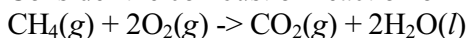Working with Hess's Law
It is often possible to calculate ΔH for a reaction from listed ΔH values of other reactions (i.e. you can avoid having to do an experiment)
Enthalpy is a *state function*
It depends only upon the *initial and final state* of the reactants/products and *not on the specific pathway* taken to get from the reactants to the products
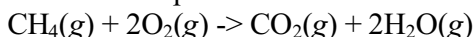Whether one can arrive at the products via either a single step or multi-step mechanism is unimportant as far as the enthalpy of reaction is concerned - they should be equal
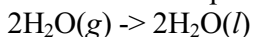Consider the combustion reaction of methane to form CO_2 and *liquid* H_2O
$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$
This reaction can be thought of as occurring in two steps:
In the first step methane is combusted to produce water vapor:
$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$
In the second step water vapor condenses from the gas phase to the liquid phase:
$2H_2O(g) \rightarrow 2H_2O(l)$
Each of these reactions is associated with a specific enthalpy change:
$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ ΔH = -802 kJ
$2H_2O(g) \rightarrow 2H_2O(l)$ ΔH = -88 Kj
(Note: under conditions of standard temperature and pressure the liquid state of water is the normal state. Thus, the gas would be expected to condense. This is an exothermic process under these conditions. In a related process, it shou ld get warmer when it rains)
Combining these equations yields the following:
$CH_4(g) + 2O_2(g) + 2H_2O(g) \rightarrow CO_2(g) + 2H_2O(g) + 2H_2O(l)$
ΔH = (-802) kJ + (-88) kJ= -890 kJ
Hess's Law
if a reaction is carried out in a series of steps, ΔH for the reaction will be equal to the sum of the enthalpy changes for the individual steps
the overall enthalpy change for the process is independent of the number of steps or the particular nature of the path by which the reaction is carried out.
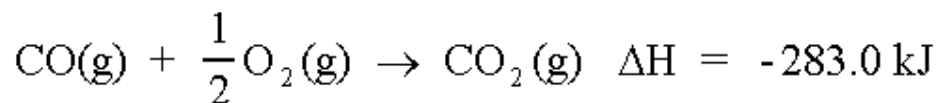*Thus we can use information tabulated for a relatively small number of reactions to calculate ΔH for a large number of different reactions*
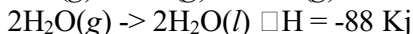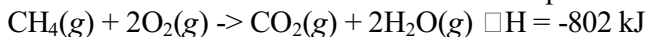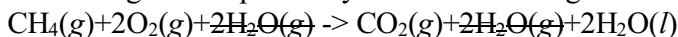
Determining ΔH for the reaction

$$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$$
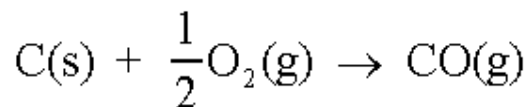
is difficult because some CO_2 is also typically produced.
However, complete oxidation of either C or CO to yield CO_2 is experimentally pretty easy to do:

$$C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H = -393.5 \text{ kJ}$$

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \quad \Delta H = -283.0 \text{ kJ}$$

We can invert reaction number 2 (making it *endothermic*) and have $CO(g)$ as a *product*. (This describes the decomposition of CO_2 to produce CO and O_2)

