

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:

$R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$; $R = 0.0820575 \text{ L atm K}^{-1} \text{ mol}^{-1}$; $k = k_B = 1.38065 \times 10^{-23} \text{ J K}^{-1}$ $k = k_B = 0.69509 \text{ cm}^{-1} \text{ K}^{-1}$;
Avogadro's Number = $N_A = 6.022142 \times 10^{23} \text{ mol}^{-1}$; $h = 6.626069 \times 10^{-34} \text{ J s}$; $e = 1.60216 \times 10^{-19} \text{ C}$;
 $m_e = 9.10938 \times 10^{-31} \text{ kg}$; $F = 96485.34 \text{ C mol}^{-1}$; $c = 2.99792458 \times 10^8 \text{ m s}^{-1}$; $\epsilon_0 = 8.854188 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$;
 $g = 9.807 \text{ m s}^{-2}$; **1 calorie** = 4.184 J.

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

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

$$\sum N_j = N = a \text{ fixed constant and}$$

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

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]

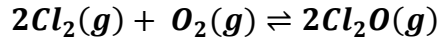
2. System 1 is an ideal gas and is composed of N 'red' atoms of mass m , $2N$ 'blue' atoms of mass m and $3N$ 'green' atoms of mass m . Atoms of the same color are indistinguishable. System 2 is another ideal gas having the same total number of atoms (each one of mass m) as in system 1, however, all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

3. Show that [4]

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

4. (a) Write the symmetry numbers and C_V (classical) for the following molecules: [2]
 (i) XeF_4 (square planar) (ii) PF_5 (tbp)
 (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 $^{16}\text{O}^{16}\text{O}$ in its ground state. [2]

5. (a) Consider the following equilibrium:



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_0 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 $q_{rot}^{class} \sim 8\pi^2 I kT$ 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:

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

- (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 ($1 \text{ eV} = 1.60216 \times 10^{-19} \text{ J}$). [3]