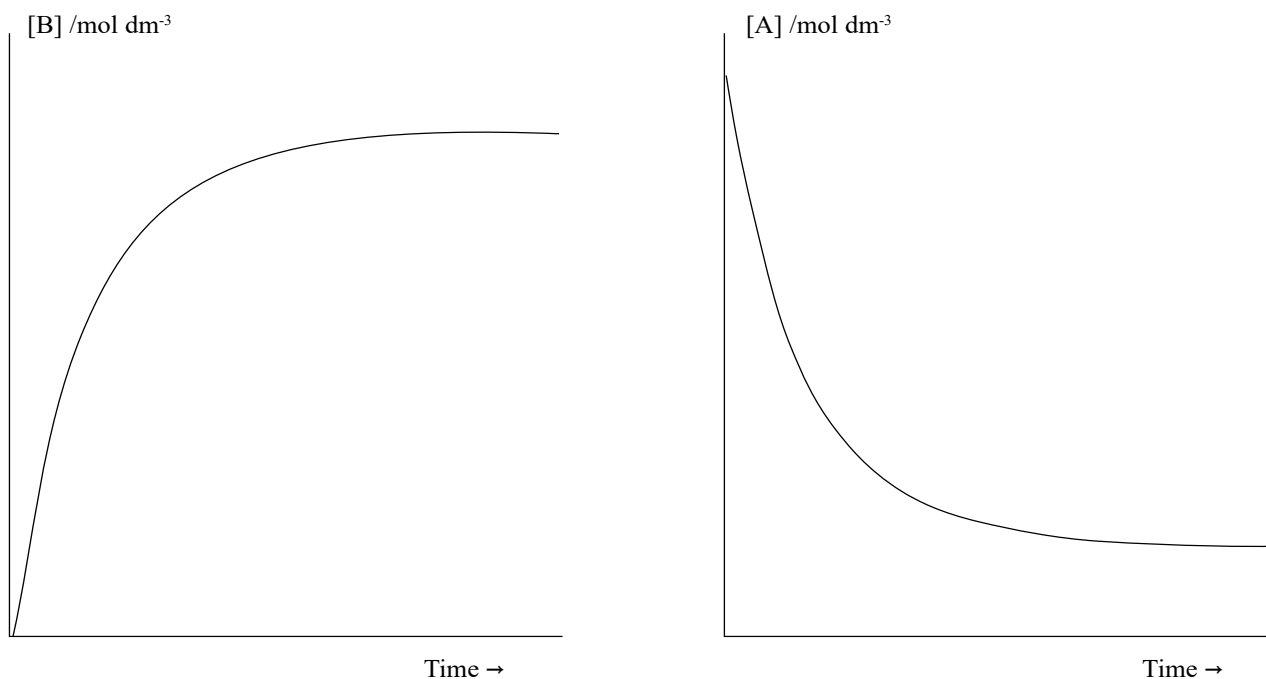# Measuring Rates of Reaction

There are many different ways of measuring the rate of a reaction. Depending on the nature of the reaction, certain methods of measurement are more practicable in the laboratory than others.

For the reaction $A \rightarrow B$,

Fig. 1

[B] /mol dm⁻³ vs Time → ; [A] /mol dm⁻³ vs Time →

All methods measure either the amount of product formed per unit time,

$Rate = \dfrac{d[B]}{dt}$, or the amount of reactant removed per unit time,

$Rate = \dfrac{-d[A]}{dt}$.

Typically, the rate of a reaction is quantified by measuring how quickly the concentration of a product or reactant changes. This yields the standard unit for the rate of a reaction, $mol\ dm^{-3}\ s^{-1}$. However, it is not always possible or simple to measure changes in concentration with time and so alternative methods are required.

Measuring the rate of appearance of a product
### 1. Collecting a gaseous product
Example reaction
$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$
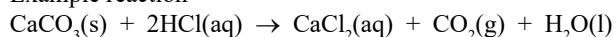
This is one of the simplest methods for measuring the rate of a reaction and can be implemented easily in school laboratories. Depending on the nature of the gas produced, one of two variations can be adopted.

Where the gas produced is insoluble or has sparing solubility in water, the gas can be collected by downward-displacement of water as shown in Fig. 2. Gases that can be collected this way include: hydrogen, carbon dioxide and oxygen. A gas burette provides a more precise measurement than a measuring cylinder but retains a smaller volume of gas.

