Chemical equilibrium (ৰাসায়নিক সাম্যাৱস্থা)

- Forward Reaction
- Backward Reaction
- Irreversible Reaction
- Reversible Reaction
- Types of chemical equilibrium
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- Characteristics of chemical equilibrium
- Law of mass action and equilibrium constant
- Relation between kp and kc
- La chatelein Principle

Forward Reaction: A forward reaction in which products are produced from reactants and it goes from left to right in a reversible reaction.

Example: $NH_2 + 3H_2 \longrightarrow 2NH_3$

Backward Reaction: A backward reaction is a reaction in which reactants are produced from products and it goes from right to left in a reversible reaction.

Example: $2NH_3 \longrightarrow NH_2 + 3H_2$

Irreversible Reaction: When an a chemical reaction all the reactants are converted to the products, or in other words the reaction proceeds in one direction, then the reaction is called an Irreversible Reaction.

Example: $2KClO_3 \xrightarrow{\Delta} 2KCl_{(s)} + 3O_{2(g)}$

$CaCO_3 \longrightarrow CaO + CO_2$

Reversible Reaction: When a chemical reaction proceeds both in forward and backword direction, then the reaction is called reversible reaction.

Example: $H_2 + I_2 \rightleftharpoons 2HI$

$NH_4Cl_{(s)} \rightleftharpoons NH_{3(g)} + HCl_{(g)}$

$CuSO_4 . 5H_2O_{(s)} \rightleftharpoons CuSO_{4\,(s)} + 5H_2O_{(g)}$

chemical equilibrium: In case of reversible reactions the reactants react with one another to produce some products and again these products reacts with one another to produce the reactants back. So in these case when the reaction among the reactants back. SO in these case when the reaction among the reactants proceeds, after some time the rate of reaction of the reactants to produce the Products equals to the rate of reaction of the products to Produce the reactants back. The state is called chemical equilibrium.

Two types of chemical equilibrium :

1. Homogeneous equilibrium (same state)
2. Heterogeneous equilibrium (Different state)

When the rate of forward reaction is equal to that of the backward reaction then the state is known as chemical equilibrium.

Homogeneous equilibrium: The chemical equilibrium in which all reactants and products are in the same physical state is called homogeneous equilibrium.

Example: ① $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$;

All products and reactants are in gaseous state.

② $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Gaseous state

③ $CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$

All reactants and products are in liquid state.

Heterogeneous equilibrium: A chemical equilibrium in which at least one product or reactant is in different physical state (or phase) than the others. is called a heterogeneous equilibrium.

Example: ① $CaCO_3(s) \overset{\Delta}{\rightleftharpoons} CaO(s) + CO_2(g)$

Two components are in solid state and one component is gaseous state.

② $3Fe_{(s)} + 4H_2O_{(g)} \overset{\Delta}{\rightleftharpoons} Fe_3O_{4(s)} + 4H_{2(g)}$

One product and one reactant in solid state but one ~~one~~ reactant and one product in gaseous state.

Characteristics of chemical equilibrium:

There are some characteristics of chemical equilibrium. They are:

1. Reversibility of Reaction: chemical equilibrium is related only to reversible reactions. It is not applicable to irreversible reaction.
2. Stability of equilibrium: If the external conditions (Pressure, temperature and concentration) are not changed, the system will stay there forever.
3. Easy approachability from both sides: The equilibrium can be attained from both directions.
4. Incompleteness of reaction: A reversible reaction is never complete, because due to backward reaction, the initial ~~reactions~~ reactants are always reproduced.
5. Ineffectiveness of catalysts: The catalysts have no effect no chemical equilibrium. catalysts speed up both the forward and backward reaction to the same degree.
6. Closed system: It is only attained in closed system, so that part of any product or reactant cannot escape out.
7. Dynamic nature: Chemical equilibrium is dynamic. Although apparently reaction stops when chemical equilibrium is attained.

But in reality the forward and backward reactions continue to occur but since their rates are equal. no change is visible.

Law of mass action and equilibrium constant:

In 1867 mathematician C.M Guldberg and chemist P. Waage of Norway invented a law regarding the rate of chemical reactions, which became known as law of mass action.

The law is as follows:

At a constant temperature the rate of a chemical reaction at any instant is directly proportional to the active mass (i.e molar concentration or partial pressure) of the reactants at that instant participitating in the reaction.

Equilibrium constant:

Let us consider following general equation reaction

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

Reactant   Product

According to the law of mass action, the rate of forward reaction,

$R_f \propto [A][B]$

$R_f = k_1 [A][B]$

where,

$[A]$ = Molar concentration of the reactant A.

$[B]$ = Molar concentration of the reactant B

k_1 = Rate constant of the forward reaction.

Similarly, the rate of Backward reaction,

$R_b \propto [C][D]$

$R_b = K_2 [C][D]$

where,

[C] = Molar concentration of the product C.

[D] = Molar concentration of the product D.

K_2 = Rate constant of the backward reaction.

