

Thermodynamic Potentials and Maxwell's Relations

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February 25, 2003

Introduction

In this lecture we introduce other thermodynamic potentials and Maxwell relations.

The energy and entropy representations

We have noted that both $S(U, V, N)$ and $U(S, V, N)$ contain complete thermodynamic information. We will use the fundamental thermodynamic identity

$$dU = TdS - pdV + \mu dN$$

as an aid to memorizing the of temperature, pressure, and chemical potential from the consideration of equilibrium conditions. by calculating the appropriate partial derivatives we have

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T,$$

$$\left(\frac{\partial U}{\partial V}\right)_{S,N} = -p,$$

and

$$\left(\frac{\partial U}{\partial N}\right)_{S,N} = \mu.$$

We can also write the fundamental thermodynamic identity in the entropy representation:

$$dS = \frac{dU}{T} + \frac{p}{T}dV - \frac{\mu}{T}dN$$

from which we find

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T},$$

$$\left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{p}{T},$$

and

$$\left(\frac{\partial S}{\partial N}\right)_{U,N} = -\frac{\mu}{T}.$$

By calculating the second partial derivatives of these quantities we find the Maxwell relations. Maxwell relations can be used to relate partial derivatives that are easily measurable to those that are not. Starting from

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T, \text{ and } \left(\frac{\partial U}{\partial V}\right)_{S,N} = -p,$$

we can calculate

$$\frac{\partial^2 U}{\partial V \partial S} = \left(\frac{\partial T}{\partial V}\right)_{S,N}, \text{ and } \frac{\partial^2 U}{\partial S \partial V} = -\left(\frac{\partial p}{\partial S}\right)_{V,N}.$$

Now since under appropriate conditions

$$\frac{\partial^2 U}{\partial V \partial S} = \text{ and } \frac{\partial^2 U}{\partial S \partial V}$$

then

$$\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial p}{\partial S}\right)_{V,N}.$$

This result is called a Maxwell relation. By considering the other second partial derivatives, we find two other Maxwell relations from the energy representation of the fundamental thermodynamic identity. These are:

$$\left(\frac{\partial T}{\partial N}\right)_{S,V} = \left(\frac{\partial \mu}{\partial S}\right)_{V,N} \text{ and } -\left(\frac{\partial p}{\partial N}\right)_{S,V} = \left(\frac{\partial \mu}{\partial V}\right)_{S,N}.$$

Similarly, in the entropy representation, starting from

$$dS = \frac{dU}{T} + \frac{p}{T}dV - \frac{\mu}{T}dN$$

and the results

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T}, \left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{p}{T}, \text{ and } \left(\frac{\partial S}{\partial N}\right)_{U,N} = -\frac{\mu}{T}.$$

we find the Maxwell relations:

$$\left(\frac{\partial \left(\frac{1}{T}\right)}{\partial V}\right)_{U,N} = \left(\frac{\partial \left(\frac{p}{T}\right)}{\partial U}\right)_{V,N}, \left(\frac{\partial \left(\frac{1}{T}\right)}{\partial N}\right)_{U,V} = -\left(\frac{\partial \left(\frac{\mu}{T}\right)}{\partial U}\right)_{V,N} \text{ and } \left(\frac{\partial \left(\frac{p}{T}\right)}{\partial N}\right)_{U,V} = -\left(\frac{\partial \left(\frac{\mu}{T}\right)}{\partial V}\right)_{U,N}.$$

Enthalpy $H(S,p,N)$

We have already defined enthalpy as $H = U + pV$. We can calculate its differential and combine it with the fundamental thermodynamic identity to show that the natural variables of H are S , p , and N .

$$H = U + pV$$

we have

$$dH = dU + d(pV) = dU + pdV + Vdp,$$

and so inserting

$$dU = TdS - pdV + \mu dN$$

we have

$$dH = TdS - pdV + \mu dN + pdV + Vdp$$

resulting in

$$dH = TdS + Vdp + \mu dN.$$

Thus, we can see that we can write $H = H(S, p, N)$, and as already noted S , p , and N are the natural variables of H . We can continue as above to generate the definitions

$$\left(\frac{\partial H}{\partial S}\right)_{p,N} = T, \quad \left(\frac{\partial H}{\partial p}\right)_{S,N} = V, \quad \text{and} \quad \left(\frac{\partial H}{\partial N}\right)_{S,p} = \mu.$$

and the Maxwell relations

$$\left(\frac{\partial T}{\partial p}\right)_{S,N} = \left(\frac{\partial V}{\partial S}\right)_{p,N}, \quad \left(\frac{\partial T}{\partial N}\right)_{S,p} = \left(\frac{\partial \mu}{\partial S}\right)_{p,N} \quad \text{and} \quad \left(\frac{\partial V}{\partial N}\right)_{S,p} = \left(\frac{\partial \mu}{\partial p}\right)_{S,N}.$$

In the above, as we transformed from U to H , we changed independent variables, *i.e.*, we replaced the variable V with its conjugate p . (Variables x and y that are related through the partial derivative of some function ξ such that $\frac{\partial \xi}{\partial x} = y$ are called conjugate variables.) This is an example of a *Legendre transform*. In a Legendre transform, to replace one independent variable with its conjugate, a new function ζ is defined by the addition or subtraction of the product of the conjugates x and y . In other words we define $\zeta = \xi \pm xy$. In the case of enthalpy we added pV , as we shall see, this was due to the presence of the term pdV in the fundamental thermodynamic identity. To eliminate the variables S and N in terms of their conjugates, it will be necessary to subtract the products of the conjugate variables, as we shall soon see.

