Unit 1-5: Free Energies

Having found the Legendre transform, we are now able to apply it to our thermodynamic problem of how to convert, for example, from the variable entropy S to the variable temperature T.

Helmholtz Free Eneregy $\boldsymbol{A(T, V, N)}$

If we want a formulation of thermodynamics in which temperature T, rather than entropy S, is regarded as an independent variable, all we have to do is to take the Legendre transform of the energy $E(S, V, N)$, transforming from the variable S to its conjugate variable $T = (\partial E/\partial S)_{V,N}$.

$$E(S, V, N), \qquad \text{with} \qquad \left(\frac{\partial E}{\partial S}\right)_{V,N} = T(S, V, N) \tag{1.5.1}$$

transform to

$$A(T, V, N) = E - TS \qquad \text{with} \qquad \left(\frac{\partial A}{\partial T}\right)_{V,N} = -S(T, V, N) \tag{1.5.2}$$

The function $A(T, V, N)$ is called the *Helmholtz free energy* (note, in some texts the Helmholtz free energy is denoted as F).

To construct $A(T, V, N)$ the prescription is:

From $\left(\frac{\partial E}{\partial S}\right)_{V,N} = T(S, V, N)$ we invert this function with respect to S to get $S(T, V, N)$. Then we substitute that in to get A,

$$A(T, V, N) = E(S(T, V, N), V, N) - TS(T, V, N) \tag{1.5.3}$$

We can explicitly confirm that $(\partial A/\partial T)_{V,N} = -S$ as follows:

By the chain rule,

$$\left(\frac{\partial A}{\partial T}\right)_{V,N} = \left(\frac{\partial E}{\partial S}\right)_{V,N} \left(\frac{\partial S}{\partial T}\right)_{V,N} - T\left(\frac{\partial S}{\partial T}\right)_{V,N} - S(T, V, N) \tag{1.5.4}$$

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

$$\left(\frac{\partial A}{\partial T}\right)_{V,N} = T\left(\frac{\partial S}{\partial T}\right)_{V,N} - T\left(\frac{\partial S}{\partial T}\right)_{V,N} - S(T, V, N) = -S(T, V, N) \tag{1.5.5}$$

Similarly we can consider the other first partial derivatives of A.

$$\left(\frac{\partial A}{\partial V}\right)_{T,N} = \left(\frac{\partial E}{\partial S}\right)_{V,N} \left(\frac{\partial S}{\partial V}\right)_{T,N} + \left(\frac{\partial E}{\partial V}\right)_{S,N} - T\left(\frac{\partial S}{\partial V}\right)_{T,N} \tag{1.5.6}$$

$$= T\left(\frac{\partial S}{\partial V}\right)_{T,N} + \left(\frac{\partial E}{\partial V}\right)_{S,N} - T\left(\frac{\partial S}{\partial V}\right)_{T,N} \tag{1.5.7}$$

$$= \left(\frac{\partial E}{\partial V}\right)_{S,N} = -p \tag{1.5.8}$$

Similarly we can show,

$$\left(\frac{\partial A}{\partial N}\right)_{T,V} = \left(\frac{\partial E}{\partial N}\right)_{S,N} = \mu(T, V, N) \tag{1.5.9}$$

So the partials of A with respect to variables that were not involved in the Legendre transform (i.e. V and N) behave just like the corresponding partials of E.

We can now write for the differential of A,

$$dA = \left(\frac{\partial A}{\partial T}\right)_{V,N} dT + \left(\frac{\partial A}{\partial V}\right)_{T,N} dV + \left(\frac{\partial A}{\partial N}\right)_{T,V} dN \tag{1.5.10}$$

$$\boxed{dA = -SdT - pdV + \mu dN} \tag{1.5.11}$$

Also, since the Euler relation gives $E = TS - pV + \mu N$, and $A = E - TS$, we have,

$$\boxed{A = -pV + \mu N} \tag{1.5.12}$$

Enthalpy $\boldsymbol{H(S, p, N)}$

When one wants to use pressure instead of volume, one constructs the *enthalpy* $H(S, p, N)$ by taking a Legendre transform of $E(S, V, N)$ from V to p.

