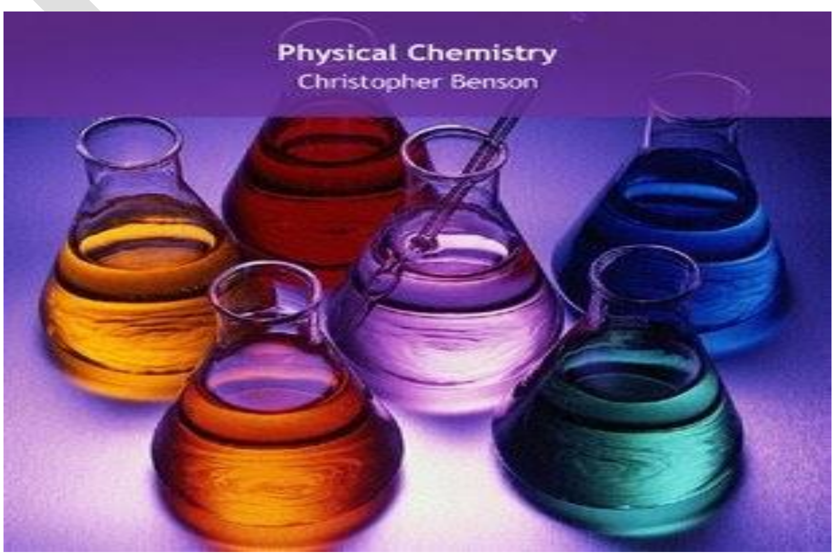
Edexcel IGCSE

Chemistry

CODE: (0620)

Unit 3

Physical Chemistry



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3.1 Energetics

Exothermic reactions

Some chemical reactions give out energy in the form of heat. A reaction that gives out heat to the surroundings is said to be exothermic. If you are holding a test-tube in which an **exothermic reaction** is occurring, you will notice that the test-tube gets warmer.

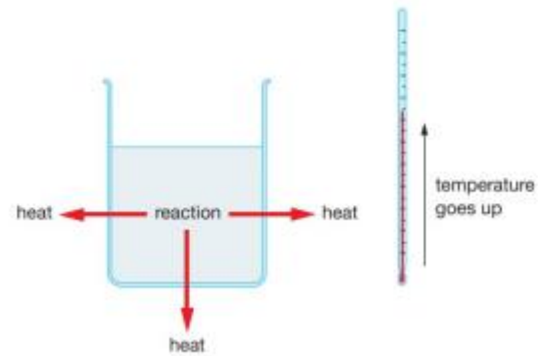

Figure 19.3 In an exothermic reaction, chemical energy is converted to heat energy. Heat is released so the temperature goes up.

Combustion reactions

Any reaction that produces a flame is exothermic. Burning things produces heat energy.
For instance, hydrogen burns in oxygen, producing water and lots of heat:

$2H_2(g) + O2(g) \rightarrow 2H_2O(l)$

Apart from burning, other exothermic changes include:
■The reactions of metals with acids
■Neutralization reactions
■Displacement reactions.

The reactions of metals with acids

When magnesium reacts with dilute sulfuric acid, for example, the mixture gets very warm:
$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$

Neutralization reactions

About the only interesting thing that you can observe happening when sodium hydroxide solution reacts with dilute hydrochloric acid is that the temperature rises:

$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$

Displacement reactions

The thermite reaction between powdered aluminium and iron (III) oxide is a displacement (competition) reaction. This reaction releases a large amount of heat, which can be used in railway welding:

$2Al(s) + Fe_2O_3(s) \rightarrow 2Fe(l) + Al_2O_3(s)$

Enthalpy change of a reaction.

You can measure the amount of heat energy taken in or released in a chemical reaction. It is called the enthalpy change of the reaction and is given the symbol ΔH. The enthalpy change is the amount of heat energy taken in or given out in a chemical reaction.

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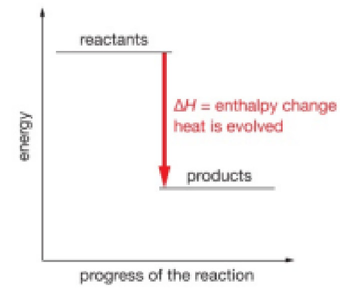
Showing and exothermic change on an energy level diagram

In an exothermic reaction, the reactants have more (chemical) energy than the products; we say that the products are more stable than the reactants. As the reaction happens, energy is given out in the form of heat. That energy warms up both the reaction itself and its surroundings.

