



বিদ্যাসাগর বিশ্ববিদ্যালয়  
**VIDYASAGAR UNIVERSITY**

**Question Paper**

**B.Sc. Honours Examinations 2021**

**(Under CBCS Pattern)**

**Semester - V**

**Subject: CHEMISTRY**

**Paper: DSE 1-T & P**

**Advanced Physical Chemistry**

**Full Marks : 60 (Theory-40 + Practical-20)**

**Time : 3 Hours**

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

*The figures in the margin indicate full marks.*

**(Theory : Marks - 40)**

**Group - A**

Answer any *three* questions :

12 × 3 = 36

- (a) What are the differences in the heat capacity model proposed by Einstein and Debye ? Write the modification introduced by Debye in order to improve the Einstein theory of specific heat of solids.

(b) Fluoride has face-centered cubic structure in the unit cell. At 25 °C the (111) reflection with x-rays of the wavelength of 1.542 nm occurs at  $\theta = 14.18^\circ$ . Calculate the length of the unit cell.

(c) Entropy is logarithmic function of thermodynamic probability — Explain.

6 + 4 + 2

2. (a) For a collection of equispaced non-degenerate levels, evaluate the partition function and from it get an expression of internal energy of the system.

(b) Find out the mutual angles formed by the following pairs of intersecting planes in the cubic system;

(i) 100, 010; (ii) 100, 110; (iii) 110, 101;

(iv) 110, 111

(c) Define weight average molecular weight.

6+4+2

3. (a) Write the Bragg equation explaining the terms. Why X-rays and not microwave are suitable for the determination of crystal structure.

(b) Discuss briefly the kinetics of copolymerization.

(c) Write down the Nernst Heat Theorem and mention one of its exceptions.

(d) Define with example of isotactic polymers.

4+4+2+2

4. (a) Derive the Barometric distribution formula from Boltzmann energy distribution.

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

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

Calculate its thermodynamic probability.

(c) Show that the separation of the (hkl) planes  $d_{hkl}$  in an ortho-rhombic crystal with sides a, b and c is given by

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

4 + 4 + 4

5. (a) NaCl and KCl have same geometric arrangements of positive and negative ions in their crystals. But X-rays diffraction indicates that KCl has a simple cubic and NaCl has a face centred cubic lattice. Explain.

(b) The total no of microstates ( $W_T$ ) of a system of N distinguishable particles distributed in two energy states is  $W_T = 2^N$ . Using Stirling approximation find the no of microstates ( $W_{1:1}$ ) for the 1 : 1 distribution. Compare  $W_T$  and  $W_{1:1}$  and comment.

(c) Given the following composition molar mass data for a polydisperse polymer mixture :

Mass %	25.0	50.0	25.0
$M_i$ (kg. mol <sup>-1</sup> )	1.00	1.20	1.40

Calculate number average and molar mass average molecular weight. Also calculate polydispersity index for the polymer mixture. 4+4+4

6. (a) The density of NaCl at 25°C is  $2.16 \times 10^3 \text{ kg m}^{-3}$ . When X-rays from a palladium target having a wavelength of 58.1 pm are used the (200) reflection of NaCl occurs at an angle of 5.91°. Calculate the number of Na<sup>+</sup> and Cl<sup>-</sup> ions in the unit cell.
- (b) For a system of N molecules, the number of molecule ( $N_i$ ) in a non-degenerate energy level ( $\epsilon_i$ ) is given by the following equation,

$$N_i = C.e^{-\beta\epsilon_i}$$

- (i) Obtain an expression for C.
- (ii) Show that  $\beta$  is always negative.
- (iii) Calculate C when  $\epsilon_i'$  are given by  $\epsilon_i = ihv, i = 1, 2, 3, \dots$
- (c) Dulong - Petit law is a consequence of equipartition principle — justify the statement. 4+6+2

### Group - B

Answer any *two* questions : 2×2=4

1. What is meant by a (110) plane and draw the plane for a simple cubic crystal.
2. Near the absolute zero, all the process should occur without any change of entropy — Justify or criticize.
3. What do you mean by kinetic chain length?
4. The distance between two successive hkl planes in a cubic crystal is  $\frac{a}{\sqrt{3}}$ , where 'a' is the length of the unit cell. Find the value of h, k and l.

**(Practical : Marks - 20)**

**Group - A**

Answer any *one* of the following questions :

15×1=15

1. Write the programme to determine the volume of 0.5 mol of van der Waals gas (carbon dioxide) at 2 226 Pa and 298 K. Take the starting volume as obtained from the ideal gas equation of state. Given:  $a = 363.76 \text{ kPa dm}^6 \text{ mol}^{-2}$ ,  $b = 0.042 67 \text{ dm}^3 \text{ mol}^{-1}$ .
2. Explain Simpson Rule for numerical integration.
3. Write down the programme to obtain the Differentiation of  $\ln(x)$ .

**Group - B**

Answer any *one* of the following questions :

5×1=5

1. Discuss the application of Gauss - Siedel method in colourimetry.
  2. Write down the programme to determine pH of a weak acid.
  3. Write a brief note on the application of molecular visualisation software.
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