

## How Fast? : The kinetics of reactions

We study the rate of reactions and factors that affect it:

- in order to be able to control reactions
- to gain insights into how reactions actually work (their mechanism)

We have already defined the rate of a reaction as:

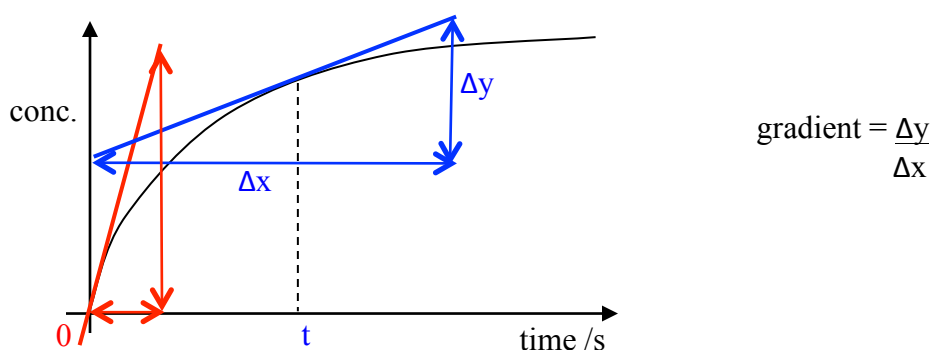
$\text{rate} = \frac{\text{change in concentration of reactant or product}}{\text{time taken for the change to take place}}$ <p style="text-align: center;">the UNITS of rate are therefore <math>\frac{\text{moles per dm}^3}{\text{second}}</math>      <b>mol dm<sup>-3</sup> s<sup>-1</sup></b></p>
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### Measuring the rate of a reaction

By **continuous monitoring**, we can construct a graph that shows the change in amount of a product or reactant as the reaction proceeds. We could, for example:

- measure pH with a probe/by titration during acid/base reactions
- measure volume of gas produced or loss in mass of reactants for a reaction that produces a gas
- measure changes in colour e.g. absorption of a specific wavelength as a coloured species is used or formed (this is called **colourimetry**)
- measure the opacity of a solution as a precipitate is formed

The gradient of such a graph at any time,  $t$ , gives the **rate of reaction at that time**. We have already seen that we can calculate the gradient by drawing a tangent to the curve and calculating its gradient. In particular, this method allows us to determine the rate at time = 0, which we call the **initial rate**. Note: we don't worry about the sign. The "changes in" are both taken as positive.



### Rate with respect to what?

We should be careful to talk about the rate of disappearance of reactant 'x' or the rate of formation of product 'y', rather than just 'the rate'. Because of the **stoichiometry**

(mole ratios), we may get a different value for the rate of the same reaction depending on which reactant or product we choose to measure.



Lets say we measure the rate of disappearance of  $\text{I}_2$  and find that it is  $1.00 \text{ mol dm}^{-3} \text{ s}^{-1}$   
The equation tells us that one mole of  $\text{I}_2$  makes 2 moles of HI, so the rate of appearance of HI will be  $2.00 \text{ mol dm}^{-3} \text{ s}^{-1}$

*Key points to watch out for in A-level questions:*

- *the rate of disappearance of a reactant will not necessarily be the same as the rate of appearance of a product; you've got to check the mole ratios*
- *exam questions may talk about "the rate" of a reaction without being specific. They mean the rate with respect to whatever reactant or product is being monitored, and this may not be specified. So long as the same substance is monitored in all such experiments "the rate" is sufficient.*

### **Determining orders for reacting species**

Each reacting substance (including any catalysts) contributes to overall rate of the reaction. The way in which each affects the rate gives us valuable information about how the reaction works. We determine the effect each reactant has on the rate experimentally.

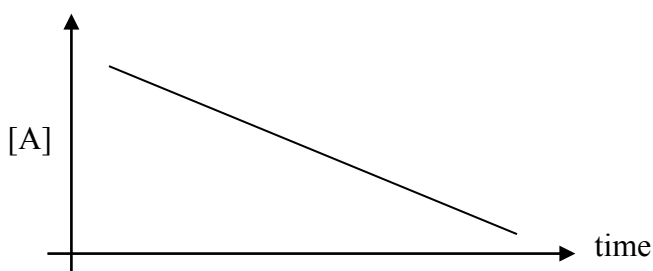
We call the effect the concentration of a reactant has on the rate of a reaction the ORDER with respect to that reactant.

