

Step by Step: Hess's Law (see at end for supplemental notes on  $\Delta H_{\text{formation}}$  with Hess's Law)

The enthalpy change ( $\Delta H_r^\circ$ ) 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:

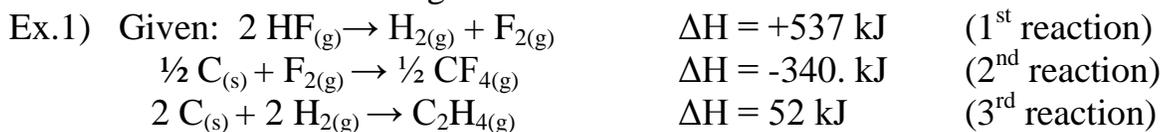
1) Check to see, if the compounds are on the correct sides of the reaction.

\*\*If not, reverse the entire reaction, and change the sign of  $\Delta H$ .

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  $\Delta H$  by that same number.

Left  $\rightarrow$  Right



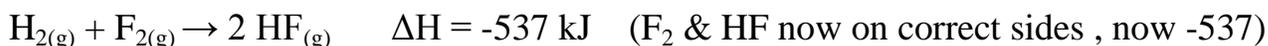
Find  $\Delta H_r^\circ$  for:  $\text{C}_2\text{H}_{4(g)} + 6 \text{ F}_{2(g)} \rightarrow 2 \text{ CF}_{4(g)} + 4 \text{ HF}_{(g)}$

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<sup>st</sup> 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<sub>2</sub> is on the right side of the 1<sup>st</sup> reaction, but it is not in the blue reaction, so that does not help.

\*The F<sub>2</sub> is on the right side of the 1<sup>st</sup> 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  $\Delta H$  sign will flip as well. The positive 537 will now be negative.



Look at the second reaction.

\*The C is on the left side of the 2<sup>nd</sup> reaction, but it is not in the blue reaction, so that does not help.

\*The F<sub>2</sub> is on the left side of the 2<sup>nd</sup> reaction and it is on the left side of the blue reaction, so that is OK.

\*The CF<sub>4</sub> is on the right side of the 2<sup>nd</sup> reaction and it is on the right side of the blue reaction, so that is OK. The 2<sup>nd</sup> reaction stays the way it is written, since F<sub>2</sub> and CF<sub>4</sub> are already on the correct sides.



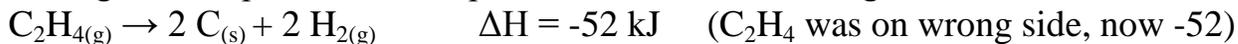
Look at the third reaction.

\*The C is on the left side of the 3<sup>rd</sup> reaction, but it is not in the blue reaction, so that does not help.

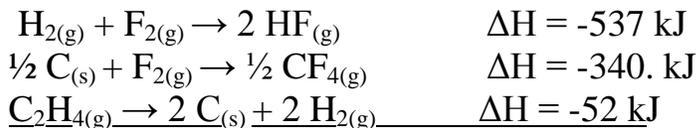
\*The H<sub>2</sub> is on the left side of the 3<sup>rd</sup> reaction, but it is not in the blue reaction, so that does not help.

\*The C<sub>2</sub>H<sub>4</sub> is on the right side of the 3<sup>rd</sup> reaction, but it is on the left side of the blue reaction. The C<sub>2</sub>H<sub>4</sub> 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.



