

Rates of reaction: factors, collision theory and graphs (O Level Chemistry notes)

These notes cover the rates of reaction topic for Cambridge O Level Chemistry 5070 and IGCSE Chemistry 0620. Learn the methods as numbered steps: practical questions are common.

1. What rate of reaction means

Rate of reaction is the change in the amount (or concentration) of a reactant or product per unit time.

We follow one changing quantity against time. Typical units:

- cm^3/s or cm^3/min when a gas volume is measured
- g/s or g/min when a mass is measured
- $\text{mol/dm}^3/\text{s}$ when a concentration is measured

For a reaction that is complete, the **average rate** can be found from:

Average rate = amount of product formed (or reactant used) $\div$ time taken

Rate is also inversely related to the time taken for a fixed change. If a reaction produces the same volume of gas in half the time, its average rate has doubled.

2. Measuring the rate of a reaction

2.1 Collecting a gas: gas syringe or inverted measuring cylinder

Suitable for any reaction that gives off a gas, for example a metal with an acid (hydrogen), a carbonate with an acid (carbon dioxide) or the decomposition of hydrogen peroxide (oxygen).

Method: volume of gas against time (magnesium and hydrochloric acid)

1. Measure a fixed volume of dilute hydrochloric acid, for example 50 cm^3 , with a measuring cylinder and pour it into a conical flask.
2. Connect a gas syringe to a bung and delivery tube. Check the syringe reads zero.
3. Add a weighed piece of magnesium ribbon (of known length or mass), insert the bung immediately and start the stopwatch.
4. Record the volume of gas in the syringe every 10 s (or 30 s) until the volume stops changing.
5. Plot volume of gas (y-axis) against time (x-axis).

Without a gas syringe, collect the gas over water in an upturned measuring cylinder. This suits hydrogen and oxygen but not carbon dioxide, which is slightly soluble.



2.2 Loss of mass on a balance

Suitable when a gas escapes from the flask. The flask sits on a top-pan balance and the mass falls as gas leaves.

Method: loss of mass (marble chips and hydrochloric acid)

1. Place a conical flask containing a known volume and concentration of dilute hydrochloric acid on a top-pan balance.
2. Add a known mass of marble chips (calcium carbonate) of a stated size.
3. Plug the neck loosely with cotton wool, which lets carbon dioxide out but stops acid spray escaping and so stops mass being lost by splashing.
4. Start the stopwatch and record the mass every 30 s until it stops changing.
5. Calculate loss in mass = starting mass – mass at each time, and plot loss in mass against time.



This suits a dense gas such as carbon dioxide ($M_r = 44$). With hydrogen ($M_r = 2$) the mass change is too small to measure accurately.

2.3 Formation of a precipitate: the disappearing cross

Suitable when a reaction produces an insoluble solid that makes the solution cloudy. The standard example is sodium thiosulfate with hydrochloric acid, which forms a pale yellow precipitate of sulfur.



Method: disappearing cross

1. Draw a dark cross on a piece of white paper and place a conical flask on it.
2. Add a measured volume of sodium thiosulfate solution to the flask.
3. Add a measured volume of dilute hydrochloric acid, swirl and start the stopwatch at the same moment.
4. Look down through the solution from above. Stop the clock when the cross can no longer be seen.
5. Repeat with different concentrations (dilute the thiosulfate with water but keep the total volume the same) or at different temperatures.
6. Use $1/\text{time}$ as a measure of the rate.

Sulfur dioxide is toxic, so work in a ventilated room. The same person should judge every end point.

2.4 Making a test fair

In every rate experiment only one variable is changed (the independent variable). The quantity measured is the dependent variable. Everything else is kept the same (control variables).

Variable being investigated	Variables to keep constant
Concentration of acid	Volume of acid, mass and size of solid, temperature

Temperature	Concentration and volume of acid, mass and size of solid
Surface area (particle size)	Total mass of solid, concentration and volume of acid, temperature
Catalyst	Concentration, volume and temperature of solution, and the mass of catalyst when comparing different catalysts

Repeat each run and take a mean to improve reliability.

