Assignment #1

Due: Sept. 10, 2003

Exercises:

1. Thermodynamics is all about energies. The standard unit of energy in chemical problems is kJ/mol (not kcal/mol!). It is useful to be able to quickly convert this basic unit into other commonly used energy measures. Express 1 kJ/mol in terms of the other “energy” units: (a) eV, (b) kcal/mol, (c) cm⁻¹, and (d) K. (You might want to use this problem as an introduction to unit conversions in Mathcad.)

Note: Remember these factors. I won’t test you on them, but the knowledge will make you a better person.

2. Use the formulas and data in Chapter 1 of M&S to calculate the energy differences between the two lowest translational, rotational, vibrational, and electronic states of Cl₂. Express your results both in units of kJ/mol and in terms of the “thermal energy” $k_B T$ at 298 K. The 1ˢᵗ electronically excited state of Cl₂ occurs at 17,160 cm⁻¹.

Note: Translational energies depend on the system volume. Pick some reasonable macroscopic volume such as 1 L.

3. (a) Using the data in Table 7.2 of the Berry, Rice, & Ross reading, determine the vibrational quantum numbers at which the actual vibrational energy level spacings (i.e. those computed using Eq. 7.10 of BR&R) of F₂ and Cl₂ deviate by 10% from the harmonic spacings based on $v_e$ alone.

(b) Compare the energies at which these deviations occur to the dissociation energies ($D_e$) of the molecules.

(c) What temperatures do these energies correspond to?

4. M&S 1-47: Express the energy both in units of cm⁻¹ and kJ/mol.

5. M&S 1-44