Ah, there's nothing more exciting than science. You get all the fun of sitting still, being quiet, writing down numbers, paying attention... Science has it all.
• We have determined enthalpy using:
  • Calorimetry experiments \((Q = mcT)\)
  • Hess’ law

• Now we will learn two other ways to find enthalpy:
  • Bond enthalpy
  • Standard enthalpy of formation
During chemical reactions, bonds are broken and new bonds are made.

Breaking bonds requires energy = endothermic ($\Delta H^+$)

Making bonds releases energy = exothermic ($\Delta H^-$)

The energy required to break a covalent bond in the gaseous phase is called a bond enthalpy.

One approach to determining an enthalpy change for a chemical reaction is to compute the difference in bond enthalpies between reactants and products.

$$\Delta H = \sum \text{Bonds broken} - \sum \text{Bonds formed}$$
The average bond enthalpies for several types of chemical bonds are shown in the table below:

<table>
<thead>
<tr>
<th>Bond</th>
<th>Enthalpy</th>
<th>Bond</th>
<th>Enthalpy</th>
<th>Bond</th>
<th>Enthalpy</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H</td>
<td>464</td>
<td>C-F</td>
<td>552</td>
<td>N≡N</td>
<td>945</td>
</tr>
<tr>
<td>O-O</td>
<td>142</td>
<td>C-Cl</td>
<td>397</td>
<td>F-F</td>
<td>155</td>
</tr>
<tr>
<td>C-O</td>
<td>351</td>
<td>C-Br</td>
<td>276</td>
<td>Cl-Cl</td>
<td>243</td>
</tr>
<tr>
<td>O=O</td>
<td>502</td>
<td>C-N</td>
<td>293</td>
<td>Br-Br</td>
<td>192</td>
</tr>
<tr>
<td>C=O</td>
<td>730</td>
<td>C≡N</td>
<td>890</td>
<td>H-H</td>
<td>435</td>
</tr>
<tr>
<td>C-C</td>
<td>347</td>
<td>N-H</td>
<td>390</td>
<td>H-F</td>
<td>565</td>
</tr>
<tr>
<td>C≡C</td>
<td>615</td>
<td>N-N</td>
<td>159</td>
<td>H-Cl</td>
<td>431</td>
</tr>
<tr>
<td>C-H</td>
<td>414</td>
<td>N≡N</td>
<td>418</td>
<td>H-Br</td>
<td>368</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H-S</td>
<td>364</td>
</tr>
</tbody>
</table>

All values are in kJ mol\(^{-1}\)
Bond enthalpy tables give the average energy to break a chemical bond. Actually there are slight variations depending on the environment in which the chemical bond is located.

For this reason, the energy calculated for a reaction may be different based on the method used to calculate.
Figure 6.4.2 In an exothermic reaction bond making releases more energy than bond breaking requires and in an endothermic reaction, bond making releases less energy than bond breaking requires.
Use average bond enthalpies (table 6.4.1) to find the heat of combustion of methane.

\[ \text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g}) \]

\[
\begin{align*}
\Delta H &= [4D_{\text{C-H}} + 2D_{\text{O=O}}] - [2D_{\text{C=O}} + 4D_{\text{H-O}}] \\
&= [4 \times 412 + 2 \times 496] - [2 \times 743 + 4 \times 463] \\
&= 2640 - 3338 \\
&= -698 \text{ kJ mol}^{-1}
\end{align*}
\]
Example 2: Calculate the enthalpy change for the reaction

$$\text{N}_2 + 3 \text{H}_2 \rightarrow 2 \text{NH}_3$$

**Bonds broken**

- $\text{N}≡\text{N}$: $= 945$
- $3 \text{H-H}$: $3(435) = 1305$

Total $= 2250 \text{ kJ}$

**Bonds formed**

$2 \times 3 = 6 \text{N-H}$: $6(390) = -2340 \text{ kJ}$

**Net enthalpy change**

$= +2250 - 2340 = -90 \text{ kJ}$
1 Explain, making reference to bond enthalpies, how a reaction could be endothermic.

