

8.4: Maxwell Relations

Let's consider the fundamental equations for the thermodynamic potentials that we have derived in [section 8.1](#):

$$\begin{aligned}dU(S, V, \{n_i\}) &= TdS - PdV + \sum_i \mu_i dn_i \\dH(S, P, \{n_i\}) &= TdS + VdP + \sum_i \mu_i dn_i \\dA(T, V, \{n_i\}) &= -SdT - PdV + \sum_i \mu_i dn_i \\dG(T, P, \{n_i\}) &= -SdT + VdP + \sum_i \mu_i dn_i .\end{aligned}$$

From the knowledge of the natural variable of each potential, we could reconstruct these formulas by using the total differential formula:

$$\begin{aligned}dU &= \underbrace{\left(\frac{\partial U}{\partial S}\right)_{V, \{n_i\}}}_T dS + \underbrace{\left(\frac{\partial U}{\partial V}\right)_{S, \{n_i\}}}_{-P} dV + \sum_i \underbrace{\left(\frac{\partial U}{\partial n_i}\right)_{S, V, \{n_{j \neq i}\}}}_{\mu_i} dn_i \\dH &= \underbrace{\left(\frac{\partial H}{\partial S}\right)_{P, \{n_i\}}}_T dS + \underbrace{\left(\frac{\partial H}{\partial P}\right)_{S, \{n_i\}}}_V dP + \sum_i \underbrace{\left(\frac{\partial H}{\partial n_i}\right)_{S, P, \{n_{j \neq i}\}}}_{\mu_i} dn_i \\dA &= \underbrace{\left(\frac{\partial A}{\partial T}\right)_{V, \{n_i\}}}_{-S} dT + \underbrace{\left(\frac{\partial A}{\partial V}\right)_{T, \{n_i\}}}_{-P} dV + \sum_i \underbrace{\left(\frac{\partial A}{\partial n_i}\right)_{T, V, \{n_{j \neq i}\}}}_{\mu_i} dn_i \\dG &= \underbrace{\left(\frac{\partial G}{\partial T}\right)_{P, \{n_i\}}}_{-S} dT + \underbrace{\left(\frac{\partial G}{\partial P}\right)_{T, \{n_i\}}}_V dP + \sum_i \underbrace{\left(\frac{\partial G}{\partial n_i}\right)_{T, P, \{n_{j \neq i}\}}}_{\mu_i} dn_i ,\end{aligned}$$

we can derive the following new definitions:

$$\begin{aligned}T &= \left(\frac{\partial U}{\partial S}\right)_{V, \{n_i\}} = \left(\frac{\partial H}{\partial S}\right)_{P, \{n_i\}} \\-P &= \left(\frac{\partial U}{\partial V}\right)_{S, \{n_i\}} = \left(\frac{\partial A}{\partial V}\right)_{T, \{n_i\}} \\V &= \left(\frac{\partial H}{\partial P}\right)_{S, \{n_i\}} = \left(\frac{\partial G}{\partial P}\right)_{T, \{n_i\}} \\-S &= \left(\frac{\partial A}{\partial T}\right)_{V, \{n_i\}} = \left(\frac{\partial G}{\partial T}\right)_{P, \{n_i\}}\end{aligned}$$

and:

$$\begin{aligned}\mu_i &= \left(\frac{\partial U}{\partial n_i}\right)_{S, V, \{n_{j \neq i}\}} = \left(\frac{\partial H}{\partial n_i}\right)_{S, P, \{n_{j \neq i}\}} \\&= \left(\frac{\partial A}{\partial n_i}\right)_{T, V, \{n_{j \neq i}\}} = \left(\frac{\partial G}{\partial n_i}\right)_{T, P, \{n_{j \neq i}\}} .\end{aligned}$$

Since T , P , V , and S are now defined as partial first derivatives of a thermodynamic potential, we can now take a second partial derivation with respect to a separate variable, and rely on Schwartz's theorem to derive the following relations:

$$\begin{aligned}
 \frac{\partial^2 U}{\partial S \partial V} &= + \left(\frac{\partial T}{\partial V} \right)_{S, \{n_{j \neq i}\}} = - \left(\frac{\partial P}{\partial S} \right)_{V, \{n_{j \neq i}\}} \\
 \frac{\partial^2 H}{\partial S \partial P} &= + \left(\frac{\partial T}{\partial P} \right)_{S, \{n_{j \neq i}\}} = + \left(\frac{\partial V}{\partial S} \right)_{P, \{n_{j \neq i}\}} \\
 - \frac{\partial^2 A}{\partial T \partial V} &= + \left(\frac{\partial S}{\partial V} \right)_{T, \{n_{j \neq i}\}} = + \left(\frac{\partial P}{\partial T} \right)_{V, \{n_{j \neq i}\}} \\
 \frac{\partial^2 G}{\partial T \partial P} &= - \left(\frac{\partial S}{\partial P} \right)_{T, \{n_{j \neq i}\}} = + \left(\frac{\partial V}{\partial T} \right)_{P, \{n_{j \neq i}\}}
 \end{aligned} \tag{8.4.1}$$

The relations in 8.4.1 are called **Maxwell relations**,¹ and are useful in experimental settings to relate quantities that are hard to measure with others that are more intuitive.

? Exercise 8.4.1

Derive the last Maxwell relation in Equation 8.4.1.

Answer

We can start our derivation from the definition of V and S as a partial derivative of G :

$$V = \left(\frac{\partial G}{\partial P} \right)_{T, \{n_i\}} \quad \text{and:} \quad -S = \left(\frac{\partial G}{\partial T} \right)_{P, \{n_i\}},$$

and then take a second partial derivative of each quantity with respect to the second variable:

$$\begin{aligned}
 \left(\frac{\partial V}{\partial T} \right)_{P, \{n_i\}} &= \frac{\partial}{\partial T} \left[\left(\frac{\partial G}{\partial P} \right)_{T, \{n_i\}} \right]_{P, \{n_i\}} \\
 - \left(\frac{\partial S}{\partial P} \right)_{T, \{n_i\}} &= \frac{\partial}{\partial P} \left[\left(\frac{\partial G}{\partial T} \right)_{P, \{n_i\}} \right]_{T, \{n_i\}}.
 \end{aligned}$$

These two derivatives are mixed partial second derivatives of G with respect to T and P , and therefore, according to Schwartz's theorem, they are equal to each other:

$$\frac{\partial}{\partial T} \left[\left(\frac{\partial G}{\partial P} \right)_{T, \{n_i\}} \right]_{P, \{n_i\}} = \frac{\partial}{\partial P} \left[\left(\frac{\partial G}{\partial T} \right)_{P, \{n_i\}} \right]_{T, \{n_i\}},$$

hence:

$$\left(\frac{\partial V}{\partial T} \right)_{P, \{n_i\}} = - \left(\frac{\partial S}{\partial P} \right)_{T, \{n_i\}},$$

which is the last of Maxwell relations, as defined in Equation 8.4.1. This relation is particularly useful because it connects the quantity $\left(\frac{\partial S}{\partial P} \right)_{T, \{n_i\}}$ —which is impossible to measure in a lab—with the quantity $\left(\frac{\partial V}{\partial T} \right)_{P, \{n_i\}}$ —which is easier to measure from an experiment that determines isobaric volumetric thermal expansion coefficients.

1. Maxwell relations should not be confused with the Maxwell equations of electromagnetism.