Maxwell Relations

Consider the derivative

\[ \left( \frac{\partial S}{\partial V} \right)_T. \] (1)

Recalling that

\[ S = - \left( \frac{\partial F}{\partial T} \right)_V, \] (2)

we have

\[ \left( \frac{\partial S}{\partial V} \right)_T = \frac{\partial^2 F(V,T)}{\partial V \partial T}. \] (3)

The function \( F(V,T) \) normally is a regular function of its two variables, and we can swap the partial derivatives:

\[ \frac{\partial^2 F(V,T)}{\partial V \partial T} = \frac{\partial^2 F(V,T)}{\partial T \partial V}. \] (4)

Then, recalling that

\[ \left( \frac{\partial F}{\partial V} \right)_T = -P, \] (5)

we see that

\[ \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V. \] (6)

This equality and analogous equalities following just from swapping variables in the mixed second-order partial derivatives are called Maxwell relations. These are general thermodynamic relations valid for all systems. To obtain all the Maxwell relations, consider the following purely mathematical situation. Suppose some quantity \( A \) is a function of two variables, \( B \) and \( C \) (just for the sake of briefness—the actual number of variables can be arbitrarily large). Then the differential of \( A \) can be written as

\[ dA = X \, dB + Y \, dC, \] (7)

where

\[ X = \left( \frac{\partial A}{\partial B} \right)_C, \quad Y = \left( \frac{\partial A}{\partial C} \right)_B. \] (8)

Then we have

\[ \left( \frac{\partial X}{\partial C} \right)_B = \frac{\partial^2 A(B,C)}{\partial C \partial B} = \frac{\partial^2 A(B,C)}{\partial B \partial C} = \left( \frac{\partial Y}{\partial B} \right)_C. \] (9)

So far, we have obtained just a direct analog of (6). But then we do the following trick. We consider the quantity

\[ \tilde{A} = A - XB, \] (10)

and note that

\[ d\tilde{A} = d(A - XB) = -B \, dX + Y \, dC. \] (11)

Hence,

\[ \left( \frac{\partial B}{\partial C} \right)_X = -\frac{\partial^2 \tilde{A}(X,C)}{\partial C \partial X} = -\frac{\partial^2 \tilde{A}(X,C)}{\partial C \partial X} = -\left( \frac{\partial Y}{\partial X} \right)_C. \] (12)

That is the relation (7) always implies

\[ \left( \frac{\partial B}{\partial C} \right)_X = -\left( \frac{\partial Y}{\partial X} \right)_C. \] (13)
Eq. (10) is called Legendre transformation.

Let us apply Legendre transformation to the function $F(V,T)$. If instead of the pair $(V,T)$ we want to have $(S,T)$, then the “transformed” $F$ is nothing else then energy, since
\[ F + TS = E , \] (14)
and
\[ dE = T dS - P dV . \] (15)

And the corresponding Maxwell relation is
\[ \left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial P}{\partial S} \right)_V . \] (16)

There are two more Legendre transformations:
\[ H = E + PV , \quad dH = T dS + V dP \quad \text{(Enthalpy)} , \] (17)
\[ G = F + PV , \quad dG = -S dT + V dP \quad \text{(Gibbs Free Energy)} . \] (18)

**Problem 41.** Establish two Maxwell relations corresponding to Eqs. (17) and (18).

**Problem 42.** Show that
\[ C_P = \left( \frac{\partial H}{\partial T} \right)_P . \] (19)

**Problem 43.** Establish all Maxwell-type relations following from the equality
\[ d\Omega = -S dT - P dV - N d\mu . \] (20)