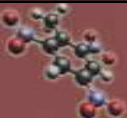


# Thermochemistry 2

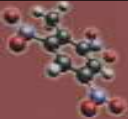
Symbols  
Bond Energy  
Hess's Law I  
Hess's Law II

Author: J R Reid



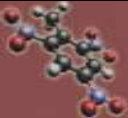
## Revision

- As we know from the level 2 chemistry work –
  - Chemical potential energy can be gained or lost from a chemical during a reaction
  - Chemical potential energy can be used to calculate the energy per mole of a certain chemical – called Enthalpy
  - When a chemical loses Enthalpy it comes out as heat and is called an **exothermic** reaction
  - When a chemical gains Enthalpy it absorbs heat and is called an **endothermic** reaction



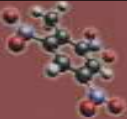
## Still Revising

- We also learnt that:
  - Atoms have the highest level of enthalpy (chemical stored energy)
  - When we make bonds we lose enthalpy - therefore bond making is exothermic
  - When we break bonds we have to put in energy - therefore it is endothermic



## Symbols and Keywords

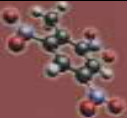
- Enthalpy (H) - the chemical potential energy (per mole) that a chemical possesses
- Change in Enthalpy ( $\Delta H$ ) - the amount of chemical potential energy lost or gained
- $\Delta_r H$  - the change in enthalpy due to a reaction
- $\Delta_f H$  - the change in enthalpy due to the formation of a chemical from its elements (in their most common form and state) e.g.  $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$
- $\Delta_c H$  - the change in enthalpy due to combustion in oxygen
- $\Delta_{fus} H$  - the change in enthalpy due to fusion (in this case a state change - from a liquid to a solid)
- $\Delta_{vap} H$  - the change in enthalpy due to vaporisation (in this case a state change - from a liquid to a gas)



## Expanding the Symbols

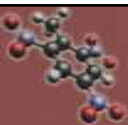
- Some symbols are shorthand for entire reactions. This means that they can be expanded:
  - $\Delta_f H$  - The reactants are elements (in their natural form and state) form the chemical e.g.  
 $\Delta_f H (\text{CO}_{2(g)})$  becomes...  $\text{C}_{(s)} + \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)}$
  - $\Delta_c H$  - The chemical burns completely with oxygen e.g.  
 $\Delta_c H (\text{C}_{(s)})$  becomes...  $\text{C}_{(s)} + \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)}$
  - $\Delta_{\text{vap}} H$  - The chemical turns from liquid to gas e.g.  
 $\Delta_{\text{vap}} H (\text{H}_2\text{O}_{(l)})$  becomes...  $\text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{O}_{(g)}$

Note: The equation must be balanced to show one mole of the 'chemical'



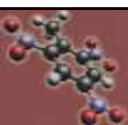
## Bond Energy

- Whatever you do, don't think that bonds have energy... in reality when we make bonds our chemicals lose energy. Remember:
  - Bond making is an exothermic process
  - Bond breaking is an endothermic process
- But... when we refer to bond energy we refer to the amount of enthalpy lost or gained when we make or break a bond. For example:
  - Making a carbon - hydrogen bond involves **losing**  $413\text{kJmol}^{-1}$  of enthalpy
  - Breaking a carbon - hydrogen bond involves **gaining**  $413\text{kJmol}^{-1}$  of enthalpy



## Examples of Bond Energies:

Bond	Bond Energy (kJmol <sup>-1</sup> )	Bond	Bond Energy (kJmol <sup>-1</sup> )
O=O	498	C-H	413
H-H	436	C-O	358
O-H	464	C=O	805
N≡N	945	C-C	347
N-H	391	C=C	612
Cl-Cl	243	C≡C	838
H-Cl	432	C-Cl	346
H-F	568		