3. Reading and sketching rate graphs

3.1 The shape of a typical curve

For volume of gas (or loss of mass) against time, the curve always has the same shape:

- **Steep at the start:** the concentration of reactant particles is highest, so collisions are most frequent and the rate is greatest.
- **Gradient decreases:** reactants are used up, so there are fewer reactant particles per unit volume and fewer collisions per second.
- **Flat (horizontal) at the end:** one reactant has been completely used up (the limiting reactant), so the reaction has stopped. The final volume shows the total amount of product.

Key rule: the gradient (steepness) of the graph at any point is the rate of reaction at that time. The steeper the line, the faster the reaction.

3.2 Finding the rate from a graph

The **average rate** over the whole reaction is the total volume of gas divided by the time at which the curve first becomes flat. The **rate at a particular time** is found by drawing a tangent to the curve at that time and calculating its gradient (change in y ÷ change in x).

Worked example: reading a gas graph

The results below were obtained when calcium carbonate reacted with excess hydrochloric acid.

Time / s	0	20	40	60
Volume of CO ₂ / cm ³	0	30	50	62

Time / s	80	100	120
Volume of CO ₂ / cm ³	68	70	70

- (a) Average rate over the first 20 s = $30 \div 20 = 1.5 \text{ cm}^3/\text{s}$.
- (b) Average rate between 60 s and 80 s = $(68 - 62) \div 20 = 0.3 \text{ cm}^3/\text{s}$. The rate has fallen as reactants are used up.
- (c) The reaction stopped at 100 s, because the volume does not change after this. Average rate for the whole reaction = $70 \div 100 = 0.7 \text{ cm}^3/\text{s}$.
- (d) Volume of gas produced in the first 50 s: read from the graph between 40 s and 60 s, about 56 cm³.

3.3 Sketching a second curve on the same axes

To sketch a second curve for a changed condition, ask two questions:

1. **Is the reaction faster or slower?** Faster means a steeper start that levels off sooner. Slower means a shallower start that levels off later.
2. **Has the amount of limiting reactant changed?** If not, the final volume (the height of the flat part) stays the same. If the amount of limiting reactant is halved, the final volume halves.

Change (acid in excess, solid limiting unless stated)	Initial gradient	Final volume of gas
Higher temperature	Steeper	Same
Powder instead of lumps (same mass)	Steeper	Same
Catalyst added	Steeper	Same
Half the mass of solid	Less steep	Half
Same volume of acid at higher concentration, acid limiting	Steeper	Greater (more moles of acid)
Acid diluted with an equal volume of water, acid limiting	Less steep	Same (same moles of acid)

Exam tip: always decide first which reactant is limiting. The final amount of product depends only on the amount (in moles) of the limiting reactant, never on temperature, particle size or a catalyst.

4. Collision theory and activation energy

Collision theory: for a reaction to happen, reactant particles must collide, and they must collide with energy equal to or greater than the activation energy.

Activation energy (E_a) is the minimum energy that colliding particles must have in order to react.

Collisions with less energy than E_a do not lead to reaction. A collision that does is a **successful** collision.

The rate of reaction depends on the frequency of successful collisions, that is the number of successful collisions per unit time (per second).

Any change that increases the number of collisions per second, or increases the fraction of collisions that have at least the activation energy, increases the rate. Always write "more frequent collisions", not just "more collisions".

5. Factors that affect the rate of reaction

5.1 Concentration of a solution

Increasing the concentration of a reacting solution increases the rate.

Explanation: there are more reactant particles in the same volume, so particles collide more frequently. There are more successful collisions per second, so the rate increases. The energy of the particles has not changed.

5.2 Pressure of a gas

For reactions between gases, increasing the pressure increases the rate.

Explanation: increasing pressure pushes the same number of gas particles into a smaller volume, which is the same as increasing their concentration. Particles collide more frequently, so there are more successful collisions per second. Pressure has almost no effect on reactions involving only solids and liquids.

5.3 Temperature

Increasing the temperature increases the rate (for many reactions a 10 °C rise roughly doubles it, but only as a rough guide).

