Thermodynamics

Thermodynamics: the physics of heat movement.

Thermochemistry: the thermodynamics of chemical reactions.

In most physical and chemical processes there is an energy change – energy is transferred and/or changes from one form (e.g. kinetic) into another (e.g. heat). (Indeed energy can be defined as the ability to cause change). In general, any system may evolve or absorb energy. This energy may be as light (e.g. chemoluminescence), electrical energy (e.g. in a battery) or as heat or energy may show up as work done on the system, e.g. the expansion or contraction of a gas (a change in volume, $\Delta V$).

Energy change ($\Delta E$) = heat absorbed or evolved + work done.

Energy can neither be created nor destroyed!

This is the first law of thermodynamics. (Though it can be converted to mass, and vice versa, so mass can be included as a form of energy).

Thus – for a system to lose energy it must give up energy to its surroundings and to gain energy it must absorb it from its surroundings.

Internal energy ($E_i$): a system may be in motion and so possess kinetic energy (energy due to motion), also it may possess potential energy (such as gravitational potential energy if it is falling) but it also contains its own internal energy.

This internal energy will be in the form of: the kinetic energy of the molecules (translational, rotational and vibrational) electronic energy (e.g. excitation of electrons to higher energy levels) and nuclear energy.

Enthalpy (H) is defined as:

$$ H = E_i + PV $$

where $E_i$ is internal energy, P is pressure and V is volume, so for a system at constant P (e.g. atmospheric pressure for a flask open to the air) and one at constant volume (for reactions in solution the volume changes are usually extremely small and so can be ignored) the enthalpy is essentially the energy of the system. (Pressure and volume changes are the main types of work performed on or by chemical systems).

In most chemical reactions most of the energy evolved or absorbed will be in the form of heat (and if it is in some other form, e.g. light then it may be eventually converted into heat).

(An interesting exception is bioluminescence in which 90% of the energy is evolved as light and only 10% as heat, whereas in a light-bulb about 90% of the energy is lost as heat!).
We cannot measure enthalpy in practise, we can only measure enthalpy changes!

This is because there is no absolute zero for energy or enthalpy – we define what zero enthalpy is and enthalpy can then be negative or positive!

- The enthalpy change ($\Delta H$) for a chemical reaction is negative if the reaction evolves heat, and such a reaction is exothermic.
- The enthalpy change ($\Delta H$) is positive for a chemical reaction that absorbs heat, and such a reaction is endothermic.

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

Left: for an exothermic reaction the enthalpy of the system decreases, $\Delta H$ is negative ($< 0$) and the reaction evolves heat (which carries away the (internal) energy lost).

Left: for an endothermic reaction the enthalpy of the system increases, $\Delta H$ is positive ($> 0$) and the reaction absorbs heat (which increases the (internal) energy of the system).
Exothermic reaction: $\Delta H$ negative, heat evolved

Endothermic reaction: $\Delta H$ positive, heat absorbed

The units of $\Delta H$:
Enthalpy changes are measured in units of energy per mole, we use kJ/mol:

\[ \text{CH}_4(g) + \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l) \]
\[ \Delta H = -890 \text{ kJ mol}^{-1} \]

\[ \text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g) \]
\[ \Delta H = +179 \text{ kJ mol}^{-1} \]

Measuring $\Delta H$: Calorimetry
We can easily measure the heat absorbed or evolved by a chemical reaction. Errors occur because some of the heat may escape before it can be measured – we need ideally to measure the total heat energy evolved or absorbed, which can be done if all the heat is transferred to a liquid whose temperature we measure, however some heat is inevitably lost to the environment.

For a reaction occurring in solution we can carry out the reaction in an insulated container (such as a polystyrene cup with a lid on it) and simply record the temperature change of the solution. Some heat escapes to the air through the walls and lid of the cup, but this introduces only a small error for most reactions.

For more accuracy we can use a bomb calorimeter. The bomb calorimeter also allows us to measure a wider range of reaction types: e.g. the energy released by burning a solid in air or oxygen can be measured in a bomb calorimeter.

Combustion reactions involve burning a fuel in oxygen and are always exothermic!
Energy must be supplied initially, e.g. as a lighted splint, but once the reaction gets underway it evolves much more heat than we supplied initially. The energy we have to supply at the beginning is called the activation energy.
Standard Conditions

$\Delta H$ varies according to physical conditions like temperature, pressure and the concentration of solutions.

