## Notes-Chapter 6 Part II-Hess's Law and Enthalpies of formation

## Hess's Law

(If you have your textbooks at home, you can read through pages 260-264.)

## Definition:

"When going from a particular set of reactants to a particular set of products, the change in the enthalpy $(\Delta H)$ of the reaction is the same whether the reaction takes place in one step or in several steps."
OR
"When a reaction takes place in more than one step, the $\Delta H$ for the reaction is equal to the sum of the changes in enthalpy ( $\Delta \mathrm{H}^{\prime} \mathrm{s}$ ) of the steps."

Example (Easy example)
Note: I will not be putting in the "phases" of the reactants or products unless more than one phase of the same element or compound appears in the steps.
Also, the "overall reaction" refers to the reaction that would be the sum of the steps (the reaction that results from the steps).

| Overall | $\mathrm{N}_{2}+2 \mathrm{O}_{2} \rightarrow 2 \mathrm{NO}_{2}$ | $\Delta \mathrm{H}=$ ? |
| :---: | :---: | :---: |
| Steps: | $\mathrm{N}_{2}+\mathrm{O}_{2} \rightarrow 2 \mathrm{NO}$ | $\Delta \mathrm{H}=+180 \mathrm{~kJ}$ |
|  | $2 \mathrm{NO}+\mathrm{O}_{2} \rightarrow 2 \mathrm{NO}_{2}$ | $\Delta \mathrm{H}=-112 \mathrm{~kJ}$ |
| Sum: | $\mathbf{N}_{2}+2 \mathrm{O}_{2} \rightarrow 2 \mathrm{NO}_{2}$ | $\Delta \mathrm{H}=+68 \mathrm{~kJ}$ |

The sum of the equation equals the Overall Rxn. Note that the NO on opposite sides of the reactions are identical in form and amount so they cancel through the laws of "algebra". The $\Delta \mathrm{H}$ of the overall reaction is therefore, +68 kJ .

Note: This was an "easy example". Sometimes we must "manipulate" the steps to have them "add" up to the overall reaction.
If I reverse a reaction step (flip it). The $\Delta \mathrm{H}$ for that step changes its sign.
Example: $2 \mathrm{NO} \rightarrow \mathrm{N}_{2}+\mathrm{O}_{2} \quad \Delta \mathrm{H}=-180 \mathrm{~kJ}$

$$
\text { (flipped) } \mathrm{N}_{2}+\mathrm{O}_{2} \rightarrow 2 \mathrm{NO} \quad \Delta \mathrm{H}=+180 \mathrm{~kJ}
$$

If you need to multiply or divide a step by a number, the $\boldsymbol{\Delta H}$ of that step needs to also be multiplied or divided by that number.
Example: $\mathrm{N}_{2}+\mathrm{O}_{2} \rightarrow 2 \mathrm{NO} \quad \Delta \mathrm{H}=+180 \mathrm{~kJ}$
(x2) $2 \mathrm{~N}_{2}+2 \mathrm{O}_{2} \rightarrow 4 \mathrm{NO} \quad \Delta \mathrm{H}=(2)(180)=+360 \mathrm{~kJ}$
Or
$(\div 2) \quad 1 / 2 \mathrm{~N}_{2}+1 / 2 \mathrm{O}_{2} \rightarrow \mathrm{NO} \quad \Delta \mathrm{H}=(180 \div 2)=+90 \mathrm{~kJ}$
Example Problem:
Overall Reaction:
Cgraphite $^{\rightarrow}$ Cdiamond
$\Delta \mathrm{H}=$ ?

| Steps: |  | $\Delta \mathrm{H}(\mathrm{Kj})$ |
| :--- | :--- | :--- |
|  | a) $\mathrm{C}_{\text {graphite }}+\mathrm{O}_{2} \rightarrow \mathrm{CO}_{2}$ | -394 |
|  | b) $\mathrm{C}_{\text {diamond }}+\mathrm{O}_{2} \rightarrow-\mathrm{CO}_{z}$ | -396 |
| (flip step b) | $\mathrm{CO}_{2} \rightarrow \mathrm{C}_{\text {diamond }}+\mathrm{O}_{2}$ | +396 (changed sign) |
|  |  |  |
| Now |  | $\Delta \mathrm{H}(\mathrm{Kj})$ |
|  |  | -394 |
|  | a) $\mathrm{C}_{\text {graphite }}+\mathrm{O}_{2} \rightarrow \mathrm{CO}_{z}$ | +396 |
| Sum: | b) $\mathrm{CO}+\mathrm{CO}_{\text {diamond }}+\mathrm{O}_{z^{-}}$ | $\Delta \mathrm{H}=+2 \mathrm{Kj}$ |

