1. (a) State the Le Chatelier's principle. For the equilibrium reactions given below, discuss how the equilibrium will shift with the change in temperature and pressure:

    o **Le Chatelier's Principle:** Le Chatelier's principle states that if a change of condition (such as temperature, pressure, or concentration) is applied to a system in equilibrium, the system will shift in a direction that counteracts the applied change, thereby re-establishing a new equilibrium.

    o **Note:** The equilibrium reactions for which the shift in equilibrium with temperature and pressure change needs to be discussed are *not provided* in the given excerpt. Therefore, a specific discussion of the shift is not possible without the reaction details.

2. (b) What are Miller Indices? Determine the Miller indices of the planes that intersect the crystallographic axes at the distance given below:

    o **Miller Indices:** Miller indices are a notation system used in crystallography to describe the orientation of planes in a crystal lattice. They are a set of three integers (hkl) that are inversely proportional to the intercepts of the plane with the crystallographic axes. They are written without commas and enclosed in parentheses, e.g., (111).

    o **Steps to Determine Miller Indices:**

        i. Determine the intercepts of the plane with the crystallographic axes (a, b, c) in terms of unit cell dimensions.

        ii. Take the reciprocals of these intercepts.

        iii. Clear the fractions to obtain the smallest set of integers.

        iv. Enclose the integers in parentheses (hkl). If an intercept is negative, a bar is placed over the corresponding index.

- (i) (1a, 3b, -c)

    - **Intercepts:** 1, 3, -1

    - **Reciprocals:** 1/1, 1/3, 1/(-1) = 1, 1/3, -1

    - **Clear Fractions (multiply by 3):** $3 \times 1 = 3$, $3 \times (1/3) = 1$, $3 \times (-1) = -3$

    - **Miller Indices: $(31\bar{3})$**

- (ii) (2a, 3b, 4c)

    - **Intercepts:** 2, 3, 4

    - **Reciprocals:** 1/2, 1/3, 1/4

    - **Clear Fractions (find LCM of 2, 3, 4, which is 12):**

        - $12 \times (1/2) = 6$

        - $12 \times (1/3) = 4$

        - $12 \times (1/4) = 3$

    - **Miller Indices: (643)**

3. (c) A first-order reflection from the (111) planes of a cubic crystal were observed at a glancing angle of 11.2° when Cu (Kα) X-rays of wavelength 154 pm were used. What is the length of the side of the unit cell? Calculate the angle at which the same crystal will give a reflection from the (123) planes.

- **Part 1: Length of the side of the unit cell (a)**

    - **Bragg's Law:** $n\lambda = 2d\sin\theta$

        - n = order of reflection = 1 (first-order)

        - λ = wavelength = 154 pm = 154×10^{-12} m

        - θ = glancing angle = 11.2°

- d = interplanar spacing for (hkl) planes

  o **For a cubic crystal, interplanar spacing d:** $d = \frac{a}{\sqrt{h^2+k^2+l^2}}$

    ▪ For (111) planes, h=1, k=1, l=1.

    ▪ $d_{111} = \frac{a}{\sqrt{1^2+1^2+1^2}} = \frac{a}{\sqrt{3}}$

  o **Substitute into Bragg's Law:**

    ▪ $1 \times (154 \times 10^{-12} \text{ m}) = 2 \times \frac{a}{\sqrt{3}} \times \sin(11.2°)$

    ▪ $154 \times 10^{-12} = \frac{2a}{\sqrt{3}} \times 0.1942$ (sin 11.2° ≈ 0.1942)

    ▪ $a = \frac{154 \times 10^{-12} \times \sqrt{3}}{2 \times 0.1942}$

    ▪ $a = \frac{154 \times 10^{-12} \times 1.732}{0.3884}$

    ▪ $a = \frac{266.628 \times 10^{-12}}{0.3884}$

    ▪ $a \approx 686.5 \times 10^{-12}$ m = **686.5 pm**

- **Part 2: Angle for (123) planes**

  o For (123) planes, h=1, k=2, l=3.

  o $d_{123} = \frac{a}{\sqrt{1^2+2^2+3^2}} = \frac{a}{\sqrt{1+4+9}} = \frac{a}{\sqrt{14}}$

  o Substitute the calculated 'a' value:

