

We begin with the now-familiar thermodynamic identity

$$dU = TdS - pdV$$

Remember in the Interlude I talked about what if one of the weights were hidden in the black box, so you could not change it, or measure its position? Now we get to see why.

Helmholtz Free Energy

Imagine for a moment that you have no decent insulation, so you cannot prevent heating of your system by its surroundings (the room), and you have no effective way to measure how much energy was transferred by heating. Under these constraints (which are pretty easy to imagine), you cannot possibly measure the internal energy by integrating the thermodynamic identity. However, the **difference between the internal energy and the amount of energy gained by heating** you could measure. That is just the work. For fixed temperature, we can write this quantity as a state property:

$$F \equiv U - TS$$

Now we can work out the total differential of F via

$$dF = dU - TdS - SdT \quad (1)$$

$$= TdS - pdV - TdS - SdT \quad (2)$$

$$= -SdT - pdV \quad (3)$$

This quantity F is called the **Helmholtz free energy** and a change in ΔF is equal to the amount of work done on a system, provided you hold the temperature fixed.

Enthalpy

The volume is also challenging. Holding the volume fixed requires a very strong container with a very low coefficient of thermal expansion. This can be awkward. Things can be much simpler if we keep the pressure fixed... even more so if we don't measure the change in volume. After all, frictionless pistons are hard to come by. So if we imagine that the pressure is fixed and we cannot conveniently measure volume, then the work done on a system becomes unmeasurable, and we cannot find the change in internal energy of a system.

As above, we can now define a state function that is like the energy with the work subtracted out for the fixed-pressure (isobaric) case:

$$H \equiv U + pV$$

Now we can work out the total differential of H via

$$dH = dU + pdV + Vdp \quad (4)$$

$$= TdS - pdV + pdV + Vdp \quad (5)$$

$$= TdS + Vdp \quad (6)$$

It is now clear that at fixed pressure a change in this **enthalpy** ΔH will tell you how much heat is released or gained by the system when a system undergoes a change. In chemistry terms, this tells us if a reaction is exothermic or endothermic.

Gibbs Free Energy

Finally, we have the case where we want to hold both the pressure and temperature fixed. This is usually a boring case, unless something “else” is changing. One example where this is very relevant is when we encounter a phase transition. As you were melting ice, you saw that the temperature and pressure both remained fixed, even though the system was changing. The Gibbs free energy in this case is not changing, meaning that the ice and water both have the same Gibbs free energy per particle. The other case where Gibbs free energy is of interest is in chemistry or biology, where the number of molecules is changing due to a chemical reaction.

The **Gibbs free energy** is given by

$$G = U + pV - TS$$

And its total differential is given by

$$dG = dU + pdV + VdP - TdS - SdT \quad (7)$$

$$= TdS - pdV + pdV + VdP - TdS - SdT \quad (8)$$

$$= -SdT + Vdp \quad (9)$$