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CHEMICAL EQUILIBRIUM

REVERSIBLE REACTIONS

"The reactions in which reactants combine together or dissociate to form products and under similar conditions of temperature and pressure, products recombine or dissociate to give back the reactants are called reversible reactions."

These reactions are represented by sign of reversibility (⇋). Here, the reaction occurring from left to right is called forward reaction, while that occurring from right to left is called backward or reverse reaction. For example,

N_2 (g) + $3H_2$ (g) ⇋ $2NH_3$ (g) + Heat (Haber's process)

$2SO_2$ (g) + O_2 (g) ⇋ $2SO_3$ (g) + Heat (Contact process)

N_2 (g) + O_2 (g) ⇋ 2NO (g) - Heat

PCl_5 (g) ⇋ PCl_3 (g) + Cl_2(g) - Heat

Reversible reactions involve the state of chemical equilibrium and it is the reason why these reactions are never completed.

THE STATE OF CHEMICAL EQUILIBRIUM –

If a reversible reaction is carried out in a closed vessel, after some time a stage comes when the rate of forward reaction becomes equal to the rate of backward reaction and concentration of any reactant or product does not change with time. This state of reversible reactions is called the state of chemical equilibrium. Thus,

"The state of a reversible reactions when the rate of forward reaction becomes equal to the rate of backward reaction and concentration of any reactant or product does not change with time is called the state of chemical equilibrium."

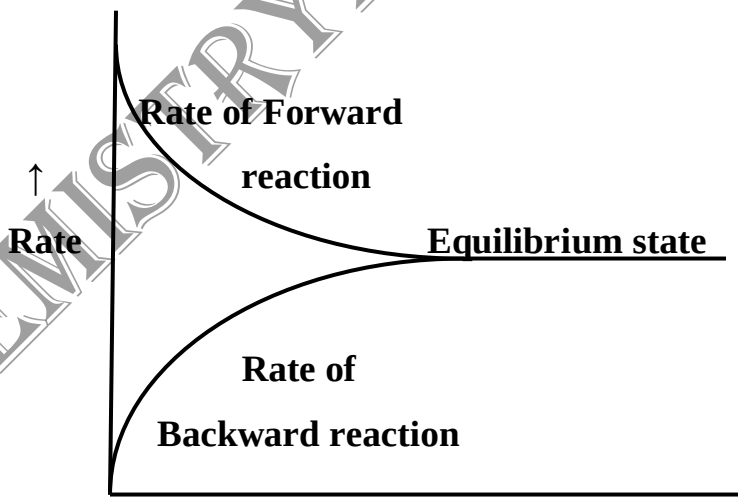


Fig.- Expression of Equilibrium state

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In fact, the rate of a chemical reaction depends upon the concentration of reactants. When a reversible reaction is carried out in a closed vessel, the concentration of reactants goes on decreasing, while that of products goes on increasing with time. Hence, the rate of forward reaction goes on decreasing, while that of backward reaction goes on increasing with time. At equilibrium state these two rates become equal.

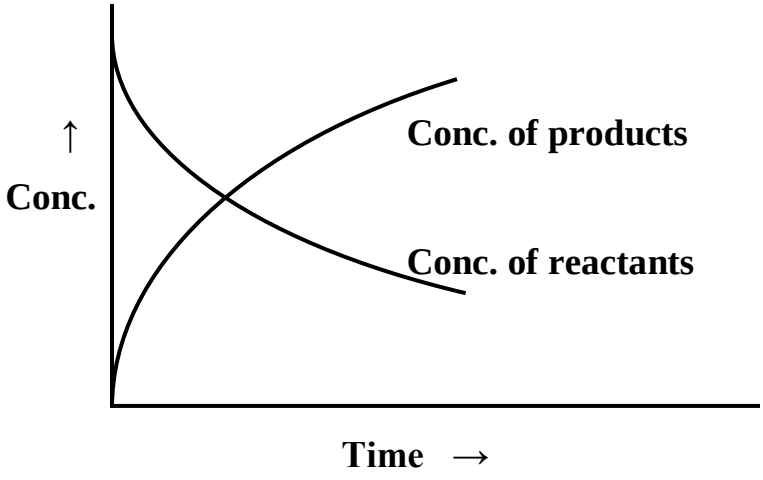


Fig. – Variation of conc. with time

CHARACTERISTICS OF EQUILIBRIUM STATE

(1) At equilibrium state, the rate of forward reaction becomes equal to the rate of backward reaction.

