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

The enthalpy change  $(\Delta H_r^{o})$  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 <u>entire</u> 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 <u>entire</u> reaction by a number so that they do cancel completely and multiply  $\Delta H$  by that same number.

Left $\rightarrow$ Right		
Ex.1) Given: $2 \text{ HF}_{(g)} \rightarrow H_{2(g)} + F_{2(g)}$	$\Delta H = +537 \text{ kJ}$	(1 <sup>st</sup> reaction)
$\frac{1}{2} C_{(s)} + F_{2(g)} \rightarrow \frac{1}{2} CF_{4(g)}$	$\Delta H = -340. \text{ kJ}$	$(2^{nd} reaction)$
$2 \operatorname{C}_{(\mathrm{s})} + 2 \operatorname{H}_{2(\mathrm{g})} \rightarrow \operatorname{C}_{2}\operatorname{H}_{4(\mathrm{g})}$	$\Delta H = 52 \text{ kJ}$	$(3^{rd} reaction)$

Find  $\Delta H_r^{o}$  for:  $C_2H_{4(g)} + 6 F_{2(g)} \rightarrow 2 CF_{4(g)} + 4 HF_{(g)}$ 

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<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.

 $H_{2(g)} + F_{2(g)} \rightarrow 2 HF_{(g)}$   $\Delta H = -537 \text{ kJ}$  (F<sub>2</sub> & HF now on correct sides , now -537)

Look at the second reaction.

\*The C is on the left side of the  $2^{nd}$  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  $2^{nd}$  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.

$$\frac{1}{2}C_{(s)} + F_{2(g)} \rightarrow \frac{1}{2}CF_{4(g)}$$
  $\Delta H = -340. \text{ kJ} \quad (F_2 \& CF_4 \text{ on correct sides already})$ 

Look at the third reaction.

\*The C is on the left side of the  $3^{rd}$  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  $3^{rd}$  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  $3^{rd}$  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 chemistrynoteslecture.com © 2011 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.

 $C_2H_{4(g)} \rightarrow 2 C_{(s)} + 2 H_{2(g)}$   $\Delta H = -52 \text{ kJ}$  ( $C_2H_4$  was on wrong side, now -52)

So this is what we have so far:

$H_{2(g)} + F_{2(g)} \rightarrow 2 HF_{(g)}$	$\Delta H = -537 \text{ kJ}$
$\frac{1}{2}C_{(s)} + F_{2(g)} \rightarrow \frac{1}{2}CF_{4(g)}$	$\Delta H = -340. \text{ kJ}$
$\underline{C_2H_{4(g)} \rightarrow 2 C_{(s)} + 2 H_{2(g)}}$	$\Delta H = -52 \text{ kJ}$

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

 $\begin{array}{ll} 2 \ ( \ H_{2(g)} + F_{2(g)} \rightarrow 2 \ HF_{(g)} \ ) & \Delta H = -537 \ kJ & X \ 2 & (need \ to \ cancel \ H_2) = \ -1074 \ kJ \\ 4 \ ( \ ^{1}\!\!\!\! 2 \ C_{(s)} + F_{2(g)} \rightarrow \ ^{1}\!\!\! 2 \ CF_{4(g)} \ ) & \Delta H = -340. \ kJ & X \ 4 & (need \ to \ cancel \ C) \ = -1360 \ kJ \\ \hline \frac{C_2 H_{4(g)} \rightarrow 2 \ C_{(s)} + 2 \ H_{2(g)}}{C_2 H_{4(g)} + 6 \ F_{2(g)} \rightarrow 2 \ CF_{4(g)} + 4 \ HF_{(g)} \quad \Delta H = -2486 \ kJ \end{array}$ 

When the reactions are added, we have  $1 C_2H_4$  on the left side.

We have 2 X 1  $F_2$  (1<sup>st</sup> reaction) added to 4 X 1 $F_2$  (2<sup>nd</sup> 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<sub>4</sub> = 2 CF<sub>4</sub>.

