13 Energetics

All chemical substances contain energy stored in their bonds. When a chemical reaction occurs, there is usually a **change in energy** between the reactants and products. This is normally in the form of **heat energy**, but may also be in the form of light, nuclear or electrical energy.

Exothermic and endothermic reactions

Based on energy changes occurring, reactions can be of **two** types:

- An **exothermic reaction** produces heat which causes the reaction mixture and its surroundings to get **hotter** (it **releases energy** to the surroundings). Exothermic reactions include neutralisation reactions, burning fossil fuels and respiration in cells.

- An **endothermic reaction** absorbs heat which causes the reaction mixture and its surroundings to get **colder** (it **absorbs energy** from the surroundings). Endothermic reactions include dissolving certain salts in water, thermal decomposition reactions and photosynthesis in plants.

Breaking and forming bonds during reactions

During any chemical reaction, existing bonds in the **reactants** are **broken** and new bonds are **formed** in the **products**:

- Energy is **absorbed** when the existing bonds in the reactants are **broken**.

- Energy is **released** when new bonds are **formed** in the products:

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reactants ⟶ **products**

existing bonds are **broken**   new bonds are **formed**

energy is **absorbed**   energy is **released**

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- In an **exothermic reaction**:

  energy **absorbed** to break bonds **<** energy **released** when forming bonds

  The extra energy is **released** to the surroundings causing the **temperature** of the surroundings to **increase**.

- In an **endothermic reaction**:

  energy **absorbed** to break bonds **>** energy **released** when forming bonds

  The extra energy is **absorbed** from the surroundings causing the **temperature** of the surroundings to **decrease**.

Enthalpy changes during reactions

The energy content of a substance is called its **enthalpy** (**H**) and cannot be measured directly. However, it is possible to measure the **enthalpy change** (**ΔH**) during a reaction.

The enthalpy change of a reaction is the difference between the enthalpy of the products and the enthalpy of the reactants:

enthalpy change of a **reaction** = (total enthalpy of **products**) − (total enthalpy of **reactants**)

or $\Delta H_{reaction} = H_{products} - H_{reactants}$

ΔH is usually expressed in kilojoules (**kJ**), or kilojoules per mol (**kJ mol⁻¹**).

- In an **exothermic reaction**:

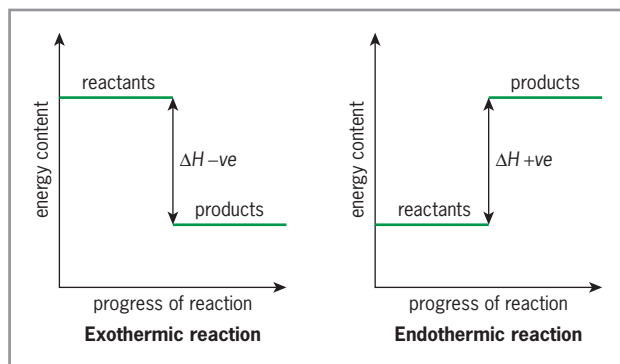 $H_{products} < H_{reactants}$

  The value of ΔH is less than zero. ΔH is **negative** (**−ve**). The extra energy from the reactants is **released** to the surroundings.

- In an **endothermic reaction**:

$$H_{\text{products}} > H_{\text{reactants}}$$

The value of ΔH is greater than zero. ΔH is **positive** (**+ve**). The extra energy gained by the products is **absorbed** from the surroundings.


Figure 13.1 *Exothermic and endothermic reactions summarised*

Energy profile diagrams

An **energy profile diagram** can be drawn to illustrate the energy change during a chemical reaction. The diagram includes the **enthalpy** of the reactants and products, the **enthalpy change** (ΔH), and the **activation energy**. Activation energy can be thought of as the **energy barrier** of a reaction.