For a reactant A:  $\text{rate} \propto [\text{A}]^a$   
where a is 0, 1 or 2 and is the ORDER with respect to A

#### Zero order

We may find experimentally that using different concentrations of A has no effect on the rate of the reaction.

The shape of a concentration vs. time graph for reactant A would be a straight line – the concentration of A will decrease steadily; the rate (gradient) would not change as A is being used up.

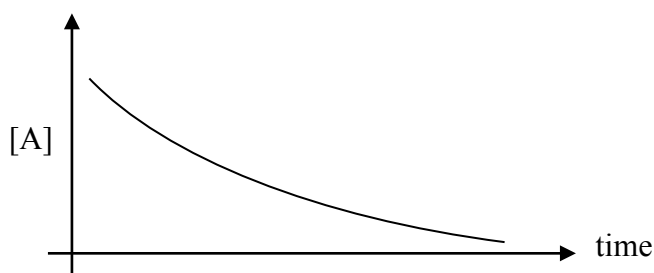


Mathematically, we can say that  $\text{rate} \propto [\text{A}]^0$  (N.B. anything to the power of 0 has a value of 1)  
 We say that the order is 0 with respect to A.

Why might this be the case – why might changing the concentration of a reactant have no effect on the rate of the reaction?

### First order

We might find experimentally that when we double the concentration of A, the rate of reaction doubles. As the reaction proceeds and the concentration of A decreases, the rate (gradient) decreases proportionally.

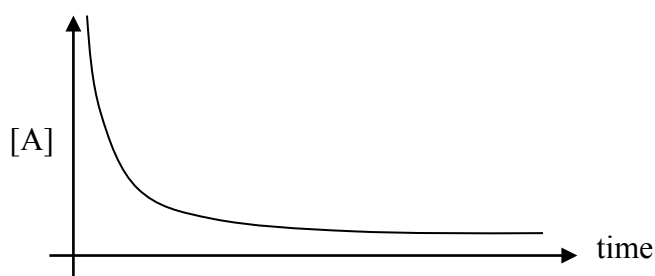


Mathematically, we can say that  $\text{rate} \propto [\text{A}]^1$  i.e.  $\text{rate} \propto [\text{A}]$  (N.B. anything to the power of 1 is itself)

We say that the order is 1 with respect to A. This is a very common situation.

### Second order

Sometimes we find that if we double concentration of A, the rate of the reaction increases by a factor of 4. As the reaction proceeds and A is used up, the rate decreases dramatically.



We can say that  $\text{rate} \propto [\text{A}]^2$ , and the order is said to be 2 with respect to A.

### **Overall order of a reaction**

The **overall order** of a reaction is the sum of the orders for each of the reactants.

For example, a reaction involving reactants A, B and C is zero-order with respect to A, first order with respect to B and second order with respect to C.

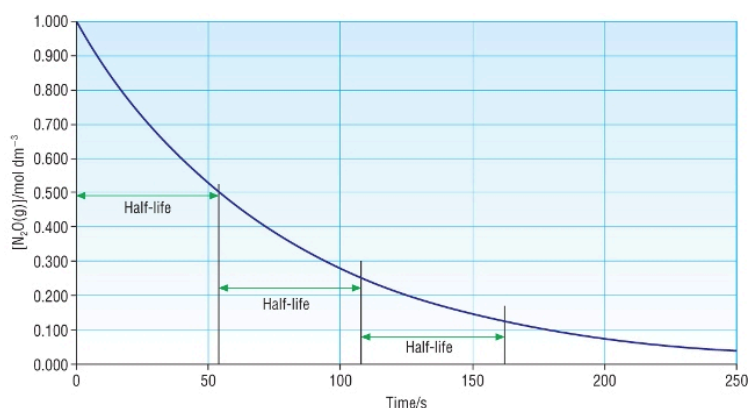
The overall order of the reaction =  $0 + 1 + 2 = 3$ . This reaction is third-order overall.

## Half-life, $t_{1/2}$

It is easy to spot when a reaction is zero-order with respect to a reactant from a graph of concentration of that reactant vs. time, but a little harder to tell first order from second order. Measuring the **half-life** allows them to be told apart, and provides other useful information.

The half life is defined as **the time taken for the concentration to reach half of its previous value**. This can be read off the graph.

