Write the answers to each Group in a separate answer-book

2010
(New and Old Syllabuses)
CHEMISTRY — HONOURS
Fifth Paper
Full Marks – 100

The figures in the margin indicate full marks

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

New Syllabus
(Under 2+1 and 1+1+1 – Old Systems)
Group – A
(Advanced Physical Chemistry)
Full Marks – 50

Answer ***any three*** questions taking ***one*** from each unit

Unit – I

1. (a) Derive thermodynamically a relation between the osmotic pressure of a dilute solution of a nonvolatile solute and its molar concentration. State the assumptions and approximations involved. 4+1

(b) For a system of N molecules the number of molecules (N_i) in a nondegenerate energy level (ϵ_i) is given by the following equation

$$N_i = Ce^{-\beta\epsilon_i}$$

(i) Obtain an expression for C.

(ii) Show that β is always positive.

(iii) Calculate C when ϵ_i's are given by

$$\epsilon_i = i\hbar\upsilon, \quad i = 0, 1, 2, 3, \ldots\ldots\ldots\ldots\ldots$$ 6

(c) Draw the phase diagrams for H_20 and CO_2 systems. Indicate the differences between the two diagrams. 4

(d) Equal volumes of two aqueous solutions, one containing 36 gm of glucose (mol. weight : 180) in 1000 gm water and the other 36 gm of urea (mol. weight : 60) in 1000 gm water are mixed. What will be the freezing point of the resulting solution ? The heat of fusion of ice at 0^0C is 80 Cal gm^{-1}. 3

2. (a) State Nernst heat theorem. Show schematically the variation of ΔG and ΔH with T on the same plot. 2+3

(b) The molecules of a gas have two states with energies zero and ϵ and degeneracies g_1 and g_2 respectively. Write down the expression for the molecular partition function. 2

(c) Two liquids A and B form an ideal solution. At 80^0C, the vapour pressures of A and B are 400 mm and 800 mm of Hg respectively. Find out the composition of the mixture that boils at 80^0C. Also find out the composition of the vapour phase remaining in equilibrium with the boiling mixture at 80^0C. 2+2

(d) Write down Duhem – Margules equation and hence show that for a binary liquid mixture at maximum boiling point vapour phase composition is same as that of liquid phase composition. 1+3

(e) State the relation between mean ionic activity, molality and mean ionic activity coefficient of a dilute solution of an electrolyte. Hence calculate mean ionic activity coefficient of $AlCl_3$ in 0.001 m solution at 25^0C. Given A = 0.509 for water at 25^0C. 1+2

Unit – II

3. (a) For a cubic crystal derive the relation

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

(Terms have their usual significance). 4

(b) Is it possible to use x-ray of wave length 3Å to determine the spacings of (111) planes of a body centered cubic crystal having side length 5.2 Å ? Justify. 3

(c) Elucidate the concept of zeta potential. Hence explain the mechanism of coagulation of colloidal particles. 2+3

(d) Explain the temperature variation of molar polarization with proper equation. Hence suggest a method for determination of the dipole moment of a molecule. 2+2

4. (a) Einstein's equation for the heat capacity of solid is given by

$$C_v = 3R\left(\frac{h\upsilon}{kT}\right)^2 \frac{\exp(h\upsilon/kT)}{[\exp(h\upsilon/kT) - 1]^2}$$

with terms having their usual significance

(i) Arrive at Dulong Petit's law from this equation.

(ii) Define Einstein characteristic temperature and give its significance.

(iii) Why does Einstein theory of heat capacity of solid fail to explain the plot of experimental heat capacity versus temperature in its entirety ? 2+2+2

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