

Chapter 8 Chemical Equilibrium

Whenever we hear the word Equilibrium immediately a picture arises in our mind an object under the influence of two opposing forces. For chemical reactions also this is true. A reaction also can exist in a state of equilibrium balancing forward and backward reactions.

Reversible and Irreversible reactions

A *chemical reaction* is said to have taken place when the concentration of reactants decreases, and the concentration of the products increases with time. The chemical reactions are classified on the basis of the extent to which they proceed, into the following two classes;

(i) **Reversible reactions** : Reaction in which entire amount of the reactants is not converted into products is termed as *reversible reaction*.

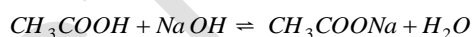
(i) **Characteristics of reversible reactions**

- (a) These reactions can be started from either side,
- (b) These reactions are never complete,
- (c) These reactions have a tendency to attain a state of equilibrium, in which Free energy change is zero ($\Delta G = 0$),

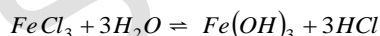
(d) This sign (\rightleftharpoons) represents the reversibility of the reaction,

(ii) **Examples of reversible reactions**

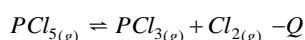
(a) *Neutralisation between an acid and a base either of which or both are weak e.g.,*



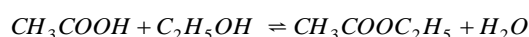
(b) *Salt hydrolysis, e.g.,*



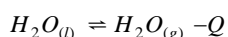
(c) *Thermal decomposition, e.g.,*



(d) *Esterification, e.g.,*



(e) *Evaporation of water in a closed vessel, e.g.,*



(2) **Irreversible reactions** : Reaction in which entire amount of the reactants is converted into products is termed as *irreversible reaction*.

(i) **Characteristics of irreversible reactions**

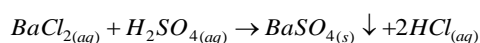
- (a) These reactions proceed only in one direction (forward direction),
- (b) These reactions can proceed to completion,
- (c) In an irreversible reaction, $\Delta G < 0$,
- (d) The arrow (\rightarrow) is placed between reactants and products,

(ii) **Examples of irreversible reactions**

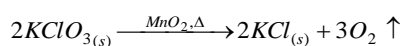
(a) *Neutralisation between strong acid and strong base e.g.,*



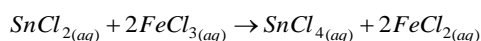
(b) *Double decomposition reactions or precipitation reactions e.g.,*



(c) *Thermal decomposition, e.g.,*

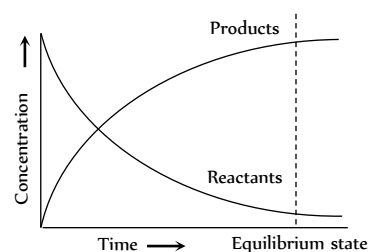


(d) *Redox reactions, e.g.,*



Equilibrium and Its dynamic nature

"Equilibrium is the state at which the concentration of reactants and products do not change with time. i.e. concentrations of reactants and products become constant."



The important characteristics of equilibrium state are,

(1) Equilibrium state can be recognised by the constancy of certain measurable properties such as *pressure, density, colour, concentration* etc. by changing these conditions of the system, we can control the extent to which a reaction proceeds.

(2) Equilibrium state can only be achieved in *close vessel*.

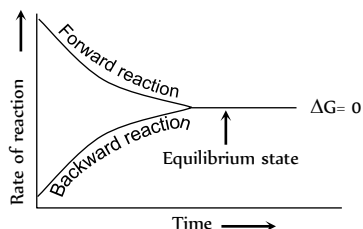
(3) Equilibrium state is *reversible* in nature.

(4) Equilibrium state is also *dynamic* in nature.

(5) At equilibrium state,

Rate of forward reaction = Rate of backward reaction

(6) At equilibrium state, $\Delta G = 0$, so that $\Delta H = T\Delta S$.



