

19.8: Pressure-Volume Work

Enthalpy

An important point is that pressure-volume work $-PdV$ is only one kind of work. It is the important one for gases but for most other systems we are interested in other kinds of work (e.g. electrical work in a battery).

A good way to measure ΔU 's is to make sure there are no work terms at all. If so:

$$\Delta U_{\text{nowork}} = q + w = q + 0 = q$$

However, this means that the $-PdV$ volume work term should also be zero and this implies we must keep volumes the same. That can actually be hard. Therefore we define a new state function ENTHALPY

$$H \equiv U + PV$$

(The \equiv symbol is used to show that this equality is actually a definition.)

If we differentiate we get:

$$dH = dU + d(PV) = dU + PdV + VdP$$

We know that under reversible conditions we have

$$dU = \delta w + \delta q = -PdV + \delta q$$

(+ other work terms that we assume zero)

Thus,

$$dH = -PdV + \delta q + PdV + VdP$$

$$dH = \delta q + VdP$$

That means that as long as there is no other work and we keep the pressure constant:

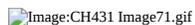
$$\Delta H = q_P$$

instead of

$$\Delta U = q_V$$

Working at constant P is a lot easier to do than at constant V . This means that the enthalpy is a much easier state function to deal with than the energy U .

For example when we melt ice volumes change whether we like or not, but as long as the weather does not change too much pressure is constant. So if we measure how much heat we need to add to melt a mole of ice we get the molar heat of fusion:



Such enthalpies are measured and tabulated.

In this case the volume change is actually quite small, as it usually is for condensed matter. Only if we are dealing with gases is the difference between enthalpy and energy really important

So, $U \approx H$ for condensed matter, but U and H differ for gases.

A good example of this is the difference between the heat capacity at constant V and at constant P . For most materials there is not much of a difference, but for an ideal gas we have

$$C_p = C_V + nR$$

Needless to say that the heat capacity is a path function: it depends on what you keep constant.

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