Chemistry 4000/5000/7001 Spring 2009 Test 1 Solutions

1. (a) True. At very low temperatures, only the ground state is occupied, and higher states are inaccessible, so U is effectively constant.

   (b) False. At higher temperatures, the population of an energy level is proportional to its degeneracy, so an excited state could have a larger population than the ground state if the former has a larger degeneracy than the latter.

   (c) False. This is an approximation which neglects coupling between (e.g.) rotational and vibrational motions.

   (d) False. The Boltzmann distribution is the dominant distribution, but it is theoretically possible, if unlikely, for a system to have a different distribution of energy at some point in time.

   (e) True. The energy of the system in this case is a sum of molecular energies. If intermolecular forces are not negligible, then the energy of the system also depends on the interaction energy between molecules, which is not a property of a single molecule.

2. (a) $kT = (0.695\,035\,6\,\mathrm{cm}^{-1}\mathrm{K}^{-1})(100\,\mathrm{K}) = 69.5\,\mathrm{K} \gg B$. We should be able to use the integrated form of the partition function.

   (b)

$$\begin{aligned}
q_R &= \frac{kT}{\sigma B} \\
&= \frac{(0.695\,035\,6\,\mathrm{cm}^{-1}\mathrm{K}^{-1})(100\,\mathrm{K})}{(1)(1.345\,257\,6\,\mathrm{cm}^{-1})} = 51.7. \\
p(J) &= \frac{(2J+1)e^{-J(J+1)B/(kT)}}{q_R}. \\
\therefore p(3) &= \frac{[2(3)+1]\exp\left(\dfrac{-3(3+1)(1.345\,257\,6\,\mathrm{cm}^{-1})}{(0.695\,035\,6\,\mathrm{cm}^{-1}\mathrm{K}^{-1})(100\,\mathrm{K})}\right)}{51.7} \\
&= 0.107.
\end{aligned}$$

3. (a) The partition function is

$$q_E = \sum_{i=1}^{4} g_i e^{-\epsilon_i/(kT)}.$$

   We can just plug our data directly into Maple to calculate the partition function with $T = 298.15\,K$. The result is $q_E = 7.83$. Note that the bottom three energy levels include nine states. The value of the electronic partition function tells us that these levels are all occupied to a significant extent at 25°C. Due to the very large energy gap and based on the value of the partition function, we can infer that the fourth level is essentially unoccupied at this temperature.

(b) The translational internal energy is just $\frac{3}{2}RT = 3718\,\mathrm{J/mol}$. The electronic internal energy is calculated by

$$U_{E,m} = RT^2 \left.\frac{\partial \ln q_E}{\partial T}\right|_V .$$

Using Maple and the relationship $R = kN_A$, I get

$$U_{E,m} = \frac{N_A \sum_{i=1}^{4} g_i \epsilon_i e^{-\epsilon_i/(kT)}}{q_E} = 338\,\mathrm{J/mol}.$$

The molar internal energy is therefore

$$U_m = U_{E,m} + U_{T,m} = 4057\,\mathrm{J/mol}.$$

4. The molar Gibbs free energy is calculated by

$$G = -RT\left[\ln Q - V \left.\frac{\partial \ln Q}{\partial V}\right|_T .\right]$$

The canonical partition function is $Q = q^N/N!$. The only quantity in this calculation which involves molecular properties is q. The molecular partition function is calculated by

$$q = q_T q_R q_V q_E,$$

i.e. the product of the translational, rotational, vibrational and electronic partition functions. We will consider each of these contributions in turn.

The only molecular parameter that the translational partition function depends on is the **molecular mass**.

Fluorobenzene is nonlinear, so it has three rotational modes. To calculate q_R, we therefore need the **three rotational constants** B_A, B_B and B_C. We also need the **symmetry number** σ, which has the value $\sigma = 2$ for fluorobenzene.

Fluorobenzene has $3(12) - 6 = 30$ **vibrational modes**. We need the **frequencies** (probably in wavenumber units) for all of these vibrational modes.

For the electronic partition function, we need the **energies** and **degeneracies** of any energy levels which are within a small multiple of kT (including the ground state itself, of course).

Bonus: The formation reaction is

$$6\mathrm{C_{(s)}} + \frac{1}{2}\mathrm{F_{2(g)}} + \frac{5}{2}\mathrm{H_{2(g)}} \rightarrow \mathrm{C_6H_5F_{(g)}}.$$

In addition to G° for fluorobenzene, we need to calculate G° for each of the reactants. For H_2 and F_2, these calculations are analogous to those for fluorobenzene, except that these are diatomics, so there is only one value of B and one vibrational frequency for each. Graphite is a solid. The only two possible contributions to Q for graphite are

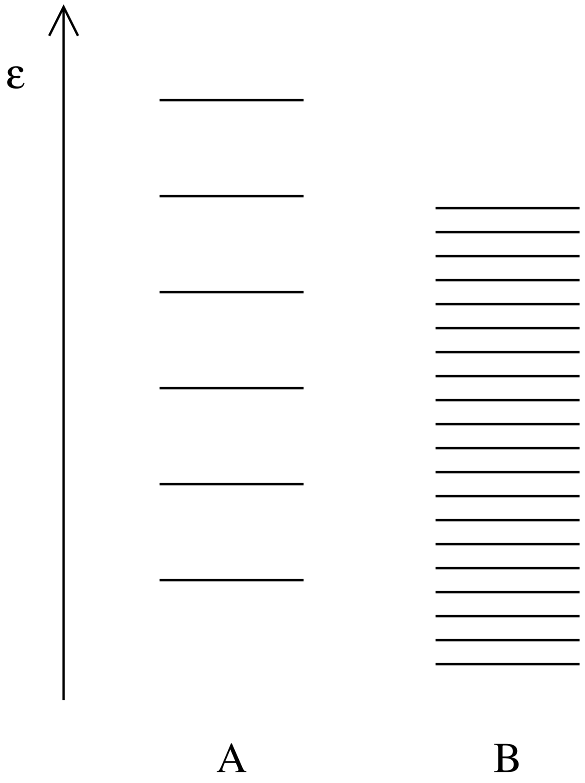

Figure 1: Schematic energy level diagrams for two molecules A and B.

vibrational and electronic contributions. We haven't talked much about solids, but let's just assume that we can calculate Q for graphite. Once we have the standard Gibbs energy for each of these compounds, we still have a problem: These will not have been computed with respect to a common zero of energy. We therefore need to correct to a common zero by adding the difference in ground-state energies, ΔE_0:

$$\Delta_f G_m^\circ(\mathrm{C_6H_5F, g}) = G_m^\circ(\mathrm{C_6H_5F, g}) - \left[6G_m^\circ(\mathrm{C, s}) + \frac{1}{2}G_m^\circ(\mathrm{F_2, g}) + \frac{5}{2}G_m^\circ(\mathrm{H_2, g})\right] + \Delta E_0.$$

5. The equilibrium constant for this reaction is given by the expression

$$K = \frac{q_\mathrm{B}}{q_\mathrm{A}} e^{-\Delta E_0/(kT)}.$$

Figure 1 shows the energy level diagrams of A and B for a case that would favor B. These diagrams have *two* features which would favor the formation of B:

   (a) The ground-state energy of B is lower than that of A, i.e. ΔE_0 is negative.

   (b) B has a greater density of energy levels than A, i.e. $q_\mathrm{B} > q_\mathrm{A}$. (This only matters if kT is not much greater than the energy level spacing of B.)