4.6 Rate and Extent of Chemical Change

Rates of Reaction

The rate of a chemical reaction can be found by measuring the amount of a reactant used or the amount of product formed over time:

Rate of reaction = $\frac{\text{Amount of reactant used}}{\text{Time}}$

Rate of reaction = $\frac{\text{Amount of product formed}}{\text{Time}}$

The quantity of reactant or product can be measured by the mass in grams or by a volume in cm^3.

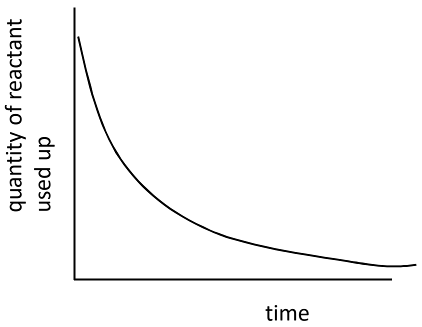
The units of rate of reaction may be given as **g/s** or **cm^3/s**.

The quantity of reactants can also be measured in terms of moles and for rate of reaction the unit can be measured in **mol/s**.

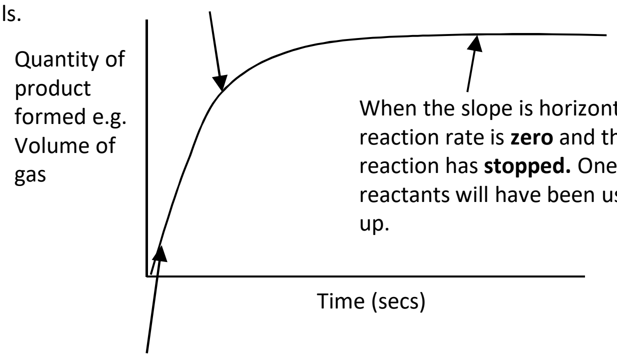
Using graphs to show reaction rates

Draw, and interpret, graphs showing the quantity of product formed or quantity of reactant used up against time.

The **slope/gradient** of these graphs is a measure of reaction rate.



The slope is less steep meaning the reaction rate drops as the concentration of reactants falls.



When the slope is horizontal the reaction rate is **zero** and the reaction has **stopped.** One of the reactants will have been used up.

Where the slope is steepest, the reaction rate is fastest. The concentration of reactants is highest here.

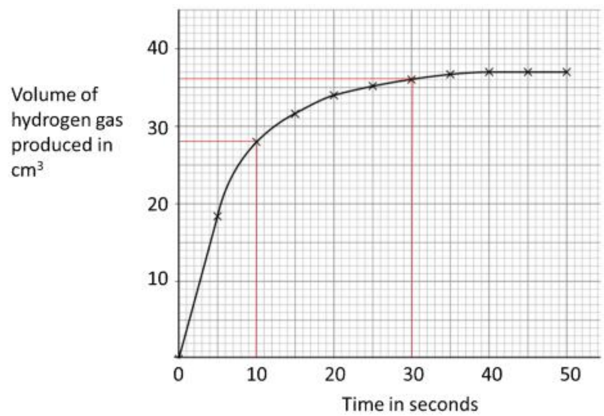
Mean rate of a reaction

Be able to calculate the **mean rate of a reaction** from given information about the quantity of a reactant used or the quantity of a product formed and the time taken.
This data could be taken from any two points on a graph of concentration against time.

Example 1
If 25 cm^3 of hydrogen gas is produced in 10 seconds then the mean rate of reaction is 25/10 = 2.5 cm^3/s

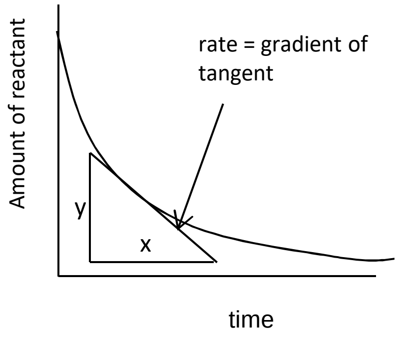
Example 2
Determine the **mean rate of reaction** between 10 and 30 seconds.
Read off from the graph the two volumes of gas.
At 10 secs = 28 cm^3
At 30 secs =36 cm^3

Mean rate = $\frac{\text{change in volume}}{\text{change in time}} = \frac{36-28}{30-10} = \frac{8}{20} = 0.4$ cm^3/s



Calculating the rate using the gradient

If a question asks you to determine the rate of reaction at **one particular time**, then you must take **a gradient** of the curve at that time.



