3.12 Hess’s Law

Hess’s law states that total enthalpy change for a reaction is independent of the route by which the chemical change takes place.

Hess’s law is a version of the first law of thermodynamics, which is that energy is always conserved.

**Hess’s Law Example**

\[ 2H (g) + 2Cl(g) \rightarrow 2HCl (g) \]

**On an energy level diagram** the directions of the arrows can show the different routes a reaction can proceed by.

The two routes must have the same starting point and the same end point.

In this example one route is arrow ‘a’
The second route is shown by arrows H plus arrow ‘b’

So by applying Hess’s law
\[ a = H + b \]
And rearranged
\[ H = a - b \]

**Interconnecting reactions** can also be shown diagrammatically.

\[ H^+ (g) + Br^- (g) \rightarrow H^+ (aq) + Br^- (aq) \]

In this example one route is arrow ‘a’ plus H
The second route is shown by arrows ‘c’ plus arrow ‘d’

So \[ a + H = c + d \]
And rearranged
\[ H = c + d - a \]

Often Hess’s law cycles are used to measure the enthalpy change for a reaction that cannot be measured directly by experiments. Instead alternative reactions are carried out that can be measured experimentally.

This Hess’s law is used to work out the enthalpy change to form a hydrated salt from an anhydrous salt.

This cannot be done experimentally because it is impossible to add the exact amount of water to hydrate the copper salt and it is not easy to measure the temperature change of a solid turning into another solid.

Instead both salts are dissolved in excess water to form a solution of copper sulfate. The temperature changes can be measured for these alternative reactions and by using Hess’s law the \( \Delta H \) for the original reaction can be calculated.
This Hess’s law is used to work out the enthalpy change for the thermal decomposition of calcium carbonate.

This cannot be done experimentally because it is impossible to add the exact energy required to decompose the solid and to measure the temperature change of a solid at the same time.

Instead both calcium carbonate and calcium oxide are reacted with hydrochloric acid to form a solution of calcium chloride. The temperature changes can be measured for these reactions.

Using Hess’s law to determine enthalpy changes from enthalpy changes of formation.

This is a very common Hess’s law cycle using standard enthalpies of formation to work out the enthalpy change for any chemical reaction. Looking at the cycle on the right we can see the two routes shown with the different coloured arrows, therefore the equation is

\[ \sum \Delta H_{\text{products}} + \Delta H_{\text{reaction}} = \sum \Delta H_{\text{reactants}} \]

As this cycle is always the same we can just use the equation below in questions.

\[ \Delta H_{\text{reaction}} = \sum \Delta H_{\text{products}} - \sum \Delta H_{\text{reactants}} \]

Example 1 Calculate the enthalpy change for this reaction.

\[ \text{Al}_2\text{O}_3 + 3 \text{Mg} \rightarrow 3 \text{MgO} + 2 \text{Al} \]

\[ \Delta H (\text{MgO}) = -601.7 \text{ kJ mol}^{-1} \]
\[ \Delta H (\text{Al}_2\text{O}_3) = -1675.7 \text{ kJ mol}^{-1} \]

Remember elements have \( \Delta H = 0 \)

\[ \Delta H = 3 \times \Delta H (\text{MgO}) - \Delta H (\text{Al}_2\text{O}_3) \]
\[ \Delta H = (3 \times -601.7) - (-1675.7) \]
\[ = -129.4 \text{ kJ mol}^{-1} \]

Note because there are 3 MgO in balanced equation then we multiply the \( \Delta H (\text{MgO}) \) by 3

The calculation can also be shown diagrammatically using an energy level diagram.
Example 2. Use the following data to calculate the enthalpy of combustion of propene.

\[ \Delta H_{\text{C}_3\text{H}_6(g)} = +20 \text{ kJ mol}^{-1} \quad \Delta H_{\text{CO}_2(g)} = -394 \text{ kJ mol}^{-1} \quad \Delta H_{\text{H}_2\text{O}(g)} = -242 \text{ kJ mol}^{-1} \]

\[ \text{C}_3\text{H}_6 + 4.5 \text{ O}_2 \rightarrow 3\text{CO}_2 + 3\text{H}_2\text{O} \]

This question is identical to example 1 in how to approach it. The only difference is the enthalpy change of reaction has been defined as an enthalpy of combustion. Many students get confused because they see the words enthalpy of combustion and enthalpy of formation in the same question and do not know what cycle to use. Draw it out to check.

\[ \Delta_c H = \Sigma \Delta_c H_{\text{products}} - \Sigma \Delta_c H_{\text{reactants}} \]

\[ \Delta_c H = [3 \times \Delta_c H (\text{CO}_2) + 3 \times \Delta_c H (\text{H}_2\text{O})] - \Delta_c H (\text{C}_3\text{H}_6) \]

\[ \Delta_c H = [(3 \times -394) + (3 \times -242)] - 20 \]

\[ = -1928 \text{ kJ mol}^{-1} \]

Using Hess’s law to determine enthalpy changes from enthalpy changes of combustion.

