

Concept of Entropy:

Spontaneous process: A process which proceeds by its own without any outside assistance is called as spontaneous process.

e.g.

-Flow of heat from hot body to cold body is spontaneous process but the reverse process is not spontaneous since it requires work to be done.

- Two different gases if enclosed in a same vessel they spontaneously mixed with each other.

In general the tendency of the process to occur naturally is called the spontaneity.

Criteria of Spontaneity:

-A spontaneous change is unidirectional

- For unstable system (when the system is not in equilibrium), a spontaneous process is unavoidable and this process will continue till equilibrium state is reached.

- Increase in randomness favours a spontaneous process. e.g. melting of ice

Entropy is a measure of the randomness or disorder of the molecules of the system. Entropy is a thermodynamic state quantity because it depends only upon initial and final state.

$\Delta S = S_f - S_i$; where ΔS = change in entropy, S_f = Entropy in final state
 S_i = Entropy in initial state

A process in which entropy of the final state (S_f) is greater than the entropy of initial (S_i) state tends to be spontaneous.

Thus , for a spontaneous process- $S_f > S_i$; $\Delta S > 0$

Absolute Entropy:

Entropy of pure crystal at absolute zero temperature is called absolute entropy. As entropy of a pure crystal at absolute zero temperature is zero, therefore it is possible by measurement and calculation to find the actual amount of entropy that a substance possesses at any temperature above 0 Kelvin.

Standard Entropy (S^0)

The absolute entropy of a substance at 25°C and one atmospheric pressure is called the standard entropy.

Standard Entropy Change

$$\Delta S^0 = \sum S^0_{\text{Product}} - \sum S^0_{\text{reactant}}$$

Standard entropy of formation:

It is the entropy of formation of 1 mole of a compound from the elements under standard conditions.

It is denoted as ΔS^0_f

$$\Delta S^0_f = \sum S^0_{\text{Compound}} - \sum S^0_{\text{Elements}}$$

Use of Entropy:

Entropy is usually expressed in terms of calories per degree, sometimes called entropy unit (e.u). Entropy is an extensive property. It, therefore, mentions the quantity of the substance involved. The quantity is usually taken as 1 mol of the substance. So the entropy units are cal per degree per mole ($\text{cal K}^{-1} \text{mol}^{-1}$) in CGS system and joule per degree per mole ($\text{JK}^{-1}\text{mol}^{-1}$) in SI units.

For a reversible change taking place at a fixed temp (T) the change in entropy (ΔS) is equal to heat energy absorbed or evolved divided by the temp (T)

$$\Delta S = q_{\text{rev}}/T$$

The statement “Entropy of the universe is always increasing” Explain??

The statement “Entropy of the universe is always increasing” is actually explained by 2nd law of thermodynamics.

Which clearly state that the entropy of the whole universe is always increasing because all naturally occurring process are spontaneous in nature which is always accompanied by an increase in entropy of the universe.

Whenever there is an irreversible process i.e., spontaneous process the entropy of universe increases.

$$(\Delta S_{\text{universe}})_{\text{irreversible}} > 0$$

Thus the statement holds true that the entropy of the universe is always increasing.

Mathematical Explanation of Entropy:

For reversible **Carnot engine** working between a higher temperature T_2 and a lower temperature T_1 with the heat absorbed q_2 and heat evolved q_1 , we have

The image shows a handwritten derivation of the Carnot cycle efficiency and the relationship between heat and temperature for reversible and irreversible cycles. The derivation starts with the efficiency of a Carnot cycle, $\frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2}$, and rearranges it to $1 - \frac{q_1}{q_2} = 1 - \frac{T_1}{T_2}$, leading to $\frac{q_1}{T_1} = \frac{q_2}{T_2}$ and $\frac{q_2}{T_2} - \frac{q_1}{T_1} = 0$ (Equation 5.15). It then defines the reduced heat $\frac{q}{T}$ and states that for a reversible Carnot cycle, the algebraic sum of the reduced heats is equal to zero. For an irreversible cycle, it shows $\frac{q_2 - q_1}{q_2} < \frac{T_2 - T_1}{T_2}$, leading to $\frac{q_2}{T_2} - \frac{q_1}{T_1} < 0$ (Equation 5.16). Finally, it states that for an infinitely small reversible cycle, Equation 5.15 can be written as $\frac{\delta q_2}{T_2} - \frac{\delta q_1}{T_1} = 0$ (Equation 5.17).

$$\frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2}$$

or $1 - \frac{q_1}{q_2} = 1 - \frac{T_1}{T_2}$

or $\frac{q_1}{T_1} = \frac{q_2}{T_2}$

or $\frac{q_2}{T_2} - \frac{q_1}{T_1} = 0 \quad \dots(5.15)$

Then term $\frac{q}{T}$ is called the reduced heat. Thus, for a reversible Carnot cycle, the algebraic sum of the reduced heats is equal to zero.

For an irreversible cycle, we have

$$\frac{q_2 - q_1}{q_2} < \frac{T_2 - T_1}{T_2}$$

or $\frac{q_2}{T_2} - \frac{q_1}{T_1} < 0 \quad \dots(5.16)$

Therefore, for an irreversible cycle, the sum of $\frac{q}{T}$ terms is less than zero.

For an infinitely small reversible cycle, Eqn. 5.15 can be written as

$$\frac{\delta q_2}{T_2} - \frac{\delta q_1}{T_1} = 0 \quad \dots(5.17)$$

Since a reversible cycle is made of a large number of infinitely small reversible Carnot cycles (Fig. 5.1), therefore for a reversible cycle, Eqn. 5.17 should be written as

$$\int \frac{\delta q_2}{T_2} - \int \frac{\delta q_1}{T_1} = 0$$

or

$$\int \frac{\delta q}{T} = 0 \quad \dots(5.18)$$

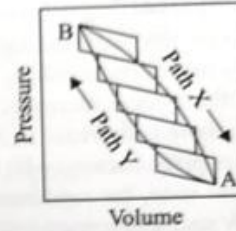


Fig. 5.1 A reversible cycle is composed of a large number of reversible Carnot cycles

Suppose the reversible cycle is so performed that the system passes from state A to state B by path X and then from state B to state A by path Y. For such a cycle, Eqn. 5.18 can be written as

$$\int_A^B \frac{\delta q(x)}{T} + \int_B^A \frac{\delta q(y)}{T} = 0$$

or

$$\int_A^B \frac{\delta q(x)}{T} = - \int_B^A \frac{\delta q(y)}{T} = \int_A^B \frac{\delta q(y)}{T} \quad \dots(5.19)$$

Therefore the term $\int \frac{\delta q}{T}$ is the same for a change from state A to state B whether the system follows path x or path y. This implies that the term $\int \frac{\delta q}{T}$ represents a function of state. This function is termed as Entropy and is represented by symbol S. Therefore.

$$\int_A^B \frac{\delta q_{rev}}{T} = S_B - S_A = \Delta S$$

Consequently,

$$dS = \frac{\delta q_{rev}}{T} \quad \dots(5.20)$$

Hence, the change in entropy dS may be defined as equal to the heat absorbed reversibly by the system divided by the temperature (in Kelvin) at which the heat is being absorbed.

Entropy change in a Chemical Reaction:

The entropy change ΔS for a chemical change is equal to the sum of the entropies of the products of that change minus the sum of entropies of the reactants.

Let us consider a hypothetical reaction,



The entropy change,

$$\begin{aligned}\Delta S &= \sum S_{\text{products}} - \sum S_{\text{reactants}} \\ &= [x \times S_C + y \times S_D] - [m \times S_A + nS_B]\end{aligned}$$

where S_A , S_B , S_C and S_D are the entropies of A, B, C and D respectively.

A positively value for ΔS ($\Delta S > 0$) indicates an increase in randomness, or disorder. A negative value for ΔS ($\Delta S < 0$) indicates decrease in randomness, or decrease in order.

Physical Significance of Entropy:

Entropy has been regarded as a measure of disorder or randomness of the system. Thus, when a system goes from a more orderly state, there is an increase in its randomness and hence entropy of the system increases. Conversely, if the change is one in which there is an increase in orderliness, there is decrease in entropy. For example, when a solid changes to a liquid an increase in entropy takes place because with the breaking of the orderly arranged molecule in the crystal to the less orderly liquid state, the randomness increases. Conversely, the process of solidification brings about more orderly state and consequently there is decrease in entropy. The process of vaporization produces an increase in entropy.

Evidently expansion of a gas in vacuum and diffusion of a solute from a concentrated to a dilute solution when the two are connected together, etc., are accompanied by increase of disorder (more of randomness) and hence there is increase in entropy.

