

Equilibrium:-

→ It is a state of reversible reaction in which there is no change in the properties of the system.

OR,

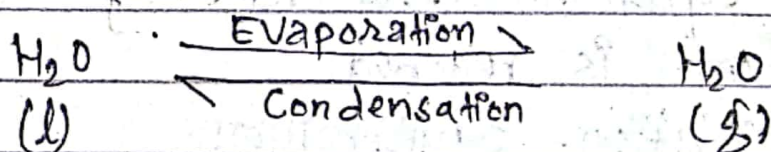
It is the state of reversible reaction in which rate of forward reaction becomes equal to rate of backward reaction. It involves two opposing process.

If the opposing process involves physical changes then equilibrium is called physical equilibrium.

If the opposing process involves chemical changes then equilibrium is called chemical equilibrium.

Physical equilibrium:-[i] Liquid-Vapour equilibrium:-

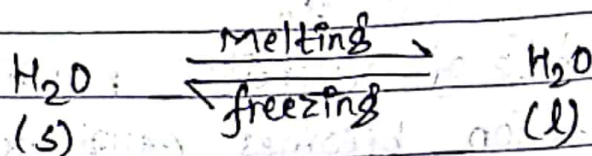
→ Liquid-Vapour system in a closed vessel at constant temperature is a good example of physical equilibrium.



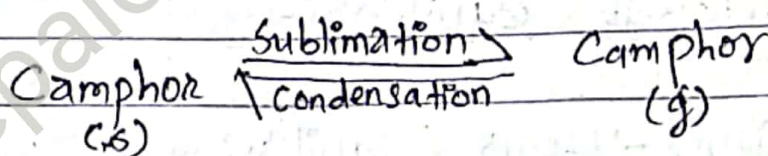
Here, two opposing process are evaporation & Condensation, When the rate of evaporation is equal to rate of Condensation, then equilibrium is reached.

(ii) Solid-Liquid equilibrium:-

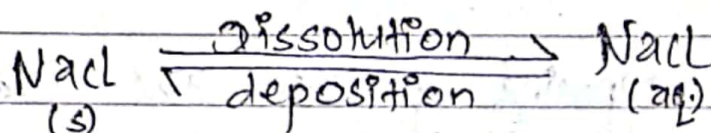
→ A mixture of ice & water at 0°C & 1 atm., pressure in a perfectly insulated vessel represents Solid-liquid equilibrium.



Here, two opposing process involved are melting & freezing. When the rate of melting of ice becomes equal to rate of freezing of water, then equilibrium is reached.

(iii) Solid-gas equilibrium:-

Here, two opposing process involved are Sublimation & Condensation. When the rate of Sublimation becomes equal to the rate of Condensation, then equilibrium is reached.

(iv) Solute-solution equilibrium:-

Here, two opposing process involved are dissolution & deposition. When the rate of dissolution becomes equal to rate of deposition then equilibrium is reached.

Differentiate between reversible & irreversible reaction:-

Reversible reaction	Irreversible reaction
i) The reaction in which reactants react to give product & vice-versa under suitable condition is called reversible reaction.	i) The reaction in which reactants react to give product but product don't react to give reactant is called irreversible reaction.
ii) It maintains equilibrium.	ii) It doesn't maintain equilibrium.
iii) It is denoted by double head arrow. i.e., \rightleftharpoons	iii) It is denoted by single head arrow. i.e., \longrightarrow
iv) It takes place in both directions.	iv) It takes place in only one direction.
v) It follows Le-chatelier's principle & Law of mass action.	v) It doesn't follow Le-chatelier's principle & Law of mass action.

Law of mass action:-

→ It states that, "The rate at which a substance reacts is directly proportional to its active mass, and the rate of chemical reaction is directly proportional to product of active masses of the reactants".

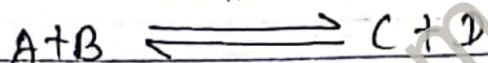
Active mass is represented by writing the species

inside square bracket $[]$ or some times by c .

