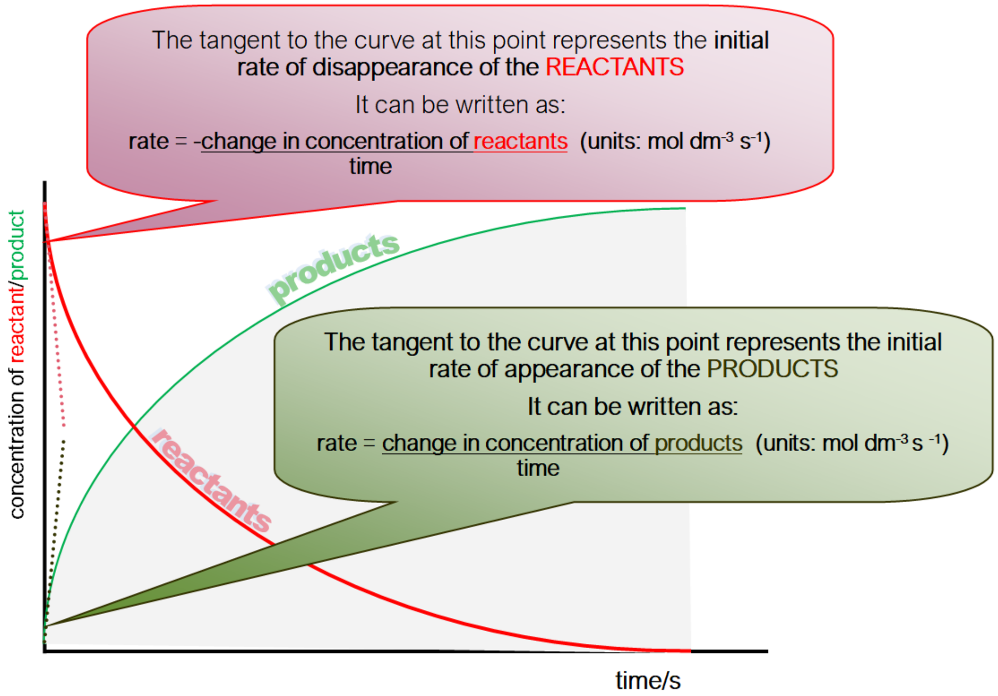
Advanced Reaction Kinetics

In GCSE Chemistry, students are typically taught a basic model of Kinetic Theory which allows us to explain the effects of temperature changes, concentration changes (including pressure in gases) and the addition of a catalyst on the rate of a chemical reaction. I don't intend to repeat that, here.

One graph from GCSE that is worth recalling is the one that we can use to work out initial rates in reaction. See below:



The tangent to the curve at this point represents the **initial** rate of disappearance of the REACTANTS

It can be written as:

$$\text{rate} = -\frac{\text{change in concentration of reactants}}{\text{time}} \quad (\text{units: mol dm}^{-3}\ \text{s}^{-1})$$

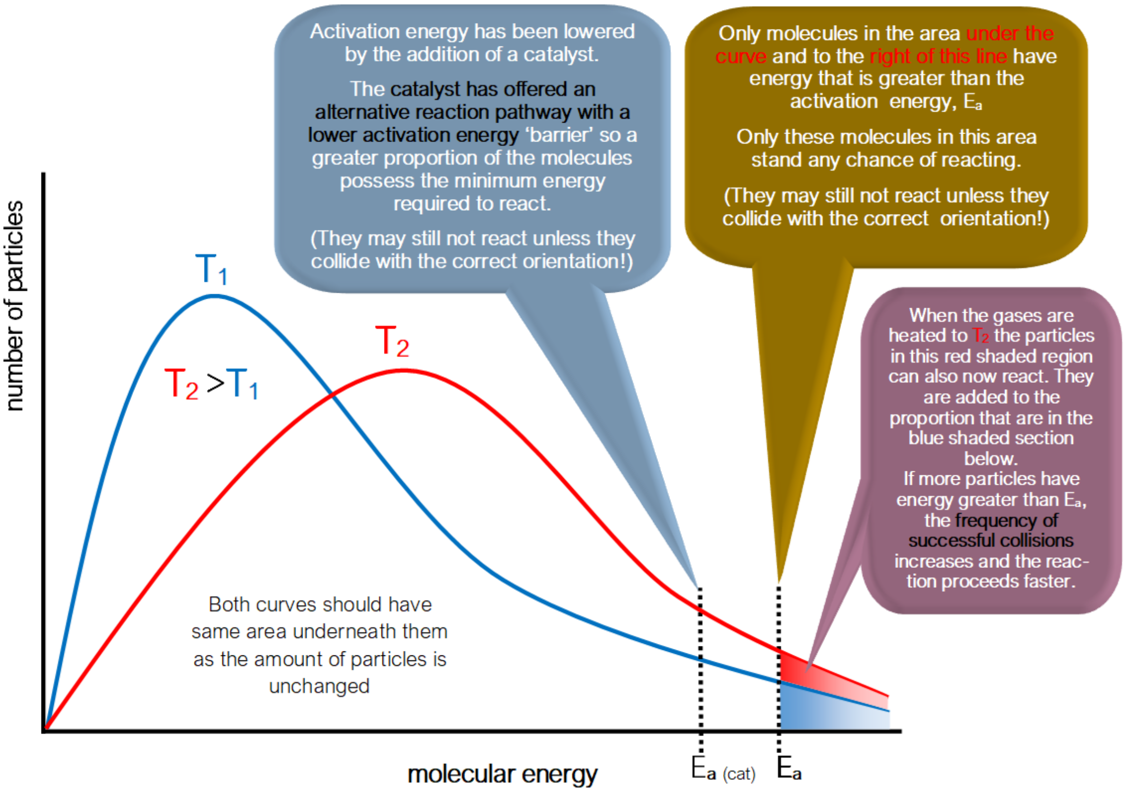
The tangent to the curve at this point represents the initial rate of appearance of the PRODUCTS

It can be written as:

$$\text{rate} = \frac{\text{change in concentration of products}}{\text{time}} \quad (\text{units: mol dm}^{-3}\ \text{s}^{-1})$$

In Y12, the GCSE explanations based around kinetic theory are often expanded a little further to include a strengthened explanation involving the Maxwell-Boltzmann distribution of molecular energies.
This is shown below. We use it to help explain why an increase in temperature speeds up a reaction. It also helps to illustrate the effect of catalysis on reaction kinetics.

Maxwell-Boltzmann Distribution of Molecular Energies



Activation energy has been lowered by the addition of a catalyst.

The catalyst has offered an alternative reaction pathway with a lower activation energy 'barrier' so a greater proportion of the molecules possess the minimum energy required to react.

(They may still not react unless they collide with the correct orientation!)

Only molecules in the area under the curve and to the right of this line have energy that is greater than the activation energy, E_a

Only these molecules in this area stand any chance of reacting.

(They may still not react unless they collide with the correct orientation!)

When the gases are heated to T_2 the particles in this red shaded region can also now react. They are added to the proportion that are in the blue shaded section below.
If more particles have energy greater than E_a, the frequency of successful collisions increases and the reaction proceeds faster.