Entropy Change Accompanying Change of Phase:

A process of change of state, e.g., melting of solid or vaporization of liquid may be carried out at constant temperature reversibly as the phases are in equilibrium for all times during the change. Suppose the process of change of state of one mol of a substance is carried out reversibly, the amount of heat absorbed will be equal to the molar heat of fusion or vaporization and the temperature will be the melting point or the boiling point.

1. **Entropy of fusion:** It is defined as the change in entropy when one mole of a solid substance transforms into the liquid form at its melting point. The molar entropy change accompanying a fusion process is given by:

$$\Delta S_f = \frac{\Delta H_f}{T_f} \quad \dots(5.21)$$

where ΔS_f is the molar entropy change (for 1 mol of a solid) accompanying fusion process, ΔH_f is the molar heat of fusion and T_f is the freezing or melting point on the absolute scale.

2. **Entropy of vaporization:** It is defined as the entropy change when one mole of a liquid changes into vapour at its boiling point. Similarly, the molar entropy change ΔS_v accompanying a vaporization process (for 1 mol of a liquid) is given by:

$$\Delta S = \frac{\Delta H_v}{T_b} \quad \dots(5.22)$$

where ΔH_v is the molar heat of vaporization and T_b is the boiling point on the absolute scale. Since ΔH_f and ΔH_v are both positive, an increase in entropy takes place during the processes of fusion and vaporization.

In the change of state from vapour to liquid or from liquid to solid, ΔH_f will be negative and during processes of condensation of vapour or freezing of a liquid decrease in entropy takes place.

3. **Entropy of Sublimation:** It is defined as the entropy involved in the transformation of a solid directly into vapour at a particular temperature called sublimation temperature. It is represented by ΔS_{sub} and is given as:

$$\Delta S_{\text{vap}} = S_{\text{vap}} - S_{\text{liquid}} = \frac{\Delta H_{\text{subs}}}{T} \quad \dots(5.23)$$

where ΔH_{sub} is the enthalpy of sublimation per mole of a solid at temperature T (in Kelvin).

4. **Entropy of Transition:** It may be defined as the change in entropy when *one mole of a solid changes from one crystalline state into the other at the transition temperature.*

$$\Delta S = \frac{\Delta H_t}{T_t} \quad \dots(5.24)$$

where ΔH_t is the molar heat of transition and T_t is the transition point.

Entropy Change in Reversible Processes:

When a system gains heat, the surroundings lose heat and hence their entropies also change. The total change in entropy will, therefore, be equal to the algebraic sum of entropy changes of the system and the surroundings *i.e.*, $\Delta S = \Delta S_{\text{sys.}} + \Delta S_{\text{sur.}}$. Consider an isothermal reversible expansion of an ideal gas. The gas absorbs $Q_{\text{rev.}}$ heat at temperature T . The entropy change of the gas, *i.e.*, system is given by

$$\Delta S_{\text{sys.}} = \frac{Q_{\text{rev.}}}{T}$$

Since expansion is reversible, the system is in equilibrium with its surroundings at all times during the expansion. Hence the surroundings lose an amount of heat equal to $Q_{\text{rev.}}$, or we can say that the surroundings absorb $-Q_{\text{rev.}}$ of heat. The entropy change of the surrounding is given by

$$\Delta S_{\text{sur.}} = - \frac{Q_{\text{rev.}}}{T}$$

So, total entropy change of the universe:

$$\Delta S = \Delta S_{\text{sys.}} + \Delta S_{\text{sur.}} = \frac{Q_{\text{rev.}}}{T} - \frac{Q_{\text{rev.}}}{T} \quad \text{or} \quad \Delta S = 0.$$

It is concluded that for a reversible process the total entropy change of the universe is zero.

Entropy change in Irreversible Processes:

When any part of the process is Irreversible, the process as a whole becomes irreversible. Suppose that the heat lost by the surroundings is Q_{irrev} . This amount of heat will be absorbed by the system, but entropy change of the heat absorbed reversibly (Q_{rev}), and not upon the heat actually absorbed. If the heat is absorbed isothermally by the system at temperature T , the entropy change of the system will be

$$\Delta S_{\text{sys.}} = \frac{Q_{\text{rev.}}}{T}$$

This is due to the fact that entropy is a state function and hence entropy increase of the system will be the same no matter the change has been brought in a reversible or an irreversible manner. But the heat actually lost by the surroundings is Q_{irrev} . The loss of heat by the surroundings to the system can be adjusted to take place reversibly and therefore the decrease in entropy is given by

$$\Delta S_{\text{sur.}} = -\frac{Q_{\text{irrev.}}}{T}$$

Hence, the net change in entropy is given by:

$$\Delta S = \Delta S_{\text{sys.}} + \Delta S_{\text{sur.}}$$

$$\Delta S = \frac{Q_{\text{rev.}}}{T} - \frac{Q_{\text{irrev.}}}{T}$$

We know that

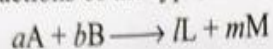
$$Q_{\text{irrev}} < Q_{\text{rev.}} \quad \text{or} \quad \Delta S > 0.$$

Thus, in an irreversible process, there is a net increase in entropy of the universe (system + surroundings).

Nernst Equation (Concentration dependence of Electrode Potential)

The emf of a cell depends both on: (i) Standard emf of cell *i.e.*, its nature, (ii) the concentrations of the species involved in the cell reaction, and (iii) temperature.

For a general cell reactions of the type,



In thermodynamics, the free energy (ΔG) accompanying the above general equation is given as:

$$\Delta G = \Delta G^\circ + RT \ln \frac{[L]^l [M]^m}{[A]^a [B]^b}$$

where ΔG° is the free energy change of the reaction under standard conditions.

Since $\Delta G = -nFE$ and $\Delta G^\circ = -nFE^\circ$

So,
$$-nFE = -nFE^\circ + RT \ln \frac{[L]^l [M]^m}{[A]^a [B]^b}$$

or

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[L]^l [M]^m}{[A]^a [B]^b}$$

$$E = E^\circ - \frac{2.303 RT}{nF} \log \frac{[L]^l [M]^m}{[A]^a [B]^b}$$

where E is the emf of the cell, E° is the standard emf of the cell:

$[A]$, $[B]$, $[L]$ and $[M]$ are the molar concentration of the species A, B, L and M respectively.

a , b , l and m are the stoichiometric co-efficients in the chemical equation, n is the number of electrons involved, R is the gas constant, T is the absolute temperature, F is one farady (96500 coulombs).

The equation is known as **Nernst equation**.

At 25°C , $R = 8.314 \text{ Joules/kelvin/mole}$, $T = 25^\circ\text{C} + 273 = 298 \text{ K}$ (at standard conditions) and $F = 96500 \text{ coulombs}$

$$\therefore \frac{2303 RT}{F} = \frac{2.303 \times 8.314 \times 298}{96500} = 0.0591$$

Substituting the value of $\frac{2303 RT}{F}$ in equation above, we get:

$$E = E^\circ - \frac{0.0591}{n} \log \frac{[L]^l [M]^m}{[A]^a [B]^b} \quad \dots(5.51)$$

or

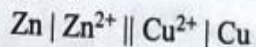
$$E = E^\circ + \frac{0.0591}{n} \log \frac{[A]^a [B]^b}{[L]^l [M]^m}$$

It is seen from Nernst equation, that if the product of the molar concentration of products is more than the product of the reactants, emf, E is less than the standard emf, E° . On the other hand, if the product of the molar concentration of the reactants is greater than that of the molar concentration of products, E is greater than E° .

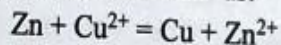
Application of Nernst Equation:

(i) Calculation of the emf of a cell

Consider for example the cell:



The cell reaction may be written as:



Applying Nernst equation

$$E = E^\circ - \frac{0.0591}{2} \log \frac{[\text{Cu}][\text{Zn}^{2+}]}{[\text{Zn}][\text{Cu}^{2+}]}$$

Here, number of electrons involved in the half cell reaction is 2.

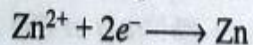
In the standard state, the activity of a solid is taken as unity.

$$E = E^\circ - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

From this equation, it is obvious that E may be equal to E° or may be greater or less than E° . E depends on the ratio of the concentration of Zn^{2+} ions and Cu^{2+} ions.

(ii) Calculation of the Single Electrode Potential

Although the standard electrode potential is fixed, the concentration of the ion in the half-cell affects its single reduction electrode potential. This is also given by Nernst's equation.



$$E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Zn}]}{[\text{Zn}^{2+}]}$$

$$= E^\circ - \frac{RT}{nF} \ln \frac{1}{[\text{Zn}^{2+}]} = E^\circ + \frac{RT}{nF} \ln [\text{Zn}^{2+}]$$

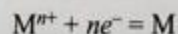
[\because Zn being solid, its concentration is taken as unity]

$$E = E^\circ + \frac{RT}{nF} \ln [\text{Zn}^{2+}]$$

$$= E^\circ - \frac{2.303RT}{nF} \log [\text{Zn}^{2+}] = E^\circ + \frac{0.0591}{n} \log [\text{Zn}^{2+}]$$

where E and E° are the single electrode potential and standard potential, n , R and F have the usual significance.