The term active mass means molar concentration
i.e. number of moles per litre volume.

$$\text{i.e., } c = \frac{\text{no. of moles}(n)}{\text{volume}(V)}$$

Let us consider a reaction;



According to law of mass action;

$$\text{Rate of forward reaction} \propto [A][B]$$

$$\text{Rate of forward reaction} = K_f [A][B]$$

Where, K_f is the velocity constant for forward reaction.

And,

$$\text{Rate of backward reaction} \propto [C][D]$$

$$\text{Rate of backward reaction} = K_b [C][D]$$

Where, K_b is the velocity constant for backward reaction.

At equilibrium;

Rate of forward reaction = Rate of backward reaction

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

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

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

Where, K is a constant known as equilibrium constant & it is defined as the ratio of velocity constant for forward reaction to velocity constant for backward reaction.



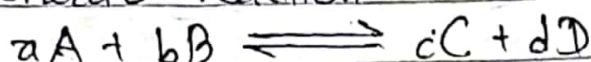
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OR//

It can be defined as the ratio of product of active mass of products to that of the reactants.

For a general reaction



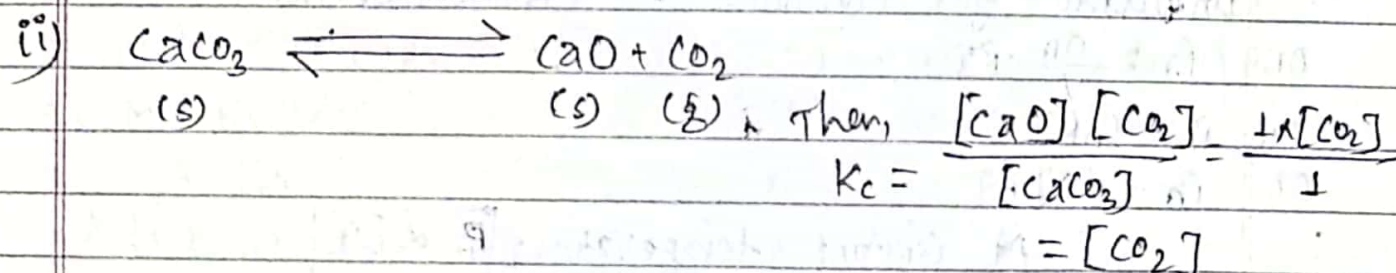
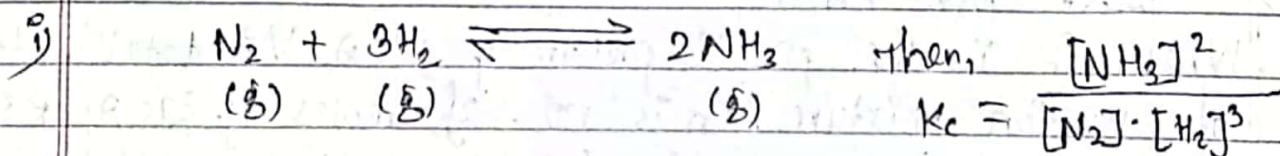
Then,

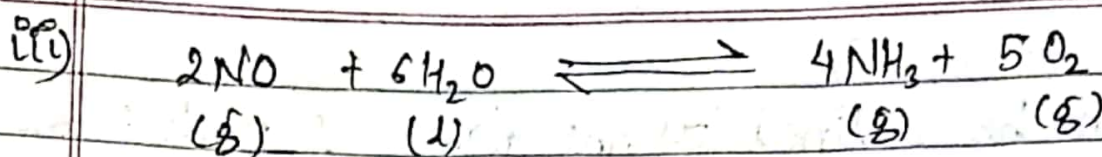
$$K = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}$$

Characteristics of equilibrium constants

- i) It is a constant for particular reaction at a particular temperature.
- ii) It doesn't depend upon the concentration of reactants.
- iii) It doesn't depend upon use of catalyst.
- iv) It depends upon temperature.

