

Chemical Physics Cumulative Examination
Wednesday, 17 February 2010

This examination is concerned with molecular thermodynamics at the level discussed in the text by McQuarrie and Simon. The exam has a total of 50 points. A list of potentially useful equations are attached below.

- A. (10 points) A certain molecule only has a non-degenerate excited state with an energy of 0.05 eV above the doubly degenerate ground state. At what temperature (in K, of course) will 10% of the population be in the upper electronic state? No credit without detailed calculations to justify your answer.
- B. (5 points each) The partition function given below describes a gas of non-interacting hard spheres. Derive expressions for **BOTH** the internal energy, E , and for the pressure, P , of this gas. The variables N , V , T , etc. have their usual meanings, b is related to the size of the spheres. Be sure to show your all your work!

$$Q(N, V, T) = \frac{(V - b)^N}{N!} \left(\frac{2\pi m k_B}{h^2} \right)^{3N/2} T^{3N/2}$$

- C. (10 points) From a statistical mechanical basis, would you expect the free energy of one mole of helium or one mole of argon to be larger? Assume that both gases are in the standard state and confined to the same volume. No points without an appropriate mathematically based justification.
- D. (5 points) Show that the low temperature limit of the molecular electronic partition function is equal to the degeneracy of the ground state.
- E. (5 points) Which molecule would you expect to have a larger heat capacity, C_V , in the standard state in the same fixed volume, ammonia or hydrogen fluoride? Justify your answer in terms of the molecular partition function. No points without an appropriate mathematically based explanation.
- F. (5 points) Would statistical mechanics predict a larger molar internal energy for carbon monoxide ($C \equiv O$) or nitrogen monoxide ($N \equiv O$), each in the standard state? Ignore the small difference in the masses of these molecules. No points without an appropriate mathematically based explanation.
- G. (5 points) Write the partition function for a single deuterium atom in an external magnetic field with a strength, B , ignoring any electronic excitations. Deuterium has a nuclear spin of $1 \hbar$ and the interaction of its magnetic moment with the external field has an energy of $E_m = m\gamma\mu_n B$ where μ_n is the nuclear magniton and γ is the gyromagnetic ratio.

$$k_B = R/N_A = 1.38066 \times 10^{-23} \text{ J } \text{ } ^\circ\text{K}^{-1}$$

$$1. \text{ amu} = 1.6605 \times 10^{-27} \text{ kg}$$

$$R = 0.08314 \text{ } \ell\text{-bar/K-mole} = 8.314 \text{ J/K-mole}$$

$$\pi = 3.1415927$$

$$1 \text{ atm} = 760 \text{ torr} = 101,325 \text{ Pa}$$

$$N_A = 6.0221 \times 10^{23} \text{ mole}^{-1}$$

$$h = 6.626 \times 10^{-34} \text{ J sec}$$

$$c = 2.99792 \times 10^8 \text{ m sec}^{-1}$$

$$\hbar = h/2\pi = 1.054 \times 10^{-34} \text{ J sec}$$

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$$

$$\text{proton mass} = 1.67263 \times 10^{-27} \text{ kg}$$

$$\text{electron mass} = 9.1094 \times 10^{-31} \text{ kg}$$

$$\text{neutron mass} = 1.67493 \times 10^{-27} \text{ kg}$$

$$\text{electron charge} = 1.60218 \times 10^{-19} \text{ Coul}$$

$$E_{\text{photon}} = h\nu$$

$$\lambda \nu = c$$

$$\lambda = hc / E_{\text{photon}}$$

$$\text{K.E.} = \frac{1}{2}mv^2$$

$$E(n) = n^2 h^2 / 8mL^2$$

$$E(n,l,m) = \left(\frac{n^2}{L_x^2} + \frac{l^2}{L_y^2} + \frac{m^2}{L_z^2} \right) h^2 / 8m$$

$$\omega = \sqrt{k/m_{\text{eff}}}$$

$$\nu = (1/2\pi) \sqrt{k/m_{\text{eff}}}$$

$$E_{\text{vib}} = \hbar\omega \left(v + \frac{1}{2} \right) = h\nu \left(v + \frac{1}{2} \right)$$

$$\text{Modes} = 3N - (5 \text{ or } 6)$$

$$\Delta E_v = \hbar\omega$$

$$m_{\text{eff}} = m_1 m_2 / (m_1 + m_2)$$

$$E_R = \hbar^2 j(j+1) / 2I$$

$$I = m_{\text{eff}} R^2$$

$$T = \lim_{P \rightarrow 0} (P\bar{V}/R)$$

$$p_j = a_j / A$$

$$\sum_{j=1} a_j = A$$

$$\sum_{\text{states}} p_j = 1$$

$$\langle E \rangle = \sum_{\text{states}} (p_j E_j)$$

$$\langle x \rangle = \sum_{\text{states}} (p_j x_j)$$

$$\langle x^2 \rangle = \sum_{\text{states}} (p_j x_j^2)$$

$$Q(N, V, \beta) = \sum_{\text{states}} \text{Exp}(-\beta E_j(N, V))$$

$$p_j(N, V, \beta) = \text{Exp}(-\beta E_j(N, V)) / Q(N, V, \beta)$$

$$\beta = 1/k_B T$$

$$\langle E \rangle = -(\partial \ln Q / \partial \beta)_{N, V} = k_B T^2 (\partial \ln Q / \partial T)_{N, V}$$

$$\langle P \rangle = k_B T (\partial \ln Q / \partial V)_{T, N}$$

$$C_V = (\partial \langle E \rangle / \partial T)_{N, V} = -1 / (k_B T^2) (\partial \langle E \rangle / \partial \beta)_{N, V}$$

$$Q(N, V, \beta) = \prod_{i=1, N} q_i(V, \beta)$$

$$q(V, \beta) = \sum_j g_j \text{Exp}(-\beta \epsilon_j)$$

$$Q(N, V, \beta) = q(V, \beta)^N / N!$$

$$q(V, \beta) = q_{\text{trans}} q_{\text{elec}} q_{\text{vib}} q_{\text{rot}}$$

$$q_{\text{rot}} = T / \sigma \Theta_{\text{rot}}$$

$$\Theta_{\text{rot}} = \hbar^2 / 2Ik_B$$

$$q_{\text{elec}} = g_1 + g_2 e^{-\beta \epsilon_2}$$

$$q_{vib} = e^{-\Theta_v/2T} / (1 - e^{-\Theta_v/T}) \quad \Theta_{vib} = h\nu/k_B \quad q_{trans} = (2\pi mk_B T/h^2)^{3/2} V$$

$$dS = \delta q_{rev}/T \quad \Delta S_{Univ} = \Delta S + \Delta S_{surr} \quad S = k_B \ln W$$

$$S = U/T + k_B \ln Q \quad S = k_B T (\partial \ln Q / \partial T)_{N,V} + k_B \ln Q$$

$$\ln N! \approx N \ln N - N \quad S(T_2) = S(T_1) + \int_{T_1}^{T_2} (C_v/T) dT$$

$$A = -k_B T \ln Q$$