Step by Step: Hess’s Law (see at end for supplemental notes on ΔH\textsubscript{formation} with Hess’s Law)

The enthalpy change (ΔH\textsubscript{r,°}) for a reaction is the sum of the enthalpy changes for a series of reactions, that add up to the overall reaction.

Steps:
For each reaction:
1) Check to see, if the compounds are on the correct sides of the reaction.
   **If not, reverse the entire reaction, and change the sign of ΔH.

2) Check to see, if all of the unwanted compounds will cancel completely.
   **If not, multiply an entire reaction by a number so that they do cancel completely and multiply ΔH by that same number.

Left \rightarrow Right

Ex.1) Given: 2 HF(g) → H\textsubscript{2}(g) + F\textsubscript{2}(g) \quad ΔH = +537 kJ \quad (1\textsuperscript{st} reaction)
½ C(s) + F\textsubscript{2}(g) → ½ CF\textsubscript{4}(g) \quad ΔH = -340. kJ \quad (2\textsuperscript{nd} reaction)
2 C(s) + 2 H\textsubscript{2}(g) → C\textsubscript{2}H\textsubscript{4}(g) \quad ΔH = 52 kJ \quad (3\textsuperscript{rd} reaction)

Find ΔH\textsubscript{r,°} for: C\textsubscript{2}H\textsubscript{4}(g) + 6 F\textsubscript{2}(g) → 2 CF\textsubscript{4}(g) + 4 HF(g)

Look at the first reaction to see, if the compounds are on the correct sides.
*The HF is on the left side of the 1\textsuperscript{st} reaction and it is on the right side of the blue reaction, so that is not OK. We need to flip this reaction and make it go the other direction.
*The H\textsubscript{2} is on the right side of the 1\textsuperscript{st} reaction, but it is not in the blue reaction, so that does not help.
*The F\textsubscript{2} is on the right side of the 1\textsuperscript{st} reaction and it is on the left side of the blue reaction, so that is not OK. We need to flip this reaction and make it go the other direction. {We cannot just move one compound, because then the reaction will not balance, so we must flip the entire reaction and make it go backwards.} If we flip the reaction, the ΔH sign will flip as well. The positive 537 will now be negative.

H\textsubscript{2}(g) + F\textsubscript{2}(g) → 2 HF(g) \quad ΔH = -537 kJ \quad (F\textsubscript{2} & HF now on correct sides, now -537)

Look at the second reaction.
*The C is on the left side of the 2\textsuperscript{nd} reaction, but it is not in the blue reaction, so that does not help.
*The F\textsubscript{2} is on the left side of the 2\textsuperscript{nd} reaction and it is on the left side of the blue reaction, so that is OK.
*The CF\textsubscript{4} is on the right side of the 2\textsuperscript{nd} reaction and it is on the right side of the blue reaction, so that is OK. The 2\textsuperscript{nd} reaction stays the way it is written, since F\textsubscript{2} and CF\textsubscript{4} are already on the correct sides.

½ C(s) + F\textsubscript{2}(g) → ½ CF\textsubscript{4}(g) \quad ΔH = -340. kJ \quad (F\textsubscript{2} & CF\textsubscript{4} on correct sides already)

Look at the third reaction.
*The C is on the left side of the 3\textsuperscript{rd} reaction, but it is not in the blue reaction, so that does not help.
*The H\textsubscript{2} is on the left side of the 3\textsuperscript{rd} reaction, but it is not in the blue reaction, so that does not help.
*The C\textsubscript{2}H\textsubscript{4} is on the right side of the 3\textsuperscript{rd} reaction, but it is on the left side of the blue reaction. The C\textsubscript{2}H\textsubscript{4} is on the wrong side of the reaction. {We cannot just move one compound, because then the
reaction will not balance, so we must flip the entire reaction and make it go backwards.} If we flip the reaction, the $\Delta H$ sign will flip as well. The positive 52 will now be negative.

$$C_2H_4(g) \rightarrow 2 C(s) + 2 H_2(g) \quad \Delta H = -52 \text{ kJ} \quad \text{(C}_2\text{H}_4 \text{ was on wrong side, now -52)}$$

