

Ionic Equilibrium discusses the dissociation of compounds such as acids, bases, salts (electrolytes), when added in water and the resultant equilibrium established between their ions and the unionised molecules in the aqueous solution.

Factors affecting Degree of Dissociation =

Degree of dissociation of an electrolyte depends on the following factors —

- ① Nature of Solute — Strong acids, alkalis, salts are 100% dissociated in their solutions. Degree of dissociation decreases with the increase in covalent character of the electrolyte.
- ② Nature of Solvent — Greater is the dielectric constant of the solvent, greater is the degree of dissociation of an electrolyte.

Water has a dielectric constant $\Rightarrow 81$ at 25°C .

- ③ Dilution — Increased dilution increases the degree of dissociation of weak electrolytes, due to increased solvation.
- ④ Temperature — An increase in temperature increases the molecular velocities, thus increasing the degree of dissociation.

Ostwald's Dilution Law.

Consider a binary electrolyte AB which dissociates into A^+ and B^- ions and the equilibrium is represented as $AB \rightleftharpoons A^+(aq.) + B^-(aq.)$

According to the Law of Mass Action, the equilibrium constant is represented as $K = \frac{[A^+](aq.)[B^-](aq.)}{[AB]}$... (i)



C	0	0
C - \alpha	\alpha	\alpha

initial concentration

active mass at equilibrium

$$\text{From eqn (i) } K = \frac{C\alpha \times C\alpha}{C - \alpha} = \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$



This equation is known as Ostwald Dilution Law. For weak electrolytes, α is very small i.e. $\alpha \ll 1$, α can be neglected in comparison to 1. Therefore $K = C\alpha^2$, or $\alpha^2 = \frac{K}{C}$, or $\alpha = \sqrt{\frac{K}{C}}$. or $\alpha \propto \sqrt{\frac{1}{C}}$ [α is directly proportional to $\frac{1}{\sqrt{C}}$]. This law holds good only for weak electrolytes.

Ionic Product of water - Pure water is a very weak electrolyte and the ionic equilibria due to self-ionisation is represented as - $2H_2O \rightleftharpoons H_3O^+ + OH^-$

Applying law of mass action, $K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$

$$\therefore K \times [H_2O]^2 = [H_3O^+][OH^-]$$

Since α is very small, $[H_2O]$ is taken as constant.

$$\therefore K \times [H_2O]^2 = [H_3O^+][OH^-] \text{ or } K_w = [H_3O^+][OH^-] \dots (ii)$$

This constant K_w is known as ionic product of water, which changes with rise in temp.

Value of K_w	Temperature $^{\circ}C$
0.11×10^{-14}	$0^{\circ}C$
0.30×10^{-14}	$10^{\circ}C$
1.00×10^{-14}	$25^{\circ}C \Rightarrow$ Standard Exptl. Condition.
7.50×10^{-14}	$100^{\circ}C$

When H_2O molecule ionises, $[H_3O^+]$ concentration in pure liquid will always be equal to its $[OH^-]$ concentration.

$$\text{i.e. } [H_3O^+] = [OH^-] = x. \text{ (Suppose)}$$

From equation (ii), we have $[H_3O^+][OH^-] = K_w = 1 \times 10^{-14}$ (at $25^{\circ}C$)

$$\therefore x \times x = 10^{-14}, \text{ or } x^2 = 10^{-14} \text{ or } x = \sqrt{10^{-14}} = 10^{-7} \text{ (M)}$$

Pure water is neither acidic nor basic i.e. neutral because in this case $[H_3O^+] = [OH^-]$

When an acid is added to pure water, the ionic product remains same (K_w remains constant) but $[H_3O^+]$ increases in comparison to $[OH^-]$ concentration. Hence in acidic medium,

$$[H_3O^+] > [OH^-] \text{ or } [H_3O^+] > 1 \times 10^{-7}$$

Again upon addition of alkali, $[OH^-]$ increases than $[H_3O^+]$. $[OH^-] > 1 \times 10^{-7}$. So increase of one entity - decreases the other and K_w remains the same.