So this is what we have so far:

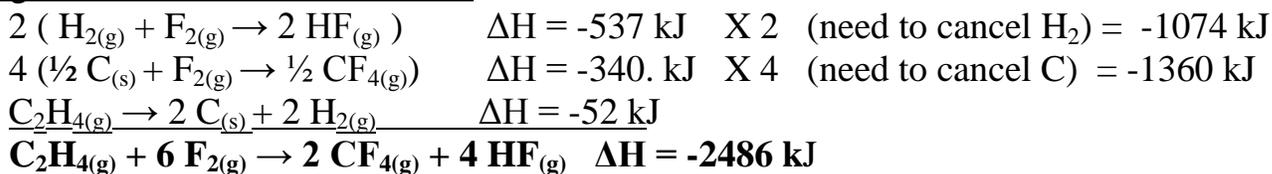


Now we must completely cancel all of the compounds that were not in the blue reaction. Look up above:  $\text{H}_2$  and  $\text{C}$  were in the 3 top reactions, but were not in the blue reaction.

To make the  $\text{H}_2$  cancel we must multiply the 1<sup>st</sup> reaction by 2. The  $\Delta H$  will also be multiplied by 2.

To make the  $\text{C}$  cancel we must multiply the 2<sup>nd</sup> 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!



When the reactions are added, we have 1  $\text{C}_2\text{H}_4$  on the left side.

We have 2 X 1  $\text{F}_2$  (1<sup>st</sup> reaction) added to 4 X 1 $\text{F}_2$  (2<sup>nd</sup> reaction) = 6  $\text{F}_2$ . {The  $\text{F}_2$  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 2 $\text{HF}$  = 4  $\text{HF}$  and 4 X  $\frac{1}{2}$   $\text{CF}_4$  = 2  $\text{CF}_4$ .

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:



Calculate  $\Delta H$  for the reaction:  $\text{S}_{(s)} + \text{O}_{2(g)} \rightarrow \text{SO}_{2(g)}$

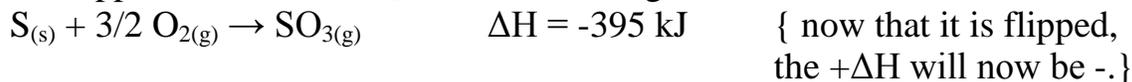
Look at the 1<sup>st</sup> reaction:

\*The  $\text{SO}_3$  is on the left side of the 1<sup>st</sup> reaction, but is it not in the blue reaction, so that does not help.

\*The S is on the right side of the 1<sup>st</sup> reaction and on the left side of the blue reaction, so that is on the wrong side.

\*The  $\text{O}_2$  is on the right side of the 1<sup>st</sup> reaction and on the left side of the blue reaction, so that is also on the wrong side.

The 1<sup>st</sup> reaction needs to be flipped, since S and  $\text{O}_2$  are on the wrong sides.



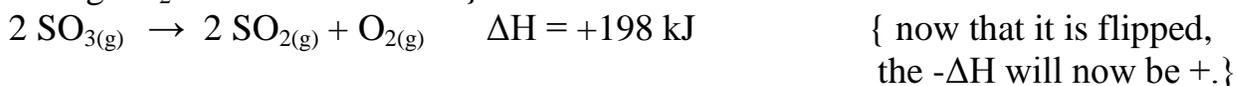
Look at the 2<sup>nd</sup> reaction:

\*The  $\text{SO}_2$  is on the left side of the 2<sup>nd</sup> reaction, but on the right side of the blue reaction. It is on the wrong side.

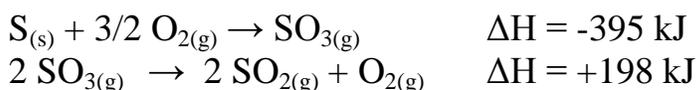
\*The  $\text{O}_2$  is on the left side of the 2<sup>nd</sup> reaction and on the left side of the blue reaction, so that is OK.

\*The  $\text{SO}_3$  is on the right side of the 2<sup>nd</sup> reaction, but it is not in the blue reaction, so that does not help.

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

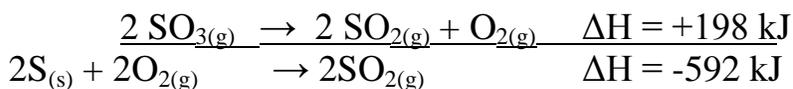


So far we have this:



Now we need to cancel out any compounds that are not in the blue reaction. That means we need to cancel the  $\text{SO}_3$ .

