CHEMISTRY

CLASS NOTES FOR CBSE

Chapter 07 Chemical and Ionic Equilibrium

01. Irreversible and Reversible Reactions

Chemical reactions can be classified as irreversible and reversible reactions. The reactions which move in one direction only are called **irreversible reactions.**

$$2HClO_3 \xrightarrow[Heat]{Mno_2} 2HCl + 3O_2$$

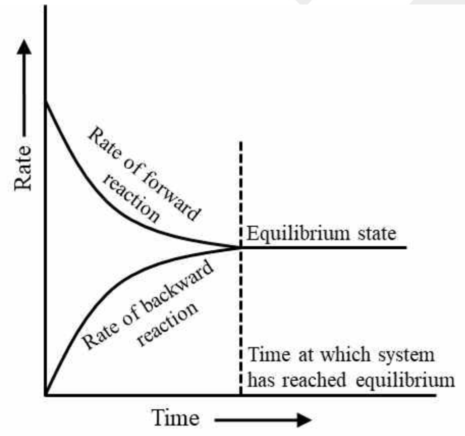
In these reactions products do not react to produce original reactants. In such reactions an arrow (→) is placed between reactants and products. $2HI \rightleftharpoons H_2 + I_2$ The chemical reactions which take place in both directions under similar conditions are called **reversible reactions.** In such reactions products also react with each other to produce reactants again. The sign (⇌) is placed between reactants and products.

02. Chemical Equilibrium

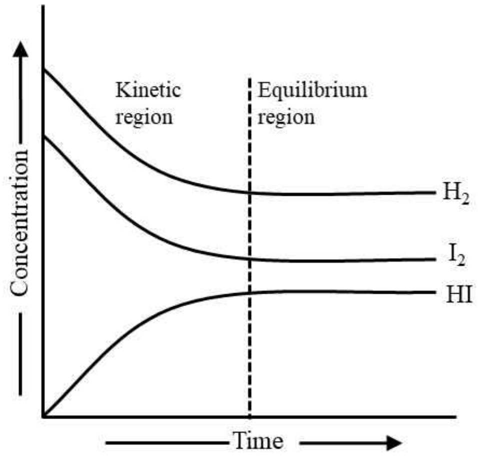
Chemical equilibrium is the most important characteristic property of reversible reactions. It is the state at which both forward and backward reactions occur at the same speed.

At equilibrium state,

Rate of forward = Rate of backward reaction



At equilibrium state, the concentrations of the reactants and products do not change with time. The following are the characteristics of the equilibrium state.



(i) It can be achieved only if the reversible reaction is carried out in a closed space.
(ii) It is characterised by constancy of certain properties such as concentration, pressure, density, colour, etc.
(iii) It can be attained from either side of the reaction.
(iv) It can be attained in lesser time by use of a catalyst.
(v) It is dynamic in nature, i.e. reaction does not stop, but both the forward and backward reactions move with the same speed.
(vi) Change of pressure, concentration or temperature favours one of the reaction and thus shifts the equilibrium point in one direction.

Reversible chemical reactions are classified into two types :

(i) **Heterogeneous reactions :** The reversible reaction in which more than one-phase is present.
(ii) **Homogeneous reactions :** The reversible reactions in which only one-phase is present. These are further classified into three types :
  (a) When there is no change in the number of molecules, i.e., $\Delta n = 0$.
  (b) When there is an increase in the number of molecules, i.e., $\Delta n = +ve$.
  (c) When there is a decrease in the number of molecules, i.e., $\Delta n = -ve$.

03. Law of Chemical Equilibrium (Application of Law of Mass Action)

Consider the general homogeneous reversible reaction in which equilibrium has been attained at a certain temperature.

$$m_1A_1 + m_2A_2 + m_3A_3 + \ldots \rightleftharpoons n_1B_1 + n_2B_2 + n_3B_3 + \ldots$$

Rate of forward reaction = Rate of backward reaction

$$k_f[A_1]^{m_1}[A_2]^{m_1}[A_3]^{m_3}\ldots = k_b[B_1]^{n_1}[B_2]^{n_1}[B_3]^{n_3}\ldots$$

or
$$\frac{\{[B_1]^{n_1}[B_2]^{n_2}[B_3]^{n_3}\ldots\}}{\{[A_1]^{m_1}[A_2]^{m_2}[A_3]^{m_3}\ldots\}} = \frac{k_f}{k_b} = K_c$$

The equilibrium constant, K_c, at a given temperature, is the ratio of rate constants of forward and backward reactions. It is also defined as the ratio between the molar concentrations of the products to the molar concentrations of the reactants with each concentration term raised to the power equal to stoichiometric coefficient in the balanced chemical equation.

The value of equilibrium constant is independent of the following factors :

(i) Initial concentration of reactants.

(ii) The direction from which equilibrium has been attained.

(iii) The presence of a catalyst.

(iv) The presence of inert materials.

The value of equilibrium constant depends upon the following factors :

(i) **The mode of representation of the reaction :** Consider the reversible reaction.

$$A + B \rightleftharpoons C + D$$

$$K_c = \frac{[C][D]}{[A][B]}$$

The products are made the reactants, i.e., the reaction is reversed.

$$C + D \rightleftharpoons A + B$$

$$K'_c = \frac{[A][B]}{[C][D]}$$

So, $$K'_c = \frac{1}{K_c}$$

(ii) **Stoichiometric representation of chemical equation :** The value of equilibrium constant will be numerically different if the reaction can be written with the help of two or more stoichiometric equations.

i.e., $2NO_2(g) \rightleftharpoons N_2(g) + 2O_2(g)$; $K_c = \dfrac{[N_2][O_2]^2}{[NO_2]^2}$

or $NO_2(g) \rightleftharpoons (1/2)N_2(g) + O_2(g)$; $K_c' = \dfrac{[N_2]^{1/2}[O_2]}{[NO_2]}$

Thus, $K_c' = \sqrt{K_c}$

(iii) **Use of partial pressures :** When the reactants and products are in gaseous state, the partial pressures can be used instead of concentrations at a definite temperature.