When a reactant is first-order with respect to a reactant, **successive half-lives are equal** e.g. in the example below the concentration halves every 55 seconds.



In comparison:

For a second-order reaction the half-life increases as the reaction progresses.

For a zero order reaction the half-life decreases as the reaction progresses.

## Rate constant and Rate Equation

Rather than keep using  $\propto$  signs all the time we can write a **rate equation**:

This has the form **rate =  $k [A]^0 [B]^1 [C]^2$**  for a reaction that is zero order with respect to A, first order with respect to B and second order with respect to C. (This reaction is third order overall.)

We can simplify for powers of 0 and 1: **rate =  $k [B][C]^2$**

Here  $k$  is called the **rate constant**. The rate constant is different for every reaction, and depends on temperature, so the value of temperature is usually stated for a specific value of the rate constant.

**It is important to appreciate that because the orders with respect to each reactant are determined experimentally and cannot be obtained from a balanced equation, so the rate equation is found experimentally not from chemical equations.**

**Value and Units of the rate constant**

Once we know the rate equation we can measure the initial rate of reaction when we use reactants of known concentrations, and plug these values into the rate equation to determine the value of the rate constant.

e.g. The reaction  $2\text{H}_2 + 2\text{NO} \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$  is found experimentally to have the following rate equation: **rate = k [H<sub>2</sub>][NO]<sup>2</sup>**

When  $6.0 \times 10^{-3} \text{ mol dm}^{-3}$  of H<sub>2</sub> was reacted with  $3.0 \times 10^{-3} \text{ mol dm}^{-3}$  NO, the initial rate was measure to be  $4.5 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$ . Calculate the value of the rate constant.

$$\begin{aligned} \text{rearranging, } k &= \text{rate} / [\text{H}_2][\text{NO}]^2 \\ &= 4.5 \times 10^{-3} / (6.0 \times 10^{-3} \times (3.0 \times 10^{-3})^2) \\ &= \mathbf{8.3 \times 10^4} \text{ ...now we need some units...} \end{aligned}$$

**Units of the rate constant**

To get the units we need to remember that units of rate are  $\text{mol dm}^{-3} \text{ s}^{-1}$  and the units of concentrations are  $\text{mol dm}^{-3}$ . We can then substitute each part of the rate equation for its units, and cancel units where possible to simplify:

So in the example above,  $k = \text{rate} / [\text{H}_2][\text{NO}]^2$

$$k = \frac{\text{mol dm}^{-3} \text{ s}^{-1}}{[\text{mol dm}^{-3}][\text{mol dm}^{-3}]^2}$$

cancelling top and bottom: units of k are  **$\text{mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$**

We would find that k has the same units for any reaction that is third order overall.

Work out the units for k in the following situations:

- zero order overall:  $\text{rate} = k[\text{A}]^0$   $= \text{mol dm}^{-3} \text{ s}^{-1}$
- first order overall:  $\text{rate} = k[\text{A}]$   $= \text{s}^{-1}$
- second order overall:  $\text{rate} = k[\text{A}][\text{B}]$   $= \text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$

**Using graphs to calculate the rate constant (first order reactions)**1: using the half life

If we have a reaction that is first order, we can find the value of the rate constant directly if we work out the half-life from the concentration vs. time graph (remember for a first order reaction this is constant).

We use the relationship  $k = \ln(2) \div t_{1/2}$   $\ln = \text{natural logarithm}$   
the value of  $\ln(2) = 0.693$  to 3 sf.

This works because the concentration-time graph for a first order reaction has an exponential shape. The graph has the form  $[A] = [A_0]e^{-kt}$  where  $[A_0]$  is the initial concentration of A (at time = 0) and  $k$  is the rate constant.

We can rearrange this equation as  $kt = \ln[A_0]/[A]$

Then we use the fact that when  $t = t_{1/2}$  the concentration  $[A]$  is half of  $[A_0]$ , so

$$kt_{1/2} = \ln([A_0] / 2 \times [A_0]) = \ln(2) \quad \text{so} \quad k = \ln(2) / t_{1/2}$$

