WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 5th Semester Examination, 2022-23

CEMADSE01T-CHEMISTRY (DSE1/2)

ADVANCED PHYSICAL CHEMISTRY

Time Allotted: 2 Hours | Full Marks: 40

The figures in the margin indicate full marks.
Candidates should answer in their own words and adhere to the word limit as practicable.
All symbols are of usual significance.

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

UNIT-I

1. (a) (i) State Hauy's law of rational intercepts. 2

(ii) Determine the Miller indices of the planes that intersect the crystal axes at $a, 2b, \infty c$ and $\frac{1}{2}a, \frac{1}{4}b, -c$. 2

(b) There exists long range order in crystals. Justify or criticize. 2

(c) What is the highest order that can be observed in Bragg's reflection from a crystal of interplanar distance 2Å by X-ray having wavelength 100 pm? 2

(d) A metal has a body centred cubic lattice and length of a unit cell is 2.95Å. If the density of the metal is 9.95 gm/cc, calculate the atomic weight of the metal. 3

(e) The molar volume of KCl is 1.3 times that of NaCl. If the glancing angle for the first order Bragg reflection from the 100 plane of NaCl is 5.9°, calculate the same for KCl. 3

2. (a) (i) Deduce Bragg's law $\lambda = 2d\sin\theta$. 3

(ii) On what factors does the intensity of the diffracted beam from different sets of planes depend? 2

(b) The characteristic K_a lines of Cr, Fe and Ni have wavelengths of 2.2009, 1.9373 and 1.6591Å respectively. (i) Can all be used to determine a lattice spacing of 1 Å? (ii) What will be the largest value of diffraction angle θ? 3

(c) The unit cell dimension 'a' of NaCl lattice is 5.63 Å. If X-ray beam of wavelength 1.1 Å falls on a family of planes with a separation of $\left(\frac{a}{\sqrt{5}}\right)$; how many orders of diffraction are observable? 3

(d) Show that the maximum proportion of available volume which may be filled by hard spheres in simple cube, body centred cube and face centred cube is in the ratio 26:34:37. 3

UNIT-II

3. (a) Consider a system of n molecules distributed among non-degenerate energy levels represented by $\varepsilon_0, \varepsilon_1, \varepsilon_2, \ldots$ etc. Write down the expression for molecular partition function for the system. Show that internal energy (U) of the system can be expressed as 3

$$U = nkT^2\left(\frac{\partial \ln Q}{\partial T}\right)_V$$

where k is the Boltzmann constant, T and V being the temperature and volume of the system respectively.

(b) What is meant by most probable macrostate? 1

(c) In a six particle system four energy states are available and energy levels are nondegenerate. The gap between the successive levels is ε. Find out the most probable configurations of the states having energy 10ε and 6ε. 2+2

(d) Calculate the relative number of microstates in water with respect to ice at 0 °C. Given $\Delta H_{fus} = 1440 \text{ cal mol}^{-1}$. 3

(e) Entropy is a function of thermodynamic probability. How can one conclude that the function is logarithmic? 2

4. (a) Define partition function. What is its physical significance? 2

(b) A system consisting of 4 identical and distinguishable particle, each possessing three available states of 1, 2 and 3 units, has a total of 10 unit energy. Calculate the number of ways, W, in which these conditions are satisfied. 3

(c) If N molecules are distributed among the possible nondegenerate energy levels $\varepsilon_1, \varepsilon_2, \varepsilon_3, \ldots$ etc in an isolated system, show that the entropy of this system can be represented as $\mathbf{S = k\beta E + NklnQ}$ (here symbols have their usual meaning). Find the value of β in terms of T. 3

(d) The relative population in two states with energies E_1 and E_2 satisfying Boltzmann distribution is given by $\frac{n_1}{n_2} = \frac{3}{2}e^{-(E_1 - E_2)/k_B T}$. What is the relative degeneracy g_2/g_1? 2

(e) State Sterling's approximation and mention the condition of its validity. 1

(f) Express Helmholtz free energy (A) in terms of partition function. 2

UNIT-III

5. (a) ΔG for a reaction as a function of temperature (T) for low value of T (T approaching zero Kelvin) is given by: 2+1+2

$$\Delta G = a + bT + cT^2$$

(i) Show that $b = 0$; (ii) Find ΔH as a function of temperature and (iii) show schematically the variation of ΔG and ΔH with T on the same plot.

(b) What is residual entropy? Calculate the residual entropy of two moles of CO molecules from the Boltzmann equation. Which has a higher residual entropy: water or methane? Explain. 1+2+1

(c) A solution contains equal number of particles with molar masses 10000 g mol^{-1} and 20000 gm mol^{-1} respectively, Calculate $\overline{M}_n$ and $\overline{M}_m$. 2

(d) What is functionality? The functionality of glycerol is three. Comment. 1+1

6. (a) (i) Evaluate the values of the constants 'x' and 'y' in the equation $C_P - C_V = TV\alpha^x\beta^y$ from dimensional considerations. Terms have their usual significances. 1

(ii) From Debye's equation for heat capacity of solids calculate the atomic heat of copper at 0°C. 2

(b) (i) Arrange the following molecules in order of increasing standard molar entropy: $C_2H_2(g)$, $C_2H_4(g)$ and $C_2H_6(g)$. Explain your answer. 3

(ii) Explain with S–T diagram the process of cooling by adiabatic demagnetisation of paramagnetic substances. 3

(c) (i) Deduce the relation between number average degree of polymerisation, '$\langle x_n \rangle$' and extent of polymerisation, 'p'. Hence show that near the completion of polymerisation reaction a small increase in 'p' leads to a large increase in '$\langle x_n \rangle$'. 2

(ii) What are conducting polymers? Give examples and account for their conducting properties. 2

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