Draw a tangent to the curve on the graph.
The tangent can be drawn at any time on the graph.
(What time does the question ask for the rate?)
Calculate the gradient of the tangent by drawing a tangent triangle.

$$\text{Gradient} = \frac{\text{difference in y}}{\text{difference in x}}$$

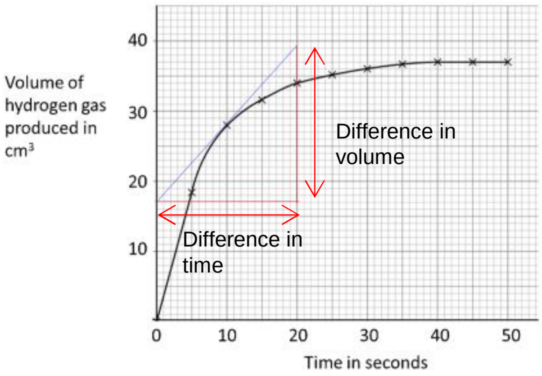
Use the slope/gradient of the tangent as a measure of the rate of reaction at that time.

Example 3

Determine the rate of reaction at 10 seconds.
Show your working on the figure.

Draw the tangent to the curve at 10 seconds.
Draw a triangle and read off the change in volume of gas and change in time.

$$\text{rate} = \frac{\text{change in volume}}{\text{change in time}} = \frac{39 - 17}{20 - 0} = \frac{22}{20} = 1.1 \text{ cm}^3\text{/s}$$

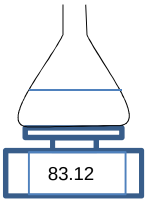


Common ways of measuring rate:

You should be able to investigate factors which affect the rate of chemical reactions by measuring:

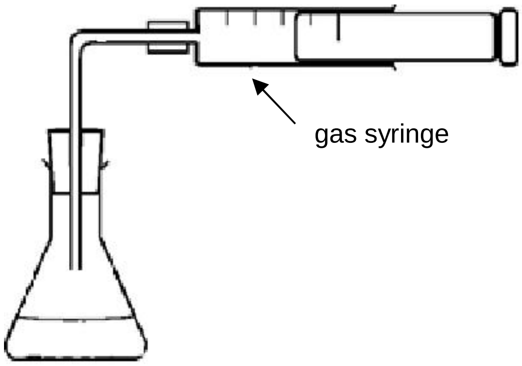
- the loss in mass of reactants
- the volume of gas produced
- the time for a solution to become opaque or coloured.

Measuring mass loss. This can be done if a heavy gas like carbon dioxide is given off. The mass drops as the gas is given off. (Hydrogen gas is too light for this method to be used)
Typically used for marble chips ($CaCO_3$) and acid reaction.



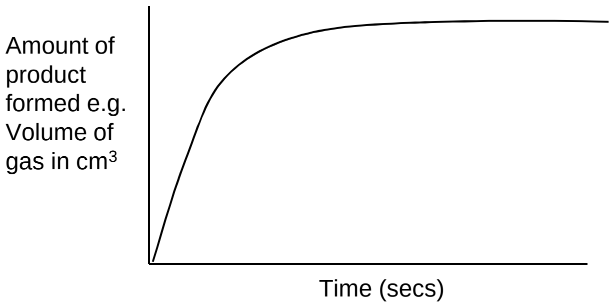
$CaCO_3$ (s) + 2HCl (aq) → $CaCl_2$ (aq) + **CO_2 (g)** + H_2O (l)

Measuring the volume of gas evolved over time using a gas syringe. Gas volume reading are taken at regular time intervals and a graph plotted.
The gradient of this graph will be equal to the reaction rate. The steeper the graph the faster the reaction.



