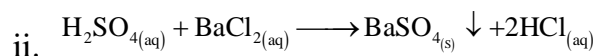
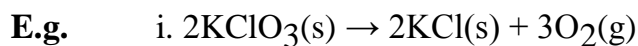


## Chemical Equilibrium -1

- 1. Irreversible Reactions:** In these reactions products cannot be converted into reactants under similar set of conditions. These reactions go to completion after certain length of time.



**2. Reversible reaction**

i. The reaction which can take place in both forward and backward directions under same conditions is called a reversible reaction.

ii. A reaction is said to be reversible, if the reaction mixture contains the reactants as well as the products and if both the forward and the backward reactions are taking place simultaneously under the given experimental conditions.

iii. Reactants change into products is known as forward reaction.

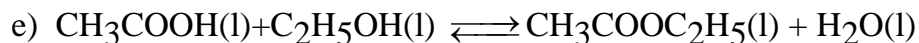
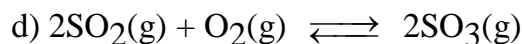
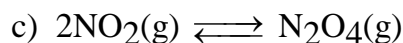
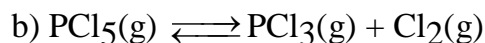
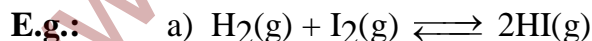
iv. Products change into reactants is known as reverse reaction (or) backward reaction.

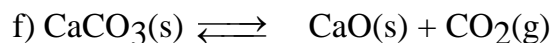
v. Reversible reactions are represented by writing a pair of half headed arrows pointing in opposite directions in between the reactants and products.



vi. A reversible reaction never goes to completion.

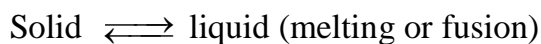
vii. Most of the reversible reactions are carried in the closed vessels.



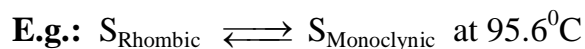


### 3. Physical Equilibrium

It is an equilibrium between the two phases of a given substance at constant temperature and pressure.



Similar equilibrium may occur between two different allotropic forms of the same substance



4. Based on the extent to which the reactions proceed, the state of chemical equilibrium in a chemical reaction may be classified into three groups.
- The reactions that proceed nearly to completion and only negligible concentrations of the reactants are left. In some cases, It may not be even possible to detect these experimentally.
  - The reactions in which only small amounts of products are formed and most of the reactants remain unchanged at equilibrium stage.
  - The reactions in which the concentrations of the reactants and products are comparable, when the system is in equilibrium.

The extent of reaction in equilibrium varies with the experimental conditions such as concentration of reactants, temperature, etc.,

Equilibrium involving ions in aqueous solutions is called as Ionic equilibrium

## Equilibrium in Physical Processes

### A) Solid-Liquid Equilibrium

**E.g.** Ice  $\rightleftharpoons$  water [kept in thermos flask at 273K and the atmospheric pressure]

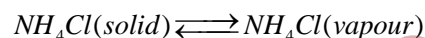
- The temperature at which the solid and liquid phases are in equilibrium is called the normal melting point **or** normal freezing point of the substance.

### B) Liquid-Vapour Equilibrium

- Water  $\rightleftharpoons$  water vapour [at atmospheric pressure and 100<sup>0</sup>C in a closed vessel]
- At one atmosphere pressure the temperature at which the liquid and vapour are in equilibrium is called normal boiling point of the liquid.

### C) Solid-Vapour Equilibrium

**Ex.** Solid iodine  $\rightleftharpoons$  iodine vapour



## 6. Equilibrium Involving Dissolution of Solid Or Gases In Liquids

### A) Solids in Liquids

In a saturated solution, a dynamic equilibrium exists between the dissolved solute molecules and undissolved solute molecules.

**E.g.1**  $sugar(solution) \rightleftharpoons sugar(solid)$ , and

The rate of dissolution of sugar = rate of crystallisation of sugar.

**E.g. 2**  $NaCl(s) + H_2O \rightleftharpoons NaCl(aq) \quad \Delta H > 0$

The dissolution of NaCl is favoured at high temperature as it is an endothermic process,

**Eg.3.**  $KOH(s) + H_2O \rightleftharpoons KOH(aq) \quad \Delta H < 0$

The dissolution of KOH is favoured at low temperature as it is an exothermic process.

