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Unique Paper Code : 32171303 Name of the Paper : Chemistry C-VII Physical Chemistry III: Phase Equilibria and Electrochemical Cells Name of the Course : B.Sc. (H) Chemistry Semester : III Duration : 3 hour \_\_\_\_\_ Maximum Marks : 75 \_\_\_\_

### Instructions for Candidates

- 1. On the first page of the answer sheet, write down the following:
- -Paper title
- -Unique Paper Code
- -Date of exam
- -Student name
- -Course name
- -University Roll No.
- 2. Attempt *four* questions in all.
- 3. Use of scientific calculator, log tables and graph paper is permitted.



Q1.

a) Solid CO2 is called dry ice. Explain.

b) A liquid has normal boiling point at 338.15 K. Using Trouton's Rule, determine the vapour pressure of a liquid at 325.15 K

c) Draw a labeled phase diagram of water. Using this phase diagram, explain why skating is possible on ice.

d) Is it possible to separate an azeotropic mixture into two pure components by isobaric fractional distillation? Explain.

3, 5, 8, 2.75

Q.2

a) Enthalpy of chemical adsorption of H2 on the surface of Ni is slightly positive yet the adsorption is spontaneous. Explain.

b) Show that the heterogenous equilibria of three components A, B and C distributed in three different phases as depicted below is in accordance with the phase rule. (Note: the three components do not react with each other)

 $A + B \rightleftharpoons B + C \rightleftharpoons A + B + C$ 

Phase 1 Phase 2 Phase 3

c) Draw a labeled phase diagram of a two-component system (A-B) with the data given

below:

(i) Melting point of  $A = 751^{\circ}C$ 

(ii) Melting point of B = 1350 °C

(iii) Melting point of a congruently melting compound AB2 =1040 °C

(iv) A compound AB melt 2s incongruently at 370°C to give a melt of 48 mass % B (v) Eutectic at 210 °C and 58 mass % of B

(vi) Eutectic at 580 °C and 88 mass % of B

d) State whether the following statements are true or false.

 $\begin{array}{c} \left( \begin{array}{c} T \\ r \end{array} \right)^{p} \left( \right) > \left( \right) \\ s \\ \stackrel{d}{\leftarrow} v \\ d \\ T \\ l \\ \stackrel{d}{\leftarrow} v \\ (ii) \\ \end{array} \right)$ 

 $s \leftarrow v = u + v \leftarrow v$  (ii) A multistage solvent extraction is more efficient process as compared to the single stage extraction.

3, 5, 8, 2.75

Q.3

a) On the basis of the critical temperatures, *T*c of the gases given below, predict and explain which of the following gases will exhibit maximum adsorption on 1 g of charcoal at room temperature.

		Gas CO2 NH3 H2		
	05.00			
/C/K4044	05 33			

b) Using Duhem-Margules equation, show that in a binary liquid mixture if one component behaves ideally then the other must also exhibit ideal behavior.



c) Consider an ideal behavior for a binary liquid mixture of two liquids A and B.(poA = 300 mm Hg and poB = 800 mm Hg). When one mole each of the two components is mixed at 323 K and the pressure over the liquid mixture is reduced, eventually the first trace of vapours is formed at a definite pressure. Calculate

i. the pressure at which this first trace of vapour forms

ii. the composition of first trace of vapour formed

iii. the composition of vapour phase when the last trace of the liquid remains to be vaporized.

d) Addition of naphthalene increases the CST of the phenol-water system at constant pressure. Explain.

3, 5, 8, 2.75

#### Q.4

a) If a gas follows the Langmuir adsorption isotherm on a surface of a solid such that at 298 K the K = 0.66 kPa-1eq. Calculate the pressure of the gas when the fraction of surface coverage is 25%.

b) Derive an expression for the reduction potential of a Metal-Metal ion half cell

c) Give the cell representation of the galvanic cell for each of the following reactions and write the expressions for the cell potential based on Nernst equation.

(i)  $Ag+(aq) + Cl-(aq) \rightleftharpoons AgCl (s)$ 

(ii) Ni2+(aq) + H(g) + 2OH−2(aq) ⇒Ni(s) + 2H2O(l)

d) Write the limitations of hydrogen electrode.

#### 3, 5, 8, 2.75

#### Q.5

(a) Explain the concept of liquid junction potential in a Galvanic cell. How can the liquid junction potential be eliminated?

(b) Describe the use of quinhydrone electrode for the measurement of pH of a solution.

(c) Calculate the mean ionic activity  $(a\pm)$  of the ions in an aqueous solution of CdI2 at 300 K using the cell potential of the following Galvanic cell. Also calculate the mean ionic molality  $(m\pm)$  in the electrolyte solution. The *E*cell value is 0.286 V at 300 K

Cd | CdI (-12aq, 0.01 mol kg) | AgI(s) | Ag Given:  $E \ominus = -0.145$  V and  $E \ominus$ I - |AgI|AgCd2 + |Cd = -0.396 V

(d) Cuprous ion is written as Cu+2and not as Cu. Explain.



3, 5, 8, 2.75

(a) Which of the following represents temperature?

the variation of physical adsorption with



(b) Determine the  $\Delta Go$  and Koeq at 298 K for the following reaction using the data given below:

 $Cu(OH)2+-2 \rightleftharpoons Cu(aq) + 2 OH(aq)$ 

Given: E<del>oo</del>

Cu(OH) - 2 + 2, OH | Cu = -0.224 V ; ECu | Cu = 0.337 V

(c) For the cell reaction,

Fe3+ (aq) + Fe (s)  $\rightleftharpoons$  Fe2+(aq)

Construct two different galvanic cells using the following three half cells and calculate the standard cell potential for each of these cells. Compare the two cell potential values and comment on the result obtained.

Given: (i) Fe2++2e- $\rightleftharpoons$  Fe  $E\Theta$  F e 2 + | F e = 0 - 0.44 V(ii) Fe3++3e- $\rightleftharpoons$  Fe  $E\Theta$  F e 3 + | F e = -0.036 V(iii) Fe3++e- $\rightleftharpoons$  Fe2+ $E\Theta$ F e 3 + , F e 2 + | P t = 0.771 V

(d) Why is phosphoric acid added while preparing the reaction mixture in the titration of Mohr's salt with potassium dichromate.

3, 5, 8, 2.75

Q.6

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