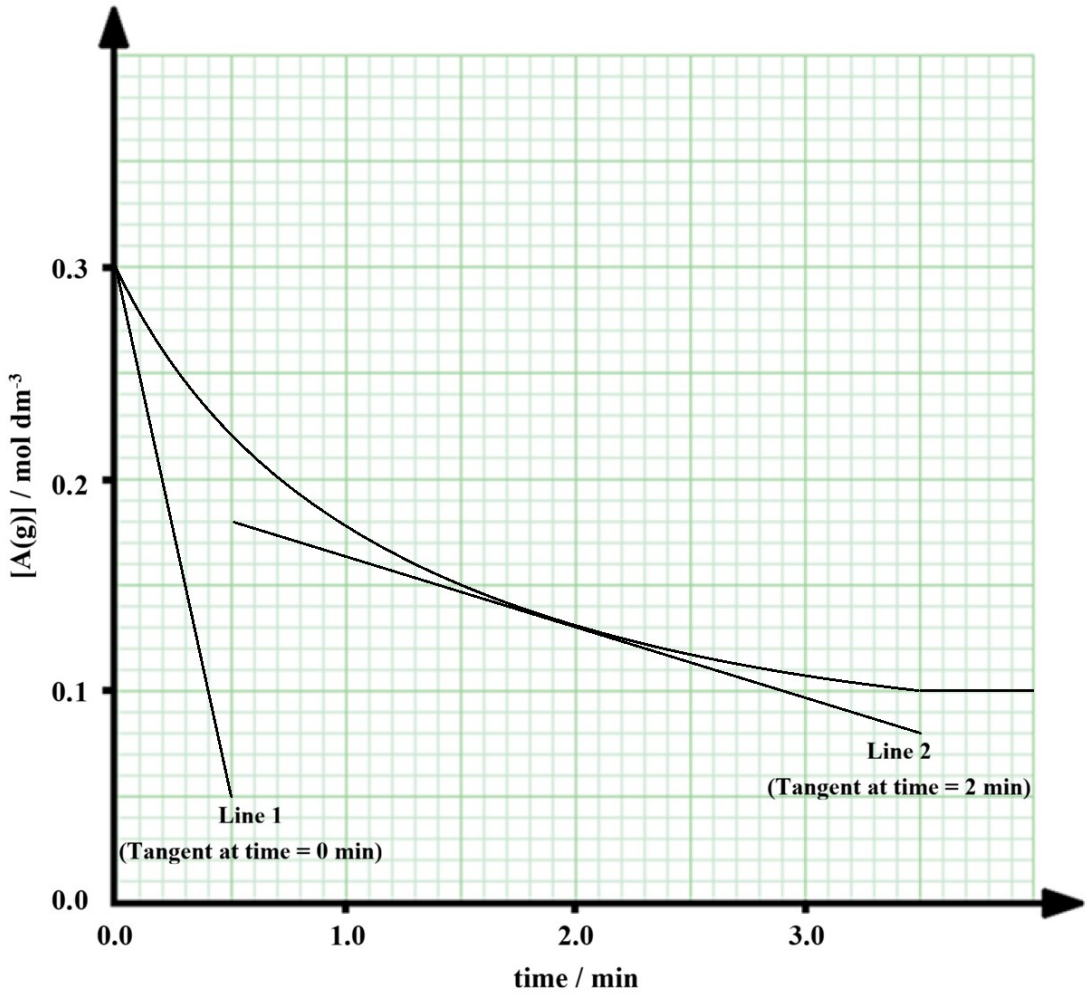
Intensive note (Topic 9: Rates of reactions)

Rate curve

Consider the chemical equation for the reaction between A(g) and B(g): $A(g) + 2B(g) \rightarrow 3C(g) + 4D(g)$

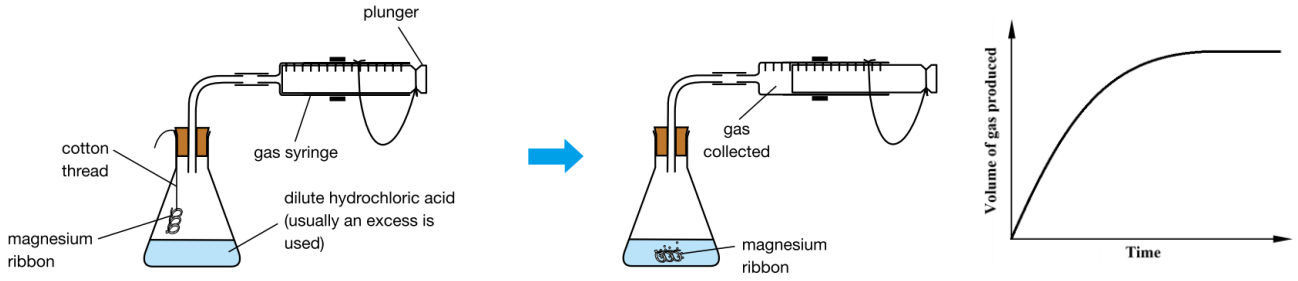
The graph below shows the variation of [A(g)] in the reaction mixture with time.



