6.1: Maxwell Relations

For a system with one constituent with fixed number of particles, from the first and second laws, and from Equation 5.1.10, we have the basic relations

$$\begin{aligned} dU &= TdS - pdV \\ dH &= TdS - Vdp \\ dF &= -SdT - pdV \\ dG &= -SdT - Vdp \end{aligned} \tag{6.1.1}$$

The quantities on the left are all **perfect differentials**. For a general differential dR of the form

$$dR = Xdx + Ydy \tag{6.1.2}$$

to be a perfect differential, the necessary and sufficient condition is

$$\left(\frac{\partial X}{\partial y}\right)_x = \left(\frac{\partial Y}{\partial x}\right)_y \tag{6.1.3}$$

Applying this to the four differentials in 6.1.1, we get

$$\begin{aligned} \left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial p}{\partial S}\right)_V \\ \left(\frac{\partial T}{\partial p}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_p \\ \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial p}{\partial T}\right)_V \\ \left(\frac{\partial S}{\partial p}\right)_T &= -\left(\frac{\partial V}{\partial T}\right)_p \end{aligned} \tag{6.1.4}$$

These four relations are called the Maxwell relations.

A Mathematical Result

Let X, Y, Z be three variables, of which only two are independent. Taking Z to be a function of X and Y, we can write

$$dZ = \left(\frac{\partial Z}{\partial X}\right)_Y dX + \left(\frac{\partial Z}{\partial Y}\right)_X dY \tag{6.1.5}$$

If now we take X and Z as the independent variables, we can write

$$dY = \left(\frac{\partial Y}{\partial X}\right)_Y dX + \left(\frac{\partial Y}{\partial Z}\right)_X dZ \tag{6.1.6}$$

Upon substituting this result into 6.1.5, we get

$$dZ = \left[\left(\frac{\partial Z}{\partial X}\right)_Y + \left(\frac{\partial Z}{\partial Y}\right)_X \left(\frac{\partial Y}{\partial X}\right)_Z\right] dX + \left(\frac{\partial Z}{\partial Y}\right)_X \left(\frac{\partial Y}{\partial Z}\right)_X dZ \tag{6.1.7}$$

Since we are considering X and Z as independent variables now, this equation immediately yields the relations

$$\begin{aligned} \left(\frac{\partial Z}{\partial Y}\right)_X \left(\frac{\partial Y}{\partial Z}\right)_X dZ &= 1 \\ \left(\frac{\partial Z}{\partial X}\right)_Y + \left(\frac{\partial Z}{\partial Y}\right)_X \left(\frac{\partial Y}{\partial X}\right)_Z &= 0 \end{aligned} \tag{6.1.8}$$

These relations can be rewritten as

$$\left(\frac{\partial Z}{\partial Y}\right)_X = \frac{1}{\left(\frac{dY}{dZ}\right)_X} \tag{6.1.9}$$

$$\left(\frac{\partial X}{\partial Z}\right)_Y \left(\frac{\partial Z}{\partial Y}\right)_X \left(\frac{\partial Y}{\partial X}\right)_Z = -1$$