Birla Institute of Technology & Science, Pilani
Pilani Campus
I Semester, 2022-2023
CHEM F4222 Statistical Thermodynamics
Mid Semester Test (Open Book)

Max. Marks: 35 **1 Nov 2022** **Duration: 1hr 30 min.**

Instructions to the student:

1) There are five questions 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) 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** = 1.38065 x 10^{-23} J K^{-1};
Avogadro's Number = $\mathbf{N_A}$ = 6.022142 x 10^{23} mol^{-1}; **h** = 6.626069 x 10^{-34} J s;
e = 1.60216 x 10^{-19} C; $\mathbf{m_e}$ = 9.10938 x 10^{-31} kg; **F** = 96485.34 C mol^{-1};
c = 2.99792458 x 10^{8} m s^{-1}; $\boldsymbol{\varepsilon_0}$ = 8.854188 x 10^{-12} C^2 N^{-1} m^{-2}; **g** = 9.807 m s^{-2}.

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1. (a) Determine whether the following functions are homogeneous or not; If homogeneous find out the degree of the function. **[4]**

(i) $f(x) = 4x^3$ **(ii)** $f(x, y) = a^x b^y - xy$

(iii) $f(x, y, z) = ax^2/y + bz + cz^2/x + dy$ **(iv)** $f(z) = z^3 + \cos z + i \sin z$

(b) Consider a function $f(x,y,z) = 2x^2 + 8y^2 + z^2$ subject to the constraint $g(x,y,z) = 6x + 4y + 4z - 72 = 0$. Write down the equations using the Lagrange multiplier method that is required to determine the extremum value of the function $f(x,y,z)$. **[3]**

2. Assume four systems (microstates), A, B, C, D belong to an ensemble. Each system can have the possible energy states of E_1=1 kT, E_2 = 2 kT, and E_3 = 3 kT. Suppose further that there are just three distributions which satisfy the conditions of namely, $\sum_j a_j = 4$, and $\sum_j a_j E_j = 8$;

Energy→ Distribution ↓	E_1	E_2	E_3
1st	a_1=1	a_2=2	a_3=1
2nd	a_1=2	a_2=0	a_3=2
3rd	a_1=0	a_2=4	a_3=0

(a) Determine the number of ways one may have the 1st, 2nd, 3rd distribution.
(b) What is the probability of observing E_3 in the 1st, 2nd, 3rd distribution?
(c) Determine the over-all probability of observing E_3. **[7]**

3. (a) Show that entropy of a system in the grand canonical ensemble can be written as

$$S = -k \sum_N \sum_j P_{Nj} \ln P_{Nj}$$

where $P_{Nj} = \frac{exp(-\beta E_{Nj} - \gamma N)}{\sum_N \sum_j exp(-\beta E_{Nj} - \gamma N)}$. **[4]**

(b) The isothermal-isobaric partition function of an ideal-monoatomic gas is

$$\Delta = \left[\frac{(2\pi m)^{3/2}(kT)^{5/2}}{ph^3}\right]^N$$

Derive an expression for chemical potential based on the above partition function. **[3]**

P.T.O.

4. (a) Write down the terms, corresponding levels and the degeneracies of each level for the excited state configuration of He, $1s^1 2p^1$. **[3]**

(b) Calculate the rotational contribution to the entropy of HD at 20 K, 100 K and 300 K using appropriate formulae, given that the θ_{rot} of HD is 42.7 K. **[4]**

5. (a) Derive an expression for the ratio of ortho to para populations of $(^{14}N)_2$ in terms of rotational parameters and temperature (Nuclear spin (I value) of $^{14}N = 1$). Based on the data given in Table 6.1. of Text Book predict this ratio at 30 K and 300 K. **[4]**

(b) Fraction of the molecules in the jth rotational level can be defined as

$$f_J = 2J(J+1)\left(\frac{\Theta_{rot}}{T}\right)e^{-\Theta_{rot}J(J+1)/T}$$

Assuming J is continuous get an expression for J_{max} value of J for which f_J is maximum. **[3]**