Seoul National University

Department of Materials Science and Engineering

Midterm Examination 1 — October 22, 2012

Physical Chemistry of Materials 2 — Professor Won Ho Jo

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1. Four bases (A, C, T, and G) appear in DNA. Assume that the appearance of each base in a DNA sequence is random.
   a. What is the probability of observing the sequence AAGACATGCA?
   b. What is the probability of finding the sequence GGGGGAAAAA?
   c. How do your answers to parts (a) and (b) change if the probability of observing A is twice that of the probabilities used in parts (a) and (b) of this question when the proceeding base is G?

2. a. The vibrational frequency of I_2 is 208 cm^{-1}. At what temperature will the population in the first excited state be half that of the ground state?
   b. The vibrational frequency of Cl_2 is 525 cm^{-1}. Will the temperature be higher or lower relative to I_2 at which the population in the first excited vibrational state is half that of the ground state? What is this temperature?

3. A system can exist in two non-degenerate states: a ground state with energy ε_1, and a higher energy (excited) state ε_2. Develop expressions for the average energy, heat capacity, entropy, and Helmholtz energy of this system as a function of temperature.

4. In 1905, Einstein proposed a simple model for an atomic crystal that can be used to calculate the molar heat capacity. He pictured an atomic crystal as *N* atoms situated at lattice sites, with each atom vibrating as a three-dimensional harmonic oscillator. Because all the lattice sites are identical, he further assumed that each atom vibrated with the same frequency. The partition function with this model is

   $$Q = e^{-\beta U_0}\left(\frac{e^{-\beta h\nu/2}}{1-e^{-\beta h\nu}}\right)^{3N}$$

   where ν, which is characteristic of particular crystal, is the frequency with which the atoms vibrate about their lattice positions and U_0 is the sublimation energy at 0 K, or the energy needed to separate all the atoms from one another at 0 K. Derive the expression for the molar heat capacity of an atomic crystal from this partition function.

5. Because the molecules in an ideal gas are independent, the partition function of a mixture of monatomic ideal gases is the form of

   $$Q\left(N_1, N_2, V, T\right) = \frac{\left[q_1(V,T)\right]^{N_1}}{N_1!}\frac{\left[q_2(V,T)\right]^{N_2}}{N_2!}$$

   where $q_j(V,T) = \left(\frac{2\pi m_j kT}{h^2}\right)^{3/2} V \qquad j = 1, 2, \cdots$

   Show that $\langle E \rangle = \frac{3}{2}(N_1 + N_2)kT$ and that $pV = (N_1 + N_2)kT$ for a mixture of monatomic gases.

6. The HCN(g) molecule is a linear molecule, and the following constants determined spectroscopically are $I = 18.816 \times 10^{-47}\ kg \cdot m^2$, $\tilde{\nu}_1 = 2096.7\ cm^{-1}$ (HC–N stretch), $\tilde{\nu}_2 = 713.46\,cm^{-1}$ (H–C–N bend, two-fold degeneracy), and $\tilde{\nu}_3 = 3311.47\ cm^{-1}$ (H–C stretch). Calculate the values of Θ_{rot} and Θ_{vib} and $C_{V,m}$ at 300 K.

7. Calculate the equilibrium constant for the reaction $I_2(g) \rightleftharpoons 2I(g)$ at 1000 K from the following data for I_2: $\tilde{\nu} = 214.36\ cm^{-1}$, $B = 0.0373\ cm^{-1}$, $\varepsilon_D = 1.5422\,eV$. The ground state of I atom is $^2P_{3/2}$, implying fourfold degeneracy.