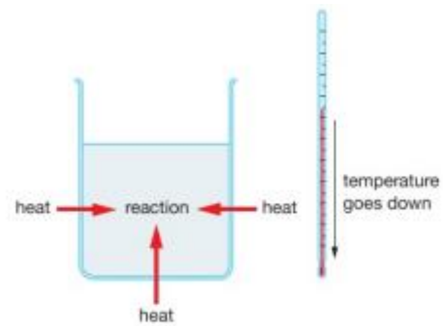


▲ Figure 19.5 An exothermic change

Endothermic reactions

A reaction that absorbs heat from the surroundings is said to be endothermic. If you hold a test-tube in which an **endothermic** reaction is occurring, you will notice that it gets colder.

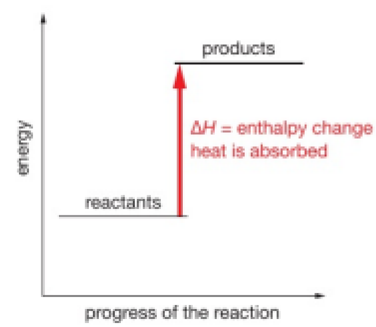
An endothermic reaction absorbs heat from the surroundings, causing it to get colder. The products have more energy than the reactants, and to convert them, heat energy needs to be absorbed from the surroundings and converted into chemical energy, causing the temperature to decrease.



▲ Figure 19.7 In an endothermic reaction, heat energy is converted to chemical energy. Heat is absorbed so the temperature goes down.

Showing and endothermic change of an energy level diagram

In an endothermic change, the products have more energy than the reactants, so we say that the products are less stable than the reactants. That extra energy must come from somewhere, and it is taken from the surroundings. In the case of the thermal decomposition of carbonates in the laboratory, it comes from the Bunsen burner.



▲ Figure 19.8 An endothermic change

Measuring enthalpy change of reactions.

Specific heat capacity

When we heat something up, it gets hotter. The **specific heat capacity** tells us about how much energy must be put in to increase the temperature of something. The specific heat capacity of a substance is defined as the amount of heat needed to raise the temperature of 1 gram of a substance by 1 °C.

Calorimetry experiments for determining the enthalpy changes of reactions.

It is uncomplicated to measure the amount of heat absorbed or given out in several kinds of chemical reactions and physical changes. The technique used to do this is called **calorimetry** and it is based on the idea that if we use the heat from a reaction to heat another substance.

If we know how many moles of reactants are used in the reaction, we can then work out the **molar enthalpy change,** ΔH, of the reaction in the unit kJ/mol.

Working out enthalpy changes for reactions involving solutions using calorimetry experiments

Why do reactions either give out or absorb heat?

During chemical reactions bonds in the reactants must be broken and new ones formed to make the products. Breaking bonds needs energy (endothermic) and making bonds releases energy (exothermic).

Think about what happens when hydrogen burns in oxygen to make water:

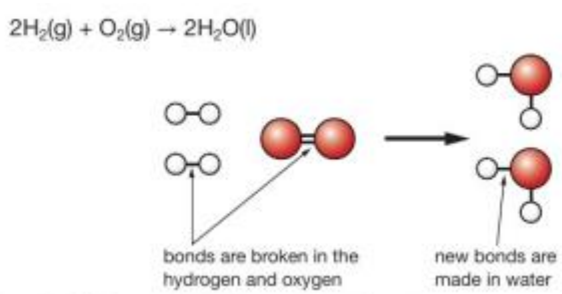


Figure 19.14 Hydrogen burning in oxygen to make water

Energy is required to break hydrogen and oxygen bonds in water molecules, releasing more energy when new bonds form. This exothermic reaction is more stable than the reactants, as the total energy released is more than needed to break the original bonds.

Calculation of enthalpy changes of reactions using bond energies

Bond energies

Chemical bonds require energy, with stronger bonds requiring more energy. Bond energies are measured in kJ/mol, like CI-CI bond energy of 243 kJ/mol. This energy is released when bonds form, and if atoms recombine, the same amount is released.