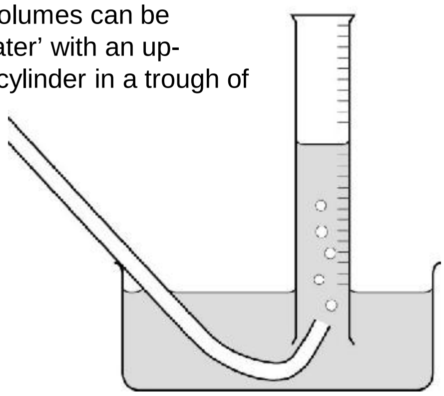
Typically used for magnesium and acid reaction

Mg (s) + 2HCl (aq) → $MgCl_2$ (aq) + **H_2 (g)**



The gradient of the slope can be used as a measure of reaction rate

Alternatively gas volumes can be measured 'over water' with an up-turned measuring cylinder in a trough of water

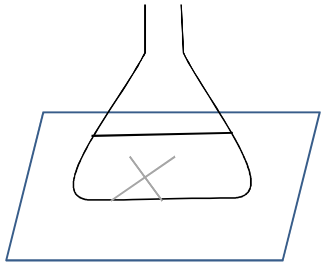


Typical method used for marble chips ($CaCO_3$) and acid (same method for magnesium).

1. Weigh 10 g of marble chips on a mass balance.
2. Place marble chips into a flask.
3. Measure 50 cm^3 of hydrochloric acid with a measuring cylinder.
4. Pour hydrochloric acid into the flask, connect the gas syringe and start a timer.
5. Record the volume of gas produced every 10 seconds.

The time for a solution to become opaque or coloured

Measuring the disappearance of a cross through a mixture of acid and sodium thiosulfate. The mixture becomes cloudy as solid sulfur is produced in this reaction. Time how long it takes for the cross on a piece of paper to disappear. The longer it takes for the cross to disappear the slower the reaction rate.



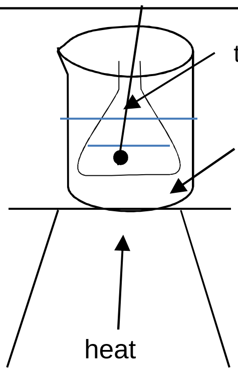
$Na_2S_2O_3$ (s) + 2HCl (aq) → 2 NaCl (aq) + SO_2 (g) +**S (s)** + H_2O (l)
sodium thiosulfate — **solid sulfur**

Method for investigating effect of changing concentration of sodium thiosulfate
- measure 25cm^3 volume of sodium thiosulfate with a measuring cylinder
- place sodium thiosulfate in conical flask
- measure 25cm^3 volume of hydrochloric acid with a measuring cylinder
- place conical flask on cross
- add hydrochloric acid to conical flask
- swirl
- start stop clock
- measure time for cross to become no longer visible
- repeat and find mean
- repeat for different concentrations of sodium thiosulfate

control variables
- concentration of hydrochloric acid
- volume of hydrochloric acid
- volume of sodium thiosulfate solution ← Do not say **amount** here. Say volume or concentration.

In this experiment **Independent variable** = concentration of sodium thiosulfate **Dependent variable** = time taken for cross to disappear

If investigating the effect of changing temperature on one of these reactions, heat the reactants up to the required temperature in a water bath.
If investigating effect of changing temperature then the control variables will be:
- volume and concentrations of the acid
- volume and concentrations of the sodium thiosulfate
- size of flask
- size of cross on paper



Factors which affect the rates of chemical reactions
include:
- the concentrations of reactants in solution,
- the pressure of reacting gases,
- the surface area of solid reactants,
- the temperature
- the presence of catalysts.

