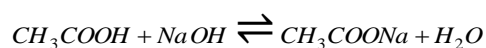# Equilibrium

Reversible and Irreversible reactions

Reversible reactions: Reversible reactions are those reactions in which the complete amount of the reactants does not converted into products.

Example:

Neutralisation reaction between an acid and a base either of which or both are weak are example of reversible reaction. e.g.,

$$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$$

This is the neutralization reaction of weak acid (CH_3COOH) and strong base (NaOH).

Irreversible reactions: Ireversible reactions are those reactions in which the complete amount of the reactants gets converted into products.

Example:

Neutralisation reaction between a strong acid (HCl) and a strong base (NaOH) are example of irreversible reaction. e.g.,

$$NaOH + HCl \rightarrow NaCl + H_2O$$
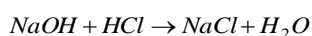
Equilibrium and Its dynamic nature

*"**Equilibrium** is the state at which the concentration of reactants and products do not change with time. i.e. concentrations of reactants and products become constant."*

Law of mass action and Equilibrium constant

"*The rate of a chemical reaction is directly proportional to the product of the molar concentrations of the reactants at a constant temperature at any given time.*"

Consider a simple reversible reaction

$$aA + bB \rightleftharpoons cC + dD \qquad \text{(At a certain temperature)}$$
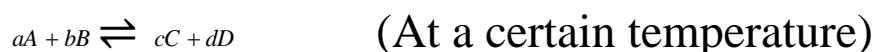
At equilibrium ,

Rate of forward reaction = Rate of backward reaction

$$k_f[A]^a[B]^b = k_b[C]^c[D]^d$$

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

Where, K_c is called equilibrium constant.

Relation between K_p, K_c and K_x

$$K_p = K_c(RT)^{\Delta n}$$

$$K_p = K_x(P)^{\Delta n}$$

Δn = number of moles of gaseous products – number of moles of gaseous reactants in chemical equation.

Relationship between equilibrium constant and $\Delta G°$

ΔG for a reaction under any condition is related with $\Delta G°$ by the relation, $\Delta G = \Delta G° + 2.303\ RT \log Q$

Standard free energy change of a reaction and its equilibrium constant are related to each other at temperature T by the relation, $\Delta G° = -2.303\ RT \log K$

For a general reaction $aA + bB \rightleftharpoons cC + dD$

$$K = \frac{(a_C)^c\ (a_D)^d}{(a_A)^a\ (a_B)^b}$$

Where a represent the activity of the reactants and products. It is unit less.

For pure solids and liquids: $a = 1$.

For gases: $a =$ pressure of gas in *atm*.

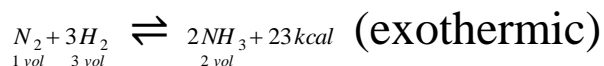For components in solution: $a =$ molar concentration.

Le-Chatelier's principle

"Change in any of the factors that determine the equilibrium conditions of a system will shift the equilibrium in such a manner to reduce or to counteract the effect of the change."

Application of Le-Chatelier's principle

The Le-Chateliers principle has a great significance for the chemical, physical systems and in everyday life in a state of equilibrium.
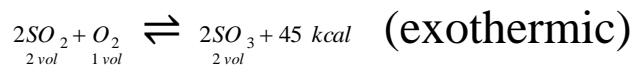
Applications to the chemical equilibrium

Synthesis of ammonia (Haber's process)

$$\underset{\underset{1\,vol}{}}{N_2} + \underset{\underset{3\,vol}{}}{3H_2} \rightleftharpoons \underset{\underset{2\,vol}{}}{2NH_3} + 23\,kcal \text{ (exothermic)}$$

(a) High pressure $(\Delta n < 0)$

(b) Low temperature

(c) Excess of N_2 and H_2

(d) Removal of NH_3 favours forward reaction.

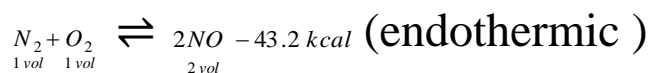### *Formation of sulphur trioxide*

$$\underset{\underset{2\,vol}{}}{2SO_2} + \underset{\underset{1\,vol}{}}{O_2} \rightleftharpoons \underset{\underset{2\,vol}{}}{2SO_3} + 45\ kcal \text{ (exothermic)}$$
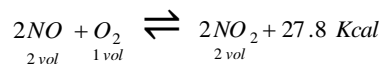
(a) High pressure $(\Delta n < 0)$

(b) Low temperature

(c) Excess of SO_2 and O_2, favours the reaction in forward direction.