*You are not expected to be able to show how this equation is derived.*

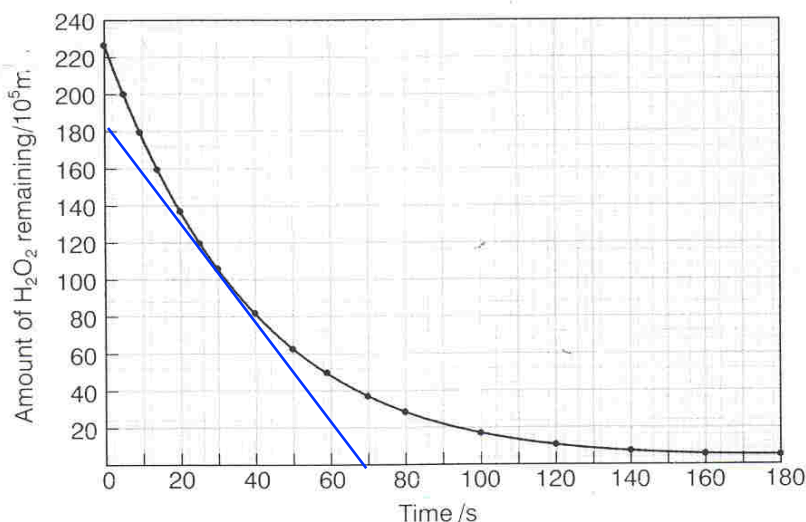
e.g. the half-life for the decomposition of  $N_2O_5$  is found to be constant, with a value of 100s. Determine (i) the rate constant, including units and (ii) the rate of this decomposition when the concentration of  $N_2O_5$  is  $0.120 \text{ mol dm}^{-3}$ .

i)  $k = \ln(2) / t_{1/2} = 0.693 / 100 = 6.92 \times 10^{-3} \text{ s}^{-1}$

ii)  $\text{rate} = k[N_2O_5] = 6.92 \times 10^{-3} \times 0.120 = 8.32 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$

## 2: using a tangent

For a reaction that is first order the rate equation has the form **rate = k[A]**, which can be rearranged to give **k = rate/[A]**. If we draw a tangent to the concentration vs. time graph at any time,  $t$ , we can calculate the rate of reaction at that time as it is equal to the gradient of the tangent. We can also use read off the concentration from the y-axis at the same time,  $t$ . These two values can then be used to calculate  $k$ .



e.g. The decomposition of hydrogen peroxide is a first order reaction.

At  $t = 30$  seconds a tangent has been drawn.

The amount of  $H_2O_2$  at this time  
 $= 102 \times 10^{-5} \text{ mol dm}^{-3}$

$$\text{Gradient of tangent} = \frac{182 \times 10^{-5}}{68} = 2.68 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$$

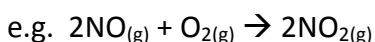
$$\text{Hence } k = \frac{2.68 \times 10^{-5}}{102 \times 10^{-5}} = 2.63 \times 10^{-2} \text{ s}^{-1}$$

### Initial Rates Method for constructing the rate equation

It isn't always possible to measure the concentration of every reacting species and track how it changes as the reaction proceeds to determine the order for that reactant.

So long as we can measure the change in concentration of ONE reactant or product with time, we can determine the order for ALL reacting species by a series of experiments, and hence construct the rate equation and determine the value of the rate constant.

What we do choose suitable initial concentrations for all the reacting species, measure the **initial rate** of the reaction (gradient at  $t = 0$ ), then repeat the experiment changing the initial concentration of one reacting species at a time and keeping the others fixed, and see what that does to the rate.



Experiment	[NO] in $\text{mol dm}^{-3}$	[O <sub>2</sub> ] in $\text{mol dm}^{-3}$	Initial rate in $\text{mol dm}^{-3} \text{s}^{-1}$
1	0.00100	0.00100	$1.82 \times 10^{-6}$
2	0.00100	0.00200 (x2)	$3.64 \times 10^{-6}$ (x2)
3	0.00200 (x2)	0.00100	$7.28 \times 10^{-6}$ (x4)

Comparing experiment 1 and 2 we can see that doubling the concentration of O<sub>2</sub> and keeping the concentration of NO the same has doubled the rate of the reaction. This means that the reaction is first order with respect to O<sub>2</sub>.

Comparing experiment 1 and 3 we can see that doubling the concentration of NO while keeping the concentration of O<sub>2</sub> the same has increased the rate x 4. This means the reaction is second order with respect to NO.