Rate	Calculation
Average rate of consumption of A(g)	– (Change in [A(g)]) / (Time needed for whole reaction) = – (0.3 – 0.1) / (3.5) = 0.0571 mol dm^{-3} min^{-1}
Average rate of consumption of A(g) in the first 2 min	– (Change in [A(g)]) / (Change in time) = – (0.3 – 0.13) / (2 – 0) = 0.085 mol dm^{-3} min^{-1}
Average rate of consumption of B(g) in the first 2 min	[Average rate of consumption of A(g)] x 2 = 0.085 x 2 = 0.17 mol dm^{-3} min^{-1}
Instantaneous rate of consumption of A(g) at 2 min	– Slope of tangent at time = 2 min (i.e. Line 2) = – (0.18 – 0.08) / (0.5 – 3.5) = 0.0333 mol dm^{-3} min^{-1}
Instantaneous rate of formation of C(g) at 2 min	[Instantaneous rate of consumption of A(g) at time = 1.5] x 3 = 0.0333 x 3 = 0.1 mol dm^{-3} min^{-1}
Initial rate of consumption of A(g) (Initial rate = instantaneous rate at time = 0)	– Slope of tangent at time = 0 min (i.e. Line 1) = – (0.3 – 0.05) / (0 – 0.5) = 0.5 mol dm^{-3} min^{-1}
Initial rate of formation of D(g)	[Initial rate of consumption of A(g)] x 4 = 0.5 x 4 = 2 mol dm^{-3} min^{-1}

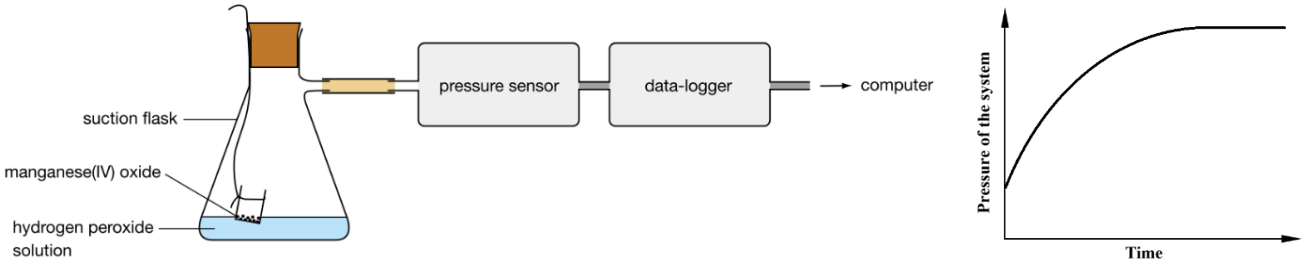
Methods for following the progress of a chemical reaction

1. Measure the volume of gas produced by gas syringe at regular time intervals



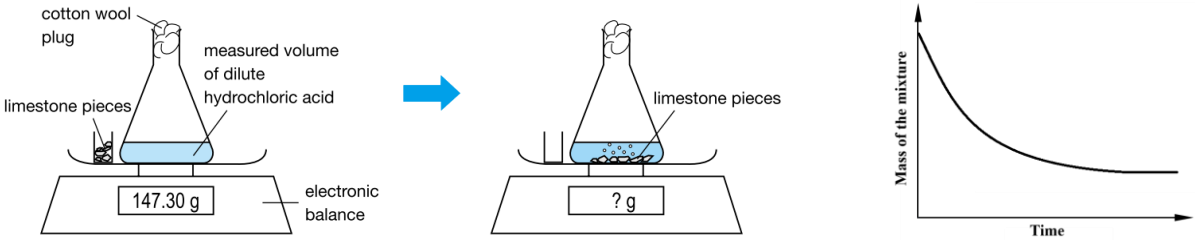
- Suitable for reactions that produce gas.
- NOT suitable for reactions that produce gas with high solubility in water (NH_3, HCl, SO_2) when water is the solvent.
- The set-up should be air-tight