Both curves should have same area underneath them as the amount of particles is unchanged

Also, it is likely that students have discussed the ways in which reactions can be **monitored** to follow their progress.
These methods include the following techniques:

- measuring the **volume** of a gas evolved by a reaction over time
- the change in **mass** of a reaction mixture if a gas is evolved over time
- a **colour change** as a reaction progresses (colorimetry)
- the change in **pH** and **conductivity**
- the change in **density** (dilatometry)

There are other highly sophisticated methods for very fast reactions including stopped-flow methods and flash-photolysis, pioneered by **Ronald Norrish** and **George Porter**. They were awarded the Nobel Prize for this work. However, the chances are, you are likely to catch gases, weigh reaction mixtures or measure colour changes.

Advanced Kinetics

Once you get beyond the basics of reaction kinetics (typically after Y12), you can begin to study reaction rates a bit more mathematically.

I typically introduce this advanced study of kinetics by asking a simple question:

"*What changes can we make to a chemical reaction that will guarantee an increase in the rate of reaction*?"

I can be certain that most students will confidently answer me by stating:

"*You can increase the concentration of reactants."*

I am then told that increasing the concentration of reactants increases the frequency of collision etc. etc.
It seems self-evident that the reaction rate must increase if the concentrations of reactants increase. This seems so obvious, doesn't it?

Well science can make predictions based on previous knowledge, but science must also test the predictions, **however obvious things appear to be**!

So, we need to think about a way of investigating the **effect of concentration** on the rate of a chemical reaction. To explain how we do this, we will consider a very simple generalised reaction between $A_{(aq)}$ and $B_{(aq)}$

Establishing a Link Between Concentration and Rate of Reaction

Consider the following simple reaction between solutions of reactants A and B.

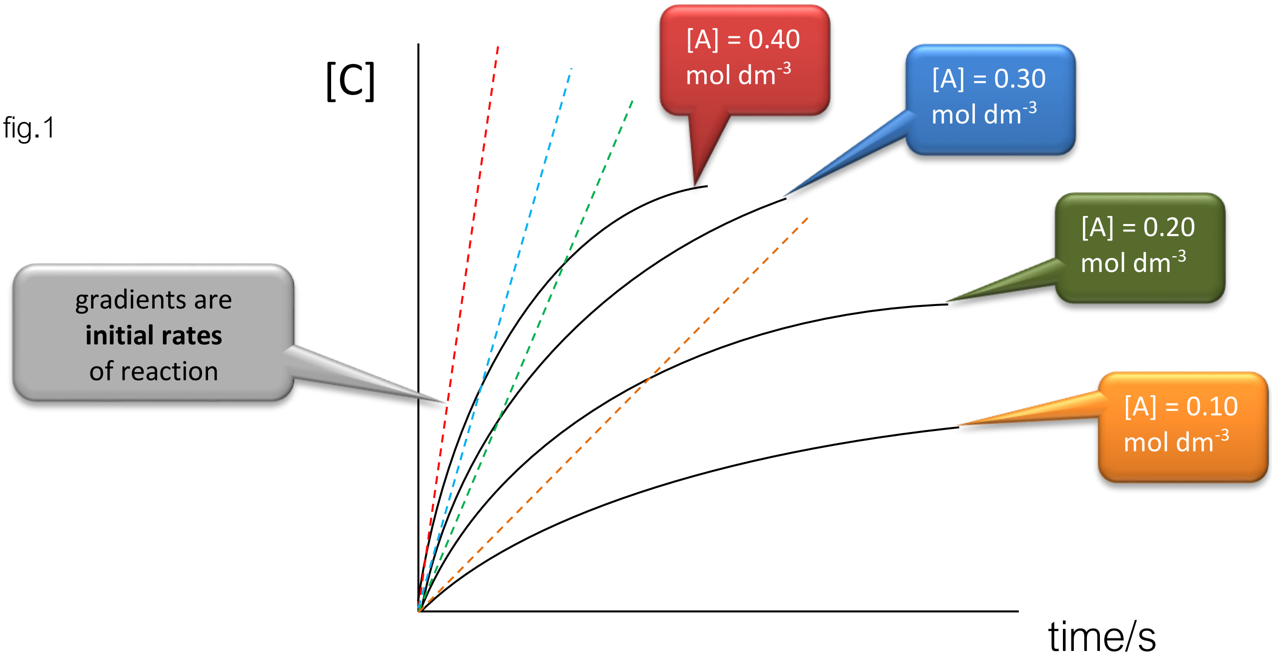
$$A_{(aq)} + B_{(aq)} \rightarrow C_{(g)}$$

We'll begin by investigating how changing the concentration of A (written, [A]), affects the rate of the reaction with B.
We need to fix the concentration of B, [B], so that we can compare reactions where only the **change in** [A] is made. (We could also make [B] large, relative to [A] so that it remains *approximately constant* throughout the reaction) We will measure the volume of gas as it is made **continuously** as the reaction progresses. This could reflect the change in the amount reactants used up or products made.

This type of method where initial rates are used to link rate with concentration is known as the **initial rates method**

In fig.1 there are results from 4 reactions where the [A] has been changed.

fig.1



It should appear obvious that there is a relationship between [A] and rate because each concentration of A produces a different **'initial rate'.** The initial rates are calculated from the coloured dotted lines which are **tangents** at the **start of the reaction**.
The value of the initial rates can be easily calculated for each concentration of A by working out the **gradient**.

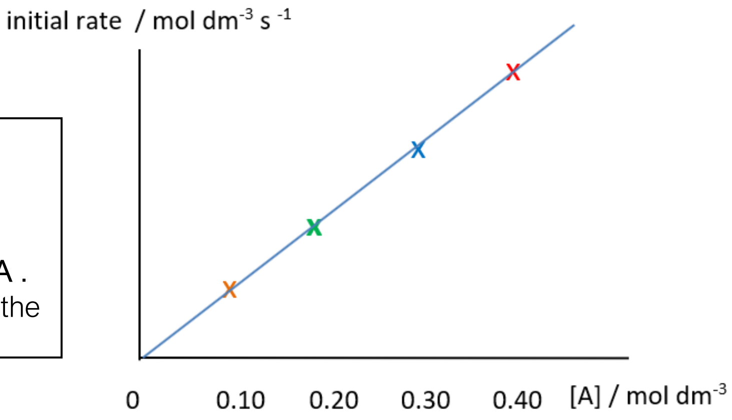
These values of **initial rate** can then be **plotted against [A]** to show the relationship between them.

fig.1

this graph shows that

rate α [A] **so rate α [A]^1**

we say that the reaction is **1st order with respect to A** .
When we double the concentration of A, we double the rate

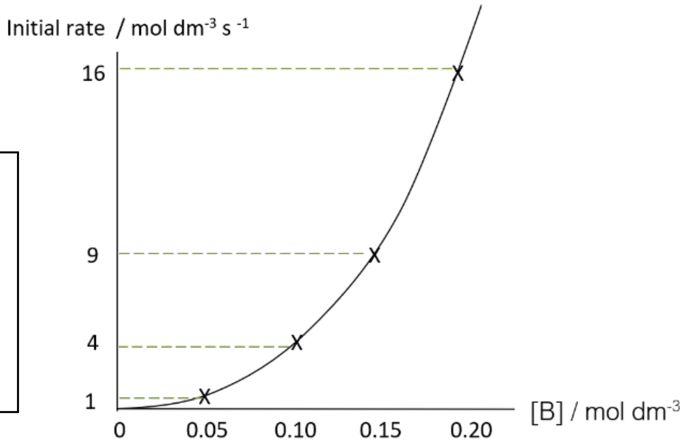


The same approach can now be applied to determine the **order with respect to B.**

Let's suppose that the initial rates are determined for 4 concentrations of B; 0.050, 0.10, 0.15 & 0.20 mol dm^{-3}

This would be done with 4 experiments just like we did with A.

