

4.4: 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 work is done, it also follows that (since $dU = dq + dw$):

$$dU = TdS - pdV$$

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!

4.4.1: 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) can be expressed:

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

Also, by inspection (comparing the two expressions for dU) it is apparent that:

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad (4.4.1)$$

and

$$\left(\frac{\partial U}{\partial V}\right)_S = -p \quad (4.4.2)$$

But the value doesn't 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 4.4.1 and 4.4.2, 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 α and/or κ_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

$$dH = dU + p dV + V dp$$

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

$$dH = T dS - \cancel{p dV} + \cancel{p dV} + V dp$$

This expression can be simplified by canceling the $p dV$ terms.

$$dH = T dS + V dp \quad (4.4.3)$$

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

$$dH = \left(\frac{\partial H}{\partial S} \right)_p dS + \left(\frac{\partial H}{\partial p} \right)_S dV \quad (4.4.4)$$

Comparing Equations 4.4.3 and 4.4.4 show that

$$\left(\frac{\partial H}{\partial S} \right)_p = T \quad (4.4.5)$$

and

$$\left(\frac{\partial H}{\partial p} \right)_S = V \quad (4.4.6)$$

It is worth noting at this point that both (Equation 4.4.1)

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

and (Equation 4.4.5)

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

are equation 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 6.2.1..

Table 6.2.1: Maxwell Relations

Function	Differential	Natural Variables	Maxwell Relation
U	$dU = T dS - p dV$	S, V	$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial p}{\partial S} \right)_V$
H	$dH = T dS + V dp$	S, p	$\left(\frac{\partial T}{\partial p} \right)_S = \left(\frac{\partial V}{\partial S} \right)_p$

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

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

✓ Example 4.4.1

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

$$\begin{aligned} \left.\frac{dU}{dV}\right|_T &= \left(\frac{\partial U}{\partial V}\right)_T \\ \left.\frac{TdS}{dV}\right|_T &= \left(\frac{\partial S}{\partial V}\right)_T \\ \left.\frac{dV}{dV}\right|_T &= 1 \end{aligned}$$

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

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

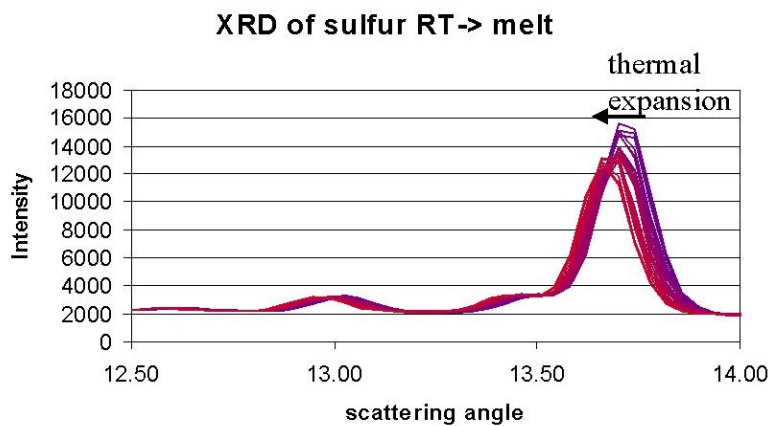
and since

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

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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