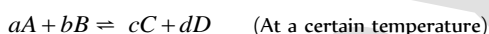
Law of mass action and Equilibrium constant

On the basis of observations of many equilibrium reactions, two Norwegian chemists **Goldberg** and **Waage** suggested (1864) a quantitative relationship between the rates of reactions and the concentration of the reacting substances. This relationship is known as *law of mass action*. It states that

“The rate of a chemical reaction is directly proportional to the product of the molar concentrations of the reactants at a constant temperature at any given time.”

The molar concentration *i.e. number of moles per litre* is also called *active mass*. It is expressed by enclosing the symbols of formulae of the substance in square brackets. For example, molar concentration of *A* is expressed as $[A]$.

Consider a simple reversible reaction



According to law of mass action

$$\text{Rate of forward reaction} \propto [A]^a [B]^b = k_f [A]^a [B]^b$$

$$\text{Rate of backward reaction} \propto [C]^c [D]^d = k_b [C]^c [D]^d$$

At equilibrium ,

Rate of forward reaction = Rate of backward reaction

$$k_f [A]^a [B]^b = k_b [C]^c [D]^d$$

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

Where, K_c is called equilibrium constant.

In terms of partial pressures, equilibrium constant is denoted by K_p and

$$K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

In terms of mole fraction, equilibrium constant is denoted by K_x and

$$K_x = \frac{(X_C)^c (X_D)^d}{(X_A)^a (X_B)^b}$$

Relation between K_p , K_x and K_c

$$K_p = K_c (RT)^{\Delta n}$$

$$K_p = K_x (P)^{\Delta n}$$

Δn = number of moles of gaseous products – number of moles of gaseous reactants in chemical equation.

As a general rule, the concentration of pure solids and pure liquids are not included when writing an equilibrium equation.

Value of Δn	Relation between K_p and K_c	Units of K_p	Units of K_c
0	$K_p = K_c$	No unit	No unit
>0	$K_p > K_c$	$(\text{atm})^{\Delta n}$	$(\text{mole l}^{-1})^{\Delta n}$
<0	$K_p < K_c$	$(\text{atm})^{\Delta n}$	$(\text{mole l}^{-1})^{\Delta n}$

Characteristics of equilibrium constant

(1) The value of equilibrium constant is independent of the original concentration of reactants.

(2) The equilibrium constant has a definite value for every reaction at a particular temperature. However, it varies with change in temperature.

(3) For a reversible reaction, the equilibrium constant for the forward reaction is inverse of the equilibrium constant for the backward reaction.

$$\text{In general, } K_{\text{forward reaction}} = \frac{1}{K'_{\text{backward reaction}}}$$

(4) The value of an equilibrium constant tells the extent to which a reaction proceeds in the forward or reverse direction.

(5) The equilibrium constant is independent of the presence of catalyst.

(6) The value of equilibrium constant changes with the change of temperature. Thermodynamically, it can be shown that if K_1 and K_2 be the equilibrium constants of a reaction at absolute temperatures T_1 and T_2 . If ΔH is the heat of reaction at constant volume, then

$$\log K_2 - \log K_1 = \frac{-\Delta H}{2.303 R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] \quad (\text{Van't Hoff equation})$$

The effect of temperature can be studied in the following three cases

(i) When $\Delta H = 0$ *i.e., neither heat is evolved nor absorbed*

$$\log K_2 - \log K_1 = 0 \quad \text{or} \quad \log K_2 = \log K_1 \quad \text{or} \quad K_2 = K_1$$

Thus, equilibrium constant remains the same at all temperatures.

(ii) When $\Delta H = +ve$ *i.e., heat is absorbed*, the reaction is *endothermic*. The temperature T_2 is higher than T_1 .

$$\log K_2 - \log K_1 = +ve \quad \text{or} \quad \log K_2 > \log K_1 \quad \text{or} \quad K_2 > K_1$$

The value of equilibrium constant is higher at higher temperature in case of endothermic reactions.