## Using Bond Energies I

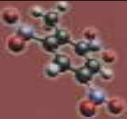
- These examples of bond energies can be used to calculate the enthalpy change of a reaction without testing it.
- To do this we must imagine that we are pulling all the reactants to pieces then we reassemble them. First we calculate the total enthalpy of the bonds broken, then we calculate how what get reassembled and find the difference between the two. For example:

$$2\text{H}_{2(\text{g})} + \text{O}_{2(\text{g})} \rightarrow 2\text{H}_2\text{O}_{(\text{l})}$$

- Bonds broken: 2 H-H bonds and 1 O=O bond
- Bonds made: 4 H-O bonds
- This can be re-written as:

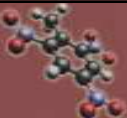
$$\Delta H_{\text{total}} = \Sigma(H_{(\text{bonds broken})}) - \Sigma(H_{(\text{bonds made})})$$

- Why do we turn the 'bonds made' values into negatives?



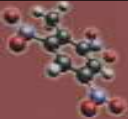
## Using Bond Energies II

- In our example:
 
$$2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$$
  - Bonds broken: 2 H-H bonds and 1 O=O bond
  - Bonds made: 4 H-O bonds
- We know (from our bond energy chart) that an
  - H-H bond is worth 436 kJmol<sup>-1</sup>
  - O=O bond is worth 498 kJmol<sup>-1</sup>
  - H-O bond is worth 464 kJmol<sup>-1</sup>
- So therefore:
 
$$\begin{aligned} \Delta H_{\text{total}} &= \Sigma(H_{\text{(bonds broken)}}) - \Sigma(H_{\text{(bonds made)}}) \\ &= (2 \times 436 + 1 \times 498) - (4 \times 464) \\ &= -486 \text{ kJmol}^{-1} \end{aligned}$$



## Using Bond Energies III

- Try this example for yourself:
 
$$\text{C}_{(\text{s})} + \text{O}_{2(\text{g})} \rightarrow \text{CO}_{2(\text{g})}$$
  - You should get the answer: -1112 kJmol<sup>-1</sup>
- Now try this example:
 
$$\text{C}_{(\text{s})} + 2\text{H}_{2(\text{g})} \rightarrow \text{CH}_{4(\text{g})}$$
  - You should get the answer: -780 kJmol<sup>-1</sup>

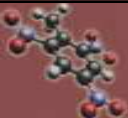


## Using $\Delta_f H$ Values I

- The formula we used on the previous page shows how we can calculate the total enthalpy of a reaction by using energy to break all the bonds then release a certain amount to make the products. Here is another formula:

$$\Delta_r H_{\text{total}} = \Sigma(\Delta_f H_{\text{(products)}}) - \Sigma(\Delta_f H_{\text{(reactants)}})$$

- Put into words this is: The total enthalpy of a reaction equals the sum of the enthalpy of formation of all the products minus the sum of enthalpy of all the reactants



## Using $\Delta_f H$ Values II

- Now lets look at using it:

$$\Delta_r H_{\text{total}} = \Sigma(\Delta_f H_{\text{(products)}}) - \Sigma(\Delta_f H_{\text{(reactants)}})$$

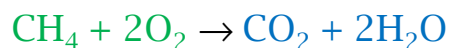
$$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$$

- The products of this reaction are  $\text{CO}_2$  and two lots of  $\text{H}_2\text{O}$
- The reactants are  $\text{CH}_4$  and two lots of  $\text{O}_2$
- Now if we know the enthalpy of formation from elements of these chemicals we can plug them straight into the formula (note -  $\text{O}_2$  is an element so we can ignore it because it takes no energy to make itself )



## Using $\Delta_f H$ Values III

- Now let's look at using it:



- Here is the data we need:

- $\Delta_f H(\text{CH}_4) = -780 \text{ kJmol}^{-1}$
- $\Delta_f H(\text{CO}_2) = -1112 \text{ kJmol}^{-1}$
- $\Delta_f H(\text{H}_2\text{O}) = -243 \text{ kJmol}^{-1}$

