Thermodynamics HW #6

Due October 7

1. **Entropy of Ice**

   (a) Included in the "Homework" folder of the class Canvas site is a text file called HW#6-heat-capicities.csv containing raw data[1] from measurements of the heat capacity c_v of one mole of ice[2] as it is heated from 10K to 273.10K. Using Schroeder equation (3.19) construct a plot of the approximate value of $S(T) - S(10\text{K})$ in units of cal./K/mol., and write down the value of $\Delta S_1 \equiv S(273.10\text{K}) - S(10\text{K})$. Compute all numbers out to 3 decimal places. The result is somewhat sensitive to just how you approximate the integral, so consider your answer correct if you are within 10%.

   Answer: $\Delta S_1 = 9.081$ cal./K/mol.

   Solution: Equation (3.19) only applies when the heat capacity is known for every temperature. In our situation the heat capacity is only known at certain temperatures $c_p(T_1), c_p(T_2), \ldots, c_p(T_N)$. There are a number of ways to approximate the heat capacity between two successive measurements (i.e. to approximate $c(T)$ when $T_n < T < T_{n+1}$ for some $1 \leq n \leq N$). The easiest way is to assume the heat capacity is constant between measurements and equal to $c(T_n)$. In this case we get

$$S(T_n) - S(T_1) = \sum_{i=1}^{n-1} c(T_i) \ln \frac{T_{i+1}}{T_i}$$

   We could also just as easily assume that $c(T)/T$ is constant between measurements, yielding

$$S(T_n) - S(T_1) = \sum_{i=1}^{n-1} \frac{c(T_i)}{T_i} (T_{i+1} - T_i)$$

   (It is strongly recommended that you try drawing a picture if the above explanation isn't obvious.) Both methods should give very similar results, and their level of agreement should improve as the measurements are made closer and closer together.

   (b) We can estimate the molar heat capacity from 0K to 10K by fitting our measurements to the low temperature limit of the Debye model, which is expected

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[1] W. F. Giauque and J. W. Stout, *Journal of the American Chemical Society* 1936 **58** (7), 1144-1150

[2] actually c_p but $c_p \approx c_v$ for incompressible materials like ice (why?)

to accurately describe the behavior of solids in this temperature regime. The model predicts:

$$c_v = \frac{12\pi^4}{5} R \left(\frac{T}{T_D}\right)^3$$

where R is the ideal gas constant (1.987 cal/K/mol), and T_D is a fitting parameter. Using $T_D = 192\text{K}$, plot this function (as a curve) from 0K to 20K along with any raw data from the text file lying in this range (as a scatter plot) and confirm that the fit is good over this range. Then use Schroeder (3.19) again (analytically this time!) to determine $\Delta S_2 \equiv S(10\text{K}) - S(0\text{K})$. *Answer:* $\Delta S_2 = .022$ cal./K/mol.

Solution: Plugging in the given expression for c_v into Schroeder (3.19) for $T_i = 0$ and $T_f = 10\text{K}$ we find:

$$\begin{aligned}
&\int_{0\text{K}}^{10\text{K}} dT \frac{\frac{12\pi^4}{5} R \left(\frac{T}{T_D}\right)^3}{T} \\
=&\frac{12\pi^4}{5} R \frac{1}{T_D^3} \int_{0\text{K}}^{10\text{K}} dT T^2 \\
=&\frac{12\pi^4}{5} R \frac{1}{T_D^3} \frac{(10\text{K})^3}{3} \\
=&\frac{4\pi^4}{5} R \left(\frac{10\text{K}}{T_D}\right)^3
\end{aligned} \tag{1}$$

(c) As it stands we have ice at 273.10°K. If $P = 23.756$ torr and we heat the system further the ice will melt. Using Schroeder equation (3.17) and a value of 1435.7 cal./mol for latent heat of melting, compute the change in the entropy $\Delta S_3 \equiv \Delta S_{s \to l}$ from melting the ice.

Answer: $\Delta S_3 = 5.257$ cal./K/mol.

Solution: Simply divide the latent heat of melting by the melting temperature to get the entropy of melting.