(2) At equilibrium, both reactants and products remain present in reaction mixture, but the concentration of any species does not change with time.

(3) At equilibrium state, all the visible properties of the system such as temperature, pressure, colour, composition, density etc. become constant. Hence, it seems that, the reaction has stopped, but the reaction actually does not stop but occurs both in forward and backward directions with equal rates. Thus, the equilibrium state seems to be static but it is actually dynamic in nature.

(4) If any of the reactants or products is gaseous, then equilibrium is always established In closed vessel and is never established in open vessel. However, if all the reactants and products are solids or liquids, then it can be established in open vessel.

(5) Equilibrium state depends upon temperature, pressure and conc. and therefore gets changed with change of these parameters.

(6) Catalysts have no effect on equilibrium. In fact, catalysts increase both forward and backward reactions for same extent and help in quick establishment of the equilibrium do not affect the equilibrium state. If catalyst is not used then also same equilibrium is established, but it takes relatively longer time.

(7) The equilibrium state can be attained from either of the directions i.e. it can be achieved by carrying out the reaction either taking reactants or taking products. In both the cases same equilibrium state is achieved.

(8) At equilibrium state, the change in free energy of the system (ΔG) is equal to zero.

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IONIC EQUILIBRIUM

Electrolytes-

The substances which pass electricity through them, either in their aqueous solutions or in their molten form are called electrolytes.

When electrolytes are dissolved in water or melted they get splitted into ions. This phenomenon is called ionization or dissociation. For example,

$$NaCl\ (s) \xrightleftharpoons{\text{Water}} \underset{\text{Ions}}{Na^+\ (aq) + Cl^-\ (aq)}$$

$$NaCl\ (s) \xrightleftharpoons{\text{Melt}} \underset{\text{Ions}}{Na^+ + Cl^-}$$

The conduction of electricity through aqueous solutions or molten form of electrolytes is due to flow of ions.

All acids (e.g. HCl, H_2SO_4, HNO_3, CH_3COOH etc.), bases (e.g. NaOH, KOH, NH_4OH, $Ba(OH)_2$ etc.) and salts (e.g. NaCl, KCl, NH_4Cl, K_2SO_4, CH_3COONa etc.) are electrolytes.

Types of Electrolytes-

Depending upon the degree of dissociation or ionization, the electrolytes may be of following two types-

(1) Strong electrolytes- Such electrolytes which dissociate almost completely in their aqueous solutions are called strong electrolytes. For example,

(i) All strong acids- e.g. HCl, H_2SO_4, HNO_3, $HClO_4$ etc.

(ii) All strong bases- e.g. NaOH, KOH, $Ba(OH)_2$ etc.

(iii) Salts of strong acids and strong bases - e.g. NaCl, KCl, Na_2SO_4, K_2SO_4, $NaNO_3$, KNO_3 etc.

(iv) Salts of strong acids and weak bases - e.g. NH_4Cl, $(NH_4)_2SO_4$, NH_4NO_3 etc.

(v) Salts of weak acids and strong bases - e.g. CH_3COONa, CH_3COOK, Na_2CO_3, K_2CO_3, NaCN, KCN etc.

(2) Weak electrolytes- Such electrolytes which dissociate very feebly or partially in their aqueous solutions are called weak electrolytes. For example,

(i) All weak acids- e.g. CH_3COOH, H_2CO_3, HCN etc.

(ii) All weak bases- e.g. NH_4OH, $Mg(OH)_2$, $Ca(OH)_2$ etc.

(iii) Salts of weak acids and weak bases - e.g. CH_3COONH_4, $HCOONH_4$, $(NH_4)_2CO_3$, NH_4CN etc.