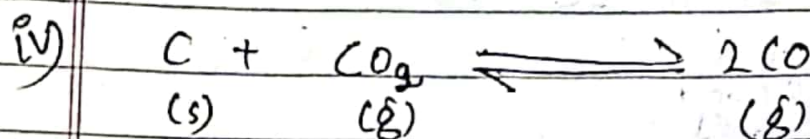
For Examples:-





Then,

$$K_c = \frac{[\text{NH}_3]^4 \cdot [\text{O}_2]^5}{[\text{NO}]^2 \cdot [\text{H}_2\text{O}]^6} = \frac{[\text{NH}_3]^4 [\text{O}_2]^5}{[\text{NO}]^2} \quad \#$$



$$\text{Then, } K_c = \frac{[\text{CO}]^2}{[\text{C}] [\text{CO}_2]} = \frac{[\text{CO}]^2}{[\text{CO}_2]}$$

Equilibrium Constant in terms of partial pressure:-

→ For gaseous reaction molar concentration is directly proportional to partial pressure. so, equilibrium constant can be expressed in terms of partial pressure.

We have,

From Ideal gas equation;

$$pV = nRT$$

$$\Rightarrow \text{ } \cdot p_A V = n_A RT$$

Where, p_A is the partial pressure of gas A, V is total volume of reaction mixture, n_A is no. of moles of gas A; R is universal gas constant & T is temperature.

$$\text{Or, } p_A = \frac{n_A}{V} \cdot RT$$

$$\text{Or, } p_A = C_A RT$$

$$\text{Or, } p_A = [A] RT$$

At constant temperature; $p_A \propto [A]$

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Relation between K_p & K_c

→ Let us consider general gaseous reaction:



The equilibrium constant in terms of concentration is written as:

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \text{--- (i)}$$

&

Equilibrium constant in terms of partial pressure is written as:

$$K_p = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b} \quad \text{--- (ii)}$$

Where, P_A, P_B, P_C & P_D are partial pressure of gas A, B, C & D respectively.

Now, from ideal gas equation:-

$$PV = nRT$$

$$\text{or } PAV = nART$$

$$\text{or } P_A = \frac{n_A}{V} RT$$

$$\text{or } P_A = [A]RT \quad \text{Similarly; } P_B = [B]RT \quad \& \quad P_C = [C]RT \quad \& \quad P_D = [D]RT$$

Putting value of P_A, P_B, P_C & P_D in eqⁿ (ii)

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

$$\Rightarrow K_p = K_c \cdot (RT)^{(c+d)-(a+b)}$$

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

Where,

$$\Delta n = (c+d) - (a+b) \quad \text{OR,}$$

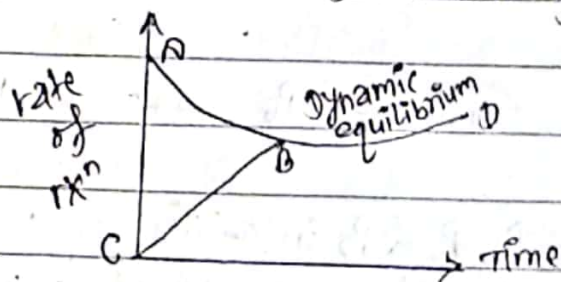
$\Delta n = \text{Change in no. of moles of products \& reactant}$

Characteristics of Equilibrium:-

- 1) At Equilibrium Constant of reactant & product remain constant.
- 2) Equilibrium is dynamic in nature.
- 3) Equilibrium maintain only in a closed vessel.
- 4) At equilibrium there is no effect of Catalyst.
- 5) It can be maintained from either direction.
- 6) The equilibrium is characterised by a constant which is known as equilibrium constant.

Dynamic nature of equilibrium:-

- ↳ In the reversible reaction, the rate of forward reaction is high at the beginning. As the reaction proceeds, the concentration of reactant decreases and rate of forward reaction also. On other hand the concentration of product increases as the rate of backward reaction also increases attains a limiting value as shown in figure:-

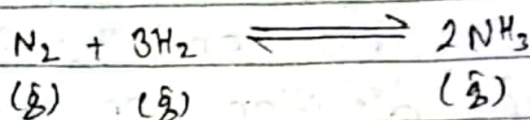


Finally, a state come at which rate of forward reaction becomes equal to rate of backward reaction. Due to equal rates there is no net change in the concentration of reactant & product but reaction doesn't stop. So, the equilibrium is dynamic in nature.

