

PHY306: Homework#7 Solutions, Spring 10

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1 Problem 5.1(5*2pts)

The energy of a mole of argon is given by the equipartition theorem:

$$U = \frac{3}{2}NkT = \frac{3}{2}nRT = \frac{3}{2}(1)(8.314J/K)(300K) = 3.74kJ.$$

The entropy is given by the Sackur-Tetrode equation:

$$S = Nk \left[\ln \left(\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right] = Nk \left[\ln \left(\frac{kT}{P} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right) + \frac{5}{2} \right],$$

where I have used the ideal gas law and equipartition in the last expression. since an argon atom has a mass of about 40 times the proton mass, the argument of the logarithm is

$$\frac{[(1.38 \times 10^{-23} J/K)(300K)]^{5/2}}{1.01 \times 10^5 N/m^2} \left(\frac{(2\pi)(40)(1.67 \times 10^{-27} kg)}{(6.63 \times 10^{-34} J \cdot s)^2} \right)^{3/2} = 1.02 \times 10^7$$

Therefore

$$S = Nk \left[\ln(1.02 \times 10^7) + \frac{5}{2} \right] = Nk(18.6) = (18.6)R = 155J/K.$$

The enthalpy is

$$H = U + PV = U + nRT = \frac{5}{2}nRT = \frac{5}{2}(8.31J/K)(300K) = 6.23kJ.$$

The Helmholtz free energy is

$$F = U - TS = (3.74kJ) - (300K)(155J/K) = -42.6kJ.$$

while the Gibbs free energy is

$$G = F + PV = F + RT = (-42.6kJ) + (8.31J/K)(300K) = -40.1kJ.$$

Since the term TS is much larger in magnitude than U or PV , both of the free energies turn out to be negative. But the sign of F or G is not any more significant than the sign of U : it is *differences* that matters, not actual values. (If we planned on tapping the rest energies, mc^2 , of the argon atoms, then we would want to include this energy in U , and then U , H , F , and G would all be increased by an enormous amount.)

2 Problem 5.2(5pts)

Because the reactants N_2 and H_2 are elements in their most stable states, the ΔH and ΔG values for this reaction are just the values for the "formation" of ammonia listed on Page 405, times 2 because we are forming two moles of ammonia. To check the relation $\Delta G = \Delta H - T\Delta S$, we also need to know ΔS , the entropy of two moles of ammonia minus the entropies of a mole of N_2 and three moles of H_2 :

$$\Delta S = 2(192.45J/K) - 191.61J/K - 3(130.68J/K) = -198.75J/K.$$

Therefore we should have

$$\Delta G = \Delta H - T\Delta S = 2(-46.11kJ) - (298K)(-198.75J/K) = -92.22kJ + 59.23kJ = -32.99kJ.$$

And indeed, the tabulated ΔG value is -16.45kJ per mole of ammonia, or -32.90 kJ for two moles, in very good agreement.

3 Problem 5.6(5+2+1+1+1pts)

(a)The data tabulated on pages 404 and 405 are (for one mole of each substance under standard conditions):(see table. 1 below),

To obtain ΔH or ΔG for the reaction $\text{glucose}+6\text{O}_2 \rightarrow 6\text{CO}_2+6\text{H}_2\text{O}$, we subtract Δ_f of the reactants

	$\Delta_f H(\text{kJ})$	$\Delta_f G(\text{kJ})$	S(J/K)
Glucose	-1273	-910	212
$\text{O}_2(\text{g})$	0	0	205
$\text{CO}_2(\text{g})$	-393.5	-394.4	214
$\text{H}_2\text{O}(\text{l})$	-285.8	-237.1	70

Table 1: Problem 5.6

from Δ_f of the products. Therefore, in kilojoules,

$$\Delta H = 6 \times (-393.5) + 6 \times (-285.8) - (-1273) = -2803$$

$$\Delta G = 6 \times (-394.4) + 6 \times (-237.1) - (-910) = -2879$$

(b)The maximum "other" work performed is just the amount by which G decreases for the system: 2879 kJ for each mole of glucose consumed.

(c)Under ideal conditions, the amount of work output, 2879kJ, is more than the amount by which the system's enthalpy decreases (2803kJ). To make up for the net loss of enthalpy, 76 kJ of heat must flow *into* the system.

(d)The total entropy of the reactants is (in J/K)

$$212 + 6 \times 205 = 1442,$$

while the total entropy of the products is (in J/K)

$$6 \times 214 + 6 \times 70 = 1704$$

Therefore the system *gains* 262J/K of entropy during this reaction. Because the entropy increases, heat can flow into the system. In the ideal case, the amount of heat entering is the maximum allowed for this entropy increase, namely $(262\text{J/K})(298\text{K})=78\text{kJ}$. (This number agrees reasonably well with the result of part(c), 76 kJ; The small difference gives some indication of the uncertainties in the data.)

