

## 4.6: Maxwell Relationships

Before we go further in our analysis of entropy, the fact that reversible heating is  $\partial q = T\partial S$  offers several opportunities for analysis that have been ignored thus far. For example:

$$\partial U = \partial q + \partial w = T\partial S - P\partial V$$

can be cast into the form of an exact differential:

$$\partial f(x, y) = \left(\frac{\partial f}{\partial x}\right)_y \partial x + \left(\frac{\partial f}{\partial y}\right)_x \partial y$$

which is exact because

$$\left(\frac{\partial}{\partial y}\right)\left(\frac{\partial f}{\partial x}\right)_y = \left(\frac{\partial}{\partial x}\right)\left(\frac{\partial f}{\partial y}\right)_x$$

If we “line up”  $\partial U$  with  $\partial f$ :

then we can see that  $f=U$ ,  $x=S$ , and  $y=V$ . This allows us to determine:

$$\left(\frac{\partial f}{\partial x}\right)_y = \left(\frac{\partial U}{\partial S}\right)_V = T$$

and:

$$\left(\frac{\partial f}{\partial y}\right)_x = \left(\frac{\partial U}{\partial V}\right)_S = -P$$

Now we can use the exactness of  $\partial U$  via the Euler Test:

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

We insert  $\left(\frac{\partial U}{\partial S}\right)_V = T$  on the left and  $\left(\frac{\partial U}{\partial V}\right)_S = -P$  on the right to reveal:

$$\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{-\partial P}{\partial S}\right)_V \quad (4.6.1)$$

Equation 4.6.1 is a Maxwell relation, which can be used to derive thermodynamic proofs that would otherwise be difficult or impossible to evaluate by any other means.

Since we determined the above using  $\partial U$ , then what about *partial H*? Is there another Maxwell relationship? Starting with  $\partial H = T\partial S + V\partial P$ , which is an exact differential, and thus we follow similar steps as before to find:

$$\left(\frac{\partial}{\partial P}\right)\left(\frac{\partial H}{\partial S}\right)_P = \left(\frac{\partial}{\partial S}\right)\left(\frac{\partial H}{\partial P}\right)_S$$

which leads to:

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad (4.6.2)$$

In the next chapter we will derive two more. In the meantime, let’s see what these Maxwell relations are good for!

### 4.6.1 Using Maxwell Relations

Equations 4.6.1 and 4.6.2 related changes in state variables under conditions of constant system entropy  $S$  due to the  $\left(\frac{\partial T}{\partial V}\right)_S$  and  $\left(\frac{\partial T}{\partial P}\right)_S$  terms.

This means that they can only be applied for systems for which  $\Delta S = 0 \text{ J/K}$ , which is only true of adiabatic reversible transitions. Furthermore, it is always true that  $\Delta S_{ext} = 0 \text{ J/K}$  for adiabatic systems due to the lack of heat exchange, which makes  $\Delta S_{tot} = 0 \text{ J/K}$ . Since there is no change in total entropy, the Maxwell relations in eqs. 4.9 and 4.10 represent equilibrium.

The utility of eqs. 4.9 and 4.10 is that it will allow us to calculate changes in the state variables volume, temperature, and pressure. Normally such derivatives  $\left(\frac{\partial V}{\partial T}\right)_P$ ,  $\left(\frac{\partial P}{\partial T}\right)_V$ , and  $\left(\frac{\partial P}{\partial V}\right)_T$  are trivial to calculate using the perfect gas law; however, they do not apply to adiabatic (equilibrium) systems since  $P$ ,  $V$ , and  $T$  are all simultaneously changing. As such, the purpose of this section is to determine  $\left(\frac{\partial V}{\partial T}\right)_S$ ,  $\left(\frac{\partial P}{\partial T}\right)_S$ , and  $\left(\frac{\partial P}{\partial V}\right)_S$  for systems at equilibrium.

#### 4.6.1.1 Maxwell relation approach:

$\left(\frac{\partial V}{\partial T}\right)_S$ . First let us tackle changing volume with temperature, although we must note that there are multiple ways to perform such a derivation.

