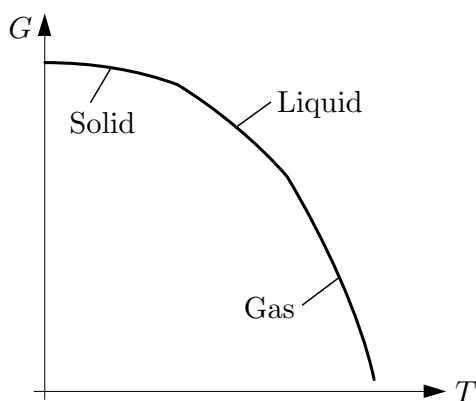

Homework Solutions 5 (Schroeder Chapter 5)

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 does not change, 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

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

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 ,

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

(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),

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

β (the volume expansion coefficient) and κ_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 1 m³ water, $C_P - C_V = 4.35 \times 10^4$ J/K, which is about 1% of its heat capacity. For 1 m³ mercury, $C_P - C_V = 2.42 \times 10^5$ J/K, which is large, about 13% of its heat capacity.
- (g) For solids, V and κ_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 H_2O . 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

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