(e)Under nonideal operation, new entropy would be created in the system during the reaction, allowing less heat to enter(or even requiring that heat be expelled, if the entropy created exceeds 262J/K). Therefore less energy would leave the system as "other" work. The values of ΔH and ΔG , however, are the same whether the operation is "ideal" or not.

4 Problem 5.12(2*5pts)

Starting with the function $U(S,V)$, we assume that this function is well enough behaved that the mixed second derivatives are equal:

$$\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S} \right) = \frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V} \right).$$

But the thermodynamic identity for U , $dU=T dS-P dV$, tells us that $(\partial U/\partial S)_V=T$ and $(\partial U/\partial V)_S=-P$. Plugging in these quantities gives us our first Maxwell relation,

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V.$$

Next, consider the enthalpy H , which due to the thermodynamic identity $dH=TdS+VdP$ is best considered a function of S and P . Equality of the mixed second derivatives tells us that

$$\frac{\partial}{\partial P} \left(\frac{\partial H}{\partial S} \right) = \frac{\partial}{\partial S} \left(\frac{\partial H}{\partial P} \right).$$

But by the thermodynamic identity for H , $(\partial H/\partial S)_P=T$ and $(\partial H/\partial P)_S=V$. Plugging in these quantities gives us a Maxwell relations for H ,

$$\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P.$$

The Helmholtz free energy, due to its thermodynamic identity $dF=-SdT-PdV$, is most naturally considered a function of T and V . the equality of mixed second derivatives is therefore,

$$\frac{\partial}{\partial V} \left(\frac{\partial F}{\partial T} \right) = \frac{\partial}{\partial T} \left(\frac{\partial F}{\partial V} \right).$$

But the thermodynamic identity for F tells us that $(\partial F/\partial T)_V=-S$, and $(\partial F/\partial V)_T=-P$. Plugging in these values gives a third Maxwell relation,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V.$$

Finally, consider the Gibbs free energy, $G(T, P)$. The relevant equality of mixed second derivatives is

$$\frac{\partial}{\partial P} \left(\frac{\partial G}{\partial T}\right) = \frac{\partial}{\partial T} \left(\frac{\partial G}{\partial P}\right).$$

The thermodynamic identity for G is $dG = -SdT + VdP$, which implies $(\partial G/\partial T)_P = -S$, and $(\partial G/\partial P)_T = V$. Plugging in these quantities gives us our fourth Maxwell relation,

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P.$$

5 Problem 5.29(3+2+5pts)

(a) The $\Delta_f G$ values on page 404 indicate that at room temperature and atmospheric pressure, kyanite has the lowest Gibbs free energy of the three phases. Furthermore, it also has the lowest molar volume of the three; this means that increasing the pressure causes its G value to increase more slowly than those of the other two phases. Since it starts out lowest and increases slowest, it will never intersect the G values of the other phases (in contrast to the graphite-diamond case illustrated in Figure 5.15).

(b) For either phase, $(\partial G/\partial T)_P = -S$. Integrating this relation from T_1 to T_2 gives

$$G(T_2) - G(T_1) = \int_{T_1}^{T_2} S(T) dT.$$

If we write this equation separately for two different phases and then subtract one equation from the other, the G 's become ΔG 's, and the S becomes ΔS , so we obtain the desired result,

$$\Delta G(T_2) = \Delta G(T_1) - \int_{T_1}^{T_2} \Delta S(T) dT.$$

(c) Taking ΔS to be independent of T , we can pull it outside the integral to obtain

$$\Delta G(T_2) = \Delta G(T_1) - (T_2 - T_1) \cdot \Delta S.$$

If we take T_2 to be the temperature at which the phase transition occurs (the two phases are in equilibrium), then $\Delta G(T_2)=0$. Solving for T_2 then gives simply,

$$T_2 = T_1 + \frac{\Delta G(T_1)}{\Delta S}.$$

Our thermodynamic data is at 298K, so we will use this value for T_1 . For the kyanite-andalusite transition, $\Delta G(T_1)=1.22\text{kJ}$ (for one mole of material), while $\Delta S=9.41\text{J/K}$. Therefore, the temperature at which andalusite becomes more stable than kyanite should be approximately

$$T_2 = 298\text{K} + \frac{1.22\text{kJ}}{9.41\text{J/K}} = 428\text{K}.$$

Similarly, for the kyanite-sillimanite transition,

$$T_2 = 298\text{K} + \frac{2.89\text{kJ}}{12.30\text{J/K}} = 533\text{K}.$$

And for the andalusite-sillimanite transition,

$$T_2 = 298\text{K} + \frac{1.67\text{kJ}}{2.89\text{J/K}} = 876\text{K}.$$

So at atmospheric pressure, kyanite should be stable up to (approximately) 428K, andalusite should be stable from 428K up to 876K, and sillimanite should be stable above 876K.

