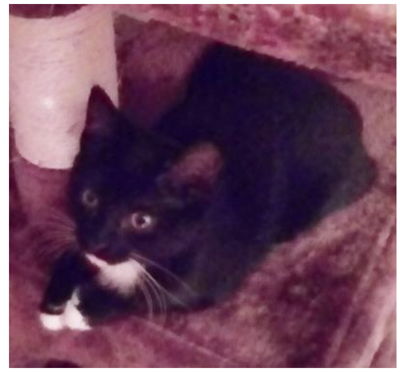
Hard Problems, for Fun!



Meet my new kitten Charlie!

Using Maxwell equations express $\left.\frac{\partial S}{\partial V}\right)_T$ and $\left.\frac{\partial V}{\partial S}\right)_P$ and $\left.\frac{\partial P}{\partial S}\right)_V$ and $\left.\frac{\partial S}{\partial P}\right)_T$ in terms of heat capacities, expansion coefficient α (ie. $\alpha = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right)_P$) and isothermal compressibility κ_T (ie. . $\kappa = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right)_T$).

We will use the Euler Chain Relation quite a bit (you know what that is!). Ok the Euler Chain formula is $\left.\frac{\partial x}{\partial y}\right)_z \left.\frac{\partial y}{\partial z}\right)_x \left.\frac{\partial z}{\partial x}\right)_y = -1$ and therefore $\left.\frac{\partial x}{\partial y}\right)_z = -\left.\frac{\partial z}{\partial y}\right)_x \left.\frac{\partial x}{\partial z}\right)_y$

1. For the first one: $\left.\frac{\partial S}{\partial V}\right)_T = \left.\frac{\partial P}{\partial T}\right)_V$ is a Maxwell equation. From there we use the Euler Chain Formula to get: $\left.\frac{\partial S}{\partial V}\right)_T = \left.\frac{\partial P}{\partial T}\right)_V = -\left.\frac{\partial V}{\partial T}\right)_P \left.\frac{\partial P}{\partial V}\right)_T$. Knowing that $\alpha = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right)_P$ and thus $\alpha V = \left.\frac{\partial V}{\partial T}\right)_P$ we can reduce this to $\left.\frac{\partial S}{\partial V}\right)_T = -\alpha V \left.\frac{\partial P}{\partial V}\right)_T$ Now we also know that $\kappa = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right)_T$ so $\frac{1}{\kappa} = -V\left.\frac{\partial P}{\partial V}\right)_T$ so $\left.\frac{\partial S}{\partial V}\right)_T = \frac{\alpha}{\kappa}$.

2. Next is $\left.\frac{\partial V}{\partial S}\right)_P$. Starting with: $\left.\frac{\partial V}{\partial S}\right)_P = \left.\frac{\partial T}{\partial P}\right)_S$ from a Maxwell Relation. Now the Euler Chain Formula: $\left.\frac{\partial V}{\partial S}\right)_P = \left.\frac{\partial T}{\partial P}\right)_S = -\left.\frac{\partial S}{\partial P}\right)_T \left.\frac{\partial T}{\partial S}\right)_P$ Knowing that $\partial H = T\partial S + V\partial P$ therefore the partial with respect to T at const. P gives: $C_P = \left.\frac{\partial H}{\partial T}\right)_P = T\left.\frac{\partial S}{\partial T}\right)_P + V\left.\frac{\partial P}{\partial T}\right)_P = T\left.\frac{\partial S}{\partial T}\right)_P$ and therefore $\frac{T}{C_P} = \left.\frac{\partial T}{\partial S}\right)_P$ we can make $\left.\frac{\partial V}{\partial S}\right)_P = -\left.\frac{\partial S}{\partial P}\right)_T \frac{T}{C_P}$. Now to get rid of the first entropy term use another Maxwell Equation $-\left.\frac{\partial S}{\partial P}\right)_T = \left.\frac{\partial V}{\partial T}\right)_P$ leaves us with $\left.\frac{\partial V}{\partial S}\right)_P = \left.\frac{\partial V}{\partial T}\right)_P \frac{T}{C_P}$ Knowing that $\alpha = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right)_P$ we can reduce this to $\left.\frac{\partial V}{\partial S}\right)_P = V\alpha\frac{T}{C_P}$.

3. Gimme more Dr. Chicken! Ok $\left.\frac{\partial P}{\partial S}\right)_V$ is equal to $-\left.\frac{\partial T}{\partial V}\right)_S$ via Maxwell Equation. Next is the Euler Chain Formula: $\left.\frac{\partial P}{\partial S}\right)_V = -\left.\frac{\partial T}{\partial V}\right)_S = \left.\frac{\partial S}{\partial V}\right)_T \left.\frac{\partial T}{\partial S}\right)_V$ Knowing that $\partial U = T\partial S - P\partial V$ therefore the partial with respect to T at const. V gives: $C_V = \left.\frac{\partial U}{\partial T}\right)_V = T\left.\frac{\partial S}{\partial T}\right)_V - P\left.\frac{\partial V}{\partial T}\right)_V = T\left.\frac{\partial S}{\partial T}\right)_V$ and

therefore $\frac{T}{C_V} = \left.\frac{\partial T}{\partial S}\right)_V$. Now we have $\left.\frac{\partial P}{\partial S}\right)_V = \left.\frac{\partial S}{\partial V}\right)_T \frac{T}{C_V}$. Last step is to recognize that we already figured out that $\left.\frac{\partial S}{\partial V}\right)_T = \frac{\alpha}{\kappa}$ in the first part of this Scratch so we get $\left.\frac{\partial P}{\partial S}\right)_V = \frac{\alpha}{\kappa}\frac{T}{C_V}$.

4. One more then its time for beddy-bye. $\left.\frac{\partial S}{\partial P}\right)_T$ is equal to $-\left.\frac{\partial V}{\partial T}\right)_P$ via a Maxwell Equation. Next is the Euler Chain Formula: $\left.\frac{\partial S}{\partial P}\right)_T = -\left.\frac{\partial V}{\partial T}\right)_P = \left.\frac{\partial P}{\partial T}\right)_V \left.\frac{\partial V}{\partial P}\right)_T$ Knowing that $\kappa = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right)_T$ gives: $\left.\frac{\partial S}{\partial P}\right)_T = -\left.\frac{\partial P}{\partial T}\right)_V V\kappa$. Last step is to recognize that we solved for $\left.\frac{\partial P}{\partial T}\right)_V$ in the first problem which is $\left.\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\kappa}$ so putting this all together gives $\left.\frac{\partial S}{\partial P}\right)_T = -\frac{\alpha}{\kappa}V\kappa = -\alpha V$.