

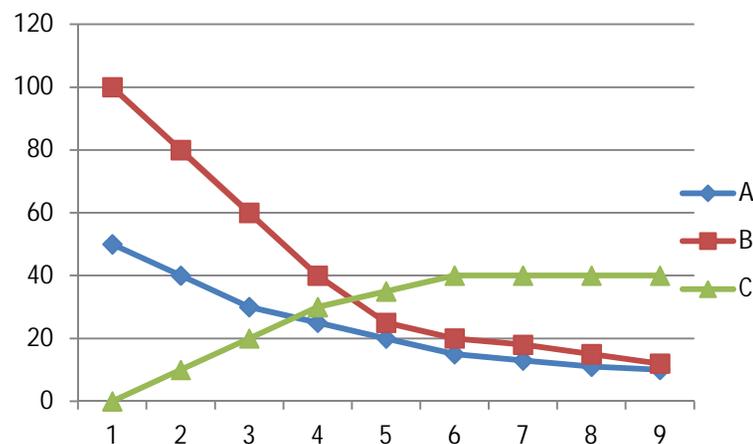
Kinetics

The main factors that affect the rate of a chemical reaction are temperature, concentration, pressure and surface area which you have covered in AS. What is a reaction rate? Well if you take the example reaction:



The concentrations of A and B will decrease with time, and C will increase with time. We could plot our results like so:

The rate of reaction is defined as the change in concentration (of any of the reactants or products) with time. Notice though how different the graphs for each one is, which means that you need to state which one you are following. In most cases you will follow C, as this is your product, and it will increase with time.



The Average Rate of a Reaction

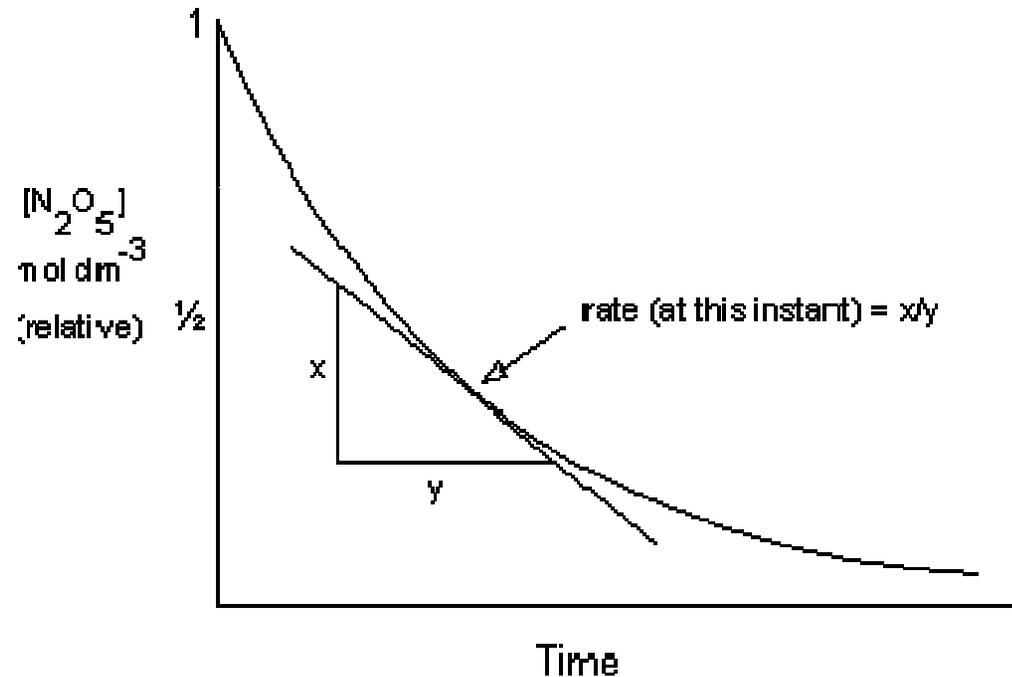
- We can find an average rate from a graph of concentration against time. The average rate of the reaction with respect to C, during a period of time Δt is the change in concentration of C divided $\Delta[C]$ by Δt .
- The average rate of reaction between t_1 and $t_2 = \Delta[C] / \Delta t$

