B.Sc. 5th Semester (Honours) Examination, 2020-2021

CHEMISTRY

Course ID: 51416   **Course Code: UG/CHEM/503/DSE-1**

Course Title: Advanced Physical Chemistry

Time: 1 Hour 15 Minutes   **Full Marks: 25**

The figures in the right hand side margin indicate marks.

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

1. Answer *any five* questions of the following: $1 \times 5 = 5$

   (a) Calculate the spacing between two successive (110) planes in an FCC lattice.

   (b) Find the number of atoms per unit cell in an FCC crystal.

   (c) If there are x numbers of energy levels then what is the condition for partition function is equal to x?

   (d) Mathematically define weight average molecular weight.

   (e) If $\ln N!$ is approximated by, $\left(N + \frac{1}{2}\right)\ln N - N$, find the approximate value of a N! itself.

   (f) What is grand canonical ensemble?

   (g) Define degree of polymerisation.

   (h) What is "residual entropy"?

2. Answer *any two* questions of the following: $5 \times 2 = 10$

   (a) (i) Write the expressions for vibrational partition function without and with zero-point energies.

   (ii) Copper has FCC structure and its atomic radius is 1.278 Å. Calculate its density. (atomic weight of Cu = 63.54) $2+3 = 5$

   (b) (i) In a Boltzmann distribution prove that, $n_{i+1}/n_i \leq 1$.

   (ii) What will be the percentage change in barometric pressure at 2000 m above the sea-level at 300K, if it is assumed that air is roughly a mixture of 20% O_2 and 80% N_2. $2.5+2.5 = 5$

(c) If partition function $f = \sum \exp(-\beta\varepsilon_i)$ then prove that $\beta = 1/kT$. Terms have their usual significance.

(d) Derive integrated rate equation for step-growth polymerisation reaction when a mineral acid is added as catalyst. Show the necessary linear plot to get the rate constant and comment on the plot, if any.

3. Answer *any one* question of the following: $10\times1 = 10$

(a) (i) Write down the Bragg's equation.

(ii) What is the lower limit to the spacing of the lattice planes to produce X-ray diffraction spectra for a given radiation?

(iii) "X-ray and not UV light can produce diffraction pattern when it passes through a crystal." Justify or criticize.

(iv) Define Schottky defects.

(v) A metal has a body centered cubic crystal having length of the unit cell is 2.95 Å. If the density of the metal be 9.95 g/cm^3, calculate the atomic weight of the metal.

$2+2+2+1+3 = 10$

(b) (i) 'For the evaluation of translational and rotational partition functions involved replacement of the summation by integration.'- Why could such integration be performed?

(ii) Indicate the shortcomings of Einstein's model for specific heats of solids.

(iii) Predict the value of $(C_P - C_V)$ at T$\rightarrow$0K.

(iv) State the third law of thermodynamics. How the absolute value of entropy of a gaseous substance can be determined from third law? $2+2+2+1+3 = 10$