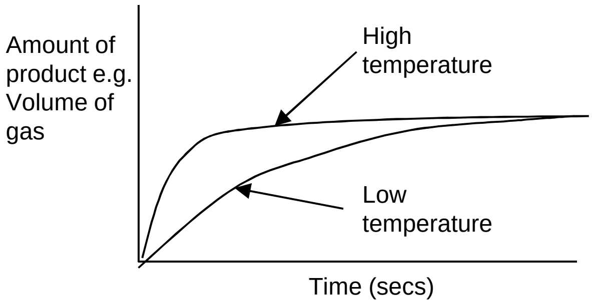
Collision Theory

Collision theory explains how various factors affect rates of reactions. According to this theory, chemical reactions can occur only when reacting particles **collide** with each other and **with sufficient energy**.

The **minimum amount of energy** that particles must have to react is called the **activation energy**..

Increasing temperature

Increasing the temperature means the **particles gain energy.** This increases the **speed of the reacting** particles so that they **collide more frequently** and **more energetically**. More of the collisions are **successful** as more particles have **energy greater** than the **activation energy**. This increases the rate of reaction.

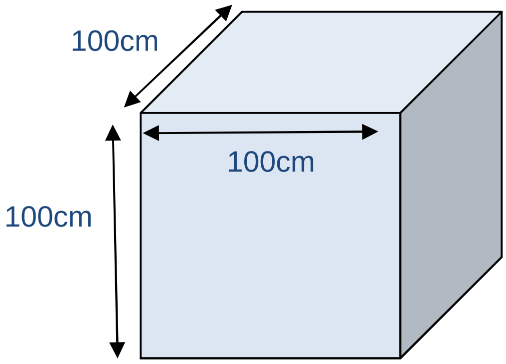


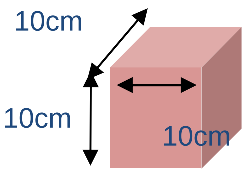
Increasing concentration
Increasing the concentration of reactants in solution, increases the number of **particles in the same volume** and so **increases the frequency of collisions** and therefore increases the rate of reaction.

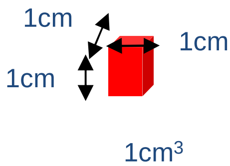
Increasing the pressure of a gas
Increasing the pressure of reacting gases, is the same as increasing concentration. It increases the number of gas **molecules in the same volume** and so **increases the frequency of collisions** and therefore increases the rate of reaction.

Increasing the surface area
If solid reactants are in smaller pieces they have a greater surface area.
Increasing the surface area of solid reactants increases the **frequency of collisions** and so increases the rate of reaction.

Be able to explain the effects on rates of reaction of changes in the size of pieces of a reacting solid in terms of surface area to volume ratio.
The smaller the piece the larger the surface area to volume ratio.







volume = 100 x100 x 100
= 1000 000 cm^3

surface area = 100 x100 x 6
= 60 000 cm^3

Surface area to volume ratio
0.06:1

volume = 10 x10 x 10
= 1000 cm^3

surface area = 10 x10 x 6
= 600 cm^3

Surface area to volume ratio
0.6:1

volume = 1 x1 x 1
= 1cm^3

surface area = 1 x1 x 6
= 6 cm^3

Surface area to volume ratio
6:1

Catalysts

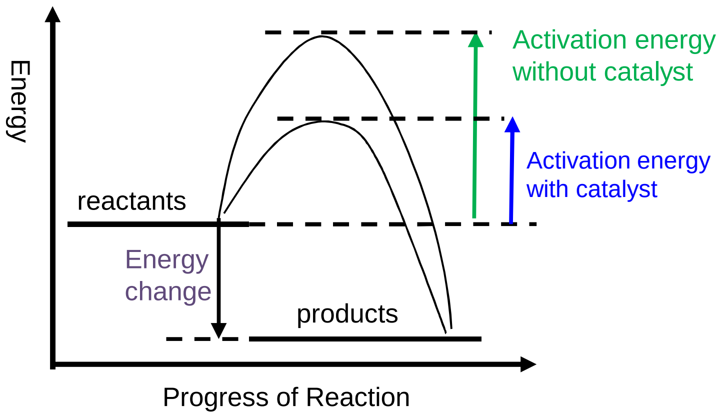
Catalysts change the rate of chemical reactions but are **not used up** during the reaction.

