WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 5th Semester Examination, 2021-22

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) A lattice point in a crystal structure must be occupied by atoms or ions. Justify or criticize. — 2+2+1+2

(ii) The unit cell has orientation but no position. Justify or criticize.

(iii) State two reasons why Miller indices are preferred to Weiss indices.

(iv) X-ray diffraction method cannot distinguish between two atoms differing only by the possession of one extra electron. Explain why.

(b) Explicitly justify that a five-fold rotational axis of symmetry is not possible in a crystal system. — 3

(c) For a given crystal the first-order reflection with a monochromatic beam of X-ray is observed at 10°12′. Find the angle at which the third-order reflection will be observed from the same plane. — 2

(d) The K_α lines of chromium, iron and nickel are observed at 2.28, 1.96 and 1.68 Å, respectively. Justify which of these radiations can be suitable for determination of a lattice spacing of 1.0 Å. — 2

2. (a) (i) Write the conditions for constructive interference in Bragg diffraction. Why is constructive interference necessary for determination of crystal structure? — 2+1+2

(ii) X-ray radiation is preferred instead of IR in the determination of crystal structure. — Comment.

(iii) In Bragg diffraction method monochromatic X-ray is customarily used. Justify whether a polychromatic beam of X-ray is suitable for determination of crystal structure.

(b) What do you understand by the term ‘space lattice’? Show that the interplanar distance in cubic system is given as $d_{hkl} = a/\sqrt{h^2+k^2+l^2}$, where, a is the edge-length of the cube and (hkl) are the Miller indices. — 1+3

(c) The first-order reflection of a beam of monochromatic X-ray from the (100) planes of sodium chloride crystal is observed at an angle of 6°35′. Find the wavelength of the X-ray used in the experiment. Also calculate the angle of reflection if X-ray of wavelength 154 pm is used. — 3

Given: Density of NaCl is 2.17 g cm^{-3}.

(d) State the criteria for obtaining sharp diffraction lines of uniform thickness in powder X-ray diffraction method. 2

UNIT-II

3. (a) The Boltzmann distribution may be represented by expressing the number of molecules (N_i) in the level ϵ_i (under isothermal conditions) as $N_i = A \exp(-b\epsilon_i)$ where A and b are constants. 2+2

Answer the following questions taking $b = 1/k_B T$:

(i) Show that $N_{i+1} < N_i$ for any finite temperature, with $\epsilon_1 < \epsilon_2$.

(ii) Obtain an expression for A in terms of b and show that it is related to the partition function.

(b) Consider a system of six distinguishable particles. One of the macrostates has the following distribution of particles: 3

Energy	0	ϵ	2ϵ	3ϵ	4ϵ
No. of particles	0	0	2	2	2

Calculate its thermodynamic probability.

(c) If the work function, A, is $A = -Nk_B T \ln Q$ 3

Then show that $P = Nk_B T \left(\dfrac{d \ln Q}{dV} \right)_T$

where N = number of molecules, Q = molecular partition function.

(d) The degeneracy of the 1st and 2nd energy levels are respectively 2 and 5. Find out the ratio $\dfrac{n_2}{n_1}$ when $\varepsilon_2 - \varepsilon_1 = 10^{-21}$ J and temperature is 400 K. 3

4. (a) Define configuration entropy and thermodynamic probability. Entropy is a logarithmic function of thermodynamic probability. — Justify. 2+2

(b) For a system, the energy levels are 0, ϵ, 2ϵ, 3ϵ where $\epsilon = 4.14 \times 10^{-21}$ and the degeneracy of the levels are respectively 1, 1, 3, 5. Find the molecular partition functions at 300 K. 3

(c) Three identical but distinguishable particles are distributed among three energy levels 0, E, $2E$. Write down the different possible distributions of the particles for total energy (i) E and (ii) $2E$. Also, obtain the thermodynamic probability for each distribution and hence the change in entropy for increasing the total energy from (i) to (ii). 2+2+2

UNIT-III

5. (a) (i) The Einstein's heat capacity model can successfully explain the lowering of heat capacity of solids with lowering of temperature. Discuss about the physical reasons underlying the success of the model. 2+2

(ii) State the physical reasons for failure of the model in the limit of very low temperature, and comment on Debye's modification.

(b) (i) The residual entropy of a substance is found to be 9.2 $JK^{-1}mol^{-1}$. Show that the number of possible orientations that a molecule of the substance can have at absolute zero is 3.024. Is this fractional value permissible? Justify your answer. 2+(2+1)

(ii) Deduce the magnitude of coefficient of thermal expansion of a pure crystalline substance in the limit of absolute zero and hence show that $C_{p,m}$ and $C_{V,m}$ of a pure crystalline substance become almost equal in the limit of absolute zero.

(c) All polymers are macromolecules, but all macromolecules are not polymers. — Justify. 2

(d) Briefly discuss about how you can monitor the progress of a step-growth polymerization reaction. 2

6. (a) Calculate the molar residual entropy of NO crystal. Compare the result with the experimental value of 2.78 $JK^{-1}mol^{-1}$ and comment. 2

(b) Provide a justification of the third law of thermodynamics from the probabilistic interpretation of entropy and hence justify the concept of origin of residual entropy. 2

(c) (i) In adiabatic demagnetization method $dq_{rev} = 0$, hence the demagnetization step is isentropic; then how does it lead to a drop in temperature? — Explain. 1+1

(ii) Gadolinium(III) sulfate octahydrate is a preferred material to the anhydrous salt for application in attainment of low temperature by adiabatic demagnetization. — Justify.

(d) Briefly discuss about the influence of the presence of polar functional moieties in the polymeric chain on the melting point/boiling point of the polymer. 2

(e) Consider the following kinetic mechanism of copolymerization: 3+1+1

$$M_1^\bullet + M_1 \rightarrow M_1^\bullet \quad \text{rate constant} = k_{11}$$

$$M_1^\bullet + M_2 \rightarrow M_2^\bullet \quad \text{rate constant} = k_{12}$$

$$M_2^\bullet + M_1 \rightarrow M_1^\bullet \quad \text{rate constant} = k_{21}$$

$$M_2^\bullet + M_2 \rightarrow M_2^\bullet \quad \text{rate constant} = k_{22}$$

Based on the given mechanism show that the ‘copolymer equation’ can be given as $\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1]+[M_2]}{[M_1]+r_2[M_2]}$ where r_1 and r_2 denote the reactivity ratios.

Use the above expression to answer the following questions:

(i) Comment on the type of copolymer formed when both the reactivity ratios are equal.

(ii) Comment on the type of polymer formed when one of the reactivity ratios is significantly greater than the other.

N.B. : *Students have to complete submission of their Answer Scripts through E-mail / Whatsapp to their own respective colleges on the same day / date of examination within 1 hour after end of exam. University / College authorities will not be held responsible for wrong submission (at in proper address). Students are strongly advised not to submit multiple copies of the same answer script.*

——×——