Chemical Equilibrium

Reversible reaction:– A reaction occurs in both the direction (direct and reverse) is called reversible reaction.

For example :– $A + B \rightleftharpoons C + D$

In the above reaction two steps are involved

Step I :– A and B react together and form the product C and D
i.e $A + B = C + D$
Reactant Product
(Direction of the reaction is direct)

Step II :– Again C and D react together and form the product A and B
$C + D = A + B$
Reactant Product
(Direction of the reaction is reverse)

Finally step I and step II may be written as

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

[Symbol ($=$) is replaced by ($\rightleftharpoons$)]

For example $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 92kJ$

or, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $\Delta H = -92kJ$

Irreversible Reaction:– Such type of reaction which go in one direction in order to complete the reaction are said to be irreversible reaction.

$$A + B = C + D$$

or $A + B \rightarrow C + D$

(Direction of the reaction is direct only)

Reaction between Acid and Base, Acid and metal - - - . etc, are irreversible reaction.

$Hcl\,(l) + NaOH\,(l) \rightarrow Nacl\,(s) + H_2O\,(l)$

$Zn\,(s) + H_2SO_4\,(l) \rightarrow ZnSO_4\,(s) + H_2(g)\uparrow$

Where l, g and s indicates liquid, gas and solid.

Chemical Equilibrium! - In a chemical reaction we see that reactant Combine to give products. As long as the reaction proced the decomposition of reactant Occurs with respect to time i.e. time and the concentration of reactants [R] decreases but Product [P] increases.

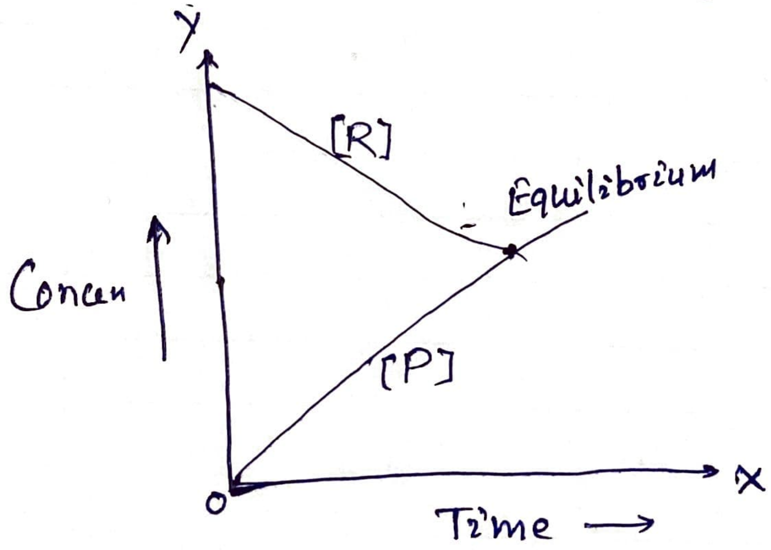
Finally, the rate of decrease in Concentration of reactant is equal to the rate of increase in the Concentration of Product with respect to time.

$$\underset{[R]}{\text{Reactant}} \xrightarrow{\text{Reaction}} \underset{[P]}{\text{Product}}$$

$$\text{or} \quad -\frac{dR}{dt} = +\frac{dP}{dt}$$

Or, we can say that reactants and Products are reacting with the same rate, This stage of chemical reaction is Called chemical equilibrium.

It may be shown by graph as follows,



For the term of reaction, it may be written as follows

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

(Reactant) (Product)

The above eqn includes two parts of reaction-direction One is direct and another is reverse.

Active Mass :—

We know that the activity (a) of the substance is directly proportional to its concentration C (in molarity)

$$a \propto C$$

$$a = f \cdot C$$

Where f is the constant called activity co-efficient. The value of f for dilute solutions, ideal gases and solids is unity. (i.e $f = 1$)

So, we can take concentration term molarity in place of activity.

Concentration term molarity or Active mass $= \frac{n}{V} = \frac{\text{no. of moles}}{\text{Volume}}$

(If, $V = 1$

Active mass = no. of moles.

So, Active mass of a substance may be defined as the number of moles per unit volume.

