Concentration of HCl solution = 0.100 N

Mass of silver deposited in the coulometer = 0.1209 g

Movement of the boundary = 7.50 cm

Cross-section of the tube = 1.24 cm^2

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

$$u_+^\circ + u_-^\circ = \frac{\lambda_+^\circ}{F} + \frac{\lambda_-^\circ}{F}$$

Where, u° is ionic mobility and λ° is molar ionic conductance. (5,5,5)

[This question paper contains 8 printed pages.]

30.12.2024(M)

Your Roll No.....

Sr. No. of Question Paper : 1151 **I**

Unique Paper Code : 2172012303

Name of the Paper : DSC: Chemical Equilibrium, Ionic Equilibrium, Conductance and Solid State

Name of the Course : **B.Sc. (Hons.) Chemistry**

Semester : III

Duration : 3 Hours Maximum Marks : 90

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt any **Six** questions in all.
3. Use of scientific calculator is permitted.

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 :

(i) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H = -923.0$ kJ

(ii) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ $\Delta H = +180.5$ kJ

(b) The dissociation of N_2O_4 is given by the equation:
$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

(i) If α is the degree of dissociation of N_2O_4 and P is the total pressure of the system, show that

$$K_P = \frac{4\alpha^2 P}{1-\alpha^2}$$

(ii) Calculate K_c and K_x of the given reaction for which $K_p = 0.157$ atm at 27°C and 1 atm pressure.

(c) Write short notes on **(Any two)** :

(i) Degree of advancement of reaction

(ii) Free energy of mixing and spontaneity

(iii) Buffer capacity (5,5,5)

2. (a) Show that the exact equation to calculate $[H_3O^+]$ in an aqueous solution containing a salt formed from a strong acid and a weak base is given by :

(b) Draw and discuss the titration curves obtained in the conductometric titration of :

(i) mixture of CH_3COOH and HCl versus NaOH in aqueous medium

(ii) HCl versus NaOH in aqueous medium

(c) A cell with electrodes that are 1.80 cm^2 in surface area and 0.50 cm apart is filled with 0.01 M MgCh solution. Molar conductivity of 0.01 M solution of MgCb is 195 S cm^2 mol^{-1} at 25°C. How much current will flow when the potential difference between the two electrodes is 5.0 V? (5,5,5)

8. (a) What is transference number? Derive the expression $t \propto v$ for an ion where, "t" is the transference number and "v" is the absolute velocity of the ion.

(b) Calculate the transport numbers of H^+ and Cl^- ions from the following data obtained from the moving boundary method using cadmium chloride as the indicator electrolyte (Atomic mass of Ag = 108 g mol^{-1}) :

(c) (i) Calculate the degree of hydrolysis of 0.10 M solution of sodium acetate at 25°C. K_a = 1.75×10^{-5} and $K_w = 1.008 \times 10^{-14}$.

(ii) Explain why a solution containing a strong base and its salt does not act as a buffer solution?

OR

(c) Why methyl orange cannot be used as indicator for titrating a weak acid against a strong base? Discuss the pH metric titration curve of a strong acid with strong base. (5,5,5)

7. (a) When a conductance cell was filled with 0.02 M KCl (with specific conductance 0.002768 S cm^{-1}) it had a resistance of 82.4 ohm at 25°C. When filled with 0.05 N K_2SO_4 it had a resistance of 326 ohm. Calculate:

(i) Cell constant

(ii) Conductance

(iii) Specific Conductance

(iv) Equivalent conductance of 0.05 N K_2SO_4

$$K_h = \frac{\left([H_3O^+] - \frac{Kw}{[H_3O^+]}\right)([H_3O^+])}{\left(c + \frac{Kw}{[H_3O^+]} - [H_3O^+]\right)}$$

where k_n and c have their usual meanings.

(b) Calculate the concentrations of H_30^+, CN^-, HCN and OH^- in a 0.01 M solution of HCN in water, given K_a (HCN) as 6.8×10^{-10} and K_w as 1.0×10^{-14} at 25°C. Indicate and justify the approximations used in the calculations.

(c) The solubility product of magnesium hydroxide, $Mg(OH)_2$ at 25°C is $1.4 \times 10^{-1}\ M^3$. Calculate the solubility of magnesium hydroxide in grams per litre. (Molar Mass of Mg = 24, O = 16, H = 1) (5,5,5)

3. (a) What do you understand by the terms "symmetry elements" and "symmetry operations"? Explain the following symmetry elements and associated operations:

(i) Plane of Symmetry/Mirror Plane

(ii) Proper Rotation Axis

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

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

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

(c) A first-order reflection from the (111) planes of a cubic crystal were observed at a glancing angle of 11.2° when Cu (K_α) 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. (5,5,5)

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.

(b) Explain the following :

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

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

(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. (5,5,5)

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.

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

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

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

(ii) (a, b, ∞c) (5,5,5)

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

(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 $K_w=10^{-14}$.