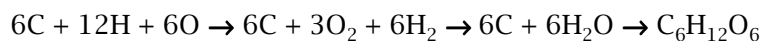
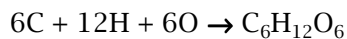
- So:

$$\begin{aligned} \Delta_r H_{\text{total}} &= \Sigma(\Delta_f H_{\text{(products)}}) - \Sigma(\Delta_f H_{\text{(reactants)}}) \\ &= (2 \times -243 + -1112) - (-780) \\ &= -1598 + 780 \\ &= -818 \text{ kJmol}^{-1} \end{aligned}$$

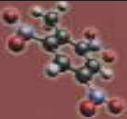


## Hess's Law

- Look at the following two reactions:

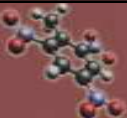


- Both reactions start and end with the same chemicals. If we go through and add up all the bond energy changes we will find out that both reactions have the same total enthalpy.
- In other words, it doesn't matter what path a reaction takes, if they start and end the same they will have the same total enthalpy



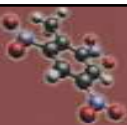
## Using Hess's Law: Part 1

- We can use this idea to say:
  - If we break all the reactants to pieces and then reassemble them, we will get the same total enthalpy.
- As seen earlier, there is a special type of  $\Delta H$  called  $\Delta_f H$ . It involves the formation of chemical from their elements. We can use this to say:
  - If we break all the reactants into their elements and then reassemble them into the products, we will get the same total enthalpy change.
- To make life easier we can put it into an equation:

$$\Delta_r H = \sum \Delta_f H_{(\text{products})} - \sum \Delta_f H_{(\text{reactants})}$$


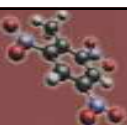
## Using Hess's Law: Part 2

- Another way to use this principle is to say:
  - Any equations that can form the products from the reactants can be substituted into the equation...!?
  - It is easier when we see it being done following some simple rules:
    1. Expand all information given to you i.e.  $\Delta_c H (C_{(s)})$  becomes...  $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$
    2. Arrange them one above the other with the equation you want to find at the bottom
    3. Reverse the direction of reactions to get the reactants and the products on the right side as the reaction you are calculating the enthalpy of - Note: when you reverse a reaction you also reverse the enthalpy - a positive becomes a negative.
    4. If the proportions are wrong you need to multiply entire reactions - Note: if you double the chemicals in a reaction you also double the enthalpy
    5. Now cancel out the chemicals that are present on both sides of the reaction
    6. If it now equals the reaction you are trying to calculate then add the enthalpies of each reaction together



## Using Hess's Law: Part 2 Example

- The equation we want to know the enthalpy of is:
 
$$\text{H}_2\text{O}_{(g)} + \frac{1}{2}\text{O}_{2(g)} \rightarrow \text{H}_2\text{O}_{2(l)}$$
- The info we've been given is:
  - $\Delta_f\text{H}(\text{H}_2\text{O}_{(l)}) = -285 \text{ kJmol}^{-1}$
  - $\Delta_f\text{H}(\text{H}_2\text{O}_{2(l)}) = -136 \text{ kJmol}^{-1}$
  - $\Delta_{\text{vap}}\text{H}(\text{H}_2\text{O}_{(l)}) = 44 \text{ kJmol}^{-1}$
- First we need to expand each reaction:
  - $\text{H}_{2(g)} + \frac{1}{2} \text{O}_{2(g)} \rightarrow \text{H}_2\text{O}_{(l)} \quad \Delta\text{H} = -285\text{kJmol}^{-1}$
  - $\text{H}_{2(g)} + \text{O}_{2(g)} \rightarrow \text{H}_2\text{O}_{2(l)} \quad \Delta\text{H} = -136\text{kJmol}^{-1}$
  - $\text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{O}_{(g)} \quad \Delta\text{H} = 44\text{Jmol}^{-1}$