These initial rates are again plotted against the [B].



this graph shows that

rate α [B]^2

We say that the reaction is 2nd **order with respect to B**
When we double the concentration of B, we quadruple the rate.

We have now **experimentally determined** the following relationships (and it CAN ONLY BE FOUND OUT BY DOING IT!)

rate α [A]^1 and rate α [B]^2 so we can combine and write a single relationship:

rate α [A]^1 x [B]^2

We now need to make this more meaningful by turning the proportionality into an equality. We introduce a constant. This is called the **rate constant, k**

$$\text{rate} = \mathbf{k}\,[A]^1 \times [B]^2$$

This is called the **rate equation**. It has been **experimentally determined** for the reaction between A and B.

rate constant

orders

initial rate (mol dm^{-3} s^{-1})

$$\boxed{\text{rate} = \mathbf{k}\,[A]^1 \times [B]^2}$$

We can write the rate equation of the **general form**

$$\boxed{\text{rate} = k\,[A]^x\,[B]^y}$$

The orders x and y are determined by experiment. You can't decide orders by looking at the chemical equation. Don't forget this.

An important thing to remember is that the units of rate constant, k, vary depending upon the orders!

The units of initial rate are mol dm^{-3} s^{-1} (in terms of moles produced or used up over time)

So, the units of **k** will be linked to the orders.

For example, in this case that we just had a look at, the units of k are worked out by rearranging the rate equation.

$$\text{rate} = \mathbf{k}\,[A]^1 \times [B]^2 \qquad \frac{\text{rate}}{[A]^1 \times [B]^2} = k \qquad \text{so} \qquad \frac{\cancel{\text{mol dm}^{-3}}\ \ s^{-1}}{\cancel{\text{mol dm}^{-3}} \times \text{mol dm}^{-3} \times \text{mol dm}^{-3}} = \text{units of } k$$

$$\frac{1 \times s^{-1}}{\text{mol dm}^{-3} \times \text{mol dm}^{-3}} = \text{units of } k \qquad \text{so} \qquad \boxed{\text{mol}^{-2}\ \text{dm}^{6}\ s^{-1} = \text{units of } \mathbf{k}}$$

Work out the units of k for the following rate equations: (Tip-You will need to rearrange the equation). Also, write down the overall order. **Overall order = sum or the orders**

a) rate = $k\,[X]^1$ units of k ……………………… overall order……
b) rate = $k\,[F]^1\ [G]^0$ units of k ……………………… overall order……
c) rate = $k\,[M]^1\ [N]^1$ units of k ……………………… overall order……
d) rate = $k\,[G]^1\ [H]^2$ units of k ……………………… overall order……

Rate constant k is temperature dependant. An increase in temperature always increases the value of k. So, for some fixed concentrations of reactants, increasing temperature must always increase the rate of the reaction

k is related to absolute temperature **T** by the famous relationship called the Arrhenius equation.

Arrhenius equation: $\boxed{k = A.e^{-Ea/RT}}$

There is a separate primer which deals with the Arrhenius equation in detail.

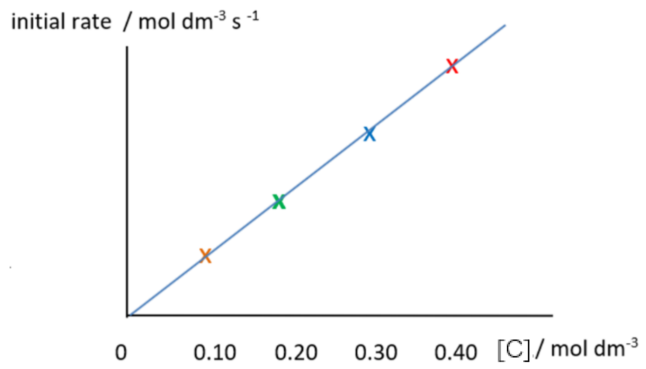
Right now, it seems that increasing the concentration of reactant always increases the rate of reaction. This is what we are encouraged to believe at GCSE. Well, this isn't necessarily true.

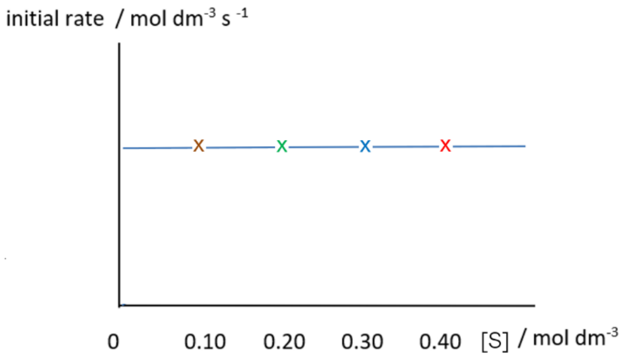
Let's consider another general simplified equation:

$$C_{(aq)} + S_{(aq)} \rightarrow D_{(aq)}$$

Using the methodology as before, we should carry out some experiments where we vary the [C] keeping [S] constant and then we should carry out experiments where we vary the [S] keeping [C] constant.

Look at the relationships between **[C] 'v' initial rate** and **[S] 'v' initial rate** found from experiment.





From the experimental results, we can see that the **initial rate is proportional** to [C].

rate α $[C]^1$

So it is 1st order w.r.t **C**

From the experimental results, varying [S] has **no effect on the initial rate.**

The way to express this mathematically is to write

rate α $[S]^0$

It is zero order w.r.t **S**

(anything to the power 0 =1. So, whatever the value of [S], the rate is unaffected.)

We can write a rate equation for this reaction between C and S.

$$\text{rate} = k\,[C]^1\,[S]^0 = k\,[C]^1 \times 1 = k\,[C]^1$$

The rather surprising discovery that the concentration of one reactant is having **no effect on the rate** needs to be explained. It seems impossible, doesn't it?

How can increasing the concentration of **S** not increase the frequency of collisions, therefore the rate?

Up to this point in chemistry, you may have assumed that chemical processes go in **one step**; many do. However, the fact that many organic reactions take place in several steps (for which we can draw separate steps in a mechanism, *e.g.* electrophilic addition) suggests that reactions can take place in **more than one step.** In this reaction between **C** and **S**, we can suggest that this reaction takes place 2 steps (at least). The assumption that particles of **C** and particles of **S** collide and react may actually be false.

This seems bizarre as **C** and **S** are the only chemicals in the overall reaction.

See below for an explanation

This is the explanation.

It could be that C undergoes a chemical change that has nothing to do with S. It may even happen when C is in the beaker on its own! This can happen by the collision of a particle of C with a solvent molecule in which it is dissolved. This is a known process.

