6. (a) Derive an expression for Fermi-Dirac statistics. Compare it with Bose-Einstein statistics. Under what conditions they become equal ?

(b) Write brief notes on the following :

(i) Gas degeneration

(ii) Thermionic emission. **12,8**

Unit IV

7. (a) Derive an expression for the rate of entropy production in a closed system of constant composition involving heat transfer from outside the system.

(b) Give an account of Qusagan's reciprocity relation. **12,8**

8. (a) Discuss the fluctuations in an open isothermal system.

(b) Derive an expression for energy fluctuation in a canonical ensemble and number density fluctuation in a grand canonical ensemble. **8,12**

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DD-300

M. Sc. EXAMINATION, Dec. 2018

(Fourth Semester)

(Re-appear Only)

(CHEMISTRY)

CH626B

Physical Chemistry Special-IV

(Statistical Thermodynamics)

Time : 3 *Hours*] [*Maximum Marks :* 100

Before answering the question-paper candidates should ensure that they have been supplied to correct and complete question-paper. No complaint, in this regard, will be entertained after the examination.

Note : Attempt *Five* questions in all, selecting at least *one* question from each Unit. All questions carry equal marks.

Unit I

1. (a) Explain distribution concept in statistical thermodynamics.

(b) Give an account of Maxwell Boltzmann law of velocities.

(c) Derive an expression for average velocity and r.m.s. velocity. **4,8,8**

2. (a) Obtain an expression for internal energy of a system of N independent particles (atoms or molecules).

(b) Give a brief account of partition function and its factorization.

(c) Using the concept of molecular partition function, show that for an ideal monoatomic gas, $P = \frac{nRT}{V}$. **8,4,8**

Unit II

3. (a) Define partition function. Give its Physical significance. Derive an expression for molecular translational p.f. of a gas in a vessel of volume V.

(b) Calculate molecular translational p.f. of CH_4 gas at 110 K in a vessel of volume 1 dm^3 **12,8**

4. (a) Derive an expression for equilibrium constant in terms of p.f. by considering a general gaseous reaction.

(b) The fundamental vibrational frequency of F_2 is 2.076×10^{13} Hz. Calculate vibrational p.f. at 25ºC. **12,8**

Unit III

5. (a) Show that the equilibrium distribution of particles the following Bose-Einstein's statistics is given by :

$$N_i = \frac{g_i}{\left[e^{-\alpha+\beta\varepsilon_i} - 1\right]}$$

(b) Give an account where in it can be reduced to Boltzman statistics. **12,8**