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Concepts of Chemical Equilibrium

Equilibrium State

"The reactions when reaches the stage where no more products are formed is said to be at equilibrium state"

Chemical Equilibrium

"The state of a reversible reaction when the two opposing reactions occur at the same rate and the concentration of the reactants and products do not change with time"

Reversible Reactions

"The reactions that do not go to completion and the products formed react to reform the reactants"

Representation

Reversible reactions can be represented by two arrows ($\rightleftharpoons$) between the reactants and products.

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

Dynamic Equilibrium

"Stage at which rate of forward reactions become equal to the rate of backward reaction is known as dynamic equilibrium."

Explanation

Consider a general reaction take place in gaseous state in a close vessel.

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

Let the initial concentration of A and B be the same. As the forward reaction proceeds, the concentration of

reactants (A and B) decrease and those of product increase continuously.
Therefore, rate of forward reaction goes on decreasing while that of backward reaction keeps on increasing. Ultimately, a stage reaches when rate of forward reaction become equal to rate of backward reaction.
At this stage concentration of reactants and products become costant. This is called state of chemical equilibrium.

Types Of Chemical Equilibrium

There are two types of chemical equilibrium;

1- Homogeneous equilibrium
2- Heterogeneous equilibrium

Homogeneous Equilibrium

In homogeneous equilibria, all the components occurs only in one phase

Example

A system containing gases or totally miscible liquids

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

Heterogeneous Equilibrium

A heterogeneous equilibria is one in which two or more phases are involved.

Example

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

Law Of Mass Action

History

This law was first enunciated by C.M Guldberg and P. Waage in 1864 that help us to find the relations between the concentrations of the reactants and products at equilibrium in a chemical reaction.

Statement

"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 reacting substances"

Rate of Reaction $\propto$ Active masses of reacting substances

Active mass

Active mass mean the molar

concentration or number of moles per dm^3 in a dilute solution

Derivation

Consider a general reaction:

$$A + B \underset{kr}{\overset{kf}{\rightleftharpoons}} C + D$$

A + B . Reactant
C + D . Products

The equilibrium concentrations in mol/dm^3 of A, B, C and D are represented in square brackets like [A], [B], [C] and [D].

Forward Reaction

Rate of forward reaction is proportional to the product of molar concentration of A and B

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

$$r_f \propto [A][B]$$

removing sign of proportionality.

$$r_f = k_f [A][B]$$

k_f is the proportionality constant known as rate constant for forward reaction.

Backward Reaction

C and D are the reactants for the backward reaction so the rate of reverse reaction is given by:

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

$$r_r \propto [C][D]$$

removing sign of proportionality.

$$r_r = k_r [C][D]$$

At Equilibrium

Rate of forward reaction = Rate of reverse reaction

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

On rearranging;

$$\frac{k_f}{k_r}[A][B] = [C][D]$$

$$\frac{k_f}{k_r} = \frac{[C][D]}{[A][B]}$$

As;

$$\frac{k_f}{k_r} = k_c$$

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

Kc

K_c is the ratio of the rate constants (k_f / k_r)

"Ratio of the product of the molar concentration of the products to that of the reactant."

For general reaction;

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

where a . b . c and d represents the number of moles of specie taking part in chemical reaction. They are called the coefficient of balanced chemical equation.

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

Value Of Kc

Value of kc is independent of the initial concentrations of the reactant and product but changes only with change in temperature.

For Gaseous Equilibrium

For gaseous equilibrium, it is convenient to express the concentrations of gases in term of their partial pressure at any given temperature. Let P_A, P_B, P_C and P_D are the partial pressure of gaseous specie than the equilibrium constant Kp may be expressed as :

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

Mole Fraction

If the concentration are expressed in teams of mole fraction. then the equilibrium constant Kx can be expressed as :

$$K_x = \frac{X_C^c}{X_A^a} \times \frac{X_D^d}{X_B^b}$$