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Unique Paper Code : 32171303_OC

Name of the Paper : Physical Chemistry III: Phase Equilibria and Electrochemical Cells

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

Semester : **III**

Duration: 3 Hours Maximum Marks: 75

Instructions for Candidate

Attempt four questions in all, selecting at least two questions from each section.

Use of scientific calculator is permitted

-1-1-1

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

Section-A

Q.1.a) Derive the Clapeyron equation and then derive Clausius-Clapeyron equation for condensed phase-vapour system. Does this relation hold good for the solid to liquid equilibria? Justify your answer.

b) Calculate the number of components in a solution containing H_2O , OH^- , Na^+ , Cl^- , Ag^+ , NO_3^- , AgCl (s) & $\text{H}_2\text{O (l)}$. Show all the constituents, reactions & restrictive conditions.

c) An aqueous solution contains 0.30 g of a solute in 100 cm³ solution. To this solution 25 cm³ of ether is added and the mixture is shaken and allowed to come to equilibrium at 298K. At this temperature, $K_d = C_{\text{ether}}/C_{\text{water}} = 4.7$

i) How much solute remains in the aqueous solution?

ii) If the extraction is carried out with two successive 20 cm³ portions of ether, how much solute remains unextracted?

d) What is Gibbs Duhem equation? Use this equation for a binary solution to derive Duhem-Margules equation.

(5, 5, 5, 3.75)

Q.2. a) Differentiate between congruent & incongruent melting point systems with an example for each. Why both of them are invariant points?

- b) Describe the phase diagram of water with due emphasis on following facts:
- How many triple points does it have?
 - Why is sublimation curve steeper than the vaporization curve at triple point?
 - Why is fusion line almost vertical & slightly tilted to the left?
 - What is the upper limit of liquid-vapour equilibrium curve?
- c) Describe the process of fractional distillation of an ideal binary solution with the help of suitable diagrams along with the principle underlying it.
- d) What are azeotropes? Give one example each of maximum boiling & minimum boiling azeotropes. Can they be purified by fractional distillation?

(5,5,5,3.75)

- Q.3. a) Plot a labeled phase diagram (with degrees of freedom) of a system with components: A (M.Pt: 1100 C) and B (M.Pt: 600 C). The eutectic temperature is 400 C and the corresponding composition is 85 mol % of B. Draw the labeled cooling curves for the solutions containing 100 mol% of A, 85 mol% of B & 56 mol% of B.
- b) Deduce Gibbs Phase rule for a non-reactive system at equilibrium in which all the components are present in all the phases.
- c) State Nernst Distribution Law. Derive the expression for Nernst Distribution Law when the solute undergoes dissociation in one of the phases.
- d) Discuss the effect of adding following impurities on CST of phenol-water system:
- NaCl
 - Succinic Acid

(5,5,5,3.75)

Section-B

- Q.4. a) Explain a method to determine the accurate value of half-cell potential graphically.
- b) Construct the galvanic cell for the following reaction and write down the expression for the cell potential,
- () () () ()
- c) Determine the standard equilibrium constant of the following reaction at 298K
- () () ()
- ()

d) Why is the Mercurous Chloride written as Hg_2Cl_2 not as HgCl ?

(5,5,5,3.75)

Q.5. a) Derive the expression for the EMF of a concentration cell with transference.

b) Write the BET equation and derive the Langmuir adsorption isotherm from it.

c) Determine the cell potential for the following cell at 25°C assuming the activity equal to molar concentration

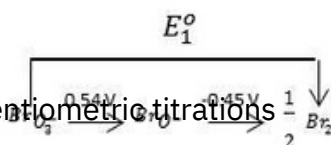
$\text{Pt} | \text{H}_2 | \text{H}^+ || \text{Cl}^- | \text{AgCl} | \text{Ag}$

d) Can a voltmeter be used to determine the EMF of a galvanic cell?

(5,5,5,3.75)

Q.6.a) Describe the construction of calomel electrode. Write the half-cell reaction and Nernst equation for it.

b) From the standard potentials shown in the following diagram, calculate the potential()



c) Write a short note on potentiometric titrations

d) What are the limitations of Quinhydrone electrode for the determination of pH of solution?

(5,5,5,3.75)

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