The general expression for electrode potential of a metal in contact with M^{n+} ions reaction involving the electrode may be written as



$$E = E^\circ + \frac{0.0591}{n} \log [M^{n+}]$$

(iii) Calculation of equilibrium constant

At the equilibrium concentration of the two metal ions, there is no potential difference between the two electrodes and the emf of the cell becomes zero.

Consider a reaction at equilibrium



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

The Nernst equation can be represented as

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

At the stage of equilibrium, $E_{\text{cell}} = 0$

Therefore, the above equation can be written as

$$\text{Zero} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log K_c$$

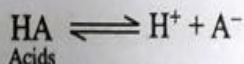
or $E^\circ_{\text{cell}} = \frac{0.0591}{n} \log K_c$, where K_c is the equilibrium constant for the reaction.

Knowledge of standard cell potential can thus be employed for calculating the equilibrium constant for the reactions.

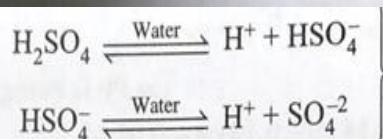
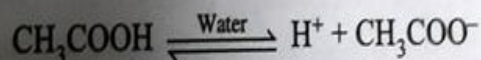
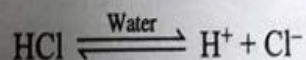
Arrhenius Concept of Acids and Bases Module4(5 of12)Acids

In the light of the behaviour of electrolytes in solution, Arrhenius provided a well-defined basis for the concept of acids and bases.

ACIDS: According to him, an acid may be defined as *a hydrogen containing substance which gives H^+ ions in aqueous solution*. Obviously the presence of ionisable hydrogen is an essential feature of all acids; thus



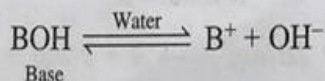
This definition could easily explain why the substances such as HCl, CH_3COOH , H_2SO_4 and H_3PO_4 etc., are recognised as acids, since each of them furnishes hydrogen ions in solution. For instance:



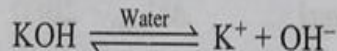
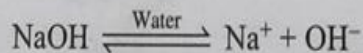
It should be noted that acids like H_2SO_4 and H_3SO_4 which contain two or more ionisable hydrogen atoms dissociate in more than one stage giving H^+ ions in each case.

The common characteristics of acids such as sour taste, turning blue litmus red, reaction with bases to form salt and H_2O were attributed to the presence of H^+ ions in aqueous solution.

Bases: A similar concept was put forward for bases. *A base is defined as a substance which contains one or more hydroxyl groups and furnishes hydroxyl $(OH)^-$ ions in aqueous solution*.



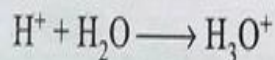
Thus, all commonly known bases such as NaOH, KOH, NH_4OH ionize in aqueous solution to give OH^- ions.



The hydroxyl ion is responsible for the basic properties exhibited by the bases.

Nature of Hydrogen Ion in Aqueous Solution:

According to Arrhenius, an acid gives H^+ ions in aqueous solution. But a hydrogen ion is only a free proton which has a very small size and an extremely high charge density. It is very strongly attracted by the negative end of water molecules and as a result it gets very readily hydrated or attracted to water molecules. Therefore, it is not very appropriate to speak of the formation of free H^+ ions or protons in solution. On the other hand, the H^+ ion always exists in solution in the more stable hydrated form, H_3O^+ , known as *hydronium ion* or hydrated proton.



In fact, even this may be an over-simplification. It has been suggested recently that hydrated proton may not be as simple as H_3O^+ . Rather it may be further to form species such as $H_9O_4^+$. But in absence of any definite evidence about the exact number of water molecules involved, the hydronium ion is commonly represented as H_3O^+ or $H^+(aq)$ or $H_3O^+(aq)$.

Limitation of Arrhenius Concept:

5.9.2 Limitations of Arrhenius Concept

Soon after Arrhenius had proposed his concept of acids and bases, it was realized, that his concept has a limited scope only. This is because it attributes all acidic and basic properties to the formation of hydrogen and hydroxyl ions *in aqueous solution only*. However, there are substances such as NH_3 , CaO etc. which do not contain the hydroxyl group but can still act as bases since they are known to neutralise acids. Similarly, there are substances such as carbon dioxide which cannot by themselves dissociate to form hydrogen ions but even then act as acids in aqueous solution.

Bronsted –Lowry Concept of Acids and Bases:

In view of the limitations of Arrhenius concept, Bronsted and Lowry proposed more general definition for acids and bases. According to their concept *an acid is a substance (molecular or ionic) which has a tendency to donate a proton*. On the other hand, *a base is a substance (molecular or ionic)*

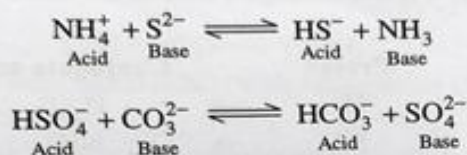
that has a tendency to **accept a proton** from any other substance. For example, the behaviour of HCl and H_3COOH in water is shown below:



As HCl donates a proton to water, hence HCl is an acid. On the other hand, H_2O accepts a proton from HCl, hence H_2O is a base. Similarly H_3COOH donates a proton to H_2O and acts as an acid, whereas H_2O accepts a proton and acts as a base.

The main features of Bronsted-Lowry concept are given as under:

1. An acid-base reaction involves the transference of a proton from a proton donor (acid) to a proton acceptor (base). Thus this concept is also called proton transfer theory of acids and bases.
2. Not only molecules but ions are also capable of acting as acids and bases. For example,



3. For an acid to act as a proton donor, a base (proton acceptor) must be present to receive proton. For example, acetic acid or HCl acts as an acid in water but not in benzene because benzene does not accept proton.



4. Whenever an acid and a base reacts another pair of acid-base is formed e.g.,



5. **Amphoteric compounds:** Certain molecules and ions may exhibit both acidic or basic behaviour under the appropriate conditions. Such species are known as amphiprotic or amphoteric. For example, water may lose a proton to a base such as NH_3 or gain a proton from an acid such as HCl and so it is classified as amphiprotic.



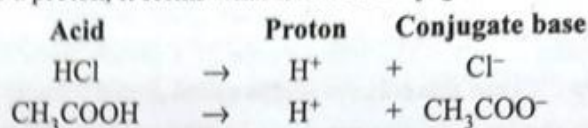
Species like HSO_3^- , HS^- , HCO_3^- are amphoteric in nature.

6. Water has a dual character. It can behave as a base in presence of acid (say HCl) and as an acid in presence of a base (say NH_3) as shown above. Its dual behaviour can be represented as:



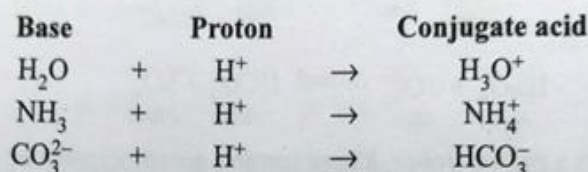
Conjugate Acid Base Pairs

When an acid loses a proton, it forms what is called conjugate base of the acid. For example,



When a base accepts a proton, it forms conjugate acid of the base.

For example,

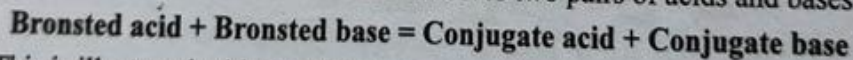


Now an acid does not form its conjugate base unless a second base (Base₂) is present to accept a proton. When the second base (Base₂) accepts the proton, it forms its conjugate acid, *i.e.*, Acid₂. For example,

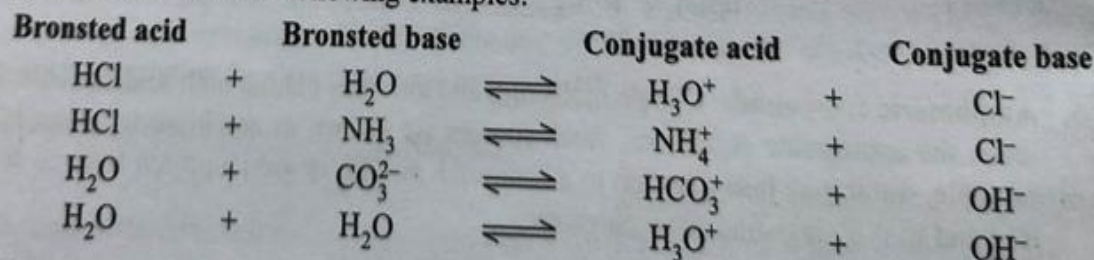


In the forward reaction, HCl donates a proton and thus behaves as an acid, water accepts a proton and thus behaves as a base. In the reverse reaction H₃O⁺ donates a proton to chloride ion and thus H₃O⁺ is an acid while Cl⁻ is a base. Such pairs of substances which are formed from one another by gain or loss of a proton are known as **conjugated acid-base pairs**. Thus hydrochloric acid is a conjugate acid of chloride ion while water is a conjugate base of hydronium ion.

