**CHAPTER NO- 02**

**Chemical Equilibrium**

**2.1 Introduction:**

In a [chemical reaction](https://en.wikipedia.org/wiki/Chemical_reaction), chemical equilibriumis the state in which both reactants and products are present inconcentrationswhich have no further tendency to change with time, so there is no observable change in the properties of the system.This state results when the forward reaction proceeds at the same rate as thereverse reaction. Thereaction ratesof the forward and backward reactions are generally not zero, but equal. There are no net changes in the concentrations of the reactants and products. Such a state is known asdynamic equilibrium.

Every change continues until no more process occurs and the system reaches to equilibrium. The conditions of minimum energy or maximum entropy are used for chemical reactions. Free energy is function of convenience used for real systems.

Entropy is the concept and criterion for the direction of natural change. Change is entropy is always greater than zero for irreversible change. Change is entropy is zero for a reversible process.

**∆S**universe **=∆S**system+ **∆S**surrounding = 0 -----reversible entropy change

**∆S**universe **=∆S**system+ **∆S**surrounding> 0 ---irreversible entropy change

Gibbs realized a single state function of the system rather than entropy change is free energy.

Consider the system exchange heat (q) with surrounding at constant temperature and pressure.

q= ∆**H and** surrounding, q = - **∆H**

**∆S**universe **=∆S**surrounding+ **∆S**system

= - **∆H/T +∆S**system

**∆S**universe **=**- **∆H/T +∆S**

-T**∆S**universe **=∆H -** T**∆S**

Gibb’s free energy (G) has mathematical equation,

G = H –TS and change in it is-

**∆**G = **∆**H - T**∆**S

**2.2 Gibbs Free Energy change for chemical reaction:**

Gibbs free energy of reaction is the difference between Gibbs free energies of products and reactants.

Consider a general reaction,

Aa+Bb + ------ →cC+dD

Let GA, GB, GC, GD be Gibbs free energies per mole of substance A,B,C and Dof reactants and products involved in a reaction.

**∆**G is free energy change of above reaction,

**∆**G = ∑Gproducts -∑ G reactants

**∆**Greaction = (cGC + dGD +-----)- (aGA + bGB +-----)

For an isothermal process, ∆G is-

**∆**G = **∆**H - T**∆**S

Where, **∆**H and **∆**S are the change in enthalpy and entropy for reaction.

∴**∆**Greaction = ( Hproducts – Hreactants ) – T (Sproducts – Sreactants )

∴**∆**Greaction= **∆**Hreaction - T**∆**Sreaction

The free energy change for any process is a state function depending on initial and final state. The absolute value of free energies of the substance is not known. The change in free energy can be calculated by the process.

The standard Gibbs free energy of the reaction **∆**G0 is interms of standard molar Gibbs energies of the reactants and products.

The standard Gibbs free energy of the reaction is the difference between the products in standard states and reactants in the stable state.

**2.3 Exergonic and Endergonic Reactions:**

We can express the spontaneity of a reaction at constant temperature and pressure in terms of the reaction Gibbs energy:

If ∆r G < 0, the forward reaction is spontaneous.

If ∆r G > 0, the reverse reaction is spontaneous.

If ∆r G = 0, the reaction is at equilibrium.

A reaction for which ∆r G < 0 is called exergonic (from the Greek words for work producing). The name signifies that, because the process is spontaneous, it can be used to drive another process, or used to do non-expansion work. In biological cells, the oxidation of carbohydrates act as the heavy weight that drives other reactions forward and results in the formation of proteins from amino acids, muscle contraction, and brain activity. Examples of exergonic reactions include cellular respiration, the decomposition of hydrogen peroxide, and combustion.

A reaction for which ∆r G > 0 is called endergonic (signifying work consuming). The reaction can be made to occur only by doing work on it, such as electrolyzingwater to reverse its spontaneous formation reaction. Reactions at equilibrium are spontaneous in neither direction: they are neither exergonic nor endergonic.An endergonic reaction is a chemical reaction with a positive standard Gibbs free energy, at constant temperature and pressure:

∆G° > 0

In other words, there is a net absorption of free energy. Chemical bonds in the products store energy. Endergonic reactions are also called unfavorable or nonspontaneous reactions because the activation energy for an endergonic reaction usually is larger than the energy of the overall reaction. Because Gibbs free energy relates to the equilibrium constant, K < 1.