Now let's say that C is being **slowly** converted into something new called π. Let's write an equation for this equilibrium process. Because this is an equilibrium process there will only be a limited amount of π at any time, especially if the equilibrium lies to the left:

STEP 1: $C \rightleftharpoons \pi$ slow reaction

As soon as is π produced, it reacts with S in a very **fast reaction** to produce the product D. The equation is:

STEP 2: $S + \pi \rightarrow D$ **fast reaction**

Overall, we add the equations together cancelling anything we can. We do this all the time in chemistry.

$C \rightarrow \cancel{\pi}$ STEP 1(slow)

$\underline{\cancel{\pi} + S \rightarrow D \text{ STEP 2 }}$(fast)

$\underline{C + S \rightarrow D \text{ Overall}}$

If you wanted to include a **solvent molecule, sol,** in the process, you could write it as follows

$C + \cancel{\text{sol}} \rightarrow \cancel{\pi}$ STEP 1(slow)

$\underline{\cancel{\pi} + S \rightarrow D} + \cancel{\text{sol}}$ STEP 2 (fast)

$\underline{C + S \rightarrow D}$ Overall (the solvent molecule was **regenerated** in step 2)

Why don't we observe this **reactive intermediate**, π?
This is because it doesn't hang around. As soon as it is made, it is **consumed very quickly by S.**
If we looked hard enough, we might be able to capture some π . This has been done in many reactions!

This has not yet been successfully explained why the reaction is zero order w.r.t. S, *i.e.* changing [S] has no effect on the rate of the production of product D. You may be getting some idea though.

To explain the fact that [S] has no effect I am going to use an analogy involving 'π'.

Here goes.

Consider the interaction that takes place in a typical dining hall at school.
Cooks and Students interact in a process that produces piles of dirty Dishes.
In our school there are 2 Cooks and hundreds of Students.
One of the favourite meals that the cooks prepare is pie. It seems to be loved by all the Students. There's meat, veg and vegan. Everyone can enjoy the pies that are loving prepared by the Cooks.

Now if you do a 'rates study' on pie day, you could monitor the rate of production of dirty Dishes (by mass, perhaps?). This would be a good way to measure the rate of the process that involves Students and Cooks.

The rate of production of dirty Dishes has nothing to do with the length of the queue. The concentration of Students in the dining room does not affect the rate of production of dirty Dishes. You can double concentration of Students by doubling the length of the queue, but the dishes won't pile up any faster.

The rate of this process of dirty Dishes production is governed by the rate at which pie is being produced and sent from the kitchen. This is a **slow** process as the pies are lovingly prepared by just 2 Cooks. As soon as it emerges from the kitchen, it's consumed in a pretty **fast** reaction and the dishes are produced. There's always a hungry queue until the pies runs out.

However, it is possible to increase the rate of dirty Dishes production if you can affect the **rate of pie production**; the **slow stage**. What limits the **overall process** is the rate at which pies are cooked and emerge from the kitchen. That's governed by the **concentration of Cooks**. If we employ double the number of Cooks, pies will be coming from the kitchen at twice the rate. These will be taken a gobbled up as fast as they emerge. There will still be a queue. Only if we employed (bakers) dozens of Cooks would be see no queue.

So, dirty Dishes production requires both Students and Cooks. If either is absent, the process can't take place.

The concentration of Students has no effect so it's **zero order** w.r.t. Students. Doubling the concentration of Cooks doubles the rate of dirty Dishes production so it is **first order** w.r.t. Cooks.

It's a **two-step process** involving

1. a **slow first step** which determines the rate (**rate determining step**) then
2. a **fast second step** which has no effect on the rate.

This is like the reaction between C and S given earlier. C could represent Cooks and S could represent Students

Big Tips! See below,
If any overall reaction has a chemical involved which is found to be **zero order**, you should assume that it must be a **multi-step reaction**, *i.e.* 2 or more steps.

At A Level, you should also assume that the **first step** in a multi-step reaction is the **rate determining step (R.D.S.)**

Second Order Explanation

You may be wondering how we can explain the situation where there is 2nd order w.r.t. a reactant.

Let's consider yet another general simplified equation:

$$X_{(aq)} + Y_{(aq)} \rightarrow Z_{(aq)}$$

Suppose we **done the kinetic study** and determined the rate equation to be:

$$\text{rate} = k\,[X]^2\,[Y]^0 = k\,[X]^2$$

This should be telling you several things.

- The reaction must be multi step (as it's zero order w.r.t. Y)
- The first step must only involve components that have an order, ***i.e.*** X
- When [X] is doubled, the rate quadruples.
- k must have units mol^{-1} dm^{3} s^{-1}
- The most subtle message is that the **first step** must consume 2 particles of X (because it is second order) but the second step must regenerate 1 particle of X (because, overall, only 1 particle of X is used up)

Here is a suggested set of steps (a mechanism):

(2 particles of X are used up) . . . . . . $X + \cancel{X} \rightarrow \cancel{X_2}$ STEP 1(slow so r.d.s.)

(1 particle of X is regenerated). . . . . . $\underline{\cancel{X_2} + Y \rightarrow Z + \cancel{X}}$ STEP 2 (fast)

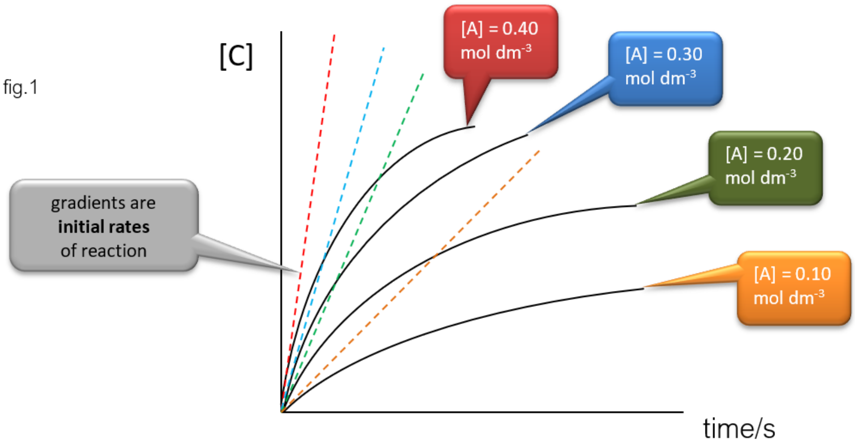
(Only 1 particle of X remains) . . . . . . $\underline{X + Y \rightarrow Z}$ Overall

The reason why the rate quadruples when [X] is doubled is clear from STEP 1.
STEP 1 involves a collision between particles X and X. If the overall concentration of X doubles, then the concentration of both X particles doubles. Each X doubling increases the rate of reaction by a factor of 2. Between them, one doubles the rate and then the other does the same again. The rate is therefore 2 x 2 times greater, i.e. 2^2 =4. Second order!