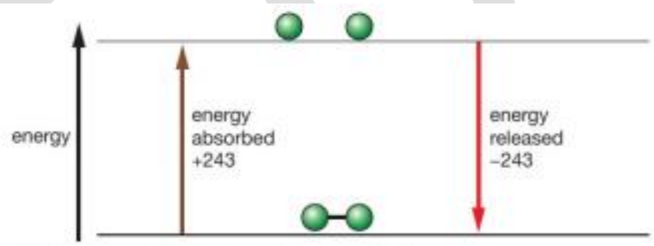


Figure 19.15 Breaking and making bonds between chlorine atoms

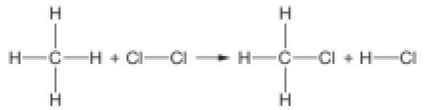
■Breaking bonds needs energy: endothermic.
■Making bonds releases energy: exothermic.

Calculation of the heat released or absorbed during a reaction.

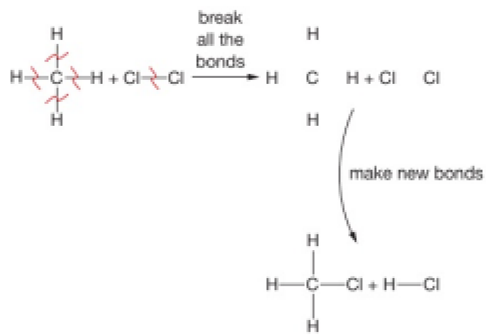
You can estimate the heat energy released or absorbed in a reaction by calculating how much energy would be needed to break the substances up into individual atoms, and then how much would be given out when those atoms recombine into new arrangements.

The reaction between methane and chloride

$$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$$



Methane reacts with chlorine in the presence of ultraviolet light to produce chloromethane and hydrogen chloride You can imagine all the bonds being broken in the methane and chlorine, and then being reformed in new ways in the products:



The negative sign of the answer shows that, overall, heat is given out as the bonds rearrange. You can show all this happening on an energy level diagram, as in Figure 19.16.

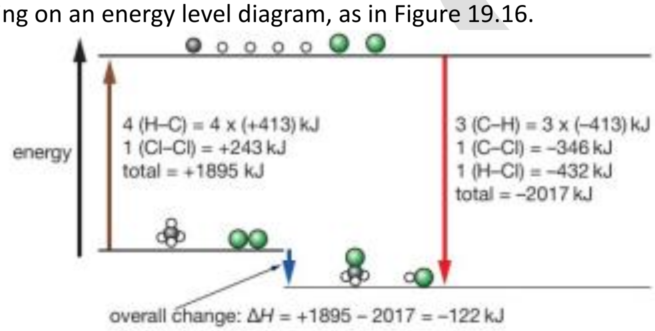


Figure 19.16 Methane reacts with chlorine to produce chloromethane and hydrogen chloride.

3.2 Rates of reaction

Experiments to measure the rate of reaction.

The rate of a reaction is the speed at which the number of reactants decreases, or the number of products increases. It is measured as a change in the concentration (or amount) of reactants or products per unit time (per second, per minute etc.).

$$\text{rate of reaction} = \frac{\text{change in concentration, volume or mass}}{\text{time}}$$

Explaining what's happening.

We can explain the shape of the curve by thinking about the particles present and how they interact. This is called the **collision theory.**

Reactions can happen only when particles collide. Not all collisions end up in a reaction. Many particles just bounce off each other. For a reaction to happen, the particles must collide with a minimum amount of energy, called the **activation energy.** The collisions with energy greater than or equal to the activation energy are usually called **successful collisions.**

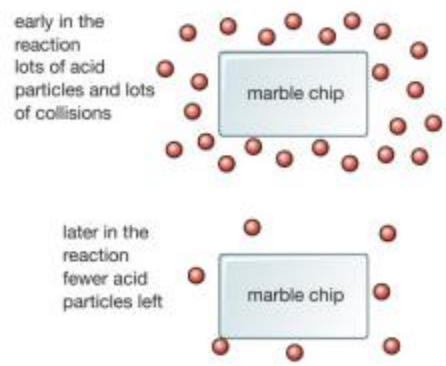


Figure 20.8 As the reaction proceeds, the collision rate of acid particles with the marble chips decreases.

A different from a graph

Normally plot graphs showing the mass or volume of product formed during a reaction. It is possible, however, that you will see graphs showing the fall in the concentration of one of the reactants - in this case, the concentration of the dilute hydrochloric acid.