## B) Gases in Liquids

This equilibrium follows Henry's law, which states that 'the mass of a gas dissolved in a given mass of a solvent at any temperature is proportional to the pressure of the gas above the solvent.'

For dissolution of solids in liquids, the solubility is constant at a given temperature.

For dissolution of gases in liquids, the concentration of a gas in liquid is proportional to the pressure (concentration) of the gas over the liquid.

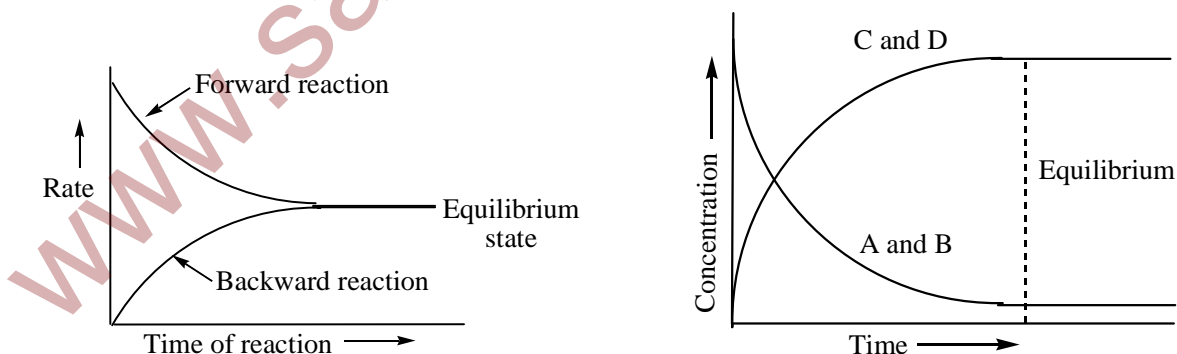
## 7. Chemical Equilibrium

**Equilibrium State:** The stage or state at which the rate of forward reaction is equal to the rate of the reverse reaction in a reversible reaction is known as the equilibrium stage or state.

Both the forward reaction and the reverse reaction continue to take place at equilibrium with equal rates. It is for this reason that reaction appears to have stopped.

Equilibrium is established in

- i) A reversible reaction
- ii) In a closed vessel
- iii) At constant temperature For  $A+B \rightleftharpoons C+D$

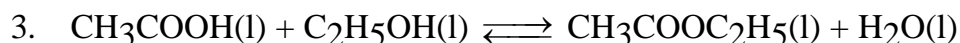
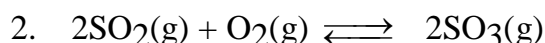
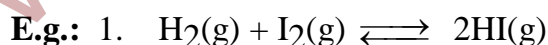


### Characteristics of Chemical Equilibrium

- i. The rate of the forward reaction is equal to the rate of the reverse reaction.
- ii. The concentrations of the reactants or the products remain unchanged with time.
- iii. The macroscopic properties like pressure, concentration, density, colour etc., remains unchanged with time.
- iv. A catalyst does not alter the state of equilibrium. It only speed up the attainment of equilibrium.
- v. At equilibrium the concentration of reactants may or may not be equal to the concentration of products.
- vi. At equilibrium state the value of Gibbs free energy change is zero i.e  $\Delta G=0$ .
- vii. Chemical equilibrium can be established from either side of the reversible reaction.
- viii. Chemical equilibrium is dynamic but not static in nature because both the forward reaction and the backward reaction continue to take place simultaneously with equal rates but never stops.
- ix. Change in temperature, pressure or concentration of substances may change the position of equilibrium.
- x. Chemical equilibrium can be homogeneous or heterogeneous,

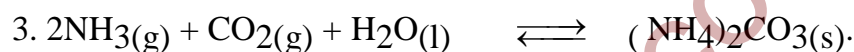
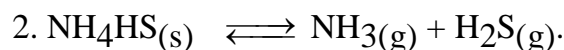
### Homogeneous Equilibrium

If the participating substances are in the same phase, the equilibrium is said to be homogeneous.



### Heterogeneous Equilibrium

If the participating substances are in two or more phases, the equilibrium is said to be heterogeneous. **Eg.1.**  $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$



### 8. Law Of Mass Action [proposed by Guldberg and Waage ]

Law of Mass action states that rate of a reaction is directly proportional to product of active masses of the reactants.

