The Mathematical Structure of Thermodynamics

Of the four state variables P, V, T and S, if we know any two, we can work out the other 2. So, from the first law:

$dU = TdS - PdV$ we can write internal energy as a function of only two state variables. we can do this by writing it as a total differential:

$$\boxed{dU = \left(\frac{\partial U}{\partial S}\right)_V dS - \left(\frac{\partial U}{\partial V}\right)_S dV}$$

From this, it also follows that:

$$\boxed{T = \left(\frac{\partial U}{\partial S}\right)_V} \qquad \boxed{P = -\left(\frac{\partial U}{\partial V}\right)_S}$$

This lets us define an unexpected relation. Using the fact that the cross derivatives are equal:

$$\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial^2 U}{\partial S \partial V}\right) = -\left(\frac{\partial P}{\partial S}\right)_V$$

we get:

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V}$$

This is one of the Maxwell Relations. These are completely general equations that apply to any system in thermodynamic equilibrium.