We will use Equation 4.9:  $\left(\frac{\partial T}{\partial V}\right)_S = -\frac{\partial P}{\partial S}_V$ , and in the next section we will demonstrate the same derivation using a slightly easier approach. The first step here is to invert Equation 4.9 as:

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

so now we are trying to solve  $-\frac{\partial S}{\partial P}_V$ . As  $\partial U = T\partial S - P\partial V$ , we solve for the change in entropy:

$$-\partial S = -\frac{1}{T}\partial U + \frac{P}{T}\partial V$$

This expression can be divided by  $\partial P$ , after which we apply the condition of constant volume:

$$-\frac{\partial S}{\partial P}_V = -\frac{1}{T}\left(\frac{\partial U}{\partial P}\right)_V + \frac{P}{T}\left(\frac{\partial V}{\partial P}\right)_V = -\frac{1}{T}\left(\frac{\partial U}{\partial P}\right)_V$$

because  $\frac{P}{T}\left(\frac{\partial V}{\partial P}\right)_V = 0 \text{ m}^3/\text{K}$  due to the condition of constant volume ( $\partial V = 0 \text{ m}^3$ ). Substituting  $\partial U = C_V\partial T$ , we find:

$$-\frac{\partial S}{\partial P}_V = -\frac{1}{T}\left(\frac{\partial U}{\partial P}\right)_V = -\frac{C_V}{T}\left(\frac{\partial T}{\partial P}\right)_V = -\frac{C_V}{T} \frac{V}{nR} = -\frac{C_V}{P}$$

where we used  $\left(\frac{\partial T}{\partial P}\right)_V = \frac{V}{nR}$  and  $\frac{V}{nRT} = \frac{1}{P}$  from the perfect gas law. As:  $\left(\frac{\partial V}{\partial T}\right)_S = -\frac{\partial S}{\partial P}_V$  and  $-\frac{\partial S}{\partial P}_V = -\frac{C_V}{P}$ , we can now show that:

$$\left(\frac{\partial V}{\partial T}\right)_S = -\frac{C_V}{P} \quad (4.6.3)$$

Clearly the derivative is negative. This means that if one compresses the volume of an adiabatic system ( $\partial V$  is negative), then the temperature rises ( $\partial T$  is positive). Of course we already knew this about thermally insulated systems!

#### 4.6.1.2 Alternative approach:

$\left(\frac{\partial V}{\partial T}\right)_S$ . Given that we are examining changes in volume at constant system entropy entices me to study a different starting point:  $\partial U = T\partial S - P\partial V$ . Under adiabatic reversible conditions  $\partial U = C_V\partial T$  and  $\partial S = 0 \text{ J/K}$ , leaving us with  $C_V\partial T = -P\partial V$ . A simple rearrangement yields  $\frac{\partial T}{\partial V} = -\frac{P}{C_V}$ , to which we must remember that we have already used the condition of constant entropy. Thus:  $\left(\frac{\partial T}{\partial V}\right)_S = -\frac{P}{C_V}$ , which rearranges to:  $\left(\frac{\partial V}{\partial T}\right)_S = -\frac{C_V}{P}$  as before.

#### 4.6.1.3 Maxwell relation approach:

$\left(\frac{\partial P}{\partial T}\right)_S$ . Similar to the previous example; starting with Equation 4.10:  $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$ , which as before is flipped over:

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

Thus, we need to determine  $\left(\frac{\partial S}{\partial V}\right)_P$ ; to do so we use  $\partial H = T\partial S + V\partial P$  to solve for entropy:

$$\partial S = \frac{1}{T}\partial H - \frac{V}{T}\partial P$$

Next, we divide by the change in volume:  $\frac{\partial S}{\partial V} = \frac{1}{T}\frac{\partial H}{\partial V} - \frac{V}{T}\frac{\partial P}{\partial V}$  and now we apply constant pressure conditions:

$$\left(\frac{\partial S}{\partial V}\right)_P = \frac{1}{T}\left(\frac{\partial H}{\partial V}\right)_P + \frac{V}{T}\left(\frac{\partial P}{\partial V}\right)_P = \frac{1}{T}\left(\frac{\partial H}{\partial V}\right)_P$$