Explanation, two parts:

1. Particles gain kinetic energy and move faster, so they collide more frequently.
2. More importantly, a greater proportion of collisions have energy equal to or greater than the activation energy, so a greater fraction of collisions are successful.

Both lead to more successful collisions per second. The second point is the main reason and is needed for full marks. E_a itself does not change.

5.4 Surface area of a solid

Using smaller pieces (powder instead of lumps) increases the rate, as long as the total mass is the same.

Explanation: a reaction with a solid can only happen at its surface. Breaking a solid into smaller pieces exposes more surface area, so more particles of the solid are available for collisions. Particles collide more frequently, so there are more successful collisions per second.

Worked example: surface area to volume

A 2 cm cube has a surface area of $6 \times (2 \times 2) = 24 \text{ cm}^2$. Cut it into eight 1 cm cubes: total surface area = $8 \times 6 \times (1 \times 1) = 48 \text{ cm}^2$. The volume and mass are unchanged, but the surface area has doubled, so the initial rate with acid would be greater.

5.5 Dangers of a very large surface area

Fine powders of combustible materials have an enormous surface area. Flour in flour mills, coal dust in mines, wood dust in sawmills and custard powder can react with oxygen in the air so quickly that the reaction becomes an explosion if a spark ignites the dust cloud. Controls include ventilation, removing dust and avoiding sparks.

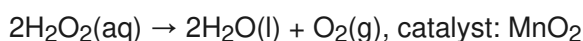
5.6 Catalysts

A catalyst is a substance that increases the rate of a reaction and is unchanged in mass and chemical composition at the end of the reaction.

Explanation: a catalyst provides an alternative reaction pathway with a lower activation energy. At the same temperature, a greater proportion of collisions now have energy equal to or greater than the (lower) activation energy, so there are more successful collisions per second.

Points to remember:

- Only a small amount is needed and it can be reused.
- A catalyst does not change the amount of product formed, and it does not change the energy change (ΔH) of the reaction.
- Transition elements and their compounds are often catalysts: iron in the Haber process, vanadium(V) oxide in the Contact process, manganese(IV) oxide for the decomposition of hydrogen peroxide.



Method: showing that a substance is a catalyst

1. Weigh a sample of manganese(IV) oxide.
2. Add it to hydrogen peroxide solution and measure the volume of oxygen given off against time. Compare with an identical flask with no MnO_2 : the catalysed reaction is much faster.
3. When the reaction stops, filter off the solid, wash it with distilled water, dry it and weigh it again.
4. The mass is the same as at the start, and the solid will catalyse a fresh sample of hydrogen peroxide. This shows it was not used up.

Enzymes are proteins that act as biological catalysts. They work best at an optimum temperature (often around 37°C for human enzymes) and pH. Above the optimum they are denatured (the active site changes shape), so the rate rises with temperature and then falls sharply.

5.7 Light

Some reactions, called photochemical reactions, are started or speeded up by light (especially ultraviolet). Increasing the light intensity increases the rate.

- **Photosynthesis:** $6\text{CO}_2 + 6\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$, which needs light energy and chlorophyll.
- **Silver halides in photography:** $2\text{AgBr} \rightarrow 2\text{Ag} + \text{Br}_2$. Light reduces silver ions to silver, which darkens the film. This is why silver salts are stored in brown bottles.
- **Methane and chlorine:** the substitution reaction $\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl}$ needs ultraviolet light and does not happen in the dark.

Explanation: light energy breaks bonds in some reactant molecules, so more particles can react.

6. Energy profile diagrams

An energy profile (reaction pathway) diagram plots energy (y-axis) against the progress of the reaction (x-axis).

6.1 Exothermic reaction

- Draw a horizontal line on the left for the reactants and a lower horizontal line on the right for the products.

- Join them with a curve that rises to a peak and then falls.
- The **activation energy** is the vertical distance from the reactants line up to the top of the peak (arrow pointing upwards).
- The **energy change ΔH** is the vertical distance from the reactants line down to the products line. It is negative because energy is released to the surroundings.