2 Why is the average bond enthalpy of C=C greater than C–C?

3 Use average bond enthalpies to calculate the heat of reaction, $\Delta H$, for the following reaction:
   \[ \text{H}_2(g) + \text{Cl}_2(g) \rightarrow 2\text{HCl}(g) \]

4 Use average bond enthalpies to calculate the heat of combustion of methanol.
   \[ 2\text{CH}_3\text{OH}(l) + 3\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 4\text{H}_2\text{O}(l) \]

5 a Use average bond enthalpies to calculate the heat of combustion of ethane.
   b Also using average bond enthalpies, calculate the heat of combustion of ethene.
   c Explain why the heat of combustion of ethene is less exothermic than that of ethane.

6 Without performing the calculations or referring to tables of combustion data, state which compound you would expect to have a greater (more negative) heat of combustion, ethyne, \( \text{C}_2\text{H}_2 \), or ethene, \( \text{C}_2\text{H}_4 \). Explain your answer.

7 a Use average bond enthalpies to find the heat of combustion of ethanoic acid, \( \text{CH}_3\text{COOH} \).
   
   b Also using average bond enthalpies, find the heat of combustion of ethanal, \( \text{CH}_3\text{CHO} \).
   
   c With reference to the bonding in these two compounds, explain the difference in their heats of combustion.
The enthalpy of formation for a compound is equal to the enthalpy change that occurs when a compound is formed from its elements.

The symbol for the bond enthalpy of formation is $\Delta H_f$.

Enthalpies of formation have been measured and tabulated for a large number of compounds.
Enthalpies of formation represent the enthalpy changes when compound forms from its elements.

The enthalpy of formation for a chemical reaction can be expressed as the difference between the enthalpy state of the products and that of the reactants.

\[ \Delta H_{\text{reaction}} = \sum \Delta H^o_{\text{products}} - \sum \Delta H^o_{\text{reactants}} \]
The enthalpy change that occurs when the reactants are converted to products, both being in their standard states is known as the standard enthalpy change.

It is designated as $\Delta H^\circ$.

$\Delta H^\circ \text{ reaction} = \Sigma \Delta H^\circ \text{ products} - \Sigma \Delta H^\circ \text{ reactants}$
# Some enthalpies of formation for common compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Enthalpy (kJ/mol)</th>
<th>Product</th>
<th>Enthalpy (kJ/mol)</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaCO$_3$</td>
<td>-1219</td>
<td>H$_2$O (g)</td>
<td>-242</td>
<td>HCl (g)</td>
</tr>
<tr>
<td>Ba(OH)$_2$</td>
<td>-998</td>
<td>H$_2$O (l)</td>
<td>-286</td>
<td>HCl (aq)</td>
</tr>
<tr>
<td>BaO</td>
<td>-554</td>
<td>H$_2$O$_2$</td>
<td>-188</td>
<td>NH$_3$ (g)</td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>-1207</td>
<td>C$_3$H$_8$</td>
<td>-104</td>
<td>NO</td>
</tr>
<tr>
<td>CaO</td>
<td>-636</td>
<td>C$<em>4$H$</em>{10}$</td>
<td>-126</td>
<td>NO$_2$</td>
</tr>
<tr>
<td>Ca(OH)$_2$</td>
<td>-987</td>
<td>CO</td>
<td>-110</td>
<td>SO$_2$</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>-796</td>
<td>CO$_2$</td>
<td>-394</td>
<td>Al$_2$O$_3$(s)</td>
</tr>
</tbody>
</table>
### Table 4.1.1 Standard Enthalpies of Formation of Selected Compounds

(Some of these values can also be found in Appendix 3 and in Table 11 of the IB Data booklet. © IBO 2007)

