

This question paper contains **4** printed pages.

Roll No. _____

Name of the Course : **B. Sc. (Honors) Chemistry-CBCS**

Semester : **III**

Name of the Paper : **Chemistry C-VII Physical Chemistry III:
Phase Equilibria and Electrochemical Cells**

Unique Paper Code : **32171303_OC**

Medium of setting the Question paper: **English**

Duration : **3 hours**

Maximum Marks : **75**

Instruction for the Candidates

- 1. Write Roll. No. on the top of paper immediately after receipt of this question paper.**
- 2. Attempt 4 questions out of 6 questions.**
- 3. Use of scientific calculator is permitted.**
- 4. Graph paper may be provided.**

Values of constant: $R=8.314 \text{ JK}^{-1}\text{Mol}^{-1}$; $F=96500 \text{ C Mol}^{-1}$

Q 1. Attempt any seven parts

- a. In a binary liquid mixture, the mutual solubility of the components may exhibit an increase with decrease in temperature. With the help of an example explain this behavior and also draw the temperature-composition diagram for such a system with proper labelling.
- b. Explain how the Nernst distribution Law forms basis of the solvent extraction separation technique.
- c.. Will dichromate ions in acidic medium be able to oxidize Fe^{2+} to Fe^{3+} ? Given: $E_{Cr_2O_7^{2-}, Cr^{3+}, H^+ | Pt}^0 = 1.33V$ and $E_{Fe^{3+}, Fe^{2+} | Pt}^0 = 0.77V$
- d. In an electrochemical reaction, explain how will E_{cell} be affected by the formation of a soluble complex with the reduced form of the metal ion involved?
- e. What are the desirable characteristics of a reference half-cell?
- f. (i) Which is irreversible; Physiosorption or Chemisorption? Why?
(ii) Adsorption is an exothermic process. Explain.

(3, 3, 3, 3, 3, 3, 3.75)

Q 2.

- a. Explain the three conditions that must be satisfied for any two phases to be in equilibrium.
- b. A substance exists as two polymorphs α and β apart from the liquid and vapor state. The normal melting point of α is lower than that of β . Solid α is denser than its liquid while solid β is less dense as compared to its liquid. Assuming that no metastable equilibria are observed, draw the P-T phase diagram explaining the significance of each point, line and region.
- c. Determine the number of components, phases and degrees of freedom for the following:
 - (i) Liquid and its vapor at equilibrium
 - (ii) Solid $CaCO_3$ heated in a sealed tube
 - (iii) A pure substance at the critical point

(6, 6, 6.75)

Q.3.

a. Freundlich Adsorption isotherm equation is written as; $\frac{x}{m} = kP^{\frac{1}{n}}$, where x is the mass of the gas adsorbed on mass m of the adsorbent at pressure p and k and n are constant for a pair of adsorbent and adsorbate. Show that Freundlich Adsorption Equation is a special case of Langmuir Adsorption Isotherm Equation.

b. Differentiate between the Physical and Chemical processes of adsorption.

c. A piece of charcoal was placed in two different aqueous solutions and the amount of solute adsorbed was recorded at equilibrium

Concentration ($\times 10^{-2}$)	2	4
x/m	0.185	0.290

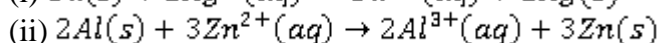
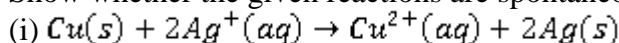
Find the values of k and n .

(6.75, 6, 6)

Q.4.

a. What do you understand by the term EMF of a cell? How does one measure the EMF? Explain with the help of a diagram.

b. Show whether the given reactions are spontaneous in the forward reaction:



Given: $E_{\text{Ag}^+|\text{Ag}}^0 = 0.7991 \text{ V}$; $E_{\text{Cu}^{2+}|\text{Cu}}^0 = 0.337 \text{ V}$;

$E_{\text{Al}^{3+}|\text{Al}}^0 = -1.66 \text{ V}$; $E_{\text{Zn}^{2+}|\text{Zn}}^0 = -0.763 \text{ V}$

c. At 25°C the potential of the cell with transference, $\text{Pt}(s)|\text{H}_2(g, f = 1)|\text{HCl}(aq, a_{\pm} = 0.009048)|\text{HCl}(aq, a_{\pm} = 0.01751)|\text{H}_2(g, f = 1)|\text{Pt}(s)$ is 0.02802 V . The corresponding cell without transference has a potential of 0.01696 V . Calculate the transference number of H^+ ion and the value of the junction potential.

(6.75, 6, 6)

Q.5.

- a. Construct a galvanic cell for the cell reaction:
 $2Cr(s) + 3Hg_2Cl_2(s) \rightarrow 2Cr^{3+}(aq) + 6Cl^-(aq) + 6Hg(l)$
Also write down the expression for the cell potential E_{cell} .
- b. Sketch the phase diagram for the system $Al_2O_3 - SiO_2$ using the following information: Al_2O_3 and SiO_2 melt at $2060^\circ C$ and $1720^\circ C$ respectively. One congruently melting compound, $Al_6Si_2O_{13}$, forms between Al_2O_3 and SiO_2 with a melting point of $1850^\circ C$. Two eutectics occur at 5 mol% of Al_2O_3 , $1595^\circ C$ and 67 mol% of Al_2O_3 , $1840^\circ C$. Label the diagram properly.
- c. What is the principle underlying potentiometric titrations? Why are potentiometric titrations preferred over volumetric titrations?

(6, 6.75, 6)

Q.6.

- a. The EMF of the cell
 $Ag(s) | AgCl(s) | KCl(aq) | Hg_2Cl_2(s) | Hg(s)$
is 0.0455V at 298 K and the temperature coefficient $\left(\frac{\partial E}{\partial T}\right)_P = 3.38 \times 10^{-4} VK^{-1}$.
What reaction is taking place in the cell? Also calculate the change in free energy, enthalpy and entropy for the cell reaction.
- b. What is underlying principle behind the steam distillation technique? Explain the process.
- c. Water and chloroform are partially miscible in each other while acetic acid is miscible in both water and chloroform in all proportions. Draw a qualitative solubility curve of the system on a triangular plot. Explain the following with the help of the plot; a plait point, a binodial curve and characteristics of the triangular plot within and outside the binodial curve.

(6.75, 6, 6)