

HEAT CAPACITIES USING MAXWELL RELATIONS

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problems 5.13 - 5.15.

We can use the Maxwell relations to derive some formulas relating to heat capacities. First, recall the thermal expansion coefficient

$$(1) \quad \beta \equiv \frac{\Delta V/V}{\Delta T}$$

which is the fractional change in volume per Kelvin, assumed to be a constant pressure. For small changes, we can write this as a partial derivative:

$$(2) \quad \beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

From the Maxwell relation derived from the Gibbs energy:

$$(3) \quad \left(\frac{\partial V}{\partial T} \right)_P = - \left(\frac{\partial S}{\partial P} \right)_T$$

so

$$(4) \quad \beta = -\frac{1}{V} \left(\frac{\partial S}{\partial P} \right)_T$$

The third law of thermodynamics says that as $T \rightarrow 0$, $S \rightarrow 0$. I'm not quite sure how we can use this to show that $\beta \rightarrow 0$ as $T \rightarrow 0$ since it's not clear how entropy depends on pressure at low temperatures. However, if $S \rightarrow 0$ for *any* system as $T \rightarrow 0$, then presumably it must be true no matter what the pressure is, so in that sense, S is independent of pressure and then $\left(\frac{\partial S}{\partial P} \right)_T = 0$. I'm not sure that constitutes a 'proof' as requested in Schroeder's problem, though.

We're on firmer ground when we wish to derive a relation between the heat capacities C_V (constant volume) and C_P (constant pressure). In terms of entropy, they are

$$(5) \quad C_V = T \left(\frac{\partial S}{\partial T} \right)_V$$

$$(6) \quad C_P = T \left(\frac{\partial S}{\partial T} \right)_P$$

If we write $S = S(V, T)$ then

$$(7) \quad dS = \left(\frac{\partial S}{\partial V} \right)_T dV + \left(\frac{\partial S}{\partial T} \right)_V dT$$

Also, starting with $V = V(P, T)$ we have

$$(8) \quad dV = \left(\frac{\partial V}{\partial P} \right)_T dP + \left(\frac{\partial V}{\partial T} \right)_P dT$$

Inserting this into 7 and setting $dP = 0$ (constant pressure) gives

$$(9) \quad dS = \left[\left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P + \left(\frac{\partial S}{\partial T} \right)_V \right] dT$$

$$(10) \quad \left(\frac{\partial S}{\partial T} \right)_P = \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P + \left(\frac{\partial S}{\partial T} \right)_V$$

$$(11) \quad C_P = T \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P + C_V$$

where we've used 5 and 6 in the last line.

From the Helmholtz energy Maxwell relation

$$(12) \quad \left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$$

we have

$$(13) \quad C_P = T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P + C_V$$

Using 2 with its relation to the isothermal compressibility:

$$(14) \quad \frac{\beta}{\kappa_T} = \left(\frac{\partial P}{\partial T} \right)_V$$

we have

$$(15) \quad C_P = C_V + \frac{TV\beta^2}{\kappa_T}$$

For an ideal gas, $PV = NkT$, so 13 becomes

$$(16) \quad C_P = T \frac{Nk}{P} \frac{Nk}{V} + C_V$$

$$(17) \quad = \frac{NkT}{PV} Nk + C_V$$

$$(18) \quad = C_V + Nk$$

which agrees with Schroeder's equation 1.48.

From 15, we can see that $C_P > C_V$ provided that the term $\frac{TV\beta^2}{\kappa_T}$ is always positive. The numerator is certainly positive, and from the definition of the isothermal compressibility

$$(19) \quad \kappa_T \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

we see that it is positive provided that an increase in pressure causes a decrease in volume, which is pretty well always true for any realistic material. Since $\beta \rightarrow 0$ for low temperatures and as we wouldn't expect V or κ_T to change much for very low temperatures (where we'd expect most substances to be solid, or possibly liquid, such as helium), then we'd expect $C_P \approx C_V$ for low temperatures, with $C_P > C_V$ as temperature increases. This agrees with Schroeder's Figure 1.14.

To put in some numbers, we can use the data from the earlier problem. For water, the values given by Schroeder are (at $25^\circ \text{C} = 298 \text{K}$):

$$(20) \quad \beta = 2.57 \times 10^{-4} \text{K}^{-1}$$

$$(21) \quad \kappa_T = 4.52 \times 10^{-10} \text{Pa}^{-1}$$

For one mole of water, the volume is $18.068 \times 10^{-6} \text{m}^3$, so

$$(22) \quad C_P - C_V = \frac{(298)(18.068 \times 10^{-6})(2.57 \times 10^{-4})^2}{4.52 \times 10^{-10}}$$

$$(23) \quad = 0.787 \text{J K}^{-1}$$

$C_P = 75.29 \text{J K}^{-1}$ for one mole of water so the difference between the heat capacities is around 1% of C_P .

For mercury we have

$$(24) \quad \beta = 1.81 \times 10^{-4} \text{ K}^{-1}$$

$$(25) \quad \kappa_T = 4.04 \times 10^{-11} \text{ Pa}^{-1}$$

One mole of mercury has a volume of $14.81 \times 10^{-6} \text{ m}^3$ so we get

$$(26) \quad C_P - C_V = \frac{(298)(14.81 \times 10^{-6})(1.81 \times 10^{-4})^2}{4.04 \times 10^{-11}}$$

$$(27) \quad = 3.58 \text{ J K}^{-1}$$

The heat capacity for one mole of mercury (from the appendix to Schroeder's book) is 27.98 J K^{-1} so the difference is around 12.8% of C_P .

Finally, we can derive 15 by starting with U and H instead of S and V . The heat capacities are defined in terms of internal energy and enthalpy as

$$(28) \quad C_V \equiv \left(\frac{\partial U}{\partial T} \right)_V$$

$$(29) \quad C_P \equiv \left(\frac{\partial H}{\partial T} \right)_P$$

Writing $U = U(V, T)$ we have

$$(30) \quad dU = \left(\frac{\partial U}{\partial V} \right)_T dV + \left(\frac{\partial U}{\partial T} \right)_V dT$$

The enthalpy is defined as $H = U + PV$, so at constant pressure

$$(31) \quad dH = dU + P dV$$

$$(32) \quad = \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] dV + \left(\frac{\partial U}{\partial T} \right)_V dT$$

Dividing through by dT at constant pressure gives

$$(33) \quad \left(\frac{\partial H}{\partial T} \right)_P = \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] \left(\frac{\partial V}{\partial T} \right)_P + \left(\frac{\partial U}{\partial T} \right)_V$$

$$(34) \quad C_P = \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] \left(\frac{\partial V}{\partial T} \right)_P + C_V$$

The Helmholtz free energy is defined as $F = U - TS$ from which we can derive the relation

$$(35) \quad P = - \left(\frac{\partial F}{\partial V} \right)_T$$

Using this, we have

$$(36) \quad C_P = \left[\left(\frac{\partial U}{\partial V} \right)_T - \left(\frac{\partial F}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_P + C_V$$

$$(37) \quad = \left(\frac{\partial (U - F)}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P + C_V$$

$$(38) \quad = T \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P + C_V$$

This is the same as 11, so from here on the derivation is the same as before, and we get 15 again.

PINGBACKS

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