Degree Part I Chem (Hons)

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Paper - I A

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TOPICS - Chemical Equilibrium

Law of Mass-action :-

The rate at which a substance reacts is proportional to its active mass and the rate of chemical reaction is proportional to the product of the active masses of the reactants.

(ACTIVE-MASS mass means molar concentration i.e. number of moles dissolved per litre of the solution.

Example :- If x g NaOH are dissolved in V litres of the solution, then concentration of NaOH solution

$= x$ g in V litres

$= \frac{x}{40}$ moles in V litres

$= \frac{x}{40 \times V}$ moles per litre

This is the active mass of given NaOH solution

$$[NaOH] = \frac{x}{40 \times V} M$$)

Mathematical Expression :-

On consider the reaction

$$A + B \longrightarrow \text{products}$$

According to Law of mass-action,

Rate at which A reacts $\propto [A]$

Rate at which B reacts $\propto [B]$

Rate at which A and B reacts together $\propto [A][B]$

$= K[A][B]$

where K is a proportionality constant or called velocity constant and is called equilibrium constant,

Again consider the more general reversible reaction

$$aA + bB + cC + \cdots \rightleftharpoons xX + yY + zZ + \cdots$$

Applying Law of Mass action as before

we get

$$\frac{[X]^x [Y]^y [Z]^z}{[A]^a [B]^b [C]^c} = K \text{ or } K_c$$

where K or K_c = Equilibrium const at const tempr.

Now, chemical equilibrium expressed in words as,

" The product of molar concentrations of the products each raised to the power equal to its coefficient divided by the product of molar concentrations of the reactants each raised to the power equal to its coefficient is constant at constant temperature and is called Equilibrium Constant.

Characteristics of Equilibrium constant :-

(i) It has a definite value for every chemical reaction at a particular temperature.

(ii) It is independent of the initial concentrations of the reacting species

(iii) It changes with the change in temperature

(IV) It depends on the nature of the reaction.

Condition of this process as:-

1. System and surroundings have to be in thermal condition.
2. Piston should be frictionless
3. Process has to be extremely slow
4. No loss of heat should take place through conduction or radiation.

CHEMICAL EQUILIBRIUM: (Equilibrium constant)

Law of chemical equilibrium is a result obtained by applying law of mass action to a reversible reaction in equilibrium

On consider the general reversible reaction

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

At equilibrium active masses of A, B, C and D are designated as [A], [B] [C] and [D] respectively. On Applying Law of mass action

Rate at which A and B react together

i.e. rate of forward reaction $\propto [A][B]$

$= K_f [A][B]$

Where K_f = velocity constant for the forward rx^n.

Similarly, rate at which C and D react together,

i.e. rate of backward reaction $\propto [C][D]$

$= K_b [C][D]$

Where K_b = velocity constant for the backward reaction

At equilibrium,

Rate of forward reaction = Rate of backward reaction

$$K_f [A][B] = K_b [C][D]$$

$$\text{or, } \frac{K_f}{K_b} = \frac{[C][D]}{[A][B]} = K \text{ or } K_c$$

At constant temperature, as K_f and K_b are constant, therefore at constant temperature $\frac{K_f}{K_b} = K$ or K_c is also constant

Again consider the following reaction

$$2A + 3B \longrightarrow \text{Products}$$

It can be written as

$$A + A + B + B + B \longrightarrow \text{Products}$$

Rate at which first A reacts $\propto [A]$

Rate at which Second A reacts $\propto [A]$

$\therefore$ Rate at which both A react $\propto [A][A]$

$\propto [A]^2$

Similarly, rate at which three B reacts $\propto [B][B][B]$

$\propto [B]^3$

$\therefore$ Rate of reaction between A and B $\propto [A]^2 [B]^3$

Hence for the general reaction

$$aA + bB + cC + \dots \longrightarrow \text{Products}$$

Therefore, Rate of reaction $\propto [A]^a [B]^b [C]^c \dots$

Thus, Law of mass action may be defined in a more general way as "The rate of a reaction is proportional to the product of active masses of reactants each raised to the power equal to its coefficient ~~each raised to the power~~ as represented by balanced chemical equation."

Reversible process :-

It is a process whose direction can be returned to its original position by inducing infinitesmal changes to some property of the system via its surrondings. Throughout the ~~en~~ entire reversible process, the system is in thermodynamic equilibrium with its surrondings.

Examples of reversible process are uniform and slow expansion or compression of a fluid, such as fluid flows in a well designed turbine.