Types of equilibrium:-

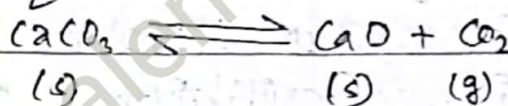
(i) Homogenous equilibrium:-

→ The equilibrium in which all the reactants & products are present in the same phase is known as homogenous equilibrium.



(ii) Heterogenous equilibrium:-

→ The equilibrium in which the reactants & products are present in the different phase is known as heterogenous equilibrium.



Le-Chatelier's principle:-

→ It states, "If a system in equilibrium is subjected to change in concentration, temperature or pressure, then equilibrium shifts in the direction so as to neutralize the effect of change."

(i) Effect of Concentration:-

→ On increasing concentration, equilibrium shifts in the direction where increased concentration is consumed. i.e., on increasing concentration of reactants equilibrium shifts in forward direction. Similarly, on increasing concentration of products

equilibrium shifts in backward direction.

(ii) Effect of temperature:-

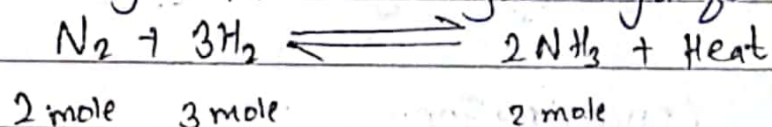
→ On increasing temperature, equilibrium shifts in the direction of where increased temperature is absorbed. Thus, endothermic reaction shifts in forward direction on increasing temperature. Similarly, exothermic reactions shift in backward direction on increasing temperature.

(iii) Effect of Pressure:-

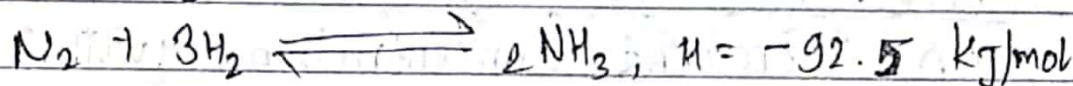
→ On increasing pressure, the equilibrium shifts in the direction where volume or no. of moles decrease. i.e., Equilibrium shifts in direction where less no. of moles or molecules are present.

Applications of Le-Chatelier's principle in Chemical Equilibrium

(i) Formation of Ammonia from Hydrogen & Nitrogen:-



2 mole 3 mole 2 mole



2) Effect of Concentration:-

→ On increasing concentration of hydrogen & Nitrogen, equilibrium shifts in the forward direction.

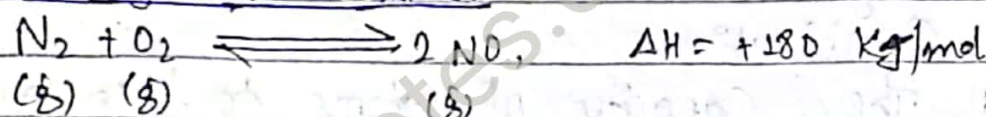
(b) Effect of temperature:-

→ On increasing temperature of H_2 & N_2 , equilibrium shifts in backward direction.

(c) Effect of pressure:-

→ On increasing pressure of H_2 & N_2 equilibrium shifts in forward direction.

(ii) Formation of Nitric oxide:-

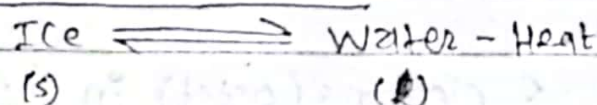


(iii) Formation of Sulphur trioxide:-

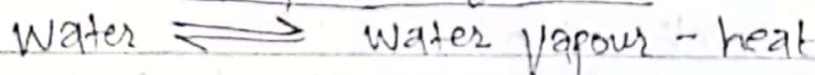


Application of Le-Chatelier's principle in physical equilibrium:-

(a) Ice-water equilibrium:-



(b) Water-water vapour equilibrium:-



(c) Gas-gas in solution:-