## Steps to follow to calculate $\Delta \mathrm{H}$ of a reaction using Hess's Law:

1) Make sure each reactant and each product in the Overall Reaction is on the correct side of the equation in the steps, flipping steps if necessary (as was done in the above example). If a reactant or a product in the overall reaction appears in more than one step, SKIP IT. It will take care of itself.
2) Make sure the coefficients of each reactant and product in the Overall Reaction is the same as the coefficients in the steps (multiply or divide by whatever number is necessary to make the coefficients the same making sure to include the $\Delta H$ when you do this.) If a reactant or a product in the overall reaction appears in more than one step, SKIP IT. It will take care of itself.
3) Cancel what is exactly the same in any step on the left with any step on the right (as done in the example above). All reactants and products in the steps must cancel if they do not appear in the overall reaction. Now add the reactants and products of the steps to show that the sum of the steps add up to the overall reaction. Add the $\Delta H^{\prime}$ s of the steps to obtain the $\Delta H$ of the reaction.

A more difficult example will follow on the next page.
You have problems assigned \#72 and \#74.
If you think you need to practice more problems, \#73 and \#75 are other problems to practice with the answers in the back of the book (if you have your book).

Example:

$$
\text { Overall Reaction: } \quad 2 B+3 \mathrm{H}_{2} \rightarrow \mathrm{~B}_{2} \mathrm{H}_{6} \quad \Delta \mathrm{H}=\text { ? }
$$

## Steps:

a) $2 \mathrm{~B}+3 / 2 \mathrm{O}_{2} \rightarrow \mathrm{~B}_{2} \mathrm{H}_{3}$
b) $\mathrm{B}_{2} \mathrm{O}_{6}+3 \mathrm{O}_{2} \rightarrow \mathrm{~B}_{2} \mathrm{O}_{3}+3 \mathrm{H}_{2} \mathrm{O}(\mathrm{g})$
c) $\mathrm{H}_{2}+1 / 2 \mathrm{O}_{2} \rightarrow \mathrm{H}_{2} \mathrm{O}$ (I)
d) $\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{g})$
$\Delta \mathrm{H}(\mathrm{kJ})$
-1273
-2035
-286
$+44$

Note: (Each of the reactants and products in the overall reaction appear in only one of the steps so none of them can be skipped in the 3 steps we need to follow.)

Step 1:
The reactants in the overall reaction are $B$ and $\mathrm{H}_{2}$. Check that they are on the correct side in the steps.
Both B (found in step " a ") and $\mathrm{H}_{2}$ (found in step " c ") are on the reactants (correct) side in the steps. Good.
The Product, $\mathrm{B}_{2} \mathrm{O}_{6}$ in step " b ", is on the reactants (wrong side) and the step needs to be "flipped".

$$
\text { It becomes } \quad \mathrm{B}_{2} \mathrm{O}_{3}+3 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \rightarrow \mathrm{B}_{2} \mathrm{O}_{6}+3 \mathrm{O}_{2} \quad \Delta \mathrm{H}=+2035 \text { (sign changes) }
$$

## Steps:

$\Delta H(k J)$
-1273
a) $2 \mathrm{~B}+3 / 2 \mathrm{O}_{2} \rightarrow \mathrm{~B}_{2} \mathrm{H}_{3}$ +2035
b) $\mathrm{B}_{2} \mathrm{O}_{3}+3 \mathrm{H}_{2} \mathrm{O}(\mathrm{g}) \rightarrow \mathrm{B}_{2} \mathrm{O}_{6}+3 \mathrm{O}_{2}$ -286
c) $\mathrm{H}_{2}+1 / 2 \mathrm{O}_{2} \rightarrow \mathrm{H}_{2} \mathrm{O}$ (I) 28
d) $\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{g})$ $+44$

Step 2:
Check the coefficients of the reactants and products in the overall reaction with their coefficients in the steps.
The coefficient for $B$ in the overall reaction is 2 . The coefficient for $B$ in step " $a$ " is also 2 . Good The coefficient for $\mathrm{H}_{2}$ in the reaction is 3 , but the coefficient for $\mathrm{H}_{2}$ in step " c " is 1. (We must multiply through step c by 3 including the $\Delta \mathrm{H}$ for that step.