So this is what we have so far:

$$H_2(g) + F_2(g) \rightarrow 2 HF(g) \quad \Delta H = -537 \text{ kJ}$$
$$\frac{1}{2} C(s) + F_2(g) \rightarrow \frac{1}{2} CF_4(g) \quad \Delta H = -340. \text{ kJ}$$
$$C_2H_4(g) \rightarrow 2 C(s) + 2 H_2(g) \quad \Delta H = -52 \text{ kJ}$$

Now we must completely cancel all of the compounds that were not in the blue reaction. Look up above: $H_2$ and $C$ were in the 3 top reactions, but were not in the blue reaction. To make the $H_2$ cancel we must multiply the 1st reaction by 2. The $\Delta H$ will also be multiplied by 2. To make the $C$ cancel we must multiply the 2nd reaction by 4. The $\Delta H$ will also be multiplied by 4. Just like the redox reactions, if the compounds are on opposite sides of the arrows, we can cancel them by subtracting from both sides of the arrow!

$$2 \left( \frac{1}{2} C(s) + F_2(g) \rightarrow \frac{1}{2} CF_4(g) \right) \quad \Delta H = -340. \text{ kJ} \quad \text{X 4 (need to cancel C)} = -1360 \text{ kJ}$$
$$C_2H_4(g) \rightarrow 2 C(s) + 2 H_2(g) \quad \Delta H = -52 \text{ kJ} \quad \text{X 2 (need to cancel H}_2\text{)} = -1074 \text{ kJ}$$

$$C_2H_4(g) + 6 F_2(g) \rightarrow 2 CF_4(g) + 4 HF(g) \quad \Delta H = -2486 \text{ kJ}$$

When the reactions are added, we have 1 $C_2H_4$ on the left side. We have 2 X 1 $F_2$ (1st reaction) added to 4 X 1 $F_2$ (2nd reaction) = 6 $F_2$. {The $F_2$ in the 2 reactions are added, since they are on the same side of the reactions. Remember they only cancel, if they are on opposite sides.}

On the right side there are 2 X 2HF = 4 HF and 4 X $\frac{1}{2}$ CF$_4$ = 2 CF$_4$.

This summation reaction should match the blue reaction, which it does. Then add all of the energies together to get the total energy of -2486 kJ.
Ex. 2) Given the following data:

\[
\text{SO}_3(g) \rightarrow S(s) + 3/2 \text{O}_2(g) \quad \Delta H = +395 \text{ kJ} \quad (1\text{st reaction})
\]

\[
2 \text{SO}_2(g) + \text{O}_2(g) \rightarrow 2 \text{SO}_3(g) \quad \Delta H = -198 \text{ kJ} \quad (2\text{nd reaction})
\]

Calculate \(\Delta H\) for the reaction: \(S(s) + \text{O}_2(g) \rightarrow \text{SO}_2(g)\)

Look at the 1\text{st} reaction:

*The SO\(_3\) is on the left side of the 1\text{st} reaction, but is not in the blue reaction, so that does not help.
*The S is on the right side of the 1\text{st} reaction and on the left side of the blue reaction, so that is on the wrong side.
*The O\(_2\) is on the right side of the 1\text{st} reaction and on the left side of the blue reaction, so that is also on the wrong side.

The 1\text{st} reaction needs to be flipped, since S and O\(_2\) are on the wrong sides.

\[
S(s) + 3/2 \text{O}_2(g) \rightarrow \text{SO}_3(g) \quad \Delta H = -395 \text{ kJ} \quad \text{now that it is flipped, the }+\Delta H \text{ will now be -.}
\]

Look at the 2\text{nd} reaction:

*The SO\(_2\) is on the left side of the 2\text{nd} reaction, but on the right side of the blue reaction. It is on the wrong side.
*The O\(_2\) is on the left side of the 2\text{nd} reaction and on the left side of the blue reaction, so that is OK.
*The SO\(_3\) is on the right side of the 2\text{nd} reaction, but it is not in the blue reaction, so that does not help.