In general, each acid base reaction involves two pairs of acids and bases as shown below:



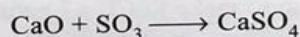
This is illustrated with the following examples:



Limitation of Bronsted-Lowry Theory:

5.10.2 Limitation of Bronsted-Lowry Theory

The theory fails to explain acid-base reactions in which no proton transfer takes place, *e.g.*, the reaction:



involves the neutralisation of basic oxide (CaO) with acidic oxide (SO₃) to form a salt (CaSO₄) without any transfer of proton between them.

Similarly, reactions taking place in non-aqueous solvents cannot be explained by this theory

e.g.,



Lewis Concept of Acids and Bases:

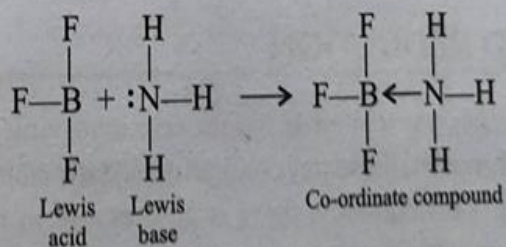
The Arrhenius as well as Bronsted-Lowry concepts limit classification of acid as substances which contain hydrogen. But G.N. Lewis put forward a more general concept which does not require hydrogen to be an essential constituent of all acids. According to Lewis, *an acid is a substance which can accept a pair of electrons while a base is a substance which can donate a pair of electrons to form a coordinate or dative bond.*

In other words, a base is an electron donor while an acid is an electron acceptor. This is the most fundamental of acid-base concepts and includes all other concepts.

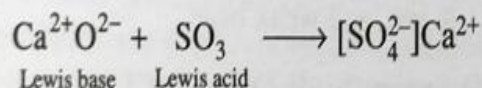
A base according to Lewis, is any substance with one or more lone pairs of electrons. It may be a neutral molecule such as: NH_3 or a negative ion such as: CN^- ion. It may be noted that any substance which can donate a pair of electrons can easily accept a proton. This means that a Lewis base is a Bronsted base.

Example of Acid Base Reactions

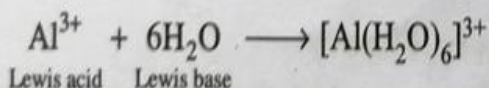
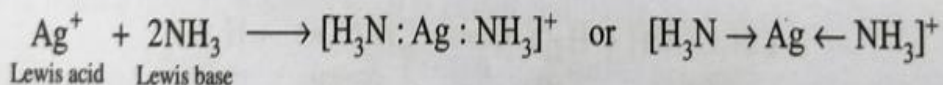
- (i) **The molecule of a Lewis acid with a central atom having incomplete octet, and a Lewis base with one or more unshared pairs of electrons** BF_3 and AlCl_3 are examples of Lewis acids of this type.



(ii) **The molecule of a Lewis acid containing multiple bonds**, *e.g.*, SO_3 has multiple bonds. It is not an Arrhenius or Bronsted acid. It is a Lewis acid and neutralizes bases.



(iii) **Simple cations**: Simple cations like Al^{3+} , Ag^+ , act as lewis acids, because they have empty orbitals in their outermost energy levels.



(iv) **The molecule of a Lewis acid having central atom with empty *d*-orbitals**. Sn in SnCl_4 has empty *d*-orbitals which are used up to make SnCl_4 a Lewis acid, the base is a negative ion, Cl^- , F^- .



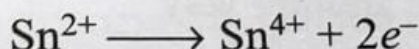
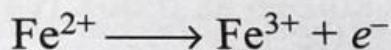
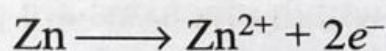
Limitations of Lewis Concept

1. It is very general and includes all the co-ordination compounds and reactions. Protonic acids do not form co-ordinate bond with bases.
2. Acid-base reactions are quite fast. But the reactions taking place forming co-ordinate compound are very slow. Thus it does not fit in normal acid-base concept.
3. The catalytic action of acids in different reactions is due to H^+ ions. Lewis acid may not contain hydrogen, so, they cannot act as catalysts.
4. The essential requirement or the main feature of Lewis concept of acid is the formation of co-ordinate bond with bases. However, protonic acids (H_2SO_4 , HCl) do not form co-ordinate bond with bases. This is against Lewis theory.

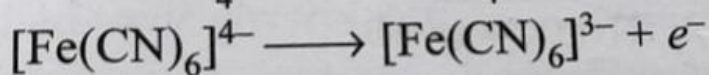
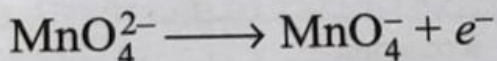
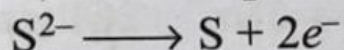
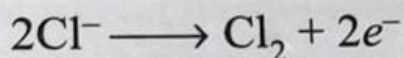
Oxidation and Reduction

Oxidation: Earlier oxidation was treated as any process involving addition of oxygen or removal of hydrogen from a substance. However, these days oxidation is defined as a process which involves the loss of electrons by a substance. Consequently, there is an increase in positive charge or decrease in negative charge of the atom or ion which undergoes oxidation. For example,

(i) *Loss of electrons resulting in an increase in positive charge*

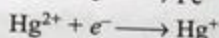
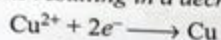


(ii) *Loss of electrons resulting in a decrease in negative charge*

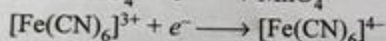


Reduction: Earlier, reduction was treated as a process involving addition of hydrogen or removal of oxygen from a substance. However, these days, reduction is defined as a process which involves the gain of electrons by a substance. Consequently, there is a decrease in positive charge or increase in negative charge of the atom or ion which undergoes reduction. For example,

(i) *Gain of electrons resulting in a decrease in positive charge*

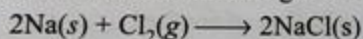


(ii) *Gain of electrons resulting in a increase in negative charge*



Further, in a chemical reaction, there is no net loss or gain of electrons. Therefore, loss and gain of electrons from one substance to another must take place simultaneously. In other words, in a chemical reaction, a substance can gain electrons only if another substance which can lose electrons is also present in the system. This means oxidation can take place only if reduction also takes place at the same time and vice versa.

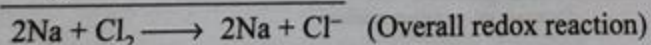
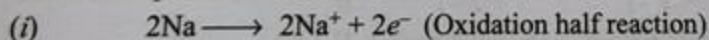
Therefore, oxidation and reduction always occurs side by side. To illustrate this, let us consider reaction between sodium metal and chlorine gas to form sodium chloride.



Now this reaction consists of two distinct, though simultaneous processes, which take place in such a way that:

Number of electrons lost = Number of electrons gained

These are represented below:

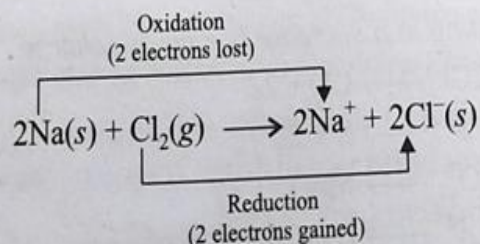


Thus, the overall reaction involves the transfer of electrons from sodium metal to chlorine. It means that sodium metal gets oxidized to Na^{+} ion while chlorine gets reduced to Cl^{-} ions so that overall reaction involves oxidation and reduction and is known as **redox reaction**.

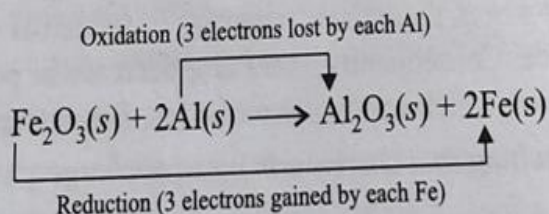
Therefore, a redox reaction may be defined as a reaction in which electrons are transferred from one to another reactant.

Every electron transfer reaction or redox reaction is the sum of oxidation half reaction in which electrons are lost and a reduction half reaction in which electrons are gained as shown above. The sum of the two half reactions in the total or net reaction known as redox reaction.

