Section 3.1 Energy Changes in Chemical Reactions

(1) Conservation of energy

An object which is capable of doing work is said to possess energy. There are many forms of energy: heat, light, chemical energy, nuclear energy, etc., but basically there are only two kinds of energy, kinetic energy and potential energy.

The energy which an object possesses because it is moving is called kinetic energy. Heat is a form of kinetic energy: it is the kinetic energy associated with the motion of atoms and molecules.

The energy which an object possesses because of its position or because of the arrangement of its component parts is called potential energy. The energy of chemical bonds is a form of potential energy, arising from the positions of atoms and molecules with respect to one another.

Bond-breaking and bond-forming in chemical reactions involve changes in potential energy.

The study of the energy changes accompany chemical reactions is called thermochemistry or chemical thermodynamics.

Laws of conservation of energy

Energy can be changed from one form into another, but it can neither be created nor destroyed. (First Law of Thermodynamics)

Energy can be converted from one form into another. Electrical energy can be converted into heat energy. Our bodies can convert the energy of the chemical bonds in food into other kinds of energy. Calculations on energy conversions show that energy is never created and never destroyed.
(2) Endothermic and exothermic reactions

In thermochemistry, all substances possess a heat content or enthalpy, H.

The enthalpy change (ΔH) of a reaction is the heat exchange with the surroundings at constant pressure before and after the reaction.

\[ \Delta H = H_2 \text{ (enthalpy of products)} - H_1 \text{ (enthalpy of reactants)} \]

Any chemical reaction involves a rearrangement of atoms. This involves two processes:

1. Bond breaking in the reactants. This is an energy absorbing process and takes in energy from the surroundings.
2. Bond formation in the products. This is an energy releasing process and gives out energy to the surroundings.

Chemical reaction results in an overall enthalpy change because the energy required to break the bonds in reactants to form free atoms is unequal to the energy given out when the free atoms recombine to form products.

**Endothermic reaction**

A reaction in which heat is absorbed from the surroundings is termed endothermic reaction.

In endothermic reactions, the energy required to break the bonds in the reactants is greater than the energy liberated in forming the bonds in the products. Energy is taken in from the surroundings.

The energy involved can be in the form of heat. When an endothermic reaction occurs, the heat required for the reaction is taken from the reacting materials. At first, the temperature of the products falls below the initial temperature. Eventually, the temperature of the products rises to room temperature again as heat is absorbed from the surroundings. The enthalpy of the products is greater than that of the reactants and the enthalpy change, ΔH, is positive.

![Enthalpy level diagram](image)

**Example**

When nitrogen gas reacts with oxygen gas in lightning, heat is absorbed:

![Enthalpy level diagram](image)
Exothermic reaction

A reaction in which heat is released to the surroundings is termed exothermic reaction.

In exothermic reactions, the energy required to break the bonds in the reactants is smaller than the energy liberated in forming the bonds in the products. Energy is given out to the surroundings.

The energy involved can be in the form of heat. When an exothermic reaction occurs, heat is given out and the temperature of the products rises above room temperature. Eventually, the temperature of the products falls to room temperature again as the heat produced is lost to the surroundings. The enthalpy of the products is less than that of the reactants and the enthalpy change, $\Delta H$, is negative.

Example 1
In the combustion of octane in a plentiful supply of air, 40 MJ of energy are obtained for every litre of octane burnt:

Example 2
When magnesium reacts with oxygen, heat is evolved:

Enthalpy level diagram
Section 3.2 Standard Enthalpy Changes

(1) Standard enthalpy change of reaction

Enthalpy change (ΔH) of a reaction is the heat exchange with the surroundings at constant pressure. It is measured in kilojoules per mole (kJ mol⁻¹). In order to compare enthalpy changes, the amounts of materials used, their physical states and the reaction conditions must be standardized.

Standard enthalpy change of reaction, ΔH°, is the enthalpy change when the molar quantities of reactants shown in a balanced chemical equation completely react to form products under standard conditions.

Standard conditions are defined as follows:
- a pressure of 1 atmosphere
- a temperature of 298 K
- if solution is used, concentration of unit activity (1 mol dm⁻³) is specified
- elements or compounds in their normal stable state at a pressure of 1 atmosphere and a temperature of 298 K

Example 1
Consider the reaction: \( \text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2 \text{HCl}(\text{g}) \) \( \Delta H^\circ = -184 \text{ kJ mol}^{-1} \)

What is the standard enthalpy change for
a. \( \frac{3}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{HCl}(\text{g}) \)

b. \( 2 \text{HCl}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \)

Note that:
1. Many reactions do not occur under standard conditions (e.g. petrol will not burn without the high temperature caused by an electrical spark or a flame). The standard enthalpy change of reaction is either calculated from a ΔH value for the direct reaction under non-standard conditions or obtained using an indirect method.