Thus, in order to compare reactions we must measure and quote their $\Delta H$ under the same standard conditions, which we chose to be:

- **Standard pressure**: one atmosphere pressure (1.01 x $10^5$ Nm$^{-2}$ or 101 kPa, where one Pascal = 1 Nm$^{-2}$).
- **Standard concentration**: 1 mol dm$^{-3}$ (1 M).
- **A specified temperature**, often room temperature (25°C which is 298K).

$\Delta H$ measured under these conditions is written as $\Delta H^\circ_{298}$ or $\Delta H^\circ$ for short (where we assume $T = 298K$). This is ‘delta H standard’. If written simply as DH we can usually safely assume this to be $\Delta H^\circ$ as in the above examples. (Note: $\phi$ is the Greek letter phi).

Standard state of a substance:

The most stable state under standard conditions (1 atmos pressure and a stated temperature, usually 298K).

E.g. carbon is in the form of graphite in its standard state, chlorine is a diatomic gas, Cl$_2$, and water is a liquid.

The enthalpy of an element in its standard state is defined to be zero.

Different Kinds of Enthalpy Change

**Standard enthalpy change for a reaction**: $\Delta H^\circ_{r,298}$ or $\Delta H^\circ$.

The enthalpy change when molar quantities of each reactant in the proportions stated in the equation react together under standard conditions. E.g.

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l); \quad \Delta H^\circ = -286 \text{ KJ mol}^{-1}$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l); \quad \Delta H^\circ = -572 \text{ KJ mol}^{-1}$$
Special types of reaction are given special names:

### Standard enthalpy change of formation: $\Delta H_f$

The enthalpy change when 1 mole of a compound is formed from its elements with both the elements and the compound being in their standard states.

E.g.

- $\text{CH}_4(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l), \quad \Delta H_f = -286 \text{ kJ mol}^{-1}$
- $\text{C(s)} + 2\text{H}_2(g) \rightarrow \text{CH}_4(g), \quad \Delta H_f = -75 \text{ kJ mol}^{-1}$

But: the last reaction does not occur under normal conditions and cannot be directly measured – we must use an enthalpy cycle (thermochemical cycle or Hess cycle) to measure it indirectly.

### Standard enthalpy change of combustion: $\Delta H_c$

The enthalpy change when 1 mole of a fuel is burned completely in oxygen under standard conditions – in practise it is impossible to burn the material under standard conditions so we burn it in the usual way and then correct the value to make it applicable to standard conditions.

E.g.

- $\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l), \quad \Delta H_c = -890 \text{ kJ mol}^{-1}$
- (methane)
- $\text{C}_8\text{H}_{18}(l) + 12\frac{1}{2}\text{O}_2(g) \rightarrow 8\text{CO}_2(g) + 9\text{H}_2\text{O}(l), \quad \Delta H_c = -5470 \text{ kJ mol}^{-1}$
- (octane)

$\Delta H_c$ is always negative!

Methane ($\text{CH}_4$) and octane ($\text{C}_8\text{H}_{18}$) are examples of hydrocarbons used as fuels. They belong to a group of hydrocarbons known as straight chain alkanes of general formula: $\text{C}_n\text{H}_{2n+2}$, where $n = 1, 2, 3, \ldots$, etc.
Hess’s Law: Thermochemical Cycles

The first law of thermodynamics, that energy is conserved (i.e. can neither be created nor destroyed) tells us that the energy change in some system due to some process is independent of the path taken by that process, so as each path starts in the same initial place and each path ends in the same final place.

For a chemical system the ‘path’ is the sequence of chemical reactions.

E.g. consider the formation of methane from carbon and hydrogen, this can be done by direct combination of the elements, or indirectly by first oxidising carbon and hydrogen:

\[
\begin{align*}
\text{C(s)} + 2\text{H}_2(\text{g}) & \rightarrow \text{CH}_4(\text{g}) \\
& \Delta H_1 \text{ path 1} \\
\Delta H_2 \text{ path 2a} & \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \\
& \Delta H_3 \text{ path 2b}
\end{align*}
\]

Above: Hess’s law: the enthalpy change is independent of reaction path, so the enthalpy change for path 1 = enthalpy change for path 2, or:

\[
\Delta H_1 = \Delta H_2 + \Delta H_3
\]