We have a problem, because the SO\(_2\) is on the wrong side, but the O\(_2\) is on the correct side. We need to figure out which is the most important! The SO\(_2\) in that 2\text{nd} reaction is the only SO\(_2\) in the first two reactions, but there is O\(_2\) in both reactions #1 and #2. The SO\(_2\) is the most important, since it is in only one location, so it must go on the correct side. The 2\text{nd} reaction will need to be flipped to get the SO\(_2\) to the right side. {The O\(_2\) will go on the wrong side, but there is O\(_2\) in the 1\text{st} reaction, that will go on the correct side. After we add the reactions and cancel, there will hopefully be enough O\(_2\) on the correct side.}

\[
2 \text{SO}_3(g) \rightarrow 2 \text{SO}_2(g) + \text{O}_2(g) \quad \Delta H = +198 \text{ kJ} \quad \text{now that it is flipped, the }-\Delta H \text{ will now be +.}
\]

So far we have this:

\[
S(s) + 3/2 \text{O}_2(g) \rightarrow \text{SO}_3(g) \quad \Delta H = -395 \text{ kJ}
\]

\[
2 \text{SO}_3(g) \rightarrow 2 \text{SO}_2(g) + \text{O}_2(g) \quad \Delta H = +198 \text{ kJ}
\]

Now we need to cancel out any compounds that are not in the blue reaction. That means we need to cancel the SO\(_3\).

To cancel the SO\(_3\) we need to multiply the 1\text{st} reaction by 2, and multiply the \(\Delta H\) by 2.

\[
2(\text{S(s) + 3/2 O}_2(g) \rightarrow \text{SO}_3(g)) \quad \Delta H = -395 \text{ kJ} \times 2 = -790 \text{ kJ}
\]

\[
\frac{2 \text{SO}_2(g) \rightarrow 2 \text{SO}_2(g) + \text{O}_2(g)}{2\text{S(s)} + 2\text{O}_2(g) \rightarrow 2\text{SO}_2(g)} \Delta H = +198 \text{ kJ} \quad \Delta H = -592 \text{ kJ}
\]

When the reactions are added we will get on the left side 2 X S = 2 S.

For the O\(_2\): On the left there are 2 X 3/2 O\(_2\) which equals 3 O\(_2\).
On the right there is $O_2$, so just 1 $O_2$.

If we have, 3 $O_2$ on the left and 1 $O_2$ on the right.

$3 \text{O}_2 \rightarrow \text{1O}_2$

2 $O_2$ → We can subtract off 1 $O_2$ from each side, leaving 2 $O_2$ on the left side.

And there are 2 $SO_2$ on the right side.

$2S(s) + 2O_2(g) \rightarrow 2SO_2(g)$ $\Delta H = -592 \text{ kJ}$

One last problem: Our reaction does not match the blue reaction, because it is two times too big. So we must divide by 2. Also divide the $\Delta H$ by 2.

$S(s) + O_2(g) \rightarrow SO_2(g)$ $\Delta H = -296 \text{ kJ}$

Supplemental Notes: $\Delta H_{\text{formation}}$ and why $\sum n\Delta H_{\text{products}} - \sum n\Delta H_{\text{reactants}}$ works.

$\Delta H_{\text{reaction}} = \sum n\Delta H_{\text{products}} - \sum n\Delta H_{\text{reactants}}$ can be explained by doing a Hess’s Law problem with the $\Delta H_{\text{formation}}$ reactions of the reactants and products in the overall reaction.

Overall Reaction: $2 \text{C}_2\text{H}_6(g) + 7 \text{O}_2(g) \rightarrow 4 \text{CO}_2(g) + 6 \text{H}_2\text{O}(g)$

1st step: Write the $\Delta H_{\text{formation}}$ reactions for each of the reactants and products.

a) When you do this, every metal, metalloid and non-metal is written as a single element, except for the gases and halogens.

(Metals: Fe(s), Na(s) etc., Metalloids: Si(s), Ge(s) etc., Non-metals: C(s), S(s) etc.)

b) Halogens and gases, that are not noble gases, are written as dimers (in two’s).

(Halogens: F$_2$(g), Cl$_2$(g), Br$_2$(l), I$_2$(s), Gases: H$_2$(g), N$_2$(g), O$_2$(g))

Noble gases have full orbital layers and are stable being alone: He$_2$(g), Ne$_2$(g) etc.

Balance the equation

$C(s) + H_2(g) \rightarrow C_2H_6(g)$ $\rightarrow \rightarrow 2 C(s) + 3 H_2(g) \rightarrow C_2H_6(g)$ $\Delta H_{\text{reaction}} = \Delta H_{\text{formation}} = -85 \text{ kJ/mol}$

$\uparrow$ of $C_2H_6$

You can find the $\Delta H_{\text{formation}}$ of the compound from the $\Delta H$, $\Delta G$, and $\Delta S$ Table in your textbook.

