Phys 114 Week 3 2018 W1

Warmup Problem

W1 Maxwell relns:

$$\alpha_P \equiv \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

a) Maxwell relation we would use is

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

$$\alpha = -\frac{1}{V}\left(\frac{\partial S}{\partial P}\right)_T .$$ The

Third law states that, in the words of Simon quoted in section 18.1 of B+B:

The contribution to S by each aspect of the system in ThermoD =ibrium tends to zero as $T \to 0$.

Thus derivatives of S (as argued in 18.2 of B+B) must vanish. Ergo:

$$\left(\frac{\partial S}{\partial P}\right)_T \to 0 \quad \text{as} \quad T \to 0$$

The result follows :)

b) We want to derive

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

My fave way is to consider relevant ThermoD pot'l. It will be the one that is a function of natural variables T & P. Hence: $G(T,P,N)$

W2

Now

$$dG = d(H - TS)$$
$$= d(E + PV - TS)$$
$$= dE + PdV + VdP - TdS - SdT$$

first law $\underbrace{dE}_{\text{of}} = \underbrace{-PdV}_{\text{work on}} + \underbrace{TdS}_{\text{heat into}}$

$$\therefore dG = VdP - SdT$$
$$= \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT$$

So since $\dfrac{\partial G}{\partial T \partial P} = \dfrac{\partial G}{\partial P \partial T}$

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

QED