Hess's Law

Hess's law states that the energy change in an overall chemical reaction is equal to the sum of the energy changes in the individual reactions comprising it. In other words, the enthalpy change of a chemical reaction (the heat of reaction at constant pressure) does not depend on the pathway between the initial and final states.

This information is extremely useful, as oftentimes a given balanced reaction may not occur spontaneously; instead Hess's law can be used to apply similar reactions that contain the same products and reactants in such a manner that the enthalpy change of the initial reaction can be deduced.

$$CS_{2(l)} + 3\ O_{2(g)} \rightarrow CO_{2(g)} + 2\ SO_{2(g)}$$

In the equation above, the enthalpy change is unknown. However, three reactions of known enthalpy change can be applied:

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)};\ \Delta H_f = -393.5\ kJ/mol$$

$$S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)};\ \Delta H_f = -296.8\ kJ/mol$$

$$C_{(s)} + 2\ S_{(s)} \rightarrow CS_{2(l)};\ \Delta H_f = 87.9\ kJ/mol$$

The goal is to determine how each reaction can be tweaked so that when summed together, they form a reaction identical to the initial. First, identify which species must be kept, and which need to be removed. If the species is not found in the initial equation, it must go.

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)};\ \Delta H_f = -393.5\ kJ/mol$$

$$S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)};\ \Delta H_f = -296.8\ kJ/mol$$

$$C_{(s)} + 2\ S_{(s)} \rightarrow CS_{2(l)};\ \Delta H_f = 87.9\ kJ/mol$$

The goal is to make sure that the red species are removed, which can only occur if it is found on both sides of the arrow. Simultaneously, the blue species must be found on the correct side of the arrow as the initial equation. Both tasks can be accomplished at once by switching equation 3. The ΔH_f can be treated as a metaphorical species in this equation, so to "flip" it, the sign must be changed from + to -

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)};\ \Delta H_f = -393.5\ kJ/mol$$

$$S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)};\ \Delta H_f = -296.8\ kJ/mol$$

Old: $-(C_{(s)} + 2\ S_{(s)} \rightarrow CS_{2(l)};\ \Delta H_f = 87.9\ kJ/mol)$

New: $CS_{2(l)} \rightarrow C_{(s)} + 2\ S_{(s)};\ \Delta H_f = -87.9\ kJ/mol$

Finally, you may notice that the mols of some of the reactants are not equal to the original problem. If the equations were summed now, for instance, one S(s) would be left over and both the O_2 and SO_2 species would be fewer in number. To remedy this, equation two can be multiplied by 2 in order for the molar ratios to remain constant. Remember, this also applies to the enthalpy value.

$C(s) + O_2(g) \rightarrow CO_2(g)$; ΔH f = -393.5 kJ/mol

Old: $2(S(s) + O_2(g) \rightarrow SO_2(g)$; ΔH f = -296.8 kJ/mol)
New: $2S(s) + 2O_2(g) \rightarrow 2SO_2(g)$; ΔH f = -593.6 kJ/mol

$CS_2(l) \rightarrow C(s) + 2\ S(s)$; ΔH f = -87.9 kJ/mol

Now, it is a matter of summing all into one singular equation, then cancelling out species that are found on both sides

$C + 3O_2 + 2S + CS_2 \rightarrow CO_2 + 2SO_2 + C + 2S$; ΔH f = -1075 kJ/mol

$3O_2 + CS_2 \rightarrow CO_2 + 2SO_2$; ΔH f = -1075 kJ/mol