5.60/BE.110: Thermodynamics and Kinetics (r08)
Recitation Handout for 10/24/2006
Office hours: W7 (4-159); R7 (1-242)

Quick summary of today's topics:

Ways we know to calculate ΔS, given a specified change of state:

- Find a reversible path between the initial and final states: $dS = \frac{dq_{rev}}{T}$
- Maxwell's relations: $\frac{\partial S}{\partial V}_T = +\frac{\partial p}{\partial T}_V$, $\frac{\partial S}{\partial p}_T = -\frac{\partial V}{\partial T}_P$, etc...
- Rearranging the fundamental equations for dS (the following show the ideal gas case):
  - $dS = \frac{C_v}{T} dT + \frac{R}{V} dV$
  - $dS = \frac{C_p}{T} dT - \frac{R}{p} dp$

Third law of thermodynamics:

- Planck statement (1913): The entropy of a *pure*, perfectly crystalline substance is zero at the absolute zero of temperature.
- Motivated by:
  - Recognizing that the integrand in $S_T - S_0 = \int_0^T \frac{C_p}{T} dT$ is always positive, *i.e.* that the entropy is a monotonically increasing function in temperature;
  - By considering the statistical definition of entropy, $S = k ln \Omega$, taking into account what is meant by "pure" (indistinguishable), and "perfect crystal" (particles located in an exact pattern of lattice sites – Castellan).
- Important conclusions:
  - Like the Kelvin scale for temperature, the third law establishes a scale for entropy such that: **entropy is always nonnegative**.
  - Since the entropy is a monotonically increasing function: $S_{gas} \gg S_{liquid} > S_{solid}$

Phase equilibrium:

- The chemical potential, μ:
  - Definition (per mole Gibbs energy): $d\mu = -\overline{S}\, dT + \overline{V}\, dp$
  - Interpretation:
    - Subject to constraints, material will exist in the state with the lowest chemical potential.
    - When chemical potentials of several phases are equal, those phases are in equilibrium.

- Clayperon equation:
  - $\frac{dp}{dT}_{coexist} = \frac{\overline{S}_a - \overline{S}_b}{\overline{V}_a - \overline{V}_b} = \frac{\Delta \overline{S}}{\Delta \overline{V}}$
  - Derived directly from the fundamental equations without additional approximations.
  - Tells us that the slope of the coexistence curve in a p vs. T phase diagram is given by the difference between the molar entropy of the two phases divided by the difference in molar volume.

“Violation of the third law”:

Suppose that we arrange different kinds of atoms A and B on the N sites of a crystal. If N_A is the number of A atoms and N_B is the number of B atoms, then $N_A + N_B = N$ is the total number of sites (as well as the total number of atoms.) At T = 0K, what is the entropy of the mixture? Is this answer consistent with the third law of thermodynamics?

[Note that the important distinction between species A and B is not necessarily that they are different atoms but that they are indistinguishable. For instance, A and B could represent the different orientation of CO in a lattice – lecture notes #16.]