Measuring and explaining the rates of reactions

To determine the rate of reaction a property that changes during the reaction must be measured against time. The property will be proportional to a concentration of a particular reactant or product.

$$\text{Rate of reaction (units } s^{-1}) = \frac{\text{change in property}}{\text{time taken (s)}}$$

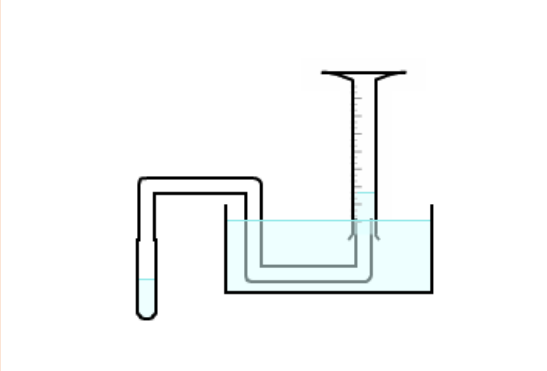
Hydrogen peroxide (H2O2 is an unstable compound that breaks down to form water and oxygen, albeit very slowly. An organic catalyst, such as catalyse (found in potato, liver or celery) or an inorganic catalyst, such as manganese(IV) oxide or lead(IV) oxide, can be used to speed up the reaction.

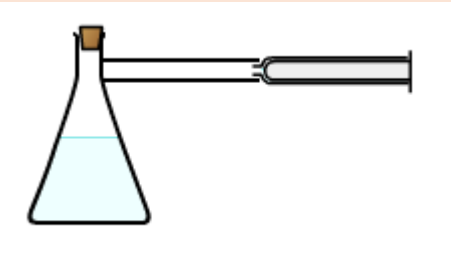
$$2H_2O_2 \rightarrow 2H_2O + O_2$$

In many living organisms, hydrogen peroxide, a product of metabolism, is toxic when concentrations build up. Therefore the catalyse enzyme breaks it down.

1. Measuring the rate of gas released:

The volume of oxygen released during the decomposition may be measured by connecting a gas syringe to a Buchner flask or Hirsch tube. An alternative method is to invert a measuring cylinder (or burette), that is filled with water, into a water trough. The reaction is conducted within a test tube and a delivery tube transports the gas released into the inverted cylinder in the water trough. This will gradually displace the water in the cylinder so the volume of gas released can be measured. The latter is called “collecting gas over water”.





In order for as much gas as possible to be collected, the system needs to be gas tight. This can be achieved by securely fitting delivery tubes, sealing them with grease (Vaseline) and ensuring holed bungs are tightly fitted.

A stopwatch may be used to measure the time. You can either measure the volume of gas at given time intervals or measure the time taken for given volumes of gas to be released.

A graph can then be plotted for the volume of gas released over reaction time. The gradient represents the rate of reaction.