<table>
<thead>
<tr>
<th>Substance</th>
<th>Formula</th>
<th>State</th>
<th>$\Delta H^\circ$ (kJ mol$^{-1}$)</th>
<th>Substance</th>
<th>Formula</th>
<th>State</th>
<th>$\Delta H^\circ$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>NH$_3$</td>
<td>g</td>
<td>$-46$</td>
<td>Ethyne</td>
<td>C$_2$H$_2$</td>
<td>g</td>
<td>$+227$</td>
</tr>
<tr>
<td>Ammonium bromide</td>
<td>NH$_4$Br</td>
<td>s</td>
<td>$-271$</td>
<td>Hydrogen bromide</td>
<td>HBr</td>
<td>g</td>
<td>$-36$</td>
</tr>
<tr>
<td>Butane</td>
<td>C$<em>4$H$</em>{10}$</td>
<td>g</td>
<td>$-125$</td>
<td>Methane</td>
<td>CH$_4$</td>
<td>g</td>
<td>$-75$</td>
</tr>
<tr>
<td>But-1-ene</td>
<td>C$_4$H$_8$</td>
<td>g</td>
<td>$+1$</td>
<td>Nitrogen monoxide</td>
<td>NO</td>
<td>g</td>
<td>$+90$</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>CO$_2$</td>
<td>g</td>
<td>$-394$</td>
<td>Pentane</td>
<td>C$<em>5$H$</em>{12}$</td>
<td>l</td>
<td>$-173$</td>
</tr>
<tr>
<td>Ethane</td>
<td>C$_2$H$_6$</td>
<td>g</td>
<td>$-85$</td>
<td>Propane</td>
<td>C$_3$H$_8$</td>
<td>g</td>
<td>$-104$</td>
</tr>
<tr>
<td>Ethanol</td>
<td>C$_2$H$_5$OH</td>
<td>g</td>
<td>$-235$</td>
<td>Propene</td>
<td>C$_3$H$_6$</td>
<td>g</td>
<td>$+20$</td>
</tr>
<tr>
<td>Ethene</td>
<td>C$_2$H$_4$</td>
<td>g</td>
<td>$+52$</td>
<td>Water</td>
<td>H$_2$O</td>
<td>g</td>
<td>$-242$</td>
</tr>
<tr>
<td>Ethylamine</td>
<td>C$_2$H$_5$NH$_2$</td>
<td>g</td>
<td>$-49$</td>
<td>Water</td>
<td>H$_2$O</td>
<td>l</td>
<td>$-286$</td>
</tr>
</tbody>
</table>
The enthalpy of formation table is stated in kJ mol\(^{-1}\).

To find the sum of enthalpies of formation for reactants or products, multiply the number of moles of each substance by the enthalpy of formation for that substance.

Then find the difference: Products - Reactants
Calcium carbonate reacts with hydrochloric acid according to the following equation:

\[
\text{CaCO}_3 (s) + 2\text{HCl} (aq) \rightarrow \text{CaCl}_2 (aq) + \text{H}_2\text{O} (l) + \text{CO}_2 (g)
\]

Calculate the enthalpy change for this reaction

\[
\Delta H^\circ_{\text{reaction}} = \Sigma \Delta H^\circ_{\text{products}} - \Sigma \Delta H^\circ_{\text{reactants}}
\]

**Solution**

<table>
<thead>
<tr>
<th>(\Delta H^\circ)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CaCO}_3)</td>
<td>-1207</td>
</tr>
<tr>
<td>(\text{HCl} (aq))</td>
<td>-167</td>
</tr>
<tr>
<td>(\text{CaCl}_2)</td>
<td>-796</td>
</tr>
<tr>
<td>(\text{H}_2\text{O} (l))</td>
<td>-286</td>
</tr>
<tr>
<td>(\text{CO}_2 (g))</td>
<td>-394</td>
</tr>
</tbody>
</table>

\[
\Sigma \Delta H^\circ_{\text{products}} = (-796) + (-286) + (-394) = -1476 \text{ kJ}
\]

\[
\Sigma \Delta H^\circ_{\text{reactants}} = (-1207) + 2(-167) = -1541 \text{ kJ}
\]

\[
\Delta H^\circ_{\text{reaction}} = -1476 - (-1541) = 75 \text{ kJ}
\]
Calculate the enthalpy change for the burning of 11 grams of propane

\[ \text{C}_3\text{H}_8 (g) + 5 \text{ O}_2 (g) \rightarrow 3 \text{ CO}_2 (g) + 4 \text{ H}_2\text{O} (g) \]

\[ \Delta H^\circ_{\text{reaction}} = \sum \Delta H^\circ_{\text{products}} - \sum \Delta H^\circ_{\text{reactants}} \]

\[
\begin{align*}
\Delta H^\circ & \quad \text{C}_3\text{H}_8 \quad -104 \\
\Delta H^\circ & \quad \text{O}_2 (g) \quad 0 \\
\Delta H^\circ & \quad \text{H}_2\text{O} (g) \quad -242 \\
\Delta H^\circ & \quad \text{CO}_2 (g) \quad -394
\end{align*}
\]