Examples of endergonic reactions include photosynthesis, theNa+/K+pump for muscle contraction and nerve conduction, protein synthesis, and dissolving potassium chloride in water.

**2.4 ChemicalEquilibrium--**

When reactants are mixed in exact stoichiometric proportion to perform a chemical reaction, it is believed that all the reactants would be converted into products with the release or absorption of energy. This is not true in all cases. many chemical reactions proceed only to a certain extent and stop. When analyzed, the resulting mixture contains both the reactants and products. It is because when reactants combine to form products, the products also start combining to give back the reactants. When such opposing processes take place at equal rates, no reaction appears to take place and it is said that a state of equilibrium has reached.

**2.4.1 Static and Dynamic Equilibrium -----**

The state equilibrium can be observed in physical and chemical systems. Equilibrium can be static or dynamic in nature. A book lying on the table is an example of static equilibrium. The forces of action and reaction cancel each other and no change takes place.

On the other hand, when an escalator is coming down and a passenger is going up at the same speed it is a case of dynamic equilibrium. Here, both are moving in opposite directions and at the same speed, no net change takes place. The equilibrium established in the above examples is in physical systems.

**2.4.2 Reversible reactions -----**

Consider the reaction between ethanol and acetic acid. When mixed in the presence of dilute Sulphuric acid they react and form ethyl acetate and water.

C2H5OH (l) + CH3COOH (l) ⎯⎯→ CH3COO C2H5 (l) + H2O (l)

On the other hand, when ethyl acetate and water are mixed in the presence of dilute sulphuric acid the reverse reaction occurs.

CH3COOC2H5 (l) + H2O (l) H +⎯⎯→CH3COOH (l) + C2H5OH (l)

The second reaction is reverse of the first one and under the same conditions, the two reactions occur simultaneously. Such reactions which occur simultaneously in opposite directions are called reversible reactions. The reactions are indicated by placing two half arrows pointing in opposite directions (⇌) between the reactants and products.

Thus the above reaction is more appropriately written as

CH3COOH (l) + C2H5OH (l) ⇌CH3COOC2H5 (l) + H2O (l)

When ethyl acetate and water are formed in the forward reaction the reverse reaction also starts in which ethanol and acetic acid are formed. After some time the concentrations of all the reactants and products become constant. This happens when the rates of forward and reverse reactions become equal; and all the properties of the system become constant. It is said that the system has attained state of equilibration. A reversible reaction is said to be in the equilibrium state when the forward and backward reaction occur simultaneously at the same rate in a closed system and the concentrations of reactants and products do not change with time.

**2.4.3Characteristics of Equilibrium State ---**

1. The state of chemical equilibrium is reached in a reversible reaction when;

(i) The temperature of the system attains a constant value.

(ii) The pressure of the system attains a constant value.

(iii) The concentrations of all the reactants and products attain constant values.

The state of equilibrium has following characteristics properties:

1. **Chemical Equilibrium is dynamic in nature**

The chemical equilibrium is the result of two equal but opposite processes occurring in the forward and reverse directions and there is no “net” change occurring in the system.

**2. Equilibrium can be attained from either side**

The same state of equilibrium characterized by its equilibrium constant can be reached whether the reaction is started from the reactants or products side. For example, the same equilibrium

N2O4 (g) ⇌2NO2 (g)

is established whether we start the reaction with N2O4 or NO2 .

3. **Equilibrium can be attained only in a closed system**

Equilibrium can be attained only if no substance among, reactants or products, is allowed to escape i.e. the system is a closed one. Any system consisting of gaseous phase or volatile liquids must be kept in a closed container,

N2 (g) + 3H2 (g) ⇌2NH3 (g)

A system consisting of only non-volatile liquid and solid phases can be kept even in an open container because such substances have no tendency to escape,

FeCl3 (aq) + 3 NH4SCN (aq) ⇌ Fe (SCN)3 (s) + 3 NH4Cl(aq)

**4. A catalyst cannot change the equilibrium state**

Addition of a catalyst speeds up the forward and reverse reactions by same extent and help in attaining the equilibrium faster. The equilibrium concentrations of reactants and products are not affected in any manner.