The rate equation is therefore  $\text{rate} = k [\text{O}_2][\text{NO}]^2$  and the overall order is 3<sup>rd</sup>, so units for the rate constant can be worked out as  **$\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$**

We can then take the concentration values from any of the experiments and use them to find the value of the rate constant. Using experiment 2:

$$k = 3.64 \times 10^{-6} / (0.002 \times 0.001^2) = \mathbf{1,820 \text{ mol}^{-2} \text{dm}^6 \text{s}^{-1}}$$

### Using graphical data

Basing a decision as to how rate is affected on a single comparison can be unreliable, so we can try a range of initial concentrations for each reactant in turn while keeping the initial concentrations of other reacting species the same. We would then plot a graph of how the initial rate (y-axis) varied as we changed the initial concentration for each reactant. The shapes of these **rate vs. concentration** graphs tell us the order with respect to each reactant, and some can be used to calculate the rate constant,  $k$ .

Measuring initial rate in practice

It is not always necessary to monitor continuously through a reaction and to determine the initial rate from a concentration vs. time graph. We may be able to measure the time taken for the reaction to proceed to a known point e.g.

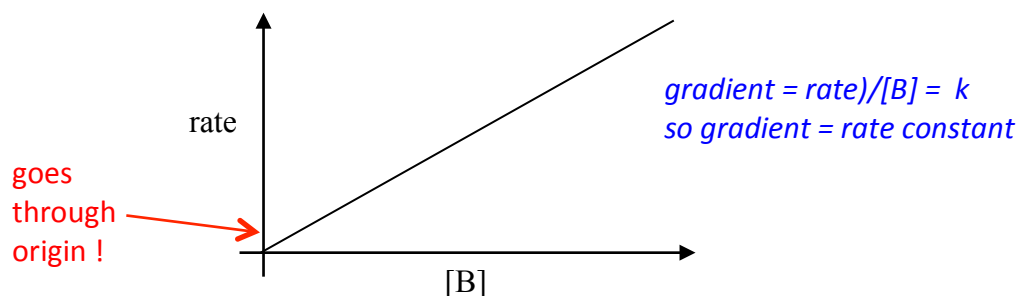
- for a specified volume of gas to be collected
- for a colour to reach a specified intensity
- for a cross to disappear, or a colour to appear (clock reactions)

If we measure time taken to that point, then  $(1 \div \text{time})$  can be taken as an approximate measure of the initial rate. **N.B. If timing with a stopwatch, the subjective nature of the measurement means we can only measure to THE NEAREST SECOND, and we must remember to not to increase the number of significant figures when we calculate  $(1 \div \text{time})$ .**

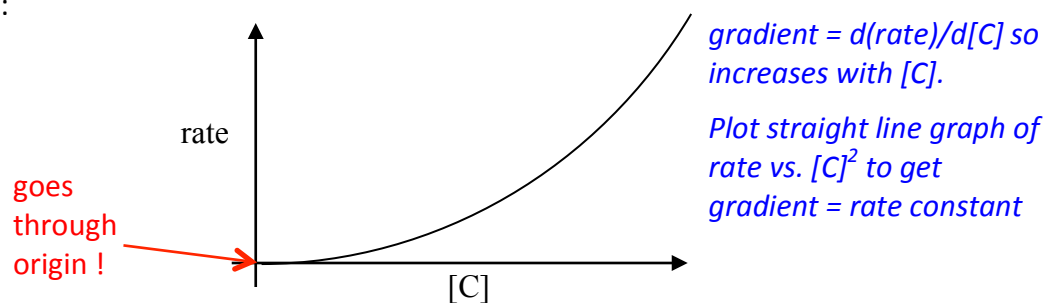
For a reactant A that is zero order, as the concentration of A changes, the rate is unaffected:



For a reactant that is first order, when the concentration of B is doubled, the rate also doubles:



For a reactant that is second order, when the concentration of C is doubled, the rate is quadrupled:





**More about the rate constant**

The rate constant tells us how fast the reaction will be

- high values of  $k$  mean fast reactions
- low values of  $k$  mean slow reactions

The rate equation shows that the rate of reaction depends on  $k$  and on the concentrations of reactants.

The Boltzmann distribution shows that the rate of reaction depends on the activation energy,  $E_A$ , for the reaction and on the temperature. When we increase the temperature without changing the concentration of the reactants, the rate of reaction increases. This means the rate constant must have increased.