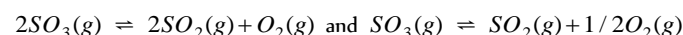
(iii) When $\Delta H = -ve$ *i.e., heat is evolved*, the reaction is *exothermic*. The temperature T_2 is higher than T_1 .

$$\log K_2 - \log K_1 = -ve \quad \text{or} \quad \log K_1 > \log K_2 \quad \text{or} \quad K_1 > K_2$$

The value of equilibrium constant is lower at higher temperature in the case of exothermic reactions.

(7) The value of the equilibrium constant depends upon the stoichiometry of the chemical equation.

For the reaction



$$K = \frac{[SO_2]^2 [O_2]}{[SO_3]^2} \text{ and } K' = \frac{[SO_2][O_2]^{1/2}}{[SO_3]}$$

$$K' = \sqrt{K} \text{ or } (K)^{1/2}$$

(i) Similarly, if a particular equation is multiplied by 2, the equilibrium constant for the new reaction (K') will be the square of the equilibrium constant (K) for the original reaction *i.e.*, $K' = K^2$

(ii) If the chemical equation for a particular reaction is written in two steps having equilibrium constants K_1 and K_2 , then the equilibrium constants are related as $K = K_1 \times K_2$

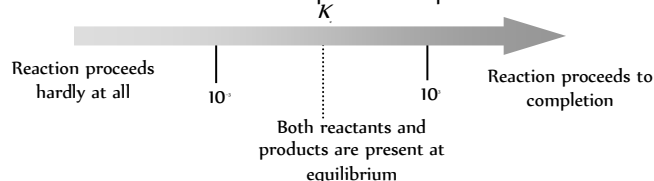
Applications of equilibrium constant

(1) Judging the extent of reaction

(i) If $K_c > 10^3$, products predominate over reactants. If K_c is very large, the reaction proceeds almost all the way to completion.

(ii) If $K_c < 10^{-3}$, reactants predominate over products. If K_c is very small, the reaction proceeds hardly at all.

(iii) If K_c is in the range 10^{-3} to 10^3 , appreciable concentration of both reactants and products are present.



(2) Predicting the direction of reaction : The concentration ratio, *i.e.*, ratio of the product of concentrations of products to that of reactants is also known as *concentration quotient* and is denoted by Q .

$$\text{Concentration quotient, } Q = \frac{[X][Y]}{[A][B]}$$

It may be noted that Q becomes equal to equilibrium constant (K) when the reaction is at the equilibrium state. At equilibrium, $Q = K = K_c = K_p$. Thus,

(i) If $Q > K$, the reaction will proceed in the direction of reactants (*reverse reaction*).

(ii) If $Q < K$, the reaction will proceed in the direction of the products (*forward reaction*).

(iii) If $Q = K$, the reaction mixture is already *at equilibrium*.

Thus, a reaction has a tendency to form products if $Q < K$ and to form reactants if $Q > K$.

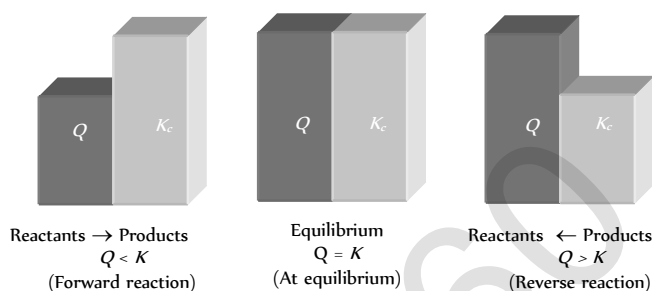
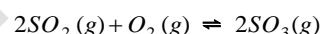
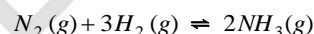
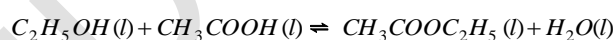


Fig. 8.1

Types of equilibria

The equilibrium between different chemical species present in the same or different phases is called chemical equilibrium. There are two types of chemical equilibrium.

(1) **Homogeneous equilibrium** : The equilibrium reactions in which all the reactants and the products are in the same phase are called *homogeneous equilibrium reactions*.



(2) **Heterogeneous equilibrium** : The equilibrium reactions in which the reactants and the products are present in different phases are called *heterogeneous equilibrium reactions*.