2. Measure the change in pressure by pressure sensor at regular time intervals



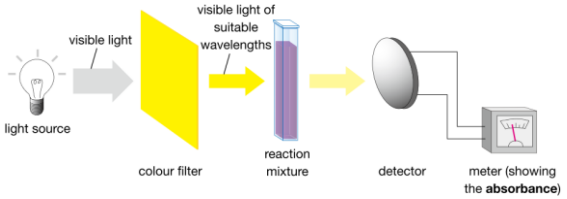
- Suitable for reactions that involve a change in the number of moles of gas (increase or decrease)
- NOT suitable for reactions that produce gas with high solubility in water (NH_3, HCl, SO_2) when water is the solvent.
- The pressure sensor is often connected to a data-logger. Advantages of using data-logger include:
  1. A data-logger can collect and store data over very short time intervals.
  2. Experimental data can be presented graphically on a computer immediately.
- The reaction system has to be a closed system with a constant volume.

3. Measure the change in mass of a reaction mixture by electronic balance at regular time intervals

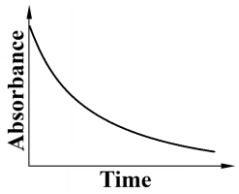


- Suitable for reactions that produce gas.
- NOT suitable for reactions that produce gas with high solubility in water (NH_3, HCl, SO_2) when water is the solvent.
- NOT suitable for reactions that produce $H_2(g)$. It is because $H_2(g)$ has a very low density. When $H_2(g)$ escapes from the flask, the change in mass of the reaction mixture cannot be accurately measured.
- Cotton wool plug can allow the escape of gas and prevent the solution from splashing out.
- Decrease in mass of the reaction mixture = Mass of gas given off

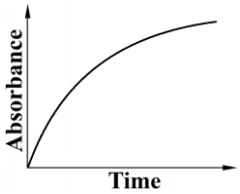
4. Measure the change in color intensity of a reaction mixture by colorimeter at regular time intervals



Example 1:



Example 2:



$Br_2(aq)$ + $HCOOH(aq)$ ➔ $2HBr(aq) + CO_2(g)$

$IO_3^-(aq) + 5I^-(aq) + 6H^+(aq)$ ➔ **$3I_2(aq)$** + $3H_2O(l)$

- Suitable for reaction that involves a change in color intensity (due to increase or decrease in coloured species)
- Consider example 1. $Br_2(aq)$ is brown in color while other chemical species are colorless. The color intensity (or absorbance, the amount of light being absorbed by the reaction mixture) is directly proportional to $[Br_2(aq)]$. When the reaction proceeds, the color intensity of the mixture decreases as $[Br_2(aq)]$ decreases during the reaction.

5. Titrimetric analysis

Example: Consider the alkaline hydrolysis of $CH_3COOCH_2CH_3$

$$CH_3COOCH_2CH_3(l) + NaOH(aq) \rightarrow CH_3COONa(aq) + CH_3CH_2OH(aq)$$

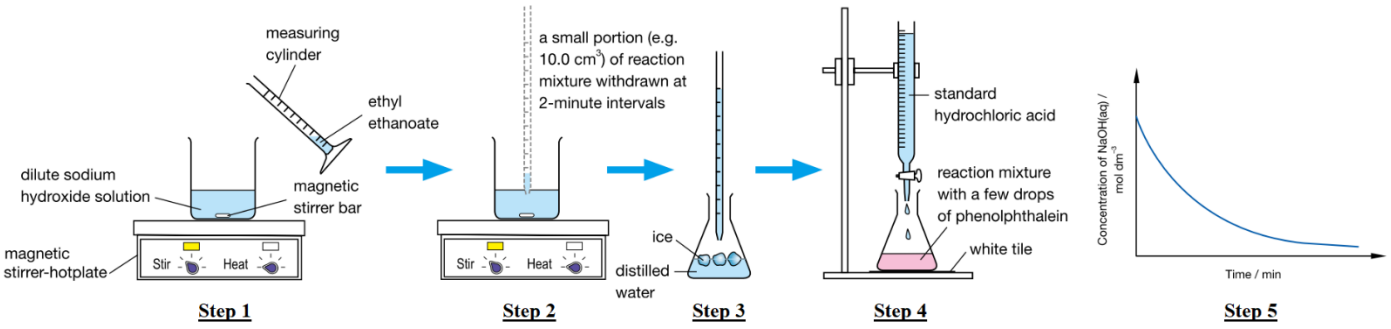
Step 1: Mix $CH_3COOCH_2CH_3(l)$ and $NaOH(aq)$ in a beaker with stirring

Step 2: Withdraw a small but fixed volume of the reaction mixture using a pipette at regular time intervals.

Step 3: *Quench the reaction in the small portions by pouring them into ice-cold distilled water.