2. The precise physical state and allotropic form must be clearly specified because changes in state and allotropic form may involve energy changes even at a fixed temperature.

Example 2
Consider the reactions:
\[ \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}) \quad \Delta H^\circ = -242 \text{ kJ mol}^{-1} \]
\[ \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}) \quad \Delta H^\circ = -286 \text{ kJ mol}^{-1} \]

Calculate the standard enthalpy change for
\[ \text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}) \]

Example 3
Consider the reactions:
\[ \text{C}_{(\text{graphite})} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \quad \Delta H^\circ = -393.5 \text{ kJ mol}^{-1} \]
\[ \text{C}_{(\text{diamond})} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \quad \Delta H^\circ = -395.4 \text{ kJ mol}^{-1} \]

Calculate the standard enthalpy change for
\[ \text{C}_{(\text{graphite})} \rightarrow \text{C}_{(\text{diamond})} \]
(2) **Standard enthalpy change of neutralisation**

**Standard enthalpy change of neutralisation,** $\Delta H^\circ_n$, is the enthalpy change when an acid and a base neutralize to form one mole of water under standard conditions.

For **strong acids and strong alkalis** the enthalpy change of neutralisation is effectively constant at about -57.3 kJ mol$^{-1}$. This is because strong acids and strong alkalis are all completely ionized in dilute solutions, so that the reaction is essentially the formation of water from H$^+$ and OH$^-$ ions.

**Example 1**

$$\text{HCl}_{(aq)} + \text{NaOH}_{(aq)} \rightarrow \text{NaCl}_{(aq)} + \text{H}_2\text{O}_{(l)} \quad \Delta H^\circ_n = -57.3 \text{ kJ mol}^{-1}$$

**Example 2**

$$2 \text{HNO}_3_{(aq)} + \text{Ca(OH)}_2_{(aq)} \rightarrow \text{Ca(NO}_3)_2{_{(aq)}} + 2 \text{H}_2\text{O}_{(l)} \quad \Delta H^\circ_n = -114.6 \text{ kJ mol}^{-1}$$

With **weak acids or weak alkalis**, unionized acid or alkali has to be converted into ions. The enthalpy change of dissociation of weak acid or weak alkali is usually positive. The overall enthalpy change of neutralisation involving either weak acids or alkalis may be smaller than –57.3 kJ mol$^{-1}$.

**Example 3**

$$\text{HCN}_{(aq)} + \text{NaOH}_{(aq)} \rightarrow \text{NaCN}_{(aq)} + \text{H}_2\text{O}_{(l)} \quad \Delta H^\circ_n = -11.7 \text{ kJ mol}^{-1}$$

Energy is required to complete the dissociation of the weak acid, HCN, as reaction proceeds. The ionization process consumes some heat produced during neutralisation, thereby reducing the magnitude of $\Delta H^\circ_n$. The enthalpy change of neutralisation is less negative (i.e. less exothermic).
Example 4: **Determination of the enthalpy change of neutralisation using a vacuum flask**

(a) When 100 g of water at 94.0 °C were added to a calorimeter at 17.5 °C, the temperature rose to 80.5 °C. Calculate the heat capacity of the calorimeter.

(b) 250 cm³ of sodium hydroxide (0.400 mol dm⁻³) were added to 250 cm³ of hydrochloric acid (0.400 mol dm⁻³) in the calorimeter. The temperature of the two solutions was 17.5 °C initially and rose to 20.1 °C. Calculate the enthalpy change of neutralisation for the reaction. (The assumptions are made that the specific heat capacity of the solutions are the same as that of water, 4.18 J g⁻¹ K⁻¹ and the density of the solutions are the same as that of water, 1.00 g cm⁻³.)

Example 5: **Determination of the enthalpy change of neutralisation using an expanded polystyrene cup**

A simple calorimeter can be made by placing an expanded polystyrene cup into a beaker with cotton wool. The cup is covered with a lid through which a thermometer can be fitted loosely. The heat capacity of the cup is usually ignored, because polystyrene is such a good insulator and the mass of the cup is so small.

50.0 cm³ of 1.00 mol dm⁻³ hydrochloric acid and 50.0 cm³ of 1.00 mol dm⁻³ sodium hydroxide solution were mixed at 25.0 °C in an expanded polystyrene cup. The temperature rose 6.8 °C. Calculate the enthalpy change of neutralisation for the reaction.