Consider the cycle below which shows the actual reactions we are considering:

\[
\begin{align*}
\text{C(s)} + 2\text{H}_2(\text{g}) & \rightarrow \text{CH}_4(\text{g}) \\
& \Delta H_1 \\
& \Delta H_2 \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \\
& \Delta H_3 \rightarrow + 2\text{O}_2(\text{g})
\end{align*}
\]

We know \(\Delta H_2\) and \(\Delta H_3\) and so we can deduce \(\Delta H_1\) which we cannot measure directly for technical reasons. However, this time:

\[
\Delta H_1 = \Delta H_2 - \Delta H_3
\]

As we need to carry out reaction 3 backwards: if we reverse a reaction \(\Delta H\) changes sign.
We want to know the enthalpy change for the following reaction:

\[
\text{NH}_3(g) + \text{HCl}(g) \rightarrow \text{NH}_4\text{Cl}(s)
\]

We can use an enthalpy cycle that makes use of the enthalpy of formations of ammonia, hydrogen chloride and ammonium chloride. These values can be obtained from data tables.

\[
\begin{align*}
\Delta H_1 &= \text{NH}_3(g) + \text{HCl}(g) \\
\Delta H_2 &= \frac{1}{2}\text{N}_2(g) + 2\text{H}_2(g) + \frac{1}{2}\text{Cl}_2(g) \\
\Delta H_3 &= \text{NH}_4\text{Cl}(s)
\end{align*}
\]

Q. What enthalpy changes are represented by \(\Delta H_1\), \(\Delta H_2\) and \(\Delta H_3\)?

A. \(\Delta H_1\):

\[
\begin{align*}
\Delta H_2 &= \Delta H_f^{\circ}(\text{NH}_3) + \Delta H_f^{\circ}(\text{HCl}) \\
\Delta H_3 &= \Delta H_f^{\circ}(\text{NH}_4\text{Cl})
\end{align*}
\]

From tables:

\[
\Delta H_f^{\circ}(\text{NH}_3) = -46.1 \text{ kJ mol}^{-1}, \quad \Delta H_f^{\circ}(\text{HCl}) = -92.3 \text{ kJ mol}^{-1}, \quad \Delta H_f^{\circ}(\text{NH}_4\text{Cl}) = -315 \text{ kJ mol}^{-1}
\]

Solution:

\[
\begin{align*}
\Delta H_1 &= -\Delta H_2 + \Delta H_3 \\
\Delta H_2 &= \Delta H_f^{\circ}(\text{NH}_3) + \Delta H_f^{\circ}(\text{HCl}) \\
\Delta H_3 &= \Delta H_f^{\circ}(\text{NH}_4\text{Cl})
\end{align*}
\]

\[
\Delta H_1 = -\Delta H_f^{\circ}(\text{NH}_3) - \Delta H_f^{\circ}(\text{HCl}) + \Delta H_f^{\circ}(\text{NH}_4\text{Cl})
\]

\[
= 46.1 \text{ kJ mol}^{-1} + 92.3 \text{ kJ mol}^{-1} - 315 \text{ kJ mol}^{-1}
\]

\[
= -176.6 \text{ kJ mol}^{-1}
\]
Using Standard Enthalpies of Formation

The (standard) enthalpy change of formation of a compound is the *enthalpy change* when one mole of a compound is formed from its elements with both the elements and the compound in their standard states.

An enthalpy change may be thought of as a change in internal energy or heat energy for our purposes (it is the change in internal energy for a system at constant temperature and pressure and this energy is usually evolved or absorbed as heat).

For a standard enthalpy change we are dealing with solutions (if applicable) of 1 mol dm\(^{-3}\) concentration and a constant pressure of 1 atmosphere (1 bar or 100 kPa) and with the reactants and products in their standard states.