$$CO_2(g) \rightarrow CO(g) + \frac{1}{2}O_2(g) \quad \Delta H = +283.0 \text{ kJ}$$
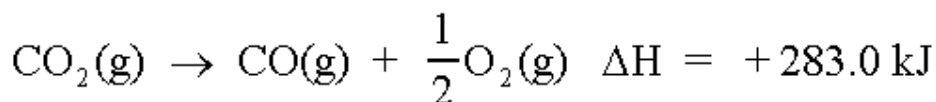
Thus, we now have two equations with known enthalpies of reaction: the first describes the combustion of carbon and oxygen to produce CO_2 and the second describes how CO_2 can be decomposed to produce carbon monoxide (and oxygen). We can combine these together to describe the production of carbon monoxide from the combustion of carbon and oxygen:
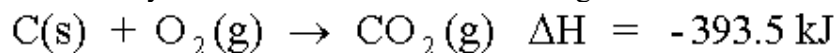
$$\Delta H = -393.5 \text{ kJ} \qquad \Delta H = +283.0 \text{ kJ}$$
$$C(s) + O_2(g) \longrightarrow CO_2(g) \longrightarrow CO(g) + \frac{1}{2}O_2(g)$$
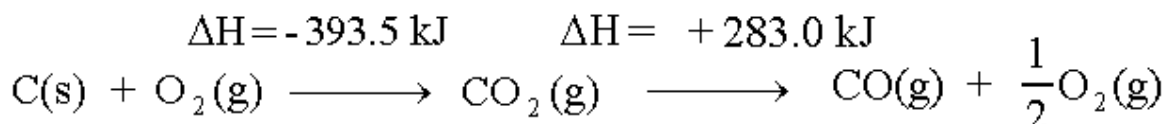
The overall reaction, going from left-hand side reactant(s) to the right-hand side product(s) would be:
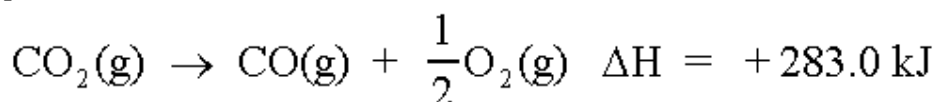
$$C(s) + O_2(g) \longrightarrow CO(g) + \frac{1}{2}O_2(g)$$
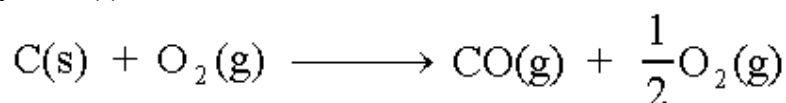
We can algebraically subtract the one-half O_2 from both sides to yield the following equation with the associated overall enthalpy:
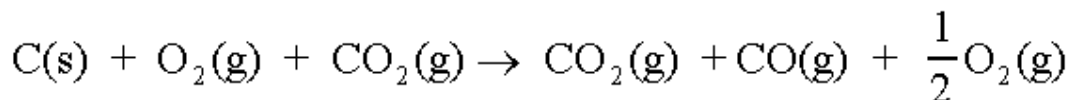
$$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) \quad \text{and } \Delta H = -110.5 \text{ kJ}$$
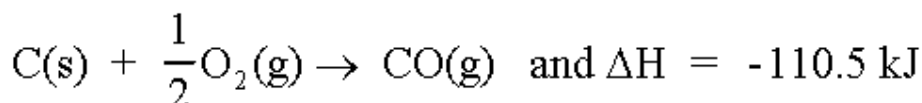
Another way to look at the method of combining reactions would be as follows:

$$C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H = -393.5 \text{ kJ}$$

plus

$$CO_2(g) \rightarrow CO(g) + \frac{1}{2}O_2(g) \quad \Delta H = +283.0 \text{ kJ}$$

gives:

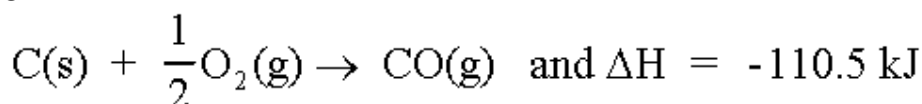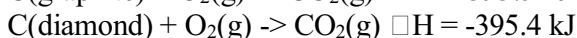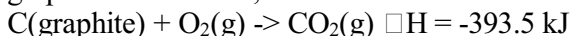$$C(s) + O_2(g) + CO_2(g) \rightarrow CO_2(g) + CO(g) + \frac{1}{2}O_2(g)$$

$\Box H = (-393.5 \text{ kJ}) + (283.0 \text{ kJ}) = -110.5 \text{ kJ}$
canceling out identical compounds from the left and right hand sides of this reaction gives

$$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) \quad \text{and } \Delta H = -110.5 \text{ kJ}$$
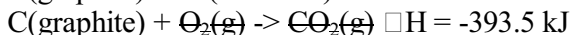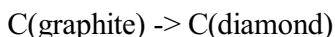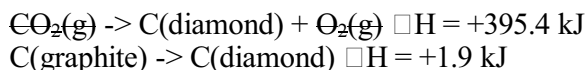
Carbon occurs in two forms: graphite and diamond. The enthalpy of combustion of graphite is -393.5 kJ, and that of diamond is -395.4 kJ
$C(graphite) + O_2(g) \rightarrow CO_2(g) \quad \Box H = -393.5$ kJ
$C(diamond) + O_2(g) \rightarrow CO_2(g) \quad \Box H = -395.4$ kJ
Calculate $\Box H$ for the conversion of graphite to diamond
What we want is $\Box H$ for the reaction:
$C(graphite) \rightarrow C(diamond)$
$C(graphite) + \cancel{O_2(g)} \rightarrow \cancel{CO_2(g)} \quad \Box H = -393.5$ kJ

$CO_2(g)$ -> C(diamond) + $O_2(g)$ $\Delta H = +395.4$ kJ
C(graphite) -> C(diamond) $\Delta H = +1.9$ kJ

We can never expect to obtain more or less energy from a chemical reaction by changing the method of carrying out the reaction ("conservation of energy"). Another way of saying this is that the particular pathway chosen to arrive at the same reactants yields the same ΔH for the overall reaction.

