This question paper contains **3** printed pages]

# AG—242—2018

**FACULTY OF SCIENCE**

**M.Sc. (III Semester) EXAMINATION**

**NOVEMBER/DECEMBER, 2018**

**(CBCS PATTERN)**

PHYSICAL CHEMISTRY

(Statistical Thermodynamics)

Paper-XVIII (CH-534/3A)

**(Monday, 3-12-2018)** **Time : 2.00 p.m. to 5.00 p.m.**

*Time*—3 *Hours* *Maximum Marks*—75

*N.B.* :— (*i*) Attempt *all* questions.

(*ii*) Use of log table and calculator is allowed.

(*iii*) Solve Q. No. **5**. (A) MCQ in one attempt only.

1. Solve any *three* : 15

(*a*) Explain in brief thermal characteristics of crystalline solid.

(*b*) Calculate the number of ways of putting 4 objects in 6 boxes.

(*c*) Write a note on mean symmetry and nuclear spin.

(*d*) Derive the relation for fluctuation in density and radioactive disintegration.

(*e*) Calculate the relative no. of distinguishable states in ice and in water at 273 K.

Given : $\Delta H_{bus} = 6.0$ kJ $mol^{-1}$ at 273 K

$k = 1.38 \times 10^{-23} JK^{-1}$.

2. Solve any *three* : 15

(*a*) Explain in detail Lagrange method of undetermined multiplier.

(*b*) Define partition function and its significance.

(*c*) Calculate the nuclear spin partition function of ortho $H_2$ and ortho $D_2$ molecules.

(*d*) Derive $S = K_b N \ln\left[\frac{qe}{N}\right] + \frac{E}{T}$

(*e*) Calculate heat capacity of an element at a temperature equal to its

P.T.O.

characteristic temperature.

3. (*a*) Derive the relation between partition function and thermodynamic function i.e. internal energy, entropy and free energy. 8

(*b*) Explain in detail limitations and modifications of Debye theory. 7

*Or*

(*a*) Derive the relation for Maxwell-Boltzmann distiribution law. 8

(*b*) Using the principle of equipartition of energy, indicate the translational, vibrations and rotational contribution to the heat capacity of hydrogen molecule. 7

4. (*a*) Derive : $C_V \left[\frac{nR}{T^2}\right]\left[\frac{\delta^2 inq}{\delta\left[T^{-2}\right]}\right]_V$ 8

(*b*) Derive the relation for rotational partition function ? Calculate the rotational partition function for HCl at 35°C. The rotation constant is 10.59 $cm^{-1}$. The value of $\frac{KT}{hC}(cm^{-1})$ at 298 K is 407.20. 7

*Or*

(*a*) Show that entropy at absolute zero in a canonical ensemble can be expressed as $S = K \log [g_0]$. 8

(*b*) Find ratio of iodine molecules in the ground, first and second excited vibration states at room temperature, the vibrational energy levels are separated by 214 $cm^{-1}$. 7

5. (A) Select the correct alternative from the following : 5

(*i*) The entropy ..... with increasing molar mass.

(*a*) Increases (*b*) Decreases

(*c*) No change (*d*) None of these

(*ii*) The entropy of Co at absolute zero temperature is .....

(*a*) +ve (*b*) –ve

(*c*) zero (*d*) None of these

(3) Partition function is a ..... quantity.

(*a*) Dimensionless (*b*) Dimension

(*c*) both (*a*) and (*b*) (*d*) All of these

(*iv*) Vibration contribution to energy at low temperature is :

(*a*) Negligible (*b*) Increases

(*c*) Decreases (*d*) None of these

(*v*) Partition function increases with ..... in temperature.

(*a*) Increase (*b*) Decrease

(*c*) Zero (*d*) None of these

(B) Solve any *two* (short note) : 10

(*i*) Combinatorial problem

(*ii*) Lattice model

(*iii*) Mean distribution and mean square deviation.