6.2 Endothermic reaction

- The products line is higher than the reactants line.
- Activation energy is still measured from the reactants up to the peak, and it is larger than ΔH .
- ΔH is positive because energy is taken in from the surroundings.

6.3 Adding a catalyst

Draw a second curve starting and finishing at the same reactant and product levels, but with a lower peak. The activation energy is smaller; ΔH is exactly the same. Label both curves "without catalyst" and "with catalyst".

Exam tip: the three most common errors are measuring E_a from the products, drawing ΔH arrows the wrong way, and changing the product level when a catalyst is added.

7. Practical method questions: how to answer them

Method answers are marked point by point. Include:

1. **Apparatus** named and sized: conical flask, gas syringe, measuring cylinder, balance, stopwatch, thermometer or water bath.
2. **Quantities** stated: a measured volume of acid of stated concentration, a weighed mass of solid.
3. **The one variable changed** and how: for temperature, warm the acid in a water bath and measure its temperature with a thermometer before mixing.
4. **What is measured and when:** volume, mass or time, at regular intervals or until an end point.
5. **Control variables** listed.
6. **Repeats** and a mean, plus how results show the trend (plot a graph, compare initial gradients or compare times).
7. **Safety:** goggles, ventilation for toxic gases.

Worked example: planning a temperature investigation

Plan an experiment to find how temperature affects the rate of reaction between sodium thiosulfate and hydrochloric acid.

Measure 50 cm³ of sodium thiosulfate solution into a conical flask and warm it in a water bath to 20 °C, checking with a thermometer. Place the flask on a paper marked with a cross. Add 5 cm³ of hydrochloric acid of fixed concentration, start the stopwatch and stop it when the cross disappears. Repeat at 30, 40, 50 and 60 °C, keeping volumes and concentrations the same and using the same paper and the same observer. Repeat each temperature and take a mean; plot 1/time against temperature. Work in a ventilated room because sulfur dioxide is produced.

Quick check

1. Define *rate of reaction* and state a suitable unit when the volume of a gas is measured.
2. Define *activation energy*.
3. State two conditions that must be met for a collision between reactant particles to lead to a reaction.
4. Describe how you would measure the rate of reaction between zinc and dilute sulfuric acid using a gas syringe. Name the gas collected.
5. In the loss of mass method, explain why cotton wool is placed in the neck of the flask, and explain why this method is not suitable for the reaction of magnesium with hydrochloric acid.
6. 50 cm³ of hydrogen peroxide solution decomposes when MnO₂ is added. Readings of oxygen volume are: 0 s, 0 cm³; 30 s, 24 cm³; 60 s, 40 cm³; 90 s, 48 cm³; 120 s, 50 cm³; 150 s, 50 cm³. Calculate the average rate in the first 30 s and between 60 s and 90 s, and explain why they are different.
7. Using the data in question 6, state the time at which the reaction finished and the total volume of oxygen produced.
8. A student repeats the experiment in question 6 with the same mass of MnO₂ but uses 25 cm³ of the same hydrogen peroxide solution diluted with 25 cm³ of water, instead of 50 cm³ of undiluted solution. Describe how the new curve would compare with the original.
9. Explain, in terms of particles, why increasing the concentration of hydrochloric acid increases the rate of its reaction with marble chips.
10. Explain fully why increasing the temperature increases the rate of a reaction.
11. Equal masses of calcium carbonate as large lumps and as powder are added to separate portions of excess acid. Compare the initial rates and the final volumes of carbon dioxide, and explain your answer.
12. Explain why a spark in a flour mill can cause an explosion.
13. Describe an experiment to show that copper(II) oxide is a catalyst for the decomposition of hydrogen peroxide and not a reactant.
14. Describe the energy profile diagram for an exothermic reaction with and without a catalyst. State what happens to the activation energy and to ΔH when the catalyst is added.
15. The reaction between methane and chlorine does not take place in the dark at room temperature but does take place in sunlight. Explain this, and give one other reaction whose rate depends on light.