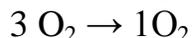
To cancel the  $\text{SO}_3$  we need to multiply the 1<sup>st</sup> reaction by 2, and multiply the  $\Delta H$  by 2.



When the reactions are added we will get on the left side  $2 \times \text{S} = 2 \text{S}$ .

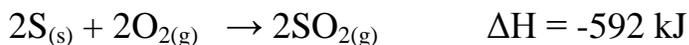
For the  $\text{O}_2$ : On the left there are  $2 \times 3/2 \text{O}_2$  which equals  $3 \text{O}_2$ .

On the right there is O<sub>2</sub>, so just 1 O<sub>2</sub>.  
 If we have, 3 O<sub>2</sub> on the left and 1 O<sub>2</sub> on the right.



We can subtract off 1 O<sub>2</sub> from each side,  
 leaving 2 O<sub>2</sub> on the left side.

And there are 2 SO<sub>2</sub> on the right side.

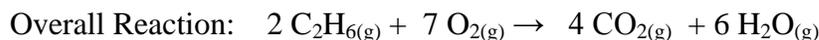


One last problem: Our reaction does not match the blue reaction, because it is two times too big. So we must divide by 2. Also divide the ΔH by 2.



Supplemental Notes: ΔH<sub>formation</sub> and why ∑nΔH<sub>products</sub> - ∑nΔH<sub>reactants</sub> works.

ΔH<sub>reaction</sub> = ∑nΔH<sub>products</sub> - ∑nΔH<sub>reactants</sub> can be explained by doing a Hess's Law problem with the ΔH<sub>formation</sub> reactions of the reactants and products in the overall reaction.



**1<sup>st</sup> step: Write the ΔH<sub>formation</sub> 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.

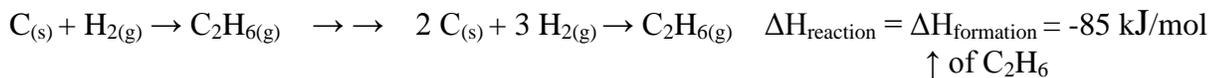
(Metals: Fe<sub>(s)</sub>, Na<sub>(s)</sub> etc., Metalloids: Si<sub>(s)</sub>, Ge<sub>(s)</sub> etc., Non-metals: C<sub>(s)</sub>, S<sub>(s)</sub> etc.)

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

(Halogens: F<sub>2(g)</sub>, Cl<sub>2(g)</sub>, Br<sub>2(l)</sub>, I<sub>2(s)</sub>, Gases: H<sub>2(g)</sub>, N<sub>2(g)</sub>, O<sub>2(g)</sub>)

Noble gases have full orbital layers and are stable being alone: He<sub>(g)</sub>, Ne<sub>(g)</sub> etc.

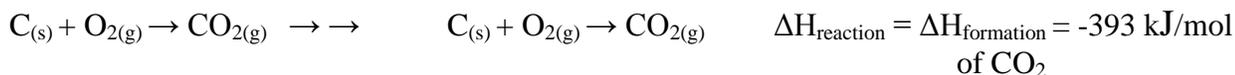
Balance the equation



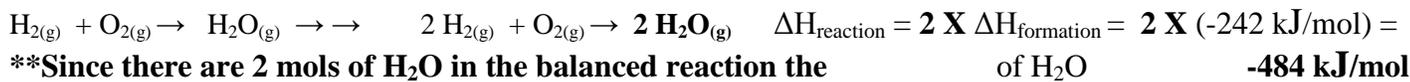
↑ of C<sub>2</sub>H<sub>6</sub>

You can find the ΔH<sub>formation</sub> of the compound from the ΔH, ΔG, and ΔS Table in your textbook.

O<sub>2(g)</sub> is just O<sub>2(g)</sub>, so there is no formation reaction.