    ▪ $d_{123} = \frac{686.5 \text{ pm}}{\sqrt{14}} = \frac{686.5}{3.7417} \approx 183.47$ pm

  o **Apply Bragg's Law again:**

    ▪ $n\lambda = 2d_{123}\sin\theta'$ (where θ' is the new glancing angle)

    ▪ $1 \times (154 \text{ pm}) = 2 \times (183.47 \text{ pm}) \times \sin\theta'$

    ▪ $154 = 366.94 \times \sin\theta'$

- $\sin\theta' = \frac{154}{366.94} \approx 0.4197$

- $\theta' = \arcsin(0.4197)$

- $\theta' \approx 24.81°$

- **Answer:**

  - The length of the side of the unit cell is approximately **686.5 pm**.

  - The angle at which the same crystal will give a reflection from the (123) planes is approximately **24.81°**.

4. (a) What is the effect of temperature change on the equilibrium constant? Derive a relation between K_p and T starting from the Gibbs Helmholtz equation.

- **Effect of Temperature Change on Equilibrium Constant:**

  - The equilibrium constant (K) of a reaction is highly dependent on temperature.

  - For an **endothermic reaction** ($\Delta H > 0$), an increase in temperature shifts the equilibrium to the right (products), leading to an **increase** in the equilibrium constant.

  - For an **exothermic reaction** ($\Delta H < 0$), an increase in temperature shifts the equilibrium to the left (reactants), leading to a **decrease** in the equilibrium constant.

  - This relationship is quantitatively described by the Van't Hoff equation.

- **Derivation of Relation between K_p and T from Gibbs-Helmholtz Equation:**

  - **Gibbs-Helmholtz Equation:** This equation relates the change in Gibbs free energy (ΔG) to temperature (T) and enthalpy change (ΔH).

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- $\left[\frac{\partial (\Delta G/T)}{\partial T}\right]_P = -\frac{\Delta H}{T^2}$ (Equation 1)

- **Relation between $\Delta G°$ and Equilibrium Constant (K_p):**

  - For a reaction in equilibrium under standard conditions:

    - $\Delta G° = -RT\ln K_p$

    - Dividing by T: $\frac{\Delta G°}{T} = -R\ln K_p$ (Equation 2)

- **Substitute Equation 2 into Equation 1:**

  - $\left[\frac{\partial (-R\ln K_p)}{\partial T}\right]_P = -\frac{\Delta H°}{T^2}$

  - $-R\left[\frac{\partial (\ln K_p)}{\partial T}\right]_P = -\frac{\Delta H°}{T^2}$

  - $\left[\frac{\partial (\ln K_p)}{\partial T}\right]_P = \frac{\Delta H°}{RT^2}$ (This is the **Van't Hoff Equation**)

- **Integrating the Van't Hoff Equation:**

  - Assuming $\Delta H°$ is constant over a small temperature range, we can integrate the Van't Hoff equation.

  - $\int d(\ln K_p) = \int \frac{\Delta H°}{RT^2} dT$

  - $\ln K_p = -\frac{\Delta H°}{RT} + C$ (where C is the integration constant)

  - **For two different temperatures (T_1 and T_2) and corresponding equilibrium constants (K_{p1} and K_{p2}):**

    - $\ln K_{p2} - \ln K_{p1} = \int_{T_1}^{T_2} \frac{\Delta H°}{RT^2} dT$

    - $\ln\left(\frac{K_{p2}}{K_{p1}}\right) = \frac{\Delta H°}{R}\left[-\frac{1}{T}\right]_{T_1}^{T_2}$

    - $\ln\left(\frac{K_{p2}}{K_{p1}}\right) = \frac{\Delta H°}{R}\left(-\frac{1}{T_2} - \left(-\frac{1}{T_1}\right)\right)$

- $\ln\left(\dfrac{K_{p2}}{K_{p1}}\right) = \dfrac{\Delta H°}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$

  o **Conclusion:** This derived relation shows that the equilibrium constant (K_p) changes with temperature (T) and is dependent on the standard enthalpy change of the reaction ($\Delta H°$).

5. (b) Explain the following:

  o (i) The molar conductivities of the alkali metal ions increase on going from Li⁺ to Cs⁺.

    ▪ **Reason:**

      • **Hydration:** In aqueous solutions, ions are surrounded by a shell of water molecules (hydrated). The size of this hydration shell is inversely proportional to the ionic radius of the bare ion and directly proportional to the charge density.