Solution

\[
\begin{align*}
\sum \Delta H^\circ_{\text{products}} &= (3)(-394) + (4)(-242) \\
&= -2150 \text{ kJ} \\
\sum \Delta H^\circ_{\text{reactants}} &= (-104) + (5)(0) \\
&= -104 \text{ kJ} \\
\Delta H^\circ_{\text{reaction}} &= -2150 - (-104) = -2046 \text{ kJ mol}^{-1}
\end{align*}
\]

Now 11 grams = 0.25 mole of propane \((11 \text{ g}/44 \text{ g mol}^{-1})\) \((0.25 \text{ mol})\)(-2046 kJ mol\(^{-1}\)) = -511.5 kJ
Use the information in table 4.1.1 to calculate the enthalpy change for complete combustion of ethene according to the following equation:

\[
\text{C}_2\text{H}_4(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})
\]

\[
\Delta H^\circ_C = \sum n\Delta H^\circ_f(\text{products}) - \sum m\Delta H^\circ_f(\text{reactants})
\]

\[
\Delta H^\circ_C = [(2 \text{ mol})\Delta H^\circ_f(\text{CO}_2) + (2 \text{ mol})\Delta H^\circ_f(\text{H}_2\text{O})] - [(1 \text{ mol})\Delta H^\circ_f(\text{C}_2\text{H}_4) + (3 \text{ mol})\Delta H^\circ_f(\text{O}_2)]
\]

\[
= [(2 \times -394) + (2 \times -242)] - [+52 + (3 \times 0)]
\]

\[
= -788 - 484 - 52
\]

\[
= -1324 \text{ kJ mol}^{-1}
\]
1. The enthalpy change of the following reaction is negative:

\[ 2\text{H}_2\text{O}_2(\text{l}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g}) \]

Describe how the stabilities of the reactants compare with those of the products.

2. Define the term *standard enthalpy change of formation, \( \Delta H^\circ \)*, and illustrate your answer with an equation, including state symbols, for the formation of methane, CH\(_4\).

3. Explain why the standard enthalpy of formation of graphite is equal to zero, while that of diamond is \(+1.90 \text{ kJ mol}^{-1}\).

4. The standard enthalpy change of formation of C\(_2\)H\(_5\)OH(g) is \(-235 \text{ kJ mol}^{-1}\). Predict how the value of \( \Delta H^\circ \) for C\(_2\)H\(_5\)OH(l) would compare with this value and explain your answer.

5. The standard enthalpy change of formation values for two oxides of sulfur are:

\[ \text{S}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{SO}_2(\text{g}) \]
\[ \Delta H^\circ = -296.1 \text{ kJ mol}^{-1} \]
\[ \text{S}(\text{s}) + \frac{3}{2} \text{O}_2(\text{g}) \rightarrow \text{SO}_3(\text{g}) \]
\[ \Delta H^\circ = -395.2 \text{ kJ mol}^{-1} \]

Calculate the enthalpy change, in kJ mol\(^{-1}\), for the reaction:

\[ 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g}) \]

6. Ethyne (also known as acetylene), C\(_2\)H\(_2\), is commonly used as a fuel for the high-temperature flame used in welding. The equation for the combustion of ethyne is:

\[ 2\text{C}_2\text{H}_2(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g}) \]

Calculate the standard enthalpy change of combustion for ethyne, using values from table 4.1.1.

7. Ethylamine can be manufactured by the reaction:

\[ \text{C}_2\text{H}_5\text{OH}(\text{g}) + \text{NH}_3(\text{g}) \rightarrow \text{C}_2\text{H}_5\text{NH}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) \]

Use values from table 4.1.1 to calculate the enthalpy change for this reaction.