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:

$$\begin{array}{c} \overline{\text{SO}}_{3(\text{g})} \rightarrow \overline{\text{S}}_{(\text{s})} + 3/2 \text{ O}_{2(\text{g})} \\ 2 \ \overline{\text{SO}}_{2(\text{g})} + \overline{\text{O}}_{2(\text{g})} \rightarrow 2 \ \overline{\text{SO}}_{3(\text{g})} \end{array} \begin{array}{c} \Delta H = +395 \text{ kJ} \\ \Delta H = -198 \text{ kJ} \end{array} \begin{array}{c} (1^{\text{st}} \text{ reaction}) \\ (2^{\text{nd}} \text{ reaction}) \end{array}$$

Calculate  $\Delta H$  for the reaction:  $S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}$ Look at the 1<sup>st</sup> reaction:

\*The SO<sub>3</sub> is on the left side of the  $1^{st}$  reaction, but is it not in the blue reaction, so that does not help. \*The S is on the right side of the  $1^{st}$  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<sup>st</sup> reaction and on the left side of the blue reaction, so that is also on the wrong side.

The  $1^{st}$  reaction needs to be flipped, since S and  $O_2$  are on the wrong sides.

$$\begin{split} S_{(s)} + 3/2 \ O_{2(g)} & \rightarrow SO_{3(g)} \\ & \Delta H = -395 \ \text{kJ} \\ & \text{the } +\Delta H \ \text{will now be } -. \end{split}$$

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

\*The SO<sub>2</sub> is on the left side of the  $2^{nd}$  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<sup>nd</sup> reaction and on the left side of the blue reaction, so that is OK. \*The SO<sub>3</sub> 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 SO<sub>2</sub> is on the wrong side, but the O<sub>2</sub> is on the correct side. We need to figure out which is the most important! The SO<sub>2</sub> in that 2<sup>nd</sup> reaction is the only SO<sub>2</sub> in the first two reactions, but there is O<sub>2</sub> in both reactions #1 and #2. The SO<sub>2</sub> 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 SO<sub>2</sub> to the right side. {The O<sub>2</sub> will go on the wrong side, but there is O<sub>2</sub> 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 
$$O_2$$
 on the correct side.}

 $2 \text{ SO}_{3(g)} \rightarrow 2 \text{ SO}_{2(g)} + \text{O}_{2(g)}$   $\Delta \text{H} = +198 \text{ kJ}$  { now that it is flipped, the - $\Delta \text{H}$  will now be +.}

So far we have this:

$$\begin{array}{ll} S_{(s)} + 3/2 \ O_{2(g)} \to SO_{3(g)} & \Delta H = -395 \ kJ \\ 2 \ SO_{3(g)} \to 2 \ SO_{2(g)} + O_{2(g)} & \Delta H = +198 \ kJ \end{array}$$

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<sub>3</sub> we need to multiply the 1<sup>st</sup> reaction by 2, and multiply the  $\Delta H$  by 2. 2 (S<sub>(s)</sub> + 3/2 O<sub>2(g)</sub>  $\rightarrow$  SO<sub>3(g)</sub>)  $\Delta H = -395$  kJ X 2 = -790 kJ

$$\frac{2 \text{ SO}_{3(g)}}{2S_{(s)} + 2O_{2(g)}} \xrightarrow{\rightarrow} 2 \text{ SO}_{2(g)} + O_{2(g)} \qquad \Delta H = +198 \text{ kJ}$$
$$\rightarrow 2SO_{2(g)} \qquad \Delta H = -592 \text{ kJ}$$

When the reactions are added we will get on the left side 2 X S = 2 S. For the O<sub>2</sub>: On the left there are 2 X 3/2 O<sub>2</sub> which equals 3 O<sub>2</sub>. chemistrynoteslecture.com © 2011

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.

> $3 O_2 \rightarrow 1O_2$  $2 O_2 \rightarrow$

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

And there are  $2 \text{ SO}_2$  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.

$$S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)} \qquad \Delta H = -296 \text{ kJ}$$

## <u>Supplemental Notes:</u> $\Delta H_{\text{formation}}$ 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:  $2 C_2 H_{6(g)} + 7 O_{2(g)} \rightarrow 4 CO_{2(g)} + 6 H_2 O_{(g)}$ 

#### <u>**1**<sup>st</sup> step:</u> Write the $\Delta H_{formation}$ 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<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  $C_{(s)} + H_{2(g)} \rightarrow C_2 H_{6(g)} \quad \rightarrow \rightarrow \quad 2 \ C_{(s)} + 3 \ H_{2(g)} \rightarrow C_2 H_{6(g)} \quad \Delta H_{reaction} = \Delta H_{formation} = -85 \ kJ/mol$  $\uparrow$  of C<sub>2</sub>H<sub>6</sub> 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.

