

Rates part 1

Kinetics just means how fast a reaction occurs. Remember from AS that if you increase the temperature, concentration, pressure, surface area or add a catalyst, then a reaction will go faster.

Finding the rate

The rate of a reaction **cannot be measured** directly in a laboratory. To work out the rate, a chemist has to calculate it from something that can be measured in a laboratory.

By definition, the rate is the **change in something measurable per unit time**. This “something” is commonly concentration, volume, mass, conductivity or absorbance.

- ✓ Another definition of rate is $1/\text{time}$. This should be common sense....if it takes longer, it is a slower rate.

Monitoring a reaction

As was said above, you have to be able to measure something to get the rate. There are several easy ways that vary depending on the reaction.

1. Colorimetry

You would use this if there was a colour change involved in the reaction. You should be looking out for the use of iodine or bromine (coloured), which can be reduced to I^- or Br^- (colourless). Other common coloured substances MnO_4^- (purple) or $\text{Cr}_2\text{O}_7^{2-}$ (orange).

2. Mass/volume

If a reaction involves a gas being given off then there will be a change in mass as the reaction proceeds. You could also collect the gas and measure how the volume of gas you collect over time.

3. Conductivity

If you have a reaction where the number of ions changes then there will be a change in conductivity. This isn't very common in questions.

4. Concentration

The most important method for this topic. In a laboratory they would take a sample from the reaction mixture at various times and then titrate it to work out the concentration.

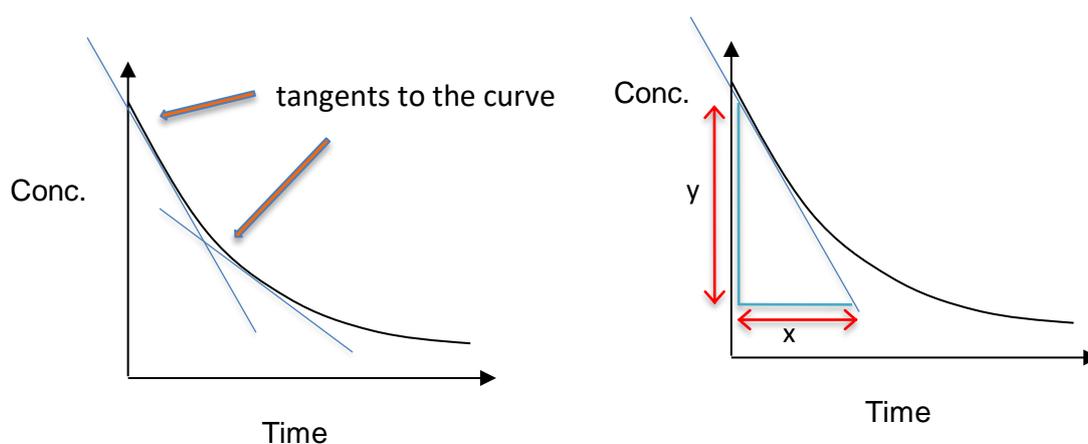
You need to 'quench' the sample after removing it to stop any further reaction. For example, if the reaction required an acid catalyst you could add a base to neutralise the acid and stop the reaction. Another way to quench is to add cold water.

- ✓ There maybe other things that you could measure such as pH. It's not limited to the list above. Concentration is by far the most common thing to look at.

A typical experiment

A very simple experiment is to measure how the concentration of a **reactant** varies with time and from that the rate can be calculated. A chemist would remove some of the sample at various time intervals, and titrate to find the concentrations.

The concentration obviously decreases as the reaction proceeds as you are using up the reactant. A chemist can then plot a graph of concentration versus time. An example is shown below. The **gradient then gives the rate**.



A chemist would draw a **tangent to the curve** at several points (shown above) to give different rate values at different concentrations. These rate values are then plotted against the concentration (see later).

A gradient is the **change in y/change in x**. So all you have to do is pick two points on the tangent line and then draw a little triangle as shown in the right hand graph above. Measure distance y and distance x then divide $y/x \rightarrow$ gradient (rate).

- ✓ **Initial rate** is usually used in questions. This is the gradient at time = 0 i.e. the steepest part of the curve as shown in the left hand graph above. They might refer to this as the initial rates method.

Rate Equations

A rate equation shows how the rate is affected by changing the concentration of reactants.

We know that if you increase the concentration, then the rate will increase. The rate equation tells you by *how much* **each reactant** affects the rate.

In the reaction $A + B \rightarrow C + D$ the rate equation takes the format:

$$\text{rate} = k[A][B]$$

where k is just a constant (the rate constant). This is “little” k and has nothing to do with “big” K in the equilibrium or acid/base topics.

The rate depends **only** on the reactants, so we don't need to bother about the products in the equation.

This is only an introduction to rate equations, we will look at the “orders” below as those are needed to complete the rate equation.

✓ If you increase the temperature, the rate increases and k also increases.

The Orders

In the laboratory we can vary the concentration of one reactant at a time and see how it affects the rate. This requires keeping the concentrations of the other reactants constant. We can do this for all the reactants and see how changing their concentrations affects the rate → orders.

by what factor each reactant affects the rate is called the **order**

Orders are either zero, first or second for each reactant.

Zero order: a reactant has **no effect** on the rate when its concentration is varied. Therefore, it is not included in the rate equation.

1st order: a **linear relationship** between the concentration of the reactant and the rate i.e. if we double the concentration then we double the rate.

2nd order: a **squared relationship** between the concentration of the reactant and the rate i.e. if you double the concentration of the reactant then the rate will increase by a factor of four (as it will be 2 squared).

If we had a rate equation such as:



We would say that this reaction is first order with respect to A and second order with respect to B.

✓ The orders **cannot** be worked out from a chemical equation. Sometimes students see a number 2 before a reactant and assume that this means second order. It doesn't! The 2 is there to balance the number of atoms.

You can only get the orders from experimental data

For example:



Someone might think that N_2O_5 is second order but from experimental data it's 1st order.

The rate equation is:

$$\text{rate} = k[\text{N}_2\text{O}_5]$$

Overall order

The overall order of a reaction is easy, all you have to do is add up the individual orders of the reactants.

So for the equation: $\text{rate} = k[\text{A}][\text{B}]^2$ we would say that the overall order is 3 (1 from A and 2 from B).

- ✓ Overall orders can be any number but individual orders can **only** be 0, 1st or 2nd. Be careful not to get these mixed up.