Activation energy is the minimum amount of energy that reactants must be given, in excess of what they normally possess, so that bonds start breaking in the reactants and products start forming.
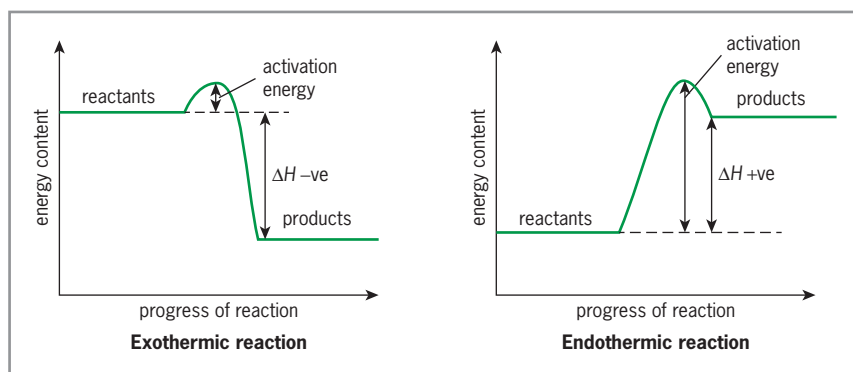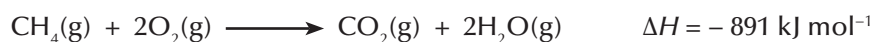

Figure 13.2 *Energy profile diagrams*

An energy profile diagram for a **specific reaction** must include:

- The **formulae** of the **reactants** and the **formulae** of the **products**.
- An arrow indicating **activation energy**.
- An arrow indicating ΔH with the **value of ΔH** written alongside.

Example

When **1 mol** of methane is completely burned in oxygen, 891 kJ of energy is **lost**, meaning that the reaction is **exothermic**:
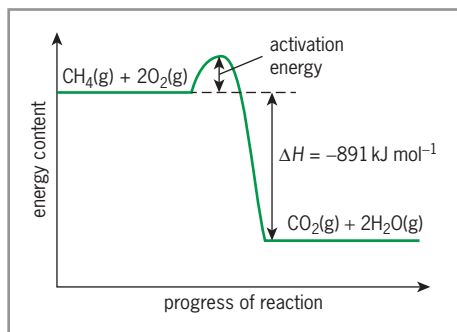
$$CH_4(g) \ + \ 2O_2(g) \ \longrightarrow \ CO_2(g) \ + \ 2H_2O(g) \qquad \Delta H = -891 \text{ kJ mol}^{-1}$$

Figure 13.3 *Energy profile diagram for the combustion of methane*

The action of a catalyst

Most **catalysts** increase the rate of a reaction. A reaction in which a catalyst is used to increase the rate has a **lower activation energy** than the same reaction without a catalyst (see Table 12.1, p. 109). The effect of using a catalyst can be shown on energy profile diagrams.
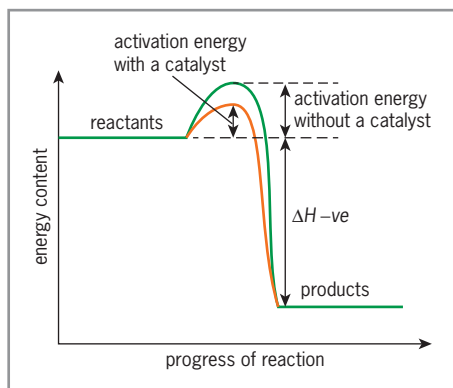

Figure 13.4 *Action of a catalyst on an exothermic reaction*

Calculating enthalpy changes

If the change in **temperature** that occurs during a reaction is measured, the **heat change**, known as the **heat of reaction**, can be determined using the formula given below.

heat change (ΔH) = mass of reactants × specific heat capacity × temperature change
(J)   (g) $(J\,g^{-1}\,°C^{-1})$ (°C)

Specific heat capacity is the quantity of heat energy required to raise the temperature of 1 g of a substance by 1 °C.

