2025

CHEMISTRY — HONOURS

Paper : DSCC-7

(Physical Chemistry - II)

Full Marks : 75

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Answer ***question nos.*** **1, 2, 3, 4** (Compulsory) and ***any four*** questions from the rest (***question nos.*** **5** to **10**).

1. Answer ***any ten*** questions : 2×10

(a) "The surface tension of a liquid decreases with increasing temperature." — Justify or criticize.

(b) In the determination of viscosity coefficient (η) of a liquid using Poiseuille's method, calculate the error in η if radius is measured with an error of 1%.

(c) How the concept of a unit cell can be obtained from a space lattice?

(d) Determine the Miller indices of the planes that intersect the crystal axis at (i) a, 2b, 3c and (ii) a, 2b, – c.

(e) Metallic gold crystallizes in fcc lattice. The length of the unit cell is 4.07Å. Calculate the closest distance between gold atoms.

(f) "The elevation of boiling point of an ideally dilute solution of a given molality is greater than the depression of freezing point of the same solution of equal molality" — Justify or criticize.

(g) Calculate degrees of freedom and the number of independent components in an aqueous solution of CH_3COOH and CH_3COONa.

(h) "Four phases of sulphur cannot exist simultaneously at equilibrium" — Justify or criticize.

(i) Write down the cell reaction for the following cell and expression for e.m.f. of the cell :

$$Ag(s)\,|\,AgCl(s)\,|\,Cl^-\,||\,Ag^+\,|\,Ag(s)$$

(j) Show with the help of phase rule that at a given pressure, the Critical Solution Temperature (CST) is a non-variant point.

(k) How liquid junction potential can be minimized?

(l) The osmotic pressure of 0.0010(M) solution of KI and sucrose are 0.432 atm and 0.24 atm respectively. What is the van't Hoff factor of KI?

2. Write short notes on :

(a) Viscosity of gases using the following points :

(i) Temperature dependence

(ii) Relation with the mean free path of gas molecules (with derivation). 2+3

Or,

(b) Close packed arrangements using the following points :

(i) 3-D hexagonal close packed structure

(ii) 3-D cubic close packed structure

(iii) Number of tetrahedral and octahedral voids. 2+2+(½+½)

3. Write short notes on :

(a) Colligative properties using the following points :

(i) Extensive or Intensive— Justification.

(ii) Assumptions leading to elevation of boiling point of an ideally dilute solution.

(iii) Colligative properties are purely entropy effect. 1+1+3

Or,

(b) Phase diagram using the following points :

(i) Definition

(ii) Phase diagram of water and CO_2, highlighting the difference(s) (with explanation). 1+(1+1+2)

4. Write short notes on :

(a) Crystal structure using the following points :

(i) FCC crystal structure.

(ii) NaCl and KCl crystal structure with explanation. 1+(2+2)

Or,

(b) Determination of pH of a solution using the following points :

(i) using Hydrogen electrode

(ii) using quinone-hydroquinone electrode

(iii) using glass electrode. 1+2+2

5. (a) At 20°C the interfacial tension between water and mercury is 375 dyne cm^{-1}. If the surface tension of mercury is 483 dyne cm^{-1} and that of water is 72.75 dyne cm^{-1}, calculate

(i) the work of adhesion between water and mercury,

(ii) the work of cohesion for mercury and water,

(iii) the spreading coefficient for mercury on water. Will mercury spread on water?

(b) A face centred lattice has all positions occupied by atom A. The body centred octahedral hole in it is occupied by an atom B. Predict the formula of the compound.

(c) Derive thermodynamically a relation between the osmotic pressure of an ideally dilute solution and its molar concentration mentioning the assumptions and approximations involved.

(1+1+2)+3+(2+½+½)

6. (a) Consider a three-dimensional cubic lattice (length of each side is 'a') and show that the separation between successive (hkl) planes is given by

$$d_{hkl} = a/(h^2 + k^2 + l^2)^{½}.$$

(b) A steel ball of density 7.9 gcm^{-3} and 4 mm diameter requires 55 sec. to fall through a distance of 1 m through a liquid of density 1.1 gcm^{-3}. Calculate the coefficient of viscosity of the liquid after obtaining the necessary equation.

(c) What is an azeotropic mixture? Differentiate it from a pure compound. What is the degrees of freedom of an azeotropic mixture in a two component liquid-vapour equilibrium? 4+(1+2)+(1+1+1)

7. (a) Draw and explain the phase diagram of phenol-water system. Calculate the degrees of freedom at different regions of the curve. What happens when some amount of NaCl is added to water?

(b) The potential of the cell

$$Cd \mid CdI_2(a_2) \mid AgI(s) \mid Ag(s)$$

is 0.2860 V at 298 K. Calculate the mean ionic activity of the ions in the solution, and the activity of the electrolyte.

Given, $E^0(Cd^{++}/Cd) = -403$ V and $E^0(Ag/AgCl(s)/Cl^-) = 0.2223$ V

(c) State and explain Fick's 1st law of diffusion. What do you mean by mutual diffusion coefficient?

(1+1+1+1)+(2+1)+(1+1+1)

8. (a) Set up a reversible cell without transference for the following cell reaction

$$HCl(a_1) \rightarrow HCl(a_2), \quad a_1 > a_2$$

and find out the e.m.f. of the cell.

(b) Consider an ideal solution of two liquids A and B. Give plots of total pressure p versus x_B^l and x_B^v separately and explain the plots, where x_B^l and x_B^v be the mole fraction of B in the liquid and vapour phase respectively.

(c) For a certain liquid, $\log \eta$ vs. $\frac{1}{T}$ plot gives straight line with slope = 2072.7 unit and intercept = –13.8 unit. Calculate η at 25° in S.I. unit.

(2+2)+(1+2)+3

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9. (a) Derive expression of van't Hoff factor

(i) for the strong electrolyte A_xB_y which dissociates in an aqueous solution,

(ii) for the species A which is polymerised into $(A)_n$.

(b) A crystal having simple cubic lattice shows first order Bragg reflection at an angle of 60° from one of its planes. If the length of the unit cell is a_0 pm and wavelength of X-ray is a_0 pm, find the Miller indices of the plane.

(c) Derive Duhem-Margules equation clearly stating the assumptions involved. Show that if Raoult's law is applicable to one of its constituents of a binary liquid mixture at all compositions, it must be equally applicable to other constituents. (2+2)+3+(2+1)

10. (a) In an X-ray diffraction experiment of powdered sample of Fe crystal, ratio of $\sin^2\theta$ values obtained is 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 etc. What is the probable Miller indices for the value 7 in the ratio? Identify the unit cell. Calculate the cell length if density = 7.92 g cm^{-3} and at wt. of Fe = 55.85 g mol^{-1}.

(b) Two liquids A and B form an ideal solution at temperature T. When the total vapour pressure above the solution is 600 torr, the mole fraction of A in the vapour phase is 0.35 and in the liquid phase is 0.70. What are the vapour pressures of pure A and pure B at temperature T?

(c) E^0 of the cell reaction

$$H_2O(e) \rightleftharpoons H^+ + OH^-$$

is -0.828 V where $a_{H^+} = 1$ and $a_{OH^-} = 1$. Calculate $E^0_{OH^-}|O_2(g)$ if ΔG^0 for the reaction $H_2(g, 1\text{ atm}) + \frac{1}{2}O_2(g, 1\text{ atm}) = H_2O(e)$ is -237.2 kJ at 298 K. Construct the cells for both the reactions. (1+1+2)+(1½+1½)+(1½+1½)