      • **Li⁺ vs. Cs⁺:** Li⁺ is the smallest alkali metal ion, and due to its high charge density (charge/radius ratio), it attracts a large number of water molecules very strongly, forming a large and tightly bound hydration shell. Cs⁺, being the largest alkali metal ion, has a much lower charge density and thus attracts fewer water molecules, forming a smaller and looser hydration shell.

      • **Effective Size and Mobility:** The species that actually moves through the solution is the hydrated ion. A smaller hydrated ion experiences less resistance from the solvent molecules and can move more freely.

      • **Trend:** Although the bare ionic radius increases from Li⁺ to Cs⁺, the size of the *hydrated* ion decreases from Li⁺ to Cs⁺. Therefore, the hydrated

Cs⁺ ion is effectively smaller and moves more easily through the solution than the heavily hydrated Li⁺ ion.

- **Molar Conductivity:** Molar conductivity is directly related to the mobility of the ions. Since the mobility of the hydrated ions increases from Li⁺ to Cs⁺, their molar conductivities also increase in that order.

o (ii) Acetate ions have lower conductivity than chloride ions.

- **Reason:**

  - **Size and Shape:** The chloride ion (Cl^-) is a relatively small, spherical inorganic anion. The acetate ion (CH_3COO^-) is a larger, polyatomic organic anion with a more complex shape.

  - **Hydration:** While both ions are hydrated, the difference in their intrinsic size and shape significantly impacts their movement through the solvent. The larger and less symmetrical acetate ion experiences greater frictional resistance as it moves through the solvent compared to the smaller, more compact chloride ion.

  - **Mobility:** Ionic conductivity is directly proportional to ionic mobility (the speed at which an ion moves under a unit electric field). Since the acetate ion is larger and less mobile due to greater resistance, its ionic mobility (and thus its conductivity) will be lower than that of the chloride ion.

  - **Delocalization of Charge:** Although not the primary factor, the negative charge in the acetate ion is delocalized over the two oxygen atoms, making the charge density somewhat lower and distributed over a larger volume compared to the

concentrated charge on the chloride ion. This can also contribute to lower effective interaction with the electric field and solvent.

6. (c) State and explain Kohlrausch's law. Illustrate how this law is used for the calculation of molar ionic conductance at infinite dilution of weak electrolytes.

- **Kohlrausch's Law (Law of Independent Migration of Ions):**

  - **Statement:** Kohlrausch's law states that at infinite dilution (or zero concentration), when the interionic interactions are negligible, the molar conductivity of an electrolyte is the sum of the individual molar ionic conductivities of its constituent cations and anions. Each ion contributes a definite amount to the total molar conductivity of the electrolyte, irrespective of the nature of the other ion present in the solution.

  - **Mathematical Expression:** $\Lambda^\circ_m = \nu_+ \lambda^\circ_+ + \nu_- \lambda^\circ_-$

    - Where:

      - Λ°_m is the molar conductivity at infinite dilution of the electrolyte.

      - ν_+ and ν_- are the number of cations and anions, respectively, produced by one formula unit of the electrolyte.

      - λ°_+ and λ°_- are the molar ionic conductivities at infinite dilution of the cation and anion, respectively.

- **Explanation:**

  - At infinite dilution, the ions are so far apart that the attractive and repulsive forces between them (interionic interactions) become negligible.

- o Under these conditions, each ion moves independently under the influence of the electric field, and its contribution to the total conductivity is solely determined by its own nature (charge, size of hydrated ion, and mobility), unaffected by the presence of the other ions.

- o This allows the total conductivity to be expressed as a simple sum of the individual contributions.

- **Calculation of Molar Ionic Conductance at Infinite Dilution of Weak Electrolytes:**

  - o Weak electrolytes (e.g., acetic acid, CH_3COOH) do not completely dissociate even at high dilutions. Therefore, their molar conductivity (Λ_m) does not reach a limiting value easily by extrapolation of Λ_m vs. $\sqrt{C}$ plots (unlike strong electrolytes).

  - o Kohlrausch's law provides a way to calculate Λ_m° for weak electrolytes indirectly, using the Λ_m° values of strong electrolytes.

  - o **Method:** We need to choose three strong electrolytes such that their combination allows us to isolate the desired ions of the weak electrolyte.

