लक्ष्यं विश्वमानम्

WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 5th Semester Examination, 2020, held in 2021

CEMADSE01T-CHEMISTRY (DSE1/2)

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) For different reflections from the same face of a crystal the glancing angle is a constant multiplier of the order of diffraction. Justify or criticize. 2

(ii) In the context of Bragg diffraction justify whether radio-wave is suitable for determination of crystal structure. 2

(b) (i) Show that for a square lattice of side-length = a the spacing between the $(hk0)$ planes is $a/\sqrt{h^2+k^2}$. 3

(ii) The spacing between two consecutive parallel $(hk0)$ planes is $a/\sqrt{11}$. Comment on the possibility of this result. 2

(c) For a unit cell having $a \neq b \neq c$ (and $\alpha = \beta = \gamma = 90^\circ$) show that the inter-planar distance between the (hkl) planes is reduced by a factor of n when the Miller indices are multiplied by the same factor. 2

(d) An element exists in two crystalline forms- a α-form that crystallizes in fcc lattice having edge-length of 370 pm, and a β form that crystallizes in bcc lattice having edge-length of 290 pm. What is the ratio of densities of the two crystalline forms? 3

2. (a) (i) Find the lower limit of interplanar spacing to produce a first-order Bragg diffraction. 2

(ii) Find the highest order of Bragg diffraction that can be observed from a crystal of interplanar distance of 2.3 Å by X-ray of wavelength 120 pm. 2

(b) Determine the Miller indices of the plane that intersects the crystal axes at 2

(i) $(-a, b, \infty)$ and (ii) $\left(\frac{3}{2}a,\ \frac{3}{2}b,\ 2c\right)$.

(c) For packing of a cubic crystal with identical atoms the edge-length of the unit cell is found to be $2/\sqrt{3}$ times the diameter of the atoms. Identify the type of the cube and calculate the percentage of void space. 3

(d) Sodium chloride and potassium chloride are known to have the same crystalline structure, but the reflection from (111) plane is observed from sodium chloride while the same is absent in potassium chloride. Explain. 3

(e) A metal (atomic weight 23.02) crystallizes in bcc lattice having edge-length of 412 pm. Calculate the density of the metal and the radius of atom. 2

UNIT-II

3. (a) Calculate the weight of the configuration in which 20 objects are distributed in the arrangement 0, 1, 5, 0, 8, 0, 3, 2, 0, 1. 2

(b) (i) What is partition function? What is its unit? 1

(ii) Show that as T approaches the absolute zero of temperature the degeneracy of the ground state becomes equal to the partition function. Evaluate the partition function for a molecule with an infinite number of equally spaced nondegenerate energy levels having energy separation ε. What is the fraction of molecules in the i-th energy state possessing an energy ε_i. 1+2+1

(c) (i) For a system of N independent and distinguishable particles show that 3

$$\langle E \rangle = k_B T^2 \left(\frac{\partial \ln q}{\partial T} \right)_{V,N}$$

(where $\langle E \rangle$ is a average energy, k_B is Boltzmann constant, q is molecular partition function).

(ii) Consider the molecular partition function of an ideal monatomic gas as $q = \exp(a + b \ln T)$ where a, b are constants. Find an expression for b and the molar heat capacity of the gas. 3

4. (a) The total number of microstates of a system comprised of N number of particles distributed in two energy states is given as $\Omega_{tot} = 2^N$. Using Stirling's approximation, find the number of microstates (Ω_{eq}) for the distribution in which the two energy states are equally populated. Compare Ω_{tot} and Ω_{eq} comment on the result. 2+2

(b) (i) Two non-degenerate energy states are separated by $200\ \text{cm}^{-1}$. At what temperature will the population of the higher state be one-third to that of the lower state? $1\frac{1}{2}$

(ii) Using the Boltzmann distribution law show that $n_{i+1} < n_i$ at any finite temperature (n_i is population of the i-th state). $1\frac{1}{2}$

(c) (i) State the physical significance of partition function. 1

(ii) The molecular partition function of an ideal gas is given as $q = (aT/b)^{3/2}V$, where a and b are constants. Find an expression for pressure of the gas. 3

(d) Starting from the expression of Helmholtz energy $A = -Nk_B T \ln q(N,V,T)$ find an expression for entropy of the system (q is molecular partition function). 2

UNIT-III

5. (a) According to the Einstein's model the molar heat capacity of monatomic crystal can be expressed as 1+3+2

$$C_{V,m} = 3R\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T}-1)^2}$$

where θ_E is the characteristic Einstein temperature.

(i) Write down the defining equation for θ_E and state its physical significance.

(ii) Find the proper expressions for $C_{V,m}$ in the limits of very low and very high temperature.

(iii) Argue on the applicability of the equation in the two limits of temperature.

(b) ΔG for a reaction is given as $\Delta G = \alpha + \beta T + \gamma T^2$. 3

(i) Show that $\beta = 0$ when $T \to 0$.

(ii) Find an expression for ΔH and ΔC_p.

(c) (i) An spontaneous polymerization reaction must be exothermic. Justify or contradict. 2+2

(ii) For a polymerization reaction show that $\langle DP \rangle_n = \dfrac{2}{2 - f\xi}$, where $\langle DP \rangle_n$ is the number-averaged degree of polymerization, ξ is the extent of polymerization, f is the average degree of functionality.

6. (a) Show that the molar entropy of a perfect crystalline substance obeying the Debye's law of heat capacity at low temperature is equal to $C_{V,m}/3$. 2

(b) Adiabatic demagnetization with a paramagnetic substance is a technique for attainment of low temperature. 2+3+2

(i) Construct with suitable explanation the S *vs.* T curve for a paramagnetic substance.

(ii) Using the S *vs.* T curve, explain the working principle of adiabatic demagnetization.

(iii) Comment on unattainability of the absolute zero of temperature by this technique and hence argue that unattainability of absolute zero is consistent with the third law of thermodynamics.

(c) Derive the integrated rate law equation for the kinetics of step-growth polymerization using a suitable example. Using your rate law equation plot the variation of $\langle DP \rangle$ with the progress of reaction (where $\langle DP \rangle$ is average degree of polymerization). 3+1

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.*

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