Helmholtz Free Energy $F(T,V,N)$

This time we as we transform from U to F , we replace the independent variable S with its conjugate T . In a Legendre transform, to replace one independent variable with its conjugate, a new function

is defined by the addition or subtraction of the product of the conjugates. Thus in this case we define the new function F by subtracting TS from U .

Starting from

$$F(T, V, N) = U(S, V, N) - TS$$

calculating the differentials

$$dF = dU - d(TS) = dU - TdS - SdT,$$

then inserting

$$dU = TdS - pdV + \mu dN$$

we find

$$dF = TdS - pdV + \mu dN - TdS - SdT$$

resulting in

$$dF = -SdT - pdV + \mu dN.$$

Thus, we have $F = F(T, V, N)$ as desired. We continue as above to generate the definitions

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S, \quad \left(\frac{\partial F}{\partial V}\right)_{T,N} = -p, \quad \text{and} \quad \left(\frac{\partial F}{\partial N}\right)_{T,V} = \mu.$$

and the Maxwell relations

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial p}{\partial T}\right)_{V,N}, \quad \left(\frac{\partial S}{\partial N}\right)_{T,V} = -\left(\frac{\partial \mu}{\partial T}\right)_{V,N} \quad \text{and} \quad \left(\frac{\partial p}{\partial N}\right)_{T,V} = \left(\frac{\partial \mu}{\partial V}\right)_{T,N}.$$

Gibbs Free Energy $G(T,p,N)$

This time we as we transform from U to G , we replace the independent variables S and V with their conjugates T and p . We can think of this as a double Legendre transform of U or a single Legendre transform of either H or F .

Starting from

$$G(T, p, N) = U(S, V, N) - TS + pV$$

calculating the differentials

$$dG = dU - d(TS) + d(pV) = dU - TdS - SdT + pdV + Vdp,$$

then inserting

$$dU = TdS - pdV + \mu dN$$

we find

$$dG = TdS - pdV + \mu dN - TdS - SdT + pdV + Vdp$$

resulting in

$$dG = -SdT + Vdp + \mu dN.$$

Thus, we have $G = G(T, p, N)$ as desired. We continue as above to generate the definitions

$$\left(\frac{\partial G}{\partial T}\right)_{p,N} = -S, \quad \left(\frac{\partial G}{\partial p}\right)_{T,N} = V, \quad \text{and} \quad \left(\frac{\partial G}{\partial N}\right)_{T,p} = \mu.$$

and the Maxwell relations

$$\left(\frac{\partial S}{\partial p}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{p,N}, \quad \left(\frac{\partial S}{\partial N}\right)_{T,p} = -\left(\frac{\partial \mu}{\partial T}\right)_{p,N} \quad \text{and} \quad \left(\frac{\partial V}{\partial N}\right)_{T,p} = \left(\frac{\partial \mu}{\partial p}\right)_{T,N}.$$

The Grand Potential $\Omega(T, V, \mu)$

This time as we transform from U to Ω , we replace the independent variables V and N with their conjugates, p and μ . We can think of this as a double Legendre transform of U or a single transform of F . The grand potential is far less common in elementary work than the other potentials. It is used in open systems, that is systems that can exchange particles with the environment. We will, however, make some use of it.

Starting from

$$\Omega(T, V, \mu) = U(S, V, N) - TS - \mu N$$

calculating the differentials

$$d\Omega = dU - d(TS) - d(\mu N) = dU - SdT - TVdS - \mu dN - Nd\mu,$$

then inserting

$$dU = TdS - pdV + \mu dN$$

we find

$$d\Omega = TdS - pdV + \mu dN - TdS - SdT - \mu dN - Nd\mu$$

resulting in

$$d\Omega = -pdV - SdT - Nd\mu.$$

Thus, we have $\Omega = \Omega(T, V, \mu)$ as desired. We continue as above to generate the definitions

$$\left(\frac{\partial \Omega}{\partial V}\right)_{T,\mu} = -p, \quad \left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu} = -S, \quad \text{and} \quad \left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V} = -N.$$

and the Maxwell relations

$$\left(\frac{\partial p}{\partial T}\right)_{V,\mu} = \left(\frac{\partial S}{\partial V}\right)_{T,\mu}, \quad \left(\frac{\partial p}{\partial \mu}\right)_{T,V} = -\left(\frac{\partial N}{\partial V}\right)_{T,\mu} \quad \text{and} \quad \left(\frac{\partial S}{\partial \mu}\right)_{T,V} = \left(\frac{\partial N}{\partial T}\right)_{V,\mu}.$$