$$E(S, V, N) \qquad \text{with} \qquad \left(\frac{\partial E}{\partial V}\right)_{S,N} = -p \tag{1.5.13}$$

transform to

$$H(S, p, N) = E + pV \qquad \text{with} \qquad \left(\frac{\partial H}{\partial p}\right)_{S,N} = V \tag{1.5.14}$$

Note, since $(\partial E/\partial V)_{S,N} = -p$, with the minus sign, the conjugate variable to V is really $-p$. That is why we define the enthalpy as $H = E - (-p)V = E + pV$, and $(\partial H/\partial(-p))_{S,N} = -V \quad \Rightarrow \quad (\partial H/\partial p)_{S,N} = V$

One can also show that,

$$\left(\frac{\partial H}{\partial S}\right)_{p,N} = T \qquad \text{and} \qquad \left(\frac{\partial H}{\partial N}\right)_{S,N} = \mu \tag{1.5.15}$$

As we saw with A, the partials with respect to the variables that are not involved in the Legendre transform remain the same as the partials of E.

The differential of the enthalpy is then

$$dH = \left(\frac{\partial H}{\partial S}\right)_{p,N} dS + \left(\frac{\partial H}{\partial p}\right)_{S,N} dp + \left(\frac{\partial H}{\partial N}\right)_{S,p} dN \tag{1.5.16}$$

$$\boxed{dH = TdS + Vdp + \mu dN} \tag{1.5.17}$$

Since the Euler relation is $E = TS - pV + \mu N$, and $H = E + pV$, we have,

$$\boxed{H = TS + \mu N} \tag{1.5.18}$$

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

When we want to use both temperature T and pressure p instead of entropy S and volume V, we make a Legendre transform with respect to both variables S and V.

$$E(S, V, N) \qquad \text{with} \qquad \left(\frac{\partial E}{\partial S}\right)_{V,N} = T, \qquad \text{and} \qquad \left(\frac{\partial E}{\partial V}\right)_{S,N} = -p \tag{1.5.19}$$

transform to the *Gibbs free energy* G,

$$G(T, p, N) = E - TS + pV \qquad \text{with} \qquad \left(\frac{\partial G}{\partial T}\right)_{p,N} = -S, \qquad \text{and} \qquad \left(\frac{\partial G}{\partial p}\right)_{T,N} = V \tag{1.5.20}$$

Also,

$$\left(\frac{\partial G}{\partial N}\right)_{T,p} = \mu \qquad \text{since} \qquad \left(\frac{\partial E}{\partial N}\right)_{S,V} = \mu \tag{1.5.21}$$

The differential of the Gibbs free energy is then,

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p,N} dT + \left(\frac{\partial G}{\partial p}\right)_{T,N} dp + \left(\frac{\partial G}{\partial N}\right)_{T,p} dN \tag{1.5.22}$$

$$\boxed{dG = -SdT + Vdp + \mu dN} \tag{1.5.23}$$

Since the Euler relation is $E = TS - pV + \mu N$, and $G = E - TS + pV$, we have,

$$\boxed{G = \mu N \qquad \text{or} \qquad \frac{G}{N} \equiv g = \mu} \tag{1.5.24}$$

The chemical potential is therefore just the Gibbs free energy per particle g.

From $G = \mu N$ we get $dG = \mu dN + Nd\mu$. Subtracting from that $dG = -SdT + Vdp + \mu dN$ one gets,

$$0 = [\mu dN + Nd\mu] - [-SdT + Vdp + \mu dN] = \boxed{SdT - Vdp + Nd\mu = 0} \tag{1.5.25}$$

which is just the Gibbs-Duhem relation!