This is another common cycle where the alternative routes involves combusting all the reactants and products in oxygen and using the enthalpies of combustion to calculate the overall enthalpy change of reaction. This cycle can only be used if all the reactants and products can be combusted in oxygen.

\[ \Delta H_{\text{reaction}} = \Sigma \Delta_c H_{\text{reactants}} - \Sigma \Delta_c H_{\text{products}} \]

Example 3. Use the following enthalpy combustion data to calculate the enthalpy of reaction for the following reaction.

\[ \text{CO (g)} + 2\text{H}_2 (g) \rightarrow \text{CH}_3\text{OH} (g) \]

\[ \Delta_c H (\text{CO(g)}) = -283 \text{ kJ mol}^{-1} \quad \Delta_c H (\text{H}_2 (g)) = -286 \text{ kJ mol}^{-1} \quad \Delta_c H (\text{CH}_3\text{OH(g)}) = -671 \text{ kJ mol}^{-1} \]

\[ \Delta H_{\text{reaction}} = \Sigma \Delta_c H_{\text{reactants}} - \Sigma \Delta_c H_{\text{products}} \]

\[ \Delta H = \Delta_c H (\text{CO}) + 2 \times \Delta_c H (\text{H}_2) - \Delta_c H (\text{CH}_3\text{OH}) \]

\[ \Delta H = -283 + 2 \times -286 - -671 \]

\[ = -184 \text{ kJ mol}^{-1} \]

Be really careful with your minus signs.

Note: unlike enthalpies of formation, elements do have an enthalpy of combustion value. Burning hydrogen in oxygen is a very exothermic reaction!
Example 4. Use the following combustion data to calculate the enthalpy of formation of propene.

\[3\text{C (s) + 3H}_2\text{(g) }\rightarrow \text{C}_3\text{H}_6\text{(g)}\]

\[\Delta h_C\text{ (s) }= -393\text{kJ mol}^{-1} \quad \Delta h\text{H}_2\text{(g)} = -286 \text{kJ mol}^{-1} \quad \Delta h\text{C}_3\text{H}_6\text{(g)} = -2058 \text{kJ mol}^{-1}\]

This another example where both enthalpies of combustion and formation appear in the same question. When constructing the original equation remember to only have one mole of the compound on the right hand side of the equation because by definition the enthalpy of formation is for 1 mole of the compound formed.

\[\Delta h = \Sigma \Delta h\text{ reactants} - \Sigma \Delta h\text{ products}\]

\[\Delta h = 3 \times \Delta h\text{(C)} + 3 \times \Delta h\text{(H}_2\text{)} - \Delta h\text{(C}_3\text{H}_6\text{)}\]

\[\Delta h = 3 \times -393 + 3 \times -286 - -2058\]

\[= +21 \text{kJ mol}^{-1}\]

You may well notice I am using the notation $\Delta fH$ and $\Delta cH$ rather than $\Delta H$ and $\Delta H_c$. I have been using the latter for many years and you will find it in almost every text book. It is actually incorrect though. The reason is in the name. $\Delta fH$ is used for enthalpy change of formation. The definition refers to change in enthalpy and $\Delta$ is the sign for change so the f or c goes next to the $\Delta$. $H$ means enthalpy and there is no such thing as $H_f$ of $H_c$ only $H$. On the new syllabus AQA are using $\Delta fH$ and $\Delta cH$ so I am changing all my notes to agree with this.
Questions about Hess’s Law

1 A student used Hess’s Law to determine a value for the enthalpy change that occurs when anhydrous copper(II) sulfate is hydrated. This enthalpy change was labelled $\Delta H_{\text{reaction}}$.

![Diagram of Hess's Law]

1 (a) State Hess’s Law.

1 (b) Write a mathematical expression to show how $H_{\text{reaction}}$, $H_1$, and $H_2$ are related to each other by Hess’s Law.

1 (c) Using the values below for the two enthalpy changes $H_1$ and $H_2$, calculate a value for $H_{\text{reaction}}$.

