

Junior honours Thermodynamics Assessed Problem 4

This question concerns phase transitions and the dissociation of diatomic molecules.

1. At the I, III, IV triple point we see that:

Increasing T takes us from III-IV-I, so this must be the order if increasing entropy.

Increasing T takes us from I-III-IV, so this must be the order if increasing density.

If we have phase coexistence, we must be on the phase boundary, so from the figure we can read off that $T=700\text{K}$.

The Clausius Clapeyron equation tells us that

$$\frac{dT}{dP} = \Delta V / \Delta S$$

and we can get the Clapeyron slope from the figure as $3 \times 10^{-9} \text{K/Pa}$. From which:

The change in entropy on melting is mainly due to the additional degrees of freedom obtained, each of which contributes $\frac{1}{2}k_B$. Very roughly, we can take this as 3 per molecule, which would give us $\Delta S = \frac{3}{4}k_B$ per atom, or equivalently $\frac{3}{4}R$ per mole.

So the volume change per mole is

$$\Delta V = \frac{dT}{dP} \Delta S = 3 \times 10^{-7} \times \frac{3}{4}R$$

i.e. about $2 \times 10^{-8} \text{m}^3$, compared to the molar volume of water/H-berg 10^{-3}m^3 means the H-ice is 0.998 times less dense than the fluid. So only 0.2% of the iceberg is above the surface.

2. Water and ice coexist at 1atm, 273K. If 1kg is supercooled until the heat of fusion becomes zero, how much useful work could be subsequently be extracted from the supercooled liquid when it freezes?

Comment on any practical difficulties.

(Assume pressure is small enough to ignore PV and assume constant $c_P = 4200 \text{J/kg/K}$, 2100J/kg/K , for water and ice respectively. Heat of fusion at STP is $L_{fus} = 334000 \text{J/kg}$).[1]

For the heat of fusion to be zero we must have

$$\Delta H = \Delta C_P (T - T_0)$$

Putting in the numbers

$$T = T_0 - 334000/4200 = 193\text{K}$$

The stable phase is the one with lower Gibbs Free Energy, $G=H-TS$. Since both phases have the same H , the stable phase must be the one with *higher* entropy. Presuming this to be the liquid, it means that water would be stable as a liquid at low temperatures. In reality, the heat capacity of supercooled water drops until it is close to that of ice, the enthalpy remaining higher, so the two curves on the graph become parallel.

Practically, it is impossible to supercool water that far, and the assumption of constant c_P is invalid because we know it must go to zero at $T=0$ from the Third Law.

3. In calculations, it is easy to obtain U and H from averaging energies of arrangements of atoms. However, even if all the atomic positions are known, there is still no way to directly calculate S, F or G. One needs to know all possible arrangements.

Prove that

$$\left(\frac{\partial(G/T)}{\partial T} \right)_P = -\frac{H}{T^2}$$

First differentiate the LHS.

$$\left(\frac{\partial(G/T)}{\partial T} \right)_P = \frac{1}{T} \left(\frac{\partial G}{\partial T} \right)_P - \frac{G}{T^2}$$

Noting that $G = U - TS + PV$; $dG = -SdT + VdP$, and so

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

so

$$\frac{1}{T} \left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T^2} = -S/T - U/T^2 + S/T - PV/T^2 = -\frac{U + PV}{T^2} - H/T^2$$

w⁵

For constant C_P , we can write $H = H_1 + C_P T$ and integrate at constant pressure:

$$\int d\left(\frac{G}{T}\right) = - \int (H_1/T^2 + C_P/T) dT$$

$$\frac{G_2}{T_2} - \frac{G_1}{T_1} = H_1 \left(\frac{1}{T_2} - \frac{1}{T_1}\right) - C_P \ln T_2/T_1$$

$$G_2 = H_1 + \frac{T_2}{T_1} (G_1 - H_1) - C_P T_2 \ln T_2/T_1$$

4. The van der Waals equation for one mole of diatomic gas is given by

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT$$

Show that the heat capacity at constant volume of a van der Waals gas depends only on the temperature. [2]
Since no work is done at constant volume, we can define

$$c_v = \left(\frac{\partial U}{\partial T}\right)_v$$

and we have from differentiating the central equation $dU = TdS - PdV$ that

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - P = T \left(\frac{\partial P}{\partial T}\right)_V - P = RT/(v - b) - P = a/v^2$$

Volume dependence is then:

$$\left(\frac{\partial c_v}{\partial V}\right)_T = T \left(\frac{\partial}{\partial V} \frac{\partial S}{\partial T}\right)_V = T \frac{\partial}{\partial T} \left(\frac{\partial S}{\partial V}\right)_T = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

Using a Maxwell relation. So for van der Waals $P = RT/(v - b) - a/v^2$; $(\frac{\partial^2 P}{\partial T^2})_v = 0$, so c_v has no volume dependence.

5. Prove that

$$\left(\frac{\partial U}{\partial V}\right)_T = T^2 \frac{\partial}{\partial T} \left(\frac{P}{T}\right)_v$$

start from the Central Equation

$$dU = TdS - PdV$$

differentiate by V at constant T .

$$\left(\frac{\partial U}{\partial V}\right)_T = T \frac{dS}{dV}_T - P$$

Now, consider the differential on the RHS of the given equation:

$$T^2 \frac{\partial}{\partial T} \left(\frac{P}{T}\right)_v = T \left(\frac{\partial P}{\partial T}\right)_v - T^2 P/T^2$$

Using a Maxwell relation and tidying up, this is $T \frac{dS}{dV}_T - P$, as required.