(d) Now we heat the liquid at constant pressure to 298.10°K at which point we hit the boiling point of water [3] and completely vaporize the liquid. We could use the same techniques as in parts (a) and (c) to find the entropy increase associated with these two steps but I'll save you the trouble and tell you that

$$\Delta S_4 \equiv S(298.10\text{K}) - S(273.10\text{K}) + \Delta S_{l \to g} = 36.800 \text{ cal./K/mol.}$$

We then perform a hypothetical compression of the gas at constant temperature from $P = 23.756$ torr to 760 torr (atmospheric pressure). I say the compression is hypothetical because we are at the boiling point so the water vapor would in reality liquify but we will instead suppose that the gas remains ideal throughout the compression. Even though the Sackur-Tetrode equation was derived assuming a monatomic gas, Schroeder equation (2.51) can be applied to determine the

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[3] Why does it boil at a temperature much lower than 100C?

entropy change $\equiv \Delta S_5$ associated with the compression of water vapor[4] Calculate ΔS_5.

Answer: ΔS_5 = -6.886 cal./K/mol.

Solution: From Schroeder equation (2.51) we find the entropy change for isothermal compression of one mole of an ideal gas is

$$\Delta S = R \ln \frac{P_i}{P_f} = R \ln \frac{23.756\text{torr}}{760\text{torr}} \approx -3.465R$$

Why is the entropy change negative? For an isothermal process of an ideal gas we have $\Delta U = 0$ (why?) so that work must be balanced exactly by heat. Since compression extracts work from the environment the gas must *return* that energy in the form of heat so that $Q < 0$. The entropy change is thus negative in light of Schroeder equation (3.17).

(e) Sum up the ΔS_n and compare to the value $S_{\text{theory}} = 45.10$ cal./K/mol. obtained from a statistical mechanics calculation[5] of the molar entropy of water vapor at STP (standard temperature and pressure): 298.10K and $P = 1$ atm. What does this imply about the entropy at 0K? What does this imply about the ground state of ice? See the discussion in Shroeder after equation (3.21).

Answer: $S_{\text{theory}} - \sum_{n=1}^{5} \Delta S_n = .82$ cal./K/mol.

Solution: The entropy at 0K appears to be positive with the experimental margin of error[6], in contradiction to the third law of thermodynamics which asserts that the entropy goes to zero at 0K. $S(0\text{K}) \neq 0$ in turn implies that the ground state is *degenerate*, i.e. that there are multiple microstates all with the lowest possible energy.

2. **Residual Entropy of Ice**

How do we account for the failure of ice to reach zero entropy at 0K? In 1935 Linus Pauling[7] came up with an explanation that has since been referred to as "one of the most successful applications of elementary statistical mechanics to real substances."[8]

From x-ray diffraction it was known that every oxygen lies at the center of a tetrahedron formed by four neighboring oxygen. The locations of the hydrogens however are typically very difficult to determine from x-ray diffraction. Using chemistry as a guide Pauling makes the following assumptions:

(a) One and only one hydrogen lies between each two oxygen atoms. This arrange maximizes the stability of the crystal by allowing for each hydrogen atom to form

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[4] Here's the idea: changing the volume of an ideal gas affects the multiplicity by changing the number of possible points in space the particles can occupy. Changing the positions of the particles, however, does not change the energy of a microstate, so the multiplicity factorizes into $\Omega(V)\Omega(U, f)$, where f is the number of degrees of freedom. In terms of entropy this means the $S_{\text{tot}} = S_V + S_{U,f}$, but since U is fixed in isothermal compression the $S_{U,f}$ term will not contribute the entropy *difference* between the initial and final states, and therefore the change in entropy from isothermal compression is independent of f. This means an expression valid for a monatomic ideal gas should hold for arbitrary f.

[5] A. R. Gordon, *J. Chem. Phys.* **2**, 65 (1934), pg. 65

[6] Which is really a testament to how accurately the scientists were able to measure the heat capacities and latent heats!

[7] L. Pauling, *J. Am. Chem. Soc.*, **1935** *57* (12), 2680-2684

[8] Elliott H. Lieb, *Phys. Rev. 162*, 162

two bonds – a chemical bond with one oxygen and a hydrogen bond with the other.