Active mass is taken as equal to the molar concentration expressed in **mole/litre** in the case of gases or substances in solution. The active mass of a solid (or) pure liquid is unity irrespective of its mass.

### 9. Equilibrium constant[ $K_C$ ] in terms of Molar concentration.

Let us consider a reversible reaction



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

#### Where

$k_f$  = forward reaction rate constant.

$k_b$  = backward reaction rate constant.

The equilibrium constant

$$= \frac{\text{product of the products concentration}}{\text{Product of the reactants concentration}}$$

Where [A], [B], [C], [D] are equilibrium concentrations of A, B, C and D respectively.

Units of  $K_C = (\text{mole/lit})^{\Delta n}$  where  $\Delta n = \text{mole of gaseous products} - \text{moles of gaseous reactants}$ .

**(b) Equilibrium Constant With Respect To Partial Pressure:**

Let us consider a reversible reaction



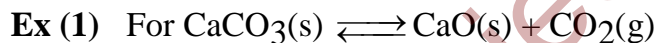
$$K_p = \frac{k_f}{k_b} = \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b}$$

Where  $P_A, P_B, P_C$  and  $P_D$  are the equilibrium partial pressures of A, B, C and D respectively.

Units of  $K_p = (\text{atm})^{\Delta n}$  where  $\Delta n = \text{mole of gaseous products} - \text{moles of gaseous reactants}$ .

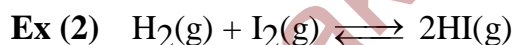
\*Equilibrium constant depends only on temperature and independent of other factors.

The active mass of a solid is unity whatever may be its mass.



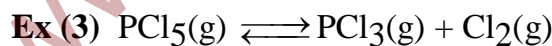
$$K_C = [\text{CO}_2], K_p = P_{\text{CO}_2}$$

**Units:**  $K_C = \text{mole/lit}, K_p = (\text{atm})$



$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}, K_p = \frac{P_{\text{HI}}^2}{P_{\text{H}_2} \cdot P_{\text{I}_2}}$$

**Units:**  $K_p$  &  $K_c$  has no units  $\because \Delta n = 0$



$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}, K_p = \frac{P_{\text{PCl}_3} \cdot P_{\text{Cl}_2}}{P_{\text{PCl}_5}}$$

**Units:**  $K_C = \text{moles/lit}, K_p = \text{atm}; \because \Delta n = 1$

### 10. Relationship Between $K_C$ & $K_P$

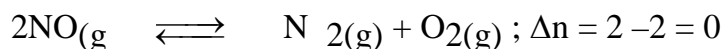
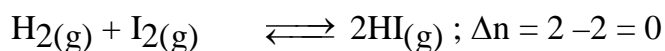
$$K_p = K_c (RT)^{\Delta n}$$

R = gas constant, T = absolute temperature

$\Delta n$  = change in number of moles

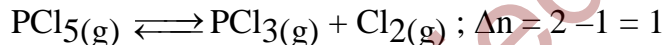
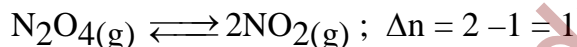
=  $n_P - n_R$  (no. of moles of gaseous products - no. of moles of gaseous reactants)

**Case (i):** If  $\Delta n$  is zero



$$K_p = K_c \text{ (or) } K_c = K_p$$

**Case (ii):** If  $\Delta n$  is positive



$$K_p = K_c (RT)^1 \text{ (or) } K_p > K_c$$

**Case (iii):** If  $\Delta n$  is negative



$$K_p = K_c (RT)^{-ve} \text{ (or) } K_p < K_c$$

**Note:** Law Of Massaction is applicable for chemical equilibria only.

### 11. Characteristics of equilibrium constant

The important characteristics of equilibrium constant are listed below.

a) The equilibrium constant has a definite value for every reaction at a particular temperature. It varies with a change in temperature. The value of equilibrium



constant increases with an increase in temperature for endothermic reactions. In case of exothermic reaction,  $K_C$  decreases with the rise of temperature.

b) The value of equilibrium constant is independent on the original concentration or pressure of the reactants at constant temperature.

c) The equilibrium constant has a greater dependence on the nature of reactants. However, it is independent of the presence of catalyst, as the catalyst affects the rates of forward and backward reactions to the same extent.

d) The value of equilibrium constant is a measure of the extent to which a reaction proceeds in the forward or backward directions. Larger  $K$  values denote greater extent of the reaction i.e. in forward direction. If  $K$  value is small, the backward reaction proceeds to a larger extent compared to the process in the forward direction.

e) Equilibrium constant is dependent on stoichiometric coefficients. If the equilibrium is reversed, the equilibrium constant is inverted. For a reversible reaction, the equilibrium constant for the forward reaction is inverse of the equilibrium constant for the reverse reaction.