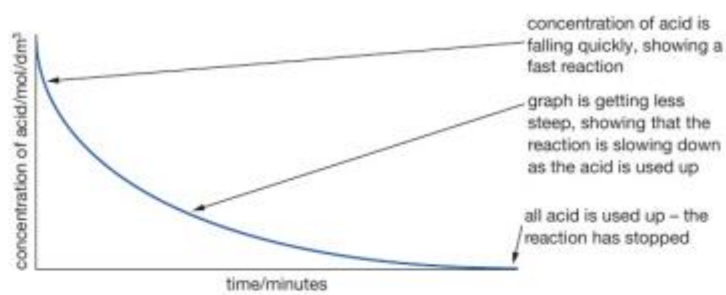


Figure 20.9 The fall in concentration of hydrochloric acid over time

Changing the surface area of the reactants

Solids and liquids reactions are faster when they are divided into smaller pieces, with finer solids resulting in faster reactions due to greater surface area and more exposed particles, increasing the frequency of successful collisions.

Large surface areas are frequently used to speed up reactions outside the lab. For example, a **catalytic converter** for a car uses expensive metals.

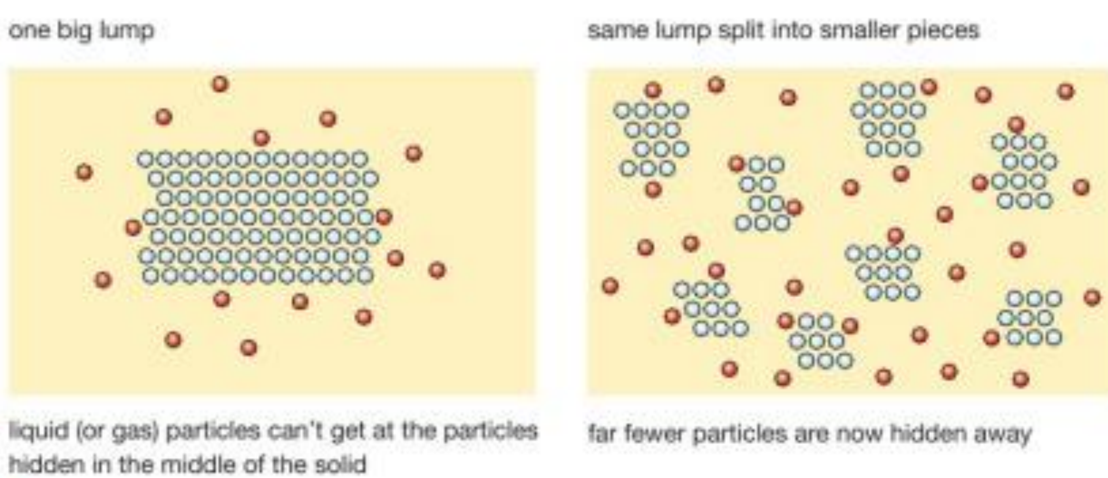


Figure 20.11 The more divided the solid, the faster the reaction

Changing the concentration of the reactions

<u>The effect of the changing concentration</u>

We can repeat our original experiment with large marble chips and hydrochloric acid. Everything is kept the same except we use hydrochloric acid of half the concentration.

We find that reducing the concentration of the acid makes the reaction slower. We can see this on our graph because the graph (red line) is less steep than for our original experiment (blue line).

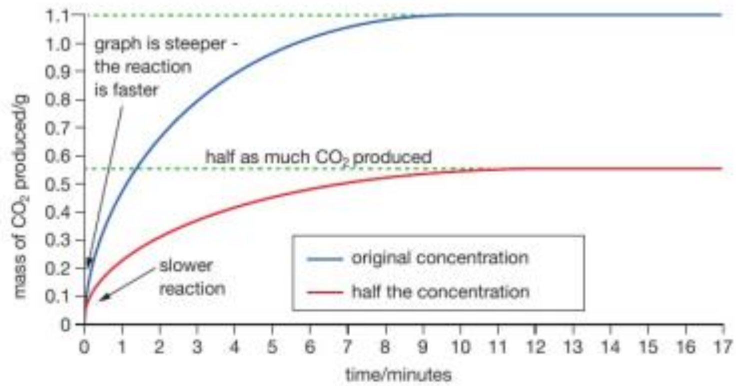


Figure 20.13 The effect of changing the concentration of the acid

Changing the temperature of the reaction

We can do the original experiment again, but this time at a higher temperature. We keep everything else the same as before.

Reactions get faster as the temperature is increased; the graph is steeper and finishes sooner. The same mass of gas is given off because we have used the same quantities of everything in the mixture.