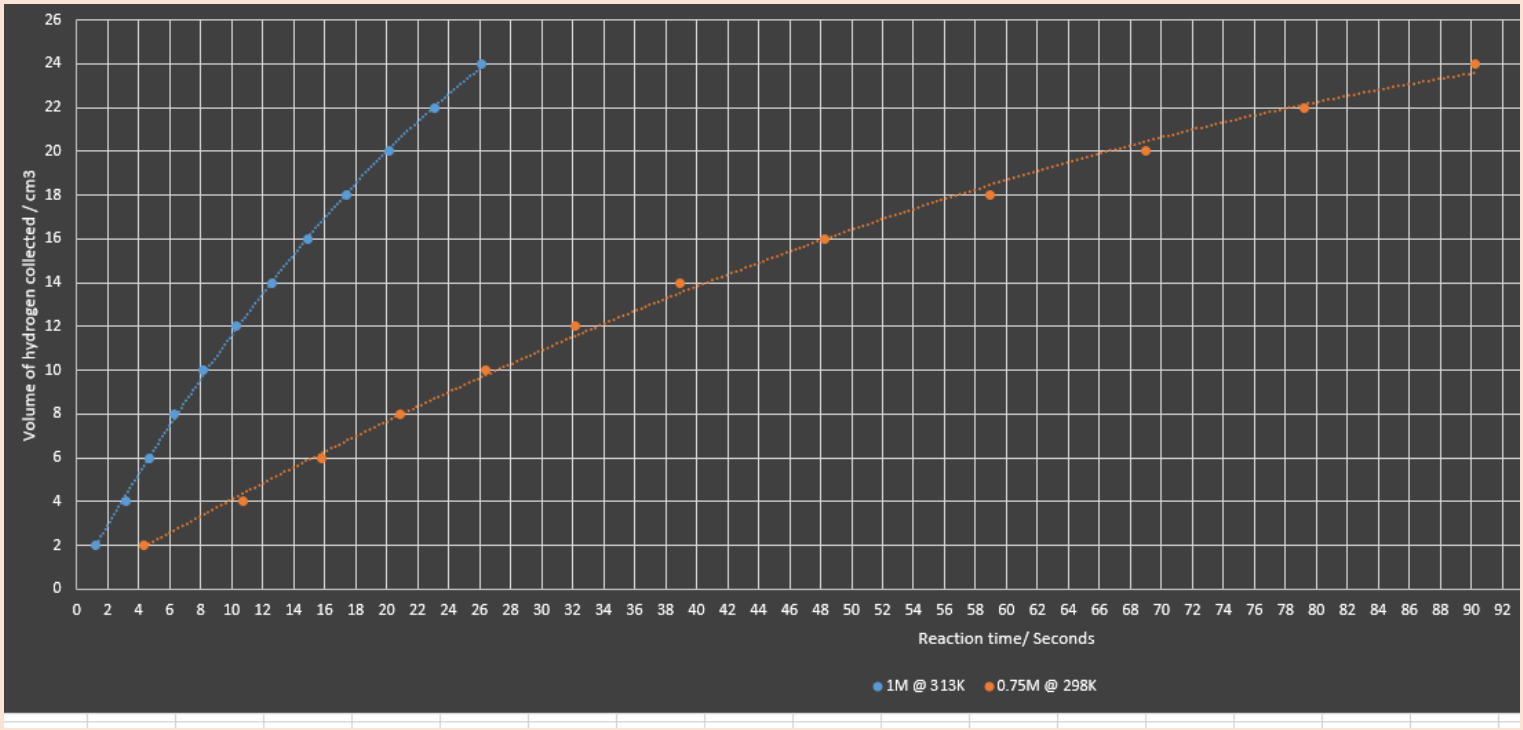
A gradient can be calculated at the very start of the reaction by drawing a tangent to the curve close to the origin. The lien is extended as far as possible to make a `triangle’. The change in volume is calculated for this tangent and divided by the change in time.

The procedure is repeated for another point on the curve further into the reaction.

The reaction rate decreases as the reaction progresses since the concentration of reactant molecules are decreasing so there are fewer collisions between reactant particles per unit time.

The rate of a reaction will plateau until it reaches 0 this signifies the reaction is complete or has reached equilibrium.

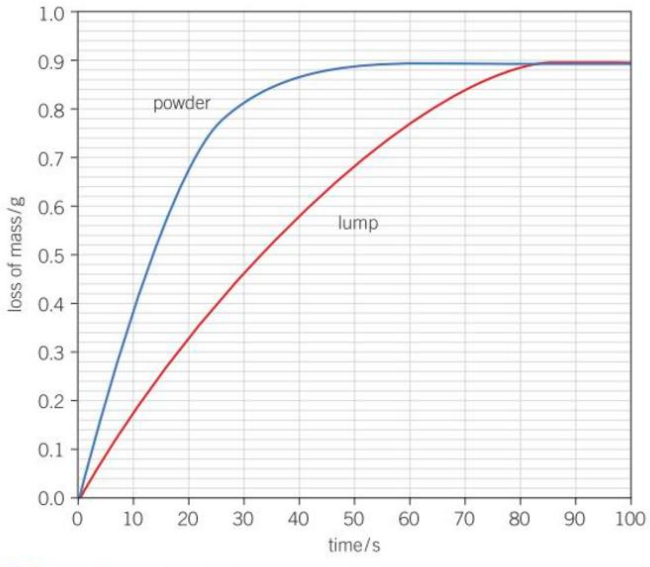
For example, for the reaction Mg + 2HCL → $MgCl_2$ + H_2



The blue curve shows the same reaction at a higher temperature and with a higher concentration of acid. The curve is steeper and plateaus sooner than the orange curve. Although neither reaction was continued to completion, it is clearly evident that the blue curve reaction took place at a faster rate.

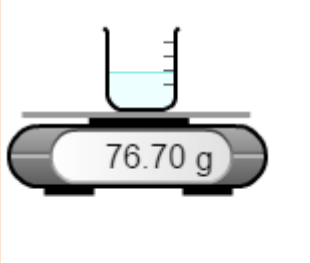
2. Measuring the mass lost from a reaction

A different way of measuring the same reaction is to measure the rate at which `mass is lost'. Following the ideas of the conservation of mass, no mass is really destroyed. It is just converted to another physicals state/phase. In most cases a gas. Calcium carbonate (marble chips) could be mixed with concentrated sulfuric acid in a beaker placed on a digital top pan balance. The initial mass is recorded.
At given time intervals the mass can be read of the balance. The mass decreases a the reaction progresses since carbon dioxide gas is given off.