Clock Reactions

‘Clock Reactions’ are a ‘short cut’ to obtaining an indication of ‘initial rate’.
Let’s go back and remind ourselves of the way in which we can obtain **actual initial rates.**
To obtain a rate equation, we need to establish a link between **concentration and initial rate.**

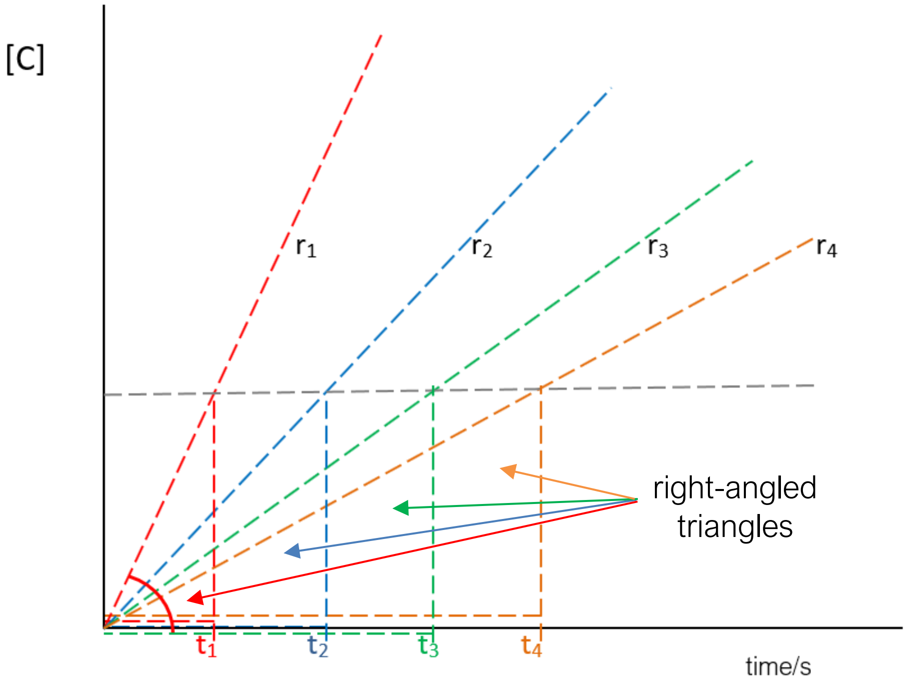
fig.1



Below is a simplified version with just the tangents remaining.

These gradients are the **initial rates, r_1, r_2, r_3, r_4**

fig. 4



It is important to understand that there is a simple relationship between the **gradient of the lines** (r_1 **to** r_4) and the **times** (t_1 to t_4). This is

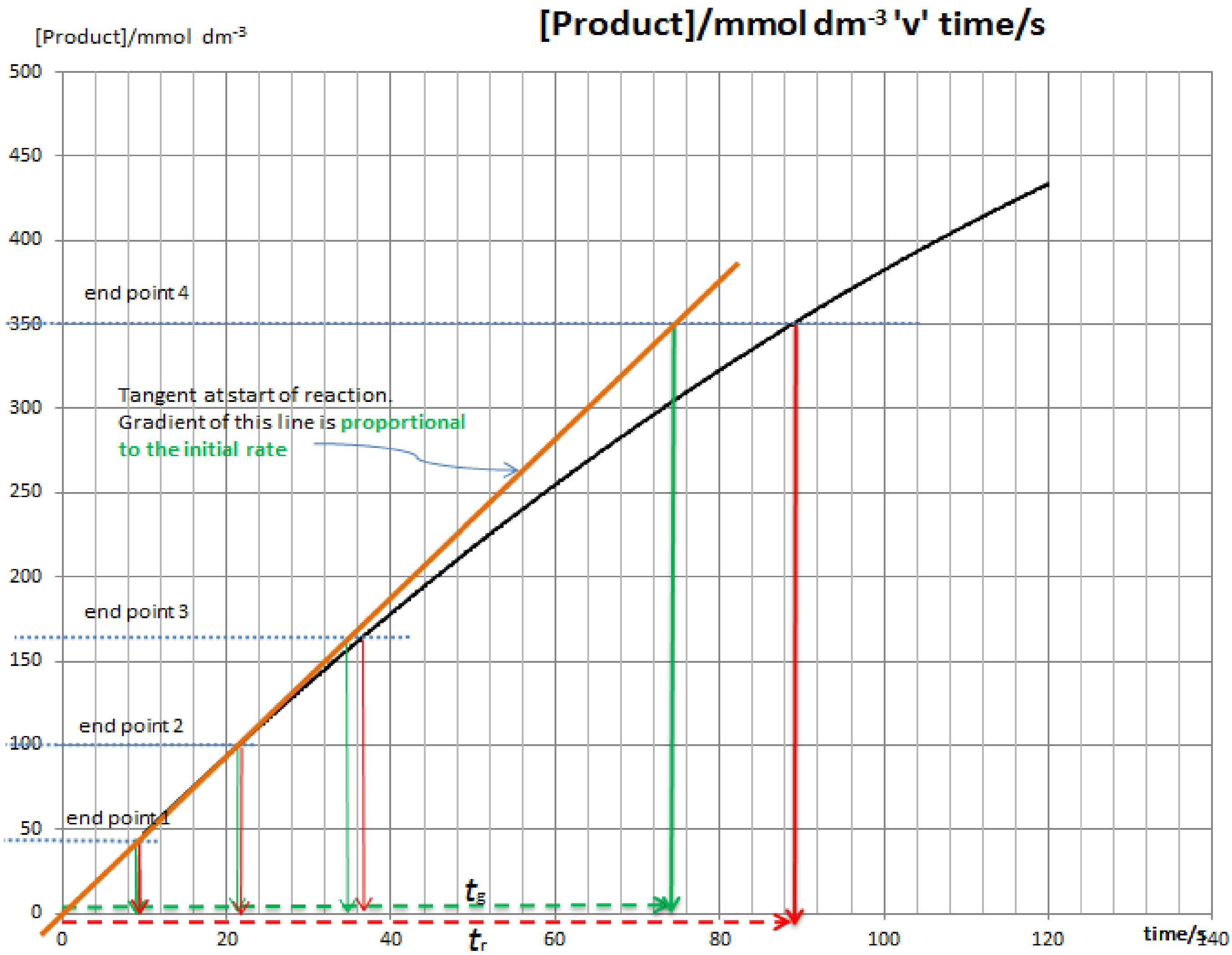
(initial rate) r α gradient α 1/t so r_1 α $1/t_1$ etc

This is because these shapes are **right angled triangles** where the base length (t_1 to t_4) is inversely proportional to the angle (and therefore the gradient!) It’s just basic geometry.

The problem is that the curves generated by the reactions aren’t exactly simple triangles. This means that the relationship of r α 1/t can’t be applied with total accuracy.

BUT, very early on in the chemical reaction, the curve gets close to being a straight line and therefore, looks more like the triangles shown above. Look at the graph below (fig.5). If there is some kind of distinct point 'end-point' (for example, a colour change or a disappearing cross) that is **early on** in the chemical reaction then **1/t** will approximate very closely to the rate. Just look how the curve and the tangent get closer towards the start of the reaction.

fig.5



t_r is the actual time that would be recorded in the experiment to get to the end point. In the case rate would be **approximately proportional to** 1/t_r

t_g is the time that would take to get to the end point in the experiment if the reaction continued at the same rate as it does at the very beginning, *i.e.* the initial gradient. In the case rate would be **exactly proportional to** 1/t_g
If an endpoint is too late in the reaction (end point 4) the difference between t_r and t_g is huge.