Therefore if in 10 seconds $[C]$ changed from 1.0 mol dm^{-3} to 1.1 mol dm^{-3} then:

$$\frac{1.1 - 1.0 \text{ mol dm}^{-3}}{10 \text{ s}} = \text{Average rate of reaction in this period}$$
$$= 0.1 / 10 = 1 \times 10^{-2} \text{ mol dm}^{-3} \text{ s}^{-1}$$

The rate of reaction at any instant

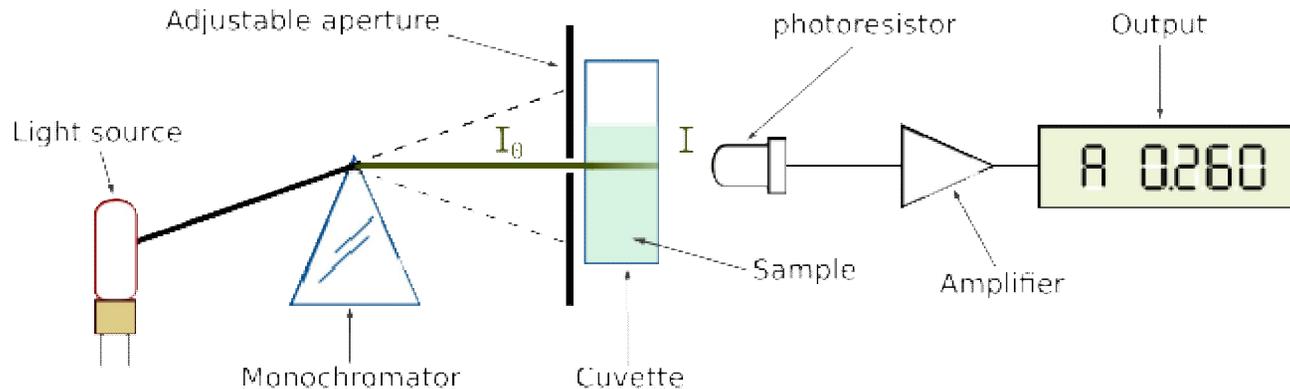
Quite often it is more useful for us to know the rate of reaction over a certain period of time. To find the rate of change of $[C]$ at a particular instant we draw a tangent to the curve at that time and then find the gradient or slope.



Measuring a reaction rate

- To measure the reaction rate we need a method to do this. This method will be different depending on the reaction that is taking place and how quickly this happens.
- Example: The reaction of Bromine and Methanoic acid. The solution starts off being brown and ends up being colourless.
- $$\text{Br}_2(\text{aq}) + \text{HCO}_2\text{H}(\text{aq}) \rightarrow 2\text{Br}^-(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{CO}_2(\text{g})$$
- For this particular reaction we use a colorimeter, which can measure the decreasing concentration of Br_2 . This relies on the Beer-Lambert Law which says that the absorption of light by a particular substance is due to the properties of the substances that it is passing through.
- It takes into account values such as the length of the path of light and concentration of the compound in solution.

Colorimeter



The essential parts of a colorimeter are:

- a light source (often an ordinary low-voltage filament lamp)
- an adjustable aperture
- a set of colored filters
- a cuvette to hold the working solution
- a detector (usually a photoresistor) to measure the transmitted light
- a meter to display the output from the detector

