

LESSON 4

CHEMICAL EQUILIBRIUM AND CHEMICAL KINETICS

1. Chemical equilibrium

- 1.1 Reversible and Irreversible Reactions:** A reaction which proceeds in both directions and ultimately reaches an equilibrium state is termed as a reversible reaction.

i.g. Thermal dissociation is a reversible process wherein the compound on being decomposed by heating is reproduced on cooling.



A reaction which proceeds only in one direction and reaches completion is known as irreversible reaction.

e.g thermal decomposition. A compound undergoes decomposition on heating but is not reproduced on cooling. This process of thermal decomposition is irreversible.



Again when calcium carbonate is heated in an open crucible, calcium oxide is formed and carbon dioxide is given off.



If, however, carbon dioxide is passed over calcium oxide, calcium carbonate is formed.



Evidently the reaction is a reversible reaction since it can proceed in either direction.



From the above equation it can be seen that a good yield of calcium oxide can be got only by removing the CO_2 as fast as it is produced.

Most reactions are reversible. By properly choosing the conditions any reaction can be made to proceed in the desired direction.

e.g. when steam is passed over red hot iron, ferrous ferric oxide and hydrogen are produced.



If, however, the reaction is carried out in a closed vessel (i.e. without allowing the products to escape) it would not go to completion but would become reversible



- 1.2. Chemical equilibrium:** If a reaction is carried out in a closed vessel, a state of equilibrium will be reached. The reactants will not be completely converted into the products of the reaction. At equilibrium, the reaction appears to have stopped. But actually it is dynamic, the rate of the forward reaction being equal to the rate of the reverse reaction.

Illustration: Let equimolecular quantities of hydrogen and iodine be heated in a sealed tube at 356°C. It is observed that only 80% of the theoretical amount of hydrogen iodide is formed, no matter how long the heating is continued. Conversely, if pure hydrogen iodide is heated in a sealed tube to the same temperature, it is partly decomposed, but 80% of it remains unchanged. No further decomposition takes place if the temperature is maintained at 356°C.

At this temperature, hydrogen, iodine and hydrogen iodide are said to be in chemical equilibrium. The system satisfies the test of a true equilibrium, which may be stated thus:

The same state of equilibrium is reached i.e., a mixture of the same composition is obtained, whether one starts with pure hydrogen iodide or with a mixture of hydrogen and iodine in molecular proportions.

At equilibrium, both the forward and reverse reactions are taking place i.e., as much HI decomposes as is formed from hydrogen and iodine. The composition of the equilibrium mixture remains constant because the speeds of the forward and reverse (or backward) reactions have become the same.



- 1.3. The Law of Mass Action:** The law states that "At a given temperature, the rate of a chemical reaction is directly proportional to the product of the active masses of the reactants".

The rate of reaction is change in concentration of the reactants in unit time.

$$\left(r = \frac{dc}{dt} \right)$$

Where dc is the change in concentration and dt is change in time.

By active mass is meant the number of moles of moles per litre.

- 1.4. Equilibrium Constant:** Let a perfectly homogeneous chemical equilibrium be represented by the equation



Let the active masses i.e., molar concentration of A, B, C and D at equilibrium be [A] [B] [C] and [D] respectively. Then by the law of mass action, the rate of the forward reaction

$$r \propto [\text{A}] [\text{B}]$$
$$\therefore r_f = K_1 [\text{A}] [\text{B}]$$

Where 'K₁' is a constant called the rate constant or velocity constant of the forward reaction.

Similarly, the rate of the reverse reaction

$$r_r = K_2 [C] [D]$$

where 'K₂' is the rate or velocity constant of the reverse reaction.

At equilibrium, the rates of the forward and reverse reactions are equal i.e.,

$$r_f = r_r$$

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

$$\therefore \frac{K_1}{K_2} = \frac{[C][D]}{[A][B]} = K$$

Where 'K' is the equilibrium constant of the reaction.

Thus the equilibrium constant of a reaction is the product of the active masses of the resultants divided by the products of the active masses of the reactants. It may also be defined as the ratio of the rate constant of the forward reaction to the rate constant of the reverse reaction ($K = K_1 / K_2$).

1.5. Expressions for equilibrium constants for various reactions:

(i) For a general reaction

$$lA + mB \rightleftharpoons pC + qD$$

$$K = \frac{[C]^p [D]^q}{[A]^l [B]^m}$$

(ii) $H_2 + I_2 \rightleftharpoons 2HI$; $K = \frac{[HI]^2}{[H_2][I_2]}$

(iii) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$; $K = \frac{[PCl_3][Cl_2]}{[PCl_5]}$

(iv) $N_2 + 3H_2 \rightleftharpoons 2NH_3$; $K = \frac{[NH_3]^2}{[N_2][H_2]^3}$

(v) $NSO_2 + O_2 \rightleftharpoons 2SO_3$; $K = \frac{[SO_3]^2}{[SO_2]^2 [O_2]}$

1.6. Application of the Law of Mass Action to the ionization of water: Water is a weak electrolyte. It dissociates according to the equation



Applying the law of mass action, the equilibrium constant K for this reaction would be

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

$[H_2O]$ is the concentration of undissociated or unionized water. Since water electrolyte $[H_2O]$ is almost the same as the initial concentration of water which is a constant.

$$\therefore [H^+] [OH^-] = K \times \text{a constant} = K_w$$

Where K is a constant called the ionic product of water.