We may depict the above redox reaction in another way



Another example of the redox reactions is:



Oxidising and Reducing Agents

5.12.1 Oxidising and Reducing Agents

On the basis of electron transfer, an oxidizing agent may be defined as the substance which can accept electrons and a reducing agent as that which can lose electrons. The oxidizing agent itself, however, gets reduced while the reducing agent gets oxidized. In the formation of NaCl from sodium and chlorine, chlorine acts as oxidizing agent and sodium acts as reducing agent.

Some common examples of oxidising agents also called *oxidants* are KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, oxygen, Ozone, HNO_3 and SO_2 etc.

Some common examples of reducing agents also called *reductants* are: Ferrous salt, oxalic acid and oxalates, HBr , HI , H_2S and C etc.

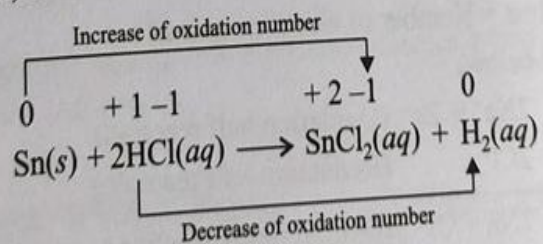
There are some substances which act as *oxidants* as well as *reductants* depending upon the conditions of the reaction e.g., H_2O_2 , HNO_2 , etc.

Redox Reaction in Terms of Oxidation Number:

5.12.2 Redox Reaction in Terms of Oxidation Number

An atom undergoes *oxidation* when it increases its oxidation number. It undergoes *reduction* when its oxidation number decreases. Since the number of electrons in a chemical reaction remains the same, reduction of one atom must accompany the oxidation of another.

Therefore, any reaction involving changes in oxidation numbers is an oxidation reduction or Redox reaction. For example, consider the reaction.



As may be seen, Sn is converted to Sn^{2+} (aq) by losing two electron and gets oxidized. On the other hand H^+ ions gains one electron and gets reduced. It may also be seen that oxidation number of Sn increases from 0 to +2 when it gets oxidized. The oxidation number of H^+ decreases from +1 to 0 when it is reduced. Therefore, *oxidation is an increase in oxidation number while reduction is decrease in oxidation number*. In the above reaction, HCl acts as *oxidising agent* while Sn acts as *reducing agent*.

Solubility Equilibria

When dissolved in suitable solvents electrolytes undergo dissociation to form charged chemical species known as *ions*. But this dissociation into ions seldom takes place to completion due to reversible nature of the process. In fact, the extent of dissociation is different in different cases. Electrolytes such as NaCl and HCl which are almost completely ionised into ions are called *strong electrolytes*.

On the other hand, electrolytes such as acetic acid (CH_3COOH) where the degree of dissociation is low, such substances which dissociate to a small extent in aqueous solution and hence conduct electricity to a small extent are called *weak electrolytes*.

In the solutions of weak electrolytes, an equilibrium is established between the ions in solution and the undissociated molecules. This is known as *ionic equilibrium*. Therefore, *ionic equilibrium is the equilibrium which is established between the undissociated molecules and the ions of the solution of weak electrolytes*.

The fraction of the total number of molecules which is ionised at the equilibrium state is known as the *degree of dissociation or ionisation*. It is usually represented by the symbol α .

$$\alpha = \frac{\text{No. of dissociated molecules}}{\text{Total no. of molecules}}$$

and

$$\text{Percentage dissociation} = \frac{\text{No. of dissociated molecules}}{\text{Total no. of molecules}} \times 100$$

Different Types of Ionic Equilibria

Reactions involving ionic equilibrium may be classified as follows:

1. Equilibria involving soluble ionic compounds such as weak acids and weak bases.
2. Equilibria involving sparingly soluble ionic compounds: solubility product.

In this chapter, we shall be discussing them as under:

Comparison of Solubility Product with Ionic product:

Table 5.2. Comparison of solubility product with ionic product

<i>Solubility product</i>	<i>Ionic product</i>
<ol style="list-style-type: none">1. It is product of the concentrations of the ions of an electrolyte, each raised to the appropriate power in a saturated solution.2. It is applicable to only saturated solutions.3. It has a constant value for an electrolyte at a constant concentration.	<ol style="list-style-type: none">1. It is the product of the concentration of the ions of an electrolyte each raised to the appropriate power in any solution.2. It is applicable to all types of solutions which may be unsaturated or saturated.3. It has variable value which can be changed by changing concentration.

Corrosion: Introduction, Causes, consequences, Mechanism, Laws of Dry Corrosion, Wet Corrosion , Factors Influencing Corrosion, Protective measures against corrosion.]

Introduction & Definition:

- Corrosion is an undesired chemical or electrochemical phenomenon and involves gradual loss of metal by the action of its environment.
- When a metal is exposed to a certain gaseous or liquid environment, its surface gradually undergoes a chemical or electrochemical reaction with the environment and gets deteriorated after some time.
- Rusting of Iron is most common example of corrosion. When a piece of iron is exposed to the atmosphere, a reddish brown coating is deposited on its surface by the combined action of air, water and CO_2 and metal is slowly eaten away.
- Corrosion starts from the surface of metal and involves a gradual loss of the metal and involves a gradual loss of the metal. All metals and alloys are susceptible (sensitive) to corrosion in one or the other environment. The extent of corrosion depends upon the nature of metal and the nature of environment.
- Even the gold which is highly resistant to corrosion under ordinary conditions gets readily corrodes when exposed to an atmosphere of mercury.
- Although corrosion is a slow process, yet the losses caused by it are substantial and sometimes heavy also. It involves the destruction of machines and equipments and sometimes may lead to shutdown of plants.

Therefore, we must be familiar with this gigantic problem and should thoroughly understand the causes and mechanism of its occurrence.

Thus corrosion may be defined as –

“The gradual disintegration or deterioration of a metal by a chemical or electrochemical action of its environment is called corrosion”

Causes of corrosion

Most of the metals occur in nature in the combined state, usually in the form of oxides, sulphides, sulphates, carbonates etc. Only a few noble metals like Au, Pt etc occur in nature in the elemental state. The form in which a metal occurs in nature is its thermodynamically stable state and corresponds to low energy of state of the system.

The process used for the extraction of metal from its ores involves the consumption of a lot of energy. Therefore, the pure metal obtained from an ore is associated with some extra amount of energy as compared to the form in which it occurred in nature. Consequently it is present in a lesser stable thermodynamic state, and has a tendency to return back to its natural thermodynamic state which is more stable. Since corrosion involves the formation of a stable compound, metals have a natural tendency to get corroded under suitable sets of conditions.

The metals like Au, Pt etc which occur in the elemental state in nature are already in their stable thermodynamic state and are much less susceptible to corrosion under ordinary conditions.

Consequences of Corrosion:

Although corrosion is a slow process, yet the losses caused by it are substantial and sometimes heavy also.

Some of the important economic and social consequences of corrosion are as follows:

- Corrosion involves the gradual eating of metals and therefore it leads to the deterioration of machines and equipments. This reduces their efficiency. It may also lead to the failure of machine and consequently the shutdown of the plants.

- *Economic consequence: Rusting is serious economic problem, and it has been estimated that approximately 15% of the total annual production of iron is mainly use to replace the iron rendered useless by rusting.*
- The cost involve in adopting the preventive measures to check corrosion are substantial. The repairing and replacement of corroded parts are also quite expensive. This adds to the cost of production and consequently the cost of production is higher.
- On account of corrosion, the products obtained may be contaminated and may lead to several problem including health hazards.
- Corrosion may also pose problems to the safe operation of the plant. It may lead to an explosion, collapse of construction due to sudden failure or fire hazard.
- Corrosion may also create pollution problem due to escaping harmful corrosion products from the corroded machine into the atmosphere.

This corrosion is highly undesirable as it leads to several economic and social problems.

Types and Mechanism of Corrosion:

1. Dry Corrosion (Chemical Corrosion)
2. Wet Corrosion (Electrochemical Corrosion)

Dry Corrosion (Chemical Corrosion)

The action caused by direct chemical action of atmosphere or environmental gases (such as O₂, SO₂, H₂S, halogen etc) or anhydrous liquids on metal surfaces is called chemical corrosion or dry corrosion.

The important types of dry corrosion are as follows –

- (i) Oxidation corrosion
- (ii) Corrosion by gases
- (iii) Liquid metal corrosion

(i) Oxidation corrosion

The oxidation corrosion occurs through the direct action of oxygen on metals, usually in the absence of moisture. This type of corrosion may occur even at ordinary temperatures. For examples- alkali metals (Li, Na, K etc) and alkali earth metals (Be, Mg, Ca etc) get oxidized even at ordinary temperatures and get corroded. Most of the other metal gets oxidized at high temperature.