This relationship between these is expressed in the Arrhenius Equation:

$$k = A \exp(-E_A/RT)$$

$k$  = the rate constant ( $\text{mol dm}^{-3} \text{s}^{-1}$ )  
 $A$  = the pre-exponential factor; a constant  
 $E_A$  = activation energy in  $\text{J mol}^{-1}$   
 $R$  = the gas constant:  $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$   
 $T$  = the temperature in Kelvin (K)

This is a powerful equation, providing a direct link between the activation energy and the rate of reaction at a given temperature. We see that there are two parts that combine to give a value for the rate constant:

The **pre-exponential factor,  $A$** : this is a measure of the frequency of collisions with the correct orientation to react successfully (regardless of the energy of the colliding particles).

The **exponential term,  $\exp(-E_A/RT)$** : this is a measure of the fraction of the particles which have energy sufficient to react successfully (i.e. have energy above the activation energy).

By measuring the rate of reaction at different temperatures, we can determine experimentally the activation energy (and pre-exponential factor) for a reaction:

Taking natural logarithms:  $\ln(k) = -E_A/RT + \ln(A)$

This is the equation of a straight line ( $y=mx + c$ ). We can calculate from the measured rates of reaction and the concentrations we used the values of  $k$  at a range of temperatures,  $T$ . We can then plot  $\ln(k)$  on the y-axis vs.  $1/T$  on the x-axis. The graph will be a straight line with gradient =  $-E_A/R$  and y-axis intercept =  $\ln(A)$ . In this way both  $E_A$  and the pre-exponential factor  $A$  can be obtained from the graph.

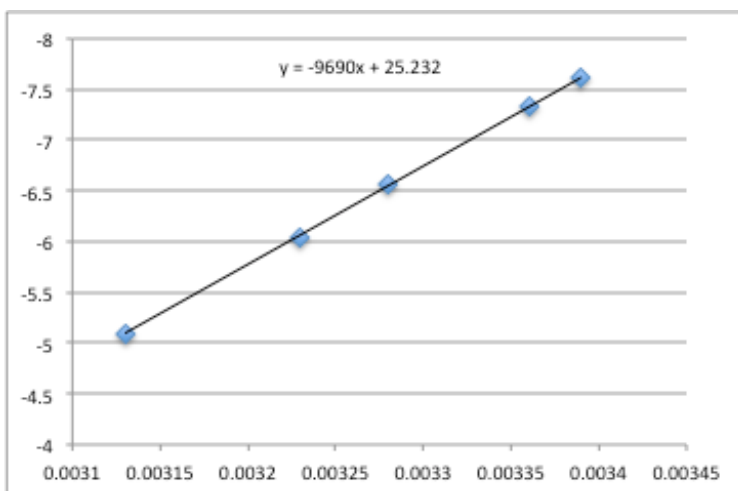
e.g. The decomposition of  $0.88 \text{ mol dm}^{-3}$  (10 vol) hydrogen peroxide was investigated at a range of temperatures. The reaction  $\text{H}_2\text{O}_2(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \frac{1}{2}\text{O}_2(\text{g})$  is first order, with a rate equation of  $\text{rate} = k[\text{H}_2\text{O}_2]$ . The following results were obtained.

$[\text{H}_2\text{O}_2]$ in $\text{mol dm}^{-3}$	Temp. in K	Initial rate in $\text{mol dm}^{-3} \text{ s}^{-1}$
0.880	295	0.000434
0.880	298	0.000577
0.880	305	0.00123
0.880	310	0.00208
0.880	320	0.00539

We need to calculate the sets of values to plot on the graph:

Initial rate	$k = \text{rate}/[\text{H}_2\text{O}_2]$	$\ln(k)$	Temp, T	$1/T$
0.000434	0.000493	-7.61	295	0.00339
0.000577	0.000656	-7.33	298	0.00336
0.00123	0.001398	-6.57	305	0.00328
0.00208	0.002364	-6.05	310	0.00323
0.00539	0.006125	-5.10	320	0.00313

And plot  $\ln(k)$  on the y-axis vs.  $1/T$  on the x-axis:



From the linear line of best fit we can determine that the gradient =  $-9690 \text{ K}$  and the intercept =  $25.232$

Hence  $-E_A/R = -9690 \text{ K}$  so  $E_A = 9690 \times 8.324 = 80563 \text{ J mol}^{-1} = \mathbf{80.6 \text{ kJ mol}^{-1}}$  (to 3 sf)

