Physics 3410 Homework #7
4 problems
Solutions

▷ **1.**

For the following four partial derivatives, write an equivalent derivative or ratio of thermo-dynamic variables. One of them is a Maxwell relation, one is a reciprocal Maxwell relation, and one involves the Gibbs-Duhem relation.

(a) $\left(\dfrac{\partial \mu}{\partial P}\right)_T$
(b) $\left(\dfrac{\partial \mu}{\partial P}\right)_{N,S}$
(c) $\left(\dfrac{\partial N}{\partial V}\right)_{F,T}$
(d) $\left(\dfrac{\partial N}{\partial V}\right)_{P,T}$

Answer:_____

(a) This involves only the intensive variables, so we can derive it from the Gibbs-Duhem relation:

$$0 = S\,dT - V\,dP + N\,d\mu$$

At constant T,

$$0 = -V\,dP + N\,d\mu \implies \frac{d\mu}{dP} = \boxed{\frac{V}{N}}$$

(b) The natural variables of this derivative are P, N, and S, so this could be part of a Maxwell relation. The enthalpy also has these natural variables:

$$dH = T\,dS + V\,dP + \mu\,dN$$

and the Maxwell relation is

$$\left(\frac{\partial \mu}{\partial P}\right)_{N,S} = \boxed{\left(\frac{\partial V}{\partial N}\right)_{P,S}}$$

Note that the cross-variables are conjugates, the natural variables (across the bottom) match on both sides, and the sign is positive because the terms $V\,dP$ and $\mu\,dN$ in dH have the same sign.

(c) This derivative involves the thermodynamic potential F, so we can get this directly from the thermodynamic identity

$$dF = -S\,dT - P\,dV + \mu\,dN$$

Because F and T are constant, we're left with

$$0 = -P\,dV + \mu\,dN \implies P\,dV = \mu\,dN \implies \frac{dN}{dV} = \boxed{\frac{P}{\mu}}$$

1

(d) The natural variables here include the conjugates P and V, so this can't be a Maxwell relation. However, the reciprocal

$$\left(\frac{\partial V}{\partial N}\right)_{P,T}$$

has natural variables corresponding to

$$dG = -D\,dT + V\,dP + \mu\,dN$$

so we can get a Maxwell relation

$$\left(\frac{\partial V}{\partial N}\right)_{P,T} = -\left(\frac{\partial \mu}{\partial P}\right)_{N,T}$$

and so

$$\left(\frac{\partial N}{\partial V}\right)_{P,T} = \boxed{-\left(\frac{\partial P}{\partial \mu}\right)_{N,T}}$$

▷ **2.**

Given one mole of diamond vs one mole of graphite,

	G	S	V
1 mol Graphite	0 J	5.74 J/K	5.30 cm^3
1 mol Diamond	2900 J	2.38 J/K	3.42 cm^3

(Assume S and V are constant over the temperatures and pressures we're considering, which is a reasonable approximation.)
(a) At room temperature $300\,\mathrm{K}$, at what pressure does diamond become more stable?
(b) At standard pressure $10^5\,\mathrm{Pa}$, at what temperature does diamond become more stable?

Answer:_____
Start with

$$dG = -S\,dT + V\,dP + \mu\,dN$$

(a) At constant temperature, the slope of the graph $G(P)$ is $\frac{dG}{dP} = V$, the volume of the material. If $P_0 = 10^5\,\mathrm{Pa}$ is standard pressure, the Gibbs free energy function is $G(P) = V(P - P_0) + G_0$ where G_0 is the Gibbs free energy at $P = P_0$. The phase transition occurs where the lines for graphite and diamond intersect:

$$G_g = G_d$$

$$V_g(P - P_0) + G_{0g} = V_d(P - P_0) + G_{0d}$$

2

$$(V_g - V_d)(P - P_0) = G_{0d} - G_{0g}$$

$$P - P_0 = \frac{G_{0d} - G_{0g}}{V_g - V_d}$$

$$P = P_0 + \frac{G_{0d} - G_{0g}}{V_g - V_d}$$

$$= 10^5\,\mathrm{Pa} + \frac{2900\,\mathrm{J} - 0\,\mathrm{J}}{5.30\,\mathrm{cm}^3 - 3.42\,\mathrm{cm}^3}$$

$$= 10^5\,\mathrm{Pa} + 1.54 \times 10^3\,\mathrm{J/cm}^3 \times \left(\frac{100\,\mathrm{cm}}{1\,\mathrm{m}}\right)^3$$

$$= 10^5\,\mathrm{Pa} + 1.54 \times 10^9\,\mathrm{Pa}$$

$$= \boxed{1.54 \times 10^9\,\mathrm{Pa}}$$

or 15 thousand atmospheres.