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \rightarrow \rightarrow CO_{2(g)} \rightarrow CO_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H_{reaction} = -393 \text{ kJ/mol}$$
of CO<sub>2</sub>

 $H_{2(g)} + O_{2(g)} \rightarrow H_2O_{(g)} \rightarrow D_{2(g)} \rightarrow 2H_{2(g)} \rightarrow 2H_2O_{(g)} \rightarrow 2H_2O_{(g)} \rightarrow \Delta H_{reaction} = 2X \Delta H_{formation} = 2X (-242 \text{ kJ/mol}) = 2X (-242 \text{$ \*\*Since there are 2 mols of H<sub>2</sub>O in the balanced reaction the of H<sub>2</sub>O -484 kJ/mol  $\Delta H_{reaction}$  will be two times the  $\Delta H_{formation}$  of H<sub>2</sub>O. Or another way of thinking about it, is that the  $\Delta H_{\text{formation}}$  will be half the  $\Delta H_{\text{reaction}}$ .

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#### 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 C<sub>2</sub>H<sub>6(g)</sub> + 7 O<sub>2(g)</sub> $\rightarrow$ 4 CO<sub>2(g)</sub> + 6 H<sub>2</sub>O<sub>(g)</sub>

Using:	$2 C_{(s)} + 3 H_{2(g)} \rightarrow C_2 H_{6(g)}$	$\Delta H_{\text{formation}} = -85 \text{ kJ/mol}$
	$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$	$\Delta H_{\text{formation}} = -393 \text{ kJ/mol}$
	$2 \operatorname{H}_{2(g)} + O_{2(g)} \rightarrow 2 \operatorname{H}_2O_{(g)}$	$\Delta H_{\text{formation}} = -484 \text{ kJ/mol}$
	$C_2H_{6(g)} \rightarrow 2 C_{(s)} + 3 H_{2(g)}$	$\Delta H_{\text{formation}} = +85 \text{ kJ/mol}$ (flipped, so $C_2H_6$ is on the left, like the reaction we are solving for, $\Delta H$ changes sign, since now backwards)
	$C_{(s)} + O_{2(g)} \to CO_{2(g)}$	$\Delta H_{\text{formation}} = -393 \text{ kJ/mol}$ (stays, since CO <sub>2</sub> is on the right, like the reaction we are solving for)
	$2 \hspace{0.1cm} H_{2(g)} \hspace{0.1cm} + \hspace{0.1cm} O_{2(g)} \hspace{0.1cm} \rightarrow \hspace{0.1cm} 2 \hspace{0.1cm} H_2 O_{(g)}$	$\Delta H_{\text{formation}} = -484 \text{ kJ/mol}$ (stays, since H <sub>2</sub> O is on the right, like the reaction we are solving for)
		<b>**</b> The energies are multiplied when the reactions are multiplied.
<b>2</b> ( C <sub>2</sub> H	$H_{6(g)} \rightarrow 2 C_{(s)} + 3 H_{2(g)}) \Delta H$	formation = +85 (X2) = 170  kJ/mol (multiply by 2 to cancel H2, making 6 H2)
<b>4</b> ( $C_{(s)}$ +	$O_{2(g)} \rightarrow CO_{2(g)}) \qquad \Delta H_{1}$	formation = -393 (X4) = -1572 kJ/mol (multiply by 4 to cancel C)
<u><b>3</b> ( 2 H<sub>2(g)</sub> +</u>	$O_{2(g)} \rightarrow 2 H_2 O_{(g)}) \qquad \Delta H_2$	$f_{\text{formation}} = -484 \text{ (X3)} = -1452 \text{ kJ/mol} (\text{multiply by 3 to cancel H}_2, \text{ making 6 H}_2)$
$2 C_2 H_{6(g)} +$	$7 O_{2(g)} \rightarrow 4 CO_{2(g)} + 6 H_2 O_{2(g)}$	$\Delta H = -2854 \text{ kJ/mol}$

#### Why this works:

The 1<sup>st</sup> reaction of the three reactions in the Hess's Law problem breaks  $C_2H_6$  apart to it's elements  $C_{(s)}$  and  $H_{2(g)}$ . This is the opposite of the  $\Delta H_{\text{formation}}$ , since  $C_2H_6$  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  $O_{2(g)}$ , 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  $C_{(s)}$ ,  $H_{2(g)}$ , and  $O_{2(g)}$  are formed into the products in the 2<sup>nd</sup> and 3<sup>rd</sup> reactions of the Hess's Law problem.

