CHAPTER 5

Chemical Equilibrium

Consider a reversible reaction,

$$aA + bB \underset{r_b}{\overset{r_f}{\rightleftharpoons}} cC + dD$$

AT EQUILIBRIUM STATE

Rate of forward reaction (r_f) = rate of backward reaction (r_b)

So, at equilibrium,

$$K_C = \frac{[C]^C[D]^d}{[A]^a[B]^b} = \frac{K_f}{K_b} \qquad \text{In terms of active mass}$$

$$K_P = \frac{[P_C]^C[P_D]^d}{[P_A]^a[P_B]^b} \qquad \text{In terms of partial pressure}$$

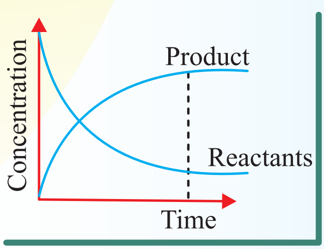
$$K_X = \frac{[X_C]^C[X_D]^d}{[X_A]^a[X_B]^b} \qquad \text{In terms of mole fraction}$$

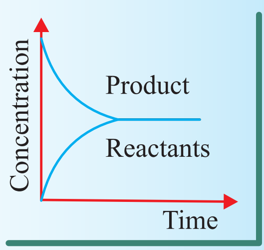
$$K_P = K_C(RT)^{\Delta n_g}$$

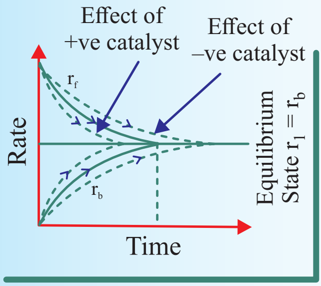
While determining Δn_g take only gaseous species.

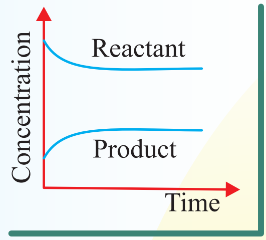
The active mass of solid & pure liquid is a constant quantity (unity) because it is an intensive property.

GRAPHS









Unit of Equilibrium constant:

$$K_C = (\text{mol } L^{-1})^{\Delta n_g};\ K_P = (\text{atm})^{\Delta n_g}$$

Application of K_C or K_P

- More is the value of K_P or K_C more is the extent of reaction.
- Stability of reactant increases when value of K decreases.
- Stability of Product increases when value of K increase.

CHARACTERISTICS OF EQUILIBRIUM CONSTANT

Predicting the direction of reaction: Reaction Quotient (Q) is expressed in the same way as for equilibrium constant, except that the concentrations may not necessarily be at equilibrium.

In general for the reversible reaction:

$$aA + bB \rightleftharpoons cC + dD$$

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

$$Q = \frac{[P_C]^C[P_D]^d}{[P_A]^a[P_B]^b} \text{ (in terms of pressure)}$$

If $Q = K_{eq}$ then system is in equilibrium

If $Q > K_{eq}$ then system proceed in backward direction to attain equilibrium.

If $Q < K_{eq}$ then system proceed in forward direction to attain equilibrium.

Degree of dissociation (α) $\dfrac{\text{No. of moles of reactant dissociated}}{\text{No. of mole of reactant present initially}}$

LE-CHATELIER'S PRINCIPLE

If a system at equilibrium is subjected to a change of any one of the factors such as concentration, pressure or temperature then the equilibrium is shifted in such a way as to nullify the effect of change.

Le-Chatelier's principle is applicable for both chemical and physical equilibrium.

CHEMICAL EQUILIBRIUM

Effect due to change in		$\Delta n_g = 0$ $A \rightleftharpoons B$	$\Delta n_g > 0$ $A \rightleftharpoons 2B$	$\Delta n_g < 0$ $2A \rightleftharpoons B$
Concentration	(i) ↑ [A] (ii) ↓ [A]	Forward direction Backward direction	Forward direction Backward direction	Forward direction Backward direction
Pressure	(i) ↑ in pressure (ii) ↓ in pressure	Unchanged Unchanged	Backward direction Forward direction	Forward direction Backward direction
Temperature	(i) ↑ in Endothermic (ii) ↑ in Exothermic	Forward direction Backward direction	Forward direction Backward direction	Forward direction Backward direction
Dissociation	(i) ↑ in pressure (ii) ↑ in volume	Unchanged Unchanged	Dissociation Decreases Dissociation Increases	Dissociation Increases Dissociation Decreases
Mixing of inert gas	(i) at constant P (ii) at constant V	Unchanged Unchanged	Dissociation Increases Unchanged	Dissociation Decreases Unchanged

Relationship between Equilibrium Constant K, Reaction Quotient Q and Gibbs Energy G

$\Delta G = \Delta G° + RT \ln Q$ …(i) where, $\Delta G°$ = Standard free energy difference between the products and reactant, T = Absolute temperature in kelvin, R = Universal gas constant.

At equilibrium, when $\Delta G = 0$ and $Q = K_c$, then equation (i) becomes

$$0 = \Delta G° + RT \ln K_c \quad \text{or} \quad \Delta G° = -RT \ln K_c \quad \text{or} \quad \ln K_c = (-\Delta G°/RT)$$

Case I: If $\Delta G° < 0$, then $(-\Delta G°/RT)$ is positive, i.e., $e^{(-\Delta G°/RT)} > 1$ hence $K_c > 1$, which implies a spontaneous reaction, i.e., the reaction proceeds in the forward reaction.

Case II: If $\Delta G° > 0$, then $(-\Delta G°/RT)$ is negative, i.e., $e^{(-\Delta G°/RT)} < 1$, hence $K_c < 1$, which implies a non-spontaneous reaction or the reaction proceeds in the forward direction to a very small extent i.e., only a very small quantity of product is formed.