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Degree of dissociation or Degree of ionization (α)

"The fraction of total number of molecules which remains dissociated at equilibrium is called degree of dissociation or degree of ionization of the electrolyte."
Mathematically,

$$\textbf{Degree of dissociation, } \alpha = \frac{\textit{The number of molecules dissociated at equilibrium}}{\textit{Total number of molecules}}$$

Strong electrolytes (e.g. HCl, H_2SO_4, HNO_3, NaOH, KOH, $Ba(OH)_2$, NaCl, KCl, NH_4Cl, K_2SO_4, CH_3COONa etc.) are electrolytes are almost completely dissociated in their aqueous solutions. Hence, for these electrolytes, the degree of dissociation is almost equal to 1. Thus, for strong electrolytes,

$$\alpha \approx 1$$

On the other hand, weak electrolytes (e.g. CH_3COOH, H_2CO_3, HCN, NH_4OH, CH_3COONH_4, $(NH_4)_2CO_3$, NH_4CN etc.) are very feebly dissociated in their aqueous solutions at equilibrium. Hence, for these electrolytes, the degree of dissociation is very very less than 1. Thus, for weak electrolytes,

$$\alpha << 1$$

Ionic Product of water (K_w)-

Water is a very weak electrolyte and undergoes autoionization (self-ionisation) to establish following equilibrium-

$$2H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + OH^-\ (aq)$$

Applying law of mass action, dissociation constant,

$$K = \frac{[H_3O^+(aq)]\,[OH^-(aq)]}{[H_2O\ (l)]^2}$$

or $$K \times [H_2O(l)]^2 = [H_3O^+][OH^-]$$

Being very weak electrolyte, the degree of dissociation of water is very small. Hence, the molar concentration of undissociated water can be taken to be almost constant. Hence,

$$K \times (\text{Constant})^2 = [H_3O^+][OH^-]$$

or $$[H_3O^+]\,[OH^-] = K_w$$

Where, K_W is a new constant called ionic product of water.

Thus, "At constant temperature, in pure water the product of the molar concentration of H_3O^+ and OH^- ions is constant, which is called ionic product of water."

At 298 K temperature, the value of K_W is found to be 1.0×10^{-14} gram-ion^2/litre^2. Thus, at 298 K temperature,

$$[H_3O^+][OH^-] = 1.0\times10^{-14}\ \text{gram-ion}^2/\text{litre}^2$$

This value of K_W depends only upon temperature and remains constant as long as temperature is constant, but it gets changed with change of temperature.

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For pure water (neutral solution),

$$[H_3O^+] = [OH^-]$$

$$\therefore \quad [H_3O^+][H_3O^+] = 1.0\times10^{-14} \text{ gram-ion}^2/\text{litre}^2$$

$$\text{or} \quad [H_3O^+] = \sqrt{1.0 \times 10^{-14} \text{ gram} - \text{ion}^2/\text{litre}^2}$$

$$= 1.0\times10^{-7} \text{ gram-ion/litre}$$

Thus, in pure water (neutral solution), H_3O^+ and OH^- ion concentrations are same and at 298K temperature these are 10^{-7} gram-ion/litre.

For acidic solutions-

$$[H_3O^+] > [OH^-]$$

$$\therefore \quad > 1.0\times10^{-7} \text{ gram-ion/litre (at 298K temperature)}$$

For basic solutions -

$$[H_3O^+] < [OH^-]$$

$$\therefore \quad < 1.0\times10^{-7} \text{ gram-ion/litre (at 298K temperature)}$$

Effect of temperature on K_W- Autonization of water is an endothermic process.

$$2H_2O\ (l) + \text{Heat} \rightleftharpoons H_3O^+\ (aq) + OH^-\ (aq)$$

Hence, on increasing temperature, following Le-chatelier's principle, this equilibrium will shift in forward direction i.e. there will occur more dissociation of water producing more concentration of H_3O^+ and OH^- ions. Thus, the ionic product of water will increase with increase of temperature. For example, at 363 K temperature, the value of K_w is found to be 10^{-12} gram-ion^2/litre^2. This value of K_w remains constant as long as the temperature is constant, but gets changed with change of temperature.