▲ Figure 4 *Recording the loss in mass*

The graph's gradient shows a rate of reaction. Using a powdered form of a solid reagent compared to a lumpy form will increase surface area. This results in more frequent collisions between reagent particles so increases the reaction rate.



3. Measuring the change in PH

This is common for neutralisation/ acid-base reactions.

A solution of hydrogen peroxide, sodium hydroxide (a strong base) and sodium ethanoate (to act as a buffer) is mixed. This solution will initially be alkaline. Then sodium thiosulfate is added: Hydrogen peroxide oxidises sodium thiosulfate to sulfuric acid.

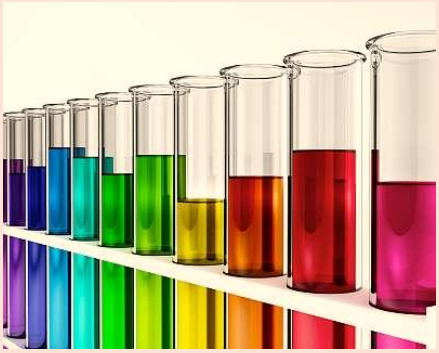
As the reaction progresses (and sulfuric acid is produced) it will gradually neutralise the sodium hydroxide.

The resulting pH change can be followed using a Universal indicator which changes from blue to green to yellow to orange-red during this reaction.

Adding an ammonium molybdate catalyst speeds up the colour change.

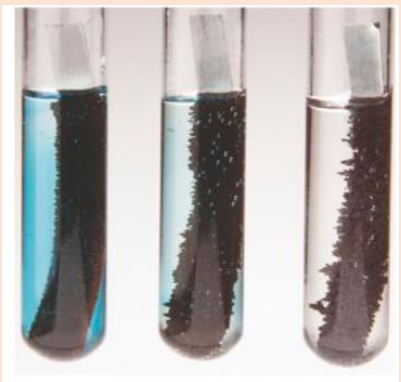
$$Na_2S_2O_3(aq) + 4H_2O_2(aq) \rightarrow Na_2SO_4(aq) + H_2SO_4(aq) + 3H_2O(l)$$

$$\mathbf{2\ NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2\ H_2O}$$



4. Colorimetry

A colorimeter (not to be confused with a **calor**imeter) measures the change in colour of a reaction. When zinc reacts with aqueous copper (II) sulphate the blue colouration of the copper sulphate solution decreases and the reaction can be followed.
A colorimeter (or visible spectrophotometer) is used to determine the concentration of a coloured solution. Coloured solutions can absorb certain wavelengths of light. The amount of this light that is



▲ **Figure 5** *When zinc reacts with copper sulfate solution the blue colour of $CuSO_4$ fades*

either absorbed - or transmitted through the solution and received by a detector - can be measured. This is proportional to the solution concentration.

A less sophisticated technique could be to place a card with a black cross beneath a beaker, during a precipitation reaction the solution becomes more clouded until eventually, you can no longer see the cross when looking down at the beaker through the solution. This can be timed.

5. Chemical analysis

The chemical analysis involves taking samples of the reaction mixture at regular intervals and stopping the reaction in the sample (quenching it), before analysis.

Iodine and propanone react in the presence of an acid catalyst. A sample can be extracted from the mixture and quenched by the addition of a base such as sodium hydrogen carbonate.
This neutralises the acid catalyst effectively stopping the reaction in the sample from progressing. The amount of unreacted iodine can then be determined using a sodium thiosulfate titration.

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

Brown — Pale yellow

We tend to add a starch solution which is initially blue/black in the presence of iodine and will turn colourless at the endpoint of the titration.

NOTE: Add the starch solution when the iodine + sodium thiosulfate mix starts to turn pale yellow/a straw colour as this signifies it is near the endpoint but not at the endpoint. We do not add starch before this point because the iodine will stick to the starch and won't react as expected with the thiosulfate, making the result unreliable.

Factors affecting the rate of a reaction:

1. **Presence of a catalyst** (offers reactions an alternative pathway of lower activation enthalpy)
2. **Surface area** of reagents/catalyst (the larger the surface area of solid exposed, the more frequent the collisions)
3. **Temperature** (Nearly all reactions go faster at higher temperatures)
4. **Concentration** (mol dm^{-3}) / **Pressure** (in gases concentration is proportional to pressure)
5. **Intensity of radiation** (especially UV for radical formation or ionisation)
6. **Kinetic energy** (stirring/shaking a reaction)