It becomes $3 \mathrm{H}_{2}+3 / 2 \mathrm{O}_{2} \rightarrow 3 \mathrm{H}_{2} \mathrm{O}(\mathrm{I})$

$$
\Delta H=(3)(-286)=-858 \mathrm{~kJ}
$$

The coefficient for $\mathrm{B}_{2} \mathrm{O} 6$ is 1 and the coefficient in step " $b$ " is 1 . Good

## Steps:

a) $2 \mathrm{~B}+3 / 2 \mathrm{O}_{2} \rightarrow \mathrm{~B}_{2} \mathrm{H}_{3}$
b) $\mathrm{B}_{2} \mathrm{O}_{3}+3 \mathrm{H}_{2} \mathrm{O}(\mathrm{g}) \rightarrow \mathrm{B}_{2} \mathrm{O}_{6}+3 \mathrm{O}_{2}$
c) $3 \mathrm{H}_{2}+3 / 2 \mathrm{O}_{2} \rightarrow 3 \mathrm{H}_{2} \mathrm{O}(\mathrm{I})$
d) $\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{g})$

## $\Delta \mathrm{H}(\mathrm{kJ})$

-1273
+2035
-858
$+44$

Step 3:
Cancel All Substances that are EXACTLY the same on opposite sides of the steps.

## Steps:

a) $2 \mathrm{~B}+3 / 2 \mathrm{O}_{z} \rightarrow \mathrm{~B}_{z} \mathrm{H}_{3}$
b) $\mathrm{B}_{2} \mathrm{O}_{3}+3 \mathrm{H}_{2} \mathrm{O}(\mathrm{g}) \rightarrow \mathrm{B}_{2} \mathrm{O}_{6}+3 \mathrm{O}_{7}$.
c) $3 \mathrm{H}_{2}+3 / 2 \mathrm{O}_{2} \rightarrow 3 \mathrm{H}_{2} \mathrm{O}$ (I)
d) $\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{g})$

## $\Delta \mathrm{H}(\mathrm{kJ})$

-1273
$+2035\left(3 / 2 \mathrm{O}_{2}+3 / 2 \mathrm{O}_{2}=3 \mathrm{O}_{2}\right)$
-858
$+44$

Problem—The $\mathrm{H}_{2} \mathrm{O}(\mathrm{I})$ and the $\mathrm{H}_{2} \mathrm{O}(\mathrm{g})$ do not cancel.
I need to multiply step "d" by 3 so all the $\mathrm{H}_{2} \mathrm{O}$ 's cancel.
"d" becomes $3 \mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightarrow 3 \mathrm{H}_{2} \mathrm{O}(\mathrm{g}) \quad \Delta \mathrm{H}=+132 \mathrm{~kJ}$

I now have the following:

Steps:

## $\Delta H(k J)$

-1273
a) $2 \mathrm{~B}+3 / 2 \mathrm{O}_{2} \rightarrow \mathrm{~B}_{2} \mathrm{H}_{3}$
b) $\mathrm{B}_{2} \mathrm{O}_{3}-+3 \mathrm{H}_{2} \mathrm{O}(\mathrm{g}) \rightarrow \mathrm{B}_{2} \mathrm{O}_{6}+3 \mathrm{O}_{2}$.
+2035
c) $3 \mathrm{H}_{2}+3 / 2 \mathrm{O}_{z} \rightarrow 3 \mathrm{H}_{z} \mathrm{O}(H$ -858
d) $3 \mathrm{H}_{2} \mathrm{O}(1) \rightarrow 3 \mathrm{H}_{2} \mathrm{O}(\mathrm{s})$
+132
Sum:
$\mathbf{2 B + 3} \mathrm{H}_{2} \rightarrow \mathrm{~B}_{2} \mathrm{O}_{6}$
+36 kJ

Note:
This example is a lengthy on. Most Hess Law problems only have 3 steps, but it is good to practice with a more lengthy problem.

