19.11: Enthalpy Changes for Chemical Equations are Additive

Hess's law

As enthalpy and energy are state functions we should expect ***additivity*** of U and H when we study chemical reactions. This additivity is expressed in **Hess's Law**. The additivity has important consequences and the law finds wide spread application in the prediction of heats of reaction.

1. The reverse reaction has the negative enthalpy of the forward one.
2. If we can do a reaction in two steps we can calculate the enthalpy of the combined reaction by adding up:

Reaction	Enthalpy
$C_{(s)}$ + ½ $O_{2(g)}$ -> $CO_{(g)}$	$\Delta_r H$ = -110.5 kJ
$CO_{(g)}$ + ½ $O_{2(g)}$ -> $CO_{2(g)}$	$\Delta_r H$ = -283.0 kJ
This means that	----------+
$C_{(s)}$ + O2(g) -> CO2(g)	$\Delta_r H$ = -393.5 kJ

By this mechanism it is often possible to calculate the heat of a reaction even if this reaction is hard to carry out. E.g. we could burn both graphite and diamond and measure the heats of combustion for both. The difference would give us the heat of the transformation reaction from graphite to diamond.

Reaction-as-written convention (caution!)

The enthalpy is for the ***reaction-as-written***. That means that if we write:

$$2C(s) + O_2(g) \rightarrow 2CO(g)$$

with $\Delta_r H$ = -221 kJ (***not***: -110.5 kJ)

Reverse reactions

Because H is a state function the reverse reaction has the same enthalpy but with opposite sign

$$2CO(g) \rightarrow 2C(s) + O_2(g)$$

with $\Delta_r H$ = +221 kJ

Combining values

It is quite possible that you cannot really do a certain reaction in practice. For many reactions we can arrive at enthalpy values by doing some bookkeeping. For example, we can calculate the enthalpy for the reaction of PCl_3 with chlorine if we know the two reactions that the elements phosphorous and chlorine can undergo.

> *You do have to make sure you balance your equations properly!*