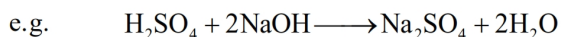# CHEMICAL EQUILIBRIUM

## IRREVERSIBLE AND REVERSIBLE REACTION

Irreversible Reaction

The chemical reaction which proceed in such a way that reactants are completely converted into products i.e. the reactions which move in one direction are called Irreversible Reaction.

e.g. $H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$

Reversible Reaction

The chemical reactions which proceed in both the direction and do not reach to completion are known as reversible reaction.

e.g. $3Fe + 4H_2O \underset{\text{Reverse}}{\overset{\text{Forward}}{\rightleftharpoons}} Fe_3O_4 + H_2$
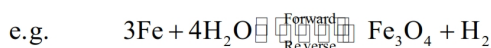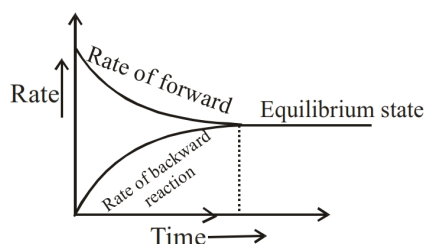
State of Chemical Equilibrium

Chemical equilibrium is that state at which both forward and backward reaction occurs at the same rate.

Thus at equilibrium state,

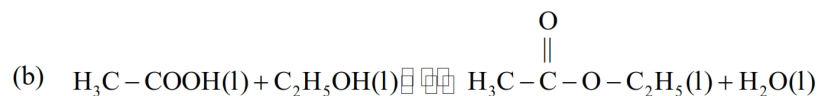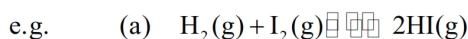Rate of forward reaction = Rate of backward reaction.

Characteristics of equilibrium state

(1) Equilibrium is dynamic in nature.

(2) At constant temperature, certain properties such as pressure, concentration, density or colour becomes constant.

(3) Equilibrium Can be attained from either side i.e. from the side of reactants or products.

$2HI \rightleftharpoons H_2 + I_2$

or $H_2 + I_2 \rightleftharpoons 2HI$

(4) Catalyst does not change the equilibrium state but it helps in attaining it rapidly.
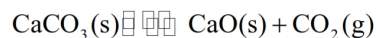
Homogeneous and Heterogeneous Equilibrium

Homogenous Reaction : The reversible reaction in which all the reactants and the products are in same physical state.

e.g. (a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

(b) $H_3C-COOH(l) + C_2H_5OH(l) \rightleftharpoons H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-O-C_2H_5(l) + H_2O(l)$

Heterogenous Reaction :

The reversible reaction in which more than one phase is present.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

LAW OF CHEMICAL EQUILIBRIUM AND EQUILIBRIUM CONSTANT

Let the reversible reaction may be represented as

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

(forward rate) $r_f = k_f[A][B]$

(backward rate) $r_b = k_b[C][D]$

where k_f and k_b are forward and backward rate constants respectively.

At equilibrium $\quad r_f = r_b$

$$k_f[A][B] = k_b[C][D]$$

$$\boxed{K = \frac{k_f}{k_b} = \frac{[C][D]}{[A][B]}}$$

$\Rightarrow$ Hence the equilibrium constant of a reversible reaction is the ratio of the velocity constants of the forward and the backward reaction and is denoted by K.

PROPERTIES OF EQUILIBRIUM CONSTANT

(a) It does not depend on initial concentration, because product will be formed in more amount when concentration of the ractants is increased, since the value of K remains constant.

(b) The value of K is constant at a fixed temperature but on increasing the temperature, value of K will change because concentration of reactants and products undergoing chemical reaction increases on increasing temperature.

(c) When the value of 'K_C' is more than 1.0 then product is formed in greater amount, i.e. forward reaction is faster but when it is less than 1.0 the product is formed in lower amount, i.e. backward reaction is faster.

(d) Value of K_C remains unaffected by the presence of catalyst, because catalyst has equal effect on the rates of forward and backward reactions.

