B. Sc. Hons Part I

Paper : Physical Chemistry (IA)
Topic : Chemical Equilibrium

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Chemical Equilibrium

Consider a simple reversible reaction, in which forward (i.e., conversion of reactant into product) and backward (i.e. conversion of product into reactant) reactions are two elementary processes

$$\underset{\text{(Reactant)}}{A} \underset{\text{Backward}}{\overset{\text{Forward}}{\rightleftharpoons}} \underset{\text{(Product)}}{B}$$

Let initially only A is present and it changes into B at a rate $r_f = k_f[A]$ where k_f is the rate constant for forward reaction and [A] is the concentration of A at a particular moment. Since the concentration of A decreases with time, so the rate of forward reaction decreases with the time.

Simultaneously, the backward reaction ($B \rightarrow A$) occurs at the rate, $r_b = k_b[B]$, where k_b is the rate constant for backward reaction and [B] is the concentration of B at that moment at which rate is being measured. Since the concentration of B increases with time, so the rate of backward reaction increases with time.

After sometime a state is attained at which the rate of forward reaction (r_f) becomes equal to the rate of backward reaction (r_b). At this state, the concentrations of reactant/s and product/s become constant and do not vary with time. This state is known as "the state of equilibrium

in a chemical process (i.e. Chemical Equilibrium).
Thus, at equilibrium

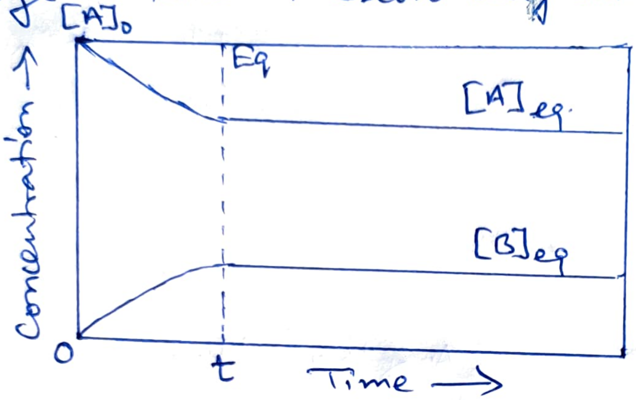
$$r_f = r_b$$

or, $$k_f [A] = k_b [B]$$

or, $$\frac{k_f}{k_b} = \frac{[B]}{[A]} = \text{Constant}, K$$

thus at equilibrium, the ratio of concentrations of products and reactants is constant and is taken as equilibrium constant.

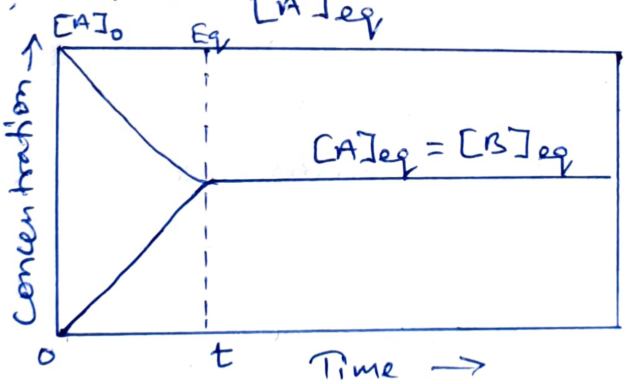
The equilibrium attained in the above chemical change is shown below diagramatically



(a) when eq. concentration of A > B, i.e.

$$[A]_{eq} > [B]_{eq}$$

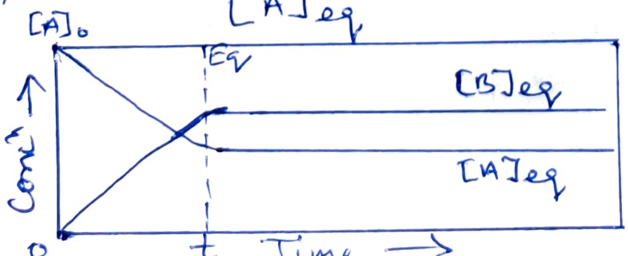
or, $$K = \frac{[B]_{eq}}{[A]_{eq}} < 1$$



(b) when eq. concentration of A = B, i.e.

$$[A]_{eq} = [B]_{eq}$$

or, $$K = \frac{[B]_{eq}}{[A]_{eq}} = 1$$



(c) When eq. concentration of B > A, i.e.