And  $\ln(A) = 25.232$  so  $A = \exp(25.232) = \mathbf{9.08 \times 10^{10}}$

## Determining Reaction Mechanisms

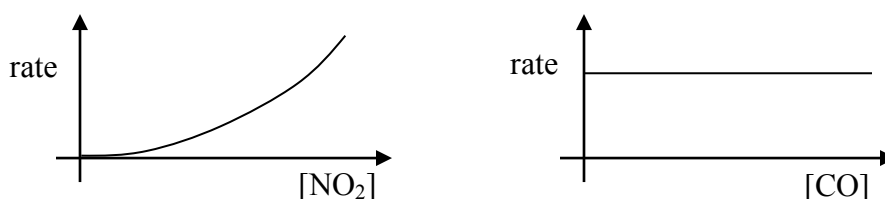
Reactions occur in a sequence of steps (a mechanism). The products from one step are often the reactants for subsequent steps. Some steps in the mechanism will happen slowly and others will be fast. One step that is slower than all the others will determine the overall rate of reaction – the overall rate can't be faster than the slowest step. We call this step the **rate-determining step**.

Any reactants which are involved in steps after the rate determining step (which by definition will be faster steps) won't have any effect on the overall rate. As a result they **won't be in the rate equation**, and will be **zero order** with respect to this reactant.

It follows that the substances reacting in the rate-determining step are the substances which are shown in the rate equation. The order with respect to that reactant tells us how many molecules of that substance are involved in this step.

### Case study 1: $\text{NO}_{2(g)} + \text{CO}_{(g)} \rightarrow \text{NO}_{(g)} + \text{CO}_{2(g)}$

Looking at the overall equation above we'd expect that  $\text{NO}_2$  collides with  $\text{CO}$  in a single step to bring about this reaction. We'd be wrong. If we do initial rates experiments:



We find that the rate equation is **rate = k [NO<sub>2</sub>]<sup>2</sup>**

We should conclude that:

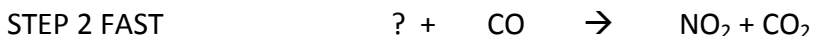
- Two  $\text{NO}_2$  collide in the rate-determining step.
- Because  $\text{CO}$  isn't in the rate-determining step but is a reactant in the overall equation, it must be being used up in a subsequent faster step, so there is evidence for a multi-step reaction.
- Because the **stoichiometry of NO is different** in the rate equation and the overall equation there must be a step subsequent to the rate determining step in which it is involved.

We can use these conclusions to propose a two-step mechanism by writing down what we know, and filling in the gaps. **Ultimately, the steps we propose for a reaction must add together to match the overall equation.**

STEP 1, SLOW (RDS)       $\text{NO}_2 + \text{NO}_2 \rightarrow ? + ?$  (from the rate equation)

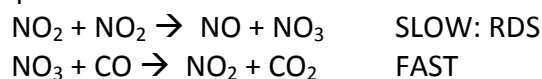
For Step 2 we know that  $\text{CO}$  is a reactant and we haven't used it in the first step, so it must be used here. We know that  $\text{CO}_2$  is a product and it can't be made in the first step

(no C atoms among the reactants, so it must be made here). We know that the overall equation has one molecule of  $\text{NO}_2$  reacting but we used two in STEP 1, so we must create an  $\text{NO}_2$  as a product in STEP 2 (the two steps must add to give the overall equation).



Now we can propose anything to fill the gaps so long as the steps add up to the overall equation. We know we haven't produced  $\text{NO}$  in STEP 2 and it is a product in the overall equation so we make it a product of STEP 1:

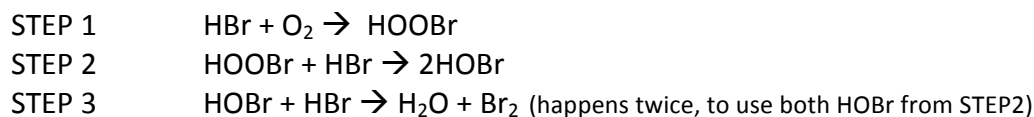
The simplest solution is:



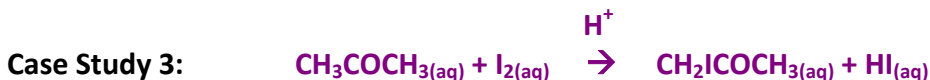
... there are other possible solutions we could propose, but steps in a mechanism represent simple sequences of collisions between reacting particles, so they rarely involve more than two reactants, and don't have fractions in the stoichiometry.