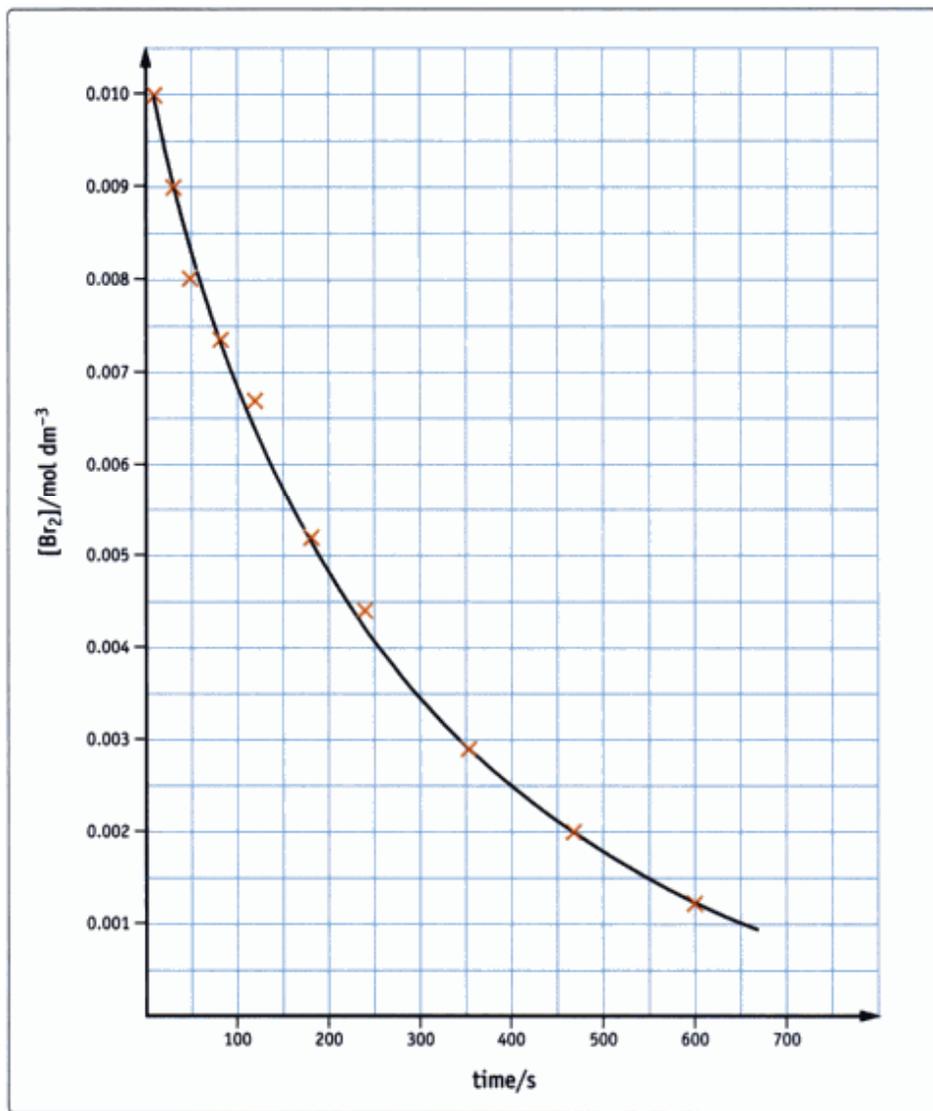
In addition, there may be:

- a voltage regulator, to protect the instrument from fluctuations in mains voltage.
- a second light path, cuvette and detector. This enables comparison between the working solution and a "blank", consisting of pure solvent, to improve accuracy.

Reaction between Bromine and Methanoic Acid

Time (s)	[Br ₂] mol dm ⁻³
0	0.0100
30	0.0090
60	0.0081
90	0.0073
120	0.0066
180	0.0053
240	0.0044
360	0.0028
480	0.0020
600	0.0013

Reaction between Bromine and Methanoic Acid



Find the rate

$t = 0s$

$t = 300s$

$t = 500s$

Reaction between Bromine and Methanoic Acid

Answers:

$$t = \frac{D[C]}{Dt}$$

1. $t = 0$ $0.010 / 215 = 4.000 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$

2. $t = 300$ $0.0035 / 585 = 1.196 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$

3. $t = 500$ $0.0053 / 750 = 7.066 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$

The rate expression and order of reaction

- The rate of a reaction depends on the concentrations of some or all of the species in the reaction vessel (reactants, products and catalysts). They will not always make the same contribution to the reaction rate. The rate expression will tell us about the contribution of the species that DO affect the reaction rate.
- Example: $X + Y \rightarrow Z$
The concentration of X [X], may have more effect on the rate than the concentration of Y [Y]. It could also be that the [X] has NO effect on the rate, or even that [Z] has an effect. All of this information can be found by experimental procedures.