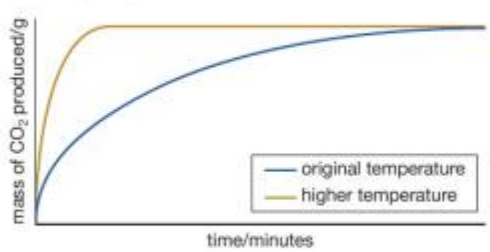


Figure 20.16 The effect of changing the temperature of the reaction

There are two factors that need to be considered when explaining why increasing temperature increases the rate of reaction:

■Increasing the temperature means that the particles are moving faster, and so collide more frequently. That will make the reaction go faster, but it only accounts for a small part of the increase in rate.

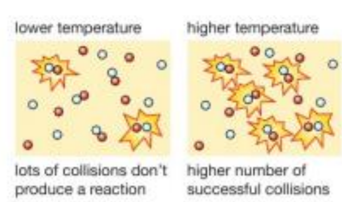


Figure 20.17 A small increase in temperature produces a large increase in the number of collisions with energy greater than the activation energy.

■We learned above that for a collision to cause a reaction (a successful collision), the particles must collide with a minimum amount of energy, called the activation energy.

Changing the pressure on the reaction

The rate of reaction in a gas reaction can be increased by increasing the pressure of the gas, which forces particles closer together, resulting in more frequent collisions, despite the change in the reaction's rate.

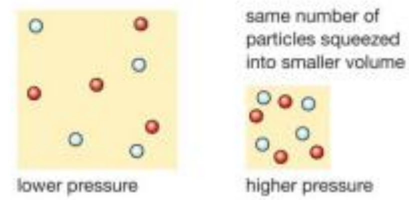


Figure 20.18 Increased pressure means gas particles collide more frequently.

Catalyst

What is catalyst?

Catalysts are substances that speed up chemical reactions but aren't used up in the process. They are still there, chemically unchanged, at the end of the reaction.

The catalytic decomposition of hydrogen peroxide

Enzymes are biological catalysts. This reaction happens almost explosively and produces a lot of heat. The same enzyme can be found in potatoes, or even liver tissues.

The reaction happening with the hydrogen peroxide is:

hydrogen peroxide → water + oxygen

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

Showing that a substance is a catalyst.

Manganese (IV) oxide accelerates hydrogen peroxide decomposition to produce oxygen. It remains chemically unchanged by the reaction, but its use can be determined by weighing it before and after adding it to the solution. Separating the oxide from the liquid, allowing it to dry, and reweighing it, should result in no change in its mass.

How does a catalyst work?

Collisions require a minimum activation energy for reactions to occur. Catalysts provide an alternative route with lower activation energy, allowing more successful collisions and faster reactions. This is because more particles have energy greater than or equal to the activation energy for the alternative route. This makes the energy of particles easier to react. However, it's important to phrase the statement correctly, as catalysts do not lower the activation energy, but rather provide an alternative route for particles to use.

3.3 Reversible reactions and equilibria

Reversibility and dynamic equilibria

DEHYDRATION OF COPPER(II) SULFATE CRYSTALS

If you heat blue copper (II) sulfate crystals gently, the blue crystals turn to a white powder and water is driven off. Heating causes the crystals to lose their water of crystallisation and white anhydrous copper (II) sulfate is formed. 'Anhydrous' simply means 'without water.'

$$\underset{\text{blue}}{CuSO_4{\cdot}5H_2O(s)} \rightarrow \underset{\text{white}}{CuSO_4(s)} + 5H_2O(l)$$ Heat is needed for this reaction to occur

If you add water to the white solid, it turns blue again; it also becomes very warm. See Figure 18.3 (page 192).

$$\underset{\text{white}}{CuSO_4(s)} + 5H_2O(l) \rightarrow \underset{\text{blue}}{CuSO_4{\cdot}5H_2O(s)}$$ Heat is released from this reaction

The original change has been exactly reversed. Even the heat that you put in originally has been given out again. This is called a **reversible** reaction and is indicated by a special arrow:

$$CuSO_4{\cdot}5H_2O(s) \rightleftharpoons CuSO_4(s) + 5H_2O(l)$$

HEATING AMMONIUM CHLORIDE

If you heat ammonium chloride, the white crystals disappear from the bottom of the tube and reappear further up. Heating ammonium chloride splits it into the colourless gases ammonia and hydrogen chloride.

$NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$ Heat is needed for this reaction to occur
white solid colourless gases

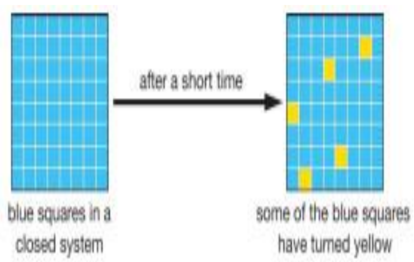
These gases recombine further up the tube, where it is cooler, to form a white solid:

$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$ Heat is released from this reaction
colourless gases white solid

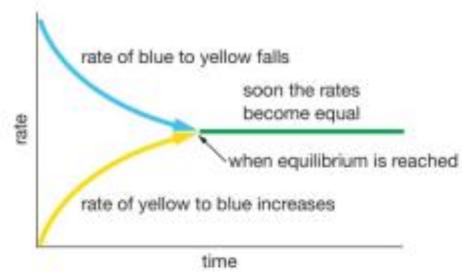
The reaction reverses when the conditions are changed from hot to cool.

REVERSABLE REACTIONS IN A SEALEAD CONTAINER

A sealed container prevents substances from entering the reaction mixture and preventing heat absorption. For example, a substance can exist in two forms: blue squares and yellow squares. The initial blue squares have a high rate of change, but as they deplete, the rate decreases. However, yellow squares can also change back to blue ones due to reversible reactions. At the start, there are no yellow squares, so the rate of change from yellow to blue is zero. As the number of yellow squares increases, the rate of change also increases. As the rates of both reactions equal, blue squares and yellow squares change at the same rate, indicating a continuous reaction. The total number of blue and yellow squares remains constant, but the reaction continues.



▲ Figure 21.3 Blue squares converting to yellow ones



▲ Figure 21.4 The rates of the forward reaction and the reverse reaction become equal when equilibrium is reached.

This is an example of a dynamic equilibrium. It is dynamic in the sense that the reactions are continuing, but the rate of the forward reaction is equal to the rate of the reverse reaction. It is an equilibrium in the sense that the total amounts or concentrations of the various things present (reactants and products) are now constant.

The position of equilibrium

Taking a general case where A reacts reversibly to give B:

$A \rightleftharpoons 2B$

The reaction from A to B (the left-to-right reaction) is described as the **forward reaction.** The reaction between from B to A (the right-to-left reaction) is called the **reverse reaction.**

If we let this reaction come to equilibrium, then measure the amount of each substance present we might find that we have.

$$\begin{array}{ccc} A & \rightleftharpoons & 2B \\ 90\% & & 10\% \end{array}$$

Because there is more A than B present at equilibrium, we say that the position of equilibrium lies to the left. It is important to realise that equilibrium does not mean 50% of reactants and products.

HOW TO PREDICT THE EFFECT OF CHANGING CONDITIONS ON THE POSITION OF EQUILIBRIUM

This section discusses how to predict the effect of changing conditions on the equilibrium position in a dynamic equilibrium system. It suggests that the reaction always counteracts any changes made, like how adjusting a temperature or pressure can affect the equilibrium mixture. The goal is to maximize the desired outcome.

Things we might try to do to influence the reaction include:
■changing the pressure
■changing the temperature
■adding a catalyst (in fact, this turns out to have no effect on the position of equilibrium).

Changing the pressure

This only really applies to reactions in which at least one of the reactants or products is a gas, and where the total numbers of gaseous molecules on both sides of the equation are different. In the example here, there are three gaseous molecules on the left, but only two on the right.

$$A(g) + 2B(g) \rightleftharpoons C(g) + D(g)$$

Pressure is caused by molecules hitting the walls of their container. If you have fewer molecules in the same volume at the same temperature, you will have a lower pressure.

Increased pressure in a reaction reduces it by converting A+ 2B into C + D, resulting in fewer gaseous molecules hitting the container walls. This shift in equilibrium position produces a smaller number of gaseous molecules.

To summarise:
Increasing pressure: the position of equilibrium shifts to the side which has fewer gas molecules.
Decreasing pressure: the position of equilibrium shifts to the side which has more gas molecules.

Changing temperature

When we write a reversible reaction showing an enthalpy change, the ΔH always shows the enthalpy change for the forward reaction. The value of AH is given as if the reaction was a one-way process.

$$A + 2B \rightleftharpoons C + D \quad \Delta H = -100\,kJ/mol$$

So, in this case ΔH being negative tells us that the forward reaction is exothermic. The reverse reaction will be endothermic by the same amount. Suppose you changed the conditions by decreasing the temperature of the equilibrium,

To summarise:
Increasing temperature: the position of equilibrium shifts in the endothermic direction.
Decreasing temperature: the position of equilibrium shifts in the exothermic direction.