So, for a **fixed point very early** in the reaction $t_r \approx t_g$

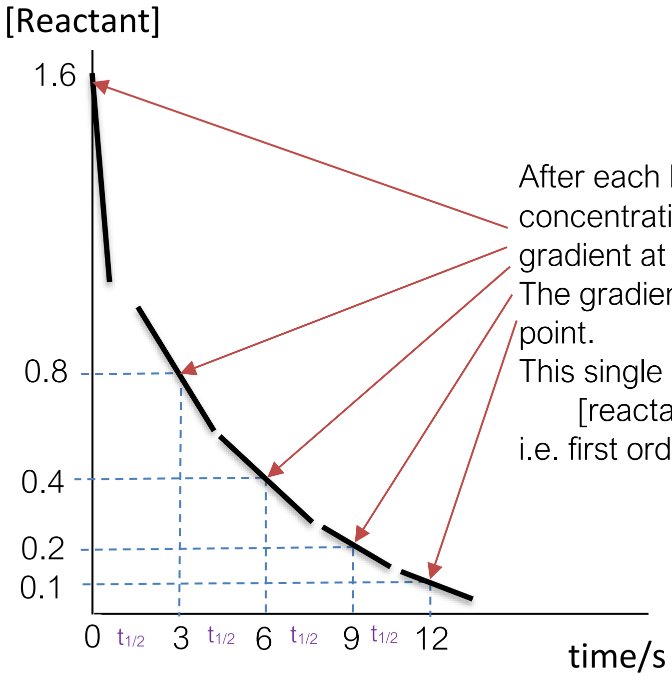
we can therefore say that:

$$\boxed{\text{initial rate } \alpha \ \frac{1}{t}}$$

This doesn't say that initial rate is equal to 1/t, they are simply proportional. This is still really useful!
Initial rates are measured in mol dm^{-3} s^{-1};1/t has units s^{-1}. But the proportionality means we can still investigate rates using 'clock reactions' because we can investigate the effect of concentration on something that 'represents rate'.
This allows us to take a **single measurement** (a time) and convert it into something that is proportional to rate. This is the background to **clock reactions.**

The First Order Graph

It can be possible to spot first order kinetics from a single graph of the decrease in concentration in a reactant.



After each half-life, $t_{1/2}$, has passed, the concentration of reactant halves and the gradient at that point halves.
The gradient is the rate of reaction at that point.
This single graph shows that :
[reactant]^1 α rate of reaction
i.e. first order with respect to that reactant

This graph is the same shape as the one that represents the **decay of a radioactive material**. Radioactive decay is a **first order process**, i.e. the rate of decay depends on the amount of radioactive nuclide remaining. This is why we see the term, half-life (that is constant)

Important thing to understand:

This graph assumes that **only the reactant we are measuring** the decrease in **affects the rate**. If any other of the reactants have an order, then their decrease in concentration will also influence the shape of this graph. The way to effectively eliminate the effect of the other reactant's concentration change, is to make sure that the other reactant is in very high relative concentration. That means that **it's concentration will remain approximately constant** and so it won't influence the rate as the reaction progresses.

Going Further: (A bridge to Undergrad Chemistry)

Some of you may be aware that there is a way of calculating the value of **k** for first order processes from a knowledge of half-life, $t_{1/2}$. OCR have this in their specification as something students need to recall and use.

This is to the relationship:

$$\boxed{k = \frac{\ln 2}{t_{1/2}}}$$

I thought that it would be interesting for some of you to see where this comes from. You can totally ignore it if it's not your idea of interesting.

Let's begin by reminding ourselves of some basics associated with 1st order process.

We know that the rate equation for a first order reactant, **R** is $\boxed{\text{rate} = k\,[R]^1}$

Let's now go a bit further:

change in [R] is negative. The negative sign is necessary as the rate of reaction is positive.

positive value

$$\boxed{\begin{array}{l}\text{rate at any point} \\ \text{in the reaction}\end{array} = -\frac{\text{change [R]}}{\text{change in t}} = \frac{\delta[R]}{\delta t}}$$

applying a bit of calculus:

$$\begin{array}{l}\text{rate at any point} \\ \text{on the } \textbf{curve}\end{array} = \frac{-\delta[R]}{\delta t} = k\,[R]^1$$

rearranging:

$$\frac{-\delta[R]}{[R]^1} = k\,\delta t$$

rearranging:

$$\frac{\delta[R]}{[R]^1} = -\,k\,\delta t$$

$$\int \frac{\delta[R]}{[R]^1} = \int -\,k\,\delta t$$

integrating both sides:

$$\int_{[R]_0}^{[R]_t} \frac{1}{[R]^1}\,\delta[R] = -\,k \int_0^t \delta t$$

concentration of R after time, t

concentration of R at the start of a period

$$\ln [R]_t - \ln [R]_0 = -\,k\,t$$

$$\boxed{[R]_t = [R]_0 \times e^{-kt}}$$

This is known as the integrated rate equation

After a period of one half-life has passed where $t = t_{1/2}$, the concentration of the reactant [R] must also have halved in value so $[R]_t = \frac{1}{2}[R]_0$ (because we know that it's first order!)

$$\text{when} \quad t = t_{1/2} \quad \text{then } [R]_t = \tfrac{1}{2}[R]_0$$

$$\tfrac{1}{2}[R]_0 = [R]_0 \times e^{-k t_{1/2}}$$

$$\tfrac{1}{2}[R]_0/[R]_0 = e^{-k t_{1/2}}$$

$$[R]_0/\tfrac{1}{2}[R]_0 = e^{k t_{1/2}}$$

$$2 = e^{k t_{1/2}}$$

$$\ln 2 = k t_{1/2} \qquad \boxed{\frac{\ln 2}{t_{1/2}} = k}$$

ln 2 has no units so the units of k must be s^{-1}

Another thing we can do with this equation:

$$\ln [R]_t - \ln [R]_0 = -kt$$

$$\ln [R]_t = -kt + \ln [R]_0$$

$$y = mx + c$$

So, a plot of ***ln*** $[R]_t$ against **t** will produce a negative gradient that is -**k** and so k can be calculated!

Link to radioactivity:

$[R]_t = [R]_0 \times e^{-kt}$ is analogous to the equation for radioactive decay which is also a **1st order process,** derived in the same way.

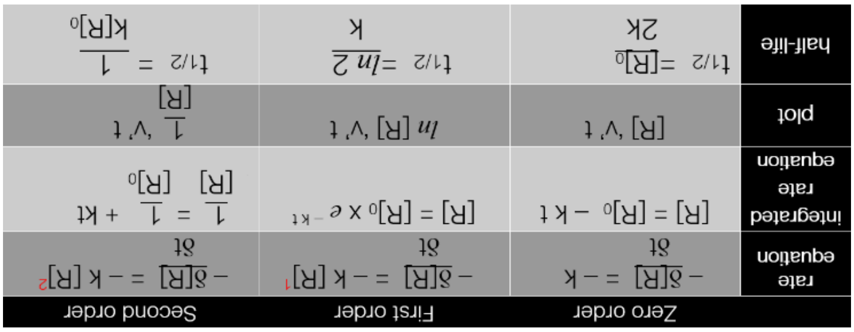
$$\boxed{N_t = N_0 \times e^{-\lambda t}}$$

N is the number of radioactive atoms remaining after a given time period
N_0 is the number of atoms at the start of a period.
λ is a constant called the radioactive decay constant.

