

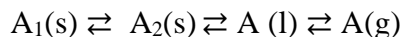
[This question paper contains 2 printed pages.]

Unique Paper Code : **32171303**
Name of the Paper : Physical Chemistry III: Phase Equilibria and
Electrochemical Cells
Name of the Course : **B.Sc. (H) Chemistry**
Semester : III
Duration : 3 Hours
Maximum Marks : 75

1. (a) Explain, giving reasons:

- (i) A eutectic mixture has a definite composition and a sharp melting point yet it is not a compound.
- (ii) In water, a large number of molecular species like H_2O , $(\text{H}_2\text{O}_2)_2$, $(\text{H}_2\text{O})_3$exist yet the number of components is only one.

(b) (i) Mr. R claims to have discovered a new element A which exists in two solid modifications A_1 and A_2 . Mr. R then studies its phase diagram and claims to have the following equilibria



Do you agree with Mr. R? Justify your answer.

- (ii) Salt is used to clear ice in sidewalks in winters. Explain.
- (c) (i) Compare physisorption and chemisorption.
(ii) Explain adsorption of gas on solids with the help of Freundlich adsorption isotherm.
- (d) Derive phase rule for a non-reactive system of C components and P phases from which component 2 is missing from phase 1 & 3.

(5, 5, 5, 3.75)

2. (a) What is the solvent extraction process? Why the multi-step extraction is more economical than the single-step extraction? Derive a general formula for the amount of solute left unextracted after n extractions using the same volume of the extracting liquid.

(b) Draw the temperature - composition diagram of a system exhibiting positive deviation from Raoult's law and explain the distillation of such a mixture with the help of the diagram. What is the term used for the distillate formed?

(c) The following data has been resulted by thermal analysis of melts containing Mg and Si:

Mass % of Mg	0	15	30	43	55	63	80	97	100
Temp. of first break in cooling curve ($^{\circ}\text{C}$)	-	1290	1150	-	1070	-	1000	-	-
Temp. of halt in cooling curve ($^{\circ}\text{C}$)	1420	950	950	950	950	1102	640	640	651

Construct the well labelled phase diagram and answer the following:

- What is the approximate melting point of the melt containing 25% by mass of Mg?
- Is the compound congruent or incongruent melting?
- What is the melting point of the compound?

(d) The enthalpy of vaporization of water is 2.259 kJ/g. What is the boiling point of water on a mountain where the barometric reading is 500 Torr?

(5, 5, 5, 3.75)

3 (a) Define C.S.T. With the help of a suitable diagram, describe the sequence of steps that take place when the composition of a mixture of partially miscible liquids exhibiting upper C.S.T is varied. What type of compounds on mixing with water show lower C.S.T and why?

(b) Calculate the E_{ijp} associated with the following cell:

$\text{Ag(s)}, \text{AgCl(s)}, \text{HCl} (m_1=1.0; \gamma_1= 0.809): \text{HCl} (m_2=0.05; \gamma_2= 0.830), \text{AgCl} (\text{s}), \text{Ag}(\text{s})$

If the transference number of H^+ is 0.83.

(c) In the distribution of benzoic acid between water and benzene, the following results were obtained:

C1 (in water)	1.50	1.95	2.97
C2 (in benzene)	24.20	41.20	97.00

Comment on molecular state of benzoic acid in both the solvents.

(d) Voltmeter cannot be used for determining the emf of a galvanic cell. Explain why?

(5, 5, 5, 3.75)

4. (a) How can an accurate value of the standard half- cell potential be determined experimentally?

(b) At 0°C and 1 atm pressure, the volume of nitrogen gas required to cover a sample of silica gel, assuming Langmuir monolayer adsorption, is found to be 130 cm³/g of the silica gel. Calculate the surface area per gram of silica gel. Given that the area occupied by a nitrogen molecule is 0.162 (nm)².

(c) Starting with the Duhem-Margules equation, derive a relation to show that the vapour phase is richer in the more volatile component for a binary system A-B.

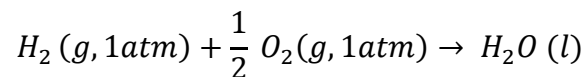
(d) Why phosphoric acid is used along with Diphenylamine in the volumetric titration of ferrous ions?

(5, 5, 5, 3.75)

5. (a) Derive Langmuir adsorption isotherm. Show that when a diatomic gas adsorbs as atom on the surface of a solid, the Langmuir adsorption isotherm becomes-

$$\theta = (Kp)^{1/2} / [1+(Kp)^{1/2}]$$

(b) The standard free energy change for the reaction



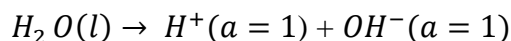
is 237.19kJ/mol at 298 K.

(i) Write the electrode reactions if the reactions to occur in a galvanic cell.

(ii) Calculate the standard electrode potential for the electrode $OH^- | O_2 | Pt$ and

$H^+ | O_2 | Pt$

The cell potential producing the reaction



is -0.827V.

(c) Consider the following cell arrangement



(i) Write down the half- cell reactions.

(ii) The standard EMF of the cell at various temperature are as follows:

T/K	291	298	303	311
E^0/mV	43.0	45.4	47.1	50.1

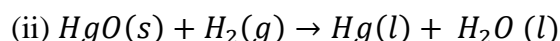
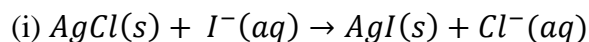
Calculate ΔG , ΔS , and ΔH for the reaction at 298K.

(d) The distribution coefficient of iodine between carbon tetrachloride and water is 85 in favour of carbon tetrachloride. Calculate the volume of carbon tetrachloride required for 85% extraction of iodine from 100 ml of aqueous solution in single stage extraction.

(5, 5, 5, 3.75)

6. (a) Derive an expression for the reduction potential of Metal-Metal insoluble salt- anion half-cell.

(b) Write the galvanic cell representation and the expression for the cell potential using Nernst Equation and show the direction of flow of electron.



(c) How the Quinhydrone electrode can be used to determine the pH of a solution? Give the limitations of using this electrode.

(d) If v is the volume of a gas (corrected to STP) adsorbed on the surface of a solid, then show that a plot of p/v versus p , where p is the gas pressure in the Langmuir adsorption isotherm, gives a straight line. Also show that for small surface coverages, a plot of (θ/p) versus θ gives a straight line.

(5, 5, 5, 3.75)