Handin 8: Thermochemistry; Entropy, Temperature, and Heat Transfer; Entropy Applications

1. Nitrous oxide, N_2O, can act as a ligand in transition metal complexes. The infrared stretching frequencies for N_2O are used to judge the strength of coordination to the metal. Nitrous oxide is also an important component of the atmosphere. The isotopic composition of nitrous oxide is a useful marker in atmospheric photochemistry. Nitrous oxide can be thought of as a resonance hybrid among: $N^-{=}N^+{=}O \leftrightarrow N{\equiv}N^+{-}O^- \leftrightarrow N{-}N^-{\equiv}O^+$. N_2O is isoelectronic with carbon dioxide. As such N_2O is linear and has a symmetric ($\tilde{\nu}_1 = 1285$ cm^{-1}) and an asymmetric ($\tilde{\nu}_3 = 2223.5$ cm^{-1}) stretching mode and two degenerate bending modes ($\tilde{\nu}_2 = 588$ cm^{-1}). Using valence force field techniques, the force constants for the NN and NO bonds in nitrous oxide have been estimated to be 1790 N m^{-1} and 1140 N m^{-1}, respectively. (a). Use these bond force constant estimates and MatLab, Mathematica, or the "eigen" Web applet to calculate the frequencies for the symmetric and asymmetric stretches for nitrous oxide. Your calculation will be very similar to the CO_2 example in Sec. 8.10. Restrict the motions to just the x-axis (e.g. neglect the bending vibrations) and estimate the force constants in a similar way. You should end up, again, with a 3x3 mass weighted force constant matrix. [Hint: k^{22}_{xx} won't be equal to 2 k^{11}_{xx} in this case because there is a nitrogen on one side and an oxygen on the other side of the central atom, atom 2] (b). Which of the three resonance structures is most representative of the true bonding in N_2O, based on the NN and NO force constants?

2. Evapotranspiration is the process of conversion of liquid water into vapor by the earth's surface. Evapotranspiration is the sum of evaporation and transpiration. Evaporation is the direct vaporization of water from water bodies, plant surfaces, and the soil. Transpiration is the conversion of liquid water into water vapor by movement of water within plants and the subsequent loss of water vapor through stomata in the leaves. Approximately 60% of the energy available from the solar flux in a forest is consumed by evapotranspiration. The solar flux at the equator at midday is about 1000 W m^{-2}. The evaporation of water results in a large increase in entropy in vegetated areas. Evapotranspiration also moderates the surface temperature and maintains the local humidity. To provide a very rough model, consider a flat surface that is heated to the boiling point of water by the sun. Assume that 60% of the solar flux is available for the vaporization of water on this surface. Calculate the rate of the production of entropy from the vaporization of water per second per m^2 at midday at the equator for a forest. The enthalpy of vaporization of water at the normal boiling point is $\Delta_{vap}H = 40.7$ kJ mol^{-1}.

3. Given that dH = TdS + VdP, prove that: $\left(\frac{\partial S}{\partial P}\right)_H = -\left(\frac{\partial H}{\partial P}\right)_S \left(\frac{\partial S}{\partial H}\right)_P = -\frac{V}{T}$

4. Use normal mode analysis to decide whether propane or 2-methylpropane has a higher absolute entropy. You can use any convenient normal mode analysis program based on molecular mechanics or molecular orbital theory.