Fig. 2

delivery tube; bung; reaction mixture; water filled measuring vessel; water filled through
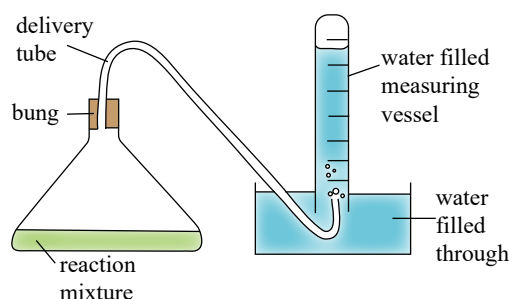
Where the gas produced is soluble in water, the gas should be collected using a glass gas syringe. Gases that should be collected this way include: ammonia, hydrogen halides, sulfur dioxide and nitrogen dioxide.

The **average** rate of the reaction can be determined by timing how long it takes to produce a specific volume of gas or the volume of gas produced in a pre-determined time period can be recorded. To find the **initial** rate of the reaction, the volume of gas should be recorded continually from the moment the reaction begins. A graph of volume of gas (y) versus time (x) should be plotted and the gradient of the steepest section of the curve calculated (see Fig. 3). A typical unit for rate yielded from the above methods is $cm^3\ s^{-1}$.

Fig. 3
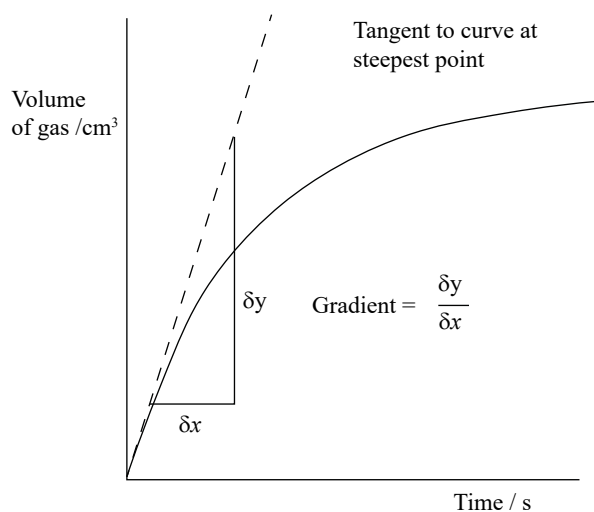
It is possible to perform a moles calculation using the volume of gas produced to determine the change in concentration of the reactants or products in aqueous solution, this gives mol dm^{-3} s^{-1}.

2. Mass loss

The example reaction given above can also be monitored using a mass loss technique as shown in Fig. 4 . The reaction takes place in an open vessel, e.g., conical flask, which has some cotton wool placed in its neck. The reaction mixture is placed on a digital balance and its mass is recorded over a period of time. The cotton wool in the neck of the flask allows the gas to escape into the atmosphere but retains any liquid substances. As the gas escapes the total mass of the reaction mixture decreases over time.

Fig. 4
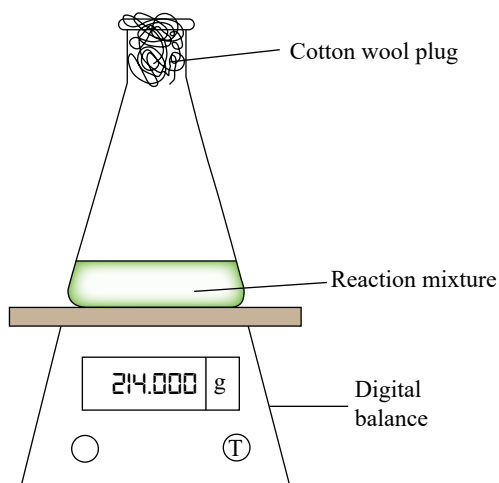
The **average** rate of the reaction in, for example, g s^{-1}, can be determined by dividing the total mass loss by the time taken. The **initial** rate of the reaction can be determined by plotting a graph of mass (y) versus time (x) and finding the gradient of the steepest section of the graph produced as shown in Fig. 5.

Fig. 5
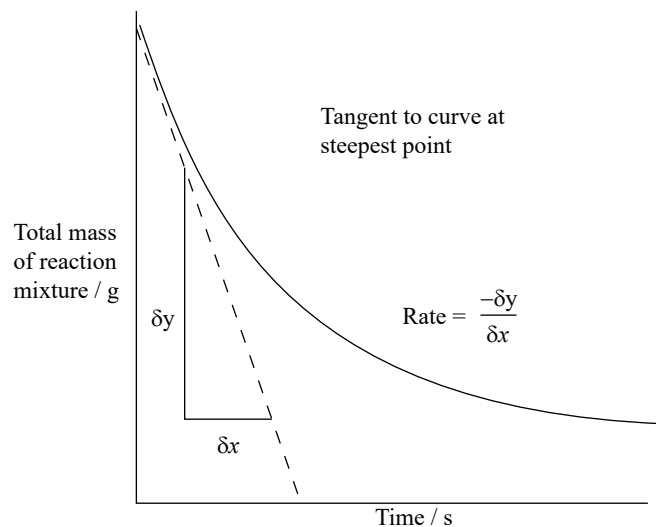
3. Light absorption of a coloured product:

