Hess's Law of Additivity of Reactions A scientist named Hess discovered that chemical reactions that, when added, equal another chemical equation (called the 'target' equation), their enthalpies  $(\Delta H)$  sum to that of the 'target' equation. Here is an example to illustrate:

These three reactions have been carefully studied in the lab. Their enthalpies have been determined:

(1) 
$$1/2N_2 + 1/2O_2 \rightarrow NO$$
  $\Delta H_1 = +90 \text{ kJ}$ 

(2) 
$$NO + 1/2O_2 \rightarrow NO_2$$
  $\Delta H_2 = -56 \text{ kJ}$ 

(3) 
$$1/2N_2 + O_2 \rightarrow NO_2$$
  $\Delta H_3 = +34 \text{ kJ}$ 

If you look closely, you can see that equations (1) + (2) equal equation (3). When you add equations, simply write all reactants and products together in one equation, then simplify. In this case, here is (1) + (2)

$$1/2N_2 + 1/2O_2 + NO + 1/2O_2 \rightarrow NO + NO_2$$

You can cancel the NO (it's on both sides), and combine the  $O_2$ 's on the left:

$$1/2N_2 + \frac{1}{2}O_2 + \frac{1}{2}O_2 + \frac{1}{2}O_2 \rightarrow \frac{1}{2}$$

This gives the simplified equation:

$$1/2N_2 + O_2 \rightarrow NO_2$$

This is the same as equation (3).

Since (1) + (2) = (3), then 
$$\Delta H_1 + \Delta H_2$$
 should equal  $\Delta H_3$ : +90 kJ + -56 kJ = +34 kJ. +34kJ is  $\Delta H_3$ .

A practical application of this concept involves calculating enthalpies of reactions that are difficult to study in the lab (some reasons are: chem's are expensive; reaction is dangerous or unpredictable).

Since literally thousands of reactions have been studied, with their enthalpies available in reference sources, it is possible to find 2 or more of these reactions that 'sum up' to some difficult reaction. The difficult reaction's enthalpy can then be calculated indirectly, without ever actually performing the reaction itself.

There is one small catch! Reactions that are used from reference sources must often be 'modified' in order to use them to solve a particular problem.

In order to modify these equations to obtain enthalpies of reactions, two basic laws about enthalpies must often be used. They deal with reversing a reaction and multiplying a reaction by a coefficient. The laws are as follows:

<u>Law 1</u>: When a chemical reaction is reversed, the sign of its  $\Delta H$  changes.

Example: This reaction is well known:

$$H_{2(g)} + 1/2O_{2(g)} \rightarrow H_2O_{(g)}$$
  $\Delta H = -241.8 \text{ kJ}$ 

Therefore, we also know the reverse reaction:

$$H_2O_{(g)} \rightarrow H_{2(g)} + 1/2O_{2(g)}$$
  $\Delta H = +241.8 \text{ kJ (note the sign change!)}$ 

(This makes perfect sense. If you reverse a reaction, the

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energy flow will also be reversed.)

<u>Law 2</u>: When a chemical reaction is multiplied by a coefficient, the same is true of its enthalpy.

Example: This reaction is well known:

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$$
  $\Delta H = -393.5 \text{ kJ}$ 

When multiplied by a coefficient, (in this case 2), the following is also true:

$$2C_{(s)} + 2O_{2(g)} \rightarrow 2CO_{2(g)}$$
  $\Delta H = -787.0 \text{ kJ (note the doubled value)}$ 

(This makes perfect sense. If you double the amount of chemical, you double the energy change.)

When you are asked to determine the enthalpy of some reaction, you won't be expected to go to references sources and find equations (from several 100 possibilities) that sum up to your 'target' equation. You will be given a list of equations to choose from, called 'known' equations. You will have to determine which ones to use and how they must be modified (reversed and/or multiplied by coefficients) in order to sum up to your target equation.

Following a set of systematic steps can help you get to the answer as quickly as possible.

Instead of looking at the 'whole' target equation and trying to solve it in one step, concentrate on one chemical at a time.

- 1) Choose the first chemical of your target equation.
- 2) Find a 'known' equation that has this chemical in it (be aware of states, they will be important in some questions). [If the chemical appears in more than one 'known' equation, skip this chemical, it will be accounted for in the end.]
- 3) Modify the 'known' equation so the chemical is on the correct side AND with the correct coefficient. Make the same change to its  $\Delta H$  (change sign and/or multiply).
- 4) Repeat steps 2 and 3 for all remaining chemicals.
- 5) Add up all of your modified 'known' equations, verifying they do in fact add up to your target equation. Add up all  $\Delta H$ 's.
- 6) The sum of the  $\Delta H$ 's will be the  $\Delta H$  of your target equation.

