STUDY MATERIAL AND NUMERICAL PROBLEMS: ELECTROLYTES, PH, BUFFERS, AND INDICATORS

1. ELECTROLYTES: STRONG, MODERATE, AND WEAK

An electrolyte is a substance that produces an electrically conducting solution when dissolved in a polar solvent, such as water. This is achieved by dissociation of the dissolved substance into cations and anions.

Types of Electrolytes:

- **Strong Electrolytes:** Substances that dissociate almost completely in solution, resulting in a high concentration of ions. Examples: Strong acids (HCl, H_2SO_4), strong bases ($NaOH$, KOH), and most salts ($NaCl$, KNO_3).
- **Moderate Electrolytes:** Substances that dissociate to a moderate extent in solution. Examples: Acetic acid (CH_3COOH) in dilute solutions, ammonium hydroxide (NH_4OH).
- **Weak Electrolytes:** Substances that dissociate only slightly in solution, resulting in a low concentration of ions. Examples: Weak acids (CH_3COOH, H_2CO_3), weak bases (NH_4OH, $C_6H_5NH_2$), and water itself.

2. DEGREE OF IONIZATION (ALPHA, A)

The degree of ionization is the fraction or percentage of a molecule of an electrolyte that dissociates into ions in a given solvent at a specific temperature. It is represented by α.

α = (Number of molecules ionized) / (Total number of molecules dissolved)

For a general electrolyte AB dissociating into A^+ and B^-, the equilibrium is:
$AB \leftrightharpoons A^+ + B^-$

If 'C' is the initial concentration and α is the degree of ionization, then at equilibrium:
Concentration of $A^+ = C\alpha$
Concentration of $B^- = C\alpha$
Concentration of undissociated $AB = C(1-\alpha)$

Factors Affecting Degree of Ionization:

- **Nature of the Electrolyte:** Strong electrolytes have high α, weak electrolytes have low α.
- **Nature of the Solvent:** The polarity of the solvent plays a crucial role. Polar solvents favor ionization more than non-polar solvents.
- **Temperature:** Generally, an increase in temperature increases the degree of ionization for most electrolytes (except for some exceptions).
- **Dilution (Presence of other ions):** According to Ostwald's dilution law, the degree of ionization of a weak electrolyte increases with dilution. The presence of common ions decreases the degree of ionization.

3. IONIZATION CONSTANT (KA, KB) AND IONIC PRODUCT OF WATER (KW)

Ionization Constant: For a weak acid HA:
$HA \rightleftharpoons H^+ + A^-$
$K_a = [H^+][A^-] / [HA] = (C\alpha)(C\alpha) / C(1-\alpha) \approx C\alpha^2$ (if α is very small)
For a weak base BOH:
$BOH \rightleftharpoons B^+ + OH^-$
$K_b = [B^+][OH^-] / [BOH] = (C\alpha)(C\alpha) / C(1-\alpha) \approx C\alpha^2$ (if α is very small)

Ionic Product of Water (Kw): Water undergoes autoionization:
$H_2O \rightleftharpoons H^+ + OH^-$
$K_w = [H^+][OH^-]$
At 25�b0;C, $K_w = 1.0 \times 10^{-14}\ mol^2/L^2$.

Relationship: For a conjugate acid-base pair, $K_a * K_b = K_w$.

4. IONIZATION OF WEAK ACIDS AND BASES

The ionization of weak acids and bases is an equilibrium process. The ionization constant (Ka or Kb) quantifies the strength of the acid or base.

Example: Acetic Acid (CH_3COOH)
$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$
$K_a = [H^+][CH_3COO^-] / [CH_3COOH]$

Example: Ammonium Hydroxide (NH_4OH)
$NH_4OH \rightleftharpoons NH_4^+ + OH^-$
$K_b = [NH_4^+][OH^-] / [NH_4OH]$

The pH of solutions of weak acids and bases can be calculated using their K_a or K_b values and initial concentrations.

5. PH SCALE

The pH scale is a measure of the acidity or alkalinity of an aqueous solution. It is defined as the negative logarithm (base 10) of the hydrogen ion concentration.

$pH = -\log_{10}[H^+]$

$pOH = -\log_{10}[OH^-]$

Relationship: $pH + pOH = 14$ (at 25�b0;C)

- $pH < 7$: Acidic solution
- $pH = 7$: Neutral solution
- $pH > 7$: Basic (Alkaline) solution

6. SALT HYDROLYSIS

Salt hydrolysis is the reaction of the ions of a salt with water, leading to the formation of an acidic or basic solution. This occurs when the cation or anion (or both) of the salt is derived from a weak acid or weak base.