Thus the ionic product of water is the product of the concentrations of hydrogen and hydroxyl ions in water.

The value of $K_w = 10^{-14}$ at 25°C .

In pure water, for every molecule of water dissociated, there will be one H^+ and one OH^- ions.

$$\therefore \text{in pure water } [H^+] = [OH^-] = 10^{-7} \text{ M at } 25^\circ\text{C}$$

If to some quantity of water, a little HCl is added, the hydrogen ion concentration would increase. Since K_w is a constant, OH^- concentration would decrease proportionately. Conversely, addition of sodium hydroxide to water increases hydroxyl ion concentration and they hydrogen ion concentration decreases proportionately.

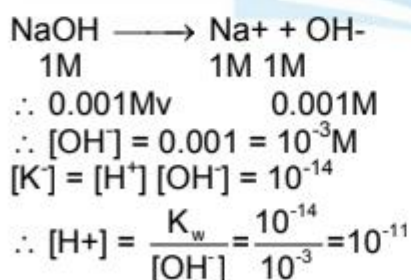
Example 1: The hydrogen ion concentration in an acidic solution is 10^{-2} mole/litre at 25°C . Calculate the hydroxyl ion concentration.

Solution

$$\begin{aligned} [H^+] &= 10^{-2} \\ K_w &= [H^+] [OH^-] = 10^{-14} \\ \therefore [OH^-] &= \frac{10^{-14}}{10^{-2}} = 10^{-12} \text{ mole/litre} \end{aligned}$$

Example 2: Calculate the hydrogen ion concentration in 0.001 M NaOH solution at 25°C .

Solution



Criteria for neutrality, acidity and alkalinity:

For a neutral solution $[H^+] = 10^{-7}$ at $25^\circ C$

For an acidic solution $[H^+] > 10^{-7}$ at $25^\circ C$

For an alkaline solution $[H^+] < 10^{-7}$ at $25^\circ C$

- 1.7. The pH scale:** In order to avoid negative exponents (such as 10^{-7}) the pH scale has been introduced to express hydrogen ion concentrations as positive integers.

pH of a solution is logarithm of the reciprocal of hydrogen ion concentration (i.e., negative logarithm to base 10 of the hydrogen ion concentration)

$$pH = \log_{10} \frac{1}{[H^+]} = - [H^+]$$

Example 3: Calculate the pH of pure water at $25^\circ C$.

Solution

In water $[H^+] = 10^{-7}$

$$\therefore pH = - \log [H^+] = - \log 10^{-7} = - (-7) = 7$$

Example 4: Calculate the pH of a solution whose hydrogen ion concentration is (a) 10^{-2} (b) 10^{-13} .

Solution

$$(a) pH = - \log 10^{-2} = - (-2) = 2$$

$$(b) pH = - \log 10^{-13} = - (-13) = 13$$

Example 5: Calculate the pH of 10^{-4} M KOH at $25^\circ C$.

Solution

$$[OH^-] = 10^{-4}$$

$$[H^+][OH^-] = 10^{-14} (K_w)$$

$$\therefore [H^+] = \frac{10^{-14}}{10^{-4}} = 10^{-10}$$

$$\therefore pH = - \log 10^{-10} = - (-10) = 10$$

- 1.8. The Le Chatelier principle:** This principle deals with the effect of alteration of one of the conditions under which a system is in equilibrium. It is stated thus: If a system in equilibrium is subjected to a change of pressure, temperature or concentration, the system shifts in such a way as to cancel or overcome the effect of the change.

Examples

- 1. Haber's synthesis of ammonia**



The forward reaction is exothermic. Hence increase of temperature will favour the reverse reaction. In the manufacture of ammonia as low a temperature as possible has to be used. The optimum temperature is 500°C.

2. Contact process for the manufacture of H₂SO₄



Since the forward reaction is exothermic, a low temperature should favour the formation of sulphur trioxide. The optimum temperature for this reaction is 400°C.

3. Manufacture of nitric acid by the are process

The first step in this manufacture is the formation of nitric oxide from air.



The forward reaction is endothermic. Hence a very high temperature of 3000°C (produced by an electric are) has to be used.

(ii) **Effect of pressure:** Increase of pressure will shift the system in a direction which there is a decrease in volume or decrease in total number of molecules.

Examples

1. Haber's synthesis of ammonia



An increase of pressure will favour the formation of ammonia.

2. Formation of hydrogen iodide



There is no change in the total volume or number of molecules on either side. Hence this equilibrium is not affected by a change of pressure.