Here is an example:

Target equation (the equation for which you are asked to get the  $\Delta H$ ):

$$6C_{(s)} + 8H_{2(g)} + O_{2(g)} \rightarrow 2C_3H_7OH_{(l)}$$
  $\Delta H = ?$ 

Calculate its  $\Delta H$  using the following known equations:

(1) 
$$C_3H_7OH_{(l)} + 9/2O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(l)}$$
  $\Delta H_1 = -2008 \text{ kJ}$ 

(2) 
$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$$
  $\Delta H_2 = -394 \text{ kJ}$ 

(3) 
$$H_{2(g)} + 1/2O_{2(g)} \rightarrow H_2O_{(1)}$$
  $\Delta H_3 = -286 \text{ kJ}$ 

Our target equation has 4 chemicals in it. Each chemical will be obtained one at a time. The end result should be the target equation. First, get the ' $6C_{(s)}$ ' reactant. C exists in known equation (2):

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$$
  $\Delta H = -394 \text{ kJ}$ 

'C' is on the correct side (reactant), but it needs a coefficient of '6', therefore we will multiply known equation (2) by 6 [noted as 6X(2)]:

$$6X(2) \qquad 6C_{(s)} + 6O_{2(g)} \rightarrow 6CO_{2(g)} \qquad \Delta H = -2364 \text{ kJ}$$

(notice how  $\Delta H$  was also multiplied by 6).

Next, we get the ' $8H_{2(g)}$ ' reactant. We will get it from 8X(3):

$$8X(3)$$
  $8H_{2(g)} + 4O_{2(g)} \rightarrow 8H_2O_{(1)}$   $\Delta H = -2288 \text{ kJ}$ 

Next, we need ' $O_{2(g)}$ ' reactant. Oxygen exists in all three known equations. It will be skipped, as it should be properly accounted for in the end.

Lastly, we need ' $2C_3H_7OH_{(l)}$ ' product. We will get it from -2X(1) [known equation (1) needs to be flipped AND multiplied by 2 to get the propanol on the correct side of the equation with the correct coefficient] -2X(1) 6 $CO_{2(g)} + 8H_2O_{(l)} \rightarrow 2C_3H_7OH_{(l)} + 9O_{2(g)} \Delta H = +4016 \text{ kJ}$ 

Next, the sum of the three modified known equations will be checked to make sure that they add up to the target equation. They are rewritten here to be more clear:

$$6C_{(s)} + 6O_{2(g)} \rightarrow 6CO_{2(g)}$$
  $\Delta H = -2364 \text{ kJ}$   
 $8H_{2(g)} + 4O_{2(g)} \rightarrow 8H_2O_{(l)}$   $\Delta H = -2288 \text{ kJ}$   
 $6CO_{2(g)} + 8H_2O_{(l)} \rightarrow 2C_3H_7OH_{(l)} + 9O_{2(g)}$   $\Delta H = +4016 \text{ kJ}$ 

Sum (all the reactants together, all the products together):

$$\begin{array}{l} 6C_{(s)} + 6O_{2(g)} + 8H_{2(g)} + 4O_{2(g)} + 6CO_{2(g)} + 8H_2O_{(l)} \rightarrow \\ 6CO_{2(g)} + 8H_2O_{(l)} + 2C_3H_7OH_{(l)} + 9O_{2(g)} \end{array}$$

The  $CO_{2(g)}$ 's and  $H_2O_{(l)}$ 's 'cancel' themselves out, and the  $O_2$ 's simplify to one  $O_2$  on the reactant side:

$$6C_{(s)} + \frac{6O_{2(g)}}{6CO_{2(g)}} + 8H_{2(g)} + \frac{4O_{2(g)}}{4O_{2(g)}} + \frac{8H_{2}O_{(l)}}{4O_{2(g)}} + \frac{8H_{2}O_{(l)}}{4$$

This simplifies to:

$$6C_{(s)} + 8H_{2(g)} + O_{2(g)} \rightarrow 2C_3H_7OH_{(l)}$$

This is exactly our target equation! That means that the sum of the  $\Delta H$ 's of the three modified equations must be the  $\Delta H$  of the target equation:

$$\Delta H = (-2364 - 2288 + 4016) \text{ kJ} = -636 \text{ kJ}$$

Therefore, the final answer looks like this:

$$6C_{(s)} + 8H_{2(g)} + O_{2(g)} \rightarrow 2C_3H_7OH_{(l)}$$
  $\Delta H = -636 \text{ kJ}$ 

There are 2 more examples on pages 324-325 you can read if you want to see more.

HW: P326 #1-3; P329 #4-5; P330 #1-4