Lecture_08

October 7, 2022

1 Revisiting Heat Capacity (again)

Ok let's use one of the tricks from the last lecture to derive some more helpful quantities. First, let's start with the fundamental thermodynamic relation, which we can write as :

$$\mathrm{d}S = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\mathrm{d}V$$

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

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

Which immediately gives

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V ; \quad \left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]$$

Using the fact that

$$\frac{\partial^2 S}{\partial V \partial T} = \frac{\partial^2 S}{\partial T \partial V}$$

leads us to

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

Recalling that

$$C_P - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)_P .$$

(from Lecture 3), we then get

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

If we now define

$$\beta_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P ; \quad -\kappa_T = \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T ;$$

where β_P is the isobaric expansivity and κ_T is the isothermal compressibility, and use the following identity

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

which gives

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

Tidying up gives that

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

These are all quantities which are easily measurable in the lab, meaning the difference in the heat capacities can be easily obtained.