$$[A]_{eq} < [B]_{eq}$$

or $$K = \frac{[B]_{eq}}{[A]_{eq}} > 1$$

General Characteristics of Chemical Equilibrium :-

1. Chemical equilibrium is attained in reversible chemical reactions only.
2. Chemical equilibrium can be established in closed vessels only, i.e. no part of the reactants or products is allowed to escape out.
3. When a chemical equilibrium is attained at a constant temperature, concentrations of the various species in the reaction mixture become constant, and do not change with time. The reaction mixture at equilibrium is called equilibrium mixture. The concentrations at equilibrium are called equilibrium concentrations and are represented by square brackets with subscript eq, i.e. $[\;]_{eq}$.
4. At equilibrium opposing reactions (i.e. forward and backward) proceeds with equal rates.
5. Chemical equilibrium is dynamic in nature, i.e., the reaction does not stop but continues in both the directions with same rate.
6. Chemical equilibrium may be attained from either side. i.e., The state of equilibrium can be approached whether we start with reactants or products. e.g.

$$2\,SO_3 \rightleftharpoons 2\,SO_2 + O_2$$

or, $$2SO_2 + O_2 \rightleftharpoons 2\,SO_3$$

7. The equilibrium concentrations are changed when reaction conditions are disturbed but equilibrium constant (i.e. K = [Product]/[Reactant]) remains constant. It changes only with temperature.
8. Equilibrium state may be attained in both homogeneous and heterogeneous systems.
9. A catalyst does not affect the equilibrium.

It's only function is to alter the time required for establishment of equilibrium. i.e. It enhances the rate of reaction (both forward and reverse to an equal extent).

10. At equilibrium the Gibbs free energy (G) is minimum, i.e. change in free energy, $\Delta G = 0$ and system has no more driving force.

Types of Chemical Equilibria :-

There are two types of equilibria :

(a) Homogeneous Equilibria in which only one phase occurs. For example, a system containing only gases or a single liquid or solid phase.

(b) Heterogeneous Equilibria in which more than a single phase appears. For example, equilibrium between solid and gas, liquid and gas, solid and liquid, solid and solid, immiscible liquids etc.

Law of Mass Action

In 1864, C.M. Guldberg and P. Waage proposed a mathematical relation between mass and activity of a substance after experimental observations of a large number of equilibrium reactions. This relation is now known as the law of mass action. This law states that at constant temperature, the rate at which a substance reacts is directly proportional to its active mass raised with suitable power and the rate of the chemical reaction is directly proportional to the product of all such active masses of reactants.

The power raised over concentration terms represents the order of reaction with respect to that reactant. Since the equilibrium is established in two elementary opposing reactions, so the stoichiometric coefficients in balanced chemica reaction are used as powers.

The term active mass of a substance is a thermodynamic quantity and is directly proportional to its concentration (either in terms of molarity, molality or mole fraction). i.e.

$$a = c.f$$

where a is the active mass of a substance, c is the molar concentration and f is its activity coefficient. For reactions involving gases and solutions, f = 1 and concentration may be substituted for active mass. In general in most of the cases, the active mass of a substance is reported in terms of molarity (i.e. molar concentration).

$$\text{Molarity} = \frac{\text{No. of g-moles}}{\text{Vol. of solution (in L)}}$$

Consider a general reversible reaction

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

According to the law of mass action, the rate of the forward reaction, r_f at any time is proportional to product of concentrations of A and B respectively and is given by

$$r_f = k_1 [A][B] \quad \text{--- (1)}$$

where k_1 is the rate constant for the forward reaction.

Similarly, the rate of the reverse reaction, r_r is given by

$$r_r = k_2 [C][D] \quad \text{--- (2)}$$

where k_2 is the rate constant for the reverse reaction.

At equilibrium,

$$r_f = r_r$$

or, $k_1 [A][B] = k_2 [C][D]$

By rearranging this equation, we get

$$\frac{k_1}{k_2} = \frac{[C][D]}{[A][B]} = K_c \quad \text{——} (3)$$

where K_c, the ratio k_1/k_2 at any specific temp. is a constant and is called Equilibrium Constant. It gives the ratio of the concentrations of the products to the concentrations of the reactants. The subscript 'c' indicates that the equilibrium condition is expressed in terms of the concentration units, i.e., moles per litre of reactants and products.

The above equation (3) is known as the equilibrium constant expression or equilibrium law.

If we consider a process involving more than a single molecule of each of the reactants and products, then the rate is proportional to the concentration of the given substance raised to a power equal to the number of molecules of the substance participating. Thus, for the reaction

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

the two rates are given by

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

and $$r_r = k_2 [C]^c [D]^d$$

and the expression for the equilibrium constant in terms of concentration, K_c is

$$\frac{[C]^c [D]^d}{[A]^a [B]^b} = \frac{k_1}{k_2} = K_c \quad \text{——} (4)$$

This equation gives the most general definition of the equilibrium constant and may be stated as: the product of the equilibrium concentrations of the products divided by the product of the equilibrium concentrations of the reactants, with each concentration term raised to a power equal to the coefficient of the substance in the balanced equation.

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