

This question paper contains 3 printed pages]

**AI—242—2017**

**FACULTY OF SCIENCE**

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

**NOVEMBER/DECEMBER, 2017**

**PHYSICAL CHEMISTRY**

Paper 534/3A

(Statistical Thermodynamics)

**(Friday, 17-11-2017)**

**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) Attempt MCQ in one attempt only.*

1. Solve any *three* : 15

(a) Explain in brief combinatorial problems.

(b) Define Partition function. Explain its significance.

(c) Derive :

$$S = K_b N \ln \left[ \frac{q_0}{N} \right] + \frac{E}{T}.$$

(d) Explain in brief mean symmetry and Nuclear spin.

(e) Estimate the heat capacity of steam at 100°C.

2. Solve any *three* : 15

(a) Write a note on mean distribution and mean square deviation.

(b) In a sample of atomic Hydrogen at 25°C what proportion of atoms are in the 1<sup>st</sup> excited state if it lies 1000 kJ mole<sup>-1</sup> above the ground state ? Calculate the proportion of atoms.

(c) Explain in brief Internal rotation of polyatomic molecules.

(d) Calculate the nuclear partition function of ortho H<sub>2</sub> and ortho D<sub>2</sub> molecules.

(e) No has doubly degenerate G.S. and doubly degenerate electrically E.S. 121.1 cm<sup>-1</sup> above the G.S. Calculate the electronic partition function [Z<sub>ele</sub>] at 25°C.

P.T.O.

3. (a) Using the principle of equipartition of energy, indicate the translational, rotational and vibrational contribution to the heat capacity ( $C_v$ ) of the hydrogen molecule. 7

*Or*

Show that entropy at absolute zero in a canonical ensemble can be expressed as  $S = K \log [g_0]$ . 7

*Or*

- (b) Derive the relation for translational partition function. Calculate the translation P.F. of a molecule oxygen gas at 1 atm. and 298 K moving in a vessel of volume 24.4 dm<sup>3</sup>. 8

*Or*

Explain in brief limitations and modifications in Debye theory. 8

4. (a) Derive the relation between P.F. and thermodynamic function i.e. Internal energy, Entropy and free energy. 8

*Or*

Compare an I.M.P. features of Maxwell-Boltzmann statistics, Bose-Einstein and Fermi-Dirac statistics. 8

- (b) Explain in brief Einstein model. Explain the comparison between Debye theory and Einstein model. 7

*Or*

Find the ratio of Iodine molecules in the ground I<sup>st</sup> and II<sup>nd</sup> Excited vibrational states at room temp. the vibrational energy levels are separated by 214.6 cm<sup>-1</sup>. 7

5. (A) Select the correct alternative : 5

(i) Thermodynamic probability and General probability are :

- (a) Same (b) Differ  
(c) Both (a) and (b) (d) None of these

(ii) Partition function increase with ..... temp.

- (a) Increases (b) Decreases  
(c) Zero (d) None of these

(iii) The translational entropy is directly proportional to ..... of the sample.

- (a) Energy (b) Molecular wt.  
(c) Density (d) None of these

- (iv) Spontaneous process leads to the ..... state of the system.
- |                      |                   |
|----------------------|-------------------|
| (a) Most probable    | (b) Less probable |
| (c) Both (a) and (b) | (d) None of these |
- (v) The entropy of CO at absolute zero is :
- |              |                   |
|--------------|-------------------|
| (a) Positive | (b) Negative      |
| (c) Zero     | (d) None of these |
- (B) Write short notes on (any *two*) : 10
- (i) Stirling approximation
  - (ii) Lattice model
  - (iii) Fluctuation in energy.