  - o **Example: Calculating Λ_m° for Acetic Acid (CH_3COOH)**

    - Acetic acid is a weak electrolyte. Its Λ_m° cannot be directly obtained by extrapolation.

    - We can use the Λ_m° values of three strong electrolytes:

      1. Sodium acetate (CH_3COONa): A strong electrolyte containing the acetate ion.

         - o $\Lambda_m^\circ(CH_3COONa) = \lambda_{CH_3COO^-}^\circ + \lambda_{Na^+}^\circ$ (Equation A)

2. Hydrochloric acid (HCl): A strong electrolyte containing the hydrogen ion.

- $\Lambda_m^\circ(HCl) = \lambda_{H^+}^\circ + \lambda_{Cl^-}^\circ$ (Equation B)

3. Sodium chloride ($NaCl$): A strong electrolyte to cancel out unwanted ions.

- $\Lambda_m^\circ(NaCl) = \lambda_{Na^+}^\circ + \lambda_{Cl^-}^\circ$ (Equation C)

- **Combination:**

  - We want to find $\Lambda_m^\circ(CH_3COOH) = \lambda_{CH_3COO^-}^\circ + \lambda_{H^+}^\circ$.

  - This can be obtained by:

    - $\Lambda_m^\circ(CH_3COOH) = \Lambda_m^\circ(CH_3COONa) + \Lambda_m^\circ(HCl) - \Lambda_m^\circ(NaCl)$

  - Substituting the expressions from Equations A, B, and C:

    - $\Lambda_m^\circ(CH_3COOH) = (\lambda_{CH_3COO^-}^\circ + \lambda_{Na^+}^\circ) + (\lambda_{H^+}^\circ + \lambda_{Cl^-}^\circ) - (\lambda_{Na^+}^\circ + \lambda_{Cl^-}^\circ)$

    - $\Lambda_m^\circ(CH_3COOH) = \lambda_{CH_3COO^-}^\circ + \lambda_{H^+}^\circ$

- **Conclusion:** By using the experimentally determined molar conductivities at infinite dilution of suitable strong electrolytes (which can be obtained by extrapolation of Λ_m vs. $\sqrt{C}$ plots), Kohlrausch's law allows us to calculate the molar conductivity at infinite dilution for weak electrolytes.

5. (a) Describe the powder method to determine the crystal structure. Explain why it is not possible to deduce the position of hydrogen atoms from X-ray diffraction.

- **Powder Method (Debye-Scherrer Method) for Crystal Structure Determination:**

- o **Principle:** The powder method is an X-ray diffraction technique used to determine the crystal structure of crystalline materials, especially when a single crystal of suitable size is not available. It utilizes the fact that a powdered sample contains a large number of tiny crystallites oriented randomly in all possible directions. When X-rays interact with this random arrangement, they will find crystallites oriented at the correct Bragg angle (θ) to produce diffraction for every possible set of (hkl) planes.

- o **Experimental Setup:**

    - ii. **X-ray Source:** A monochromatic beam of X-rays (e.g., Cu Kα) is used.

    - iii. **Sample:** The crystalline material is finely ground into a powder (to ensure random orientation of crystallites) and placed in a thin-walled capillary tube or pressed into a flat disc.

    - iv. **Detector:** A cylindrical photographic film (Debye-Scherrer camera) or an electronic detector (diffractometer) is placed around the sample.

- o **Procedure:**

    - v. The monochromatic X-ray beam is directed at the powdered sample.

    - vi. As the X-rays pass through, crystallites oriented at the Bragg angle (for various sets of planes) will diffract the X-rays.

    - vii. Because of the random orientation of the crystallites, for each set of (hkl) planes, the diffracted X-rays will form a cone (with the beam as the axis) at an angle of 2θ to the incident beam.

    - viii. When these cones intersect the cylindrical film, they produce a series of concentric dark rings (lines on the

unrolled film). In an electronic diffractometer, peaks of intensity are recorded at specific 2θ angles.

ix. The positions of these diffraction lines/peaks (2θ) and their intensities are measured.

o **Data Analysis and Structure Determination:**

x. From the measured 2θ values, the interplanar spacings (d) for each set of planes can be calculated using Bragg's Law: $n\lambda = 2d\sin\theta$.

xi. For a given crystal system (e.g., cubic, tetragonal), specific relationships exist between 'd' and the unit cell parameters (a, b, c) and Miller indices (h, k, l). By indexing the observed d-spacings to possible (hkl) values, the unit cell parameters can be determined.

xii. The intensities of the diffraction lines provide information about the positions of atoms within the unit cell (structure factor calculations). By comparing observed intensities with calculated intensities for various structural models, the crystal structure can be elucidated.