Representation of Active mass :— The active mass of a substance is represented by either concentration term C or Square Bracket.

C or [ ]

Let us consider a chemical reaction in which a mole of A b mole of B, c mole of C and d mole of D has participated in a reversible chemical reaction and its active mass maybe represented as,

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

Active Mass of A = $[A]^a$ or C_A^a

" " of B = $[B]^b$ or C_B^b

" " " C = $[C]^c$ or C_C^c

" " " D = $[D]^d$ or C_D^d

—x—

Law of Mass-action :-

The law of mass-action was proposed by Gulberg and Bage in 1807 to explain quantitatively occurrence of a chemical reaction.

The law of mass action may be stated as

"The rate of any chemical reaction is proportional to the product of active masses of reacting substances.

Let us consider the following reversible reaction.

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

If the reaction is on progress, the concentration of reactant decreases and that of product increase and at equilibrium, the rate of decrease ~~of~~ in reactant concentration becomes equal to that of product.

$$A + B \rightarrow C + D \quad \text{[Direct reaction]}$$

So, the rate of direct reaction $\propto [A][B]$

Rate of direct reaction $= K_1 [A][B]$

Where K_1 is rate constant of direct re^n

$$C + D \rightarrow A + B \quad \text{[Reverse reaction]}$$

Similarly the rate of reverse reaction $\propto [C][D]$

$= K_2 [C][D]$

K_2 is another rate constant of reverse reaction

At, the point of equilibrium,

Rate of direct reaction = Rate of reverse reaction

$$K_1 [A][B] = K_2 [C][D]$$

$$\frac{K_1}{K_2} = \frac{[C][D]}{[A][B]}$$

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

Where Kc is constans called equilibrium constant.

Significance of Kc (Equilibrium Constant) :-

The equilibrium Constant Kc depends on temperature. It tells about the extent of Completion of a reaction.

If Kc = 1, Equilibrium will be established, when half of the reaction will be Completed.

If Kc > 1, Equilibrium will be found when more than half of the Product is formed.

If Kc < 1, Equilibrium will be found when less than half of the product is formed.

If Kc is very high (10^{10}) Direct reaction will be almost Complete

If Kc is very low (10^{-10}) Reverse reaction will be almost Complete.

The Value of Kc also depends on mode and manner of Chemical reaction.

—x—

Relation between K_c, K_p and K_x : -

K_c is equilibrium Constant in term of molar Concentration, represented by [ ] squre bracket or C. In case of gaseous reaction it is difficult to Calculate molar Concentration. Hence Partial pressure is used in place of molar Concentration for gases and K_p is the equilibrium in terms of Partial Pressure and K_x is the equilibrium Constant in terms of mole fractions.

We know the gas equation,

$$PV = nRT$$ where R is a gas Constant.

$$\text{or, } P = \frac{n}{V} RT$$

$$= C\,RT \qquad \left[\because \frac{n}{V} = C \text{ or } [\;]\right]$$

$$= [\;].RT$$

It is Clear that Partial Pressure (P) is proportional to molar Concentration C or squre bracket, [ ].

Let us Consider the general equation,

$$aA + bB + \cdots\cdots = cC + dD + \cdots\cdots$$

Now the value of K_c on applying law of mass action may be given as

$$K_c = \frac{[C]^c \cdot [D]^d \times \cdots\cdots}{[A]^a \cdot [B]^b \times \cdots\cdots}$$

On replacing Concentration term by Patial Pressure we have,

$$K_p = \frac{P_C^c \times P_D^d \times \cdots\cdots}{P_A^a \times P_B^b \times \cdots\cdots}$$

$$= \frac{[C]^c\,(RT)^c \times [D]^d\,(RT)^d \times \cdots\cdots}{[A]^a\,(RT)^a \times [B]^b\,(RT)^b \times \cdots\cdots}$$

$$= \frac{[C]^c \times [D]^d \times (RT)^{c+d} \cdots}{[A]^a \times [B]^b \times (RT)^{a+b} \cdots}$$

$$K_p = K_c \times (RT)^{(c+d)-(a+b)}$$ [Applying law of indices

$$= K_c \cdot R \cdot T^{(c+d)-(a+b)}$$

$$= K_c \cdot RT^{\Delta n}$$ [R is gas Const.]

$$K_p = K_c \cdot R \cdot T^{\Delta n} \qquad \text{——— (1)}$$

Δn = Sum of the moles of Product − Sum of the moles of reactants

Now equation (i) is the desired relation between K_p and K_c.

