[This question paper contains 4 printed pages.]

**Sr. No. of Question Paper : 807** **E** **Your Roll No.....**

Unique Paper Code : 217405

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

Name of the Paper : Physical Chemistry-III (CHHT-410)

Semester : IV

Duration : 3 Hours Maximum Marks : 75

**Instructions for Candidates**

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **six** questions in all, selecting at least two question from each Section.
3. Question No. **1** is compulsory.
4. Use of Scientific Calculator is allowed.

1. Answer any **five** question given below:

   (a) Give the number of components present in the solution containing $Na^+$, $Cl^-$, $Ag^+$, $NO_3^-$, AgCl(s) and $H_2O$.

   (b) Why does the plait point lies either to the left or the right of the maximum of the binodal curve.

   (c) Why does the addition of succinic acid to phenol water system decreases the critical solution temperature.

   (d) The role of salt bridge is to reduce the liquid junction potential. Comment

   (e) The compounds of active metal such as Zn and Na are not reducible by hydrogen gas under standard condition while those of noble metals such as Cu and Ag are reducible by hydrogen gas. Explain.

   (f) Would you use silver spoon to stir a solution of $Cu(NO_3)_2$? (3×5=15)

*P.T.O.*

## Section A

2. (a) The melting point of mercury at external pressure of 10 atm and 3540 atm are 234.3 K and 257.2 K, respectively. Predict whether the transformation of solid Hg to liquid Hg involves an increase or a decrease of volume. (2)

   (b) Write a short note on pressure - composition diagram of completely miscible liquid exhibiting non ideal behaviour. (4)

   (c) Draw a labelled phase diagram of sulphur. (6)

3. (a) An ideal solution of two components with vapour pressure of 400 mmHg and 300 mmHg when pure contains two moles of the more volatile component and five moles of the less volatile one. Calculate:

      (i) Total vapour pressure of the solution.

      (ii) Composition of the vapour in equilibrium with a solution of this composition. (5)

   (b) Define and derive Lever Rule. (3)

   (c) Write a short note on Fractional distillation. (3)

4. (a) The system $CaF_2$ (melting point, 1360 °C) and $CaCl_2$ (melting point, 772 °C) shows an incongruent behaviour, forming a compound at 1 : 1 ratio. The compound melts at 737 °C giving a liquid containing 60 mol % of $CaCl_2$. The eutectic point is at 625 °C. with the eutectic composition of 80 mol % of $CaCl_2$ Draw the phase diagram and label it. (5)

   (b) Draw cooling curve for solution containing 25 mol% and 60 mol% of $CaCl_2$ (3)

   (c) Derive phase rule for a non reactive system. (4)

5. (a) A mixture of an organic liquid A (molar mass, 123 g $mol^{-1}$) and water is distilled under one atmosphere pressure at 372.2 K. What mass of steam would be condensed to obtain 1.0 g of liquid A in the distillate. The vapour pressure of water at 372.2 K is 739 Torr. (4)

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(b) Write a short note on system consisting of three components exhibiting formation of one pair of partially miscible liquids. (4)

(c) Define and derive Konowaloffs Rule. (4)

## Section B

6. (a) How will you determine accurately the ionic product of water with the help of an electrochemical cell? (4)

(b) Given the cell:

$Pt\ |Q, QH_2, H^+\ (aq.)\ ||\ KCL\ (1\ m), Hg_2Cl_2\ (s)|\ Hg(s)|\ Pt$

Find out the cell potential at 298 K when pH = 5 in the left half cell,

Given that $E^\circ_{calomel} = 0.280$ V, $E^\circ_{Q,H2Q,H+|Pt} = 0.6996$ V (4)

(c) Write short note on the glass electrode. (4)

7. (a) Discuss the principle underlying potentiometric titrations. What are the advantages of potentiometric titrations? (4)

(b) Calculate the solubility product of AgBr at 25°C.

($E^\circ_{Br-|AgBr|Ag} = 0.0731$ V, $E^\circ_{Ag+|Ag} = 0.799$ V) (4)

(c) Between 0°C and 90°C, the potential of the cell

$Pt\ |\ H_2\ (g, 1\ atm)\ |\ HCl\ (m = 0.1)\ |\ AgCL\ (s)\ |\ Ag$ is given by

$E_{(volts)} = 0.3551 - 0.3422 \times 10^{-4}t$

Where t is the temperature in Celsius. Write the cell equation and calculate $\Delta G$, $\Delta H$ and $\Delta S$ for the cell at 50°C. (4)

8. (a) The standard equilibrium constant for the following reaction at 298K, is

$1.646 \times 10^6$.

$2Cu^{+}$ (aq) $\longleftrightarrow$ $Cu^{2+}$ (aq) + $Cu_{(s)}$

Construct the cell having the above cell reaction and calculate the standard potential of the cell. (4)

(b) The potential of the cell

$Cd|CdI_2$ $(a_2)$ $|AgI(s)|Ag$

is 0.2860 V at 25°C. Calculate the mean ionic activity and activity of the electrolyte, given that $E^{\circ}_{I-|AgI|Ag}$ = 0.1522 V and $E^{\circ}_{cd^{2+}|cd}$ = -0.404 V (4)

(c) What is a reference half- cell? Outline its merits relative to that of the hydrogen-hydrogen ion half-cell. (4)

9. (a) The E.m.f of the cell

$Pt|H_2$ (g, 1 atm)|HCl ($a_{\pm}$ =0.00905) |HCl($a_{\pm}$ =0.00905) |$H_2$(g, 1atm)|Pt

is 0.02802 V at 25°C and the corresponding cell without transference has an EMF of 0.01696 V. Calculate the transport number of hydrogen ion and liquid junction potentail. (4)

(b) Derive an expression for EMF of the concentration cell without tranference.

$Pt|H_2$ (g, 1 atm)|HCl (al), AgCl(s)|Ag-Ag|Cl(s), HCl ($a_2$)| $H_2$ (g, 1 atm)|Pt (4)

(c) What are the redox indicators? Describe the working of the redox indicator. (4)