- **Why it is not possible to deduce the position of hydrogen atoms from X-ray diffraction:**

  o **Interaction with X-rays:** X-rays primarily interact with the electron clouds of atoms. The intensity of X-ray scattering by an atom is directly proportional to the number of electrons it possesses (its atomic number, Z).

  o **Hydrogen's Low Atomic Number:** Hydrogen has an atomic number (Z) of 1, meaning it has only one electron. This makes it an extremely weak scatterer of X-rays.

  o **Visibility Issue:** Compared to heavier atoms (even carbon, oxygen, nitrogen), the scattering contribution from hydrogen atoms is so small that it is often masked by the stronger

scattering from other atoms in the crystal. The electron density associated with hydrogen is usually too low to be resolved accurately in an X-ray diffraction experiment.

- o **Alternative for Hydrogen:** To accurately locate hydrogen atoms, alternative diffraction techniques like **neutron diffraction** are used. Neutrons interact with the nucleus of atoms, and hydrogen (specifically deuterium, which has a higher scattering cross-section than protium) has a significant scattering cross-section for neutrons, making it "visible" in neutron diffraction patterns.

6. (b) Draw the planes for which the Miller indices are (112) and (200).

- **Understanding Miller Indices:**

  - o (hkl) means the plane intercepts the axes at a/h, b/k, and c/l.

  - o If an index is zero (e.g., (110)), it means the plane is parallel to that axis (intercept at infinity).

  - o A bar over an index (e.g., ($\bar{1}$11)) means the intercept is on the negative side of the axis.

- **Plane (112):**

  - o **Intercepts:** Reciprocals are 1/1, 1/1, 1/2.

    - ▪ Intercepts on a, b, c axes are: 1a, 1b, 1/2c.

  - o **Drawing (Conceptual for a cubic unit cell):**

    - ▪ Imagine a cube (unit cell).

    - ▪ Mark a point at 1 unit along the 'a' axis.

    - ▪ Mark a point at 1 unit along the 'b' axis.

    - ▪ Mark a point at 1/2 unit along the 'c' axis.

- Connect these three points to form the plane. The plane will cut across the unit cell.

  (Visual Description):

  - Origin at one corner (0,0,0).

  - X-axis (a-axis) extends right.

  - Y-axis (b-axis) extends up.

  - Z-axis (c-axis) extends out.

  - The plane would pass through (1,0,0), (0,1,0), and (0,0,0.5).

  - The plane would slice the cube, starting from the corner (1,0,0) on the x-axis, going to (0,1,0) on the y-axis, and then to (0,0,0.5) on the z-axis.

- **Plane (200):**

  o **Intercepts:** Reciprocals are 1/2, 1/0, 1/0.

    - Intercepts on a, b, c axes are: 1/2a, ∞b, ∞c.

  o **Drawing (Conceptual for a cubic unit cell):**

    - The plane intersects the 'a' axis at 1/2 (halfway along the 'a' axis).

    - It is parallel to the 'b' axis (y-axis) and parallel to the 'c' axis (z-axis).

    - This means the plane is a simple slice parallel to the bc-plane, located at x = 1/2.

      (Visual Description):

      - Origin at one corner (0,0,0).

      - X-axis (a-axis) extends right.

- Y-axis (b-axis) extends up.

- Z-axis (c-axis) extends out.

- The plane would be a vertical slice through the middle of the unit cell, perpendicular to the x-axis. It would pass through the points (0.5, 0, 0), (0.5, 1, 0), (0.5, 0, 1), (0.5, 1, 1).

7. (c) What are Weiss indices? What are the corresponding Miller indices of the Weiss indices of crystal planes given below:

- **Weiss Indices:**

  - Weiss indices are a notation system used to describe the orientation of crystal planes. They represent the intercepts of a plane with the crystallographic axes (a, b, c) in terms of multiples of the unit cell dimensions.

