Problem set 6

Due April 16, 2025

1. Demonstrate that the reversible work exerted by an ideal gas (n moles) that expands from volume V_1 to volume V_2, $V_2 > V_1$, at constant absolute temperature T and constant external pressure p is equal to the change of its free energy. Does the energy change upon reversible isothermal expansion of an ideal gas? Prove your statement.

   Hint: Use the formula for work exerted under the above conditions that has been derived during the lecture on the Carnot cycle and use the Guggenheim diagram to compute the derivative of the free energy in volume at constant temperatures.

2. Estimate the change of entropy after bringing 1 mol of manganese (Mn^{2+}) cations from a weak ligand field, in which each of the five d electrons occupies a different d orbital, to a strong octahedral ligand field in which the d electrons have only a total of three t_{2g} group orbitals to populate. Assume that Hund's rule applies in the first situation and mind Pauli's exclusion principle.

3. Methane is a gas at normal conditions but the energy of the interactions between two methane molecules *in vacuo* amounts to about 0.3 kcal/mol. In the molecular-modeling community, the statement that any system tends to reach the global energy minimum tends to be a common knowledge. Why, then, methane apparently is not at the global energy minimum?

4. Crystalline potassium nitrate when dissolved in water makes the temperature of the solution decrease and the amount of dissolved salt increases with heating. On the other hand, dissolving crystal calcium acetate results in increasing the temperature and its solubility decreases upon heating. Based on the thermodynamical argument, explain the behaviors of the two salts.