If the product of a reaction absorbs visible light, for example, 1,2-benzoquinone produced by the oxidation of catechol, the rate of its appearance can be quantified using **colorimetry**.
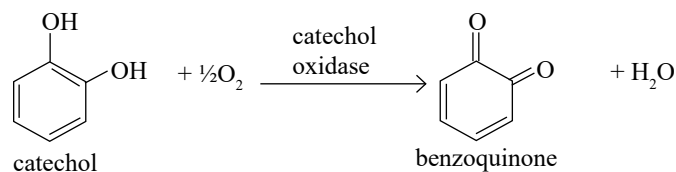
Colorimetry involves shining light of a particular wavelength (one that is absorbed by one of the substances present) through the reaction mixture and measuring the intensity of light that passes through the mixture as a function of the intensity of the original light source. As more product is formed, the intensity of the light passing through the mixture decreases (as more light is absorbed by the product). Typically, colorimeters give a digital output in arbitrary units of **absorbance**. As with the collection of gas method, the time taken to reach a particular value of absorbance or the absorbance reading after a set period of time will yield the **average** rate of the reaction. Finding the gradient of the steepest section of a plot of absorbance (y) versus time (x) will yield the **initial** rate in units of, e.g., s^{-1}.

Absorbance is directly proportional to concentration and either a calibration curve or the Beer-Lambert Law, $A = \varepsilon cl$, can be used to convert the absorbance readings to concentrations and give rate as mol dm^{-3} s^{-1}.

4. Clock reactions
Example reaction
$2KI(aq) + H_2O_2(aq) + H_2SO_4(aq) \rightarrow I_2(aq) + K_2SO_4(aq) + 2H_2O(l)$
In the above reaction, the reactants are colourless but the iodine produced forms a yellow-brown solution. This could be quantified using colorimetry but it is also possible to convert this reaction into a so-called clock reaction. In a clock reaction, a substance is added that immediately reacts with one of the products of the main reaction (in a side-reaction) thereby delaying the appearance of this product until all of the additional substance is used up. Typically, some form of indicator is added so that as soon as the side reaction finishes and product appears permanently, there is a rapid and obvious colour change.

In the example reaction given, a small, known amount of sodium thiosulfate solution, $Na_2S_2O_3(aq)$, is added. This reacts with the iodine as soon as it is formed and converts it back to iodide ions.

$$2Na_2S_2O_3(aq) + I_2(aq) \rightarrow 2NaI(aq) + Na_2S_4O_6(aq)$$
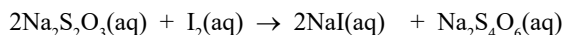
No colour change occurs until all of the sodium thiosulfate solution has reacted. Once this happens, any iodine formed remains in solution. Some starch solution is normally included in the reaction mixture so that when the first trace of iodine appears permanently it suddenly forms a vivid blue-black complex with the starch.

Iodide mixed with acidified peroxide to start reaction to produce iodine	Iodine instantly converted back to iodide by thiosulfate in mixture → no colour change	All thiosulfate in mixture consumed → colour change to blue-black by I_2 complexing with starch

$$t = 0 \qquad t < t_{rx} \qquad t = t_{rx}$$
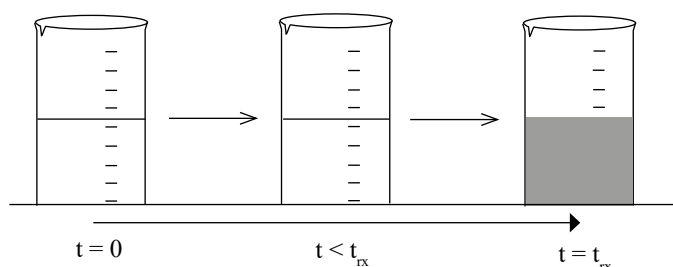
The rate of reaction can be determined by timing how long it takes (t_{rx}) for the reaction to change from colourless to blue-black. Taking the reciprocal of the time taken ($1/t_{rx}$) yields the rate of reaction in units of s^{-1}. It is possible to perform a moles calculation using the known amount of sodium thiosulfate added initially in order to find the rate in $mol\ dm^{-3}\ s^{-1}$. As the rate is only determined from a single point, the rate determined is the **average** rate of the reaction. It is not possible to determine the initial rate using this method.

