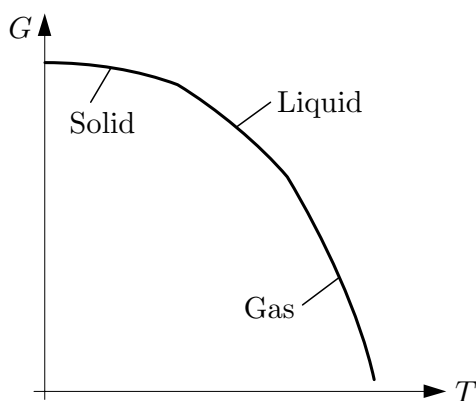


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## Homework Solutions 4 (Schroeder Chapter 5)

**9** Since  $S = -(\partial G/\partial T)_{P,N}$ , and  $S > 0$ , this means that the slope of the  $G$ - $T$  graph should always be negative. Typically  $S$  is an increasing function of  $T$ , so therefore the slope should be increasingly negative. At a phase transformation, the entropy increases while the temperature changes, so there should be discontinuity in the slope as the slope becomes more negative. So the graph should look like:



**12** For well-behaved functions, the mixed second derivatives are identical. So, starting with  $U$ ,

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

Now, using  $(\partial U/\partial S)_V = T$  and  $(\partial U/\partial V)_S = -P$ , the Maxwell relation is

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

$H$  is next:

$$\frac{\partial}{\partial P} \left( \frac{\partial H}{\partial S} \right) = \frac{\partial}{\partial S} \left( \frac{\partial H}{\partial P} \right) \quad \text{and} \quad \left( \frac{\partial H}{\partial S} \right)_P = T \quad , \quad \left( \frac{\partial H}{\partial P} \right)_S = V$$

Therefore

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

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Now  $F$ :

$$\frac{\partial}{\partial V} \left( \frac{\partial F}{\partial T} \right) = \frac{\partial}{\partial T} \left( \frac{\partial F}{\partial V} \right) \quad \text{and} \quad \left( \frac{\partial F}{\partial T} \right)_V = -S, \quad \left( \frac{\partial F}{\partial V} \right)_T = -P$$

Therefore

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

Finally,  $G$ :

$$\frac{\partial}{\partial P} \left( \frac{\partial G}{\partial T} \right) = \frac{\partial}{\partial T} \left( \frac{\partial G}{\partial P} \right) \quad \text{and} \quad \left( \frac{\partial G}{\partial T} \right)_P = -S, \quad \left( \frac{\partial G}{\partial P} \right)_T = V$$

Therefore

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

## 14

(a) Expanding,

$$dS = \left( \frac{\partial S}{\partial T} \right)_V dT + \left( \frac{\partial S}{\partial V} \right)_T dV = \frac{C_V}{T} dT + \left( \frac{\partial S}{\partial V} \right)_T dV$$

(b) Then,

$$dV = \left( \frac{\partial V}{\partial T} \right)_P dT + \left( \frac{\partial V}{\partial P} \right)_T dP$$

With constant pressure,  $dP = 0$  and

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

Therefore, multiplying by  $T$ ,

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

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(c) Using the previously derived  $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ ,

$$C_P - C_V = T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

And now, using the result of 1.46(c),

$$C_P - C_V = -T \frac{\left(\frac{\partial V}{\partial T}\right)_P^2}{\left(\frac{\partial V}{\partial P}\right)_T}$$

$\beta$  (the volume expansion coefficient) and  $\kappa_T$  (the isothermal compressibility) are defined as

$$\beta \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \quad \text{and} \quad \kappa_T \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$$

In that case,

$$C_P - C_V = \frac{TV\beta^2}{\kappa_T}$$

(d) For an ideal gas,  $\beta = Nk/VP = 1/T$  and  $\kappa_T = NkT/VP^2 = 1/P$ . So

$$C_P - C_V = \frac{PV}{T} = Nk$$

as it should be.

- (e)  $\beta^2 \geq 0$ ,  $\kappa_T \geq 0$  since increasing pressure can't increase the volume,  $V \geq 0$ , and since this isn't some kind of spin-temperature situation that can produce negative temperature. Therefore  $C_P - C_V \geq 0$ .
- (f) For water,  $C_P - C_V = 0.0435$  J/K, which is about 1%. For mercury,  $C_P - C_V = 3.58$  J/K, which is large, about 13%.
- (g) For solids,  $V$  and  $\kappa_T$  only change slightly with  $T$ . So the temperature dependence of  $C_P - C_V$  mostly comes from  $T\beta^2$ .  $\beta = 0$  at  $T = 0$ , and is relatively constant at higher temperatures.

## 32 (no d)

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(a) The slope of the phase boundary is  $\Delta S/\Delta V$ . Now,  $\Delta S = L/T > 0$ , while  $\Delta V < 0$  for  $\text{H}_2\text{O}$ . Therefore the slope is negative.

(b) Things will remain linear with a one-degree temperature difference. So

$$\frac{\Delta P}{\Delta T} \approx \frac{dP}{dT} = \frac{L}{T\Delta V} \Rightarrow \Delta P = \frac{L\Delta T}{T\Delta V} = 1.35 \times 10^7 \text{ Pa}$$

(c) The pressure is due to the weight of the mass above, just as in a fluid. So  $\Delta P = \rho g z$  where  $z$  is the depth. Solving,  $z = P/\rho g = 1500 \text{ m}$ . Glaciers are not that thick.

**48** Differentiating the van der Waals equation,

$$\frac{\partial P}{\partial V} = -\frac{NkT}{(V - Nb)^2} + \frac{2aN^2}{V^3} \quad \text{and} \quad \frac{\partial^2 P}{\partial V^2} = \frac{2NkT}{(V - Nb)^3} - \frac{6aN^2}{V^4}$$

Both are zero at the critical point, therefore

$$\frac{NkT_c}{(V_c - Nb)^2} = \frac{2aN^2}{V_c^3} \quad \text{and} \quad \frac{2NkT_c}{(V_c - Nb)^3} = \frac{6aN^2}{V_c^4}$$

Dividing the two equations gives  $\frac{1}{2}(V_c - Nb) = \frac{1}{3}V_c$ , or  $V_c = 3Nb$ . We can now use this in the same equations. After some algebra,  $kT_c = 8a/27b$  drops out. For  $P_c$ , use these results in the van der Waals equation:

$$P_c = \frac{NkT_c}{V_c - Nb} - \frac{aN^2}{V_c^2} = \frac{8Na/27b}{2Nb} - \frac{aN^2}{9N^2b^2} = \frac{a}{27b^2}$$

**51** With the reduced variables, the van der Waals equation becomes

$$pP_c = \frac{NktT_c}{vV_c - Nb} - \frac{aN^2}{v^2V_c^2}$$

Using the results from problem 48 and doing some algebra, we end up with

$$p = \frac{8t}{3v - 1} - \frac{3}{v^2}$$