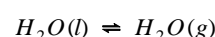
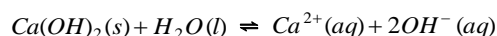
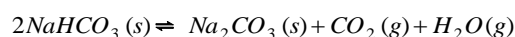


Table : 8.1 Homogeneous equilibria and equations for equilibrium constant (Equilibrium pressure is P atm in a V L flask)

	$\Delta n = 0$; $K_p = K_c$	$\Delta n < 0$; $K_p < K_c$			$\Delta n > 0$; $K_p > K_c$
	$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$		$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
Initial mole	1 1 0	1 3 0	2 1 0	1 0 0	
Mole at Equilibrium	(1-x) (1-x) 2x	(1-x) (3-3x) 2x	(2-2x) (1-x) 2x	(1-x) x x	
Total mole at equilibrium	2	(4-2x)	(3-x)	(1+x)	
Active masses	$\left(\frac{1-x}{V}\right) \left(\frac{1-x}{V}\right) \frac{2x}{V}$	$\left(\frac{1-x}{V}\right) 3\left(\frac{1-x}{V}\right) \left(\frac{2x}{V}\right)$	$\left(\frac{2-2x}{V}\right) \left(\frac{1-x}{V}\right) \left(\frac{2x}{V}\right)$	$\left(\frac{1-x}{V}\right) \left(\frac{x}{V}\right) \left(\frac{x}{V}\right)$	
Mole fraction	$\left(\frac{1-x}{2}\right) \left(\frac{1-x}{2}\right) \frac{2x}{2}$	$\frac{1-x}{2(2-x)} \frac{3(1-x)}{2(2-x)} \frac{x}{(2-x)}$	$\left(\frac{2-2x}{3-x}\right) \left(\frac{1-x}{3-x}\right) \left(\frac{2x}{3-x}\right)$	$\left(\frac{1-x}{1+x}\right) \left(\frac{x}{1+x}\right) \left(\frac{x}{1+x}\right)$	

Partial pressure	$p\left(\frac{1-x}{2}\right) p\left(\frac{1-x}{2}\right) p\left(\frac{2x}{2}\right)$	$P\left(\frac{1-x}{2(2-x)}\right) P\left(\frac{3(1-x)}{2(2-x)}\right) \frac{Px}{(2-x)}$	$P\left(\frac{2-2x}{3-x}\right) p\left(\frac{1-x}{3-x}\right) p\left(\frac{2x}{3-x}\right)$	$p\left(\frac{1-x}{1+x}\right) p\left(\frac{x}{1+x}\right) p\left(\frac{x}{1+x}\right)$
K_c	$\frac{4x^2}{(1-x)^2}$	$\frac{4x^2V^2}{27(1-x)^4}$	$\frac{x^2V}{(1-x)^3}$	$\frac{x^2}{(1-x)V}$
K_p	$\frac{4x^2}{(1-x)^2}$	$\frac{16x^2(2-x)^2}{27(1-x)^4P^2}$	$\frac{x^2(3-x)}{P(1-x)^3}$	$\frac{Px^2}{(1-x^2)}$

Table : 8.2 Heterogeneous equilibria and equation for equilibrium constant (Equilibrium pressure is P atm)

	$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$			$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$			$NH_2CO_2NH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$		
Initial mole	1	0	0	1	1	0	1	0	0
Mole at equilibrium	(1-x)	x	x	(1-x)	(1-x)	2x	(1-x)	2x	x
Total moles at equilibrium (solid not included)	2x			(1+x)			3x		
Mole fraction	$\frac{x}{2x} = \frac{1}{2}$			$\left(\frac{1-x}{1+x}\right)$			$\frac{2}{3}$		
				$\left(\frac{2x}{1+x}\right)$			$\frac{1}{3}$		
Partial pressure	$\frac{P}{2}$			$P\left(\frac{1-x}{1+x}\right)$			$\frac{2P}{3}$		
				$P\left(\frac{2x}{1+x}\right)$			$\frac{P}{3}$		
K_p	$\frac{P^2}{4}$			$\frac{4P \cdot x^2}{(1-x^2)}$			$\frac{4P^3}{27}$		

Relationship between equilibrium constant and ΔG°

ΔG for a reaction under any condition is related with ΔG° by the relation, $\Delta G = \Delta G^\circ + 2.303 RT \log Q$

Standard free energy change of a reaction and its equilibrium constant are related to each other at temperature T by the relation, $\Delta G^\circ = -2.303 RT \log K$

For a general reaction $aA + bB \rightleftharpoons cC + dD$

$$K = \frac{(a_C)^c (a_D)^d}{(a_A)^a (a_B)^b}$$

Where a represent the activity of the reactants and products. It is unit less.

