

# CHEMICAL EQUILIBRIUM

## Types of Reactions

	Reversible	Irreversible
(i)	A reaction in which not only the reactants react to form products but also the products react to form reactants under the same conditions is called reversible reaction.	A reaction which cannot take place in the reverse direction is called an irreversible reaction
(ii)	A few examples are given below $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$	A few examples are given below $\text{AgNO}_3(\text{aq}) + \text{NaCl}(\text{aq}) \rightarrow \text{AgCl}(\text{s}) + \text{NaNO}_3(\text{aq})$ $\text{BaCl}_2(\text{aq}) + \text{Na}_2\text{SO}_4(\text{aq}) \rightarrow \text{BaSO}_4(\text{s}) + 2\text{NaCl}(\text{aq})$

## Characteristics of Equilibrium State

- ❖ A reaction (or a process) is said to be in equilibrium when the rate of forward reaction (process) becomes equal to the rate of backward reaction (process).
- ❖ At equilibrium, the concentration of each of the reactants and products become constant.
- ❖ Chemical equilibrium is dynamic in nature and not static *i.e.*, even after equilibrium is attained, the forward as well as the backward reaction take place but at equal speeds.
- ❖ A chemical equilibrium can be established only if none of the products is allowed to escape out.
- ❖ Chemical equilibrium can be attained from either direction.
- ❖ When reaction attains equilibrium at certain temperature and pressure,  $\Delta_r G = 0$
- ❖ Catalyst increases rate of reaction in forward as well as backward direction upto same extent.

## Law of Mass Action

It was put forward by Guldberg and Waage. It states that the rate at which a substance reacts is directly proportional to its active mass raised with suitable powers and hence the rate at which substances react together is directly proportional to the product of their active masses. Active mass means molar concentration.

## Law of Chemical Equilibrium

For the reaction  $aA(aq) + bB(aq) \rightleftharpoons xX(aq) + yY(aq)$

$$K_c = \frac{[X]^x [Y]^y}{[A]^a [B]^b}$$

Where  $K_c$  is called equilibrium constant at constant temperature.

## Types of Equilibrium Constants

$$K_c = \text{Equilibrium constant in terms of molar concentration} = \frac{[X]^x [Y]^y}{[A]^a [B]^b}$$

$$K_p = \text{Equilibrium constant in terms of pressure} = \frac{P_X^x \cdot P_Y^y}{P_A^a \cdot P_B^b}$$

$$K_x = \text{Equilibrium constant in terms of mole fraction} = \frac{(X_x)^x (X_y)^y}{(X_A)^a (X_B)^b}$$

## Unit of Equilibrium Constant

Unit of  $K_p = (\text{atm})^{\Delta n_g}$  (where  $\Delta n_g$  = change in gas mole of reaction)

Unit of  $K_c = M^{\Delta n_g}$

Unit of  $K_x$  = Unitless

**Relationship between  $K_p$  and  $K_c$ :**  $K_p = K_c (RT)^{\Delta n_g}$

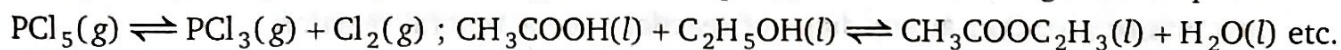
where  $R$  = universal gas constant,  $T$  = temperature

**Relationship between  $K_p$  and  $K_x$ :**  $K_p = K_x (P)^{\Delta n_g}$

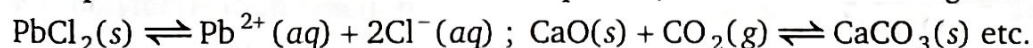
where  $P$  = equilibrium pressure in container.

## Types of Chemical Equilibria

❖ Homogeneous equilibrium. When in an equilibrium reaction, all the reactants and products are present in the same phase (*i.e.* gaseous or liquid), it is called homogeneous equilibrium.

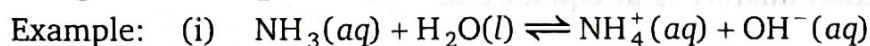


❖ Heterogeneous equilibrium. When in an equilibrium reaction, the reactants and the products are present in two or more than two phases, it is called a heterogeneous equilibrium.

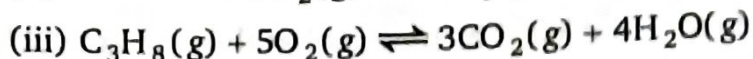
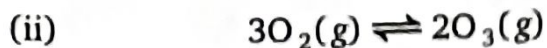


## Expression of $K$ for Equilibrium Reaction

❖ Homogeneous equilibria in gases







Equilibrium constant expression for them are

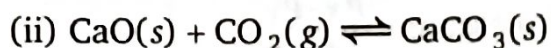
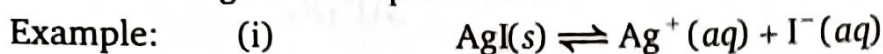
$$(i) \quad K_c = \frac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]} \quad ; \quad [ ] \text{ represents concentration in mol/litre at equilibrium.}$$

$$(ii) \quad K_c = \frac{[O_3]^2}{[O_2]^3} ; K_p = \frac{P_{O_3}^2}{P_{O_2}^3} \quad (iii) \quad K_c = \frac{[CO_2]^3[H_2O]^4}{[C_3H_8][O_2]^5} ; K_p = \frac{P_{CO_2}^3 \cdot P_{H_2O}^4}{P_{C_3H_8} \cdot P_{O_2}^5}$$

**Note:** Equilibrium constant for gaseous homogeneous equilibrium can be expressed in two ways  $K_p$  and  $K_c$ . This means value of equilibrium constant depends upon choice of standard state in which concentration of reactants and products are expressed.