$O_2(g)$ is just $O_2(g)$, so there is no formation reaction.

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\rightarrow \rightarrow C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H_{\text{reaction}} = \Delta H_{\text{formation}} = -393 \text{ kJ/mol}$

of $CO_2$

$H_2(g) + O_2(g) \rightarrow H_2O(g)$ $\rightarrow \rightarrow 2 H_2(g) + O_2(g) \rightarrow 2 H_2O(g)$ $\Delta H_{\text{reaction}} = 2 \times \Delta H_{\text{formation}} = 2 \times (-242 \text{ kJ/mol}) = -484 \text{ kJ/mol}$

**Since there are 2 mols of $H_2O$ in the balanced reaction the $\Delta H_{\text{reaction}}$ will be two times the $\Delta H_{\text{formation}}$ of $H_2O$. Or another way of thinking about it, is that the $\Delta H_{\text{formation}}$ will be half the $\Delta H_{\text{reaction}}$.**
2nd step: Use the above reactions in a Hess’s Law problem to solve for the overall reaction.

Find $\Delta H_{\text{reaction}}$ for: $2 \text{C}_2\text{H}_6(\text{g}) + 7 \text{O}_2(\text{g}) \rightarrow 4 \text{CO}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{g})$

Using:

- $2 \text{C}_6\text{H}_6(\text{g}) \rightarrow 2 \text{C}_2\text{H}_6(\text{g})$  $\Delta H_{\text{formation}} = -85 \text{ kJ/mol}$
- $\text{C}_2\text{H}_6(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$  $\Delta H_{\text{formation}} = -393 \text{ kJ/mol}$
- $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{g})$  $\Delta H_{\text{formation}} = -484 \text{ kJ/mol}$

- $2 \text{C}(\text{s}) + 3 \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$  $\Delta H_{\text{formation}} = +85 \text{ kJ/mol}$ (flipped, so $\text{C}_2\text{H}_6$ is on the left, like the reaction we are solving for, $\Delta H$ changes sign, since now backwards)
- $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$  $\Delta H_{\text{formation}} = -393 \text{ kJ/mol}$ (stays, since $\text{CO}_2$ is on the right, like the reaction we are solving for)
- $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{g})$  $\Delta H_{\text{formation}} = -484 \text{ kJ/mol}$ (stays, since $\text{H}_2\text{O}$ is on the right, like the reaction we are solving for)

**The energies are multiplied when the reactions are multiplied.**

\[
\begin{align*}
2 \text{C}_2\text{H}_6(\text{g}) & \rightarrow 2 \text{C}(\text{s}) + 3 \text{H}_2(\text{g}) \quad \Delta H_{\text{formation}} = +85 \times 2 = +170 \text{ kJ/mol} \\
4 \text{C}(\text{s}) + \text{O}_2(\text{g}) & \rightarrow \text{CO}_2(\text{g}) \quad \Delta H_{\text{formation}} = -393 \times 4 = -1572 \text{ kJ/mol} \\
3 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) & \rightarrow 2 \text{H}_2\text{O}(\text{g}) \quad \Delta H_{\text{formation}} = -484 \times 3 = -1452 \text{ kJ/mol}
\end{align*}
\]

\[
\text{C}_2\text{H}_6(\text{g}) \rightarrow 2 \text{C}_2\text{H}_6(\text{g}) \quad \Delta H_{\text{formation}} = +85 \text{ kJ/mol}
\]

\[
\begin{align*}
\text{C}(\text{s}) + \text{O}_2(\text{g}) & \rightarrow \text{CO}_2(\text{g}) \quad \Delta H_{\text{formation}} = -393 \text{ kJ/mol} \\
2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) & \rightarrow 2 \text{H}_2\text{O}(\text{g}) \quad \Delta H_{\text{formation}} = -484 \text{ kJ/mol}
\end{align*}
\]

\[
\begin{align*}
2\text{C}_2\text{H}_6(\text{g}) + 7\text{O}_2(\text{g}) & \rightarrow 4\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g}) \\
\Delta H & = -2854 \text{ kJ/mol}
\end{align*}
\]

**Why this works:**

The 1st reaction of the three reactions in the Hess’s Law problem breaks $\text{C}_2\text{H}_6$ apart to it’s elements $\text{C}(\text{s})$ and $\text{H}_2(\text{g})$. This is the opposite of the $\Delta H_{\text{formation}}$, since $\text{C}_2\text{H}_6$ is broken apart and not formed. (The reaction was flipped and $\Delta H$ changed sign.) Hess’s Law has no reaction for the breaking down and forming of $\text{O}_2(\text{g})$, since it is already in it’s elemental state.