Synthesis of nitric oxide

$$\underset{\substack{1\,vol \quad 1\,vol}}{N_2 + O_2} \rightleftharpoons \underset{\substack{2\,vol}}{2NO} - 43.2\,kcal \text{ (endothermic)}$$
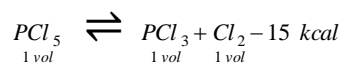
(a) High temperature

(b) Excess of N_2 and O_2

(c) Since reaction takes place without change in volume *i.e.*, $\Delta n = 0$, pressure has no effect on equilibrium.

Formation of nitrogen dioxide

$$\underset{\substack{2\,vol}}{2NO} + \underset{\substack{1\,vol}}{O_2} \rightleftharpoons \underset{\substack{2\,vol}}{2NO_2} + 27.8\,Kcal$$

(a) High pressure

(b) Low temperature

(c) Excess of NO and O_2 favours the reaction in forward direction.

(v) *Dissociation of phosphours pentachloride*

$$\underset{\substack{1\,vol}}{PCl_5} \rightleftharpoons \underset{\substack{1\,vol}}{PCl_3} + \underset{\substack{1\,vol}}{Cl_2} - 15\,kcal$$
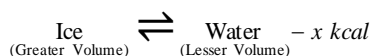
(a) Low pressure or high volume of the container, $\Delta n > 0$ (b) High temperature (c) Excess of PCl_5.

Applications to the physical equilibrium

(i) **Melting of ice** (Ice – water system).

$$\underset{\text{(Greater Volume)}}{\text{Ice}} \rightleftharpoons \underset{\text{(Lesser Volume)}}{\text{Water}} - x\ kcal$$

(There is no chemical reaction is involve in the ice-water system, so this an example of physical equilibrium. In this equilibrium the quantity decreases from 1.09 c.c. to 1.01 c.c. per gram.)

(a) As it absorbs more heat that's why more water is produced at high temperature.

(b) Produce more water at high pressure, because there is the volume reduction.

(c) Reduces the melting point of ice at high pressure, while the boiling point of water rises.

(ii) **Melting of sulphur**:
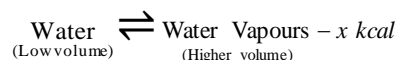
$$S_{(s)} \rightleftharpoons S_{(l)} - x\ kcal$$
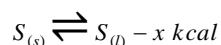
(This equilibrium reaction follows increase in volume.)

(a) More liquid sulphur is formed at high temperature.

(b) The melting point of the sulphur is raised at high pressure.

(c) Less sulphur can melt at higher pressure, as the melting increases volume.

(iii) **Boiling of water**(water- water vapour system).

$$\underset{\text{(Low volume)}}{\text{Water}} \rightleftharpoons \underset{\text{(Higher volume)}}{\text{Water Vapours}} - x \; kcal$$

(a) More vapors are produced at high temperature.

(b) Vapors will be converted to liquid at higher pressure, the volume decreases.

(c) Boiling point of water is raised at high pressure.

(iv) **Solubility of salts**:
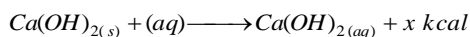
If a salt's solubility is accompanied by heat absorption, its solubi lity increases with rise in temperature.

e.g., NH_4Cl, K_2SO_4, KNO_3 etc.

$$KNO_{3(s)} + (aq) \longrightarrow KNO_{3(aq)} - x \; kcal$$
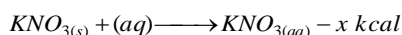
If after heat development, solubility will decrease with increase in temperature.

e.g., $CaCl_2, Ca(OH)_2, NaOH, KOH$ *etc.*

$$Ca(OH)_{2(s)} + (aq) \longrightarrow Ca(OH)_{2(aq)} + x \; kcal$$

Arrhenius theory of electrolytic dissociation

Postulates of Arrhenius theory

(i) In aqueous solution, the molecules of an electrolyte undergo spontaneous dissociation to form positive and negative ions.

(ii) Degree of ionization (α)

$$= \frac{\text{Number of dissociated molecules}}{\text{Total number of molecules of electrolyte before dissociation}}$$

(iii) At moderate concentrations, there exists an equilibrium between the ions and undissociated molecules, such as, $NaOH$

$\rightleftharpoons Na^+ + OH^-$; $KCl \rightleftharpoons K^+ + Cl^-$
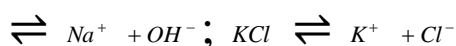
This equilibrium state is called *ionic equilibrium.*

(iv) Each ion behaves osmotically as a molecule.

Factors affecting degree of ionisation

(i) $\alpha \propto$ Dielectric constant

Higher the dielectric constant of a solvent more is its ionising power. Water is the most powerful ionising solvent since it has the highest dielectric constant.

(ii) $\alpha \propto \dfrac{1}{\text{Con. of solution}}$

(iii)

With temperature rise, the degree of ionization of an electrolyte in solution increases.