Different reactions need different catalysts. Enzymes act as catalysts in biological systems.

Catalysts increase the rate of reaction by providing a different pathway for the reaction that has a lower activation energy.

Be able to identify catalysts in reactions from their effect on the rate of reaction and because they are **not included** in the **chemical equation** for the reaction

A reaction profile for a catalysed reaction can be drawn in the following form:



4.6 Reversible Reactions

In some chemical reactions, the products of the reaction can react to produce the original reactants. Such reactions are called **reversible reactions** and are represented:
A + B ⇌ C + D

When a reversible reaction occurs in apparatus which prevents the escape of reactants and products (called a **closed system**) an **equilibrium** is reached.

Equilibrium is reached:

- when the **forward** and **reverse** reactions occur at **exactly the same rate.**
- When reaction occurs in apparatus which prevents the escape of reactants and products.

At equilibrium the amounts of reactants and products **remain constant**

If a reversible reaction is exothermic in one direction, it is endothermic in the opposite direction. The same amount of energy is transferred in each case. For example:

hydrated copper sulfate (blue) $\underset{\text{exothermic}}{\overset{\text{endothermic}}{\rightleftharpoons}}$ anhydrous copper sulfate (white) + water

Changing Conditions

The relative amounts of all the reactants and products at equilibrium depend on the conditions of the reaction.

The direction of reversible reactions can be changed by changing the conditions.
For example:

$$\text{Ammonium chloride} \underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}} \text{ammonia + hydrogen chloride}$$

The effects of changing conditions on a system at equilibrium can be predicted using **Le Chatelier's Principle:**
If a system is at equilibrium and **a change** is made to any of the **conditions,** then the system responds to **counteract the change**.

Changing concentration

If the concentration of one of the reactants or products is changed, the system is no longer at equilibrium and the concentrations of all the substances will change **to counteract the change** until equilibrium is reached again.
If the concentration of a **reactant is increased**, **more products** will be **formed** until equilibrium is reached again and the concentration of the reactant is reduced.
If the concentration of a **product is decreased**, **more reactants will react** until equilibrium is reached again.

Changing temperature

If the **temperature is increased** the equilibrium will always move in the **endothermic direction** so that the increase in temperature is reduced.
If the temperature is increased, the yield from the endothermic reaction increases and the yield from the exothermic reaction decreases.

e.g . If temp is increased in the following reaction
$SO_2 + ½ O_2 \rightleftharpoons SO_3$ (exothermic in forward)
The yield of SO_3 will decrease because the reaction will move in the endothermic reaction, which is the **reverse** direction.

If the temperature of a system at equilibrium is increased:
- the relative amount of products at equilibrium increases for an endothermic reaction
- the relative amount of products at equilibrium decreases for an exothermic reaction.

Changing pressure

In gaseous reactions, if **pressure is increased** the equilibrium will move towards the side of the reaction that has the **least number of gaseous molecules** so that the increase in pressure is reduced
e.g . If pressure is increased in the following reaction

$$N_2 + 3 H_2 \rightleftharpoons 2NH_3$$

The yield of NH_3 will increase as the reaction will move to **the right side** which has **fewer moles of gas**.

An increase in pressure causes the equilibrium position to shift towards the side with the smaller number of molecules as shown by the symbol equation for that reaction.
A decrease in pressure causes the equilibrium position to shift towards the side with the larger number of molecules as shown by the symbol equation for that reaction.

If a reaction has the **same number of gaseous** molecules on both sides of the equation, then increasing pressure will have **no effect** on the position of equilibrium e.g. $2 HI \rightleftharpoons H_2 + I_2$

Increasing temperature and pressure will also increase the rate of reaction. Explain this by using the collision theory from earlier in this chapter.

Catalysts do not affect the position of equilibrium as they speed up the forward and the backward reactions by the same amount.