### Equilibrium constants for a general reaction

Chemical equation	Equilibrium constant
$aA + bB \rightleftharpoons cC + dD$	$K_C$
$cC + dD \rightleftharpoons aA + bB$	$K'_c = (1/K_c)$
$naA + nbB \rightleftharpoons ncC + ndD$	$K''_c = (K_c)^n$

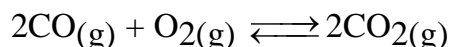
f) The equilibrium constant for an exothermic reaction decreases as the temperature increases.

The equilibrium constant for an endothermic reaction increases as the temperature increases.

## 12. Predicting the Direction of the Reaction

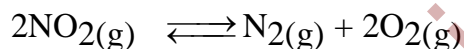
The numerical value of equilibrium constant is an important measure to predict information regarding the reversible reactions in the laboratory as well as in industries. Some applications of the equilibrium constant are discussed below.

**Application-1:** The magnitude of equilibrium constant helps to predict the extent of reaction. Larger the value of  $K$ , greater will be the equilibrium concentrations of the products relative to those of the reactants. The  $K_c$  for the reaction,



At 1000K is  $2.3 \times 10^{22} \text{ L mol}^{-1}$ . This high value of  $K$  denotes that the molar concentration of  $\text{CO}_2$  in the equilibrium mixture is quite large at 1000K.

The  $K_c$  for the reaction,



At 298K is  $6.7 \times 10^{-16} \text{ mol L}^{-1}$ .

This low value of  $K$  denotes that the molar concentration of  $\text{NO}_2$  in the equilibrium mixture is large, suggesting that  $\text{NO}_2$  is quite stable at room temperature.

If  $K > 10^3$ , products predominate over reactants at equilibrium. The reaction proceeds nearly to completion. If  $K < 10^{-3}$ , reactants predominate over products at equilibrium. The reaction hardly proceeds. If  $K$  is in the range  $10^{-3}$  and  $10^3$ , both reactants and products are present at equilibrium.

**Application-2:** The magnitude of equilibrium constant helps in predicting the direction of the reaction. The value of  $K$  helps to find the direction in which an arbitrary reaction mixture of reactants and products will proceed.

The ratio of concentration of products to that of reactants at any instant of time is called reaction quotient ( $Q$ ).

At equilibrium, the reaction quotient (Q) and the equilibrium constant (K) are equal.

If  $Q = K$ , the reaction is at equilibrium and no net reaction occurs.

If  $Q > K$ , the reverse reaction will proceed, predominantly, before attaining equilibrium.

If  $Q < K$ , the forward reaction proceeds predominantly, before attaining equilibrium.

A chemical reaction has tendency to form products if  $Q < K$  and to form reactants if  $Q > K$ .

**Application-3:** The value of equilibrium constant helps to calculate the equilibrium concentrations and partial pressures.

If the concentration or partial pressure of substances are known at equilibrium, the equilibrium constant of a reaction can be calculated. On the other hand, if the equilibrium constant is known, either concentrations or partial pressures of equilibrium mixture are also calculated.

**Application-4:** The spontaneous nature of the reaction can also be obtained using the value of equilibrium constant.

The standard free energy change  $\Delta G^0$  is related to the equilibrium constant ( $K_c$ ) as

$\Delta G^0 = -2.303RT \log K_c$ . The equation may also be written as

$$\ln K = -\Delta G^0 / RT \quad \text{or} \quad K = e^{-\Delta G^0 / RT}$$

The above equation helps to predict spontaneity in terms of the value of  $\Delta G^0$ . When  $K > 1$ , the standard free energy change  $\Delta G^0 < 0$ .

This implies a spontaneous reaction. The reaction proceeds in forward direction to such an extent that the products are present predominantly.

When  $K < 1$ , the standard free energy change  $\Delta G^0 > 0$ .

This implies a non-spontaneous reaction. The reaction proceeds in backward direction to such an extent that only small quantity of products are present.

One can generally expect that strong exothermic reactions and spontaneous redox reaction have large value of equilibrium constant. Such reactions go to near completion on their own.