Birla Institute of Technology & Science, Pilani (Raj)
CHEM F422 Statistical Thermodynamics
Comprehensive Exam, I Semester, 2023-2024
(Open Book)

Max. Marks: 35 **20 Dec 2023** **Duration: 180 min.**

Instructions to the student:
1) There are four questions in total; answer all the questions.
2) Data: The following constant values may be used wherever required.

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}.
Binomial theorem: $(x+y)^n = \sum_{k=0}^{n}\binom{n}{k}x^k y^{n-k}$

1. Following the random walk model, a particle is moving along x-direction, where p is the probability that the step is to the right and $q = 1 - p$ probability that the step is to the left. The particle has undergone a total of N steps consisting of n_1 steps to the right and n_2 steps to the left.
(a) For $N = 3$, what is the probability of (i) $n_1 = 3$ and $n_2 = 0$ (ii) $n_1 = 2$ and $n_2 = 1$(iii) $n_1 = 1$ and $n_2 = 2$ (iv) $n_1 = 0$ and $n_2 = 3$. [4]
(b) Write down the general formula of the probability in a total of N steps, of making n_1 steps to the right. [2]
(c) What is mean number of $\bar{n}_1$ of steps to the right? [2]
(d) Determine the dispersion, $\overline{(\Delta n_1)^2} \equiv \overline{(n_1 - \bar{n}_1)^2}$. [2]

2. (a) Show that in a two component open, isothermal ensemble

$$\overline{N_1 N_2} - \bar{N}_1\bar{N}_2 = kT\left(\frac{\partial \bar{N}_1}{\partial \mu_2}\right)_{V,T,\mu_1} = kT\left(\frac{\partial \bar{N}_2}{\partial \mu_1}\right)_{V,T,\mu_2}$$

Remember that the probability that a system in the ensemble has N_1 and N_2 particles and is in the state j is $\frac{e^{\beta\left(N_1\mu_1 + N_2\mu_2 - E_{N_1 N_2,j}\right)}}{\Xi}$ where $\Xi(\mu_1, \mu_2, T, V) = \sum_{N_1,N_2,j} e^{\beta\left(N_1\mu_1 + N_2\mu_2 - E_{N_1 N_2,j}\right)}$. [3]
(b) Show that Debye frequency $\nu_D = \left(\frac{3N}{4\pi V}\right)^{1/3} v_0$. [2]

3.(a) Given that the values of θ_{rot} and θ_{vib} for H_2 are 85.3 K and 6332 K, respectively calculate these quantities for HD and D_2. [3]
(b) What molar constant-volume heat capacities would you expect under classical conditions for the following gases: (a) Ne (b) O_2 (c) H_2O (d) CO_2 (e) $CHCl_3$ [5]
(c) NO_2 (g) is a bent triatomic molecule. The following data determined from spectroscopic measurements are $\bar{\nu}_1 = 1319.7$ cm^{-1}, $\bar{\nu}_2 = 749.8$ cm^{-1}, $\bar{\nu}_3 = 1617.75$ cm^{-1}, $\bar{A}_0 = 8.0012$ cm^{-1}, $\bar{B}_0 = 0.43304$ cm^{-1} and $\bar{C}_0 = 0.41041$ cm^{-1}. Determine the three characteristic vibrational temperatures and the characteristic rotational temperatures for each of the principle axes of NO_2 (g) at 1000 K. [4]

4. (a) Determine the equilibrium constant at 1200 K for the reaction $CO_2(g) + H_2(g) \rightleftharpoons CO\,(g) + H_2O\,(g)$. Write the expression and calculate the partition function of all components. [5]

(b) Square-well potential is defined as

$$u(r) = \begin{cases} \infty, & r < \sigma \\ -\varepsilon, & \sigma < r < \lambda\sigma \\ 0, & r > \lambda\sigma \end{cases}$$

Show that the second virial coefficient $B_2(T) = b_0\{1 - (\lambda^3 - 1)(e^{\beta\mu} - 1)\}$ where $b_0 = 2\pi\sigma^3/3$ [3]