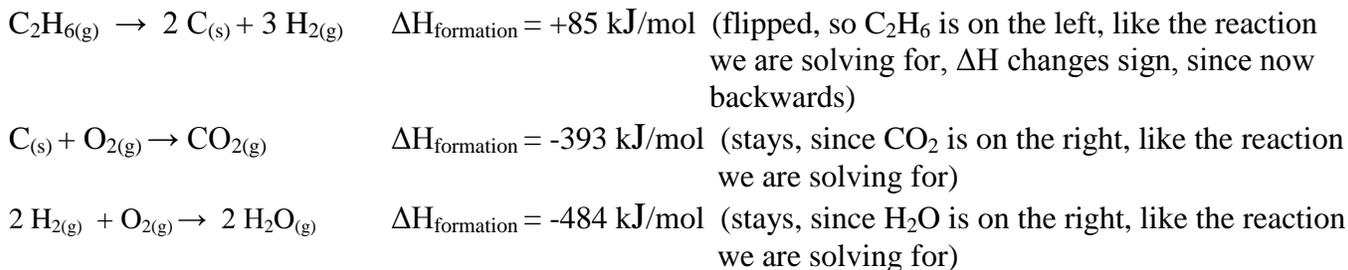
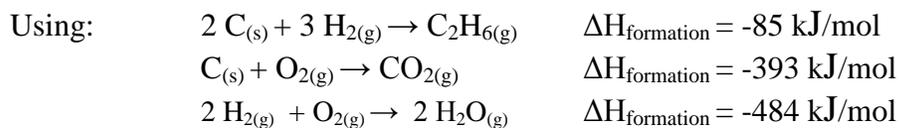
of CO<sub>2</sub>



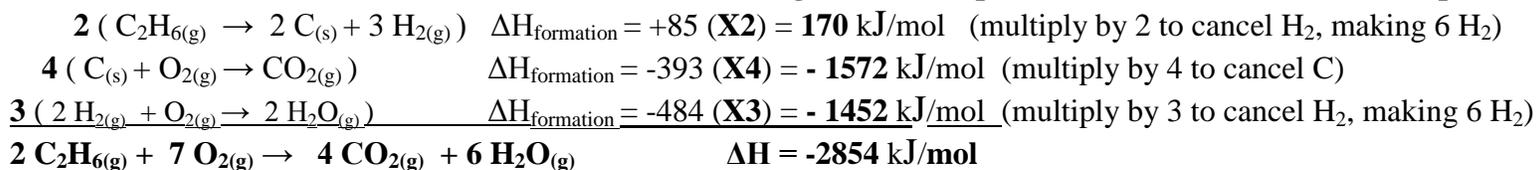
**\*\*Since there are 2 mols of H<sub>2</sub>O in the balanced reaction the ΔH<sub>reaction</sub> will be two times the ΔH<sub>formation</sub> of H<sub>2</sub>O. Or another way of thinking about it, is that the ΔH<sub>formation</sub> will be half the ΔH<sub>reaction</sub>.**

**2<sup>nd</sup> step: Use the above reactions in a Hess's Law problem to solve for the overall reaction.**

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



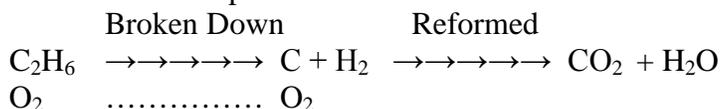
**\*\*The energies are multiplied when the reactions are multiplied.**



**Why this works:**

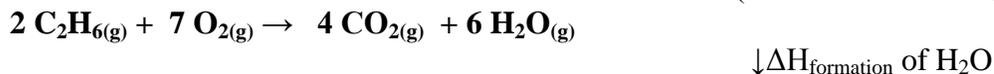
The 1<sup>st</sup> reaction of the three reactions in the Hess's Law problem breaks  $\text{C}_2\text{H}_6$  apart to its elements  $\text{C}_{(\text{s})}$  and  $\text{H}_{2(\text{g})}$ . This is the opposite of the  $\Delta H_{\text{formation}}$ , since  $\text{C}_2\text{H}_6$  is broken apart and 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 its 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 2<sup>nd</sup> and 3<sup>rd</sup> reactions of the Hess's Law problem.



