Birla Institute of Technology & Science Pilani
Pilani Campus
I Semester 2022-2023
CHEM F422 Statistical Thermodynamics
Comprehensive Examination
(Open Book)

Max. Marks: 35 **20 December 2022** **Duration: 3 hrs.**

Instructions to the student:

1) There are six questions (two pages) in total; answer all the questions.
2) Start answering each question on a fresh page and answer all parts of a question together.
3) Write brief answers to the point with proper justification.
4) Mobile phones, lap-tops etc. are to be switched off and kept away from you.
5) Open book test. Textbook, Ref. books, class notes, and printed slides are allowed. However, exchange of these materials is not allowed.
6) Any unfair means, if identified, will be sternly dealt with.
7) Data required are available in Text and/or Reference books. However, for quick reference the following constant values are given.

DATA:

R = 8.3145 J mol^{-1} K^{-1}; **R**= 0.0820575 L atm K^{-1} mol^{-1}; **k = k_B** = 1.38065 x 10^{-23} J K^{-1} **k = k_B** = 0.69509 cm^{-1} K^{-1}; **Avogadro's Number** = **N_A** = 6.022142 x 10^{23} mol^{-1}; **h** = 6.626069 x 10^{-34} J s; **e** = 1.60216 x 10^{-19} C; **m_e** = 9.10938 x 10^{-31} kg; **F** = 96485.34 C mol^{-1}; **c** = 2.99792458 x 10^{8} m s^{-1}; **ε_0** = 8.854188 x 10^{-12} C^2 N^{-1} m^{-2}; **g** = 9.807 m s^{-2}; 1 **calorie** = 4.184 J.

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1. **(a)** Give an example of any function f(x,y,z) which is both homogeneous and even. **[2]**

(b) Maximize

$W(N_1, N_2, \ldots, N_M) = \frac{N!}{\prod_{j=1}^{M} N_j!}$ with respect to each N_j under the constraints that

$\sum N_j = N = a\ fixed\ constant$ and

$\sum E_j N_j = \mathcal{E} = another\ fixed\ constant$

Hint: Consider N_j's to be continuous, large enough to use Stirling's approximation of $N_j!$, and leave your answer in terms of the two undermined multipliers. **[4]**

2. System 1 is an ideal gas and is composed of N 'red' atoms of mass m, 2N 'blue' atoms of mass m and 3N 'green' atoms of mass m. Atoms of the same color are indistinguishable. System 2 is another ideal gas having the same total number of atoms (each one of mass m) as in system 1, however, all the atoms of system 2 are of same color 'white'. **(a)** Write the canonical partition functions for system1 and system 2 in terms of 'molecular' partition functions. **(b)** Find out the entropy difference between system 2 and system 1 in terms of N and k. Given: **S = kT(∂ ln Q /∂T)$_{V,N_B}$ + k ln Q**. **[2+3 = 5]**

3. Show that **[4]**

$$\overline{(E-\overline{E})^3} = k^2\left\{T^4\left(\frac{\partial C_V}{\partial T}\right) + 2T^3 C_V\right\}$$

4. **(a)** Write the symmetry numbers and C_V (classical) for the following molecules:
(i) XeF_4 (square planar) (ii) PF_5 (tbp) **[2]**

(b) Arrange the following quantities in the increasing order of their numerical values:
$\theta_v^{H_2}, \theta_{rot}^{H_2}, \theta_v^{Cl_2}, \theta_{rot}^{Cl_2}, \theta_v^{HCl}, \theta_{rot}^{HCl}$. Briefly justify your answer. **[2]**

(c) Discuss about the kind of rotational levels (odd/even) possible for the molecule $^{16}O^{16}O$ in its ground state. **[2]**

5. (**a)** Consider the following equilibrium:

$$2Cl_2(g) + O_2(g) \rightleftharpoons 2Cl_2O(g)$$

Write an expression for the equilibrium constant (K_p) in terms of the molecular partition functions. No need for any numerical calculations. But write in detail the expressions in terms of characteristic temperatures of rotation, vibration and D_o etc. **[4]**

(b) Calculate the value of K_p at 750 K for the above equilibrium in terms of appropriate atmospheric units, using the data given in Table 9-6 of the textbook. **[4]**

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6. (**a)** Derive $q_{rot}^{class} \sim 8\pi^2 IkT$ for rigid rotor starting from

$$q_{rot} \sim \int_{-\infty}^{\infty} \int dp_\theta \, dp_\phi \int_\theta^{2\pi} d\phi \int_\theta^{\pi} d\theta e^{-\beta H}$$

where

$$H = \frac{1}{2I}\left(p_\theta{}^2 + \frac{p_\phi{}^2}{\sin^2\theta}\right)$$

Note:

$\int_{-\infty}^{\infty} e^{-ax^2} dx = 2\int_0^{\infty} e^{-ax^2} dx = 2\sqrt{\frac{\pi}{4a}}$ **[3]**

(**b)** Calculate the number of Schottky defects per mole of crystal at 500 K and 1500 K given that it takes 1.5 eV to bring an atom or ion from an interior lattice site to a surface lattice site (1 eV = 1.60216×10^{-19} J). **[3]**

End.