Home work week 2

1. Calculate the change in entropy when 1 kg of liquid water, initially at 300 K is heated by 20 K at constant pressure. From wikipedia I found that the heat capacities of water at constant pressure is: c_P = 4.1813 $\mathrm{Jg^{-1}K^{-1}}$. You can assume c_P to remain constant over the temperature range of interest.

   As a side note, the heat capacity of water is quite a bit higher than of most other materials. Can you speculate why that is?

2. Calculate the change in entropy of an ideal gas when the gas is expanded isothermally from V_1 to V_2.

   - Does it matter whether the expansion is done reversibly or irreversibly?
   - What is the change in entropy for the bath (environment) if the expansion is done reversibly? And how large is the change in the entropy of the gas plus environment (ΔS^{tot})?
   - What is the entropy change for the bath if the expansion done irreversibly by simply letting the piston go? What is then the change in the entropy of the gas plus environment (ΔS^{tot})?

3. Calculate the change in entropy of an ideal gas isolated from the environment (adiabatic) when the gas is expanded reversibly from V_1 to V_2. What if we would do the expansion irreversibly, but still in isolation (*i.e.*, $dQ = 0$)?

4. In the lecture we derived the direction of flow of energy between two compartments using the Clausius principle. Use the same derivation to find the equilibrium conditions, when the wall separating the two compartments is movable, but does not allow heat to flow through (a movable adiabatic wall). At equilibrium, any change in volume of the compartments should

not change the total entropy of the combined systems:

$$\left(\frac{\partial S_{AB}}{\partial V_A}\right)_{E_A,N_A,E_B,N_B} = 0 \tag{1}$$

We know from common sense that at equilibrium the pressures are the same on both sides $p_a = p_B$. Can you use this information to derive an expression for the pressure in terms of a derivative of the entropy?

5. Consider 1,000,000 two-level systems (e.g. 1,000,000 spin-$\frac{1}{2}$ nuclei in a magnetic field), with an energy gap of 3 10^{-20} J between the levels. How many of these system are in the lower energy level and in the upper level at

   (a) 0 K?

   (b) 10 K?

   (c) 100 K?

   (d) 1000 K?

   (e) 10,000 K?

   Assume that these N nuclei are not interacting with one another. $k =$ 1.3806 10^{-23} JK^{-1}

6. Write down the partition function for a quantum harmonic oscillator. If you don't recall the solution, check your books, or wikipedia. For this exercise it suffices, however, to know that the discrete eigenvalues (energies) of the Schrödinger equation are

   $$E_i = (i + \frac{1}{2})\hbar\omega \tag{2}$$

   and integer i runs from 0 (ground state) to infinity. If the angular frequency $\omega = \sqrt{\frac{k}{m}} = 125\ 10^{12}$ Hz (vibrational frequency of hydrogen molecule, H_2)

what is the ratio between the occupation (*i.e.* probability) of the ground state ($i = 0$) and of the first vibrationally excited state ($i = 1$) at

(a) 1 K?

(b) 10 K?

(c) 100 K?

(d) 1,000 K?

(e) 10,000 K?

use that $\hbar = 1.0546\ 10^{-34}$ Js and $k = 1.3806\ 10^{-23}$ JK^{-1}

Next, compute the average energy at these temperatures. What do you notice when you plot the average energies versus temperature?

Hint 1: $e^{abc} = (e^{ab})^c = (e^{ac})^b = (e^{bc})^a$

Hint 2: $\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$ if $|x| < 1$.

Hint 3: The program Mathematica makes hint 1 & 2 obsolete...