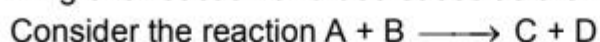
(iii) **Effect to catalyst:** A catalyst accelerates the forward and reverse reactions to the same extent. Hence it does not alter the position of equilibrium in a reversible reaction. It only decreases the time required for reaching the equilibrium.

Examples

- | | | |
|--|---|---|
| 1. Haber Process
(ammonia) | : | Iron + a little molybdenum
(as promoter) |
| 2. Contact Process
(Sulphuric acid) | : | Vanadium pent oxide |
| 3. Ostwald's Process
(Nitric acid) | : | Finely divided platinum |

2. CHEMICAL KINETICS

2.1. Rate of Reaction: The velocity of a reaction is never uniform. It is high at the beginning of a reaction and decreases as the reaction proceeds.\



The rate at which A and B react depends on their molar concentration. As the reaction proceeds, the molar concentration of A and B would decrease.

i.e., the reaction rate diminishes with time.

If in a smaller interval of time dt , the amount of reactant transformed into product is dx , the velocity i.e., rate of change of concentration with respect to time would be $\frac{dx}{dt} = K(a - x)$; where 'K' is the velocity constant, 'a' is the initial concentration of the reactant, 'a - x' is the concentration at any given time 't'.

The rate at time 't' (from the start of the reaction) may also be denoted by $\frac{-dc_A}{dt}$; where $-dc_A$ is a small decrease in the molar concentration of A in a short interval of time dt .

The rate is also equal $\frac{-dc_B}{dt}$ for, in the time 1 mole of A reacts, 1 mole of B also would react. The rate can also be expressed by $+\frac{dc_C}{dt}$ or $+\frac{dc_D}{dt}$, because 1 mole of A reacts with 1 mole of B to produce 1 mole of C and 1 mole of D.

$$\text{Rate} = -\frac{dc_A}{dt} = -\frac{dc_B}{dt} = +\frac{dc_C}{dt} = +\frac{dc_D}{dt}$$

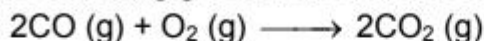
- (i) A system containing several gases constitutes only one-phase because gases are miscible and form a homogeneous mixture.
- (ii) A liquid system such as alcohol and water which are miscible with one another is a one-phase system. But in a liquid system such as water and ether which are not miscible, the number of phases is equal to the number of layers. The mixture of water and ether thus constitutes a two-phase system.
- (iii) In a solid system, each solid constitutes a separate phase, except solid in solutions. E.g., a perfectly homogeneous mixture of two solids such as brass, an alloy of copper and zinc.

2.2. Types of reactions: Chemical reactions are broadly classified into two types depending upon the number of phases present in the reacting system.

1. homogeneous reactions and
2. heterogeneous reactions

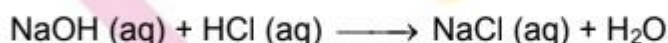
A phase is a homogeneous part of a system, which is separated from other homogeneous parts (phases) by boundary surface. A phase has the same properties and composition throughout.

Let the following gaseous reaction be considered



In this reaction, both the reactants and products are in the same phase (i.e. gaseous phase) Hence it is a homogeneous reaction.

The neutralization reaction

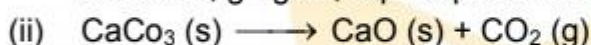


Taking place in solution is another example of a homogeneous reaction. A heterogeneous reaction is one in which more than one phase is present.

Examples



s = solid ; g= gas ; aq = aqueous solution



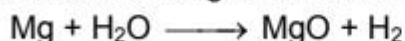
2.3. Factors which influence rates of reactions: Rates of reactions are influenced by several factors such as

- (i) Nature of the reactants
- (ii) The physical nature of the reacting substances
- (iii) Concentration
- (iv) Temperature
- (v) Catalyst

(i) **Nature of the reactants:** Metals such as sodium, potassium and calcium react with cold water liberating hydrogen



Metals such as magnesium decompose hot water.



Metals such as zinc and iron in the red hot condition displace hydrogen from steam



Metals such as copper, mercury and silver do not displace hydrogen from water.

- (ii) **The physical nature of the reacting substances:** In a heterogeneous reaction the greater the surface area of contact between the reactants, the faster is the reaction. In other words the reaction is faster with a fine powder than with a lump of a reactant.



Takes place quickly if the calcium carbonate (limestone or marble) is in the form of fine powder rather than in the form of a lump.

- (iii) **Concentration:** Increase in concentration of one of the reactants increases the rate of the reaction.

e.g. concentrated acid reacts much faster than dilute acid.
In the case of gases increase of pressure increases the reaction rate.

- (iv) **Temperature:** The influence of temperature on the rate of a reaction is very great. Actually, the reaction rate is doubled when the temperature is raised by just 10°C .

- (v) **Catalyst:** A catalyst is a substance, which by its mere presence, without undergoing any permanent change in itself, changes the rate of a reaction.

E.g. manganese dioxide acts as a very good catalyst in the decomposition of potassium chlorate.