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<td>2. Heat lost to the surroundings due to conduction, convection, radiation and evaporation.</td>
<td>2. Replace the polystyrene cup by a vacuum flask calorimeter.</td>
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<td>3. Thermometer is not precise enough.</td>
<td>3. Use a <strong>Beckmann thermometer</strong> for higher accuracy in recording temperatures.</td>
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<td>4. Specific heats of solutions may not be exactly 4.18 Jg⁻¹K⁻¹ as that of water.</td>
<td>4. Determine the exact specific heat capacity of the solutions.</td>
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</table>
(3) Standard enthalpy change of solution

Standard enthalpy change of solution, \( \Delta H_{\text{soln}} \), is the enthalpy change when one mole of a substance is completely dissolved in an infinite amount of solvent under standard conditions.

The solute should be dissolved in such a large excess of solvent that further addition of solvent produces no further enthalpy change.

Example 1

When 1 mole of sodium chloride is dissolved in large excess of water, 5.0 kJ of energy is absorbed from the surroundings under standard conditions. There is no further enthalpy change if the solution is further diluted.

Example 2: Determining the enthalpy change of solution of copper(II) sulphate

When 8.0 g of anhydrous copper(II) sulphate are added to 100 cm\(^3\) water in a polystyrene cup, there is a temperature rise of 8 °C in the solution.

(a) Calculate the molar enthalpy change of solution of anhydrous copper(II) sulphate.

\[
\begin{align*}
\text{[Molar heat capacity of water} &= 76.5 \text{ J K}^{-1} \text{ mol}^{-1}; \\
\text{molar mass of water} &= 18.0 \text{ g mol}^{-1}; \\
\text{molar mass of anhydrous copper(II) sulphate} &= 159.5 \text{ g mol}^{-1}\]
\end{align*}
\]

(b) Indicate four assumptions which are made in calculating the molar enthalpy change of solution in (a).
1. The thermal capacities of polystyrene cup and thermometer are negligible.
2. The specific heat capacity of copper(II) sulphate solution is similar to that of water.
3. The density of copper(II) sulphate solution is similar to that of water (1.0 g cm\(^{-3}\)).
4. Anhydrous copper(II) sulphate dissolves quickly such that heat losses are negligible.
5. Further dilution of the solution would cause no further heat change.

(c) Indicate sources of error in this experiment. How could these errors be minimized?

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<td>6. Anhydrous copper(II) sulphate may have absorbed moisture from air.</td>
<td>6. Gently heat the sample in an oven for several hours and keep it in a desiccator.</td>
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(4) Standard enthalpy change of atomisation

Standard enthalpy change of atomisation, $\Delta H^\circ_a$, is the enthalpy change when one mole of gaseous atoms is formed from the element under standard conditions.

Example 1

\[ \frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{Cl}(\text{g}) \quad \Delta H^\circ_a \left[ \frac{1}{2} \text{Cl}_2(\text{g}) \right] = +121 \text{ kJ mol}^{-1} \]

Note that atomisation is always an endothermic process. For diatomic molecules in gaseous state, $2 \times \Delta H^\circ_a$ is equal to the energy required to break 1 mole of the covalent bonds.

\[ 2 \times \Delta H^\circ_a \left[ \frac{1}{2} \text{Cl}_2(\text{g}) \right] = \text{Bond enthalpy of Cl}_2(\text{g}) = +242 \text{ kJ mol}^{-1} \]

Example 2

Write thermochemical equations from the following data:

(a) $\Delta H^\circ_a \left[ \frac{1}{2} \text{N}_2(\text{g}) \right] = +473 \text{ kJ mol}^{-1}$

(b) $\Delta H^\circ_a \left[ \frac{1}{4} \text{P}_4 \text{ (white, s)} \right] = +315 \text{ kJ mol}^{-1}$

(c) $\Delta H^\circ_a \left[ \text{Ca(s)} \right] = +178 \text{ kJ mol}^{-1}$

(e) $\Delta H^\circ_a \left[ \text{C(graphite, s)} \right] = +718 \text{ kJ mol}^{-1}$
Standard enthalpy change of combustion, $\Delta H^\circ_c$, is the enthalpy change when one mole of a pure substance is completely burnt in oxygen under standard conditions.

Example 1
Write thermochemical equations from the following data:
(a) $\Delta H^\circ_c [\text{CO (g)}] = -283 \text{ kJ mol}^{-1}$

(b) $\Delta H^\circ_c [\text{H}_2 (g)] = -286 \text{ kJ mol}^{-1}$

(c) $\Delta H^\circ_c [\text{C}_2\text{H}_5\text{OH (l)}] = -1368 \text{ kJ mol}^{-1}$

(d) $\Delta H^\circ_c [\text{C}_6\text{H}_{14} (l)] = -4195 \text{ kJ mol}^{-1}$

(e) $\Delta H^\circ_c [\text{Zn (s)}] = -348 \text{ kJ mol}^{-1}$

Example 2: Experimental method for finding enthalpy change of combustion
A simple method obtaining an approximate value for the enthalpy change of combustion of a fuel is shown below:

When ethanol was burnt in the apparatus, the results were: $m_1 = 1.50 \text{ g}$, $m_2 = 500 \text{ g}$, $t = 19.5 \circ \text{C}$. Find the enthalpy change of combustion of ethanol. Compare the experimental value with the listed value of $-1368 \text{ kJ mol}^{-1}$.
Standard enthalpy change of formation, $\Delta H^\circ_f$, is the enthalpy change when one mole of a pure substance is formed from its elements in their normal physical states under standard conditions.