## Using Hess's Law: Part 2 Example

- Now we line them up:
  - $\text{H}_{2(g)} + \frac{1}{2} \text{O}_{2(g)} \rightarrow \text{H}_2\text{O}_{(l)} \quad \Delta\text{H} = -285\text{kJmol}^{-1}$
  - $\text{H}_{2(g)} + \text{O}_{2(g)} \rightarrow \text{H}_2\text{O}_{2(l)} \quad \Delta\text{H} = -136\text{kJmol}^{-1}$
  - $\text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{O}_{(g)} \quad \Delta\text{H} = +44\text{Jmol}^{-1}$

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- $\text{H}_2\text{O}_{(g)} + \frac{1}{2}\text{O}_{2(g)} \rightarrow \text{H}_2\text{O}_{2(l)} \quad \Delta\text{H} = ?$
- Now we decide which reactions need to be turned around:
  - $\text{H}_2\text{O}_{(l)} \rightarrow \text{H}_{2(g)} + \frac{1}{2} \text{O}_{2(g)} \quad \Delta\text{H} = +285\text{kJmol}^{-1}$
  - $\text{H}_{2(g)} + \text{O}_{2(g)} \rightarrow \text{H}_2\text{O}_{2(l)} \quad \Delta\text{H} = -136\text{kJmol}^{-1}$
  - $\text{H}_2\text{O}_{(g)} \rightarrow \text{H}_2\text{O}_{(l)} \quad \Delta\text{H} = -44\text{Jmol}^{-1}$

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- $\text{H}_2\text{O}_{(g)} + \frac{1}{2}\text{O}_{2(g)} \rightarrow \text{H}_2\text{O}_{2(l)} \quad \Delta\text{H} = ?$

## Using Hess's Law: Part 2 Example

- Note the changes in sign of the enthalpy
  - $\text{H}_2\text{O}_{(l)} \rightarrow \text{H}_{2(g)} + \frac{1}{2} \text{O}_{2(g)} \quad \Delta H = +285\text{kJmol}^{-1}$
  - $\text{H}_{2(g)} + \text{O}_{2(g)} \rightarrow \text{H}_2\text{O}_{2(l)} \quad \Delta H = -136\text{kJmol}^{-1}$
  - $\text{H}_2\text{O}_{(g)} \rightarrow \text{H}_2\text{O}_{(l)} \quad \Delta H = -44\text{kJmol}^{-1}$
- 
- $\text{H}_2\text{O}_{(g)} + \frac{1}{2}\text{O}_{2(g)} \rightarrow \text{H}_2\text{O}_{2(l)} \quad \Delta H = ?$
- Then we multiply any reactions to get the right number of reactants and products on each side (not necessary here)
- Next we cancel out the chemicals present on both sides, compare it to the one we want to calculate and add up the enthalpies:
  - $\text{H}_2\text{O}_{(l)} \rightarrow \text{H}_{2(g)} + \frac{1}{2} \text{O}_{2(g)} \quad \Delta H = +285\text{kJmol}^{-1}$
  - $\text{H}_{2(g)} + \frac{1}{2} \text{O}_{2(g)} \rightarrow \text{H}_2\text{O}_{2(l)} \quad \Delta H = -136\text{kJmol}^{-1}$
  - $\text{H}_2\text{O}_{(g)} \rightarrow \text{H}_2\text{O}_{(l)} \quad \Delta H = -44\text{kJmol}^{-1}$
- 
- $\text{H}_2\text{O}_{(g)} + \frac{1}{2}\text{O}_{2(g)} \rightarrow \text{H}_2\text{O}_{2(l)} \quad \Delta H = 105\text{kJmol}^{-1}$
- Note - changes in state MUST be accounted for

## Exam Practice - 2006

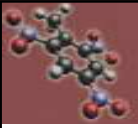
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