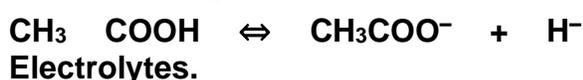


IONIC EQUILIBRIUM

- **Ionic Equilibrium:** The equilibrium established between the unionised molecules and the ions in the solution of weak electrolytes is called ionic equilibrium. e.g.,



- Chemical substances which can conduct electricity in their aqueous state or in molten state are called electrolytes.

STRONG AND WEAK ELECTROLYTES

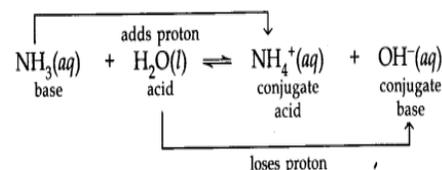
- Many electrolytes, when dissolved in water, are almost completely converted into ions. Such electrolytes are called **strong electrolytes**. *Ex.* all ionic compounds like NaCl, KCl, KNO₃, NH₄Cl.
- Many electrolytes ionize only partially. Such electrolytes are called **weak electrolytes**. *Ex.* many covalent compounds like CH₃COOH, NH₄OH, C₆H₅NH₂ are weak electrolytes.
- **Degree of ionization, (α):** It is defined as the fraction or percentage of the total amount (or concentration) of the electrolyte that is present in the form of ions.
- **Ostwald's dilution law :** Degree of dissociation of weak electrolyte,

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

GENERAL CONCEPTS OF ACIDS AND BASES

- **Arrhenius Concept of Acids and Bases:** According to Arrhenius theory, acids are substances that dissociates in water to give hydrogen ions H⁺(aq). Bases: Bases are substances that produce OH⁻(aq) after dissociation in water.
- **The Bronsted-Lowry Acids and Bases:** According to Bronsted-Lowry,

an acid is a substance which is capable of donating a hydrogen ion H⁺ and bases are substances capable of accepting a hydrogen ion H⁺.



- **Lewis Concept of Acids and Bases:** According to Lewis, acid is a substance which accepts electron pair and base is a substance which donates an electron pair.
- Electron deficient species like AlCl₃, BH₃, H⁺ etc. can act as **Lewis acids** while species like H₂O, NH₃ etc. can donate a pair of electrons, can act as **Lewis bases**.

Conjugate Acid or Base:

- Species - H⁺ = Conjugate base
- Species + H⁺ = Conjugate acid
- **Ionization of Acids and Bases:** Strength of acid or base is determined with the help of extent of ionization in aqueous solution.
- **pH Scale:** Hydrogen-ion concentration are measured as the number of gram ions of hydrogen ions present per litre of solution. Since these concentrations are usually small, the concentration is generally expressed as the pH of the solution. pH being the logarithm of the reciprocal of the hydrogen ion concentration.

$$\text{pH} = -\log \{[\text{H}^+]/\text{mol L}^{-1}\}$$

pH of pure water at 25°C is given as

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

Acidic solution has pH < 7

Basic solution has pH > 7

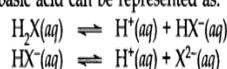
Neutral solution has pH = 7

$$\text{pH} = -\log [\text{H}_3\text{O}^+] \text{ or } [\text{H}^+] = 10^{-\text{pH}}$$

$$\text{pH} + \text{pOH} = \text{p}K_w = 14 \text{ at } 298\text{K}$$

- **Di and Polybasic Acids:** Acids which contain more than one ionizable proton per molecule are called Dibasic acids or polybasic acids or polyprotic acids. Common examples are oxalic acid, sulphuric acid, phosphoric acid etc.

The ionization reactions for a dibasic acid can be represented as.



Their equilibrium constants can be written as

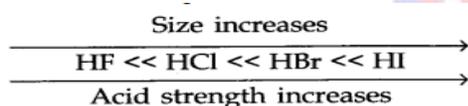
$$K_{a_1} = \frac{[\text{H}^+][\text{HX}^-]}{[\text{H}_2\text{X}]}, K_{a_2} = \frac{[\text{H}^+][\text{X}^{2-}]}{[\text{HX}^-]}$$

K_{a_1} and K_{a_2} are called first and second ionization constants respectively.

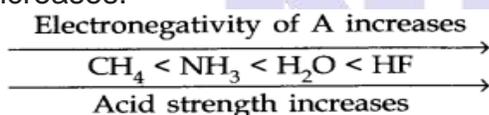
• $K_{a_1} > K_{a_2}$ for dibasic acid.