- $H_1 = -156 \text{ kJ mol}^{-1}$
- $H_2 = +12 \text{ kJ mol}^{-1}$

2) Using for following table of date and scheme of reactions, calculate a value for $H_{\text{reaction}}$.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Enthalpy change kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl (g) $\rightarrow$ H$^+$ (aq) + Cl$^-$ (aq)</td>
<td>-75</td>
</tr>
<tr>
<td>H (g) + Cl (g) $\rightarrow$ HCl (g)</td>
<td>-432</td>
</tr>
<tr>
<td>H (g) + Cl (g) $\rightarrow$ H$^+$ (g) + Cl$^-$ (g)</td>
<td>+963</td>
</tr>
</tbody>
</table>

3) On strong heating, zinc carbonate decomposes to zinc oxide and carbon dioxide:

$$\text{ZnCO}_3(s) \rightarrow \text{ZnO}(s) + \text{CO}_2(g)$$

Owing to the conditions under which the reaction occurs, it is not possible to measure the enthalpy change directly. An indirect method uses the enthalpy changes when zinc carbonate and zinc oxide are neutralized with hydrochloric acid.

(i) Write the equation for the reaction of zinc carbonate with hydrochloric acid. And label this $H_1$.

(ii) The reaction of zinc oxide with hydrochloric acid is

$$\text{ZnO}(s) + 2\text{HCl}(aq) \rightarrow \text{ZnCl}_2(aq) + \text{H}_2\text{O}(l)$$

$H_2$

Use the equations in parts (i) and (ii) to complete the Hess’s Law cycle below to show how you could calculate the enthalpy change for the decomposition of $H_{\text{reaction}}$. Label the arrows in your cycle.

![Diagram of Hess's Law with reaction cycle]

(iii) Write an expression for the $H_{\text{reaction}}$ in terms of $H_1$ and $H_2$.

(b) Suggest two reasons why the value obtained by carrying out these two experiments and using the equation gives a value different to the data booklet value for the decomposition reaction of zinc carbonate.
Questions using Enthalpy Change of Formation Data

<table>
<thead>
<tr>
<th>Compound</th>
<th>Enthalpy change of formation / Kj mol⁻¹</th>
<th>Substance</th>
<th>Enthalpy change of formation / Kj mol⁻¹</th>
<th>Compound</th>
<th>Enthalpy change of formation / Kj mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃(s)</td>
<td>-1669</td>
<td>Fe(l)</td>
<td>+14</td>
<td>NH₃(g)</td>
<td>-46</td>
</tr>
<tr>
<td>BaO(s)</td>
<td>-558</td>
<td>Fe₂O₃(s)</td>
<td>-822</td>
<td>NF₃(g)</td>
<td>-114</td>
</tr>
<tr>
<td>CH₄(g)</td>
<td>-75</td>
<td>H₂O(l)</td>
<td>-286</td>
<td>NH₄NO₃(s)</td>
<td>-365</td>
</tr>
<tr>
<td>C₅H₇O₂H(l)</td>
<td>-304</td>
<td>H₂O(g)</td>
<td>-242</td>
<td>NH₄F(s)</td>
<td>-467</td>
</tr>
<tr>
<td>C₂H₄O₂H(l)</td>
<td>-327</td>
<td>H₂O₂(g)</td>
<td>-133</td>
<td>N₂H₄(g)</td>
<td>+74</td>
</tr>
<tr>
<td>CH₃COCH₃(l)</td>
<td>-248</td>
<td>HCl (g)</td>
<td>-92</td>
<td>NO₂(g)</td>
<td>+34</td>
</tr>
<tr>
<td>CO(g)</td>
<td>-111</td>
<td>MgCl₂(s)</td>
<td>-642</td>
<td>N₂O(g)</td>
<td>+82</td>
</tr>
<tr>
<td>CO₂(g)</td>
<td>-394</td>
<td>MgO(s)</td>
<td>-602</td>
<td>SO₂(g)</td>
<td>-297</td>
</tr>
</tbody>
</table>

For the following questions use the enthalpy change of formation data in the table above:

1) Calculate the enthalpy change for the following reaction
   \[ \text{NH}_4\text{NO}_3(s) + \frac{1}{2} \text{C}(s) \rightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(g) + \frac{1}{2} \text{CO}_2(g) \]

2) Calculate the enthalpy change for the following reaction
   \[ \text{MgO}(s) + 2\text{HCl}(g) \rightarrow \text{MgCl}_2(s) + \text{H}_2\text{O}(l) \]

3) Calculate the enthalpy change for the following reaction
   \[ \text{N}_2\text{H}_4(g) + 2\text{H}_2\text{O}_2(g) \rightarrow \text{N}_2(g) + 4\text{H}_2\text{O}(g) \]

4) Calculate the enthalpy change for the following reaction
   \[ 4\text{NH}_3(g) + 3\text{F}_2(g) \rightarrow \text{NF}_3(g) + 3\text{NH}_4\text{F}(s) \]

5) Use the data above and the following equation to calculate a value for the standard enthalpy of formation for nitric acid.
   \[ \text{H}_2\text{O}(l) + 2\text{NO}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow 2\text{HNO}_3(l) \quad \Delta H = -128 \text{kJ mol}^{-1} \]