N.B. For any element, by definition: \(\Delta H^\phi_f[\text{element}] = 0\) kJ mol\(^{-1}\)

e.g. \(H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l), \quad \Delta H^\phi_f,298 = -286\) kJ mol\(^{-1}\)

For a *thermochemical cycle* in which we use standard enthalpy changes of formation to calculate the enthalpy change of a reaction:

e.g.

\[
\begin{align*}
\text{NH}_3(g) + \text{HCl}(g) & \quad \Delta H_1 \text{ or } \Delta H_r \quad \rightarrow \quad \text{NH}_4\text{Cl}(s) \\
& \downarrow \quad \Delta H_2 \quad \Delta H_3 \\
\frac{1}{2}\text{N}_2(g) + 2\text{H}_2(g) + \frac{1}{2}\text{Cl}_2(g) \\
\end{align*}
\]

\[\Delta H_r = -\Delta H_2 + \Delta H_3\]

\[\Delta H_r = \{ \text{sum of } \Delta H^\phi_f[\text{products}] \} - \{ \text{sum of } \Delta H^\phi_f[\text{reactants}] \}\]

\[\Delta H_r = \{ \sum \Delta H^\phi_f[\text{products}] \} - \{ \sum \Delta H^\phi_f[\text{reactants}] \}\]

(\(\Sigma\) is the Greek capital sigma and means ‘sum of’).
Worked Example – Enthalpies of Formation

Calculate the enthalpy change for the reaction of hydrazine with oxygen to form nitrogen and steam.

\[ \Delta H_f[N_2H_4(l)] = +50.6 \text{ kJ mol}^{-1} \]
\[ \Delta H_f[H_2O(g)] = -241.8 \text{ kJ mol}^{-1} \]

1. Write the balanced equation for the reaction:
   \[ N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2H_2O(g) \]

2. Recall that by definition:
   \[ \Delta H_f[\text{element}] = 0 \text{ kJ mol}^{-1} \]

3. \[ \Delta H_r = \{ \text{sum of } \Delta H_f[\text{products}] \} - \{ \text{sum of } \Delta H_f[\text{reactants}] \} \]
   \[ \Delta H_r = \{ \Delta H_f[N_2(g)] + 2 \times \Delta H_f[H_2O(g)] \} - \{ \Delta H_f[N_2H_4(l)] + \Delta H_f[O_2(g)] \} \]
   \[ \Delta H_r = \{ 0 \text{ kJ mol}^{-1} + 2 \times (-241.8 \text{ kJ mol}^{-1}) \} - \{ (+50.6 \text{ kJ mol}^{-1}) + 0 \text{ kJ mol}^{-1} \} \]
   \[ \Delta H_r = -534.2 \text{ kJ mol}^{-1}. \]

Note: putting quantities in brackets with their signs helps avoid sign errors, e.g. \((+ 50 \text{ kJ mol}^{-1}) - (-30 \text{ kJ mol}^{-1}) = 80 \text{ kJ mol}^{-1}\).
Enthalpy: Practise Questions

Q.1 The following question is taken from the OCR Salters Jan 2008 paper.

MTBE, $C_5H_{12}O$, is added to petrol to make it burn more efficiently. The equation for the complete combustion of MTBE is shown below:

$$C_5H_{12}O(l) + 7.5O_2(g) \rightarrow 5CO_2(g) + 6H_2O(l)$$

Use the standard enthalpy change of formation data in the following table to calculate a value for the standard enthalpy change of combustion, $\Delta H^\circ_c$, of MTBE.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Standard enthalpy change of formation, $\Delta H^\circ_f$/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTBE $[C_5H_{12}O(l)]$</td>
<td>-283</td>
</tr>
<tr>
<td>$CO_2(g)$</td>
<td>-394</td>
</tr>
<tr>
<td>$H_2O(l)$</td>
<td>-286</td>
</tr>
</tbody>
</table>

Q.2 Find the standard enthalpy of formation of CO if the standard enthalpies of combustion, $\Delta H^\circ_c$, of carbon and carbon monoxide are -393 kJ mol$^{-1}$ and -285 kJ mol$^{-1}$ respectively. [Hint: first write a balanced equation for the reaction, including state symbols, then construct an enthalpy cycle diagram.]

Q.3 When calculating standard enthalpies of reactions involving water, why is it important to specify whether or not the $H_2O$ is present as water or steam?

Q.4 The standard enthalpy of combustion of butane, $C_4H_{10}$, is -2876 kJ mol$^{-1}$. Write a balanced equation with state symbols for the reaction for which $\Delta H^\circ_c = -2879$ kJ mol$^{-1}$. 


Where does the energy come from?

During a combustion reaction, for example, the bonds in the fuel and oxygen break and new bonds form to make new molecules.

Energy is needed to break bonds.

**Bond breaking is endothermic.**

Energy is released as bonds form.