The rate expression

- The rate expression describes how the rate of the reaction depends on the concentration of species involved in the reaction. All the reactants may not appear in the rate expression, this is because these particular species have no effect on the rate. For example:
- The rate expression for $X + Y \rightarrow Z$ may have the rate expression $\propto [X][Y]$ where \propto means 'proportional to'.
- This would mean that both $[X]$ and $[Y]$ have an equal effect on the rate. Doubling either one of these would double the rate of reaction. Doubling the concentration of both would quadruple the rate.
- It could be that the rate expression is $\propto [X][Y]^2$
This would mean that doubling $[X]$ would double the rate of reaction but doubling $[Y]$ would quadruple the rate.

The rate constant k

- We can remove the proportionality sign if we introduce a constant to the expression. This constant is k and is different for every reaction and varies with temperature, so the temperature needs to be stated. If the concentration of all the species is 1 mol dm⁻³ then the rate of reaction is k.

Therefore if the rate expression were $\propto [X][Y]^2$

This can be written as $k[X][Y]^2$

The order of a reaction

Take the rate equation:

$$\text{Rate} = k[X][Y]^2$$

This means that $[Y]$, which is raised to the power of 2, has double the effect on the rate than that of $[X]$. The order of reaction with respect to one of the species, is the power to which the concentration of that species is raised to. It tells us how the rate depends on the concentration of that species.

So for our particular example the order of reaction with respect to Y is two and to X is one.

The overall order of reaction would be the sum of the orders of all the species. So this reaction is first order in respect to X , second order in respect to Y and third order overall.

Chemical equations and the rate equation

The rate equations tells us about the species which affect the rate. The species in a chemical equation may not appear in the rate equation, also the coefficient of a species in the chemical equation has no relevance on the rate expression. For example:



After experiment, the rate equation was found to be:

$$\text{Rate} = k[\text{CH}_3\text{COCH}_3(\text{aq})] [\text{H}^+(\text{aq})]$$

So we could say that this reaction is first order in respect to propanone, first order in respect to H^+ ions and second order overall. The rate is zero order in respect to iodine or $[\text{I}]^0$.

Units of the rate constant, k

The units of the rate constant varies depending on the overall order of reaction.

For a first order reaction, such as:

$$\text{Rate} = k[\text{A}]$$

The units of rate are $\text{mol dm}^{-3}\text{s}^{-1}$ and the units of [A] are mol dm^{-3} so the units of k are s^{-1} .
Therefore if you cancel out the units:

$$\text{mol dm}^{-3}\text{s}^{-1} = k \times \text{mol dm}^{-3} \quad == \quad k = \text{mol dm}^{-3} \text{s}^{-1} / \text{mol dm}^{-3}$$

Therefore the unit of k for a first order reaction is s^{-1} .

Another example, this time for a second order reaction:

$$\text{Rate} = k[\text{B}][\text{C}]$$

$$\text{mol dm}^{-3}\text{s}^{-1} = k \times \text{mol dm}^{-3} \times \text{mol dm}^{-3} \quad == \quad k = \text{mol dm}^{-3} \text{s}^{-1} / \text{mol dm}^{-3} \times \text{mol dm}^{-3}$$

Therefore the unit of k for a second order reaction is $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$

Finding the order of reaction from a graph

The results from most reaction rate experiments will give you a series of concentration readings for one particular species. Usually the first step to finding the order with respect to that species is by plotting these readings on a concentration – time graph.

To help the interpretation of the experiment, we make sure that the concentrations of all the reactants, other than the one being measured, stay the same. We do this by making their concentration so large compared with the reactant being investigated, that any change is negligible. Example:



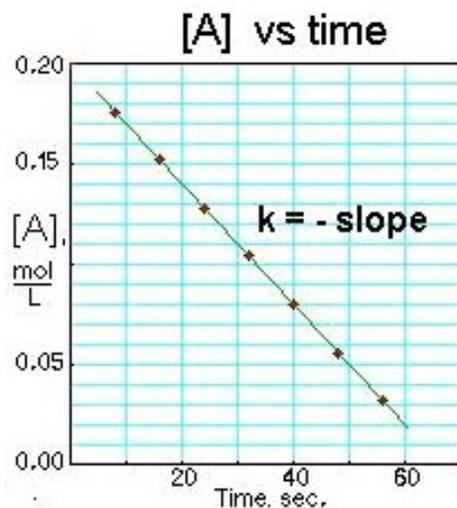
At the start of the reaction we make [B] very large compared with [R]. For example:

