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 CO_2 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 H_2 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)

$$\underset{\text{Phase 1}}{A + B} \quad \rightleftharpoons \quad \underset{\text{Phase 2}}{B + C} \rightleftharpoons \quad \underset{\text{Phase 3}}{A + B + C}$$

c) Draw a labeled phase diagram of a two-component system (A-B) with the data given below:
   (i) Melting point of A = 751°C
   (ii) Melting point of B = 1350 °C
   (iii) Melting point of a congruently melting compound AB_2 =1040 °C
   (iv) A compound A_2B melts 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.
   (i) $\left(\frac{dp}{dT}\right)_{s \rightleftharpoons v} > \left(\frac{dp}{dT}\right)_{l \rightleftharpoons v}$
   (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	CO_2	NH_3	H_2
T_c / K	404	405	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.($p_A^o = 300$ mm Hg and $p_B^o = 800$ 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 $K_{eq} = 0.66\ kPa^{-1}$. 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) $Ni^{2+}(aq) + H_2(g) + 2OH^-(aq) \rightleftharpoons Ni(s) + 2H_2O(l)$

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 CdI_2 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

$$Cd \mid CdI_2\ (aq,\ 0.01\ mol\ kg^{-1}) \mid AgI(s) \mid Ag$$

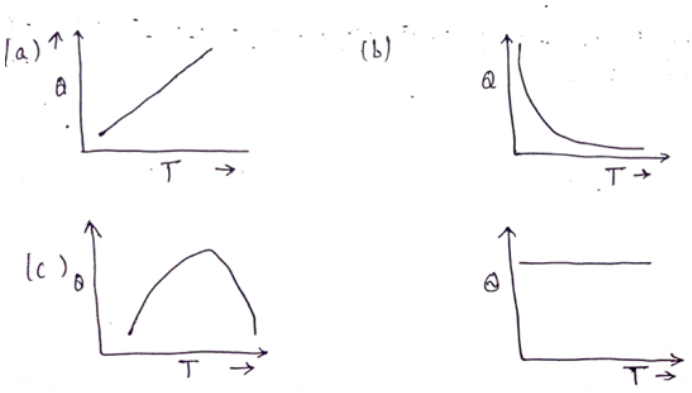
Given: $E^{\ominus}_{I^-|AgI|Ag} = -0.145\ V$ and $E^{\ominus}_{Cd^{2+}|Cd} = -0.396\ V$

(d) Cuprous ion is written as Cu_2^{2+} and not as Cu^+. Explain.

3, 5, 8, 2.75

Q.6

(a) Which of the following represents the variation of physical adsorption with temperature?



(b) Determine the ΔG^o and K_{eq}^o at 298 K for the following reaction using the data given below:

$$Cu(OH)_2 \rightleftharpoons Cu^{2+}(aq) + 2\ OH^-(aq)$$

Given: $E^{\ominus}_{Cu(OH)_2,OH^-|Cu} = -0.224\ V$; $E^{\ominus}_{Cu^{2+}|Cu} = 0.337\ V$

(c) For the cell reaction,

$$Fe^{3+}\ (aq) + Fe\ (s) \rightleftharpoons Fe^{2+}(aq)$$

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) $Fe^{2+} + 2e^- \rightleftharpoons Fe$ $\quad E^{\ominus}_{Fe^{2+}|Fe} = 0 - 0.44\ V$

(ii) $Fe^{3+} + 3e^- \rightleftharpoons Fe$ $\quad E^{\ominus}_{Fe^{3+}|Fe} = -0.036\ V$

(iii) $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $\quad E^{\ominus}_{Fe^{3+},Fe^{2+}|Pt} = 0.771\ V$

(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