Mechanism:

When a metal is exposed to air, absorption of oxygen takes place even at ordinary temperatures. This absorption is purely physical in nature and is due to Vanderwaal's forces. However due to climatic changes, the absorbed oxygen may gradually enter into chemical combination with the metal by electron transfer between the metal atoms and oxygen as shown below---

Mechanism of Oxidation Corrosion

Metal gets oxidized ($M \longrightarrow M^{n+} + ne^{-}$) and electrons so released lead to the reduction of O_2 ($\frac{1}{2} O_2 + 2e^{-} \longrightarrow O^{2-}$). Formation of metal oxide ($M_2 O_n$) takes place at the point of meeting of M^{n+} and O^{2-} . The resulting metal oxide scale forms a barrier to restrict further oxidation. As the size of M^{n+} is much smaller than that of O^{2-} , hence faster outward diffusion of metal through the scale leads to continuation of oxidation, provided metal oxide barrier is sufficiently porous. It is to be noted that slow inward diffusion of O^{2-} through scale also takes place because size of O^{2-} is large and hence its mobility is also less.

On account of the above electron transfer reactions, a metal oxide scale is formed at the metal surface. This scale acts as a barrier and tends to prevent the underlying metal atoms to come in contact with oxygen. Further oxidation can take place only when either the underlying metal gets diffused outwards through the scales to the surface or oxygen gets penetrated inwards through the scales.

In fact, both the processes take place simultaneously but the outward diffusion of metal is faster as compared to the inward diffusion of oxygen because metal ions being smaller than oxygen ions possess high mobility. Thus, once the metal surface is covered with a monolayer of oxide film, the growth of the oxide film takes place perpendicular to the metal surface and this results in the formation of thick oxide film.

The nature of oxide film formed on the metal surface plays an important role in oxidation corrosion, as is clear from following discussion.

(a) When the oxide film is stable e.g. Al, Sn, Pb, Cu

(b) When the oxide film is unstable e.g. Ag, Au, Pt

(c) When the oxide film is volatile e.g. Molybdenum (MoO_3)

(d) When the oxide film is porous e.g. Alkali metals & Alkaline earth metal

(a) When the oxide film is stable: It cuts off the penetration of oxygen to the underlying metal and acts as protective coating. Such a film prevents the further corrosion of metal. The film formed in the oxidation corrosion of Al, Sn, Pb, Cu etc are this type.

(b) When the oxide film is unstable : It decomposes back into the metal and oxygen.

Metal Oxide \rightleftharpoons Metal + Oxygen

In such case, oxidation corrosion is not possible. Such films are formed in the cases of Ag, Au, Pt etc. This is why these metal donot undergo oxidation corrosion.

(c) When the oxide film is volatile: Oxide film volatilizes as soon as it is formed, the underlying metal gets exposed to the further attack. This causes rapid and continuous corrosion. Such film s formed in the case of Molybdenum (MoO_3 is volatile)

(d) When the oxide film is porous:

When the oxide film is porous, the atmospheric oxygen can penetrate inward easily and can attack the underlying metal. Hence the corrosion will continue unobstructed till the entire metal gets completely converted into its oxide. Such films are formed by alkali metals and alkaline earth metals.

This can be explained on the basis of Pilling –Bed worth ratio.

Pilling –Bed worth ratio: The ratio of the volume of oxide formed to the volume of metal consumed is called Pilling-Bed worth ratio.

In case of alkali metals and alkaline earth metals, the volume of oxide film formed on the surface is much less as that of the metal consumed. Consequently the oxide film develops cracks and pores and allows free access of oxygen to the underlying metal. On the other hand, in case of metals such as Pb, Sn, Al etc the volume of the oxide film formed on the metal surface is greater than that of the metal

consumed. Hence, the oxide layer is non-porous and protects the underlying metal from further oxidation.

(ii) Corrosion by gases:

Several gases such as SO_2 , H_2S , Cl_2 , F_2 etc also cause corrosion of metals. The extent to which a gas corrodes a metal depends upon the chemical affinity of the gas for the metal. In such case, the degree of attack depends upon whether the film formed is porous or nonporous. When the film formed on the metal surface is porous, it allows the penetration of the gas to the underlying metal and the entire metal gets spoiled. e.g. corrosion of steel by H_2S , Corrosion of tin by Chlorine.

On the other hand, when the film formed on the metal surface is non-porous, it restrict the penetration of the gas and protects the underlying metal. Thus, the intensity of corrosion decreases. e.g. corrosion of silver by chlorine

Corrosion by Hydrogen: When a metal is exposed to hydrogen environment, hydrogen diffuses into the metal lattice in the form of atoms and collects in the interstitial spaces present in the lattice. Further diffusion helps hydrogen atoms to combine together to form H_2 gas. This develops pressure inside the lattice and causes cracking or blistering of metals.

(iii) Liquid metal corrosion:

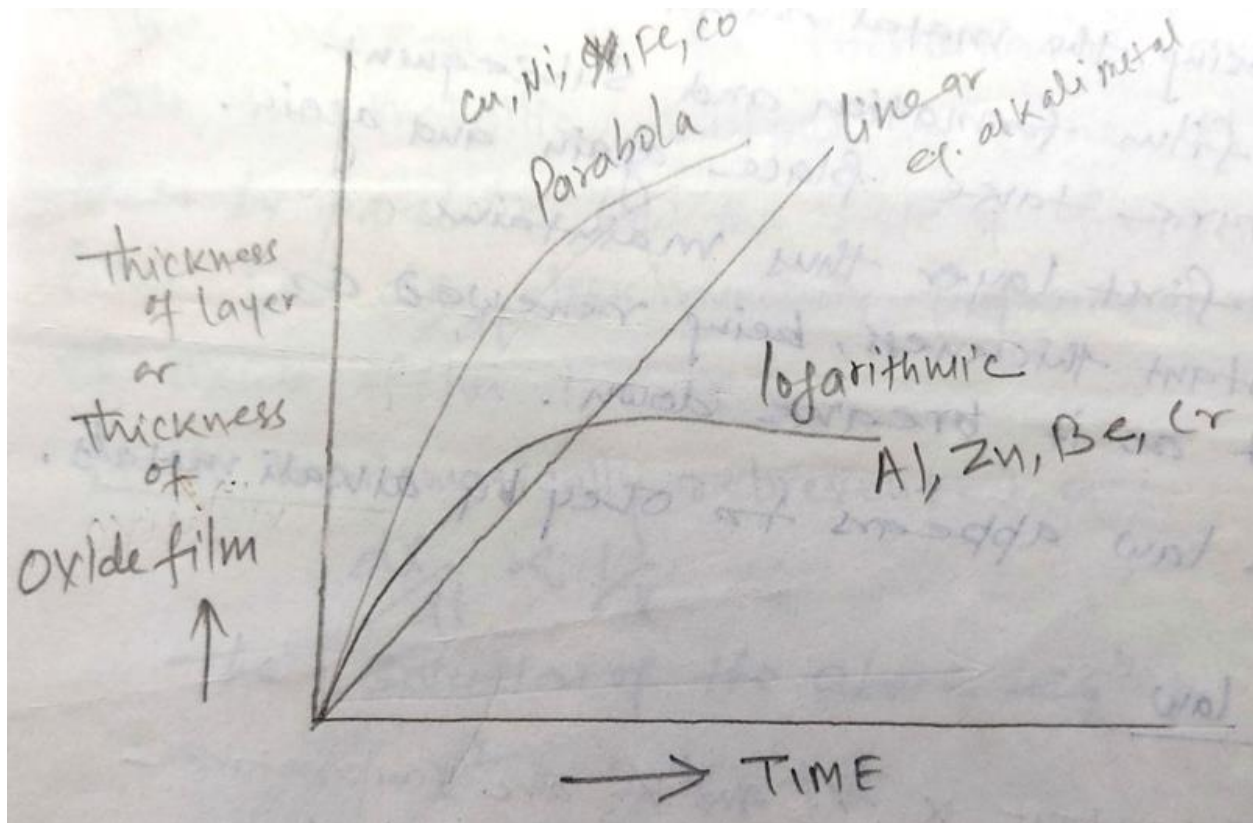
When a liquid metal is made to flow at high temperatures over a solid metal or alloys, the solid metal or alloy usually gets weakened. This type of corrosion is called liquid metal corrosion and is common in nuclear energy devices. The liquid metal corrosion is due to the dissolution of the solid metal by the following liquid metal or by the internal penetration of the liquid metal into the solid metal.

Laws of Dry Corrosion:

On the metallic surfaces, the growth of an oxide film or scale appears to follow three growth laws-

- (i) Parabolic law
- (ii) Linear law
- (iii) Logarithmic law

These laws describe how the thickness of the oxide film varies with time.