Adding a catalyst

A catalyst accelerates reactions in a reversible change by increasing the rate at which equilibrium is reached. This means that adding a catalyst does not alter the equilibrium position, but rather increases the rate at which forward and reverse reactions are accelerated.

The effect of pressure

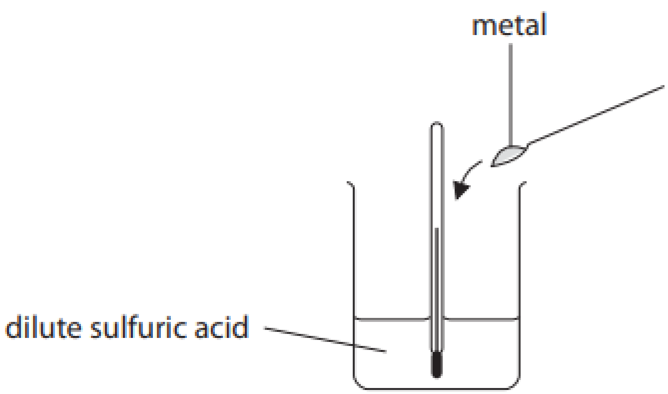
Increased pressure shifts the equilibrium position by producing fewer gaseous molecules, resulting in more dinitrogen tetroxide. Conversely, decreased pressure shifts the equilibrium position to the right, producing more gaseous molecules and a higher proportion of brown nitrogen dioxide in the equilibrium mixture.

The effect of temperature

The equation explains the exothermic change from nitrogen dioxide to dinitrogen tetroxide, with the negative sign indicating heat production. Lowering the temperature shifts the equilibrium position to produce more heat, resulting in more dinitrogen tetroxide and a faded reaction mixture color. Conversely, increasing the temperature shifts the equilibrium position to lower it, resulting in more nitrogen dioxide and a darkening gas color.

Revision questions

1) A student uses this apparatus to investigate the temperature changes that take place when certain metals are added to dilute sulfuric acid.



This is the student's method:

- use the five metals aluminium, copper, iron, magnesium and zinc
- add the same amount of each metal separately to 25cm3 of acid
- in each case the acid is in excess
- stir the mixture and record the highest temperature reached

(a) Use the diagrams of the thermometer in the table to record the highest temperature reached in each experiment. Record all temperatures to the nearest 0.5 °C

	Metal				
	aluminium	opper	iron	magnesium	zinc
Thermometer	45 40 35	30 25 20	35 30 25	50 45 40	35 30 25
Highest temperature in °C					

b)(i) In each experiment the initial temperature of the acid is 25 °C. Which metal produces the largest temperature rise?
(ii) Explain the result obtained with copper.
(c) The same amount of magnesium is added to 50cm3 of dilute sulfuric acid. Explain the effect this would have on the temperature change observed

2) Aluminium and iron have some similar properties. Both metals

- are malleable
- are ductile (can be drawn into a wire)
- are good conductors of electricity
- are good conductors of heat
- have a high melting point

(a) (i) Choose two properties from the list that make iron a suitable metal for saucepans.
(ii) Choose two properties from the list that make aluminium a suitable metal for power cables.
(b) Steel is an alloy containing iron. These are three differences between steel and aluminium

- steel can rust but aluminium resists corrosion
- steel has a higher density than aluminium
- steel is much stronger than aluminium

(i) Use information from the list to suggest why steel is the better metal for making bridges
(ii) Use information from the list to suggest why aluminium is the better metal for making aircraft bodies.

3) Molybdenum (Mo) is a metal. It is often used to make an alloy with iron. Like iron, it is extracted from its oxide. Unlike iron, it occurs mainly as its sulfide.

(a) Molybdenum sulfide is converted into molybdenum oxide by heating in air. The equation for this reaction is;

$$2MoS_2 + 7O_2 \rightarrow 2MoO_3 + 4SO_2$$

(i) Why is molybdenum said to be oxidised in this reaction?
(ii) The sulfur dioxide formed in the reaction could form acid rain if it escaped into the atmosphere. Write a chemical equation for the formation of an acid from sulfur dioxide.
(b) The table shows the melting points of molybdenum oxide and sulfur dioxide.