### ❖ Heterogeneous equilibria

If reactants and products are present in two or more phases, the equilibria describing them is called heterogeneous equilibrium.



Equilibrium expression for them can be written as

$$(i) \quad K_c = [Ag^+(aq)][I^-(aq)] \quad (ii) \quad K_p = \frac{1}{P_{CO_2}} ; K_c = \frac{1}{[CO_2(g)]}$$

$$(iii) \quad K_p = P_{Br_2}(g) ; K_c = [Br_2(g)]$$

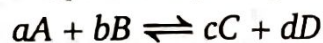
### Predicting the Extent of a Reaction

High value of equilibrium constant indicates that product(s) concentration is high and its low value indicates that concentration of the product(s) in equilibrium mixture is low.

Large values of  $K_p$  or  $K_c$  (larger than about  $10^3$ ), favour the products strongly. For intermediate values of  $K$  (approximately in the range of  $10^{-3}$  to  $10^3$ ), the concentrations of reactants and products are comparable. Small values of equilibrium constant (smaller than  $10^{-3}$ ), favour the reactants strongly.

### Predicting the Direction of the Reaction

For this purpose, we calculate the reaction quotient,  $Q$ . The reaction quotient is defined in the same way as the equilibrium constant (with molar concentrations to give  $Q_c$ , or with partial pressure to give  $Q_p$ ) at any stage of reaction. For a general reaction



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

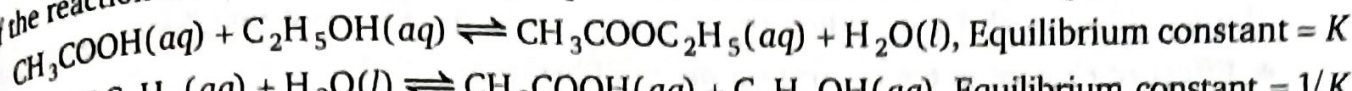
Then, if  $Q_c > K_c$ , the reaction will proceed towards direction of reactants.

If  $Q_c < K_c$ , the reaction will move towards direction of the products.

If  $Q_c = K_c$ , the reaction mixture is at equilibrium

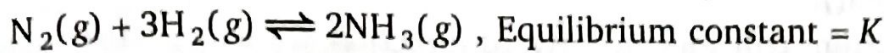
## Important Point about Equilibrium Constant

♦ If the reaction is reversed, the value of equilibrium constant is inverted e.g.,



♦ For  $\text{CH}_3\text{COOC}_2\text{H}_5(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3\text{COOH}(aq) + \text{C}_2\text{H}_5\text{OH}(aq)$ , Equilibrium constant =  $1/K$

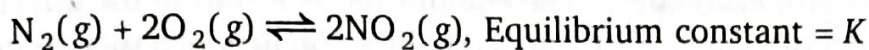
♦ If the reaction is divided by 2, equilibrium constant is the square root of the original e.g.,



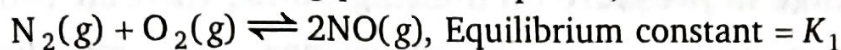
for  
then for  $\frac{1}{2}\text{N}_2(g) + \frac{3}{2}\text{H}_2(g) \rightleftharpoons \text{NH}_3(g)$ , Equilibrium constant =  $\sqrt{K}$

♦ If the reaction is multiplied by 2, equilibrium constant is the square of the original.

♦ If the reaction is written in two steps, equilibrium constant is equal to the product of the equilibrium constants of the step reactions e.g., if for



and for the same reaction taking place in steps i.e.,



and  $\text{NO}(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}_2(g)$ , Equilibrium constant =  $K_2$

then  $K = K_1 \times K_2$

♦ Effect of temperature: According to van't Hoff equation,  $\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$

where  $K_1$  and  $K_2$  are the equilibrium constants at temperatures  $T_1$  and  $T_2$  respectively and  $\Delta H$  is the molar enthalpy change in the temperature range  $T_1$  to  $T_2$ .

For exothermic reaction, as temperature increases  $K$  decreases.

For endothermic reaction, as temperature increases  $K$  increases.

## Relationship Between Degree of Dissociation ( $\alpha$ ) and Vapour Density

♦ For dissociation reaction:  $A_n(g) \rightleftharpoons nA(g)$

$$\begin{aligned} \text{Degree of dissociation } (\alpha) &= \frac{\text{No. of moles dissociated}}{\text{Total no. of moles taken}} \\ &= \frac{D - d}{d(n - 1)} = \frac{M_t - M_0}{M_0(n - 1)} \end{aligned}$$

where  $M_t$  = theoretical (calculated) molecular mass

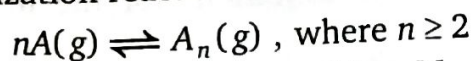
$M_0$  = observed (experimental) molecular mass

$D$  = theoretical vapour density,  $d$  = observed vapour density.

$n$  = number of moles of product formed from 1 mole reactant

$$\text{Density of gas mixture} = \frac{PM}{RT}$$

♦ For polymerization reaction



$$\alpha = \frac{D - d}{d\left(\frac{1}{n} - 1\right)} = \frac{M_t - M_0}{M_0\left(\frac{1}{n} - 1\right)}$$