Step 4: Titrate the NaOH(aq) present in the quenched portions against standard HCl(aq)

Step 5: A rate curve can be obtained by sketching a graph of the variation of [NaOH(aq)] in the reaction mixture with time.



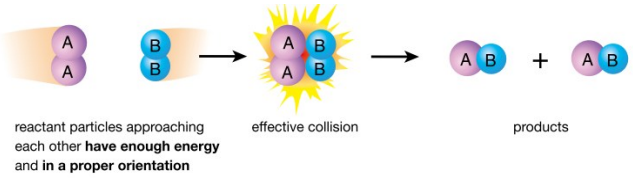
* The reaction in these small portions has to be slowed down or even stopped (i.e. quenched) before carrying out the analysis. This prevents further changes in the concentration of the reactant or product in the small portions. It can be done by:

1. Cooling the reaction mixture rapidly in ice
2. Diluting the reaction mixture with a sufficient amount of cold water
3. Remove the catalyst

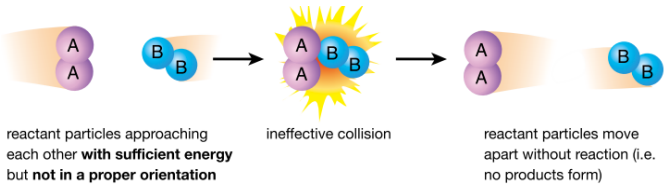
- Limitations of using titrimetric analysis to follow the progress of a reaction:
  1. The original reaction mixture is disturbed when small portions of the mixture are withdrawn for titrimetric analysis.
  2. Continuous monitoring of the progress of a reaction is impossible.

Effective collisions

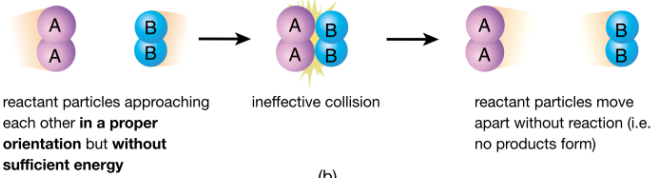
Reactant particles must have sufficient energy to react and collide in a proper orientation in order for a reaction to occur.



Effective collision



Ineffective collision



Ineffective collision

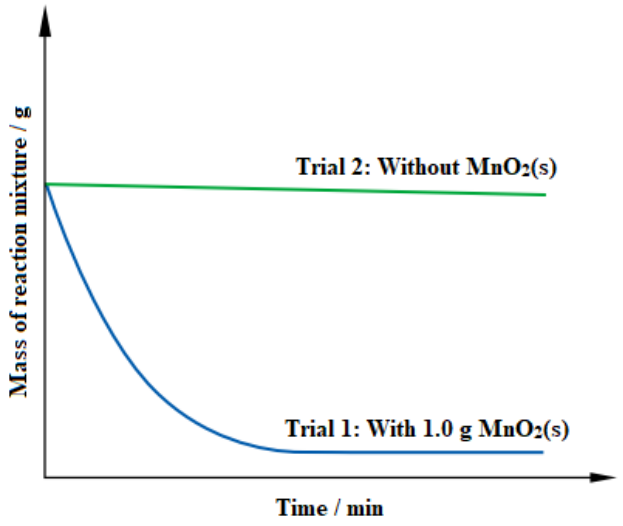
Factors affecting rate of reaction: Catalyst

A **catalyst** is a substance which can change (usually increase) the rate of a reaction but itself remains chemically unchanged at the end of reaction.

Example: Consider the decomposition reaction of $H_2O_2(aq)$:

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

The mass of the reaction mixture is measured at regular time intervals.



For the rate curve in trial 1, the curve is steepest at the beginning.

➔ It is because $[H_2O_2(aq)]$ is highest at the beginning.

The curve becomes less steep with time.

➔ It is because $[H_2O_2(aq)]$ is decreasing during the reaction.

The curve becomes horizontal finally.

➔ It is because all H_2O_2 is used up.

The curve of trial 1 is much steeper than that of trial 2.

➔ Rate of reaction in trial 1 is much faster than that in trial 2

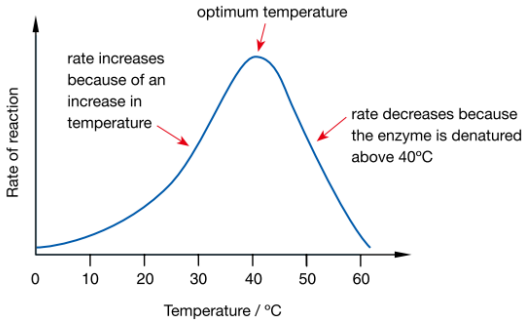
➔ $MnO_2(s)$ catalyzes the decomposition of $H_2O_2(aq)$.

