

## 6.2: Combining the First and Second Laws - Maxwell's 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  $dU = dq + dw$ ):

$$dU = TdS - pdV \quad (6.2.1)$$

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 6.2.1 can be expressed:

$$dU = \left( \frac{\partial U}{\partial S} \right)_V dS + \left( \frac{\partial U}{\partial V} \right)_S dV \quad (6.2.2)$$

Also, by inspection (comparing the two expressions for  $dU$  in Equations 6.2.1 and 6.2.2) it is apparent that:

$$\left( \frac{\partial U}{\partial S} \right)_V = T \quad (6.2.3)$$

and

$$\left( \frac{\partial U}{\partial V} \right)_S = -p \quad (6.2.4)$$

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 6.2.3 and 6.2.4, 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.

$$dH = TdS + Vdp \quad (6.2.5)$$

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

$$dH = \left( \frac{\partial H}{\partial S} \right)_p dS + \left( \frac{\partial H}{\partial p} \right)_S dV \quad (6.2.6)$$

Comparing Equations 6.2.5 and 6.2.6 show that

$$\left( \frac{\partial H}{\partial S} \right)_p = T \quad (6.2.7)$$

and

$$\left( \frac{\partial H}{\partial p} \right)_S = V \quad (6.2.8)$$

It is worth noting at this point that both Equation 6.2.3

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

and Equation 6.2.7

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

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 6.2.1.

Table 6.2.1: 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
$H$	$dH = TdS + Vdp$	$S, p$	$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$
$A$	$dA = -pdV - SdT$	$V, T$	$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$
$G$	$dG = Vdp - SdT$	$p, T$	$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$

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

### ✓ Example 6.2.1

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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