6. Using the previous results, prove that the molar energy of a diatomic van der Waals gas is given by

$$u_{vdW}(V, T) = \frac{5}{2}RT - a/v$$

and hence show that C_v is the same for the ideal and van der Waals gases.

Consider a constant temperature process.

$$dU = \int \frac{\partial U}{\partial V}_T dV = \int T^2 \left(\frac{\partial}{\partial T} \frac{P}{T}\right)_v dV$$

For vdW $P/T = R/(v - b) - a/Tv^2$ so

$$T^2 \left(\frac{\partial}{\partial T} \frac{P}{T}\right)_v = a/v^2$$

and $ds = \int a/v^2 dV = -a/v$

Now, if we integrate from very large volume

$$u(T, v) - u(T, v_\infty) = -a/v$$

(Hint: a constant of integration can be determined by using the constraint that, at very large volumes, the van der Waals gas behaves like an ideal gas.) But we know that as $v \rightarrow \infty$ we obtain the ideal gas result, so

$$u(T, v) = c_{v,ideal}T - a/v = \frac{5}{2}RT - a/v$$

Explain the physical reason for why the constant a appears in this equation, but not the constant b .

a represents binding of molecules, so can be assumed to be related to an energy. b is the molecular size, and doesn't contribute to bonding or kinetic energy.

7. Show that the change in entropy when one mole of a van der Waals gas converts from (T_0, V_0) to (T, V) is

$$dS = \left(R \ln \frac{V-b}{V_0-b} + C_v \ln \frac{T}{T_0} \right)$$

$$dS = \left(\frac{\partial S}{\partial V} \right)_T dV + \left(\frac{\partial S}{\partial T} \right)_V dT = C_v dT/T + \frac{\partial P}{\partial T}_V dV = C_v dT/T + R dV/(V-b)$$

$$S - S_0 = C_v \ln(T/T_0) + R \ln\left(\frac{V-b}{V_0-b}\right)$$

The van der Waals equation only describes intermolecular interactions. For a diatomic gas, u_{bond} is the additional energy in the chemical bond holding the atoms together, which can be taken as a constant.

$$u_{vdW}(V, T) = \frac{5}{2}RT - a/v - u_{bond}$$

$$u_{ideal}(V, T) = \frac{5}{2}RT - u_{bond}$$

If the molecules dissociate, we obtain two moles of monatomic gas. The monatomic gas can be also described by the van der Waals equation:

$$\left(P + \frac{a_1}{v^2}\right)(v - b_1) = RT$$

Where v is the volume per mole. Explain why $a = 4a_1$ and $b = 2b_1$ is a reasonable assumption for the parameters.

8. You are given that at $T_0=300K$, $P_0=1atm$, a particular ideal gas has the same Gibbs free energy in both monatomic and diatomic forms. Calculate the equation for the P,T phase boundary between diatomic and monoatomic gases in terms. Sketch this phase diagram.

Gibbs Free Energy of the diatomic phase

$$G_2 = U + PV - TS = \frac{5}{2}RT - u_{bond} + RT - \frac{7}{2}RT \ln(T) + RT \ln(P) + X_2 = RT \left(\frac{7}{2} - \frac{7}{2} \ln T + \ln P \right) - u_{bond} + X_2$$

Gibbs Free Energy of the monatomic phase

$$G_1 = U + PV - TS = 3RT + 2RT - 5RT \ln(T) + 2RT \ln(P) + X_1$$

where X is an undetermined constant of integration.

At T_0 , P_0 these are equal, so

$$X_1 - X_2 - u_{bond} = \frac{3}{2}RT_0 - \frac{3}{2}RT_0 \ln(T_0) + RT_0 \ln(P_0)$$

So because we are dealing with the same amount of stuff in each case, the equation of the phase boundary becomes: $G_1 = G_2$

$$3(T_0/T - 1) = -3 \ln T/T_0 + 2 \ln P/P_0$$

or

$$P = P_0(T/T_0)^{3/2} \exp\left(\frac{3(T - T_0)}{2T}\right)$$

Monatomic favoured at low pressure and high T

9. Under what circumstances will we observe (i) a monatomic gas (ii) a diatomic gas (iii) a mixture of monatomic and diatomic molecules

(i) High T, low P (interstellar space) (ii) Low T, high P (inside a planet or dead star) (iii) Constant volume boundary conditions (inside a hot planet)

10. Briefly, relate this to plasma physics. [3]

A hydrogen atom can be treated as a “diatomic molecule” of a proton and an electron, bound by 13.6eV. At sufficiently high temperature (or ridiculously low pressure) entropy causes ionization, separating the charged particles into a plasma.

The expression will be the same as above, except that u_{bond} is now very much higher. The question asks only for an estimate, so we can take the temperature where the entropy TS term is similar to the binding, i.e.

$$T = 13.6 \times 1.6 \times 10^{-19} / 1.3806485210^{-23} \equiv 150000K$$

[1] These assumptions aren't really valid, supercooled water actually becomes glassy and the heat capacity becomes similar to ice, but for purposes of the question we'll use these assumptions to make the maths tractible.

[2] Hint: it is sufficient to show that $\frac{dc_v}{dV}_T = 0$. One method is to start from the central equation, use the fact that entropy is a state variable, and apply a Maxwell relation.

[3] Yes, I know you haven't studied plasma physics: you will have to look it up! The question is how