Example 1
The standard enthalpy change of formation of ethanol can be represented by the following thermochemical equation:

Example 2
From the definition, the standard enthalpy change of formation of an element in its standard state is zero.

\[
\begin{align*}
\text{Cl}_2(g) & \rightarrow \text{Cl}_2(g) \quad \Delta H^\circ_f [\text{Cl}_2(g)] = 0 \text{ kJ mol}^{-1} \\
\text{Na}(s) & \rightarrow \text{Na}(s) \quad \Delta H^\circ_f [\text{Na}(s)] = 0 \text{ kJ mol}^{-1}
\end{align*}
\]

Example 3
Write thermochemical equations from the following data:
(a) $\Delta H^\circ_f [\text{CH}_3\text{Cl}(l)] = -81 \text{ kJ mol}^{-1}$

(b) $\Delta H^\circ_f [\text{NH}_4\text{I}(s)] = -201 \text{ kJ mol}^{-1}$

(c) $\Delta H^\circ_f [\text{MgCl}_2.6\text{H}_2\text{O}(s)] = -2500 \text{ kJ mol}^{-1}$

Standard enthalpy change of formation provides useful information about the energetic stability of the compound relative to its elements.

Example 4
The following equations show the formation of nitrogen monoxide and dinitrogen pentoxide from their elements under standard conditions:

$\text{NO}(g)$ is an example of an endothermic compound, that is, enthalpy is absorbed on its formation.

$\text{N}_2\text{O}_5(s)$ is an example of an exothermic compound, that is, enthalpy is lost on its formation. The two enthalpies of formation can be compared on an enthalpy level diagram. Clearly, nitrogen pentoxide, and not nitrogen monoxide, is the more energetically stable of the oxides.

\[
\begin{align*}
\text{H} & \quad \text{Enthalpy} \\
0 & \quad \text{Enthalpy}
\end{align*}
\]

In many cases, standard enthalpy change of formation cannot be measured directly because the elements will not combine under experimental conditions. Fortunately, standard enthalpy change of formation can be calculated from the other enthalpy change terms.
(1) **Hess’s Law**

The standard enthalpy change of reaction depends only on the difference between the standard enthalpy of the reactants and the standard enthalpy of the products and not on the route by which the reaction occurs.

**Hess’s law** states that if a reaction can take place by more than one route, the overall change in enthalpy is the same, whichever route is followed.

Hess’s law is derived from the First Law of Thermodynamics: **Law of Conservation of energy**. As shown in the following figure, the standard enthalpy in going from A to B by the direct route 1 is $\Delta H^\circ_1$. The standard enthalpy in going from A to B by the indirect route 2 is $\Delta H^\circ_2 + \Delta H^\circ_3$.

If the sum ($\Delta H^\circ_2 + \Delta H^\circ_3$) were less than $\Delta H^\circ_1$, it would be possible to create energy by making A from B by route 1 and then converting A to B by route 2. This would be contrary to the Law of Conservation of Energy. It follows that

$$
\Delta H^\circ_1 = \Delta H^\circ_2 + \Delta H^\circ_3
$$

and the standard enthalpy change is the same for the different routes. It follows also that the standard enthalpy change for the reaction $B \rightarrow A$ is $-\Delta H^\circ_1$.

Hess’s law can be used **to determine enthalpy changes which are not easily obtainable by experiment**. Usually, an enthalpy level diagram or an enthalpy cycle is drawn to link the enthalpy changes of different routes.

**Example 1**

Given that:

- $\Delta H^\circ_c [\text{CO (g)}] = -283 \text{ kJ mol}^{-1}$
- $\Delta H^\circ_c [\text{C (graphite)}] = -393 \text{ kJ mol}^{-1}$

Find the standard enthalpy change of formation of carbon monoxide, $\Delta H^\circ_f [\text{CO (g)}]$.