  - They are written as a ratio or set of integers representing the actual intercept values along the a, b, and c axes. For example, (a, 2b, 3c) means the plane intercepts the 'a' axis at 'a', the 'b' axis at '2b', and the 'c' axis at '3c'. Infinity (∞) is used if the plane is parallel to an axis.

- **Conversion from Weiss Indices to Miller Indices:**

  - The conversion involves the same steps as determining Miller indices from intercepts:

    xiii. Write down the Weiss indices (intercepts in terms of a, b, c).

    xiv. Take the reciprocals of these intercept coefficients.

    xv. Clear the fractions to get the smallest set of integers.

    xvi. Enclose in parentheses (hkl).

  - (i) (2a, 2b, 2c)

- **Intercept Coefficients:** 2, 2, 2

- **Reciprocals:** 1/2, 1/2, 1/2

- **Clear Fractions (multiply by 2):** $2 \times (1/2) = 1$, $2 \times (1/2) = 1$, $2 \times (1/2) = 1$

- **Corresponding Miller Indices: (111)**

  - (ii) (a, b, ∞c)

    - **Intercept Coefficients:** 1, 1, ∞

    - **Reciprocals:** 1/1, 1/1, 1/∞ = 1, 1, 0

    - **Clear Fractions:** (Already integers)

    - **Corresponding Miller Indices: (110)**

6. (a) Deduce the relation between K_h, K_a and Kw for a salt of a weak acid and a weak base. Also, find the pH of the hydrolyzed salt solution.

- **Hydrolysis of a Salt of Weak Acid and Weak Base:**

  - Consider a salt of a weak acid (HA) and a weak base (BOH), such as NH_4CH_3COO (ammonium acetate).

  - When this salt dissolves in water, both the cation (B^+) and the anion (A^-) undergo hydrolysis:

    - Cation hydrolysis: $B^+(aq) + H_2O(l) \rightleftharpoons BOH(aq) + H^+(aq)$

    - Anion hydrolysis: $A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)$

  - The overall hydrolysis reaction can be written by summing these two reactions and simplifying:

    - $B^+(aq) + A^-(aq) + H_2O(l) \rightleftharpoons BOH(aq) + HA(aq)$

  - The equilibrium constant for this hydrolysis is K_h.

- $K_h = \frac{[BOH][HA]}{[B^+][A^-]}$ (Equation 1)

- **Relation between K_h, K_a, and K_w:**

  o We know the following equilibrium expressions:

    - **For the weak acid (HA):** $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

      - $K_a = \frac{[H^+][A^-]}{[HA]}$ (Equation 2)

    - **For the weak base (BOH):** $BOH(aq) \rightleftharpoons B^+(aq) + OH^-(aq)$

      - $K_b = \frac{[B^+][OH^-]}{[BOH]}$ (Equation 3)

    - **For water dissociation:** $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$

      - $K_w = [H^+][OH^-]$ (Equation 4)

  o Now, manipulate these equations to derive K_h:

    - From Equation 2, $[A^-] = \frac{K_a[HA]}{[H^+]}$

    - From Equation 3, $[B^+] = \frac{K_b[BOH]}{[OH^-]}$

    - From Equation 4, $[OH^-] = \frac{K_w}{[H^+]}$

    - Substitute these into the K_h expression (Equation 1):

      - $K_h = \frac{[BOH][HA]}{\left(\frac{K_b[BOH]}{[OH^-]}\right)\left(\frac{K_a[HA]}{[H^+]}\right)}$

      - $K_h = \frac{[BOH][HA] \times [OH^-][H^+]}{K_b[BOH]K_a[HA]}$

      - $K_h = \frac{[H^+][OH^-]}{K_aK_b}$

      - $K_h = \frac{K_w}{K_aK_b}$

- o **Relation:** $K_h = \dfrac{K_w}{K_a K_b}$

- **pH of the Hydrolyzed Salt Solution:**

  - o For a salt of a weak acid and a weak base, both the cation and anion hydrolyze.

  - o The net effect on pH depends on the relative strengths of the weak acid and weak base (i.e., the relative values of K_a and K_b).

  - o From the overall hydrolysis reaction: $B^+(aq) + A^-(aq) + H_2O(l) \rightleftharpoons BOH(aq) + HA(aq)$

  - o Let 'x' be the concentration of HA and BOH formed at equilibrium.

  - o Initial concentration of salt = C.

