

5.2: Gibbs Energy

Gibbs energy is the ultimate Legendre transform as we must remove both natural variables of internal energy (S and V) and put them on their conjugates, T and -P. Hopefully this is rather obvious at this point:

$$G = U + PV - TS \quad (5.2.1)$$

We can establish the natural variables by determining the change in the Gibbs energy function:

$$\partial G = \partial U + \partial(PV) - \partial(TS)$$

Since $\partial U = -P\partial V + T\partial S$, $\partial(PV) = P\partial V + V\partial P$, and $\partial(TS) = T\partial S + S\partial T$:

$$\partial G = -P\partial V + T\partial S + P\partial V + V\partial P - T\partial S - S\partial T$$

which simplifies to:

$$\partial G = V\partial P - S\partial T \quad (5.2.2)$$

We can derive Equation 5.6 faster if we started with enthalpy, since $H = U + PV$ and H already has P as a natural variable. We simply Legendre transform away enthalpy's dependence on entropy:

$$G = H - TS \quad (5.2.3)$$

Taking the change of this function reveals:

$$\partial G = \partial H - \partial(TS) = V\partial P + S\partial T - T\partial S - S\partial T$$

which simplifies to Equation 5.6:

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

Regardless of the approach we see that the natural variables of Gibbs energy are pressure and temperature, i.e. G(T,P).

As with Helmholtz energy, Gibbs energy has special meanings when its natural variables are held constant. For instance, under constant temperature conditions $\partial G = V\partial P$. We expected ∂G to be reversible work, just like the change in Helmholtz energy at constant temperature, but that doesn't appear to be the case. Or is it? To investigate further, first calculate the change in G with respect to V at constant T:

$$\left(\frac{\partial G}{\partial V}\right)_T = V\left(\frac{\partial P}{\partial V}\right)_T$$

If we insert the perfect gas law then:

$$\left(\frac{\partial G}{\partial V}\right)_T = V\left(\frac{-nRT}{V^2}\right) = V\left(\frac{-P}{V}\right) = -P$$

Since we can "juggle" the partials algebraically, we can bring ∂V to the right to show:

$$\partial G = -P\partial V = \partial w_{rev}$$

under constant temperature conditions. So, like Helmholtz energy, Gibbs energy is also reversible work at constant T.

Last, under consideration is at constant temperature and pressure a negative change in Gibbs energy is the same as a positive change in total entropy. This proof of spontaneity is left to you as a problem at the end of this chapter. Regardless, Gibbs energy is special because nearly all processes that occur in Nature are under constant temperature and pressure conditions. Note that we also told you in high school that only negative changes in Gibbs energy were spontaneous. This was a lie, because if we lived in a constant entropy and volume world you would have learned that only negative changes in internal energy define spontaneity.

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