We know that $p'V = n'RT$ and $PV = nRT$

So,
$$\frac{p'}{P} = \frac{n'}{n} = X$$

or $\frac{p'}{P} = X$ [Where X is mole fraction]

or, $p' = P \cdot X$

or $p' \propto X$

In a gaseous mixture, the Partial Pressure (p') of a Constituent is equal to the product of the mole fraction X of the Substance and total Pressure (P) of the mixture. or, $p_c^c = X_c^c \cdot P^c$ ......

Therefore
$$K_p = \frac{p_c^c \times p_D^d \times \cdots\cdots}{p_A^a \times p_B^b \times \cdots\cdots} = \frac{P^c \cdot X_c^c \times P^d X_D^d \times \cdots\cdots}{P^a \cdot X_A^a \times P^b X_B^b \times \cdots\cdots}$$

$$K_p = \frac{X_c^c \cdot X_D^d \times P^{(c+d+\cdots)}}{X_A^a \cdot X_B^b \times P^{(a+b+\cdots)}}$$

$$= \frac{X_c^c \cdot X_D^d}{X_A^a \cdot X_B^b} \cdot P^{(c+d+\cdots\cdots)-(a+b+\cdots\cdots)}$$

$$K_p = K_x \cdot P^{\Delta n} \qquad \text{——— ②}$$

Where Δn is the difference in the number of moles of Product and that of reactants.

From equation ① and ②

$$K_p = K_c \cdot R \cdot T^{\Delta n} = K_x \cdot P^{\Delta n}$$

or, $$K_c \cdot R \cdot T^{\Delta n} = K_p = K_x \cdot P^{\Delta n}$$

or, $$K_c \cdot R\, T^{\Delta n} = K_x\, P^{\Delta n}$$

or, $$K_x = K_c \cdot \frac{(RT)^{\Delta n}}{P^{\Delta n}} = K_c \cdot \left(\frac{RT}{P}\right)^{\Delta n}$$

or, $$K_x = K_c\, V_m^{\Delta n}$$

Where V_m is the Partial molar Volume of the gas in the gas mixture

Kinetic derivation of Law of mass-action

If substances are reacting it means their molecules are in Collision with each other. So the rate of reaction is proportional to the number of Collisions of the reactant molecules per second.

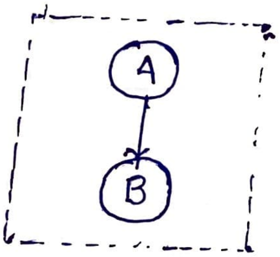
Let us Consider a homogeneous gas Phase reaction of A and B.

If we have One molecule of A and One molecule of B per unit volume, then there Can be only One Collision between them per second
i.e. 1 × 1 = 1

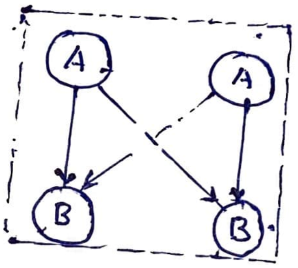
If the number of molecules of A and B are two each, then the number of Possible Collisions between them per second = 2×2 = 4.

If we have three molecules of A and two molecules of B per unit volume, then the number of possible Collision between them per Second = 3×2 = 6

If the number of molecules of A and B are three each, then the number of Possible Collision between them per Second = 3 × 3 = 9 and so on.



1 × 1 = 1



2 × 2 = 4

Therefore it is Concluded that the number of Collisions between the Reactant molecules depends upon the product of the number of reactant molecules per unit Volume. It means the prouct of the molar Concentration of reactant molecules. Thus it tells that the rate of reaction is definietly proportional to the product of molar concentration of reacting molecules.

Hence this statement is same to the statement of the Law of mass-action.