# IONIC EQUILIBRIUM, P$^H$ AND HYDROLYSIS

## Physical Equilibrium

It is the equilibrium between the same chemical species in different phases. e.g.

(*i*) Equilibrium between a liquid and its vapour.

(*ii*) Equilibrium between a vapour and its saturated solution.

## Homogeneous Equilibrium

A reversible reaction having all the species in same phase throughout, is called in homogeneous equilibrium.

Here, $$\underset{\text{Hydrogen}}{H_2(g)} + \underset{\text{Iodine}}{I_2(g)} \rightleftharpoons \underset{\text{Hydrogen iodide}}{2HI(g)}$$

Here all reactants and products are gases.

## Heterogeneous Equilibrium

A reversible reaction having its species in two or more phases, is called in heterogeneous equilibrium.

Here, $$\underset{\text{Calcium carbonate}}{CaCO_3\,(s)} \rightleftharpoons \underset{\text{Calcium oxide}}{CaO\,(s)} + \underset{\text{Carbon dioxide}}{CO_2\,(g)}$$

In this reaction $CaCO_3$ and CaO are solids, but $CO_2$ is a gas.

## Ionic Equilibrium

A reversible reaction between species and its ions is called in ionic equilibrium.

e.g. $$H_2O\,(l) \rightleftharpoons H^+\,(aq) + OH^-\,(aq)$$

### Relationship between $K_c$ and $K_p$

$K_c$ = Equilibrium constant expressed in

$K_p$ = Equilibrium constant expressed in pressures.

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

where R = 0.08206 litre atm $K^{-1}$ $mol^{-1}$.

T = absolute temperature.

$\Delta n$ = number of moles of the gaseous products – number of moles of the gaseous reactants in the balanced equation.

## Le-Chatelier Principle

It states that if some change is introduced in a system at equilibrium, the system proceeds in such a way that the effect of change is minimised.

Factors influencing equilibrium

(*i*) Concentration of reactant or a product

(*ii*) Reaction volume or applied pressure.

(*iii*) Temperature

## Electrolytes and non-electrolytes

**Electrolyte:** A compound whose aqueous solution or melt conducts electricity, is known as an electrolyte.

**Non-electrolyte:** A compound whose aqueous solution or melt does not conduct electricity, is known as a non-electrolyte.

**Strong electrolyte:** A substance which dissociates completely into its ions in an aqueous solution and hence is a very good conductor of electricity, is known as strong electrolyte.

**Weak electrolyte:** A substance which dissociates to a small extent is an aqueous solution, is known as weak electrolyte.

**Degree of dissociation or ionisation (α):** Fraction of electrolyte that dissociates into its ions when it is dissolved in water, is known as its degree of dissociation or ionisation, α is 1 for strong electrolytes and less than one for weak electrolytes.

## Ionisation Constant of a Weak Electrolyte

According to this law, for a weak electrolyte, the degree of ionisation is inversely proportional to the square root of its molar concentration. It can be proved as follows –

Here,

$$AB + H_2O \rightleftharpoons A^+\,(aq) + B^-\,(aq)$$

$$\Rightarrow \qquad AB\,(aq) \rightleftharpoons A^+\,(aq) + B^-\,(aq)$$

| | | | |
|---|---|---|---|
| Moles before dissociation: | $1$ | $0$ | $0$ |
| Moles after dissociation: | $(1-\alpha)$ | $\alpha$ | $\alpha$ |

If C mol/litre is initial concentration of the electrolyte AB.

$$[AB] = C(1-\alpha) \text{ mol/litre}$$

$$[A^+] = [B^-] = C\alpha \text{ mol/litre}$$

According to, law of equilibrium,

$$K = \frac{\left[A^+\right]\left[B^-\right]}{[AB]}$$

$$= \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

where K is ionisation constant for weak electrolytes. For weak electrolytes, $\alpha << 1$, so $\alpha$ can be neglected as compared to 1 *i.e.* $1 - \alpha \approx 1$.

$$\therefore \quad K = C\alpha^2$$

$$\Rightarrow \quad \alpha = \sqrt{\frac{K}{C}}$$

## Arrhenius Concept of Acids and Bases

**Acid:** An acid is a substance which contains hydrogen and which when dissolved into water gives hydrogen ions ($H^+$). The acid ionizes completely when dissolved in water, is called strong acid. An acid ionizes partially when dissolved in water, is called **weak acid**.

A **weak acid** solution contains unionized molecules in addition to ions. In general,

$$\underset{\text{Acid}}{\mathrm{HA\,(aq)}} \rightleftharpoons \mathrm{H^+\,(aq)} + \mathrm{A^-\,(aq)}$$

**Base:** A base is a substance which contains hydroxyl group and which when dissolved into water gives hydroxyl ions ($OH^-$).