To determine the heat of reaction, the reaction is carried out in an insulated container called a **calorimeter**. The temperatures of the reactants are measured before mixing. The maximum or minimum temperature reached when the reactants are mixed is then measured and used to determine the **temperature change**. Three **assumptions** are made in calculating the heat of reaction:

- The **density** of a dilute aqueous solution is the same as pure water, **1 g cm⁻³**. This means that 1 cm³ of solution has a mass of 1 g.
- The **specific heat capacity** of a dilute aqueous solution is the same as pure water, **4.2 J g⁻¹ °C⁻¹**. This means that it requires 4.2 J to increase the temperature of 1 g of water by 1 °C.
- A **negligible amount of heat** is lost to, or absorbed from, the surroundings during the reaction.

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Determining the heat of solution

*The **heat of solution** is the heat change when 1 mol of solute dissolves in such a volume of solvent that further dilution by the solvent produces no further heat change.*

When a solute dissolves in a solvent:

- Bonds **break** between the solute particles; **ionic bonds** between ions break in ionic compounds and **intermolecular forces** between the molecules break in covalent substances. This **absorbs** energy from the surroundings.

- **Intermolecular forces** between the solvent molecules also **break**. This **absorbs** energy from the surroundings.

- Attractions form between the ions or molecules of the solute and the molecules of the solvent, a process is called **solvation**. This **releases** energy to the surroundings.

The reaction is **exothermic** if the energy **absorbed** to break bonds in the solute and solvent is **less** than the energy **released** during solvation.

The reaction is **endothermic** if the energy **absorbed** to break bonds in the solute and solvent is **greater** than the energy **released** during solvation.

When determining the heat of solution, the **initial** temperature of the water and the **maximum** or **minimum** temperature of the solution must be measured. The **temperature increase** or **decrease** and the **number of moles** of solute that dissolved must then be calculated.

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Sample question

Dissolving 15.15 g of potassium nitrate in 100 cm³ of distilled water resulted in a temperature decrease of 10.2 °C. Calculate the heat of solution of potassium nitrate.

To determine the **number of moles** of KNO_3 dissolved:

Mass of 1 mol KNO_3 = 39 + 14 + (16 × 3) g = **101 g**

$\therefore$ number of moles in 15.15 g = $\dfrac{15.15}{101}$ mol

$= \textbf{0.15 mol}$

To determine the **heat of solution**:

Volume of water = 100 cm³

$\therefore$ mass of water = **100 g**

Final mass of solution = 100 + 15.15 g = **115.15 g**

Temperature decrease = **10.2 °C**

Specific heat capacity of the solution = **4.2 J g⁻¹ °C⁻¹**

Heat change = mass of solution × specific heat capacity × temperature change
     (J)   (g)   (J g⁻¹ °C⁻¹)   (°C)

$\therefore$ heat absorbed in dissolving **0.15 mol KNO_3** = 115.15 × 4.2 × 10.2 J

$= \textbf{4933 J}$

and heat absorbed in dissolving **1 mol KNO_3** = $\dfrac{4933}{0.15}$ J

$= 32\ 887$ J

$= \textbf{32.9 kJ}$

Heat of solution, ΔH = **+32.9 kJ mol⁻¹**

The heat of solution, ΔH, is **positive** because the temperature of the reaction **decreased** indicating that it **absorbed** energy from the surroundings. The reaction was **endothermic**.

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Determining the heat of neutralisation

*The **heat of neutralisation** is the heat change when **1 mol of water** is produced in a neutralisation reaction between an alkali and an acid.*

When determining the heat of neutralisation, the temperature of both solutions must be measured and used to determine the **average initial** temperature. The **maximum** temperature of the solution after mixing must then be measured and used to calculate the **temperature increase**. Finally the **number of moles** of water made in the reaction must be determined.

50 cm³ of sodium hydroxide solution with a temperature of 29.4 °C and concentration of 2.0 mol dm⁻³ is added to 50 cm³ of sulfuric acid of concentration 1.0 mol dm⁻³ and temperature 30.0 °C. The maximum temperature of the solution after mixing is 43.2 °C. Determine the heat of neutralisation.
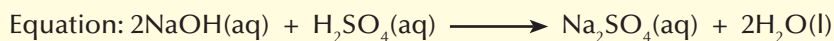
To determine the **number of moles of water** made in the reaction:

1000 cm³ NaOH(aq) contains 2.0 mol NaOH

∴ 50 cm³ NaOH(aq) contains $\frac{2.0}{1000} \times 50$ mol NaOH

= 0.1 mol NaOH

1000 cm³ H_2SO_4(aq) contains 1.0 mol H_2SO_4

∴ 50 cm³ H_2SO_4(aq) contains $\frac{1.0}{1000} \times 50$ mol H_2SO_4

= 0.05 mol H_2SO_4

Equation: $2NaOH(aq) + H_2SO_4(aq) \longrightarrow Na_2SO_4(aq) + 2H_2O(l)$

i.e. 2 mol NaOH reacts with 1 mol H_2SO_4 forming 2 mol H_2O(aq)

∴ **0.1 mol NaOH** reacts with **0.05 mol H_2SO_4** to form **0.1 mol H_2O**

0.1 mol H_2O is made in the reaction

To determine the **heat of neutralisation**:

Total volume of solution = 50 + 50 = 100 cm³

∴ mass of solution = **100 g**

Average initial temperature = $\frac{29.4 + 30.0}{2}$ °C = 29.7 °C

Final temperature = 43.2 °C

∴ temperature increase = 43.2 − 29.7 °C = **13.5 °C**

Specific heat capacity of the solution = **4.2 J g⁻¹ °C⁻¹**

Heat change = mass of solution × specific heat capacity × temperature change

     (J)   (g)   (J g⁻¹ °C⁻¹)   (°C)

∴ heat evolved in forming **0.1 mol H_2O** = 100 × 4.2 × 13.5 J

= 5670 J

and heat evolved in forming **1 mol H_2O** = $\frac{5670}{0.1}$ J

= 56 700 J

= 56.7 kJ

Heat of neutralisation, ΔH = **−56.7 kJ mol⁻¹**

The heat of neutralisation, ΔH, is **negative** because the temperature of the reaction **increased**, indicating that it **lost energy** to the surroundings. The reaction was **exothermic**.

When any strong alkali reacts with any strong acid, the heat of neutralisation is always approximately **−57 kJ mol⁻¹**. This is because the energy change is for the common reaction occurring between the **OH⁻ ions** of the alkali and the **H⁺ ions** of the acid:

$$OH^-(aq) + H^+(aq) \longrightarrow H_2O(l) \qquad \Delta H = -57 \text{ kJ mol}^{-1}$$
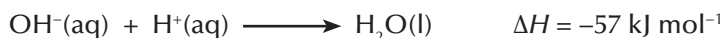
Revision questions

1 Distinguish between an exothermic reaction and an endothermic reaction.

2 Explain what happens during an exothermic reaction in terms of bonds breaking and bonds forming.

3 Hydrogen peroxide (H_2O_2) decomposes according to the following equation:

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g) \qquad \Delta H = -98.2 \text{ kJ mol}^{-1}$$

The reaction can be speeded up by adding a catalyst.

a State, with a reason, if the reaction is exothermic or endothermic.

b Explain the change in enthalpy which occurs during the reaction.

c Draw a fully labelled energy profile diagram for the reaction.

d On your energy profile diagram, show the effect of adding a catalyst to the reaction.

4 What is the name of the main piece of apparatus used when determining heats of reaction?

5 Give the formula used to calculate heat change occurring during a reaction.

6 What are THREE assumptions that are made when calculating heats of reaction?

7 To determine the heat of solution of ammonium chloride, a student dissolved 7.49 g of the solid in 100 cm³ of distilled water at 29.7 °C. He stirred the solution and recorded a minimum temperature of 22.8 °C.

a Define 'heat of solution'.

b State, with a reason, if the reaction was exothermic or endothermic.

c Calculate the heat of solution of ammonium chloride, assuming that the specific heat capacity of the solution is 4.2 J g⁻¹ °C⁻¹.

d Draw a fully labelled energy profile diagram for the reaction.

8 **a** Define 'heat of neutralisation'.

b Explain why the heat of neutralisation for the reaction between sodium hydroxide and nitric acid has the same value as the heat of neutralisation for the reaction between potassium hydroxide and sulfuric acid.