5. Formation of a precipitate
Example reaction
$$Na_2S_2O_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + S(s) + SO_2(g) + H_2O(l)$$
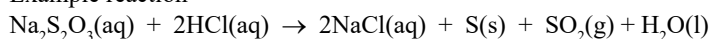
For reactions in which a precipitate forms slowly, the **average** rate of the reaction can be determined by trying to measure the time it takes to produce a fixed quantity of precipitate. This is usually done via a crude method in which the reaction takes place is a glass vessel placed above a dark cross. The experimenter observes the reaction from directly above and attempts to determine when the cross beneath the vessel has been completely obscured.

observer's eye

glass vessel

reaction mixture

black cross drawn on surface under reaction vessel
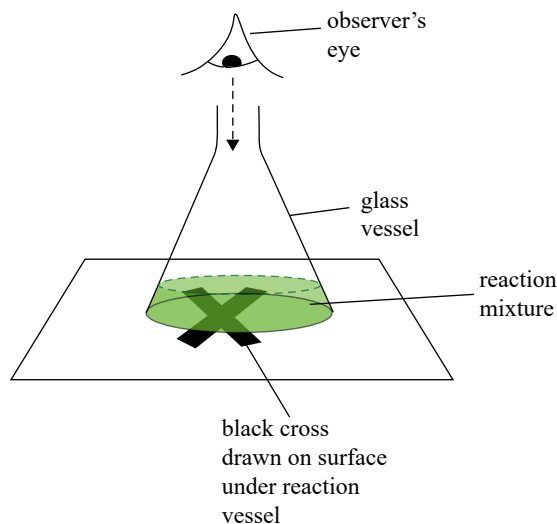
This method is subject to numerous errors but, with practice it can yield useful data. The **average** rate of the reaction, in s^{-1}, can be calculated by taking the reciprocal of the time taken for the cross to be obscured.

6. Other methods
Depending on the reaction it may also be possible to determine the rate of a reaction by measuring:
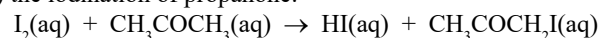
(a) the change of pH of the solution with time: any reaction which involves changes in concentrations of H^+ or OH^- should give a change in pH over time. However, due to the logarithmic nature of pH, sometimes the change may be too small to measure with any great precision.

(b) the change in electrical conductivity with time: any reaction that involves a change in the number of free ions present in solution should give a change in the electrical conductivity of the solution over time. Reactions that produce an ionic or metallic precipitate or produce covalent compounds from ionic ones could potentially be monitored this way.

Measuring the Rate of Disappearance of a Reactant
Most reactions performed at school in order to determine a rate of reaction involve measuring the rate of formation of a product. The techniques used to measure the disappearance of a reactant are similar, if not identical, and are used when the formation of a product cannot be quantified easily.

Examples of reactions that measure the disappearance of a reactant include:

(a) the iodination of propanone:
$$I_2(aq) + CH_3COCH_3(aq) \rightarrow HI(aq) + CH_3COCH_2I(aq)$$
In this case, the initial mixture is coloured and the products are colourless so the time it takes for the initial colour (of the iodine solution) to disappear can be measured. This can be done by eye or using colorimetry.

(b) $Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$
In this case, one of the reactants is a solid and neither of the products is solid. The **average** rate of this reaction, and those like it, can be measured by timing how long it takes for all of the solid to disappear (assuming it is the limiting reactant).

There are more sophisticated techniques that can be employed in industrial or research settings to measure the rates of more complex or obscure reactions. The methods detailed above are those that can be used within the setting of the school laboratory with relative simplicity.

Questions

1. Suggest, with reasons, which methods for measuring the rate of a reaction would best apply to the following reactions:
   (a) oxidation of a secondary alcohol using acidified potassium dichromate(VI) solution.
   (b) production of chlorine gas from concentrated HCl and solid potassium manganate(VII).
   (c) reaction of marble chips with dilute nitric acid.

2. Why is it **not** effective to measure the rate of the reaction, $Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$ via the mass loss technique?

3. When measuring the rate of formation of a precipitate by observing a cross beneath the reaction mixture, why is it essential to keep the total volume of the solution and the apparatus used the same across all experiments?

Answers

1 (a) Colorimetry (mixture changes colour from orange to green), pH change (initial solution is acidified and H^+ is removed; though pH change may be very small), electrical conductivity change (the number of ions is reduced significantly as the reaction progresses).

   (b) Collection of gas using a gas syringe (product is gaseous but soluble in water).

   (c) Collection of gas using downward-displacement of water or a gas syringe (gaseous product is only sparingly soluble in water), mass loss (gaseous product can be lost to the atmosphere and has significant mass), disappearance of solid reactant (marble chips are converted to a salt solution and will disappear if limiting), pH change (the acid is neutralised by the marble chips and so the pH changes, works best if acid is limiting).

2. H_2 is a light molecule and so the amount of mass that is lost as hydrogen gas is very small and difficult to measure on typical school laboratory balances.

3. Ensures the depth of the solution above the cross is the same and so the amount of precipitate required to obscure the cross is similar between experiments.