- **Factors Affecting Acid Strength**

When the strength of H-A bond decreases

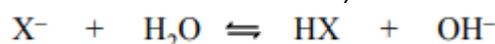


- The energy required to break the bond decreases, H-A becomes a stronger acid. As the size of A increases down the group, H-A bond strength decreases and so the acid strength increases. In a period, as the electro negativity of A increases the strength of the acid increases.



- **Common ion effect:** The depression of ionisation of weak electrolyte by the presence of common ion from a strong electrolyte is called common ion effect. For example degree of dissociation of NH_4OH decreases in the presence of strong electrolyte NH_4Cl .
- **Hydrolysis of salts and pH of their solutions:** Hydrolysis of salt is defined as the reaction of cation or anion with water as a result of which the pH of water changes.

- 1. Salts of strong and strong bases (e.g., NaCl) do not hydrolyse. The solution pH will be 7.
- 2. Salts of weak acids and strong bases (e.g., CH_3COONa) hydrolyse, $\text{pH} > 7$ (The anion acts as a base).



(Weak acid)

(Strong base)

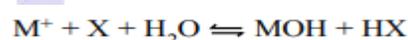
$$\text{pH} = 7 + \frac{1}{2} (\text{p}K_a + \log C)$$

- Salt of strong acids and weak bases (e.g., NH_4Cl) hydrolyse, $\text{pH} < 7$. (The cation acts as an acid).



$$\text{pH} = 7 - \frac{1}{2} (\text{p}K_a + \log C)$$

- Salt of weak acids and weak base (e.g., $\text{CH}_3\text{COONH}_4$) hydrolyse. The cation acts as an acid and anion as a base but whether the solution is anodic or basic depends upon the relative values of K_a and K_b for these ions.



$$\text{pH} = 7 + \frac{1}{2} (\text{p}K_a - \text{p}K_b)$$

- **Buffer solutions:** The solutions, which resist the change in pH on dilution or addition of small amounts of acid or base, are called buffer solutions.

- **Basic buffer:** Solution of weak base and its salt with strong acid, For e.g., $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$
- **Acidic buffer:** Solution of weak acid and its salt with strong base, For e.g., $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$.

- Henderson's Equation for the pH of Buffer solution—

- **Solubility Product (K_{sp}):** The equilibrium constant that represent the equilibrium between undissolved salt (solute) and its ions in a saturated solution is called solubility product constant (K_{sp}).



$$K_{sp} = [A^{y+}]^x [B^{x-}]^y$$

If ionic product $< K_{sp}$; salt remain dissolve.

If ionic product $> K_{sp}$; salt will be precipitated.

• **Relationship between solubility (S) and solubility product (K_{sp}):**

$$K_{sp} = x^x \cdot y^y \cdot S^{x+y}$$

For binary salts (e.g., AgCl, AgBr, AgI)

$$K_{sp} = S^2$$

For Ternary salts (e.g., PbI_2)

$$K_{sp} = 4S^3$$

- There are three different concepts of acids and bases proposed by Arrhenius, Brønsted and Lowry and Lewis respectively.
- According to Arrhenius Concept an acid is a substance capable of producing hydrogen ions by dissociating in aqueous solution while a base is a substance capable of providing a hydroxyl ion.
- Since a hydrogen ion H^+ is very small with high charge density it does not exist free in a polar solvent like water. It binds itself to a water molecule and form a hydronium ion (H_3O^+)
- According to Brønsted and Lowry, an acid is defined as a proton (H^+) donor, and a base is defined as a proton acceptor.
- According to Brønsted and Lowry definition the species in either side of the acid-base equilibrium, differ by the gain or loss of a proton. These are called a conjugate acid-base pair. In such a pair a strong acid has a weak conjugate base while a weak acid has a strong conjugate base.
- Lewis definition is quite broad, according to

him, an acid is defined as, 'any atom, molecule or ion that can accept an electron pair from any other atom, molecule or ion, while a base is 'any atom, molecule or ion that can donate a pair of electron'. The product of a reaction between an acid and a base is called an adduct.

