

3.26 Maxwell relations

The fundamental equations represent exact differentials, e.g.

$$dG = Vdp - SdT \quad , \text{ i.e. } \quad \left(\frac{\partial^2 G}{\partial p \partial T} \right) = \left(\frac{\partial^2 G}{\partial T \partial p} \right) \quad ; \text{ thus } \quad - \left(\frac{\partial S}{\partial p} \right)_T = \left(\frac{\partial V}{\partial T} \right)_p \quad (3.62)$$

Generally

$$df(x, y) = gdx + hdy \quad \text{gives} \quad \left(\frac{\partial g}{\partial y} \right)_x = \left(\frac{\partial h}{\partial x} \right)_y \quad (3.63)$$

So from the other fundamental equations we get further Maxwell relations:

$$\begin{aligned} \left(\frac{\partial S}{\partial V} \right)_T &= \left(\frac{\partial p}{\partial T} \right)_V \\ \left(\frac{\partial T}{\partial V} \right)_S &= - \left(\frac{\partial p}{\partial S} \right)_V \\ \left(\frac{\partial T}{\partial p} \right)_S &= \left(\frac{\partial V}{\partial S} \right)_p \\ \left(\frac{\partial V}{\partial T} \right)_p &= - \left(\frac{\partial S}{\partial p} \right)_T \end{aligned} \quad (3.64)$$

These Maxwell relations allow for drastic simplification and replacements of difficult-to-measure relations by easy-to-measure relations and thus contribute strongly to the powerful toolbox of thermodynamics as we will see in some subsequent examples.