p^H value

In order to express acidic, basic or neutral nature of the aqueous solutions, Sorenson has introduced a scale called p^H scale. On this scale, the molar concentration of H_3O^+ ions of the solution is expressed as the negative power of the base 10, where the numerical value of the negative power of the base 10 corresponds to the p^H value of the solution. Thus,

If in a solution,

$$[H_3O^+] = 10^{-x} \text{ gram-ion/litre}$$

Then, pH of the solution = x

Thus,
$$[H_3O^+] = 10^{-pH} \qquad \text{---------- (1)}$$

"The numerical value of the negative power raised to the base 10 to express the molar concentration of H_3O^+ ions of the solution is called the p^H value of the solution."

Taking algorithm of eq. (1),

$$\log [H_3O^+] = -p^H (\log 10)$$

$$\because \quad \log 10 = 1$$

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$\therefore \quad \log [H_3O^+] = - p^H$

or $\quad pH = - \log [H_3O^+]$ ---------- (2)

Thus, "The negative logarithm of the molar concentration of H_3O^+ ions of a solution is called p^H value of the solution."

From eq. (2)-

$$pH = \log \frac{1}{[H_3O^+]} \quad \text{---------- (3)}$$

Thus, "The logarithm of the reciprocal of the molar concentration of H_3O^+ ions of a solution is called p^H value of the solution."

At 298 K temperature, in pure water (neutral solution),

$[H_3O^+] = 10^{-7}$ gram-ion/litre

$\therefore \quad pH = - \log (10^{-7})$

$= 7$

Thus, at 298K temperature, the p^H value of pure water (neutral solution) is 7.

For acidic solutions-

$[H_3O^+] > 10^{-7}$ gram-ion/litre (at 298K temperature)

$\therefore \quad pH < 7$

For basic solutions -

$[H_3O^+] < 10^{-7}$ gram-ion/litre (at 298K temperature)

$\therefore \quad pH > 7$

In fact, at 298K temperature, the p^H value of the aqueous solutions ranges from 0 to 14. Here, if the p^H value of the solution is from 0 – 2, it is highly acidic. If it is 2 – 5, then the solution is moderately acidic and if it is from 5 – 7, then the solution is weakly acidic in nature. At p^H 7, the solution is completely neutral. On the other hand, if the p^H value of the solution is from 7 – 9, it is weakly basic. If it is 9 – 12, then the solution is moderately basic and if it is from 12 – 14, then the solution is highly basic in nature.

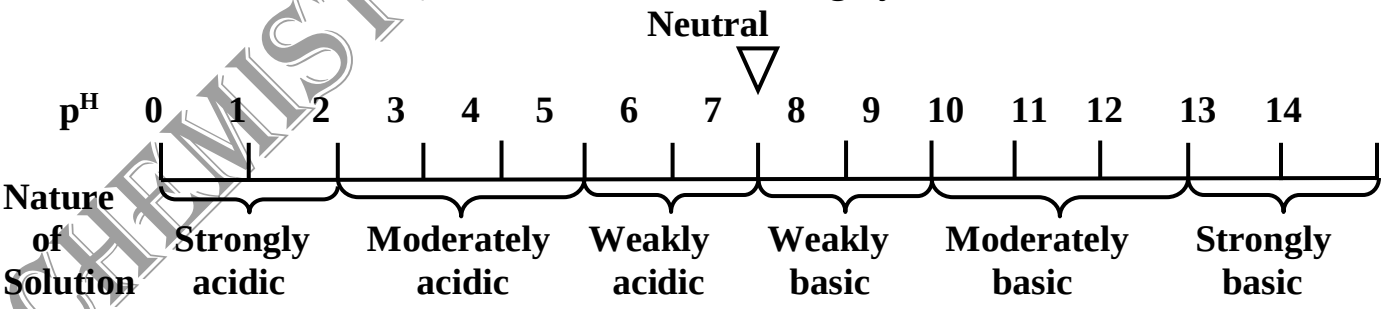


Fig. - p^H Scale

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