**Bond forming is exothermic.**

\[ \begin{align*}
\Delta H_1 : & \text{enthalpy change (or energy change) – the energy needed to break one mole of O=O bonds + energy needed to break 2 moles of H-H bonds, endothermic:} \\
& \Delta H_1 = (+358 \text{ kJ mol}^{-1}) + 2 \times (+436 \text{ kJ mol}^{-1}) = +1230 \text{ kJ mol}^{-1}. \\
\Delta H_2 : & \text{energy evolved or given out when 4 moles of O-H bonds are formed, exothermic:} \\
& \Delta H_2 = 4 \times (-464 \text{ kJ mol}^{-1}) = -1856 \text{ kJ mol}^{-1}. \\
\Delta H_3 : & \text{energy released during reaction to form 2 moles of water, i.e. the enthalpy change of the reaction (exothermic):} \\
& \Delta H_3 = \Delta H_1 + \Delta H_2 = (+1230 \text{ kJ mol}^{-1}) + (-1856 \text{ kJ mol}^{-1}) = -626 \text{ kJ mol}^{-1}. 
\end{align*} \]

The bond dissociation enthalpy, **bond enthalpy or bond energy** is the energy needed to break a particular bond in a particular molecule, e.g. the O-H bond in water.

We usually use **average bond enthalpies**, e.g. the average bond energy of the O-H bond in a range of different compounds, as this simplifies matters whilst introducing only a small error. It is measured for molecules in the gaseous state.
Potential-energy curve for a diatomic molecule.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Average bond enthalpy / kJ mol⁻¹</th>
<th>Bond length / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–C</td>
<td>+347</td>
<td>0.154</td>
</tr>
<tr>
<td>C=O</td>
<td>+612</td>
<td>0.134</td>
</tr>
<tr>
<td>C≡C</td>
<td>+838</td>
<td>0.120</td>
</tr>
<tr>
<td>C−O</td>
<td>+358</td>
<td>0.143</td>
</tr>
<tr>
<td>C=O (for CO₂)</td>
<td>+805</td>
<td>0.116</td>
</tr>
<tr>
<td>C−H</td>
<td>+413</td>
<td>0.108</td>
</tr>
<tr>
<td>O−H</td>
<td>+464</td>
<td>0.096</td>
</tr>
<tr>
<td>O=O</td>
<td>+498</td>
<td>0.121</td>
</tr>
<tr>
<td>N≡N</td>
<td>+945</td>
<td>0.110</td>
</tr>
</tbody>
</table>

Bond enthalpies are measured indirectly using Hess’s Law.

Q.1 How does bond enthalpy change as the number of bonds increases between a given element, e.g. C–C, C=O, C≡C bonds?

Q.2 How does bond enthalpy relate to bond length?

Q.3 Why is a double bond shorter than a single bond and a triple bond shorter than a double bond?
**Worked example – Using Bond Enthalpies**

Find $\Delta H_1$, the enthalpy of combustion, $\Delta H_f^c$, for methane:

We are breaking 4 C-H bonds and 2 O=O double bonds, so:

$$\Delta H_2 = 4 \times (+413 \text{ kJ mol}^{-1}) + 2 \times (+498 \text{ kJ mol}^{-1}) = +2648 \text{ kJ mol}^{-1}.$$  

We are forming 2 C=O double bonds and 4 O-H bonds, so:

$$\Delta H_3 = 2 \times (-805 \text{ kJ mol}^{-1}) + 4 \times (-464 \text{ kJ mol}^{-1}) = -3466 \text{ kJ mol}^{-1}.$$  

$$\Delta H_1 = \Delta H_2 + \Delta H_3 = (+2648 \text{ kJ mol}^{-1}) + (-3466 \text{ kJ mol}^{-1})$$  

$$\Delta H_1 \equiv \Delta H_f^c = -818 \text{ kJ mol}^{-1}.$$  

This value will not exactly match the standard enthalpy of combustion for methane as listed in tables, which is $-890 \text{ kJ/mol}$, since we used H2O(g) not H2O(l) – we used water gas (steam) as required for bond enthalpies, not the standard state of water.

Q. Use bond enthalpies to calculate the overall enthalpy (energy) change for the reaction:

$$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g}).$$

Use the following average bond enthalpy values:

- H-H bond enthalpy = +436 kJ mol\(^{-1}\).
- I-I bond enthalpy = +151 kJ mol\(^{-1}\).
- H-I bond enthalpy = +299 kJ mol\(^{-1}\).