(d) The change in entropy as the temperature is increased is given by equation 3.50,

$$S(T_2) = S(T_1) + \int_{T_1}^{T_2} \frac{C_p}{T} dT$$

If we write this equation for two different phases and then subtract, we obtain

$$\Delta S(T_2) = \Delta S(T_1) + \int_{T_1}^{T_2} \frac{\Delta C_P}{T} dT$$

Suppose, for the sake of a rough estimate, that ΔC_P is independent of temperature. Then,

$$\Delta S(T_2) = \Delta S(T_1) + \Delta C_P \cdot \ln(T_2/T_1)$$

For kyanite \rightarrow andalusite, $\Delta C_P = 1.01$ J/K (at room temperature). Taking $T_1 = 298$ K and $T_2 = 428$ K, I find that the final term in this equation is 0.37 J/K, compare to $\Delta S(T_1) = 9.41$ J/K. So over this range, ΔS is reasonably independent of temperature. However, for andalusite \rightarrow sillimanite, $\Delta C_P = 1.80$ J/K and we should take $T_2 = 876$ K; with these numbers I get a correction term of 1.94 J/K, compared to $\Delta S(T_1) = 2.89$ J/K. With ΔS varying by nearly 70% over the temperature range of interest, I conclude that the calculated temperature of the transition could be off by as much as 100-200K. To make a significantly improved calculation, however, we would really need heat capacity data over the whole temperature range.

6 Problem 5.32(10pts)

(a) As ice melts into water, the change in entropy (or the latent heat) is positive, while the change in volume is negative (since ice is less dense), so the slope of the phase boundary, $\Delta S/\Delta V$, must be negative. In more fundamental terms, converting ice to water lets the entropy of the environment increase (by making more volume available), and this effect is more important at high pressure since $P = T(\partial S/\partial V)$. So high pressures tend to push the equilibrium in the direction of the phase that takes up less volume.

(b) Instead of considering a mole of ice/water, let's just consider one gram. Then the latent heat is 333J, the volume of the ice is $(917000)^{-1} m^3 = 1.091 \times 10^{-6} m^3$, and the volume of the water is $1.000 \times 10^{-6} m^3$. Therefore the slope of the phase boundary is

$$\frac{dP}{dT} = \frac{L}{T\Delta V} = \frac{333J}{(273K)(-0.091 \times 10^{-6}m^3)} = -1.35 \times 10^7 Pa/K = -135bar/K.$$

So if the temperature decreases by one degree (from 0 to $-1^\circ C$), the pressure must increase by 135 bars to remain on the phase boundary. In other words, ice will melt at $-1^\circ C$ if pressure is above 135 bars (or 133 atmospheres).

(c) Treating the glacier ice as a fluid, the increase in pressure at depth z is simply ρgz , where ρ is

the density. (To derive this formula, consider a column of ice extending down to depth z . The weight of the column per unit area is ρgz , and this must be balanced by the pressure from below.) In our case, to reach a pressure of 135 bars,

$$z = \frac{P}{\rho g} = \frac{135 \times 10^5 \text{ N/m}^2}{(917 \text{ kg/m}^3)(9.8 \text{ N/kg})} = 1500 \text{ m}.$$

That's pretty deep, just to lower the melting temperature by one degree. Apparently the flow of glaciers is not caused primarily by lowering of the melting point under pressure.

(d) The blade of an ice skate measure a few millimeters across by perhaps 25 cm long, so the total area is perhaps 10 cm^2 . Even if you are leaning on the "corner" of the blade, the total area in contact with the ice is probably more than $1 \text{ cm}^2 = 10^{-4} \text{ m}^2$. If your mass is 50 kg, then your weight is about 500N. So the pressure on the blade is roughly 50 bars. Under this pressure the melting temperature drops by only $50/135 \approx 0.4^\circ\text{C}$. This mechanism of friction reduction would work only if the ice temperature is already within less than half a degree of melting, and even then, only when you are minimizing the area of the blade in contact with the ice. In practice, the ability to glide does not depend so critically on the ice temperature or on how the blade touches the ice, so I do not think this mechanism can be very important.

7 Problem 5.35(5pts)

Neglecting the volume of the condensed phase and using the ideal gas law for the volume of the gas, the difference in volume between the two phases is approximately,

$$\Delta V \approx V_g \approx \frac{RT}{P},$$

Assuming one mole. Therefore the Clausius-Clapeyron equation becomes,

$$\frac{dP}{dT} = \frac{LP}{RT^2}, \text{ or } \frac{dP}{P} = \frac{L}{R} \frac{dT}{T^2}$$

Integrating both sides then gives,

$$\ln P = -\frac{L}{RT} + (\text{const}), \text{ or } P = (\text{const})e^{-L/RT}$$