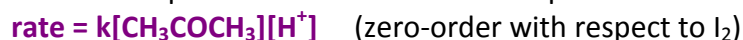
Looking at the overall equation, we can be confident that this is a multistep reaction because there is no probability of five reacting molecules all colliding simultaneously. The following possible mechanism is suggested:



Experimental evidence to support this mechanism would come from initial rates experiments to determine the rate equation and see whether it is consistent with the proposed STEP 1. If so, we'd expect to find that the reaction is first order with respect to both  $\text{O}_2$  and  $\text{HBr}$ , so that the rate equation would be **rate =  $k[\text{HBr}][\text{O}_2]$**



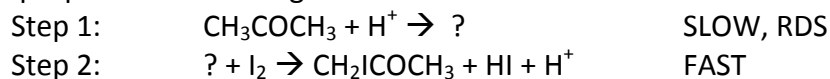
When we do the experiments we find the rate equation is:



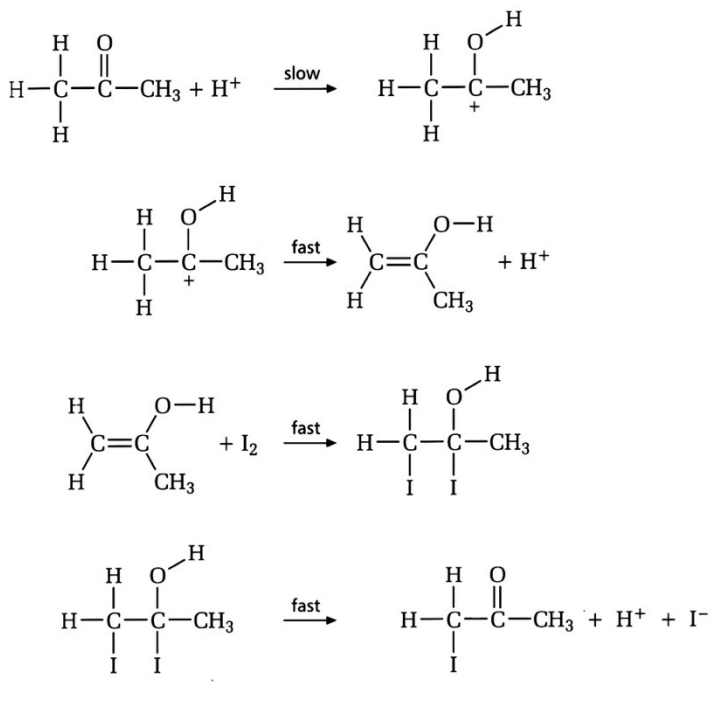
We should conclude that:

- The first, rate-determining step is a reaction between  $\text{CH}_3\text{COCH}_3$  and  $\text{H}^+$ .
- Because  $\text{I}_2$  is a reactant and is not in STEP 1 there must be one or more subsequent steps, one of which uses the  $\text{I}_2$ .
- Because  $\text{H}^+$  is used in the rate-determining step but is not in the overall equation, it must be formed again in a subsequent step: it is a catalyst (used in one step and regenerated in a subsequent step).

We can propose the following:

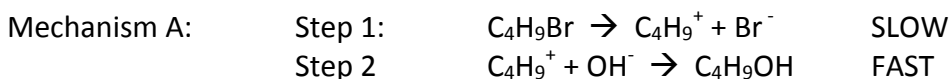


From which it is clear that  $[\text{CH}_3\text{C}(\text{OH})\text{CH}_3]^+$  must be the intermediate indicated as '?'.  
 In fact the mechanism is as follows, showing it is consistent with the evidence we have obtained.



#### Case Study 4: $\text{C}_4\text{H}_9\text{Br} + \text{OH}^- \rightarrow \text{C}_4\text{H}_9\text{OH} + \text{Br}^-$

This is a nucleophilic substitution we have met before. Two possible mechanisms have been proposed.



We can use rate of reaction experiments to determine the rate equation and hence determine which mechanism is correct.

The actual rate equation for the primary haloalkane 1-bromobutane is found to be first order with respect to both  $[\text{OH}^-]$  and  $[\text{C}_4\text{H}_9\text{Br}]$ , so the correct mechanism is the single-step one where the C-Br bond breaks as the C-O bond forms.

When the experiment is repeated with a different isomer, the tertiary haloalkane