	Melting point in °C
molybdenum oxide	800
sulfur dioxide	–75

The melting point indicates the type of bonding and structure in a compound.
(i) What is the type of bonding in a molecule of sulfur dioxide?
(ii) Explain why the melting point of sulfur dioxide is low

4) (i) What is meant by the term catalyst?
(ii) State one reason why cryolite is used in the extraction of aluminium
(iii)Several equations can be written for the reactions occurring in the extractions. (i) Write the chemical equation for the reaction between iron(III) oxide (Fe_2O_3) and carbon monoxide (CO).
(ii) This equation represents a reaction used to remove impurities in the extraction of iron

$$CaO + SiO_2 \rightarrow CaSiO_3$$

State the type of reaction occurring in this equation.

5) Soluble salts can be made by reacting an acid with a metal hydroxide, a metal oxide, or a metal carbonate. Insoluble salts can be made by using a precipitation reaction.

(a) Complete the table to show which acid or metal compound is used to make each salt listed. For each metal compound, state whether it would be used as a solid or in aqueous solution.

Salt made	Acid used	Metal compound	
		Name	Solid or aqueous solution
copper(II) sulfate		copper(II) oxide	
silver chloride	hydrochloric acid		aqueous solution
potassium nitrate		potassium carbonate	

(b) An acid is a source of hydrogen ions, H+ Write an equation to show the ions formed when sulfuric acid is dissolved in water.
(c) Lead(II) chloride is an insoluble salt that can be prepared by reacting lead(II) nitrate with sodium chloride. Describe how you would prepare a pure, dry sample of lead(II) chloride starting from solid lead(II) nitrate and solid sodium chloride.

6) This question is about the insoluble salt lead(II) bromide.
(a) A student uses the precipitation method to prepare lead(II) bromide. The equation for the reaction she uses is

$$Pb(NO_3)_2(aq) + 2NaBr(aq) \rightarrow PbBr_2(s) + 2NaNO_3(aq)$$

Describe how she could use solutions of lead(II) nitrate and sodium bromide to obtain a pure, dry sample of lead(II) bromide.
(b) The student writes this half-equation to show the reaction in which the brown substance forms.

$$2Br^- + 2e^- \rightarrow 2Br$$

Identify the two mistakes in her half-equation.
(iii) Explain why the lamp stops working after the teacher stops heating the lead(II) bromide.

7)some magnesium powder is added to dilute sulfuric acid in a test tube. A colourless solution is formed and a gas is given off. When more magnesium is added, the reaction continues for a while and then stops, leaving some magnesium powder in the test tube. When a flame is placed at the mouth of the test tube, the gas burns with a squeaky pop.
(i) Identify the gas produced.
(ii) Suggest why the reaction stops
(iii) State the name of the colourless solution
(iv) How could you separate the magnesium powder from the colourless solution?

8) Several methods are used to prepare salts. The method chosen depends on whether the salt is soluble or insoluble in water. (a) An insoluble salt is prepared by mixing solutions of silver nitrate and sodium chloride.

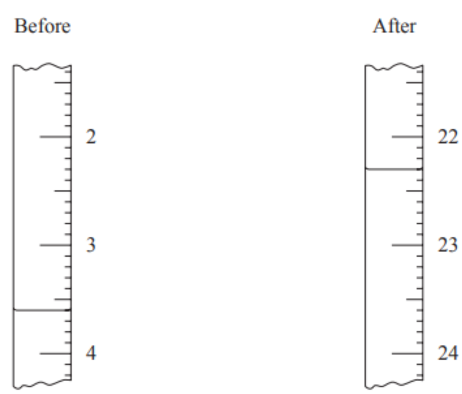
(i) State the name of the insoluble salt formed.

(ii) Write a chemical equation for the reaction occurring

(b) The chemical equation for the preparation of the insoluble salt lead(II) sulfate is shown below. Complete the equation by adding state symbols.

$$Pb(NO_3)_2(\dots\dots) + Na_2SO_4(\dots\dots) \rightarrow PbSO_4(\dots\dots) + 2NaNO_3(\dots\dots)$$

(c) A soluble salt is prepared from solutions of an acid and an alkali. (i) Identify the acid and the alkali used to prepare sodium nitrate
(ii) The diagrams show the readings on a burette before and after a student added an alkali to an acid during a titration



Use these diagrams to complete the table below, entering all values to the nearest 0.05 cm^3 .

Burette reading after adding alkali in cm^3	
Burette reading before adding alkali in cm^3	
Volume of alkali added in cm^3	