Consider the previous example of the combustion of methane to produce gaseous H_2O and then the condensation of the gaseous H_2O to the liquid state. How is this represented in an Enthalpy Diagram?
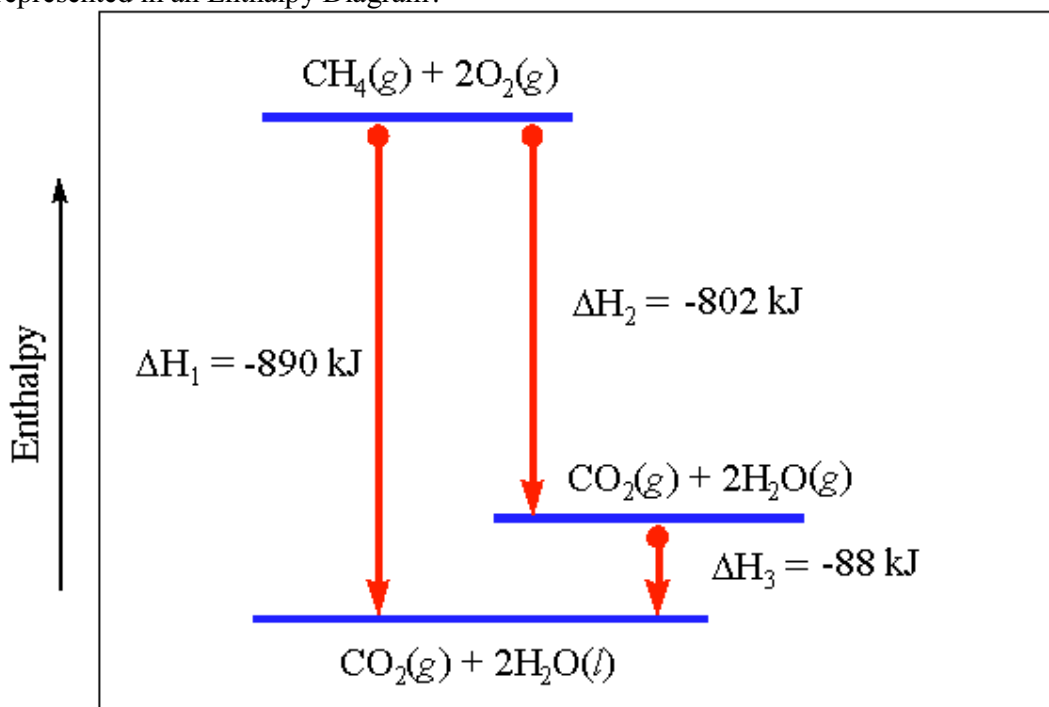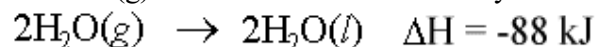

The key features are the following:

1. Each line represents a set of reactants or products for a balanced chemical reaction. When going from one line to another, the atoms must balance. For example, if we were to ask what is the enthalpy associated with the condensation of water we would have (from the above data):

$$CO_2(g) + 2H_2O(g) \rightarrow CO_2(g) + 2H_2O(l) \quad \Delta H = -88 \text{ kJ}$$
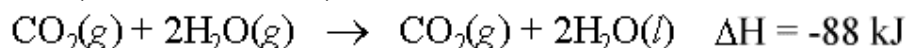
The $CO_2(g)$ on both sides will cancel to yield:

$$2H_2O(g) \rightarrow 2H_2O(l) \quad \Delta H = -88 \text{ kJ}$$

2. The relative distance of each line must reflect the relative enthalpy difference (ΔH) between the reactants/products. If the enthalpy change in going from reactants to products is negative, then the line for the products must be below the reactants. Furthermore, the length of the distance must be proportional. For example, the distance reflecting the enthalpy associated with the condensation of water ($\Delta H = -88$ kJ) is only about 10% as long as the distance between the reactants and products for the combustion of methane to CO_2 and liquid water ($\Delta H = -890$ kJ)