(i) Parabolic law:

Let the oxide film on the metallic surface be x . The increase in the formation of oxide film on the metallic surface in time dt be dx , then by parabolic law the rate of formation of oxide film dx/dt is inversely proportional to the thickness of oxide film i.e., x

It is mathematically represented as

$$dx/dt \propto 1/x$$

The solution of the above equation is

$$x^2 = 2K_1 t$$

Where x^2 = thickness of the oxide film

K_1 = Constant (diffusion coefficient)

t = time

from the above equation, if we plot x against t , we get a parabola. That's why this is called as parabolic law of corrosion or Parabolic law of oxidation.

(ii) Linear law:

According to linear law of dry corrosion, the rate of formation of oxide film be constant. It means that there is no change in the formation of oxide film i.e., it increases uniformly.

It is mathematically expression of linear law is -

$$dx/dt = \text{Constant}$$

The solution of the above equation is

$$x = K_2 t + \text{constant}$$

Where

K_2 = Constant for linear law

The alkali metals obeys this law

(iii) Logarithmic law:

The mathematical expression for logarithmic laws of dry corrosion is

$$x = K_3 \log (at + 1)$$

Where K_3 and a are constants

According to logarithmic laws, the values of K_3 and a is the function of temperature and the metallic surfaces. It means that value of K_3 and a increase with the increase of temperature and changes on the changing the surface of the metals.

The rate constant K_1 , K_2 and K_3 are temperature dependent.

Q. How much rust ($Fe_2O_3 \cdot 3H_2O$) will be formed, when 100kg of Iron have completely rusted away?

Answer: We know that atomic wt of Fe=56, O=16, H=1

So, molecular weight of rust

$$Fe_2O_3 \cdot 3H_2O = (2 \times 56) + (3 \times 16) + 3(2 \times 1 + 16) \\ = 214 \text{ gm/mole}$$

Each $Fe_2O_3 \cdot 3H_2O$ has 2Fe atoms or 112 gm iron

Since 214 gram of rust contain 112 gm iron

Therefore, 112 gm of iron produces =214 gm rust

$$\text{Or } 100\text{kg of iron produces} = 214 \times 100 / 112 \\ = 191.07 \text{ kg rust}$$

Q. Iron corrodes faster than aluminum, even though iron is placed below aluminum in electrochemical series why?

Or

Aluminium is highly corrosive metal; even then it is used freely in electrical lines for long time. Justify.

Answer:

This can be explained by the fact that aluminum form non-porous (Stable), very thin tightly adhering protective oxide film (Al_2O_3) on its surface and this film doesn't permit corrosion to occur.

Q. Rusting of iron is quicker in saline water than in ordinary water. Give reason.

Or

Why metals corrode faster near sea-shores?

Answer: Water is saline near sea-shores. Saline water has sodium chloride in it, which leads to increase conductivity of water. When such a water is contact with the iron surface, corrosion current increases and rusting is speeded up.

Factors Influencing Corrosion:

Rate of Corrosion depends on: (1) Nature of the metal (2) Nature of the Environment

(1) Nature of the metal:**(i) Purity of metals:**

Lesser is the percentage purity of metal, faster is the rate of corrosion.
For example, in the case of Zn metal

% Purity	99.999	99.99	99.95	99.0
Corrosion rate	1	2650	5000	7200

The impurities present in a metal caused heterogeneity and thus, tiny electrochemical cells are set up at the exposed part of the impurity and corrosion of metal around the impurity. Thus, Corrosion resistance of metal can be improved by increasing its purity.

(ii) Physical state of matter:

Physical state of metal means orientation of crystals, grain –size, stress etc. The larger the grain size of metal/alloy, the smaller will be its solubility and lesser will be its corrosion.

(iii) Nature of the oxide film:

Greater oxidation is caused due to oxide film formation as oxide film will be porous through which oxygen can diffuse and bring about further corrosion.

(iv) Position in the galvanic series :

The greater the oxidation potential, when the metal is in higher up in the galvanic series, greater is its tendency to become anodic and hence greater is the rate of corrosion.

(v) Relative area of the anode and cathode:

The rate of corrosion of metal is less when the area of the cathode is small, because demand for electron will be less with small cathode area.

(vi) Solubilities of the corrosion products:

Corrosion rate increases with increase in solubilities of corrosion products, because insoluble corrosion products function as physical barrier.

(vii) Volatility of corrosion products:

Corrosion rate increase with increase in volatility of corrosion products, because volatile products leave the underlying surface for further attack.

(2) Nature of the Environment

(i) Temperature:

The rate of corrosion increases with rise in temperature. This is due to the fact that the anodic attack by the anions, the cathodic evolution of hydrogen gas and solubility of oxygen decreases with rise of temperature.

As poorly oxygenated area behave as anode, so corrosion due to differential aeration gets slowed down at higher temperatures. This is due to faster diffusion of oxygen into pits and crevices.

(ii) Humidity:

The greater is the humidity, the greater is the rate and extent of corrosion. This is due to the fact that moisture acts a solvent for O_2 , H_2S , SO_2 , $NaCl$ etc. to furnish the electrolyte essential for setting up a *corrosion cell*. For example

(a) Atmospheric corrosion of iron is slow in dry air compared to moist air.

(b) Gases like H_2S and SO_2 increases the acidity of medium by their dissolution in water and hence, increases the corrosion rate.

(c) Dissolution of $NaCl$ in water leads to the increased conductivity and thereby increased corrosion rate.

(iii) Effect of pH

Corrosion of metals, which are readily attacked by acids, can be reduced by increasing the pH of the attacking environment. *For example* corrosion of Zn can be minimized by increasing the pH to 11. *In general, acidic media are more corrosive than alkaline and neutral media.*

(iv) Nature of Electrolyte: The nature of the electrolyte also influences the rate of corrosion.

(a) *Anion*: If the electrolyte consists of silicate ions, they form insoluble silicate and prevent further corrosion. If the electrolyte consists of chloride ions, they destroy the protective film and the surface is exposed for further corrosion. *For example, rapid corrosion of Al in sea water.*

(b) *Cation*: Corrosion of many metals is rapid in presence of NH_4^+ ions in corroding media.

(c) *Conductance of the corroding medium*: The corrosion current depends upon the internal resistance of the short-circuited cells, which in turn depends on the conductance of the electrolyte medium. If the conductance of the soil is more, the corrosion of under-ground structure will also be more. Consequently, there will be more severe damage to the metallic structures in the presence of stray currents from power leakages.

(v) Formation of Oxygen Concentration Cell: with the increase in supply of oxygen to the moist metal surface, the corrosion is promoted as it helps in the formation of oxygen concentration cell. The less oxygen concentration part becomes anodic while the more oxygen concentration part becomes cathodic.

Due to differential aeration, “Oxygen –concentration cell” sets up and anodic part having less oxygen concentration suffers corrosion. *For example- waterline corrosion occurs due to formation of differential –oxygen concentration cell.*

(vi) Presence of impurities in atmosphere: Corrosion of metals is more in areas near the industry and sea. This is due to the fact that corrosive gases (like H_2S , SO_2 , CO_2) and fumes of H_2SO_4 and HCl in industrial areas and NaCl of sea water lead to increased conductivity of the liquid layer in contact with the metal surface, thereby increasing the corrosion rate.

(vii) Presence of Suspended Particle in the atmosphere:

- (a) Active suspended particle like NaCl enhance atmospheric corrosion because they absorb moisture and act as strong electrolyte.
- (b) Inactive suspended particles like charcoal also slowly enhance corrosion rate because they can absorb moisture.

Protective measures against corrosion:

The methods used to protect a metal from corrosion mainly operate by preventing corrosion reactions from taking place. One of the best ways of doing this is to protect the metal from water and oxygen.