The mass of $MnO_2(s)$ collected at the end of experiment in trial 1 should be 1.0 g (i.e. remains unchanged) as catalyst is NOT consumed in a chemical reaction.

Enzymes are biological catalysts. They are proteins (a polymer made of amino acids). Unlike other catalysts, their catalytic properties do NOT increase with temperature as they can be denatured at high temperatures (or extreme pH values).

e.g. Yeast (a fungus) can produce zymase (an enzyme) which catalyzes the fermentation of glucose to ethanol and carbon dioxide

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$



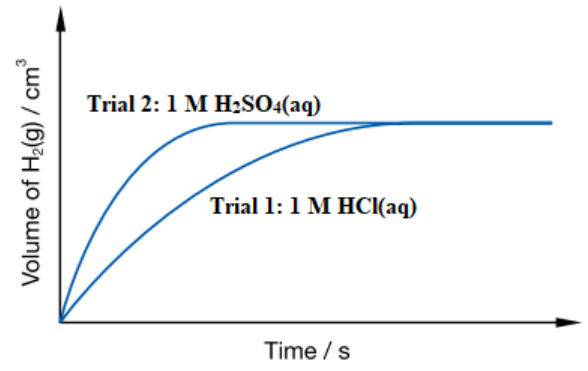
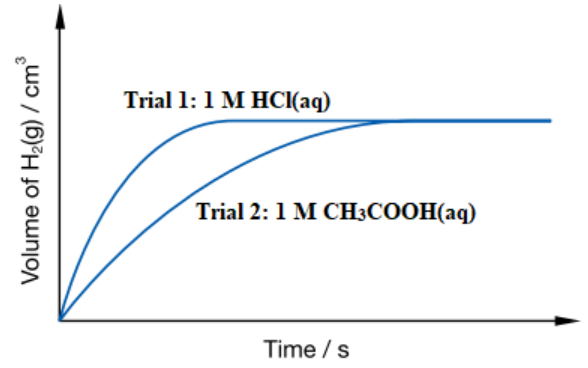
Intensive note (Topic 9: Rates of reactions)

Factors affecting rate of reaction: Concentration of reactants

Example 1: Consider the reaction between magnesium and dilute acids:

$$Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$$

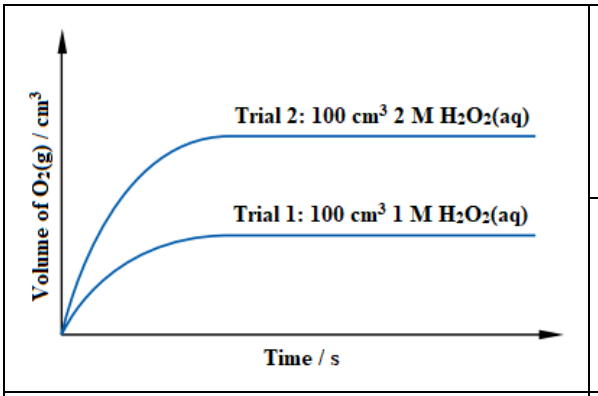
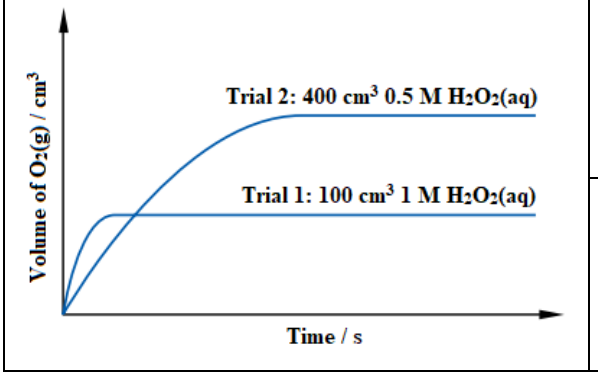
The same mass of Mg(s) and the same volume of **excess** acids are used each time. The volume of $H_2(g)$ collected is measured.

	**Steepness of curve:** $H_2SO_4(aq)$ is a dibasic acid while HCl(aq) is a monobasic acid. $[H^+(aq)]$ in trial 2 is higher than that in trial 1. This increases the frequency of effective collisions and hence the reaction rate in trial 2 increases. The curve of trial 2 is steeper as it has a higher reaction rate.
	Final volume of $H_2(g)$: As the amount of limiting reactant Mg(s) used in both trials are the same, volume of $H_2(g)$ produced should be the same
	**Steepness of curve:** $CH_3COOH(aq)$ is a weak acid while HCl(aq) is a strong acid. $[H^+(aq)]$ in trial 2 is lower than that in trial 1. This decreases the frequency of effective collisions and hence the reaction rate in trial 2 decreases. The curve of trial 2 is less steep as it has a lower reaction rate.
	Final volume of $H_2(g)$: As the amount of limiting reactant Mg(s) used in both trials are the same, volume of $H_2(g)$ produced should be the same

Example 2: Consider the decomposition reaction of $H_2O_2(aq)$ using $MnO_2(s)$ as catalyst:

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

The volume of $O_2(g)$ collected is measured at regular time intervals.