(b) The hydrogen atoms will lie closer to one oxygen (forming a strong chemical bond with bond length 0.95Å) than the other (forming a weaker hydrogen bond with bond length 1.81Å). He denies the possibility that the hydrogens should lie exactly halfway between the two, arguing that "the magnitudes of the changes in the properties of steam to ice are not sufficently great to permit us to assume that this distance [the gas phase O-H bond length of 0.95Å] is increased to 1.38Å."

(c) Each oxygen will possess two chemical bonds and two hydrogen bonds. This is justified by the scarcity of OH^- and H_3O^+ ions in water's liquid state.

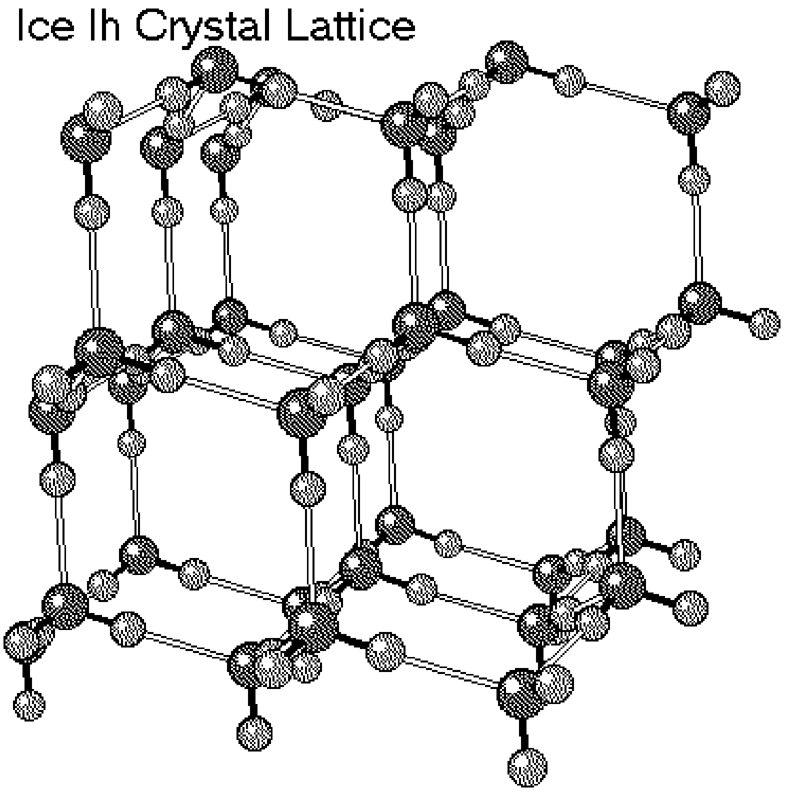

Figure 1: Diagram of the microscopic structure of ice. The larger darker spheres are oxygen and the smaller lighter ones are hydrogen.

See figure 1 for an illustration of the above three rules. Pauling argues that the non zero entropy of ice at 0K is due to the large number of ways (i.e. multiplicity) of arranging the hydrogens in ice while obeying the above three rules.

(a) Show that the number of ways of arranging the hydrogens while obeying rules (a) and (b) is 2^{2n}, where n is the number of oxygen atoms in the solid.

Solution: To satisfy rule (a) we must take all of the $2n$ hydrogen atoms and put each one between two neighboring oxygen atoms. Let's call a "neighborship" a pair of neighboring oxygen atoms. How many total neighborships do we have? Well each oxygen atom has four neighbors and thus a participant in four

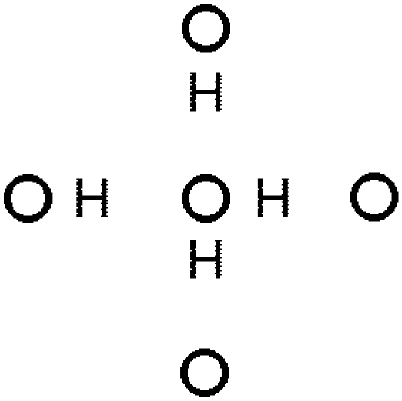

Figure 2: The environment arround an oxygen. The configuration shown is valid in that it obeys rules (a), (b), and (c).

neighborships. Each neighborship however requires two participants so we have $\frac{1}{2}4n = 2n$ neighborships[9] So we have just as many neighborships as hydrogen atoms, so there is exactly one way to distribute the hydrogen atoms among the different neighborships.

