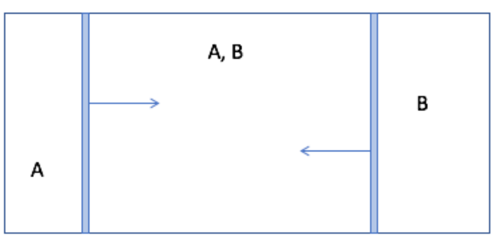
Physics 408 Problem Set 2 Due Weds, Sep. 15 at beginning of class

1) Callen 15.1.2

2) Mixing: (a) Consider ideal gases A and B which are allowed to intermix: they start at the same T and P, in two separated regions of a cylinder, then a valve is opened so that they can mix with each other. With no interactions between molecules, T & P will not change due to mixing. There are $N{\cdot}x$ A molecules and $N{\cdot}(1 - x)$ B molecules, e.g. N is the total number and x is the fraction which are type A. Using the result that the multiplicity of a gas is proportional to V^N, find an expression for the entropy change due to mixing. Plot this function and identify the mole fraction x giving the largest entropy change.
(b) Similarly, consider solids made of elements A and B allowed to mix by diffusion. Assume that the two solids are crystals of identical structure (so that atoms can statistically occupy lattice sites or "bins" of equivalent type on both sides), and that they can freely mix (no energy difference between A-B vs. A-A or B-B). Suppose there are $N{\cdot}x$ atoms in the A crystal and $N{\cdot}(1 - x)$ atoms in the B crystal. Use binomial statistics to determine the entropy change due to mixing, and show using the Stirling approximation (large N) that the function is the same as for the mixing of gases from part (a).
(c) Consider the solid mixing case with $x = \frac{1}{2}$, and assume that the solids have constant heat capacity $3Nk_B$ for room temperature and above (e.g. the classical partition function expression for N 3D harmonic oscillators). Starting at 300 K, to what temperature must the two solids be heated for the entropy to change by an equivalent amount as the mixing entropy change?

3) Un-mixing: A cylinder has volume V, and is in thermal contact with the outside world, keeping it at temperature T. Initially it contains a uniform mixture of ideal gases A and B, in equal numbers. Semi-permeable pistons are slowly moved from the far right and left ends of the cylinder as shown until they meet in the middle, dividing the cylinder into two equal halves. The pistons are semi-permeable: the one on the right allows B atoms to pass freely, but A atoms cannot go through, while on the left is the opposite situation with only A passing freely. (Membranes sometimes used to desalinate seawater work in approximately this way.) Determine the work required to do this, and the change in entropy of the universe, due to this "unmixing" process.



4) Consider the spin-1/2 paramagnet with N spins as considered in class, with "up" and "down" spins, N^+ and N^-. Show that, in the limit of large N, the entropy per atom follows a universal curve vs. the energy per atom, independent of the size of the system. Also find the maximum value of S per atom from your result.

5) Consider a 3D Einstein solid with 2 vibrational quanta per mode, e.g. 6 per atom.
a) For the case of N = 1 atom, show the specific arrangements of vibrational quanta in the different modes, and count them, showing that the result is equivalent to the relationship for the multiplicity given in class and in the text.

b) Now consider the case of a solid that includes 2 atoms, with 12 quanta. Find the multiplicity for this case. Note that although the system is doubled in extent, the number of available states does not change by a factor of 2; explain why not.

c) Considering the large-N limit, again with a total vibrational energy corresponding to 2 quanta per mode, show that the entropy per atom approaches a value that is independent of N, and find this value. (This is as required by the extensivity property of the entropy.)

d) Find the temperature of the large-N system in equilibrium with 2 quanta per mode for the case that the oscillator frequency is 5 THz, which is in the range of typical values of vibrational-mode frequencies for crystalline solids.