Note: If one were dealing with a system with more than one species of particles, i.e. N_1 of type 1, N_2 of type 3, N_3 of type 3, etc., then the energy E, and so the Gibbs free energy G, would depend on each N_i separately. We then have,

$$\left(\frac{\partial E}{\partial N_i}\right)_{S,V,N_{j\neq i}} = \left(\frac{\partial G}{\partial N_i}\right)_{T,p,N_{j\neq i}} = \mu_i \qquad \text{the chemical potential for species } i \tag{1.5.26}$$

The Euler relation becomes $E = TS - pV + \mu_1 N_1 + \mu_2 N_2 + \mu_3 N_3 + \ldots$, and then we get

$$G(T, p, N_1, N_2, N_3, \ldots) = \mu_1 N_1 + \mu_2 N_2 + \mu_3 N_3 + \ldots \tag{1.5.27}$$

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

Now we wish to use temperature T and chemical potential μ instead of entropy S and number of particles N. So we make a Legendre transform on both S and N.

$$E(S, V, N) \qquad \text{with} \qquad \left(\frac{\partial E}{\partial S}\right)_{V,N} = T, \qquad \text{and} \qquad \left(\frac{\partial E}{\partial N}\right)_{S,V} = \mu \tag{1.5.28}$$

transform to the *Grand Potential* Φ,

$$\Phi(T,V,\mu) = E - TS - \mu N \qquad \text{with} \qquad \left(\frac{\partial \Phi}{\partial T}\right)_{V,\mu} = -S, \qquad \text{and} \qquad \left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} = -N \tag{1.5.29}$$

Also

$$\left(\frac{\partial \Phi}{\partial V}\right)_{T,\mu} = -p \qquad \text{since} \qquad \left(\frac{\partial E}{\partial V}\right)_{S,N} = -p \tag{1.5.30}$$

The differential of the Grand Potential is then,

$$d\Phi = \left(\frac{\partial \Phi}{\partial T}\right)_{V,\mu} dT + \left(\frac{\partial \Phi}{\partial V}\right)_{T,\mu} dV + \left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} d\mu \tag{1.5.31}$$

$$\boxed{d\Phi = -SdT - pdV - Nd\mu} \tag{1.5.32}$$

Since the Euler relation is $E = TS - pV + \mu N$, and $\Phi = E - TS - \mu N$, we have,

$$\boxed{\Phi = -pV \qquad \text{or} \qquad -\frac{\Phi}{V} = p} \tag{1.5.33}$$

The pressure p is $(-)$ the grand potential per unit volume.

The free energies discussed above were obtained, working in the energy formulation, as Legendre transforms of the energy $E(S,V,N)$. We could also have gotten similar results working in the entropy formulation, by taking Legendre transforms of the entropy $S(E,V,N)$. It is useful to summarize this alternative way.

Recall, for $S(E,V,N)$,

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T}, \qquad \left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{p}{T} \qquad \left(\frac{\partial S}{\partial N}\right)_{E,NV} = -\frac{\mu}{T} \tag{1.5.34}$$

So if we take the Legendre transform of S from E to $\frac{1}{T}$ we get $S - \frac{E}{T}$. Recalling $A = E - TS$ then gives $S = \frac{E}{T} - \frac{A}{T}$, and so,

$$\boxed{S - \frac{E}{T} = -\frac{A}{T}} \tag{1.5.35}$$

If we take the Legendre transform of S from E to $\frac{1}{T}$ *and* from V to $\frac{p}{T}$ we get $S - \frac{E}{T} - \frac{pV}{T}$. Recalling $G = E - TS + pV$ then gives $S = \frac{E}{T} + \frac{pV}{T} - \frac{G}{T}$, and so,

$$\boxed{S - \frac{E}{T} - \frac{pV}{T} = -\frac{G}{T}} \tag{1.5.36}$$

And if we take the Legendre transform of S from E to $\frac{1}{T}$ *and* from N to $-\frac{\mu}{T}$ we get $S - \frac{E}{T} + \frac{\mu N}{T}$. Recalling $\Phi = E - TS - \mu N$ then gives $S = \frac{E}{T} - \frac{\mu N}{T} - \frac{\Phi}{T}$, and so,

$$\boxed{S - \frac{E}{T} + \frac{\mu N}{T} = -\frac{\Phi}{T}} \tag{1.5.37}$$

So when taking the Legendre transform of S, we get the corresponding potential that we get when transforming E, multiplied by $-1/T$.