If you feel confident with the maths, why not attempt to derive the integrated rate equations for zero order and 2nd order rate equations. Start with the rate equations and go from there.

You could try to figure out what graph plots would give the **rate constant** and the relationship between **half-life and k**.

Answers are given below: REMEMBER this won't appear in your A level chemistry examination. It is undergraduate level chemistry.



	Zero order	First order	Second order
rate equation	$-\frac{\delta[R]}{\delta t} = -k$	$-\frac{\delta[R]}{\delta t} = -k[R]^1$	$-\frac{\delta[R]}{\delta t} = -k[R]^2$
integrated rate equation	$[R] = [R]_0 - kt$	$[R] = [R]_0 \times e^{-kt}$	$\frac{1}{[R]} = \frac{1}{[R]_0} + kt$
plot	[R] 'v' t	*ln* [R] 'v' t	$\frac{1}{[R]}$ 'v' t
half-life	$t_{1/2} = \frac{[R]_0}{2k}$	$t_{1/2} = \frac{\ln 2}{k}$	$t_{1/2} = \frac{1}{k[R]_0}$

Typical Questions on Reaction Kinetics

The typical way that questions are posed at A level is to give you with a table containing experimental data.

Presented below is a worked example:

QUESTION:

Nitric oxide radicals, **NO** are known to deplete ozone. One process is shown below.

$$NO_{(g)} + O_{3(g)} \rightarrow NO_{2(g)} + O_{2(g)}$$

Shown below are some **experimental data** obtained for this reaction. Using an initial rates method, initial rates have been calculated for two concentrations of each of **NO** and **O_3**.
From this data, work out the **orders** of reaction, the **rate equation** for the reaction and calculate the value of **rate constant, k**. Give the **units** of k.

Experiment	$[NO_{(g)}]$/mol dm^{-3}	$[O_{3(g)}]$/mol dm^{-3}	Initial rate/ mol dm^{-3}s^{-1}
1	0.100	0.100	0.300
2	0.100	0.200	0.600
3	0.200	0.100	0.600

What is the **order with respect to** NO in this reaction? ________

What is the **order with respect to** O_3 in this reaction? ________

Write down the **rate equation** for this reaction ________________________

Now Calculate the value of the **rate constant, *k*** ________

How to answer this:

a. Look at the results **between experiments 1 and 2**. The initial rate doubles. Something changed between experiments 1 and 2 that made the reaction go twice as fast.

   The only thing that changed between these experiments was $[O_3]$. The value of $[O_3]$ doubles.
   There was no change to [NO].

$$\text{rate} \propto [O_3]^1$$

   We conclude the reaction is first order w.r.t. O_3

b. Looking at the data **between experiments 2 and 3**, there is no change in initial rate even though [NO] doubles.
   There was no change to $[O_3]$.

$$\text{rate} \propto [NO]^0$$

   We conclude the reaction is zero order w.r.t. NO

c. So the rate equation is $\text{rate} = k\,[O_3]^1\,[NO]^0 = k\,[O_3]^1$

You now need to calculate the **value of rate constant, k**. To do this, rearrange the equation to get k on its own:

$$\text{rate} / [O_3]^1 = k$$

Now select some data from the table. You can select any experiment (k is a constant so its doesn't matter which experiment you chose). Inert the data into the rearranged equation. We can also get the units of k.

I'm going to choose data from experiment 1.

value

$$\frac{0.300\ \cancel{\text{mol dm}}^{-3}\text{s}^{-1}}{0.100\ \cancel{\text{mol dm}}^{-3}} = \mathbf{k = 3.00\ s^{-1}}$$

units

Now for a slightly harder example:

QUESTION

Haloalkanes can react with aqueous solutions of **hydroxide ions** in a reaction known as a **nucleophilic substitution**

Rates studies of the reaction of haloalkanes with hydroxide ions have been studied extensively. It's kinetic studies in physical organic chemistry that have helped chemists work out what is happening in the reaction and to allow them to suggest mechanisms for the organic reactions.

Rates studies are a means to an end. Rate equations give a window into the reactions.

Let's consider the reaction between 1-bromobutane and hydroxide ions:

$$\text{1-bromobutane}_{(aq)} + OH^-_{(aq)} \rightarrow \text{butan-1-ol}_{(aq)}$$

Experimental data:

Experiment	[1-bromobutane] /mol dm^{-3}	[$OH^-_{(aq)}$] /mol dm^{-3}	initial rate /mol dm^{-3}s^{-1}
1	0.200	0.200	2.40
2	0.400	0.200	4.80
3	0.800	0.400	19.2

a. Look at the results **between experiments 1 and 2.** The initial rate doubles
   The only thing that changed between these experiments was [1-bromobutane].

   The value of [1-bromobutane] doubles.

   There was no change to [$OH_{(aq)}$]

   Therefore: $\text{rate}\ \alpha\ [\text{1-bromobutane}]^1$

   We conclude the reaction is first order w.r.t. 1-bromobutane

b. Looking at the data **between experiments 2 and 3**, the initial rate quadruples
   Now we need to recognize that there were changes to both [$OH_{(aq)}$] and [1-bromobutane]
   We have already worked out that doubling [1-bromobutane] doubles initial rate. But the rate has been doubled again so this must be due to the doubling of [OH^-] that took place at the same time.

   Therefore: $\text{rate}\ \alpha\ [OH^-_{(aq)}]^1$

   We conclude the reaction is first order w.r.t. **OH^-**

c. So, the rate equation is

$\boxed{\text{rate} = k\,[\text{1-bromobutane}]^{1}\,[OH^{-}_{(aq)}]^{1}}$

$\text{rate} / [\text{1-bromobutane}]^{1}\,[OH^{-}_{(aq)}]^{1} = k$

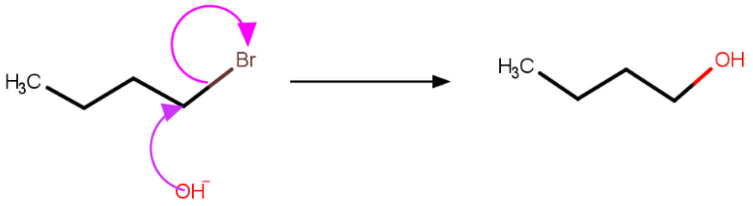
$$\frac{2.40\ \cancel{\text{mol dm}^{-3}}\text{s}^{-1}}{0.200\ \cancel{\text{mol dm}^{-3}} \times 0.200\ \text{mol dm}^{-3}} = k = 60.0\ \text{mol}^{-1}\,\text{dm}^{3}\,\text{s}^{-1}$$

Now we need to think about what this study is telling us.