Types of Salt Hydrolysis:

- **Salt of Strong Acid & Strong Base (e.g., $NaCl$):** No hydrolysis occurs, solution remains neutral ($pH = 7$). Cation (Na^+) and anion (Cl^-) are spectator ions.
- **Salt of Strong Acid & Weak Base (e.g., NH_4Cl):** The cation derived from the weak base hydrolyzes. The solution becomes acidic.
  $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$
  Hydrolysis Constant, $K_h = K_w / K_b$ (where K_b is for the base NH_3).
  Degree of Hydrolysis, $h = \mathrm{sqrt}(K_h/C)$ where C is the salt concentration.
  $pH = 7 - 0.5*pK_b - 0.5*\log C$
- **Salt of Weak Acid & Strong Base (e.g., CH_3COONa):** The anion derived from the weak acid hydrolyzes. The solution becomes basic.
  $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$
  Hydrolysis Constant, $K_h = K_w / K_a$ (where K_a is for the acid CH_3COOH).
  Degree of Hydrolysis, $h = \mathrm{sqrt}(K_h/C)$.
  $pOH = 7 - 0.5*pK_a - 0.5*\log C$, therefore $pH = 7 + 0.5*pK_a + 0.5*\log C$

- **Salt of Weak Acid & Weak Base (e.g., $CH3COONH4$):** Both cation and anion hydrolyze. The pH depends on the relative strengths of the acid and base.
  $Kh = Kw / (Ka * Kb)$.
  If $Ka > Kb$, the solution is acidic. If $Ka < Kb$, the solution is basic. If $Ka = Kb$, the solution is neutral.
  $pH = 7 + 0.5*pKa - 0.5*pKb$

Conductometric Determination of Hydrolysis Constant: The change in conductivity of water upon addition of a salt of a weak acid/base can be used to determine the degree of hydrolysis and subsequently the hydrolysis constant.

7. BUFFER SOLUTIONS

A buffer solution is a solution that resists changes in pH when a small amount of acid or base is added to it. It typically consists of a weak acid and its conjugate base, or a weak base and its conjugate acid.

Buffer Action: The components of the buffer react with added acid/base, converting them into a weak acid/base or water, thus minimizing the pH change.

Buffer Capacity (β): A measure of the buffer's ability to resist pH change. It is defined as the amount of strong acid or base added per unit change in pH of one liter of buffer solution.
$\beta = dC_b / dpH = -dC_a / dpH$

Buffer Range: The pH range over which the buffer is effective. It is generally considered to be $pH = pKa \pm 1$ for an acid buffer.

Henderson-Hasselbalch Equation:

- **Derivation for Weak Acid Buffer (HA/A-):**
  $HA \leftrightharpoons H+ + A-$
  $Ka = [H+][A-] / [HA]$
  $[H+] = Ka * [HA] / [A-]$
  $-log10[H+] = -log10(Ka) - log10([HA] / [A-])$
  $pH = pKa + log10([Conjugate Base] / [Weak Acid])$
  $pH = pKa + log10([A-] / [HA])$
- **Derivation for Weak Base Buffer (B/BH+):**
  $B + H2O \leftrightharpoons BH+ + OH-$
  $Kb = [BH+][OH-] / [B]$
  $[OH-] = Kb * [B] / [BH+]$
  $-log10[OH-] = -log10(Kb) - log10([B] / [BH+])$
  $pOH = pKb + log10([Conjugate Acid] / [Weak Base])$

$pOH = pKb + log10([BH+] / [B])$
Using pH + pOH = 14, we get $pH = 14 - pOH = 14 - (pKb + log10([BH+] / [B]))$

Applications: Maintaining pH in biological systems (blood buffers), chemical reactions, pharmaceutical preparations, and industrial processes.

8. THEORY OF ACID–BASE INDICATORS

Acid-base indicators are weak organic acids or bases that change color over a specific pH range. They function based on the principle of equilibrium.

Ostwald's Theory: An indicator is a weak acid (HIn) or weak base (InOH). Its undissociated form and ionic form have different colors.

For an acid indicator (HIn):
HIn (acidic color) ⇋ H+ + In- (alkaline color)
The color change occurs when the ratio [In-]/[HIn] reaches a certain value, typically 10:1 or 1:10, within the indicator's dissociation constant (Kind).
$Kind = [H+][In-] / [HIn]$
The pH range of color change is approximately pKind ± 1.

Selection of Indicators: The indicator should have a pH range that matches the steep part of the titration curve.
* For strong acid-strong base titrations, any indicator (e.g., phenolphthalein, methyl orange) can be used.
* For strong acid-weak base titrations, methyl orange (pH range 3.1-4.4) is suitable as the equivalence point is acidic.
* For weak acid-strong base titrations, phenolphthalein (pH range 8.2-10.0) is suitable as the equivalence point is basic.

Limitations: The color change might not be sharp if the solution is highly colored or contains colloidal matter. The pH range of indicators can be affected by the presence of other salts (salt effect) or organic solvents.

NUMERICAL PROBLEMS

Problem 1: Degree of Ionization

Calculate the degree of ionization of a 0.1 M acetic acid solution if its Ka is 1.8 x 10^-5.

Solution:
For acetic acid, $CH3COOH \leftrightharpoons H+ + CH3COO-$
$Ka = 1.8 \times 10^{-5}$, $C = 0.1$ M
Using the approximation $Ka \approx C\alpha^2$ (since α is expected to be small):
$1.8 \times 10^{-5} = 0.1 * \alpha^2$
$\alpha^2 = (1.8 \times 10^{-5}) / 0.1 = 1.8 \times 10^{-4}$
$\alpha = \text{sqrt}(1.8 \times 10^{-4}) = 0.0134$
The degree of ionization is approximately 0.0134 or 1.34%.