**Step 1**: Draw an enthalpy cycle or enthalpy level diagram to link the thermochemical equations involved.

**Enthalpy cycle**

<table>
<thead>
<tr>
<th>H</th>
<th>Enthalpy KJ mol$^{-1}$</th>
</tr>
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<tr>
<td>0</td>
<td></td>
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**Step 2**: By Hess’s law,

**Question**: Why is it impossible to obtain $\Delta H^\circ_f [\text{CO (g)}]$ directly?

- It is difficult to control the extent of the reaction.
- Carbon may react with oxygen to form carbon dioxide gas which is more exothermic.
Example 2: **Determination of the enthalpy change of hydration of MgSO$_4$(s)**

It is impossible to measure the enthalpy change of hydration of anhydrous magnesium sulphate because the process is very slow and cannot be controlled.

By using Hess’s law, this enthalpy change can be obtained by measuring the enthalpy change of solution for the two solids.

**Experiment A**

When 3.01 g of anhydrous magnesium sulphate were added to 50.0 cm$^3$ of water in a polystyrene cup and the solution stirred to dissolve the solid as quickly as possible, there was a maximum rise in temperature of the solution by 11.0 °C.

**Experiment B**

When 6.16 g of magnesium sulphate-7-water were added to 50.0 cm$^3$ of water in a polystyrene cup and the solution stirred to dissolve the solid as quickly as possible, there was a maximum fall in temperature of the solution by 1.5 °C.

[ Specific heat capacity of water = 4.18 J g$^{-1}$ K$^{-1}$; density of water = 1.00 g cm$^{-3}$; molar mass of MgSO$_4$ = 120.4 g mol$^{-1}$; molar mass of MgSO$_4$.7H$_2$O = 246.4 g mol$^{-1}$]

(a) From experiments A, calculate the enthalpy change of solution of anhydrous magnesium sulphate.

(b) From experiments B, calculate the enthalpy change of solution of magnesium sulphate-7-water.

(c) Draw an enthalpy cycle linking the equations for the reactions which took place in experiment A and B with the hydration reaction. Find the value for the enthalpy change of hydration of anhydrous magnesium sulphate.

(d) The value of standard enthalpy change of hydration of MgSO$_4$ from data book is – 104 kJ mol$^{-1}$. What are the possible sources of errors in these experiments? Suggest how they can be reduced.

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<td>7. The experiments are not performed under standard conditions.</td>
<td>7. Perform the experiments at 298 K and under 1 atm.</td>
</tr>
</tbody>
</table>
(2) Calculations involving enthalpy changes of reactions

1. Finding the standard enthalpy change of formation of a compound indirectly

Example 1
To find the standard enthalpy change of formation of ethyne from practical measurements is impossible, as attempts to make ethyne from carbon and hydrogen will result in the formation of a mixture of hydrocarbon. By Hess’s law, the standard enthalpy change of formation of ethyne can be calculated from the following standard enthalpy changes of combustion which can be measured accurately:

\[ \Delta H^\circ_{oc} [H_2 (g)] = -286 \text{ kJ mol}^{-1} \]
\[ \Delta H^\circ_{oc} [C_{(\text{graphite})}] = -393 \text{ kJ mol}^{-1} \]
\[ \Delta H^\circ_{oc} [C_2H_2 (g)] = -1300 \text{ kJ mol}^{-1} \]

Example 2
Calculate the standard enthalpy change of formation of methanol, using the following data:

\[ \Delta H^\circ_{oc} [H_2 (g)] = -286 \text{ kJ mol}^{-1} \]
\[ \Delta H^\circ_{oc} [C_{(\text{graphite})}] = -393 \text{ kJ mol}^{-1} \]
\[ \Delta H^\circ_{oc} [\text{CH}_3\text{OH} (l)] = -726 \text{ kJ mol}^{-1} \]

Example 3
Find the standard enthalpy change of combustion of propan-2-ol, given

\[ \Delta H^\circ_{oc} [H_2 (g)] = -286 \text{ kJ mol}^{-1} \]
\[ \Delta H^\circ_{oc} [C_{(\text{graphite})}] = -393 \text{ kJ mol}^{-1} \]
\[ \Delta H^\circ_{f} [\text{CH}_3\text{CH(OH)}\text{CH}_3 (l)] = -318 \text{ kJ mol}^{-1} \]
2. Finding the standard enthalpy change of reaction from standard enthalpy changes of formation

Example 1

Ethanol reacts with phosphorus pentachloride according to the reaction:

\[ \text{C}_2\text{H}_5\text{OH}(l) + \text{PCl}_5(s) \rightarrow \text{C}_2\text{H}_5\text{Cl}(l) + \text{POCl}_3(l) + \text{HCl}(g) \]