	**Steepness of curve:** $[H_2O_2]$ in trial 2 is higher than that in trial 1. This increases the frequency of effective collisions and hence the reaction rate in trial 2 increases. The curve of trial 2 is steeper as it has a higher reaction rate.
	Final volume of $O_2(g)$: Mol of limiting reactant H_2O_2 in trial 1 = (100/1000) x 1 = 0.1 Mol of limiting reactant H_2O_2 in trial 2 = (100/1000) x 2 = 0.2 Volume of O_2 produced in trial 2 should be the double of trial 1
	**Steepness of curve:** $[H_2O_2]$ in trial 2 is lower than that in trial 1. This decreases the frequency of effective collisions and hence the reaction rate in trial 2 decreases. The curve of trial 2 is less steep as it has a lower reaction rate.
	Final volume of $O_2(g)$: Mole of limiting reactant H_2O_2 in trial 1 = (100/1000) x 1 = 0.1 Mole of limiting reactant H_2O_2 in trial 2 = (400/1000) x 0.5 = 0.2 Volume of O_2 produced in trial 2 should be the double of trial 1

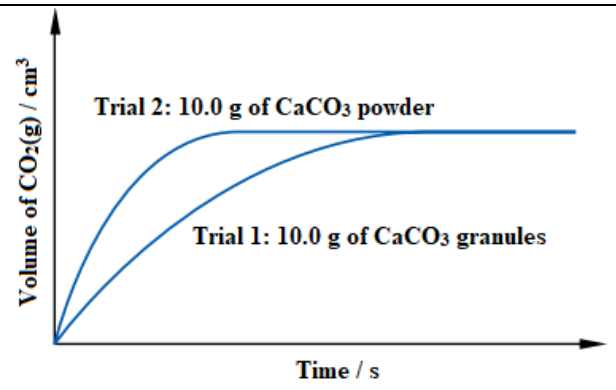
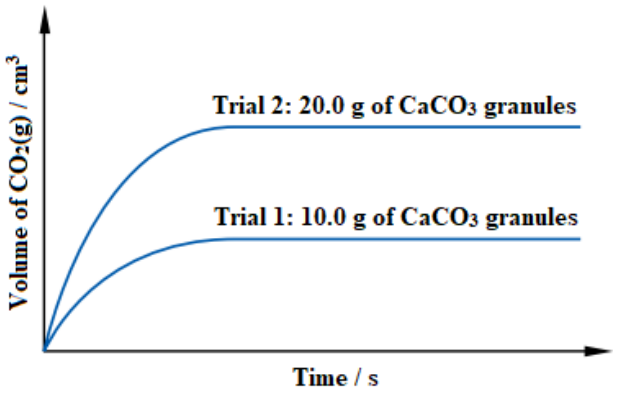
Factors affecting rate of reaction: Surface area of solid reactants

Example 1: Consider the reaction between calcium carbonate and dilute hydrochloric acid:

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

$CaCO_3(s)$ and **excess** 1 dm^3 of 1 M HCl(aq) are used each time. The volume of $CO_2(g)$ collected is measured.

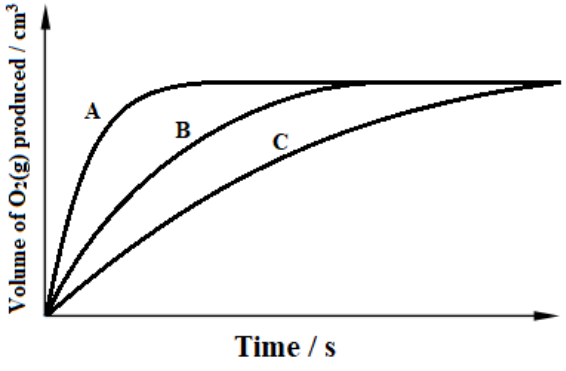
*To obtain more accurate results, HCl(aq) should be saturated with $CO_2(g)$ first before the experiment as $CO_2(g)$ produced is slightly soluble in water.