6) Use the data above and the following equation to calculate a value for the standard enthalpy of formation for carbon disulphide.
   \[ \text{CS}_2(l) + 3\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{SO}_2(g) \quad \Delta H = -1076 \text{kJ mol}^{-1} \]

7) Calculate the enthalpy change for the following reaction
   \[ 3\text{BaO}(s) + 2\text{Al}(s) \rightarrow 3\text{Ba}(s) + \text{Al}_2\text{O}_3(s) \]

8) Calculate the enthalpy change for the following reaction
   \[ 2\text{NH}_3(g) + 2\text{O}_2(g) \rightarrow \text{N}_2\text{O}(g) + 3\text{H}_2\text{O}(l) \]

9) Calculate the enthalpy change for the following reaction
   \[ \text{Fe}_2\text{O}_3(s) + 3\text{CO}(g) \rightarrow 2\text{Fe}(l) + 3\text{CO}_2(g) \]

10) Calculate the standard enthalpy change of combustion of propanone using equation below
    \[ \text{CH}_3\text{COCH}_3(l) + 4\text{O}_2(g) \rightarrow 3\text{H}_2\text{O}(l) + 3\text{CO}_2(g) \]

11) Calculate the standard enthalpy change of combustion of an alcohol C₃H₇OH, as shown by the equation:
    \[ \text{C}_3\text{H}_7\text{OH}(l) + 4 \frac{1}{2} \text{O}_2(g) \rightarrow 3\text{CO}_2(g) + 4\text{H}_2\text{O}(l) \]

12) Write an equation for the combustion of methane (CH₄) and use it to calculate the enthalpy change of combustion of methane using the data in the above table

13) Write an equation for the combustion of butanol (C₄H₉OH(l)) and use it to calculate the enthalpy change of combustion of butanol using the data in the above table

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Questions using Enthalpy Change of Combustion Data

<table>
<thead>
<tr>
<th>Substance</th>
<th>Enthalpy change of combustion / Kj mol⁻¹</th>
<th>Substance</th>
<th>Enthalpy change of combustion / Kj mol⁻¹</th>
<th>Substance</th>
<th>Enthalpy change of combustion / Kj mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(s)</td>
<td>-393.5</td>
<td>C₄H₆ (g)</td>
<td>-2542</td>
<td>C₂H₅OH(l)</td>
<td>-1370</td>
</tr>
<tr>
<td>H₂(g)</td>
<td>-285</td>
<td>C₆H₁₂ (l)</td>
<td>-4003</td>
<td>C₂H₅SH(l)</td>
<td>-1170</td>
</tr>
<tr>
<td>S(s)</td>
<td>-297</td>
<td>C₇H₈ (l)</td>
<td>-4163</td>
<td>CH₃COOH(l)</td>
<td>-870</td>
</tr>
<tr>
<td>CH₄(g)</td>
<td>-890</td>
<td></td>
<td></td>
<td>C₄H₄O₄(s)</td>
<td>-1356</td>
</tr>
<tr>
<td>CO(g)</td>
<td>-283</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For the following questions use the enthalpy change of combustion data in the table above.

1) Calculate the enthalpy change for the following reaction
   C₆H₁₂(l) + H₂(g) → C₆H₁₄(l)

2) Calculate the enthalpy change for the following reaction
   CH₄(g) + 1½O₂(g) → CO(g) + 2H₂O(l)

3) Use the data above and the following equation to calculate a value for the standard enthalpy of combustion for gaseous methanol.
   CO(g) + 2H₂(g) → CH₃OH(g)  \[ H = -91 \text{ kJmol}⁻¹ \]

4) Calculate the standard enthalpy change of formation of C₄H₆ using the equation below and the data above.
   4C(s) + 3H₂(g) → C₄H₆(g)

5) Calculate the standard enthalpy change of formation of C₇H₈ using the equation below and the data above.
   7C(s) + 4H₂(g) → C₇H₈(l)

6) Calculate the standard enthalpy change of formation of Maleic acid C₄H₄O₄ using the equation below and the data above.
   4C(s) + 2H₂(g) + 2O₂(g) → C₄H₄O₄(s)

7) Calculate the standard enthalpy change of formation of ethanoic acid CH₃COOH using the equation below and the data above.
   2C(s) + 2H₂(g) + O₂(g) → CH₃COOH(l)

8) Calculate the standard enthalpy change of formation of C₂H₅SH using the equation below and the data above.
   2C(s) + 3H₂(g) + S(s) → C₂H₅SH(l)

9) Write an equation for the formation of ethanol (C₂H₅OH(l)) from its elements and use it to calculate the enthalpy change of formation of ethanol using the data in the above table.