  - o At equilibrium: $[B^+] \approx C, [A^-] \approx C, [HA] = x, [BOH] = x$. (Assuming low degree of hydrolysis)

  - o From the acid dissociation: $K_a = \dfrac{[H^+][A^-]}{[HA]} \Longrightarrow [H^+] = \dfrac{K_a[HA]}{[A^-]}$

  - o From the base dissociation: $K_b = \dfrac{[B^+][OH^-]}{[BOH]} \Longrightarrow [OH^-] = \dfrac{K_b[BOH]}{[B^+]}$

  - o Also, $[H^+][OH^-] = K_w \Longrightarrow [OH^-] = \dfrac{K_w}{[H^+]}$

  - o Substitute $[OH^-]$: $\dfrac{K_w}{[H^+]} = \dfrac{K_b[BOH]}{[B^+]}$

  - o So, $[H^+] = \dfrac{K_w[B^+]}{K_b[BOH]}$

  - o Since $[HA] \approx [BOH]$ and $[A^-] \approx [B^+]$ for the hydrolysis (assuming the degree of hydrolysis is small and initial salt concentration is 'C'), we can write:

    - ▪ $\dfrac{[H^+]}{K_a} \approx \dfrac{[HA]}{[A^-]}$ and $\dfrac{[H^+]}{K_w} \approx \dfrac{[BOH]}{K_b[B^+]}$

- From the hydrolysis equilibrium, $[HA] \approx [BOH]$.

- Multiplying the expressions for $[H^+]$ from acid and base hydrolysis and using $[HA] = [BOH]$:

  - $[H^+]^2 = \frac{K_w \cdot K_a \cdot [B^+] \cdot [HA]}{K_b \cdot [BOH] \cdot [A^-]}$

  - Since $[B^+] \approx [A^-]$ and $[HA] \approx [BOH]$ in the overall hydrolysis.

  - $[H^+]^2 = \frac{K_w \cdot K_a}{K_b}$

  - $[H^+] = \sqrt{\frac{K_w \cdot K_a}{K_b}}$

  o Taking negative logarithm on both sides:

  - $-\log[H^+] = -\frac{1}{2}\log K_w - \frac{1}{2}\log K_a + \frac{1}{2}\log K_b$

  - $pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b$

  - **pH** $= 7 + \frac{1}{2}(pK_a - pK_b)$ (at 25°C, where $pK_w = 14$)

  o **Interpretation of pH:**

  - If $K_a = K_b$ (or $pK_a = pK_b$), then pH = 7 (neutral solution).

  - If $K_a > K_b$ (or $pK_a < pK_b$), then pH < 7 (acidic solution).

  - If $K_a < K_b$ (or $pK_a > pK_b$), then pH > 7 (basic solution).

7. (b) What is pH scale? Calculate the pH of a solution obtained by mixing 25 mL of 0.2 M HCl with 50 mL of 0.25M NaOH. Take Kw=10^{-14}.

- **pH Scale:**

  o The pH scale is a logarithmic scale used to specify the acidity or basicity of an aqueous solution. It primarily measures the

concentration of hydrogen ions (H^+ or hydronium ions, H_3O^+) in a solution.

- o **Definition:** pH is defined as the negative logarithm (base 10) of the molar concentration of hydrogen ions ($[H^+]$).

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

- o **Range:** The pH scale typically ranges from 0 to 14 at 25°C:

  - pH < 7: Acidic solution (higher $[H^+]$ than pure water)

  - pH = 7: Neutral solution (equal $[H^+]$ and $[OH^-]$)

  - pH > 7: Basic (alkaline) solution (lower $[H^+]$ than pure water, higher $[OH^-]$)

- o **Significance:** The pH scale provides a convenient way to express very large or very small hydrogen ion concentrations in a compact and understandable manner. It is widely used in chemistry, biology, environmental science, and many industries to monitor and control acidity/basicity.

- **Calculation of pH of the Mixed Solution:**

  - o **Reactants:** HCl (strong acid) and NaOH (strong base)

  - o **Reaction:** $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

  - o **Calculate moles of HCl:**

    - Volume of HCl = 25 mL = 0.025 L

    - Molarity of HCl = 0.2 M

    - Moles of HCl = Molarity × Volume = 0.2 mol/L × 0.025 L = 0.005 mol

  - o **Calculate moles of NaOH:**

    - Volume of NaOH = 50 mL = 0.050 L

- Molarity of NaOH = 0.25 M

- Moles of NaOH = Molarity × Volume = 0.25 mol/L × 0.050 L = 0.0125 mol

- **Determine Limiting Reactant and Excess:**

  - From the stoichiometry (1:1), 0.005 mol of HCl will react with 0.005 mol of NaOH.

