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.

Δn = 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,

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

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

Moles before dissociation: $1 \quad 0 \quad 0$

Moles after dissociation: $(1-\alpha) \quad \alpha \quad \alpha$

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,

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

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

where K is ionisation constant for weak electrolytes. For weak electrolytes, $\alpha << 1$, so α 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,

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

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,

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

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

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

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. $P^{Ka} = -\log K_a$
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. $K_h = \dfrac{K_w}{K_a}$, for hydrolysis of anion of weak acid

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

$K_h = \dfrac{K_w}{K_a . K_b}$, 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,

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