Calculate the standard enthalpy change of reaction, using the following data:

\[ \Delta H_{\text{f}}^{\circ} [\text{C}_2\text{H}_5\text{OH} (l)] = -277 \text{ kJ mol}^{-1} \]
\[ \Delta H_{\text{f}}^{\circ} [\text{PCl}_5 (s)] = -443 \text{ kJ mol}^{-1} \]
\[ \Delta H_{\text{f}}^{\circ} [\text{C}_2\text{H}_5\text{Cl} (l)] = -136 \text{ kJ mol}^{-1} \]
\[ \Delta H_{\text{f}}^{\circ} [\text{POCl}_3 (l)] = -597 \text{ kJ mol}^{-1} \]
\[ \Delta H_{\text{f}}^{\circ} [\text{HCl} (g)] = -92 \text{ kJ mol}^{-1} \]

Alternative method of calculation:

\[ \text{C}_2\text{H}_5\text{OH}(l) + \text{PCl}_5(s) \rightarrow \text{C}_2\text{H}_5\text{Cl}(l) + \text{POCl}_3(l) + \text{HCl}(g) \]

Example 2

The platinum-catalyzed oxidation of ammonia,

\[ 4 \text{NH}_3(g) + 5 \text{O}_2(g) \rightarrow 4 \text{NO}(g) + 6 \text{H}_2\text{O}(l) \]

is used in the manufacture of nitric acid. Calculate the standard enthalpy change of reaction using the following data:

\[ \Delta H_{\text{f}}^{\circ} [\text{NH}_3 (g)] = -46 \text{ kJ mol}^{-1} \]
\[ \Delta H_{\text{f}}^{\circ} [\text{NO} (g)] = +90 \text{ kJ mol}^{-1} \]
\[ \Delta H_{\text{f}}^{\circ} [\text{H}_2\text{O} (l)] = -286 \text{ kJ mol}^{-1} \]
The Apollo 11 project landed the first man on the moon on 21 July 1969. During this project, engines of the lunar module used methylhydrazine (CH$_3$NHNH$_2$) and dinitrogen tetraoxide (N$_2$O$_4$). These liquids were carefully chosen since they ignite spontaneously and very exothermically on contact.

Write the equation for the reaction and calculate the standard enthalpy change of reaction using the following data:

\[
\Delta H^\circ_f [\text{CH}_3\text{NHNH}_2 (l)] = + 53 \text{ kJ mol}^{-1} \\
\Delta H^\circ_f [\text{N}_2\text{O}_4 (l)] = - 20 \text{ kJ mol}^{-1} \\
\Delta H^\circ_f [\text{H}_2\text{O} (l)] = - 286 \text{ kJ mol}^{-1} \\
\Delta H^\circ_f [\text{CO}_2 (g)] = - 393 \text{ kJ mol}^{-1}
\]

3. Finding the enthalpy change of reaction by algebraic method

Example:

Given the following thermochemical data at 298 K:

1. Standard enthalpy change of formation of CO$_2$(g)  
   $\Delta H^\circ_f [\text{CO}_2 (g)] = - 394.80 \text{ kJ mol}^{-1}$

2. Standard enthalpy change of formation of CH$_3$CO$_2$H(l)  
   $\Delta H^\circ_f [\text{CH}_3\text{CO}_2\text{H} (l)] = - 488.88 \text{ kJ mol}^{-1}$

3. Enthalpy of vaporization of H$_2$O(l) to H$_2$O(g)  
   $\Delta H^\circ_v [\text{H}_2\text{O} (l) \rightarrow \text{H}_2\text{O} (g)] = + 39.48 \text{ kJ mol}^{-1}$

Enthalpy of reactions:

4. H$_2$(g) + $\frac{1}{2}$ O$_2$(g) $\rightarrow$ H$_2$O(g)  
   $\Delta H^\circ_r = - 242.76 \text{ kJ mol}^{-1}$

5. CH$_4$(g) + 2 O$_2$(g) $\rightarrow$ CO$_2$(g) + 2 H$_2$O(g)  
   $\Delta H^\circ_r = - 809.34 \text{ kJ mol}^{-1}$

(a) Calculate the standard enthalpy change of formation of H$_2$O(l) at 298 K.

(b) Calculate the enthalpy change for the following reaction at 298 K:

CH$_3$CO$_2$H(l) $\rightarrow$ CH$_4$(g) + CO$_2$(g)
Section 3.4  Spontaneity of changes

(1) Spontaneous change

A spontaneous change is a change that happens naturally. It tends to occur without the need to be driven by an external influence. Spontaneous exothermic reactions are common. Endothermic reactions are only spontaneous if there is a large increase in the degree of disorder.

In the following spontaneous changes a relatively ordered system has been replaced by a more disordered system:

Example 1
When gases come into contact they diffuse to form a homogeneous mixture. Instead of a tidy arrangement of different molecules in different containers, the molecules become mixed up in a random arrangement. The pattern is that mass tends to become more disordered.