For pure solids and liquids: $a = 1$.

For gases: a = pressure of gas in atm.

For components in solution: a = molar concentration.

Le-Chatelier's principle

Le-Chatelier and Braun (1884), French chemists, made certain generalizations to explain the effect of changes in concentration, temperature or pressure on the state of system in equilibrium. When a system is subjected to a change in one of these factors, the equilibrium gets disturbed and the system readjusts itself until it returns to equilibrium. The generalization is known as **Le-Chatelier's principle**. It may be stated as :

"Change in any of the factors that determine the equilibrium conditions of a system will shift the equilibrium in such a manner to reduce or to counteract the effect of the change."

The principle is very helpful in predicting **qualitatively** the effect of change in concentration, pressure or temperature on a system in equilibrium.

Table : 8.3 The effect of varying conditions on the equilibrium $aA + bB \rightleftharpoons cC + dD$, $\Delta n = (c + d) - (a + b)$

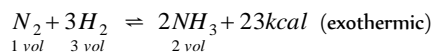
Change imposed on the system in equilibrium	Equilibrium position moves	Equilibrium constant	Any other points
Conc. of A and/or B increased	To right	No change	No change
Conc. of C and /or D increased	To left	No change	No change
Pressure increased	To right if $(c + d) < (a + b)$, i.e. $\Delta n = -ve$ To left if $(c + d) > (a + b)$, i.e. $\Delta n = +ve$ No change if $(c + d) = (a + b)$, i.e. $\Delta n = 0$	No change No change No change	Very little effect, if any, on reactions in liquid solution.
Temperature increased	To left if $\Delta H = -ve$ (exothermic) To right if $\Delta H = +ve$ (endothermic)	Value decreased Value increased	Equilibrium achieved faster
Addition of catalyst	No change	No change	Equilibrium achieved faster

Application of Le-Chatelier's principle

The Le-Chatelier's principle has a great significance for the chemical, physical systems and in every day life in a state of equilibrium.

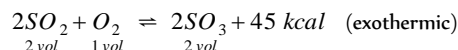
(i) Applications to the chemical equilibrium

(i) *Synthesis of ammonia (Haber's process)*



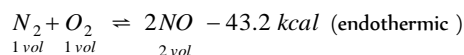
- (a) High pressure ($\Delta n < 0$)
- (b) Low temperature
- (c) Excess of N_2 and H_2
- (d) Removal of NH_3 favours forward reaction.

(ii) *Formation of sulphur trioxide*



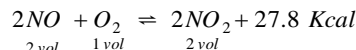
- (a) High pressure ($\Delta n < 0$)
- (b) Low temperature
- (c) Excess of SO_2 and O_2 , favours the reaction in forward direction.

(iii) *Synthesis of nitric oxide*



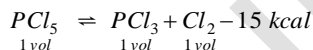
- (a) High temperature
- (b) Excess of N_2 and O_2
- (c) Since reaction takes place without change in volume i.e., $\Delta n = 0$, pressure has no effect on equilibrium.

(iv) *Formation of nitrogen dioxide*



- (a) High pressure
- (b) Low temperature
- (c) Excess of NO and O_2 favours the reaction in forward direction.

(v) *Dissociation of phosphorus pentachloride*



- (a) Low pressure or high volume of the container, $\Delta n > 0$
- (b) High temperature
- (c) Excess of PCl_5 .

(2) Applications to the physical equilibrium

(i) *Melting of ice (Ice - water system)*



(In this reaction volume is decreased from 1.09 c.c. to 1.01 c.c. per gm.)