At the start:	[R] = 0.01 mol dm ⁻³	[B] = 1.00 mol dm ⁻³
At the end:	[R] = 0 (all used up)	[B] = 0.99 mol dm ⁻³

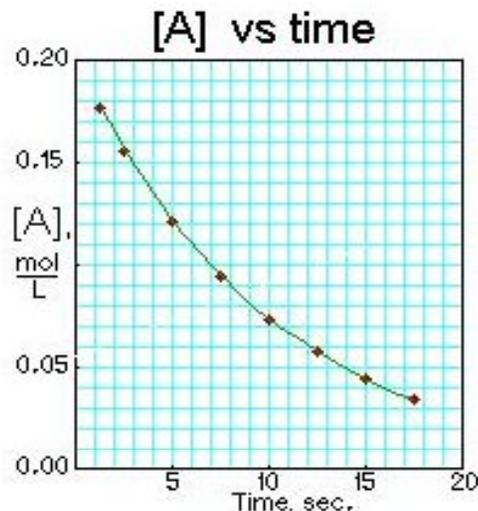
So during the whole reaction [B] is practically constant.

Finding the order of reaction from a graph

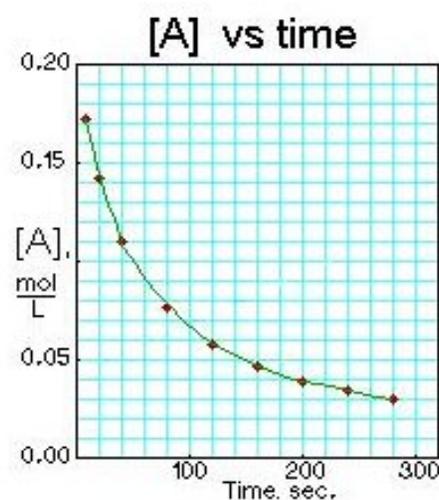
The graph of $[R]$ plotted against time will look different depending on the order.



Zero Order



First Order

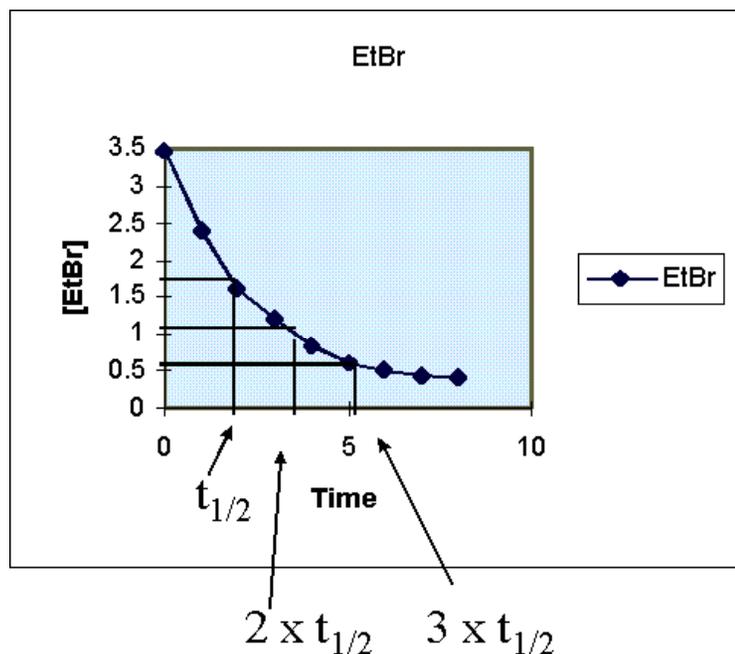


Second Order

Notice that in all of the graphs the concentration of R decreases with time. This is because R is the reactant and is therefore being used up. Just by looking at the graph can often tell you what the order of reaction is. If it is a straight line the order of reaction is zero, this is because the rate is the same whatever the concentration of R is. First and second order reactions both give curves by the second order is deeper than the first order one.