Example 2
Potassium chloride dissolves endothermically. The solid is a highly ordered arrangement of potassium ions and chloride ions. When it dissolves, this regular arrangement is replaced by a random distribution of ions in solution.

\[
\text{KCl(s) + aq. \rightleftharpoons KCl(aq)} \quad \Delta H_{\text{solution}}^\circ = +19 \text{ kJ mol}^{-1}
\]

Example 3
When ice melts the regular hydrogen-bonded structure of ice is replaced by the fluid association of water molecules in liquid water. When water vaporizes the association of water molecules is replaced by changes of state occur spontaneously and endothermically.

Example 4
Ammonium carbonate dissociates spontaneously

\[
\text{(NH}_4\text{)}_2\text{CO}_3(s) \rightleftharpoons 2 \text{NH}_3(g) + \text{CO}_2(g) + \text{H}_2\text{O}(g) \quad \Delta H^\circ = +68 \text{ kJ mol}^{-1}
\]

One mole of a solid with an ordered crystalline structure is replaced by four moles of gases. The system becomes less ordered.

The extent of disorder of a system is measured by a quantity called entropy (symbol S). Low entropy means little disorder; high entropy means a high degree of disorder. Natural changes tend to increase the degree of disorder of matter and of energy.

Second law of Thermodynamics: Entropy tends to increase.

The entropy of a substance can be increased by heating. This increases the motion of particles and therefore the degree of disorder. Entropy can be increased by providing more space into which particles can spread.

A solid is an ordered three-dimensional structure with low entropy. When a solid melts, the particles have more freedom to move: the liquid is more disordered than the solid and has higher entropy. When a substance vaporizes the particles have almost complete freedom of movement and they occupy a much higher volume than in the liquid or solid state. Gases therefore have much higher entropies than liquids and solids at the same temperature.

A perfect crystal at temperature zero K has perfect order and zero entropy. As the substance is heated the entropy increases.
(2) Entropy change \( (\Delta S) \)

Entropy is given the symbol \( S \), standard entropy, \( S^\ominus \), and change in entropy, \( \Delta S \).

An increase in the degree of disorder of a system shows in a positive value of \( \Delta S \).

A decrease in the degree of disorder of a system shows in a negative value of \( \Delta S \).

Example 1

The equation \( \text{NH}_4\text{NO}_3(s) \rightarrow \text{N}_2\text{O}(g) + 2 \text{H}_2\text{O}(g) \)

Shows that 1 mole of the crystalline solid, ammonium nitrate, forms 1 mole of a gas, dinitrogen oxide, and 2 moles of water vapour, a total of 3 moles of gas. The value of \( \Delta S \) is positive.

Under standard conditions, the water formed is a liquid, and the increase in entropy is less: \( \Delta S^\ominus \) has a smaller positive value.

Example 2

\[ \text{CaO}(s) + \text{H}_2\text{O}(l) \rightarrow \text{Ca(OH)}_2(s) \quad \Delta S^\ominus \text{negative} \]

Example 3

\[ \text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g) \quad \Delta S^\ominus \text{positive} \]

Example 4

For each of the following reactions, state whether the entropy change of the system will be positive, negative or approximately zero:

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

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

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

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

(e) \( \text{NaCl}(s) + \text{aq.} \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \)

(f) \( \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(l) \)

(g) amino acids \( \rightarrow \) proteins

(h) starch \( \rightarrow \) glucose
(3) Free energy change (ΔG)

Both factors, the change in enthalpy and the change in entropy, are important in deciding whether a physical or chemical change will occur. They are combined in the equation:

\[ \Delta G = \Delta H - T \Delta S \]

where \( \Delta G \) is the free energy change (kJ mol\(^{-1}\)), \( \Delta H \) is the enthalpy change (kJ mol\(^{-1}\)), \( \Delta S \) is the entropy change (kJ mol\(^{-1}\)K\(^{-1}\)), and T is the absolute temperature (K).

All spontaneous physical and chemical changes involve a decrease in free energy, a negative value of \( \Delta G \).

In an exothermic reaction, \( \Delta H \) is negative.

If \( \Delta S \) has a positive value, then
\[ \Delta G = \text{(negative value)} \times \text{(positive value)} = \text{negative value} \]

If the reaction is strongly exothermic but \( \Delta S \) has a small negative value,
\[ \Delta G = \text{(large negative value)} \times \text{(small negative value)} = \text{negative value} \]

In an endothermic reaction, \( \Delta H \) is positive,

therefore \( \Delta G \) is negative only if \( T \Delta S \) has a large positive value:
\[ \Delta G = \text{(positive value)} \times \text{(large positive value)} = \text{negative value} \]

The value of the entropy change is multiplied by the temperature; therefore the role of entropy change in deciding whether or not a reaction is spontaneous becomes more important at higher temperatures. A large value of \( \Delta S \) and a high temperature help to make the \( T \Delta S \) term outweigh a positive value of \( \Delta H \).

