Birla Institute of Technology and Science, Pilani (Rajasthan)

CHEM F422 : Statistical Thermodynamics

Comprehensive Examination **Semester I (2016-17)**

Max. Marks: 80 (24+56) **Duration: 1+2 hours** **Date: 8st December, 2016, FN**

Part B : Open book (Max Marks 56)

General Instructions:

1. Enter your name, ID number, course no., course title, tutorial section no. etc. on the front page of answer-sheet and the supplementary answer-sheet(s) clearly and legibly. Incomplete, incorrect or illegible information may result in deduction of up to 5 marks.

2. All the questions are compulsory. You may attempt the questions in any order but the sub-questions of a question must be solved together before attempting the next question(s).

3. Use of non-programmable scientific calculators only is allowed for calculations. Do not use pencil for writing answers.

4. Indicate the "Rough work" clearly. Rough work must be done only on the last page of the main answer-sheet/supplementary answer-sheet(s).

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1. We studied how to derive the Fermi-Dirac distribution function (FDDF): $\bar{n}_i = \frac{\lambda e^{-\beta\epsilon_i}}{1+\lambda e^{-\beta\epsilon_i}} = \frac{1}{1+e^{\beta(\epsilon_i-\mu)}}$ using a Grand-canonical ensemble approach. However, the equation shows that the average number of fermions, $\bar{n}_i$, in a given energy level depends on the energy of that particular level only. Thus, it must be possible to derive FDDF using micro-canonical ensemble more easily. In this problem, you are exactly going to do that. Consider a closed system of fermions. Let n_i be the number of fermions in the i^{th} energy level with degeneracy g_i. Analogous to the procedure used in Chapter 2, obtain FDDF, by maximizing $W = f\{w_i(n_i, g_i)\}$, under the constraints of total energy of the system and constant total number of fermions of the system; where, $w_i(n_i, g_i)$ is the number of ways of distributing n_i fermions (of energy ϵ_i) in g_i states. (Hints: The energy states are usually very large in number as compared to the particles in the system. Think for a while for understanding the form of $f\{w_i(n_i, g_i)\}$. This is a crucial step. Use the conventional undetermined multipliers relevant to the constraints.) **[14]**

2. Show that entropy of a system of bosons can be expressed as $k\sum_j \ln\left[(\bar{n}_j+1)^{\bar{n}_j+1}/n_j^{\bar{n}_j}\right]$. **[14]**

3. (a) Estimate the reaction enthalpy of the forward reaction: $H_2(g) + T_2(g) \rightleftarrows 2HT(g)$ within the temperature range of 273 K through 373 K. **(b)** Derive a simplified expression for variance in the pressure in a canonical ensemble. **[8+6]**

4. **(a)** If universe would be two-dimensional, what would be the number of vibrational degrees of freedom? Explain your answer in no more than one line. **(b)** For a two-dimensional monatomic crystal, using Debye theory, derive the expression for $g(\nu)d\nu$ assuming that longitudinal and transverse velocities are same. **(c)** Obtain the expression for the Debye frequency. Refer to your answers to (a) and (b) for this. **[2+8+4]**

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