## Enthalpies of Formation

In any chemical reaction, the bonds in the reactants are broken and new bonds in the products are formed.
Every compound has an Enthalpy of Formation-The amount of energy needed to form one mole of a substance

## from its elements in their standard states.

Elements in their standard or natural states have an enthalpy of formation of zero (0) $\mathrm{kJ} / \mathrm{mol}$.
The Enthalpies of formation $\left(\Delta \mathrm{H}_{\mathrm{f}}\right)$ for elements and compounds are listed in the appendix in the back of your book.
I will send you a picture of that appendix.
You can also google them but you must make sure you have the correct "state".
You only have one problem over this for homework.

If you want to find the Enthalpy of a Reaction $\left(\Delta \mathrm{H}_{\mathrm{rxn}}\right)$, you need to add all the enthalpies of formation of the products
multiplied by their coefficients (\#moles)and subtract the sum of all the enthalpies of formation of the reactants
multiplied by their coefficients (\#moles). Because, when a reaction takes place, the reactants break apart (un-form) and the products come together (form).
By subtracting the sum of the reactants, we are changing the signs of the enthalpies of formation because we are reversing the process.

The formula for finding the Enthalpy of a Reaction $\left(\Delta \mathrm{H}_{\mathrm{rxn}}\right)$ is
The sum of (add) the enthalpies of formation of the Products ( $\Delta \mathrm{H}_{\text {prod }}$ ) times their coefficients
minus The sum of (add) the enthalpies of formation
of the reactants $\left(\Delta H_{f}\right)$ times their coefficients.
It is written: $\Delta \mathrm{H}_{\mathrm{rxn}}=\sum \mathrm{n}\left(\Delta \mathrm{H}_{\mathrm{f}}\right)_{\text {products }}--\sum \mathrm{n}$
$\left(\Delta H_{f}\right)_{\text {reactants }}$
" $\Sigma$ " means "the sum of" so it means to add.
The change in enthalpy of formations are in the back of the book.
"n" means \#moles. You need to multiply the coefficients of the

Products and Reactants by their enthalpies before adding.

When you use the appendix I will post, you are looking to use the $\Delta H^{0}{ }_{f}$ values.(Not the $\Delta \mathrm{G}$ or S values)

Example:

$$
2 \mathrm{C}_{8} \mathrm{H}_{18}(\mathrm{I})+25 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow 16 \mathrm{CO}_{2}(\mathrm{~g})+18 \mathrm{H}_{2} \mathrm{O}(\mathrm{I})
$$

$\Delta \mathrm{H}_{\mathrm{f}}$ of $\mathrm{C}_{8} \mathrm{H}_{18}=-269 \mathrm{~kJ} \quad \Delta \mathrm{H}_{\mathrm{f}}$ of $\mathrm{O}_{2}=0 \quad \Delta \mathrm{H}_{\mathrm{f}}$ of $\mathrm{CO}_{2}=-394 \mathrm{~kJ} \quad \Delta \mathrm{H}_{\mathrm{f}}$ of $\mathrm{H}_{2} \mathrm{O}=-286 \mathrm{~kJ}$

$$
\left.\begin{array}{rl}
\Delta \mathrm{H}_{\mathrm{rxn}} & =2 \mathrm{C}_{8} \mathrm{H}_{18}(\mathrm{I})+25 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow 16 \mathrm{CO}_{2}(\mathrm{~g})+18 \mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \\
& =(2)(-269)+(25)(0) \\
& =-538+0(16)(-394)+(18)(-286) \\
& =-538
\end{array} \quad \rightarrow-6304+-5148\right)
$$

Now: Products - Reactants (remember, you need to flip the sums)

$$
\begin{aligned}
(-11452)-(-538)= & -10,914 \mathrm{~kJ} \\
& 1.09 \times 10^{4} \mathrm{~kJ}
\end{aligned}
$$