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

**3<sup>rd</sup> 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.)

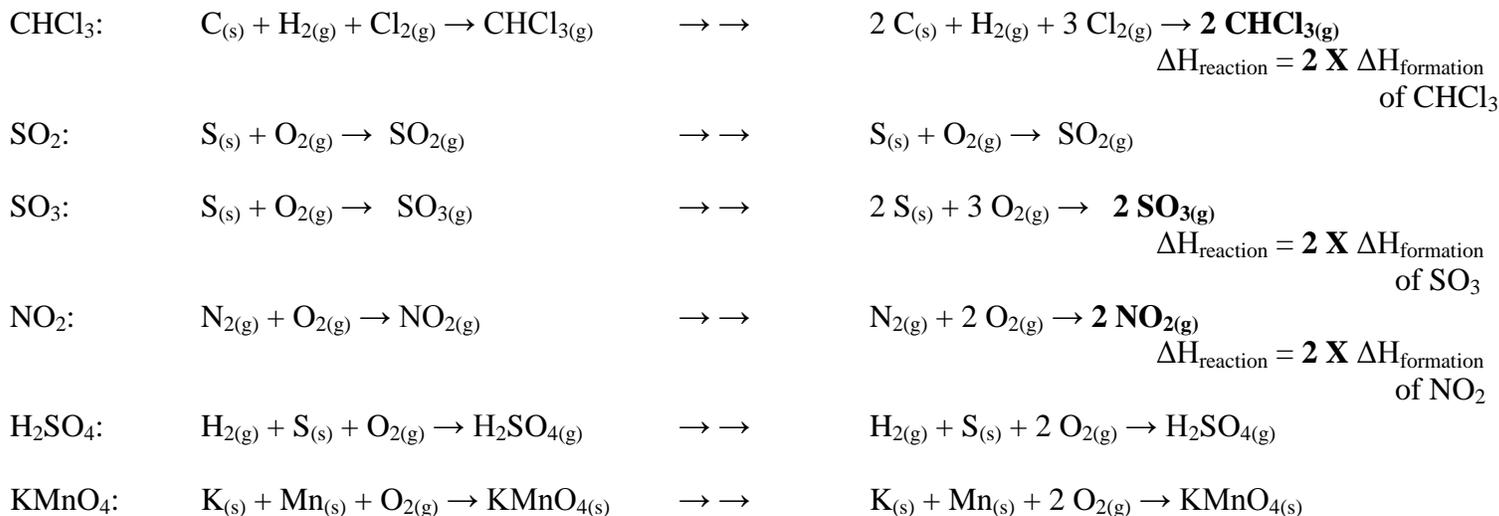


$$\Delta H_{\text{reaction}} = [(4 \text{ mol CO}_2) (-393 \text{ kJ/mol}) + (6 \text{ mol H}_2\text{O}) (-242 \text{ kJ/mol})] - [(2 \text{ mol C}_2\text{H}_6) (-85 \text{ kJ/mol}) + (7 \text{ mol O}_2) (0 \text{ kJ/mol})]$$

$$\Delta H_{\text{reaction}} = -1572 - 1452 + 170 = \mathbf{-2854 \text{ kJ/mol}}$$

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 $\Delta H_{\text{formations}}$ :



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

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

(Halogens: F<sub>2(g)</sub>, Cl<sub>2(g)</sub>, Br<sub>2(l)</sub>, I<sub>2(s)</sub> Gases: H<sub>2(g)</sub>, N<sub>2(g)</sub>, O<sub>2(g)</sub>)

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

**\*End of Notes\***