Dissociation constant for weak base: NH_4OH is a weak base and its equilibrium can be represented as,
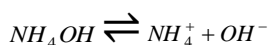
$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

On applying the law of mass action, $K_b = \dfrac{[NH_4^+][OH^-]}{[NH_4OH]}$

K_b is equilibrium constant of weak base at a definite temperature. It does not change with the change of concentration.

Common ion effect

An electrolyte's(weak) degree of dissociation is suppressed by adding another electrolyte (strong) containing a common ion, it is called common ion effect.

Solubility product

In a saturated solution of sparingly soluble electrolyte two equilibria exist and can be represented as, $\underset{\text{Solid}}{AB} \rightleftharpoons \underset{\substack{\text{Unionised}\\(\text{Dissolved})}}{AB} \rightleftharpoons \underset{ions}{A^+ + B^-}$

Applying the law of mass action, $\frac{[A^+][B^-]}{[AB]} = K$

Relative strength of acids and Bases

For two weak acids HA_1 and HA_2 of ionisation constant K_{a_1} and K_{a_2} respectively at the same concentration c, we have,

$$\frac{\text{Acid strength of } HA_1}{\text{Acid strength of } HA_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

Similarly, relative strengths of any two weak bases at the same concentration are given by the ratio of the square-roots of their dissociation constants. i.e.,
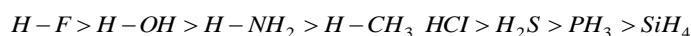
$$\frac{\text{Basic strength of } BOH_1}{\text{Basic strength of } BOH_2} = \sqrt{\frac{K_{b_1}}{K_{b_2}}}$$
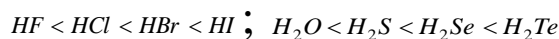
Relative strength of Inorganic acids

(i) *Hydrides*

(a)

As the electronegativity of the element directly attached with the hydrogen increases, the acidic strength increases.
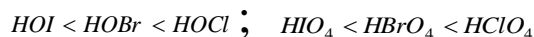
$H - F > H - OH > H - NH_2 > H - CH_3 \quad HCl > H_2S > PH_3 > SiH_4$

(b) With the increase in atomic size the acidic strength increases,
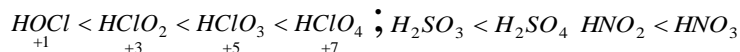
$HF < HCl < HBr < HI \; ; \; H_2O < H_2S < H_2Se < H_2Te$

(ii) *Oxyacids*

(a)

With the electronegativity, acidic nature increases among oxyacids of the same kind produced by different elements;

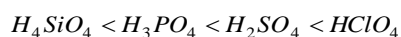$HOI < HOBr < HOCl \; ; \quad HIO_4 < HBrO_4 < HClO_4$

(b) The acidic nature of oxydants of the same element increases with its oxidation number.

$\underset{+1}{HOCl} < \underset{+3}{HClO_2} < \underset{+5}{HClO_3} < \underset{+7}{HClO_4} \; ; H_2SO_3 < H_2SO_4 \quad HNO_2 < HNO_3$

(c) The strength of oxyacids increases from left to right across a period

$H_4SiO_4 < H_3PO_4 < H_2SO_4 < HClO_4$

(d)   Acid strength decreases with increase in atom size for the same oxidation state and configuration of the elements.

$HNO_3 > HPO_3$; $H_3PO_4 > H_3AsO_4$ $HClO_4 > HBrO_4 > HIO_4$
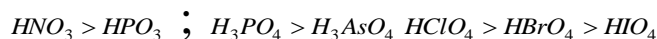
Hydrogen ion concentration – *pH* scale

"pH of a solution is the negative logarithm to the base 10 of the concentration of H⁺ ions which it contains."

$pH = -\log[H^+]$ or $pH = \log \dfrac{1}{[H^+]}$

Just as *pH* indicates the hydrogen ion concentration, the *pOH* represents the hydroxyl ion concentration, *i.e.,*

$pOH = -\log[OH^-]$

Considering the relationship, $[H^+][OH^-] = K_w = 1 \times 10^{-14}$

Buffer solutions

A solution whose pH is not altered to any great extent by the addition of small quantities of either sirong acid (H^+ ions) or a sirong base (OH^- ions) is called the buffer solution.

pH of an acidic or a basic buffer can be calculated by Henderson- Hasselbalch equation.

For acidic buffers, $pH = pK_a + \log \frac{[salt]}{[acid]}$

When $\frac{[salt]}{[acid]} = 10$, then, $pH = 1 + pK_a$ and

when $\frac{[salt]}{[acid]} = \frac{1}{10}$, then, $pH = pK_a - 1$