The various protective measures includes

- (i) Modification of the Environment
- (ii) Modification of the properties of metal
- (iii) Use of protective coating
- (iv) Cathodic protection

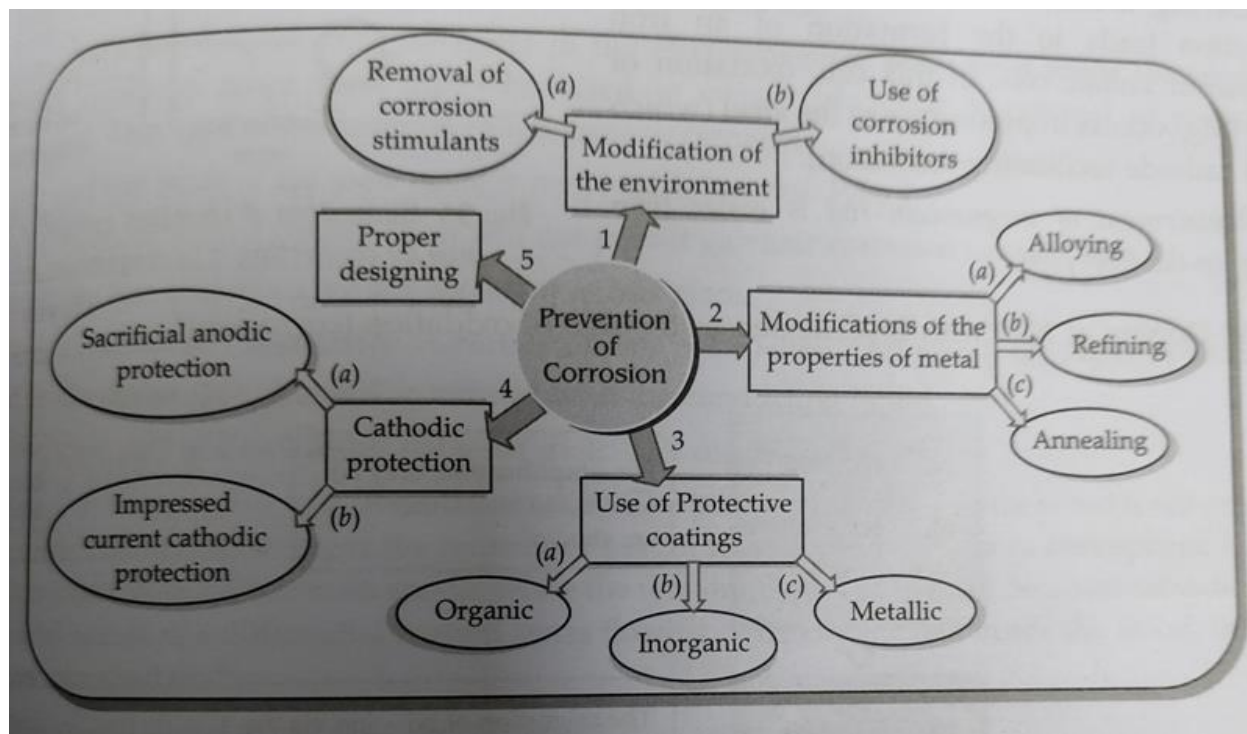


Figure: Various methods for prevention of corrosion

(i) Modification of the Environment:

In this category, the metal are protected from corrosion either by removal of corrosion stimulates or by the use of *inhibitors* (i.e. the substance which effectively decrease the corrosion rate)

- (a) Removal of corrosion stimulates
- (b) Use of corrosion inhibitors

(a) Removal of corrosion stimulates :

- To prevent corrosion due to the oxygen, dissolved oxygen from water is removed by physical or chemical means.

[Either deaeration is done or reducing substance are added like N_2H_4 , Na_2SO_3 etc]

- To prevent corrosion by acids, they are neutralized with lime
- To prevent corrosion by salts, they are removed by using ion-exchange resins.
- To prevent corrosion by moisture, moisture from air is removed by dehumidification using silica gel.

(b) Use of corrosion inhibitors:

Inhibitors are inorganic or organic substances which when added to the environment are able to reduce the rate of corrosion. Inhibitors are chemical substances which reduce the corrosion rate when added in small quantities to the corrosive environment.

Corrosion inhibitors are of following three types—

- (i) Anodic inhibitors
- (ii) Cathodic inhibitors
- (iii) vapour phase inhibitors- are organic inhibitors which readily sublime and form a protective layer on surface of metal.

Q. What are organic inhibitors?

Answer: Organic inhibitors are S- or N-containing organic compounds which retard corrosion processes even in acid solutions by getting adsorbed all over the metal surface. e.g. Amines , organic nitrates, substituted thiocarbamides and heterocyclic compound

(ii) Modification of the properties of metal:

The properties of the metal can be modified to decrease the effect of corrosion. The following methods used to modify the properties of metals-

1. Alloying: The alloying additions for increasing corrosion resistance may be for Passivating:- The phenomenon in which a metal or an alloy exhibits a much higher corrosion resistance than expected from the position in the galvanic series is called Passivating. Al, Cr, Ti, Ni, Mo as protective oxide layers make steel less corrosive.

Inhibiting- Arsenic or Sn in brass prevents dezincification

Neutralizing - Tantalum(73) , Niobium (41), Titanium (22) combine with C to form respective carbides and thus make the stainless steel corrosion resistant.

2. Refining: It is done to lower the content of S and P in the steel and C in the stainless steel.

3. Annealing: It is a heat treatment given to metal to remove the residual stresses

(iii) Use of protective coating:

(i) Metallic Coating:

(a) Anodic Coating: - The metal which is used for coating is more anodic than the metal to be protected. e.g. Coating of Al, Cd and Zn on steel surface

(b) Cathodic coating: - These coatings protect the underlying base metals due to their noble character and higher corrosion resistance. E.g. coating of Sn on Fe.

(ii) Inorganic coating: These are non-metallic coating-

(a) Chemical dip coating

(b) Anodized oxide coating

(c) Porcelain enamel coating

(iii) Organic Coating : two important functions of organic coatings are-

- To impart decorative and aesthetic appeal
- To protect the metal from corrosion.

Organic coatings are of two types :-

(a) Those that protect the metal from environment by an impervious film.

(b) Organic films which contain an inhibitor.

These two types of organic coatings are combined in paints etc. In general , there is primary coating in paints which contains zinc chromate and red lead which overcoat of organic coating containing ferric oxide which gives mechanical protection.

Metallic Coating:

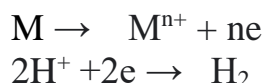
Iron and steel are the most commonly used construction material due to their low cost, easy availability and ease of fabrication into desired structures. Iron and steel can be protected from corrosion by covering their surface with metallic coatings. Surface coatings made up of metals are known as metallic coatings.

The metallic coating often used are Zinc, tin , nickel , chromium , aluminum , copper etc. These coatings separate the base metal from the corrosive environment and also function as an effective barrier for the protection of base metals. There are two types of metallic coating (i) Anodic coating (ii) Cathodic coatings.

(iv) Cathodic protection:

In cathodic protection the metal to be protected is forced to behave like a cathode, since there is not any anodic area on the metal, corrosion doesn't occur.

Consider corrosion of metal in acid medium. The reaction occurring are oxidation of the metal and reduction of hydrogen ions.



Cathodic protection can be achieved by supplying electrons to the metal. This will tend to suppress corrosion and increase the rate of hydrogen evolution

Two types of cathodic protection are:--

(a) Sacrificial Anodic protection: In this method the metal to be protected is connected by a wire to a more anodic metal. The more active metal loses electrons and gets corroded slowly thereby protecting the parent cathodic metal. e.g. Galvanization process where iron is protected by covering with zinc.

Some sacrificial anodes commonly used are Mg, Zn, Al etc. Application of this method include underground cables, water tanks etc

(b) Impressed Current Method/ Electrical cathodic protection: In this method an impressed current is applied in opposite direction to nullify the corrosion current and convert the corroding metal from anode to cathode. The current is derived from direct sources like battery (or rectifier) on a.c. line with an insoluble anode (like graphite etc) This technique is used for long term operations.

Questions

1. Explain the term (i) internal energy, (ii) enthalpy. What is the main difference between these terms? Can we know the absolute value of internal energy of a system? Give reason for your answer.
2. Derive relation between change in internal energy and change in enthalpy.
3. Explain the term Entropy show that it is a state function. Give its units.
4. Discuss the entropy change in reversible and irreversible processes. Comment on the statement: *Entropy of the Universe is always increasing*.
5. Define spontaneity and free energy. Describe the relationship between Helmholtz free energy and Gibb's free energy.
6. Derive Nernst equation for single electrode potential and explain in terms involved in it. Write its application.
7. Explain in terms (i) Oxidation (ii) Reduction (iii) Oxidising agent
8. Comment upon the statement: Oxidation and reduction reactions go side by side.
9. Give Arrhenius definition of acid and a base? What is meant by strong and weak acids and bases? What is the Lewis concept of acids and bases?
10. What is meant by common ion effect?

11. What is Ellingham diagram? How can it be constructed? What are its important characteristics?
12. Define corrosion of metals. What are different types of corrosion? Explain electrochemical theory of wet corrosion, giving its mechanism.
13. Explain rusting of iron with the help of electrochemical theory of corrosion.
14. Explain the mechanism of following types of corrosion (i) Stress corrosion (ii) Waterline Corrosion (iii) Pitting Corrosion
15. Explain sacrificial anodic protection of controlling corrosion.
16. Explain why impure metals are more susceptible to corrosion than pure metals.
17. What is pilling –Bed worth rule? Explain it.
18. Discuss various factors affecting corrosion.
19. Differentiate wet corrosion from dry corrosion.
20. Discuss in details the various methods of corrosion control with chemical equations.