Birla Institute of Technology & Science, Pilani (Raj)
CHEM F422 Statistical Thermodynamics
Mid-Semester Exam, I Semester, 2023-2024
(Open Book)
(Based on Lectures No 1-19 – (first 6 chapters of TB) as per the course handout)

Max. Marks: 35 **14 Oct 2023** **Duration: 90 min.**

Instructions to the student:
1) There are three 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** = 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. (I) The binomial coefficient, $\frac{N!}{N_1!N_2!}$ where $N = N_1 + N_2$. Using Method of Lagrange Multipliers show that $N_1 = N_2 = N/2$, the coefficient exhibits the extremum. 4

(II) The Poisson probability distribution function can describe the evolutionary process of amino acid substitutions in proteins. The probability $p_s(t)$ that exactly s substitutions occur over an evolutionary time t is $p_s(t) = \frac{e^{-\alpha t}(\alpha t)^s}{s!}$ where α is the rate of amino acid substitutions. Fibrinopeptides evolve rapidly, $\alpha = 9 \times 10^{-9}$ year^{-1}. Lysozyme is intermediate: $\alpha = 1 \times 10^{-9}$ year^{-1} and histone evolve slowly, $\alpha = 0.01 \times 10^{-9}$ year^{-1}.

(a) What is the probability that a fibrinopeptide has no substitution at a given site in t=1 billion years?
(b) What is the probability that lysozyme has three substitution in 100 million years?
(c) Show that the expected number of substitutions that will occur in time t is αt.
(d) Determine the ratio of the expected number of substitutions in a fibrinopeptide to the expected number of substitutions in histone protein. 1+1+4+2=8

2. (a) For an ideal gas the number of states between energy E and $E + \Delta E$ ($E \gg \Delta E$) is $\Omega = \frac{1}{\Gamma(N+1)\Gamma(3N/2)}\left(\frac{2\pi m a^2}{h^2}\right)^{3N/2} E^{(3N/2-1)}\Delta E$ where $a^3 = V$. Using $S = k \ln \Omega$ and $E = \frac{3}{2}NkT$, show that $S = Nk \ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{Ve^{5/2}}{N}\right]$.

(b) Show that for grand canonical ensemble $\bar{E}(V,\beta,\gamma) = -\left(\frac{\partial \ln \Xi}{\partial \beta}\right)_{V,\gamma}$ and $\bar{N}(V,\beta,\gamma) = -\left(\frac{\partial \ln \Xi}{\partial \gamma}\right)_{V,\beta}$ where $\Xi(V,\beta,\gamma) = \sum_N \sum_j e^{-\beta E_{Nj}(V)} e^{-\gamma N}$.

(c) Derive the connection formula for S (entropy) in terms of the grand canonical ensemble starting from $\boldsymbol{pV = kT} \ln \Xi$ and $\boldsymbol{d(pV) = SdT + Nd\mu + pdV}$. 4+4+2=10

3. (a) Write down $q_{\mathrm{rot,nucl}}$ for D_2 (Nuclear Spin I=1).
(b) Show that at high temperatures the amount of ortho-D_2 to para-D_2 is equal to 2.
(c) Show that at low temperatures true equilibrium corresponds to almost pure ortho- D_2.
(d) Show that at the maximum of a plot of fraction of molecules in Jth rotational state, f_J, versus J, the values of J is given by $J_{\max} = \left(\frac{T}{2\theta_{\mathrm{rot}}}\right)^{1/2} - \frac{1}{2}$, where θ_{rot} is the characteristic temperature of rotation.

2+4+4+3=13