# 22.3: The Maxwell Relations

Modeling the dependence of the Gibbs and Helmholtz functions behave with varying temperature, pressure, and volume is fundamentally useful. But in order to do that, a little bit more development is necessary. To see the power and utility of these functions, it is useful to combine the First and Second Laws into a single mathematical statement. In order to do that, one notes that since

$$dS = \frac{dq}{T}$$

for a reversible change, it follows that

$$dq = TdS$$

And since

$$dw = TdS - pdV$$

for a reversible expansion in which only p-V works is done, it also follows that (since $dU = dq + dw$ ):

$$dU = TdS - pdV \tag{22.3.1}$$

This is an extraordinarily powerful result. This differential for $dU$ can be used to simplify the differentials for $H$, $A$, and $G$. But even more useful are the constraints it places on the variables $T$, $S$, $p$, and $V$ due to the mathematics of exact differentials!

## Maxwell Relations

The above result suggests that the natural variables of internal energy are $S$ and $V$ (or the function can be considered as $U(S,V)$). So the total differential ($dU$) in Equation 22.3.1 can be expressed:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \tag{22.3.2}$$

Also, by inspection (comparing the two expressions for $dU$ in Equations 22.3.1 and 22.3.2) it is apparent that:

$$\left(\frac{\partial U}{\partial S}\right)_V = T \tag{22.3.3}$$

and

$$\left(\frac{\partial U}{\partial V}\right)_S = -p \tag{22.3.4}$$

But the value does not stop there! Since $dU$ is an exact differential, the Euler relation must hold that

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V\right]_S = \left[\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S\right]_V$$

By substituting Equations 22.3.3 and 22.3.4, we see that

$$\left[\frac{\partial}{\partial V}(T)_V\right]_S = \left[\frac{\partial}{\partial S}(-p)_S\right]_V$$

or

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

This is an example of a **Maxwell Relation**. These are very powerful relationship that allows one to substitute partial derivatives when one is more convenient (perhaps it can be expressed entirely in terms of $\alpha$ and/or $\kappa_T$ for example.)

A similar result can be derived based on the definition of $H$.

$$H \equiv U + pV$$

Differentiating (and using the chain rule on $d(pV)$) yields

$$dH = dU + pdV + Vdp$$

Making the substitution using the combined first and second laws ($dU = TdS - pdV$) for a reversible change involving on expansion (p-V) work

$$dH = TdS - \cancel{pdV} + \cancel{pdV} + Vdp$$

This expression can be simplified by canceling the $pdV$ terms.

$$dH = TdS + Vdp \tag{22.3.5}$$

And much as in the case of internal energy, this suggests that the natural variables of $H$ are $S$ and $p$. Or

$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dV \tag{22.3.6}$$

Comparing Equations 22.3.5 and 22.3.6 show that

$$\left(\frac{\partial H}{\partial S}\right)_p = T \tag{22.3.7}$$

and

$$\left(\frac{\partial H}{\partial p}\right)_S = V \tag{22.3.8}$$

It is worth noting at this point that both Equation 22.3.3

$$\left(\frac{\partial U}{\partial S}\right)_V$$

and Equation 22.3.7

$$\left(\frac{\partial H}{\partial S}\right)_p$$

are equal to $T$. So they are equation to each other

$$\left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_p$$

Moreover, the Euler Relation must also hold

$$\left[\frac{\partial}{\partial p}\left(\frac{\partial H}{\partial S}\right)_p\right]_S = \left[\frac{\partial}{\partial S}\left(\frac{\partial H}{\partial p}\right)_S\right]_p$$

so

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

This is the Maxwell relation on $H$. Maxwell relations can also be developed based on $A$ and $G$. The results of those derivations are summarized in Table 22.3.1.

Table 22.3.1: Maxwell Relations

| Function | Differential | Natural Variables | Maxwell Relation |
|---|---|---|---|
| $U$ | $dU = TdS - pdV$ | $S, V$ | $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$ |
| | | | |

| Function | Differential | Natural Variables | Maxwell Relation |
|---|---|---|---|
| $H$ | $dH = TdS + Vdp$ | $S, p$ | $\left(\dfrac{\partial T}{\partial p}\right)_S = \left(\dfrac{\partial V}{\partial S}\right)_p$ |
| $A$ | $dA = -pdV - SdT$ | $V, T$ | $\left(\dfrac{\partial p}{\partial T}\right)_V = \left(\dfrac{\partial S}{\partial V}\right)_T$ |
| $G$ | $dG = Vdp - SdT$ | $p, T$ | $\left(\dfrac{\partial V}{\partial T}\right)_p = -\left(\dfrac{\partial S}{\partial p}\right)_T$ |

The Maxwell relations are extraordinarily useful in deriving the dependence of thermodynamic variables on the state variables of $p$, $T$, and $V$.

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✔ **Example 22.3.1**

Show that

$$\left(\frac{\partial V}{\partial T}\right)_p = T\frac{\alpha}{\kappa_T} - p$$

**Solution**

Start with the combined first and second laws:

$$dU = TdS - pdV$$

Divide both sides by $dV$ and constraint to constant $T$:

$$\left.\frac{dU}{dV}\right|_T = \left.\frac{TdS}{dV}\right|_T - p\left.\frac{dV}{dV}\right|_T$$

Noting that

$$\left.\frac{dU}{dV}\right|_T = \left(\frac{\partial U}{\partial V}\right)_T$$

$$\left.\frac{TdS}{dV}\right|_T = \left(\frac{\partial S}{\partial V}\right)_T$$

$$\left.\frac{dV}{dV}\right|_T = 1$$

The result is

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p$$

Now, employ the Maxwell relation on $A$ (Table 6.2.1)

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

to get

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

and since

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa_T}$$

It is apparent that

$$\left(\frac{\partial V}{\partial T}\right)_p = T\frac{\alpha}{\kappa_T} - p$$

*Note*: How cool is that? This result was given without proof in Chapter 4, but can now be proven analytically using the Maxwell Relations!

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