Once the reactants are broken apart to their elements, they can be reformed into their products. So the $\text{C}(\text{s})$, $\text{H}_2(\text{g})$, and $\text{O}_2(\text{g})$ are formed into the products in the 2nd and 3rd reactions of the Hess’s Law problem.

\[
\begin{align*}
\text{Broken Down} & \quad \text{Reformed} \\
\text{C}_2\text{H}_6 & \rightarrow \text{C} + \text{H}_2 \\
\text{O}_2 & \rightarrow \text{O}_2
\end{align*}
\]

The total of the energies for these changes was calculated in Hess’s Law.

3rd step: Prove that this equation works: $\Delta H_{\text{reaction}} = \sum n\Delta H_{\text{products}} - \sum n\Delta H_{\text{reactants}}$

These $\Delta H$’s are $\Delta H_{\text{formations}}$ of the compounds.

\[
\begin{align*}
2 \text{C}_2\text{H}_6(\text{g}) + 7 \text{O}_2(\text{g}) & \rightarrow 4 \text{CO}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{g}) \\
\Delta H_{\text{reaction}} & = [(4 \text{ mol CO}_2) (-393 \text{ kJ/mol}) + (6 \text{ mol H}_2\text{O}) (-242 \text{ kJ/mol})] - [(2 \text{ mol C}_2\text{H}_6) (-85\text{kJ/mol}) + (7 \text{ mol O}_2) (0 \text{ kJ/mol})] \\
\Delta H_{\text{reaction}} & = -1572 -1452 + 170 = -2854 \text{ kJ/mol}
\end{align*}
\]

The above equation has $\Delta H_{\text{products}} - \Delta H_{\text{reactants}}$, because the product $\Delta H_{\text{formations}}$ remain positive in the Hess’s Law problem and the reactant $\Delta H_{\text{formations}}$ are negative, since they are flipped in the Hess’s Law problem.
Other Sample $\Delta H_{\text{formation}}$: 

CHCl₃: $C(s) + H_2(g) + Cl_2(g) \rightarrow CHCl_3(g)$ $\rightarrow \rightarrow$ $2 C(s) + H_2(g) + 3 Cl_2(g) \rightarrow 2 CHCl_3(g)$

SO₂: $S(s) + O_2(g) \rightarrow SO_2(g)$ $\rightarrow \rightarrow$ $S(s) + 2 O_2(g) \rightarrow SO_2(g)$

SO₃: $S(s) + O_2(g) \rightarrow SO_3(g)$ $\rightarrow \rightarrow$ $2 S(s) + 3 O_2(g) \rightarrow 2 SO_3(g)$

NO₂: $N_2(g) + O_2(g) \rightarrow NO_2(g)$ $\rightarrow \rightarrow$ $N_2(g) + 2 O_2(g) \rightarrow 2 NO_2(g)$

H₂SO₄: $H_2(g) + S(s) + O_2(g) \rightarrow H_2SO_4(g)$ $\rightarrow \rightarrow$ $H_2(g) + S(s) + 2 O_2(g) \rightarrow H_2SO_4(g)$

KMnO₄: $K(s) + Mn(s) + O_2(g) \rightarrow KMnO_4(s)$ $\rightarrow \rightarrow$ $K(s) + Mn(s) + 2 O_2(g) \rightarrow KMnO_4(s)$

Remember: Every metal, metalloid and non-metal is written as a single element, except for the gases and halogens. (Metals: Fe(s), Na(s) etc., Metalloids: Si(s), Ge(s) etc., Non-metals: C(s), S(s) etc.)

**Halogen and gases, that are not noble gases, are written as dimers (in two’s).** (Halogens: F₂(g), Cl₂(g), Br₂(l), I₂(s) Gases: H₂(g), N₂(g), O₂(g))

Noble gases have full orbital layers and are happy as loners: He(g), Ne(g) etc.

*End of Notes*