<table>
<tr><td rowspan="2"> 
</td><td>Steepness of curve:
$CaCO_3(s)$ powder has a higher surface area than $CaCO_3(s)$ granules. This increases the chance for collision and hence the frequency of effective collisions in trial 2. The curve of trial 2 is steeper as it has a higher reaction rate.</td></tr>
<tr><td>Final volume of $CO_2(g)$:
As the amount of limiting reactant $CaCO_3(s)$ used in both trials are the same, volume of $CO_2(g)$ produced should be the same</td></tr>
<tr><td rowspan="2"> 
</td><td>Steepness of curve:
20.0 g of $CaCO_3(s)$ granules has a higher surface area than 10.0 g of $CaCO_3(s)$ granules. This increases the chance for collision and hence the frequency of effective collisions in trial 2. The curve of trial 2 is steeper as it has a higher reaction rate.</td></tr>
<tr><td>Final volume of $CO_2(g)$:
Mole of limiting reactant $CaCO_3$ in trial 1 = 10/100.1 = 0.1
Mole of limiting reactant $CaCO_3$ in trial 2 = 20/100.1 = 0.2
Volume of CO_2 produced in trial 2 should be the double of trial 1</td></tr>
</table>

Example 2: Consider the decomposition reaction of $H_2O_2(aq)$ using $MnO_2(s)$ as catalyst:

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

100 cm^3 of 1 M $H_2O_2(aq)$ and $MnO_2(s)$ with different masses and sizes of are used each time. The volume of $O_2(g)$ collected is measured at regular time intervals.

<table>
<tr><th>Trial A: 10.0 g $MnO_2(s)$ powder</th><th>Trial B: 5.0 g $MnO_2(s)$ powder</th><th>Trial C: 5.0 g $MnO_2(s)$ lumps</th></tr>
<tr><td rowspan="2"> 
</td><td colspan="2">Steepness of curve:
Surface area of $MnO_2(s)$: A > B > C
Chance of collision and frequency of effective collisions: A > B > C
Rate of reaction: A > B > C
Steepness of curve: A > B > C</td></tr>
<tr><td colspan="2">Final volume of $CO_2(g)$:
As the amount of limiting reactant $H_2O_2(aq)$ used in all trials are the same, volume of $O_2(g)$ produced should be the same</td></tr>
</table>

Factors affecting rate of reaction: Temperature of reactants

Example: Consider the reaction between sodium thiosulphate ($Na_2S_2O_3$) and dilute sulphuric acid (H_2SO_4)

$$S_2O_3^{2-}(aq) + 2H^+(aq) \rightarrow SO_2(g) + H_2O(l) + S(s)$$

- The above reaction produces a creamy yellow precipitate of S(s). The solution turns turbid and reduces the amount of light transmitted through the solution.

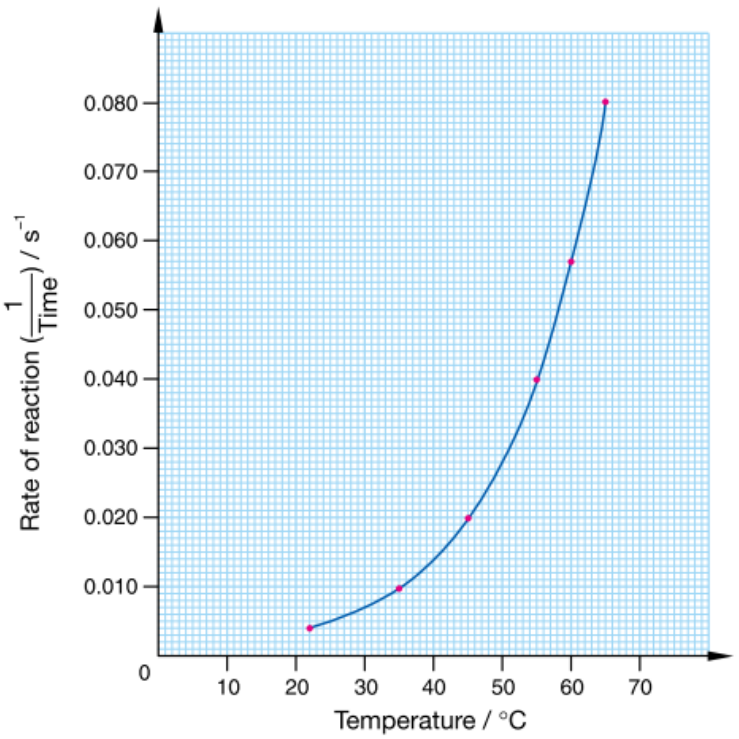
- The faster the reaction, the shorter is the time taken to 'blot out' the cross. The time taken to 'blot out' the cross is inversely proportional to the average rate of reaction

$$\text{average rate} \propto \frac{1}{\text{time taken to 'blot out' the cross}}$$