- (a) At high temperature more water is formed as it absorbs heat.
- (b) At high pressure more water is formed as it is accompanied by decrease in volume.
- (c) At higher pressure, melting point of ice is lowered, while boiling point of water is increased.

(ii) *Melting of sulphur*: $S_{(s)} \rightleftharpoons S_{(l)} - x \text{ kcal}$

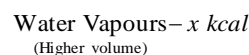
(This reaction accompanies increase in volume.)

- (a) At high temperature, more liquid sulphur is formed.

(b) At higher pressure, less sulphur will melt as melting increases volume.

(c) At higher pressure, melting point of sulphur is increased.

(iii) *Boiling of water (water- water vapour system)*

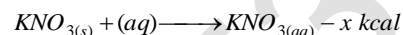


(It is accompanied by absorption of heat and increase in volume.)

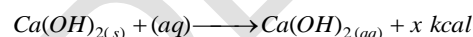
- (a) At high temperature more vapours are formed.
- (b) At higher pressure, vapours will be converted to liquid as it decreases volume.

(c) At higher pressure, boiling point of water is increased (principle of pressure cooker).

(iv) *Solubility of salts*: If solubility of a salt is accompanied by absorption of heat, its solubility increases with rise in temperature; e.g., NH_4Cl , K_2SO_4 , KNO_3 etc.

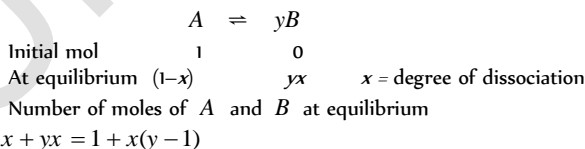


On the other hand if it is accompanied by evolution of heat, solubility decreases with increase in temperature; e.g., $CaCl_2$, $Ca(OH)_2$, $NaOH$, KOH etc.



Relation between vapour density and Degree of dissociation

In the following reversible chemical equation.



If initial volume of 1 mole of A is V, then volume of equilibrium mixture of A and B is, $= [1 + x(y - 1)]V$

Molar density before dissociation,

$$D = \frac{\text{molecular weight}}{\text{volume}} = \frac{m}{V}$$

Molar density after dissociation,

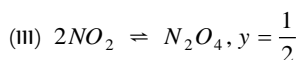
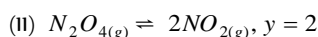
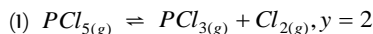
$$d = \frac{m}{[1 + x(y - 1)]V}; \frac{D}{d} = [1 + x(y - 1)]; x = \frac{D - d}{d(y - 1)}$$

y is the number of moles of products from one mole of reactant.

$\frac{D}{d}$ is also called **Van't Hoff factor**.

$$\text{In terms of molecular mass, } x = \frac{M - m}{(y - 1)m}$$

Where M = Initial molecular mass,
 m = molecular mass at equilibrium
 Thus for the equilibria



$$\therefore x = \frac{D - d}{d} \quad (\text{for I and II}) \quad \text{and} \quad x = \frac{2(d - D)}{d} \quad (\text{for III})$$

Also $D \times 2 = \text{Molecular weight (theoretical value)}$

$d \times 2 = \text{Molecular weight (abnormal value) of the mixture.}$

T Tips & Tricks

- ✍ Pure ice can be made to melt at a temperature slightly below 0°C by increasing the pressure. As the water so obtained on melting is below 0°C , it refreezes when pressure is reduced. It is called regelation of ice.
- ✍ Increase in external pressure always increases the boiling point and vice-versa.
- ✍ If the reaction is multiplied by 2, the equilibrium constant is squared.
- ✍ When a bottle of coca or beer is opened, the pressure is decreased and dissolved CO gas escapes out with a fizzle.
- ✍ Increase in pressure favours melting of ice into water
- ✍ Flash evaporation is a technique generally used for concentrating certain aqueous solutions which cannot be concentrated by normal boiling.
- ✍ Freeze drying is a technique where water is made to sublime off at a temperature below 0°C .