1. It is suggesting that both reacting particles are present in first step (the rate determining step)
2. Also, as there are only 2 particles involved in the overall equation (one of each) the reaction is probably a **single step reaction.**

From these results chemists have suggested a mechanism which is shown below:

Mechanism



Both the haloalkane and OH^{-} are involved in this single step This is known as an S$_{N}$2 mechanism as it is Substitution Nucleophilic Bimolecular (2nd order overall)

Let's consider the reaction between a **structural isomer of 1-bromobutane**. The reaction is between 2-bromomethylpropane (a 3° haloalkane) and hydroxide ions:

$$\text{2-bromomethylpropane}_{(aq)} + OH^{-}_{(aq)} \rightarrow \text{methylpropan-2-ol}_{(aq)}$$

Experimental data:

Experiment	[2-bromomethylpropane $_{(aq)}$] /mol dm^{-3}	[OH$^{-}_{(aq)}$] /mol dm^{-3}	initial rate /mol dm^{-3}s^{-1}
1	0.200	0.200	2.4
2	0.400	0.200	4.8
3	0.800	0.400	9.6

a. Look at the results **between experiments 1 and 2.** The initial rate doubles
The only thing that changed between these experiments was [2-bromomethylpropane $_{(aq)}$]

The value of [2-bromomethylpropane] doubles.

There was no change to [OH^{-}]

Therefore: $\text{rate} \propto [\text{2-bromomethylpropane}]^{1}$

We conclude the reaction is first order w.r.t. 2-bromomethylpropane

b. Looking at the data **between experiments 2 and 3**, the initial rate doubles.
We have already worked out that doubling [2-bromomethylpropane] doubles initial rate. This alone accounts for the doubling of rate between experiments 2 and 3. The concentration of OH^- clearly has no additive effect so it must me zero order.

Therefore: $\text{rate}\ \alpha\ [OH^{-}_{(aq)}]^{0}$

We conclude the reaction is zero order w.r.t. OH^-

c. So, the rate equation is $\boxed{\text{rate} = k\ [\text{2-bromomethylpropane}]^{1}}$

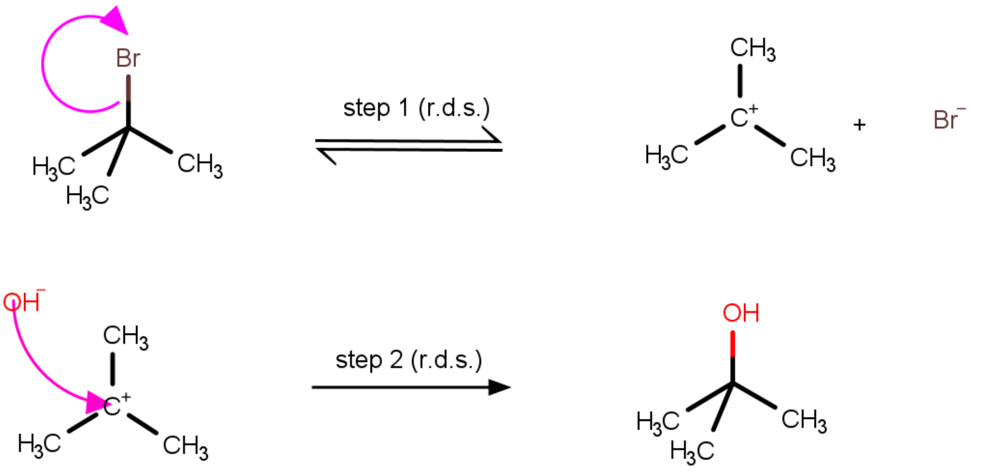
$$\text{rate} / [\text{2-bromomethylpropane}]^{1} = k$$

$$\frac{2.40\ \cancel{\text{mol dm}^{-3}}\text{s}^{-1}}{0.200\ \cancel{\text{mol dm}^{-3}}} = \mathbf{k = 12.0\ s^{-1}}$$

Now we need to think about what this study is telling us and how it differs from the study with its structural (chain) isomer.

1. It suggests that there in more than one step because only one particle appears in the rate determining step but there are 2 particles in the overall equation.
2. It suggests that only one particle of 2-bromomethylpropane is involved in the first step.
3. It suggests that OH^- is almost certainly involved in a later step.

Chemists have suggested a mechanism which is shown below:



Only the haloalkane is involved in the first step. This is known as an S_N1 mechanism as it is Substitution Nucleophilic Unimolecular (1nd order overall)

In summary, studies of reaction kinetics are done go give information about reactions and allow suggestions to be made about possible mechanisms.

There's a separate primer on **Suggesting Mechanisms from Rate Equations** on *CramNow* !

Another example for you to have a go at.

1. Reaction:

$$H_2O_{2(aq)} + I^-_{(aq)} + H^+_{(aq)} \rightarrow I_{2(aq)} + H_2O_{(aq)}$$

Experiment	$[H_2O_2]$ /mol dm^{-3}	$[I^-]$ /mol dm^{-3}	$[H^+]$ /mol dm^{-3}	initial rate /mol dm^{-3}s^{-1}
1	0.11	0.31	0.19	4.50×10^{-3}
2	0.11	0.31	0.38	4.50×10^{-3}
3	0.22	0.31	0.19	9.00×10^{-3}
4	0.44	0.93	0.68	5.40×10^{-2}
5		0.62	0.74	3.60×10^{-2}

This requires you to do a bit of thinking! Also, care with the numbers

a) What is the **order with respect to** H_2O_2 in this reaction? ________

b) What is the **order with respect to** I^- in this reaction? ________

c) What is the **order with respect to** H^+ in this reaction? ________

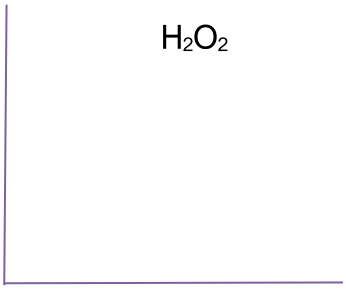
d) Write down the **rate equation** for this reaction ________________________

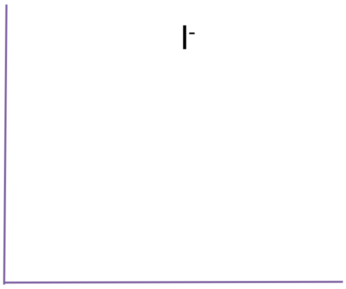
e) Calculate the value of the **rate constant, *k*** ________

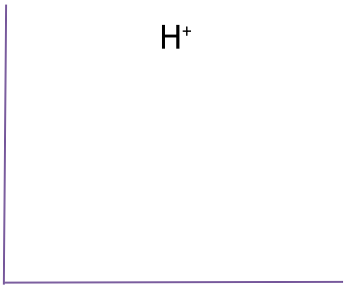
f) State the **units of *k*** ________

g) Fill in the blank box in the table.

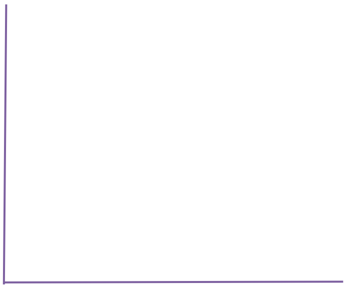
h) Sketch 3 simple graphs showing how the **initial rate of reaction** varies with the $[H_2O_2]$, $[I^-]$ and $[H^+]$. The initial rate should be plotted on the y axis.







i) Sketch a simple graph showing how **$[H^+]$ varies with time.** Assume that the concentrations of [R] and [S] do not change during the reaction! Can you suggest how the concentrations of [R] and [S] could be kept **effectively** constant during the reaction?



These are some more of these questions in a quiz on *CramNow* in the M5 folder.