- The effect of temperature on the reaction rate can be investigated by repeating the experiment at different temperatures, using the same amount of $Na_2S_2O_3(aq)$ and HCl(aq)

Temperature of mixture / ℃	**22**	**35**	**45**	**55**	**60**	**65**
Time taken to 'blot out' the cross / s	250	100	50	25	17.5	12.5
1/time / s^{-1}	0.004	0.010	0.020	0.040	0.057	0.080

Experimental results:



- The rate of reaction against temperature is an exponential curve. This indicates that reaction goes faster at higher temperatures (exponentially)

- At higher temperatures, the reactant particles have more energy and move faster. As a result, they collide more frequently with each other. In addition, more reactant particles have sufficient energy to react. Thus, there is an increase in the frequency of effective collisions.

Molar volume of gases at room temperature and pressure

4 equations in mole calculations:

$\text{Mole of gas (mol)} = \frac{\text{Volume of gas (dm}^3\text{)}}{\text{Molar volume of gas (dm}^3\text{ mol}^{-1}\text{)}}$	$\text{Mole (mol)} = \frac{\text{Mass (g)}}{\text{Molar mass (g mol}^{-1}\text{)}}$
$\text{Mole (mol)} = \text{volume (dm}^3\text{)} \times \text{concentration (mol dm}^{-3}\text{)}$	$\text{Mole (mol)} = \frac{\text{Number of formula unit}}{\text{Avogadro's constant (mol}^{-1}\text{)}}$

- At room temperature and pressure, molar volume of gas = 24 dm^3 mol^{-1}

Example 1

In an experiment, excess $NaHCO_3(s)$ is added to 500 cm^3 of $H_2SO_4(aq)$.

$$2NaHCO_3(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2CO_2(g) + 2H_2O(l)$$

The volume of $CO_2(g)$ collected is 1200 cm^3 (measured at room temperature and pressure).

(a) Calculate the mass of $NaHCO_3(s)$ reacted.

Answer: Mole of $CO_2(g)$ produced = (Volume of gas) / (Molar volume of gas) = (1200/1000) / 24 = 0.05

Mole of $NaHCO_3(s)$ reacted = 0.05

Mass of $NaHCO_3(s)$ reacted = 0.05 x 84 = 4.2 g

(b) Calculate the concentration of $H_2SO_4(aq)$ used.

Answer: Mole of $CO_2(g)$ produced = (Volume of gas) / (Molar volume of gas) = (1200/1000) / 24 = 0.05

Mole of $H_2SO_4(aq)$ reacted = 0.05 x 1/2 = 0.025

Concentration of $H_2SO_4(aq)$ used = 0.025 / (500/1000) = 0.05 M

(c) $NaHCO_3(s)$ can also be decomposed to give $CO_2(g)$ under heating

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(l)$$

If 12.6 g of $NaHCO_3(s)$ is decomposed, calculate the theoretical volume of $CO_2(g)$ produced, measured at room temperature and pressure. (Formula mass of $NaHCO_3$ = 84)

Answer: Mole of $NaHCO_3(s)$ = 12.6 / 84 = 0.15

Mole of $CO_2(g)$ produced = 0.15 x 1/2 = 0.075

Theoretical volume of $CO_2(g)$ produced = 0.075 x 24 = 1.8 dm^3

Example 2 (Mole ratio = Volume ratio)

Consider the following reaction:

$$2\ C_4H_{10} + 13\ O_2(g) \rightarrow 8\ CO_2(g) + 10\ H_2O(l)$$

If 100 cm^3 of $C_4H_{10}(g)$ burns in 800 cm^3 of $O_2(g)$, what would be the volume of the resulting gaseous mixture at room conditions?

Answer: Since mole of $C_4H_{10}(g)$: mole of $O_2(g)$ = 2 : 13, volume of $C_4H_{10}(g)$: volume of $O_2(g)$ will also be 2 : 13

Volume of $O_2(g)$ needed to react completely with 100 cm^3 $C_4H_{10}(g)$ = 100 x 13/2 = 650 cm^3

Volume of $O_2(g)$ remained = 800 – 650 = 150 cm^3

Since mole of $C_4H_{10}(g)$: mole of $CO_2(g)$ = 2 : 8, volume of $C_4H_{10}(g)$: volume of $CO_2(g)$ will also be 2 : 8

Volume of $CO_2(g)$ produced = 100 x 8/2 = 400 cm^3

Volume of the resulting gaseous mixture = 150 + 400 = 550 cm^3

(Note that at room conditions, H_2O is a liquid.)