1. Rate of reaction is the change in the amount or concentration of a reactant or product per unit time. Suitable unit: cm³/s (or cm³/min).
2. Activation energy is the minimum energy that colliding particles must have in order to react.
3. The particles must collide, and the collision must have energy equal to or greater than the activation energy.
4. The gas is hydrogen: $\text{Zn} + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2$. Measure a fixed volume (for example 50 cm³) of sulfuric acid of known concentration into a conical flask. Connect a gas syringe to a bung with a delivery tube and check it reads zero. Add a weighed mass of zinc granules, replace the

bung at once and start the stopwatch. Record the gas volume every 10 s until it stops changing. Plot volume against time; the gradient gives the rate.

5. Cotton wool lets carbon dioxide escape but stops droplets of acid spraying out, so the only mass lost is the mass of gas. Magnesium with hydrochloric acid produces hydrogen, which has a very small M_r (2). The mass lost is so small that a school balance cannot measure the change accurately, so a gas syringe should be used instead.

6. First 30 s: $24 \div 30 = 0.8 \text{ cm}^3/\text{s}$. Between 60 s and 90 s: $(48 - 40) \div 30 = 8 \div 30 = 0.27 \text{ cm}^3/\text{s}$ (2 s.f.). The rate is lower later because hydrogen peroxide is being used up, so its concentration falls. There are fewer H_2O_2 particles per unit volume, so collisions with the catalyst surface (and successful collisions) are less frequent.

7. The volume stops changing at 120 s, so the reaction finished at (or just before) 120 s. Total volume of oxygen = 50 cm^3 .

8. The diluted solution contains only 25 cm^3 of the original solution, so it has half the moles of H_2O_2 , and its concentration is also half. The new curve starts with a smaller gradient (slower, because of the lower concentration) and levels off at half the final volume, 25 cm^3 , because hydrogen peroxide is the limiting reactant and only half as much is present.

9. A more concentrated acid has more hydrogen ions (acid particles) in the same volume. The acid particles collide with the surface of the marble chips more frequently, so there are more successful collisions per second and the rate increases.

10. At a higher temperature the particles have more kinetic energy and move faster, so they collide more frequently. Also, a greater proportion of the collisions have energy equal to or greater than the activation energy. Both effects give more successful collisions per second, so the rate increases. The second effect is the more important one.

11. The powder has a much larger surface area, so more calcium carbonate particles are exposed to the acid. Acid particles collide with them more frequently, giving more successful collisions per second, so the initial rate is greater with the powder. The final volume of carbon dioxide is the same, because the mass (and so the number of moles) of calcium carbonate, the limiting reactant, is the same and the acid is in excess.

12. Flour dust in the air is a very fine powder with an extremely large surface area in contact with oxygen. Flour is combustible, so once a spark supplies the activation energy, the combustion reaction spreads through the dust cloud extremely quickly. The rapid release of energy and hot gas causes an explosion.

13. Weigh a sample of copper(II) oxide. Set up two flasks with equal volumes of the same hydrogen peroxide solution at the same temperature. Add the copper(II) oxide to one flask only and measure the volume of oxygen given off against time in each. Oxygen is produced much faster with the copper(II) oxide, showing that it increases the rate. When the reaction stops, filter off the copper(II) oxide, wash it with distilled water, dry it and reweigh it. The mass is unchanged and it speeds up fresh hydrogen peroxide, so it has not been used up. It is therefore a catalyst, not a reactant.

14. Axes: energy against progress of reaction. The reactants are on a higher level on the left and the products on a lower level on the right. The uncatalysed curve rises to a high peak and falls to the products. The catalysed curve starts and ends at the same levels but has a lower peak.

Activation energy is shown as the height from the reactants to each peak, so it is smaller with the catalyst. ΔH is the drop from reactants to products, which is negative (exothermic) and is unchanged by the catalyst.

15. The reaction is photochemical. Ultraviolet light supplies the energy needed to break the Cl–Cl bond in chlorine molecules, so particles can react. In the dark at room temperature too few collisions have enough energy to overcome the activation energy, so no reaction is seen. Other examples: photosynthesis ($6\text{CO}_2 + 6\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$) or the decomposition of silver bromide in photography ($2\text{AgBr} \rightarrow 2\text{Ag} + \text{Br}_2$).