Now rule (b) requires each hydrogen to lie in one of two positions along the line joining the neighboring oxygen atoms in that hydrogen's neighborship, giving then 2^{2n} different ways of distributing the hydrogen atoms overall (i.e. what are the number of possible outcomes of $2n$ coin flips?).

(b) Consider a single one of the n oxygens and the four hydrogens surrounding it (figure 2). Of the 2^{2n} total configurations satisfying rules (a) and (b), show that $\frac{3}{8}^{\text{ths}}$ of them satisfy rule (c) for this particular oxygen atom only.

Solution: Here we are asking "If all of the four hydrogens can be either close to or far from the center oxygen, then what fraction of the possible configurations result in exactly two hydrogens close to the center oxygen?" This is mathematically equivalent to the question "What is the probability of flipping a coin four times and getting two heads?" By now it should be clear that this probability is

$$\frac{1}{2^4}\binom{4}{2} = \frac{1}{16}\frac{4!}{2!(4-2)!} = \frac{3}{8}$$

(c) Suppose then that we consider the $\frac{3}{8}2^{2n}$ configurations satisfying not only rules (a) and (b) for all the oxygen atoms but also rule (c) for one of the oxygen atoms. Assume (without proof!) that again $\frac{3}{8}^{\text{ths}}$ of these configurations satisfy rule (c) for some second oxygen atom. Suppose this same trend continues for the third, fourth, fifth, ..., n^{th} oxygen atom. Show then that of the original 2^{2n} configurations satisfying rules (a) and (b) there are only $\left(\frac{3}{2}\right)^n$ configurations that also satisfy rule (c).

Solution: Let Ω_n be the number of configurations satisfying rules (a), (b), and

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[9] We are ignoring here any funny business which may occur at the surface of the ice crystal since surface atoms constitute a negligible fraction of the total atoms.

(c) for the first n oxygen atoms. From the part (a) we found that

$$\Omega_0 = 2^{2n}$$

and in this question we are asked to suppose

$$\Omega_n = \frac{3}{8}\Omega_{n-1}$$

from this we can use part (c) to prove from induction (or better yet, claim that "it is obvious") that

$$\Omega_n = \left(\frac{3}{8}\right)^n 2^{2n} = \left(\frac{3 \cdot 2^2}{8}\right)^n = \left(\frac{3}{2}\right)^n$$

To prove a mathematical theorem from induction you must

- show it to be true for the case $n = 1$ and
- show that if the theorem holds for n then it also holds for $n + 1$.

If you've never done a proof by induction before, try it out for this problem (you will never find an easier example :))

(d) Compute the "residual entropy" associated with this $\left(\frac{3}{2}\right)^n$ multiplicity of ice at 0K. Compare this with the experimentally determined molar entropy of ice at 0K computed in part (e) of the previous problem.

Solution: The two entropies are remarkably close. Pauling in my opinion was either extremely lucky or possessed some sort of ungodly physical intuition. The assumption made in part (c) that the *distribution* of configurations satisfying rule (c) for the first n atoms is in some sense the same for any n is certainly not exactly true. This can be seen be noting that $\left(\frac{3}{2}\right)^n$ is not even a whole number as it must be. The accuracy of the part (c) assumption is difficult to analyze and depends on exactly how the oxygens link up into an overall network, and what you decide to do with the surface atoms. If you assume, for example, that the oxygen link in a square-like grid (which is *not* how they link up in ice), then it turns you can determine the residual entropy exactly (see the paper by Lieb cited in the footnotes) and you get an answer that is in *worse* agreement with experiment than Pauling's estimate! Interesting stuff.

Answer: $R \ln \frac{3}{2} = .805$ cal/K/mol.