A base that ionizes completely into its ions when dissolved in water, is called a **strong base**, and a base ionizes partially when dissolved in water is called a **weak base**. In general,

$$\underset{\text{Base}}{\mathrm{BOH\,(aq)}} \rightleftharpoons \mathrm{B^+\,(aq)} + \mathrm{OH^-\,(aq)}$$

**Neutralisation** is the process in which hydrogen ions and hydroxyl ions combine to form unionized molecules of water.

$$\mathrm{H^+\,(aq)} + \mathrm{OH^-\,(aq)} \rightleftharpoons \mathrm{H_2O\,}(l)$$

## Bronsted-Lowry Concept of Acids and Bases

An **acid** is defined as a substance which has the tendency to give a proton ($H^+$).

A **base** is defined as a substance which has a tendency to accept a proton ($H^+$).

**Conjugate base:** The remainder part of an acid after donating a proton, is called conjugate base.

$$\underset{\text{Acid}}{HCl\ (g)} + H_2O\ (l) \rightarrow H_3O^+\ (aq) + \underset{\text{Conjugate base}}{Cl^-(aq)}$$

**Conjugate acid:** Base when accepts a proton released by an acid is called as conjugate acid.

$$\underset{\text{Base}}{H_2O\ (l)} + H^+\ (\text{from an acid}) \rightarrow \underset{\text{Conjugate acid}}{H_3O^+\ (aq)}$$

**Amphoterism:** A particular can behave as an acid by donating a proton in one reaction and as a base in another by accepting a proton. Such a species is called as an amphoteric species. such as water.

$$\underset{\text{Acid}_1}{H_2O} + \underset{\text{Base}_2}{H_2O} \rightleftharpoons \underset{\text{Base}_1}{OH^-} + \underset{\text{Acid}_2}{H_3O^+}$$

## Lewis Concept of Acids and Bases

**Acid :** An acid is a substance or an ion which is capable of accepting a pair of electrons and is called as Lewis acid.

**Base :** Base is a substance or an ion which is capable of donating an unshared pair of electrons and is called as Lewis base.

## Types of Lewis Bases

(*i*) *Neutral molecules* having at least one lone pair of electrons. e.g. $NH_3$, R–$NH_2$, $R_2$–NH, R–OH, H–OH etc.

(*ii*) All negative ions like $F^-$, $Cl^-$, $Br^-$, $OH^-$, $CN^-$ etc.

## Types of Lewis Bases

(*i*) Electron deficient compounds or molecules having a central atom with incomplete octet : *e.g.* $BF_3$, $AlCl_3$ etc.

(*ii*) Cations e.g. $Ag^+$, $Cu^{2+}$, $Fe^{3+}$, etc.

(*iii*) Molecules with multiple bonds between two atoms of different electronegativities *e.g.* $CO_2$.

(*iv*) Molecules whose central atoms has empty d-orbitals, *e.g.* $SnCl_4$, $SiF_4$, $PF_5$, $PCl_5$ etc.

## Some Important Results

1. $P^H = -\log [H^+]$
2. $[H^+] = 10^{-P^H}$
3. $P^{OH} = -\log [OH^-]$
4. $P^{K_a} = -\log K_a$
5. $P^{K_b} = -\log K_b$

6. $P^{K_w} = -\log K_w$
7. $P^H$ of acidic solution $< 7$
8. $P^H$ of neutral solution $= 7$
9. $P^H$ of basic solution $> 7$
10. $P^H + P^{OH} = P^{K_w} = 14$
11. $K_w$ is called ionic product of water $= [H^+][OH^-] = 10^{-14}$ at 25°C
Thus in pure $H_2O$; $[H^+] = [OH^-] = 10^{-7}$ molar
12. $K_h = \frac{K_w}{K_a}$, for hydrolysis of anion of weak acid

$K_h = \frac{K_w}{K_b}$, for hydrolysis of cation of weak base.

$K_h = \frac{K_w}{K_a . K_b}$, for hydrolysis of weak acid-weak base salt.

where, $K_h$ is hydrolysis constant, $K_a$ is ionisation constant for an acid otherwise called acid dissociation constant and $K_b$ is ionisation constant for a base otherwise called base dissociation constant.

13. **$P^H$ of an acidic buffer solution and $P^{OH}$ of an alkaline buffer solution.**

(a) **Acidic Buffer :** (Weak acid and its salt which is a strong electrolyte; e.g., $CH_3COOH$ and $CH_3COONa$); in general, $H \rightleftharpoons HA^+ + A^-$

$P^H = P^{K_a} + \log \frac{[A^-]}{[HA]}$ (Henderson's equation)

(b) **Basic Buffer :** (Weak base and its salt which is a strong electrolyte; e.g., $NH_4OH$ and $NH_4Cl$) in general,

$$BOH \rightleftharpoons B^+ + OH^-, P^{OH} = P^{K_b} + \log \frac{[B^-]}{[BOH]}$$