Example 1

\[
\text{NH}_4\text{Cl}(s) \rightarrow \text{NH}_4^{+}(aq) + \text{Cl}^{-}(aq) \quad \Delta G = -6.7 \text{ kJ mol}^{-1} ; \quad \Delta H = +16 \text{ kJ mol}^{-1}
\]

Why does ammonium chloride dissolve spontaneously under standard conditions even under standard conditions even though \( \Delta H \) for the process is positive?

The dissolution of ammonium chloride involves an increase in entropy (\( \Delta S \) is positive). A positive \( T \Delta S \) term outweighs a positive value of \( \Delta H \), hence free energy change (\( \Delta G \)) for the dissolution process is negative.

Example 2

\[
\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(s) \quad \Delta G = +0.6 \text{ kJ mol}^{-1} ; \quad \Delta H = -44.1 \text{ kJ mol}^{-1}
\]

Why does liquid water not freeze under standard conditions even though \( \Delta H \) for the process is negative?

The freezing of water involves a decrease in entropy (\( \Delta S \) is negative). The change in free energy is positive at standard conditions (25 °C and 1 atm) and thus liquid water does not freeze. The \( T \Delta S \) term becomes a smaller value at lower temperature, therefore free energy change (\( \Delta G \)) for the freezing process is negative at or below the freezing point of water (0 °C).
(4) Feasibility of chemical reaction

A chemical reaction with a negative value of $\Delta G$ is said to be feasible. This means that, if the reaction takes place, it will go in the direction of the reactants forming the products and not in the reverse direction.

A feasible reaction does not tell anything about the rate of the reaction. The reactants may have to surmount an energy barrier before they can react. Whether the reaction is exothermic or endothermic, it will not occur in the absence of a certain minimum amount of energy, known as the activation energy, $E_a$. The reactants will be kinetically stable if the activation energy is very high.

If $\Delta G^\Theta$ for a change is negative, the reactants are thermodynamically unstable relative to that change.

Example 1
In the presence of sunlight, hydrogen and chlorine gases will explode at room temperature:

$$\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$$

The reactants are kinetically unstable as the activation energy is very low. They are also thermodynamically unstable because the free energy change for the reaction is negative.

Example 2
When methane is burnt in oxygen, there is a considerable release of free energy.

$$\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \quad \Delta G^\Theta = -580 \text{ kJ mol}^{-1}$$

The activation energy for the combustion is quite high, and methane is said to be thermodynamically unstable but kinetically stable, relative to its combustion products. Methane does not react with air at a measurable rate at room temperature. The reactant molecules must be given enough energy to surmount the energy barrier in order to react.

Example 3
What happens if the $\Delta G$ for a change is positive?

The reaction can be made to occur by driving it with energy from an external source.

The reaction $2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \quad \Delta G^\Theta = +494 \text{ kJ mol}^{-1}$
can be made to occur by sending an electric current through water.
### Summary: Possible combination of $\Delta H$ and $\Delta S$

<table>
<thead>
<tr>
<th>$\Delta H$</th>
<th>$\Delta S$</th>
<th>$\Delta G = \Delta H - T \Delta S$</th>
<th>Result</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>+</td>
<td>-</td>
<td>Change occurs spontaneously (if rate is reasonable).</td>
<td>mixing of gases</td>
</tr>
<tr>
<td>0</td>
<td>-</td>
<td>+</td>
<td>Change does not occur spontaneously.</td>
<td>unmixing of gases</td>
</tr>
<tr>
<td>-</td>
<td>+</td>
<td>-</td>
<td>Change occurs spontaneously (if rate is reasonable).</td>
<td>exothermic reactions producing gases, e.g. burning most fuels</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>+ or -</td>
<td>Change may occur spontaneously depending on conditions. Most likely at low temperatures.</td>
<td>exothermic reactions in which number of moles of gas decreases, e.g. $N_2(g) + 3 H_2(g) \rightarrow 2 NH_3(g)$ or condensing of a gas.</td>
</tr>
<tr>
<td>+</td>
<td>+</td>
<td>+ or -</td>
<td>Change may occur spontaneously depending on conditions. Most likely at high temperatures.</td>
<td>endothermic reactions in which number of moles of gas increases, e.g. liquids evaporating</td>
</tr>
<tr>
<td>+</td>
<td>-</td>
<td>+</td>
<td>Change does not occur spontaneously.</td>
<td>endothermic reactions in which number of moles of gas decreases, e.g. $6 C(s) + 3 H_2(g) \rightarrow C_6H_6(g)$ or photosynthesis</td>
</tr>
</tbody>
</table>