(b) At constant pressure, the slope of the graph $G(T)$ is $\frac{dG}{dT} = -S$, and the formula for $G(T)$ is $G(T) = -S(T - T_0) + G_0$ where $T_0 = 300\,\mathrm{K}$ is room temperature. The phase transition occurs at the temperature where

$$G_g = G_d$$

$$-S_g(T - T_0) + G_{0g} = -S_d(T - T_0) + G_{0d}$$

$$(S_d - S_g)(T - T_0) = G_{0d} - G_{0g}$$

$$T = T_0 + \frac{G_{0d} - G_{0g}}{S_d - S_g}$$

$$= 300\,\mathrm{K} + \frac{2900\,\mathrm{J} - 0\,\mathrm{J}}{2.38\,\mathrm{J/K} - 5.74\,\mathrm{J/K}}$$

$$= 300\,\mathrm{K} - 863\,\mathrm{K}$$

$$= \boxed{-563\,\mathrm{K}}$$

But this is less than absolute zero. Thus, at standard pressure, there is no temperature at which diamond is more stable than graphite: you cannot make diamonds without increased pressure.

▷ **3.**
The fictional compound *hillonium* has two different solid phases, miranite and kevinite. At

standard temperature and pressure,

- 1 mole of miranite has $G = 0\,\text{J}$, entropy $S = 3\,\text{J/K}$, and volume $V = 4\,\text{cm}^3$
- 1 mole of kevinite has $G = 500\,\text{J}$, entropy $S = 5\,\text{J/K}$, and volume $V = 3\,\text{cm}^3$

(a) Which is more stable at room temperature? That is, which one is more common?

(b) At what temperature does the other compound become stable?

Answer:

(a) The more stable phase has the lower Gibbs free energy; therefore miranite is the more stable at STP.

(b) If the temperature of the two substances change, the Gibbs free energy also changes by the amount

$$dG = -S\,dT$$

So if T_i is room temperature, G_i is the Gibbs free energy at room temperature, and $G(T)$ is the Gibbs free energy at some other temperature T, then

$$G(T) - G_i = -S(T - T_i) \implies G(T) = G_i - S(T - T_i)$$

For miranite, this equation is

$$G_m(T) = -(3\,\text{J/K})(T - 300\,\text{K})$$

and for kevinite,

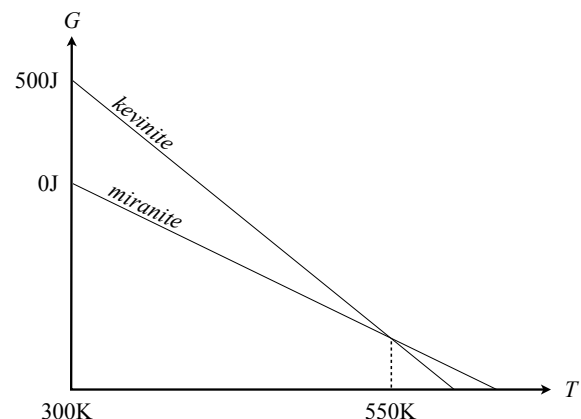$$G_k(T) = 500\,\text{J} - (5\,\text{J/K})(T - 300\,\text{K})$$

The critical temperature T_c is where $G_m(T_c) = G_k(T_c)$, or where

$$-3(T_c - 300) = 500 - 5(T - 300)$$

$$\implies 2(T_c - 300) = 500$$

$$\implies T_c - 300 = 250$$

$$\implies T_c = \boxed{550\,\text{K}}$$

Thus when the temperature is greater than $550\,\text{K}$ (or $277°\,\text{C}$), kevinite becomes more stable.

It may help to look at a graph of these two equations, to the right.

4

▷ **4.**

Use the Clausius-Clapeyron relation to find the slope of the liquid-gas phase transition line at the natural boiling point of water (i.e. $P = 10^5$ Pa, $T = 373$ K). Assume that the water vapor is an ideal gas, and that the water has mass density $\rho = 958$ kg/m^3. (You'll also need that each molecule of water has mass $m = 3 \times 10^{-26}$ kg.)

Answer:_____

The Clausius-Clapeyron relation says that the phase boundary line has the slope

$$\frac{dP}{dT} = \frac{S_g - S_l}{V_g - V_l} = \frac{L}{T\Delta\left(\frac{1}{\rho}\right)}$$

We can look up the latent heat of vaporization to convert liquid water to steam:

$$L = 2265 \text{ kJ/kg} = 2.27 \times 10^6 \text{ J/kg}$$

The temperature is $T = 373$ kg. We're given the density of liquid water, but to get the density of the vapor we need to use the ideal gas law. The number density of water molecules in the gas is

$$\frac{N}{V} = \frac{P}{kT} = \frac{10^5 \text{ Pa}}{(1.38 \times 10^{-23} \text{ J/K})(373 \text{ K})} = 1.94 \times 10^{25} \text{ molecules/m}^3$$

We're given $m = 3 \times 10^{-26}$ kg kg/molecule, so the mass density is

$$\rho = m\frac{N}{V} = (3 \times 10^{-26} \text{ kg/molecule})(1.94 \times 10^{25} \text{ molecule/m}^3) = 0.583 \text{ kg/m}^3$$

Thus

$$\Delta\left(\frac{1}{\rho}\right) = \frac{1}{\rho_g} - \frac{1}{\rho_l} = \frac{1}{0.583 \text{ kg/m}^3} - \frac{1}{958 \text{ kg/m}^3} = 1.71 \text{ m}^3/\text{kg}$$

and so

$$\frac{dP}{dT} = \frac{(2.27 \times 10^6 \text{ J/kg})}{(373 \text{ K})(1.71 \text{ m}^3/\text{kg})} = \boxed{3560 \text{ Pa/K}}$$