- Strong Arrhenius acids and bases dissociate completely in aqueous solutions where as the weak acids and bases undergo partial ionisation. Higher the extent of ionisation stronger the acid or the base.
- In Brønsted- Lowry concept, the relative strength of an acid is defined as its relative tendency to lose/donate a proton to water.
- The ionisation equilibria of weak acids and bases are characterized by equilibrium constants called ionisation constants. The values of these constants are a measure of their relative strength.
- Water can act both as a weak acid as well a weak base. In a sample of water a small number of water molecules undergo autoionisation, in which half the ions act as an acid while the other half acts as a base.
- The presences of common ions in a solution of a weak acid or a weak base suppress its dissociation. Such solutions act as buffer solutions which resist a change in their pH on addition of small amount of an acid or a base. The pH of buffer solutions depend on their composition and can be found by using a simple equation called **Henderson Hasselbalch equation**.
- The aqueous solutions of certain salts also behave as acids or bases due to the hydrolysis of their cation or anion or both.

Check Yourself

1. The solubility of $\text{Ca}_3(\text{PO}_4)_2$ in water is y mol/L. Its solubility product is:

- (A) $6y^2$ (B) $36y^4$
 (C) $64y^5$ (D) $108y^5$

2. Which of the following aqueous solutions will have highest pH?

- (A) NaCl (B) CH_3COONa
 (C) Na_2CO_3 (D) NH_4Cl

3. What is the pH of a 0.10 M solution of barium hydroxide, $\text{Ba}(\text{OH})_2$?

- (A) 11.31 (B) 11.7
 (C) 13.30 (D) None of these

4. Which of the following oxides is not expected to react with sodium hydroxide?

- (A) CaO (B) SiO_2
 (C) BeO (D) B_2O_3

5. The pH of a 10^{-10} M NaOH solution is nearest to

- (A) 10 (B) 7
 (C) 4 (D) -10

Stretch Yourself

1. Explain why pure liquids and solids can be ignored while writing the value of equilibrium constants.

2. The value of K_c for the reaction $3\text{O}_2(\text{g}) \rightleftharpoons 2\text{O}_3(\text{g})$ is 2.0×10^{-50} at 25°C . If equilibrium concentration of O_2 in air at 25°C is 1.6×10^{-2} , what is the concentration of O_3 ?

3. What is meant by conjugate acid-base pair? Find the conjugate acid/base for the following species: HNO_2 , CH_3^- , HClO_4 , OH^- , CO_3^{2-} , S^{2-}

4. Which of the following are Lewis Acids?

H_2O , BF_3 , H^+ and NH_4^+

5. What will be the conjugate bases for the Bronsted acids? HF, H_2SO_4 and H_2CO_3 ?

Test Yourself

Question: The concentration of hydrogen ions in a sample of soft drink is 3.8×10^{-3} M. What is the pH value?

Answer: The pH of a solution is the negative logarithm of hydrogen ion concentration.

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log(3.8 \times 10^{-3})$$

$$\text{pH} = 2.42$$



Answers

Check Yourself

Answer: 1(D); 2(C); 3(C); 4(A); 5(C)

Stretch Yourself

1. Pure solids and liquids are not included in the equilibrium constant expression. This is because they do not affect the reactant amount at equilibrium in the reaction, so they are disregarded and kept at 1.

2. $3\text{O}_2(\text{g}) = 2\text{O}_3(\text{g})$
 Equilibrium constant (K_c) = $\frac{[\text{O}_3]^2}{[\text{O}_2]^3}$
 $2 \times 10^{-50} = \frac{[\text{O}_3]^2}{(1.6)^3 \times 10^{-6}}$
 $[\text{O}_3]^2 = \frac{2 \times 10^{-50} \times (1.6)^3 \times 10^{-6}}{1} = 8.192 \times 10^{-56}$
 $[\text{O}_3] = \sqrt{8.192 \times 10^{-56}}$
 $[\text{O}_3] = 2.86 \times 10^{-28} \text{M}$

3. Conjugate acid base pairs differ by a proton.
 For example, HCl, Cl^- represents conjugate acid base pair.
 The conjugate acid/base for the species HNO_2 , CN^- , HClO_4 , F^- , OH^- , CO_3^{2-} and S^{2-} are NO_2^- , HCN , ClO_4^- , HF , H_2O (acid) or O^{2-} (base), HCO_3^- and HS^- respectively.

4. BF_3 , H^+ and NH_4^+ are Lewis acids whereas H_2O is a Lewis base.

5. The conjugate bases for the Bronsted acids HF, H_2SO_4 and HCO_3^- are F^- , HSO_4^- and CO_3^{2-} respectively.