$m_1A_1 + m_2A_2 + m_3A_3 + \ldots \rightleftharpoons n_1B_1 + n_2B_2 + n_3B_3 + \ldots$

$$K_p = \frac{(P_{B_1})^{n_1}(P_{B_2})^{n_2}(P_{B_3})^{n_3}\ldots}{(P_{A_1})^{m_1}(P_{A_2})^{m_2}(P_{A_3})^{m_3}\ldots}$$

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

where, Δn = total number of molecules of products – total number of molecules or reactants.

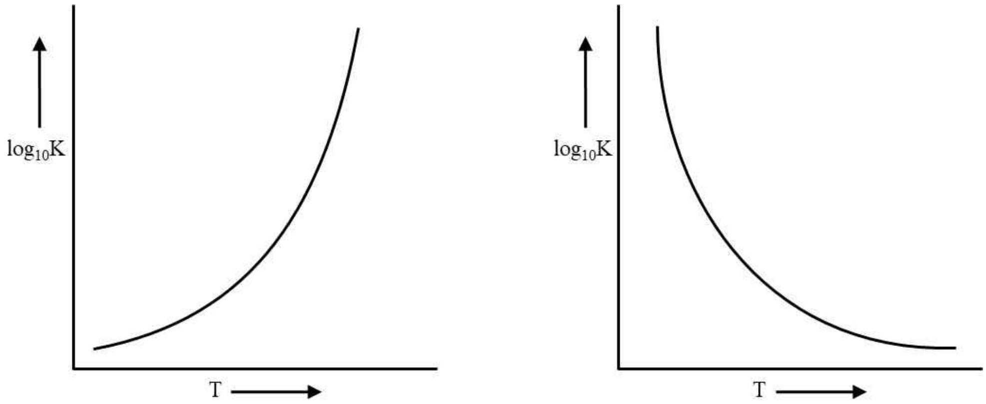
When $\Delta n = 0$, $K_p = K_c$;

$\Delta n = +ve$, $K_p > K_c$;

and $\Delta n = -ve$, $K_p > K_c$;

(iv) **Temperature :** The value of equilibrium constant changes with temperature. The values of equilibrium constants at two different temperatures are related by the following equation:

$$\log K_2 - \log K_1 = -\frac{\Delta H}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \quad T_2 > T_1$$



(a) Endothermic reaction (b) Endothermic reaction
(Plots or log K versus T)

When, $\Delta H = 0$, i.e. heat of reaction at constant volume is zero,
$K_2 = K_1$

When $\Delta H = +ve$, i.e., endothermic reaction,
$K_2 > K_1$

Units of equilibrium constant : Partial pressures are measured in terms of atmospheres. Therefore, units of K_p will be $(atm)^{\Delta n}$. Since, concentrations are measured in terms of moles per litre, the units of K_c are $(mol\ L^{-1})^{\Delta n}$.

K_p and K_c will be pure numbers when, $\Delta n = 0$.

04. Equilibrium Expressions for Some Reactions

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Initially	a	b	0
At equilibrium	(a−x)	(b−x)	(2x)

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x)^2}{(a-x)(b-x)} = \frac{4x^2}{(a-x)(b-x)}$$

$$K_p = \frac{[pHI]^2}{pH_2 \times pI_2} = \frac{(a+b)^2}{\left(\frac{a-x}{a+b}.P\right)\left(\frac{b-x}{a+b}.P\right)} = \frac{4x^2}{(a-x)(b-x)}$$

So, $K_c = K_p$

06. Relation Between Free Energy Change and Equilibrium Constant

$$\Delta G^\circ = -2.303\ RT \log Kp$$
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

When, ΔG° = −ve, the value of equilibrium constant will be large positive quantity and when ΔG° is positive, the value of K is less than 1, i.e., low concentration of products at equilibrium state.

08. Heterogeneous Equilibria

Law of mass action can also be applied to the heterogeneous system. In such systems the concentrations of pure solids and liquids are not considered in equilibrium expressions.

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

$$K_p = \frac{p_{CO} \times p_{H_2}}{p_{H_2O}} \quad \text{or} \quad K_c = \frac{[CO][H_2]}{[H_2O]}$$

i.e., concentration of C(*s*) is not taken into account.

09. Le Chatelier's Principle

It is a qualitative principle which can describe the effect of change in concentration, pressure and temperature on the reversible system whether physical or chemical. It is stated as "If the system at equilibrium is subjected to a change of any one of the factors such as concentration, temperature or pressure, the system adjusts itself in such a way as to annul the effect of that change." The following conclusions have been derived from this principle :

(i) Increase in concentration of any substance favours the reaction in which it is used up.
(ii) High pressure is favourable for the reaction in which there is decrease in volume.
(iii) A rise in temperature favours the endothermic reaction.

Effect of inert gas addition

Condition		Effect
$\Delta V = 0$, V = constant	$\Delta n = 0$, +ve or −ve	No effect
$\Delta V \neq 0$, $V \neq$ constant	$\Delta n = 0$	No effect
$\Delta V \neq 0$, $V \neq$ constant	$\Delta n > 0$	Forward shift
$\Delta V \neq 0$, $V \neq$ constant	$\Delta n < 0$	Backward shift

where, Δn = number of gaseous moles of product – number of gaseous moles or reactant