 $\begin{array}{ccc} & \text{Broken Down} & \text{Reformed} \\ C_2H_6 & \longrightarrow \longrightarrow \longrightarrow & C+H_2 & \longrightarrow \longrightarrow \longrightarrow & CO_2+H_2O \\ O_2 & \dots & O_2 \end{array}$ 

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

# <u>**3**<sup>rd</sup> step:</u> Prove that this equation works: $\Delta H_{reaction} = \sum n \Delta H_{products} - \sum n \Delta H_{reactants}$

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

 $\begin{array}{rcl} 2 \ C_2 H_{6(g)} + \ 7 \ O_{2(g)} \rightarrow & 4 \ CO_{2(g)} + 6 \ H_2 O_{(g)} & & & \downarrow \Delta H_{formation} \ of \ H_2 O \\ \Delta H_{reaction} = \left[ (4 \ mol \ CO_2) \ (-393 \ kJ/mol) + (6 \ mol \ H_2 O) \ (-242 \ kJ/mol) \ \right] - & \\ & & \left[ \ (2 \ mol \ C_2 H_6) \ (-85 kJ/mol) + (7 \ mol \ O_2) \ (0 \ kJ/mol) \right] \end{array}$ 

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

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

CHCl <sub>3</sub> :	$C_{(s)} + H_{2(g)} + Cl_{2(g)} \rightarrow CHCl_{3(g)}$	$\rightarrow \rightarrow$	$2 C_{(s)} + H_{2(g)} + 3 Cl_{2(g)} \rightarrow 2 CHCl_{3(g)}$ $\Delta H_{reaction} = 2 X \Delta H_{formation}$ of CHCl <sub>3</sub>
SO <sub>2</sub> :	$S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}$	$\rightarrow \rightarrow$	$S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}$
SO <sub>3</sub> :	$S_{(s)} + O_{2(g)} \rightarrow SO_{3(g)}$	$\rightarrow \rightarrow$	$2 \mathbf{S}_{(s)} + 3 \mathbf{O}_{2(g)} \rightarrow 2 \mathbf{SO}_{3(g)}$ $\Delta \mathbf{H}_{\text{reaction}} = 2 \mathbf{X} \Delta \mathbf{H}_{\text{formation}}$ of SO <sub>2</sub>
NO <sub>2</sub> :	$N_{2(g)} + O_{2(g)} \longrightarrow NO_{2(g)}$	$\rightarrow \rightarrow$	$N_{2(g)} + 2 O_{2(g)} \rightarrow 2 NO_{2(g)}$ $\Delta H_{reaction} = 2 X \Delta H_{formation}$ of NO <sub>2</sub>
$H_2SO_4$ :	$H_{2(g)} + S_{(s)} + O_{2(g)} \longrightarrow H_2 SO_{4(g)}$	$\rightarrow \rightarrow$	$H_{2(g)} + S_{(s)} + 2 O_{2(g)} \rightarrow H_2SO_{4(g)}$
KMnO <sub>4</sub> :	$K_{(s)} + Mn_{(s)} + O_{2(g)} \rightarrow KMnO_{4(s)}$	$\rightarrow \rightarrow$	$K_{(s)} + Mn_{(s)} + 2 O_{2(g)} \rightarrow KMnO_{4(s)}$

# Remember: Every <u>metal, metalloid and non-metal is written as a single element, except</u> 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:  $F_{2(g)}$ ,  $Cl_{2(g)}$ ,  $Br_{2(l)}$ ,  $I_{2(s)}$  Gases:  $H_{2(g)}$ ,  $N_{2(g)}$ ,  $O_{2(g)}$ ) Noble gases have full orbital layers and are happy as loners:  $He_{(g)}$ ,  $Ne_{(g)}$  etc.

# \*End of Notes\*