Finding the half-life of a first order reaction

- The half life of a reaction, $t_{1/2}$, is the time take for $[R]$ to fall from any chosen value to half that value. The first half-life is often taken from the start of the reaction. The second half-life is from the end of the first etc.



In a first order reaction all the half lives are the same. For a second order reaction and greater, successive half lives increase.

Finding the order of a reaction by using rate-concentration graph

Another way of determining the order of a reaction with respect to a particular species is by plotting a graph of rate against concentration (rather than concentration against time).

We start off by drawing a usual graph of $[R]$ against time and draw tangents at the different values of $[R]$. The gradients of these tangents are the reaction rates (changes in concentration over time) at different concentrations. The values for these rates can then be used to construct a second graph of rate against concentration.

If the graph is a horizontal straight line, this means that the rate is unaffected by $[R]$ so the order is zero.

If this graph is a sloping straight line through the origin then rate is proportional $[R]$ so the order is one.

If the graph is not a straight line then it is probably second order. To prove this plot rate against $[R]^2$, if this is a straight line then it is second order.

The initial rate method

The previous method we discussed allows us to find the order of reaction with respect to the one reactant whose concentration we measured. This method allows us to find the order of reactant with respect to any species in the reaction mixture.

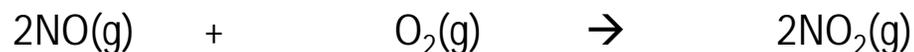
With this method a series of experiments are carried out, Each experiment starts with a different combination of initial concentrations of reactants, catalysts etc. The experiments are designed so that for any pair of experiments, there is only one concentration that varies, the rest stay the same. Then for each experiment, the concentration of one reactant is followed and the concentration-time graph plotted.

On the graph a tangent at time=0 is drawn and the gradient of this line is the initial rate. The good thing about this method is that the concentrations of ALL the substances in the reaction mixture are known exactly at this time.

Comparing the initial concentration and the initial rates for pairs of experiments allows the order with respect to each reactant to be found.

The initial rate method

An example of this is the reaction:



Experiment Number	Initial [NO]/10 ⁻³ mol dm ⁻³	Initial [O ₂]/10 ⁻³ mol dm ⁻³	Initial rate/10 ⁻⁴ mol dm ⁻³ s ⁻¹
1	1	1	7
2	2	1	28
3	3	1	63
4	2	2	56
5	3	3	189

Comparing experiment 1 and 2: [NO] is doubled but [O₂] stays the same. The rate is shown to quadruple (7 – 28) which suggests rate $\propto [\text{NO}]^2$. This can be confirmed by looking at experiment 1 and 3 where [NO] is trebled while [O₂] is kept the same. Here the rate increases nine fold as we would expect. So the order with respect to NO is two.

Now you can compare experiment 2 and 4. Here [NO] is constant but [O₂] doubles. The rate doubles from (28 – 56) so it looks as if rate $\propto [\text{O}_2]$. This can be confirmed by looking at experiments 3 and 5. Again [NO] is constant, but [O₂] triples. The rate triples too, confirming that the order in respect to [O₂] is one. Therefore:

$$\text{rate} \propto [\text{NO}]^2$$

$$\text{rate} \propto [\text{O}_2]^1$$

$$\text{rate} \propto [\text{NO}]^2[\text{O}_2]^1$$

Provided that no other species affect reaction rate:

$$\text{rate} = k [\text{NO}]^2[\text{O}_2]$$

Finding the rate constant k

To find k in the equation mentioned before, we simply substitute any set of values for rate, [NO] and [O₂] in the equation. Remember to work the units out as well as the units for k change depending on the order of reaction. So taking the values for experiment 2:

$$28 \times 10^{-4} = k \times (2 \times 10^{-3})^2 \times (1 \times 10^{-3})$$

$$28 \times 10^{-4} = k \times (4 \times 10^{-9})$$

$$28 \times 10^{-4}$$

$$\frac{\quad}{4 \times 10^{-9}} = 7 \times 10^5$$

$$4 \times 10^{-9}$$

Now units:

