SH-V/CHEM/503/DSE-1/19

B.Sc. 5th Semester (Honours) Examination, 2019-20

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: 1×5=5

(a) What is Thermodynamic Probability? How does it differ from Mathematical Probability?

(b) What is Stirling's Approximation? Calculate the percentage of error in using Stirling's formula where $n = 10$.

(c) Deduce the Miller indices of a plane in an orthorhombic crystal which cuts intercepts of $3a$, $-2b$, $3c/2$ along the three axes.

(d) Why does cooling occur during adiabatic demagnetization of a paramagnetic salt?

(e) Write down the Lewis and Randall statement of the third law of thermodynamics.

(f) State the basic difference between the Einstein's and Debye treatment of solids.

(g) Define Condensation polymer.

(h) Represent Canonical-ensemble by its characteristic constants.

2. Answer *any two* questions: 5×2=10

(a) (i) Derive Bragg's equation $n\lambda = 2d\sin\theta$ employing a suitable diagram.

(ii) If the 1st order reflection maxima of NaCl crystal occurs at an angle 5·9º, then at what angle 2nd order maxima will be obtained? 3+2=5

(b) The Boltzmann distribution law for the number of molecules in the energy level ε_i is given by: $N_i = C.e^{-\beta\varepsilon_i}$.

(i) How 'C' can be expressed in terms of β and ε_i?

(ii) Write down the expression for the probability of the i^{th} energy level being occupied.

(iii) Show that $N_{i+1} < N_i$.

(iv) Under what condition of temperature, $N_{i+1} = N_i$. 1+1+2+1=5

(c) (i) State and explain Nernst heat theorem. Point out its limitations.

(ii) Define residual entropy. How it is originated? 3+2=5

(d) (i) Define weight-average molar mass ($\bar{M}_w$) of a polymer. Calculate $\bar{M}_w$ for a system containing equal no. of particles with molecular weights 10,000 and 20,000.

(ii) Explain the following.

Why averaging is essential to assign the molar mass of a polymer? From Osmotive pressure measurement of a polymer the molar mass obtained is $\bar{M}_w$ or $\bar{M}_n$? 3+2=5

3. Answer any *one* question: 10×1=10

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

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

Where, *k*=Boltzmann constant, T and V being the temperature and volume of the system.

(ii) Assuming the expression for the energy associated with an oscillator vibrating with frequency (γ) in one direction, deduce Einstein equation for the head capacity of solids. Show that at high temperature the equation reduces to Dulong-Petits' law. (1+4)+(3+2)=10

(b) (i) State and explain Havy's law of rational intercepts.

(ii) Calculate the ratio of number of molecules at two different energy levels A and B with $(\epsilon_B - \epsilon_A) = K_BT$ and ${}^{g_B}/_{g_A} = 3$ (g's are the degeneracies of the respective levels)

(iii) For a polymer, ${}^{\pi}/_{C}$ vs. C plot on extrapolation to zero concentration gave an intercept with ordinate equals to $3{\cdot}47\times10^{-4}$ L. atm g^{-1} at 27°C. Determine the molar mass of the polymer.

(iv) Show that $\bar{M}_w \geq \bar{M}_n$ for macromolecules. 2+3+3+2=10

———