At the equilibrium, the rate of forward reaction = the rate of backward reaction.

$$R_f = R_b$$

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

$$\text{or,} \quad \frac{[A][B]}{[C][D]} = \frac{K_2}{K_1}$$

$$\text{or,} \quad \frac{K_1}{K_2} = \frac{[C][D]}{[A][B]}$$

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

∴ K_c is called the molar equilibrium constant or simply equilibrium constant of the reaction.

∴ $K_c = \frac{[C][D]}{[A][B]}$ This is the mathematical expression for the law of chemical equilibrium.

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

Forward reaction, $R_f \propto [A]^a [B]^b$

$$R_f = k_1 [A]^a [B]^b$$

Rate of backward reaction, $R_b \propto [C]^c [D]^d$

$$R_b = k_2 [C]^c [D]^d$$

At equilibrium,

$$R_f = R_b$$

$$k_1 [A]^a [B]^b = k_2 [C]^c [D]^d$$

or, $$\frac{k_1}{k_2} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

or, $$K_c = \frac{C_C^c \times C_D^d}{C_A^a \times C_B^b}$$

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

Relation between k_p and k_c:

Let us consider a general reversible gaseous ~~equation~~ reaction.

$$aA + bB + cC \rightleftharpoons dD + eE + fF \quad \text{--- (1)}$$

The rate of forward reaction,

$$R_f \propto [A]^a [B]^b [C]^c$$

$$R_f = k_1 [A]^a [B]^b [C]^c \quad \text{--- (2)}$$

The rate of backward reaction,

$$R_b \propto [D]^d [E]^e [F]^f$$

$$R_b = k_2 [D]^d [E]^e [F]^f \quad \text{--- (3)}$$

At equilibrium,

$$R_f = R_b$$

or, $k_1 [A]^a [B]^b [C]^c = k_2 [D]^d [E]^e [F]^f$

or, $$\frac{k_1}{k_2} = \frac{[D]^d [E]^e [F]^f}{[A]^a [B]^b [C]^c}$$

or, $$k_c = \frac{[D]^d [E]^e [F]^f}{[A]^a [B]^b [C]^c} \quad \text{--- (4)}$$

or, $$k_c = \frac{C_D^d \times C_E^e \times C_F^f}{C_A^a \times C_B^b \times C_C^c} \quad \text{--- (5)}$$

or, $$k_p = \frac{P_D^d \times P_E^e \times P_F^f}{P_A^a \times P_B^b \times P_C^c} \quad \text{--- (6)}$$

Now, we know, $PV = nRT$

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

or, $P = CRT \quad \text{--- (7)}$

Putting the value of p in equation ⑥

$$k_p = \frac{(CRT)_D^d \times (CRT)_E^e \times (CRT)_F^f}{(CRT)_A^a \times (CRT)_B^b \times (CRT)_C^c}$$

or, $$k_p = \frac{C_D^d \times (RT)^d \times C_E^e \times (RT)^e \times C_F^f \times (RT)^f}{C_A^a \times (RT)^a \times C_B^b \times (RT)^b \times C_C^c \times (RT)^c}$$

or, $$k_p = \frac{C_D^d \times C_E^e \times C_F^f \times RT^{(d+e+f)}}{C_A^a \times C_B^b \times C_C^c \times (RT)^{a+b+c}}$$

or, $$k_p = \frac{C_D^d \times C_E^e \times C_F^f}{C_A^a \times C_B^b \times C_C^c} \times RT^{(d+e+f)-(a+b+c)}$$

or, $k_p = k_c \times RT^{(n_2-n_1)}$ [From equation ⑤]

or, $k_p = k_c \times RT^{\Delta n}$

Question pattern: Establish the relation between k_p and k_c for the given reactions.

Le-chatelier Principle:

If a change occurs in one of the controlling factors, such as temperature, pressure, concentration etc. under which a system is in equilibrium the system will tend to adjust itself in such a way so as to reduce the effect of that change.

There are three ways in which the stress can be caused on a chemical equilibrium:

① changing the concentration of a reactant or Product
② changing the pressure (or volume) of the system
③ changing the temperature.

◫ If a change in concentration pressure or temperature is caused to a chemical reaction in equilibrium, the equilibrium will shift to the right or the left so as to minimize the change.

Effect of change in concentration:

When concentration of any of the reactants or products is changed, the equilibrium shifts in a direction so as to reduce the change in concentration that was made.

$$N_{2}(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

when N_2 or H_2 is added to the equilibrium stage, the equilibrium will shift to the right side so as to reduce the concentration of the N_2/H_2.

To have a better yeild of NH_3, One of the reactants should be added in excess.

Effect of change of temperature:

When temperature of a reaction is increased the equilibrium shifts in a direction in which heat is absorbed. ~~Ammonia~~

Ammonia Synthesis reaction:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \quad \Delta H = -92kg$$

As heat is increased in this reaction, an increase of reaction will cause the equilibrium to shift to the left, NH_3 Production will be decreased.

Effect of change of Pressure:

When pressure ~~t~~ is increased on a gaseous equilibrium reaction, the equilibrium will shift in a direction which tends to decrease the pressure,