Where the  $2^{nd}$  term is removed because  $\frac{V}{T}\left(\frac{\partial P}{\partial V}\right)_P = 0 \text{ Pa/K}$  due to the condition of constant pressure ( $\partial P = 0 \text{ Pa}$ ). Substituting  $\partial H = C_P\partial T$ :

$$\left(\frac{\partial S}{\partial V}\right)_P = \frac{C_P}{T}\left(\frac{\partial T}{\partial V}\right)_P = \frac{C_P}{T} \frac{P}{nR} = \frac{P \cdot C_P}{nRT} = \frac{C_P}{V}$$

where  $\left(\frac{\partial T}{\partial V}\right)_P = \frac{P}{nR}$  and  $\frac{P}{nRT} = \frac{1}{V}$  are from the perfect gas law. As:  $\left(\frac{\partial P}{\partial T}\right)_S = \left(\frac{\partial S}{\partial V}\right)_P$  and  $\left(\frac{\partial S}{\partial V}\right)_P = \frac{C_P}{V}$ , we can now show that:

$$\left(\frac{\partial P}{\partial T}\right)_S = \frac{C_P}{V} \quad (4.6.4)$$

This derivative is always positive, which means that pressurizing a thermally insulated system increases the temperature.

#### 4.6.1.4 Alternative approach:

$\left(\frac{\partial P}{\partial T}\right)_S$ . Let's tackle  $\left(\frac{\partial P}{\partial T}\right)_S$  again starting with the change in enthalpy:  $\partial H = T\partial S + V\partial P$ . Under adiabatic reversible conditions  $\partial S = 0$  J/K and  $\partial H = C_P\partial T$ , leaving us with  $C_P\partial T = V\partial P$ . A simple rearrangement yields:  $\left(\frac{\partial T}{\partial P}\right)_S = \frac{V}{C_P}$ . This of course rearranges to:  $\left(\frac{\partial P}{\partial T}\right)_S = \frac{C_P}{V}$  as we determined above.

#### 4.6.1.5

$\left(\frac{\partial P}{\partial V}\right)_S$ . This is a harder one because we don't have a good starting point. In this case, we use the Euler Chain formula:  $\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial x}{\partial z}\right)_y$  as:

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

Here we incorporate eqs. 4.11 and 4.12:  $\left(\frac{\partial P}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_S = \frac{P}{C_V}$  and  $\left(\frac{\partial S}{\partial V}\right)_P = \frac{\partial P}{\partial T}_S = \frac{C_P}{V}$ . Putting these together yields:

$$\left(\frac{\partial P}{\partial V}\right)_S = -\frac{C_P}{C_V} \frac{P}{V} \quad (4.6.5)$$

Since the right side is composed of all positive quantities with a negative sign, then we see that pressure increases if volume decreases (and vice versa). While we already knew this, just like the examples above, it is nonetheless comforting to see that our derivations are consistent with the incredibly obvious. You can also use such derivations to determine how adiabatic systems respond to pressure and temperature changes. For example, if we rearrange Equation 4.13 as  $\frac{\partial P}{P} = -\frac{C_P}{C_V} \frac{\partial V}{V}$  and integrate we discover:

$$\ln\left(\frac{P_f}{P_i}\right) = -\frac{C_P}{C_V} \ln\left(\frac{V_f}{V_i}\right)$$

which can be manipulated further into the form:  $\frac{P_f}{P_i} = \left(\frac{V_i}{V_f}\right)^{\frac{C_P}{C_V}}$

Note that you can also arrive at this result using the adiabatic equation of state:  $\left(\frac{T_f}{T_i}\right)^{\frac{C_V}{nR}} = \frac{V_i}{V_f}$  from section 2.5.1.1 by substituting in the perfect gas law for the temperatures; in fact the example problem on pg. demonstrates this exact derivation.

**Conclusion.** Entropy is unequivocally the most important thermodynamic variable. And now you see that energy is not as important as you thought; in fact, all it does is allow you to measure total entropy changes more easily. Up until now all our thermodynamic understandings have come from internal energy and enthalpy, which have entropy as a natural variable. From here on, we will now study constant temperature processes using energy equations that have temperature as a natural variable. And in the process, we will use a Legendre transform to define a thermodynamic variable that you learned so much about in high school and Freshman chemistry- the Gibbs energy.

4.6: Maxwell Relationships is shared under a [not declared](#) license and was authored, remixed, and/or curated by LibreTexts.