

5.4: Advanced Derivations - Maxwell Relationships II

We had a brief introduction to Maxwell relationships in Sec. 4.5. In case you don't recall, a Maxwell relation is based on the Euler test for exactness of a partial function. For the change in a function (i.e., the differential):

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

then if ∂f is an exact partial differential:

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

Since state variables (U, H, A, G, and S) have exact partials, we can use them to derive Maxwell relations with the Euler test. Starting with internal energy:

$$\partial U = T \partial S - P \partial V$$

therefore:

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

, and since $\left(\frac{\partial U}{\partial S} \right)_V = T$ and $\left(\frac{\partial U}{\partial V} \right)_S = -P$, then:

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V \quad (5.4.1)$$

Likewise $\partial H = T \partial S + V \partial P$, which leads to

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

and thus:

$$\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P \quad (5.4.2)$$

These are the relationships derived from Ch. 4. More interesting relationships are derived from:

$$\partial A = -S \partial T - P \partial V \quad \text{and} \quad \partial G = -S \partial T + V \partial P$$

such as:

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V \quad (5.4.3)$$

and:

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P \quad (5.4.4)$$

Equations 5.4.3 and 5.4.4 are especially useful for understanding changes in entropy, which tends to be a very difficult subject.

5.4.1 Using Maxwell Relations

Maxwell relations can reveal many thermodynamic principles, some we have seen already and some that we have not. For example, what can we do with the fact that $\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$ from Equation 5.11? The derivative on the right is easy to determine using the perfect gas equation: $\left(\frac{\partial P}{\partial T} \right)_V = \frac{\partial \left(\frac{nRT}{V} \right)}{\partial T} = \frac{nR}{V}$. Thus, $\left(\frac{\partial S}{\partial V} \right)_T = \frac{nR}{V}$ which is always positive as there is no such thing as negative values for n, R, and V. This means that increasing the volume of a perfect gas at constant temperature will increase the entropy. This makes sense because we previously derived the equation: $\Delta S = nR \cdot \ln \left(\frac{V_f}{V_i} \right)$ that demonstrates the same. In fact, we can re-derive this using:

$$\left(\frac{\partial S}{\partial V} \right)_T = \frac{nR}{V}, \text{ which is rearranging as: } \partial S = \frac{nR}{V} \partial V \text{ and then integrated: } \int_{S_i}^{S_f} \partial S = \Delta S = \int_{V_i}^{V_f} \frac{nR}{V} \partial V = nR \cdot \ln \left(\frac{V_f}{V_i} \right).$$

What if we had started with the Helmholtz Maxwell relation: $\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P$ from Equation 5.12? The derivative on the right is easy to determine using the perfect gas equation: $- \left(\frac{\partial V}{\partial T} \right)_P = - \frac{\partial \left(\frac{nRT}{P} \right)}{\partial T} = - \frac{nR}{P}$. Thus, $\left(\frac{\partial S}{\partial P} \right)_T = - \frac{nR}{P}$ which is always negative. This means that increasing the pressure of a perfect gas at constant temperature will lower the entropy. This makes sense because you must

lower the gas's volume to increase pressure, which we already know will cause the entropy to drop. We can in fact determine the relationship between entropy and pressure changes using: $\left(\frac{\partial S}{\partial P}\right)_T = -\frac{nR}{P}$, which is rearranged as: $\partial S = -\frac{nR}{P} \partial P$ and then integrated: $\int_{S_i}^{S_f} \partial S = \Delta S = -\int_{P_i}^{P_f} \frac{nR}{P} \partial P = nR \cdot \ln\left(\frac{P_i}{P_f}\right)$. If we insert the perfect gas equation for the pressure we find $\Delta S = nR \cdot \ln\left(\frac{\frac{nRT}{V_f}}{\frac{nRT}{V_i}}\right) = nR \cdot \ln\left(\frac{V_i}{V_f}\right)$ as stated before.

5.4.2 Compressibilities

Maxwell relations allow us to understand the thermodynamics behind some measurable physical properties of materials, specifically the expansion coefficient $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$ and the isothermal compressibility $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$. Specifically, we can show that $\left(\frac{\partial S}{\partial V}\right)_T$, $\left(\frac{\partial V}{\partial S}\right)_P$, $\left(\frac{\partial P}{\partial S}\right)_V$, and $\left(\frac{\partial S}{\partial P}\right)_T$ can all be expressed as functions of α and κ_T using the Euler Chain formula $\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$, which rearranges to $\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial x}{\partial z}\right)_y$. $\left(\frac{\partial S}{\partial V}\right)_T$. Start with the Helmholtz Maxwell equation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$. From there we use the Euler Chain Formula: $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T$. Knowing that $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$ and thus $\alpha V = \left(\frac{\partial V}{\partial T}\right)_P$ we can reduce the above to: $\left(\frac{\partial S}{\partial V}\right)_T = -\alpha V \left(\frac{\partial P}{\partial V}\right)_T$. We were given that: $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$, which is rearranged as: $\frac{1}{\kappa_T} = -V \left(\frac{\partial P}{\partial V}\right)_T$ to yield the final result:

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{\alpha}{\kappa_T}$$

$\left(\frac{\partial V}{\partial S}\right)_P$. Starting with the enthalpy Maxwell equation $\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S$ and applying the Euler Chain Formula on the right side: $\left(\frac{\partial T}{\partial P}\right)_S = -\left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial T}{\partial S}\right)_P$. Knowing that $\partial H = T \partial S + V \partial P$, the partial with respect to T at constant P gives $C_P = \left(\frac{\partial H}{\partial T}\right)_P = T \left(\frac{\partial S}{\partial T}\right)_P + V \left(\frac{\partial P}{\partial T}\right)_P = T \left(\frac{\partial S}{\partial T}\right)_P$ and therefore $\frac{T}{C_P} = \left(\frac{\partial T}{\partial S}\right)_P$. Thus the Euler Chain formula above reduces to: $\left(\frac{\partial V}{\partial S}\right)_P = -\frac{T}{C_P} \left(\frac{\partial S}{\partial P}\right)_T$. To get rid of the entropy term we use the Gibbs energy Maxwell Equation $-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$, which leaves us with: $\left(\frac{\partial V}{\partial S}\right)_P = \frac{T}{C_P} \left(\frac{\partial V}{\partial T}\right)_P$. Knowing that $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$ we can reduce this to:

$$\left(\frac{\partial V}{\partial S}\right)_P = \frac{TV\alpha}{C_P}$$

Conclusion

After nearly ~100 pages and 5 chapters of Physical Chemistry I, you finally know all there is to know about how a gas expands and contracts. Congratulations! Now we move into the more practical aspects of thermodynamics, which are the energetics of chemical reactions. The greatest use of this science is the ability to accurately predict reaction yields, which is very useful for industry that produces chemicals on megaton-scales. However, we will now see how limited our understanding of energy is, and how we can at best only relatively understand thermodynamic principles of energy.

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