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BR—374—2016

FACULTY OF SCIENCE

M.Sc. (Second Year) (Third Semester) EXAMINATION

OCTOBER/NOVEMBER, 2016

(CBCS Pattern)

PHYSICAL CHEMISTRY

Paper XVIII (534/3A)

(Statistical Thermodynamics)

(Wednesday, 23-11-2016) **Time : 2.00 p.m. to 5.00 p.m.**

Time—Three 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) in one attempt only.

1. Solve any *three* out of five : 15

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

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

(*c*) Derive :

$$S = K_b N \ln \left[\frac{q_e}{N}\right] + \frac{E}{T}$$

(*d*) Calculate the nuclear partition function of ortho H_2 and ortho D_2 molecules.

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

2. Solve any *three* out of five : 15

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

P.T.O.

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

(*c*) Calculate the relative number of distinguishable states in ice and in water at 273 K.

Given : ΔH_{fus} = 6.0 kJ mol^{-1} at 273 K

$K = 1.38 \times 10^{-23}$ JK^{-1}]

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

(*e*) No has doubly degenerate ground state and doubly degenerate electrically excited state 121.1 cm^{-1} above ground state. Calculate electronic partition function at 25°C.

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

Or

Derive the relation for Maxwell-Boltzmann distribution law.

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

Or

Using the principle of equipartition of energy, indicate the translational, vibrational and rotational contribution to the heat capacity of hydrogen molecule.

4. (*a*) Derive : 8

$$C_v = \left[\frac{nR}{T^2}\right]\left[\frac{\delta^2 \ln q}{\delta[T^{-2}]}\right]_v$$

Or

Derive the relation for rotational partition function. Calculate the rotational partition function for HCl at 25°C. The rotational constant of HCl is 10.59 cm^{-1}. The value of $\frac{kT}{hc}(cm^{-1})$ at 298 K is 207.20

(*b*) Show that the entropy at absolute zero in a cannonical ensemble can be expressed as $s = k \log [g_0]$ 7

Or

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}.

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 is ..... .

(*a*) Positive (*b*) Negative

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

(*iii*) Partition function is a ..... quantity.

(*a*) dimensionless (*b*) dimension

(*c*) both (*a*) and (*b*) (*d*) none of these

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

(*a*) negligible (*b*) increases

(*c*) decreases (*d*) none of these

P.T.O.

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

(*a*) increase (*b*) decrease

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

(B) Write short notes on any *two* of the following : 10

(*i*) Combinatorial problem

(*ii*) Lattice model

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