$$\text{mol dm}^{-3} \text{s}^{-1} = k \times \text{mol}^2 \text{dm}^{-6} \times \text{mol dm}^{-3}$$

$$\text{mol dm}^{-3} \text{s}^{-1}$$

$$\frac{\quad}{\text{mol}^3 \text{dm}^{-9}} = \text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$$

$$\text{mol}^3 \text{dm}^{-9}$$

OVERALL:

$$7 \times 10^5 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$$

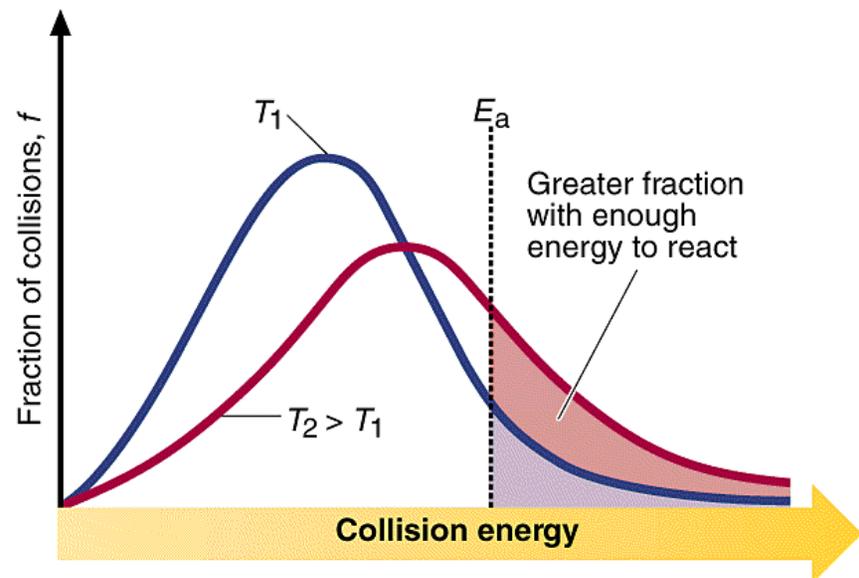
The effect of temperature on k

Small changes in temperature produce large changes in reaction rates. A rule of thumb is that for every 10K rise in temperature, the rate of reaction doubles. Suppose the rate expression for a reaction is $\text{rate} = k [A][B]$. We know that $[A]$ and $[B]$ do not change with temperature, so therefore the rate constant, k , must increase with temperature.

The rate constant, k , is a measure of the speed of a reaction. The larger the value of k , the faster the reaction. k increases with temperature, and this is true for all reactions.

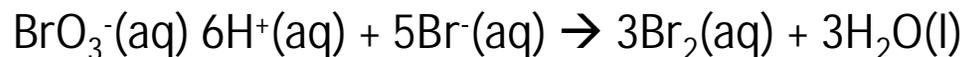
You should already be aware that increasing the temperature increases reaction rate.

You should also know that the reason for this is because raising the temperature will give colliding particles enough energy to start bond breaking, or giving them enough energy to overcome the E_A (activation energy).



The rate determining step

Most reactions take place in more than one step. The separate steps that lead from reactants to products are together called the reaction mechanism. For example look at the reaction below:

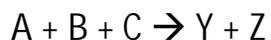


The above reaction has 12 ions, the chances of these all hitting each other at the same time, and having enough energy is VERY slim. What happens is the steps in between have very short lived intermediates. The problem is, as these intermediates are usually impossible to isolate and identify, therefore we must find other ways of working out the mechanism.

The rate determining step

In a multi step reaction the steps nearly always follow after each other, so that the product(s) of one step is/are the starting material(s) for the next. Therefore the slowest step is the one that governs the rate of the whole process. The slowest step forms a bottleneck called the rate determining step.

