Unique Paper Code	: 32171102
Name of the Paper	: Physical Chemistry-I
Name of the Course	: B.Sc. (Hons.) Chemistry
Semester	: I
Duration	: 3 hours
Maximum Marks	: 75

## **Instructions for Candidates:**

- i. The candidate **must write** the following details on the **first page** of the answer sheet: University roll No, Unique paper code, Course, Semester, and Paper name.
- ii. Write page numbers on every page of the answer script.
- iii. Attempt any Four questions in all. All questions carry equal marks.
- iv. Attempt all parts of a question together.
- **1.** (a) Write the mathematical expression for Maxwell's distribution of molecular speed and derive the expression for the most probable and root mean square velocity of the gas.
  - (b) Define the surface tension of the liquid. Describe the drop number method for the determination of the surface tension of a liquid.
  - (c) Explain the following:
    - (i) The cleansing action of detergents.
    - (ii) Why the addition of NaCl increases the surface tension of water whereas the addition of acetone reduces the surface tension of water.
  - (d) Will a precipitate form if 50 cm<sup>3</sup> of 0.01 M AgNO<sub>3</sub> and 50 cm<sup>3</sup> of 0.0004 M NaCl are mixed? Given  $K_{sp}$  of AgCl =  $1.7 \times 10^{-10} M^2$ .

(6, 5, 4, 3.75)

- **2.** (a) Starting from van der Waals equation of state, derive the mathematical expression of Boyle's temperature.
  - (**b**) The critical constants for water are 647 K, 22.09 MPa, and 0.0566 dm<sup>3</sup> mol<sup>-1</sup>. Calculate the values of van der Waals constants a, b and R and also explain the abnormal value of R.
  - (c) (i) What are buffer solutions? Explain clearly how does a buffer act?
    (ii) Determine *Exact* pH of 10<sup>-8</sup> M NaOH.
  - (d) With the given viscometer, the times of flow at 20°C for water and an unknown liquid  $(d = 1.22 \text{ g cm}^{-3})$  were found to be 155 sec and 80 sec respectively. Calculate the absolute viscosity of the unknown liquid at 20°C if viscosity and density of water are 1.005 centipoise and 1 g cm<sup>-3</sup> respectively.

(5, 4, 5, 4.75)

- **3.** (a) Describe the powder diffraction method to determine crystal structure. Explain how this method can be used to analyze the structure of a cubic system.
  - (b) X-ray diffraction is not useful for distinguishing between atoms that differ by only the possession of one additional electron. Explain.
  - (c) Show that the pH of an aqueous solution of salt formed from a strong acid and weak base is given by

 $pH = 7 - \frac{1}{2}(pK_b + \log c)$ 

(d) Silver is known to be crystallized in cubic form. The Bragg angles using copper  $K_{\alpha}$  X-rays with  $\lambda = 154.1$  pm, for the first six diffraction lines are as follows:

 $\begin{array}{cccc} \theta & 19.08^{\circ} & 22.17^{\circ} & 32.26^{\circ} & 38.74^{\circ} & 40.82^{\circ} & 49.00^{\circ} \\ \end{array}$  What is the type of cubic crystal formed by Silver?

(6, 3, 5, 4.75)

- 4. (a) Explain the terms  $\sigma$ ,  $\lambda$ ,  $Z_1$  and  $Z_{11}$ . Discuss the effect of temperature and pressure on these terms.
  - (**b**) Calculate  $\lambda$ , Z<sub>1</sub>, and Z<sub>11</sub> for oxygen at 298 K and 10<sup>-3</sup> mmHg. Given  $\sigma = 3.61 \times 10^{-8}$  cm.
  - (c) Write a short note on *any three* of the followings:
    - (i) Continuity of state
    - (ii) Law of constancy of interfacial angles.
    - (iii) Law of rational indices
    - (iv) Symmetry elements
  - (d) Determine pH of water at 363 K ( $K_w$  at 363 K =  $1 \times 10^{-12} M^2$ ). Will it be neutral at 363 K? Explain.

(6, 4, 6, 2.75)

- 5. (a) What is an acid-base indicator? How does its color change with the  $H^+$  ion concentration of the solution? What is the indicator range?
  - (b) Starting from the postulate of the kinetic theory of gases, derive the kinetic gas equation.
  - (c) Calculate the temperature at which the average velocity of SO<sub>2</sub> equals that of O<sub>2</sub> at 20 K.
  - (d) A solution is 0.1 M in Cl<sup>-</sup> and .001 M in CrO<sub>4</sub><sup>2-</sup>. If solid AgNO<sub>3</sub> is gradually added to this solution, which will precipitate first, AgCl or Ag<sub>2</sub>CrO<sub>4</sub>? Assume that the addition causes no change in volume. Given:  $K_{sp}$  (AgCl) = 1.7 x 10<sup>-10</sup> M<sup>2</sup> and  $K_{sp}$  (Ag<sub>2</sub>CrO<sub>4</sub>) = 1.9 ×10<sup>-12</sup> M<sup>3</sup>.

(5, 5, 3.75, 5)

**6.** (a) Show that the concentration of  $H_3O^+$  in an aqueous solution of a diprotic acid  $H_2A$  is given by

$$[H_{3}O^{+}] = \left\{ \begin{array}{c} [H_{2}A]_{0} K_{1} \\ \hline [H_{3}O^{+}] + K_{1} + \frac{K_{1}K_{2}}{[H_{3}O^{+}]} \end{array} \right\} \left\{ 1 + \frac{2 K_{2}}{[H_{3}O^{+}]} \right\} + \frac{Kw}{[H_{3}O^{+}]}$$

Under what conditions can the following expressions be used

(i) 
$$[H_3O^+] = \begin{cases} [H_2A]_0 K_1 \\ [H_3O^+] + K_1 + \frac{K_1K_2}{[H_3O^+]} \end{cases} \begin{cases} 1 + \frac{2K_2}{[H_3O^+]} \end{cases}$$

(ii) 
$$[H_3O^+] = \frac{[H_2A]_0 K_1}{[H_3O^+] + K_1}$$

(b) Define solubility and solubility product. Determine the solubility of Mg(OH)<sub>2</sub> in pure water and a buffer solution having pH=12.  $K_{sp}$  of Mg(OH)<sub>2</sub> =  $1.2 \times 10^{-11}$  M<sup>3</sup>.

(c) Explain why the titration of a weak acid and weak base is not carried out using an acid-base indicator.

(d) What is capillary action? Derive:  $\gamma = \pm \frac{1}{2}$  hpgr, where the symbols have their usual meanings. (6, 5, 3, 4.75)

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