Problem 2: pH of a Weak Acid

Calculate the pH of a 0.05 M solution of benzoic acid ($C6H5COOH$), given $Ka = 6.3 \times 10^{-5}$.

Solution:
$C6H5COOH \leftrightharpoons H+ + C6H5COO-$
$Ka = 6.3 \times 10^{-5}$, $C = 0.05$ M
$\alpha^2 = Ka / C = (6.3 \times 10^{-5}) / 0.05 = 1.26 \times 10^{-3}$
$\alpha = \text{sqrt}(1.26 \times 10^{-3}) = 0.0355$
$[H+] = C\alpha = 0.05 * 0.0355 = 0.001775$ M
$pH = -\log10[H+] = -\log10(0.001775) \approx 2.75$

Problem 3: pH of a Salt of Weak Acid and Strong Base

Calculate the pH of a 0.1 M sodium acetate ($CH3COONa$) solution. Ka for acetic acid is 1.8×10^{-5}.

Solution:
This is a salt of a weak acid ($CH3COOH$) and a strong base ($NaOH$).
$Kh = Kw / Ka = (1.0 \times 10^{-14}) / (1.8 \times 10^{-5}) \approx 5.56 \times 10^{-10}$
$C = 0.1$ M
$h = \text{sqrt}(Kh/C) = \text{sqrt}(5.56 \times 10^{-10} / 0.1) = \text{sqrt}(5.56 \times 10^{-9}) \approx 7.46 \times 10^{-5}$
$[OH-] = C*h = 0.1 * 7.46 \times 10^{-5} = 7.46 \times 10^{-6}$ M
$pOH = -\log10(7.46 \times 10^{-6}) \approx 5.13$
$pH = 14 - pOH = 14 - 5.13 = 8.87$

Alternatively, using the direct formula:
$pKa = -\log10(1.8 \times 10^{-5}) \approx 4.74$
$pH = 7 + 0.5*pKa + 0.5*\log C = 7 + 0.5*(4.74) + 0.5*\log(0.1) = 7 + 2.37 + 0.5*(-1) = 7 + 2.37 - 0.5 = 8.87$

Problem 4: Buffer Solution pH

Calculate the pH of a buffer solution containing 0.2 M acetic acid and 0.3 M sodium acetate. Ka for acetic acid is 1.8 x 10^-5.

Solution:
Using Henderson-Hasselbalch equation:
pH = pKa + log10([Conjugate Base] / [Weak Acid])
pKa = -log10(1.8 x 10^-5) ≈ 4.74
[Conjugate Base] = [CH3COO-] = 0.3 M
[Weak Acid] = [CH3COOH] = 0.2 M
pH = 4.74 + log10(0.3 / 0.2)
pH = 4.74 + log10(1.5)
pH = 4.74 + 0.176 = 4.92

Problem 5: Buffer Capacity

A buffer solution is prepared by mixing 100 mL of 0.1 M NH3 and 100 mL of 0.1 M NH4Cl. Calculate the buffer capacity of this solution if 1 mL of 1 M HCl is added. (Kb for NH3 = 1.8 x 10^-5).

Solution:
Initial moles of NH3 = 0.1 M * 0.1 L = 0.01 mol
Initial moles of NH4Cl = 0.1 M * 0.1 L = 0.01 mol
Initial pH: pKb = -log10(1.8 x 10^-5) ≈ 4.74. pOH = pKb + log10([Acid]/[Base]) = 4.74 + log10(0.1/0.1) = 4.74. pH = 14 - 4.74 = 9.26.

When 1 mL of 1 M HCl is added:
Moles of HCl added = 1 x 10^-3 L * 1 M = 0.001 mol.
This HCl will react with NH3 (the base component of the buffer):
NH3 + H+ → NH4+
New moles of NH3 = 0.01 - 0.001 = 0.009 mol
New moles of NH4+ = 0.01 + 0.001 = 0.011 mol

New pH: The total volume is now 200 mL + 1 mL = 201 mL = 0.201 L.
New [NH3] = 0.009 mol / 0.201 L ≈ 0.0448 M
New [NH4+] = 0.011 mol / 0.201 L ≈ 0.0547 M
New pOH = pKb + log10([Acid]/[Base]) = 4.74 + log10(0.0547 / 0.0448) = 4.74 + log10(1.22) = 4.74 + 0.086 = 4.826
New pH = 14 - 4.826 = 9.174

Change in pH = ΔpH = 9.174 - 9.26 = -0.086

Amount of acid added = 0.001 mol per liter of buffer.
Buffer Capacity (β) = (moles of acid added) / (volume of buffer in L * ΔpH)
$\beta \approx (0.001 \text{ mol}) / (0.201 \text{ L} * 0.086) \approx 0.0727 \text{ mol/L}$