In a chemical reaction, any step that occurs after the rate determining step will not affect the rate. The reason for this is as follows. Consider this expression:



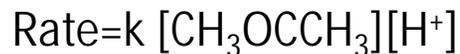
This could happen like this:

1. $A + B \rightarrow D$ (FAST)
2. $D \rightarrow E$ (SLOW)
3. $E + C \rightarrow Y + Z$

Step 2 is the slowest step and so determines the rate. As soon as some E is produced it rapidly reacts with C to produce Y and Z. BUT the rate of step 1 might affect the overall rate – the concentration of D depends on this. So any species involved before the rate-determining step could affect the rate and therefore appear in the rate expression.

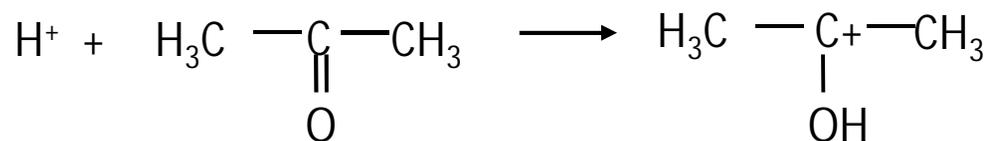
The rate determining step

The reaction between iodine and propanone. The rate expression is found to be:

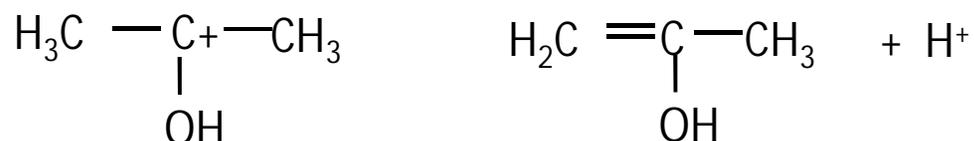


- Various mechanisms could be proposed for this reaction. One of them is as follows:-
-
- Step 1 The propanone is protonated (picks up an H^+ ion) – slow
- Step 2 This ion undergoes rearrangement and forms a $\text{C}=\text{C}$ double bond – fast
- Step 3 Iodine adds across the double bond – fast
- Step 4 The carbonyl $\text{C}=\text{O}$ bond is re-established by the elimination of a proton (restoring the catalyst) and an iodide ion – fast

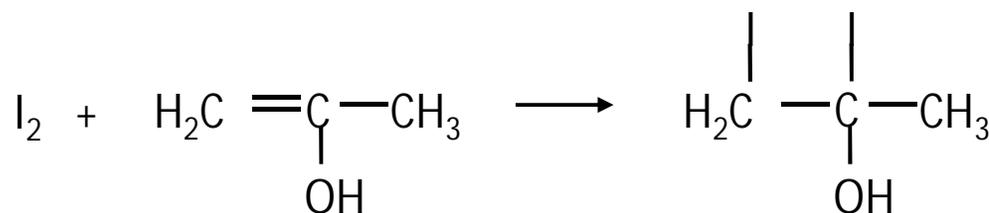
Step 1: slow



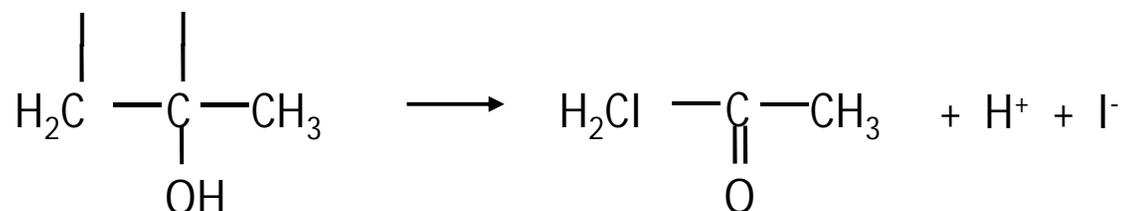
Step 2: fast



Step 3: fast



Step 4: fast



Step 1 is obviously the RDS and it involves only the propanone and the acid catalyst. The iodine molecules are not involved in the mechanism until later, so the overall rate does not depend on the concentration of iodine. This is consistent with the experimental evidence.

It is important to realise, however, that the mechanistic suggestion above was not deduced from the kinetic evidence; the evidence was merely shown to be consistent with the suggestion.