(e) If the same reaction is brought to equilibrium by two different methods the values of equilibrium constant will be different under the two conditions.
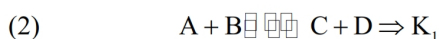
(1) $\quad N_2 + 3H_2 \rightleftharpoons 2NH_3 \Rightarrow K_1$

$$K_1 = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3 \Rightarrow K_2$$

$$K_2 = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{\frac{3}{2}}} \qquad\qquad \text{Therefore} \qquad \boxed{K_2 = \sqrt{K_1}}$$

(2) $\qquad A + B \rightleftharpoons C + D \Rightarrow K_1$

and for, $\quad C + D \rightleftharpoons A + B \Rightarrow K_2$

Than $\quad \boxed{K_2 = \frac{1}{K_1}}$

RELATIONSHIP BETWEEN K_p AND K_C

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

Δn = no. of moles of gaseous product − no. of moles of gaseous reactant

Three cases may arise

1st Case : when $\Delta n_g = 0$

$$K_p = K_C$$

IInd Case : when $\Delta n_g < 0 \left(\Delta n_g = -ve \right)$

$$K_p < K_C$$

IIIrd Case : when $\Delta n_g > 0 \left(\Delta n_g = +ve \right)$

$$K_p > K_C$$

APPLICATION OF LAW OF MASS ACTION ON HOMOGENOUS EQUILIBRIUM

(a) (1) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Assuming that 'a' mole of H_2 reacts with 'b' mole of I_2 in a closed container of 'V' litre. At equilibrium 'x' mole of H_2 reacts with 'x' mole I_2 to form '2x' mole of HI.

H_2	+	I_2	$\rightleftharpoons$	2HI	
a		b		0	......Number of initial molecules
(a–x)		(b–x)		2x	......Molecules at equlibrium
$\dfrac{a-x}{V}$		$\dfrac{b-x}{V}$		$\dfrac{2x}{V}$	......Active mass at equilibrium

$$K_C = \frac{4x^2}{(a-x)(b-x)}$$

Calculation of K_p :

H_2	+	I_2	$\rightleftharpoons$	2HI	
a		b		0	----- Number of initial mole
(a–x)		(b–x)		2x	----- Mole at equilibrium

Number of total mole in the reaction at equilibrium = a − x + b − x + 2x = a + b

$$K_p = \frac{(P_{HI})^2}{(P_{H_2})(P_{I_2})}$$

$$K_p = \frac{4x^2}{(a-x)(b-x)}$$

Therefore, $\boxed{K_c = K_p}$

Pressure does not appear in the equation of K_p. Therefore such a reaction does not depend on pressure.

LE CHATELIER'S PRINCIPLE

If a system at equilibrium is subjected to a change the equilibrium shifts in that direction where the effect of the brought change is nullified.

(1) <u>Change of Concentration :</u> In general, in a chemical equilibrium, increasing the concentrations of reactants results in shifting the equilibrium in favour of product and vice-versa.

(2) <u>Change of pressure :</u> It can effect the equilibrium when $\Delta n \neq 0$. An increase in pressure to a system at equilibrium, favours the reaction in that direction on where less number of moles of gases are formed and vice-versa.

(3) <u>Change in Temperature</u>

    (a) Endothermic Reaction

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$
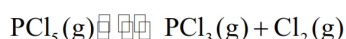
    Increase in temperature will shift the reaction towards right i.e product side.

    (b) Exothermic Reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) ; \quad \Delta H = -ve$$

    Increase in temperature will shift the reaction towards left.

EQUILIBRIUM CONSTANT AND ITS UNIT

Equilibrium constant can be dimensional if the standard state of the substance is not considered. In that case,

$$\text{Unit of } K_C = (Mol/L)^{\Delta n} \text{ and Unit of } K_p = (bar \text{ or } atm)^{\Delta ng}$$

In modern days we express equilibrium constants as dimensionless quantities by specifying the standard state of the reaction and product.

Example :

The standard state for pure gas is 1 bar and now the partial pressures are measured with respect to this standard.

Thus a pressure of 2bar in terms of this standard state is equal to, $\dfrac{2bar}{1bar} = 2$ a dimensionless number.