  - Moles of NaOH in excess = Moles initial - Moles reacted = 0.0125 mol − 0.005 mol = 0.0075 mol

  - Since NaOH is in excess, the final solution will be basic.

- **Calculate Total Volume of Solution:**

  - Total Volume = Volume of HCl + Volume of NaOH = 25 mL + 50 mL = 75 mL = 0.075 L

- **Calculate Concentration of excess OH^- ions:**

  - $[OH^-] = \dfrac{\text{Moles of excess OH}^-}{\text{Total Volume (L)}} = \dfrac{0.0075 \text{ mol}}{0.075 \text{ L}} = 0.1$ M

- **Calculate pOH:**

  - $pOH = -\log_{10}[OH^-] = -\log_{10}(0.1) = -(-1) = 1$

- **Calculate pH (using K_w):**

  - We know that $pH + pOH = pK_w$

  - Given $K_w = 10^{-14}$, so $pK_w = -\log(10^{-14}) = 14$.

  - $pH = pK_w - pOH = 14 - 1 = 13$

- **Answer:** The pH of the solution is **13**.

7. (c) Define ionic mobility and show that, the ionic mobility of a solution (1:1 Electrolyte) at infinite dilution is given by

  - $u°_+ + u°_- = \lambda°_+/F + \lambda°_-/F$

○ Where, u° is ionic mobility and λ° is molar ionic conductance.

- **Ionic Mobility (u°):**

  ○ **Definition:** Ionic mobility is defined as the velocity (or speed) with which an ion moves in an electric field of unit potential gradient (i.e., when the electric field strength is 1 Volt per meter). It is a measure of how easily an ion can move through a solvent under the influence of an electric field.

  ○ **Units:** Typically expressed in $m^2V^{-1}s^{-1}$.

  ○ **Relationship to Velocity:** $v = uE$, where v is the velocity of the ion, u is its ionic mobility, and E is the electric field strength.

- **Derivation of the Relation:** $u°_+ + u°_- = λ°_+/F + λ°_-/F$

  ○ **Molar Ionic Conductance ($λ°$):** Molar ionic conductance at infinite dilution ($λ°$) is the contribution of a single type of ion (cation or anion) to the total molar conductivity of an electrolyte when there are no interionic interactions. It represents the conductivity generated by one mole of that ion.

  ○ **Fundamental Relationship:** The molar ionic conductance ($λ°$) is related to ionic mobility (u°) by the following equation:

    ▪ $λ° = zFu°$

    ▪ Where:

      • $λ°$ is the molar ionic conductance (in S m^2mol^{-1})

      • z is the charge number of the ion (e.g., for Na^+, z=1; for Mg^{2+}, z=2)

      • F is Faraday's constant (approximately 96485 C mol^{-1}), which is the charge carried by one mole of electrons.

      • u° is the ionic mobility (in $m^2V^{-1}s^{-1}$)

- o **For a Cation ($_+$) at infinite dilution:**

  - $\lambda^\circ_+ = z_+ F u^\circ_+$

  - For a 1:1 electrolyte (e.g., NaCl, HCl), $z_+ = 1$.

  - So, $\lambda^\circ_+ = 1 \times F \times u^\circ_+$

  - Therefore, $u^\circ_+ = \frac{\lambda^\circ_+}{F}$ (Equation A)

- o **For an Anion ($-$) at infinite dilution:**

  - $\lambda^\circ_- = z_- F u^\circ_-$

  - For a 1:1 electrolyte, $z_- = 1$.

  - So, $\lambda^\circ_- = 1 \times F \times u^\circ_-$

  - Therefore, $u^\circ_- = \frac{\lambda^\circ_-}{F}$ (Equation B)

- o **Summing the Mobilities:**

  - Adding Equation A and Equation B:

    - $u^\circ_+ + u^\circ_- = \frac{\lambda^\circ_+}{F} + \frac{\lambda^\circ_-}{F}$