

Rates part 2

Orders and graphs

In the last tutorial we showed that the gradient of a concentration/time graph \rightarrow rate.

Below I have drawn the three **concentration/time graphs** on the left (obtained from experiments) for 0, 1st and 2nd order. 0 order is easy to see as it is a straight line but 1st and 2nd orders are similar in shape.

From these graphs, we can take the gradient at several points \rightarrow **rate versus concentration** graphs, which are shown on the right side below.

Rate versus concentration graphs

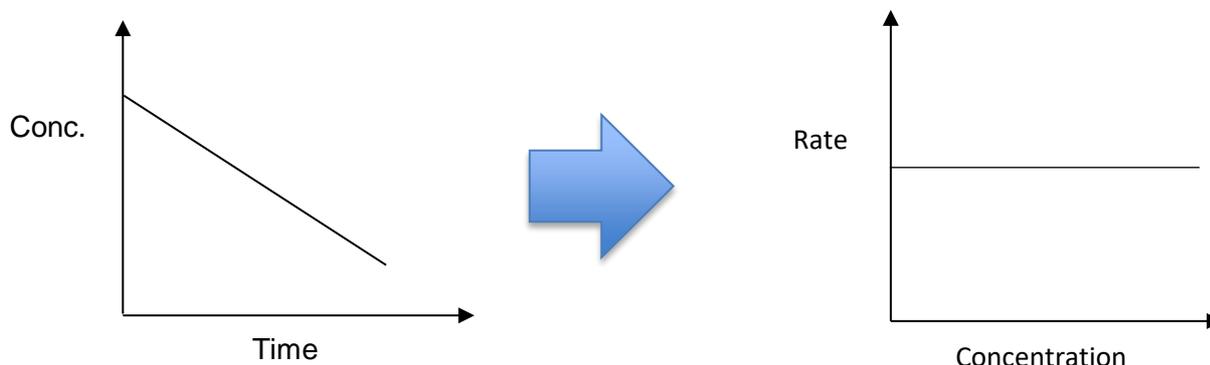
zero order is always a **horizontal line** as it has no affect on the rate.

1st order is a **straight line** through the origin as concentration and rate are proportional to each other.

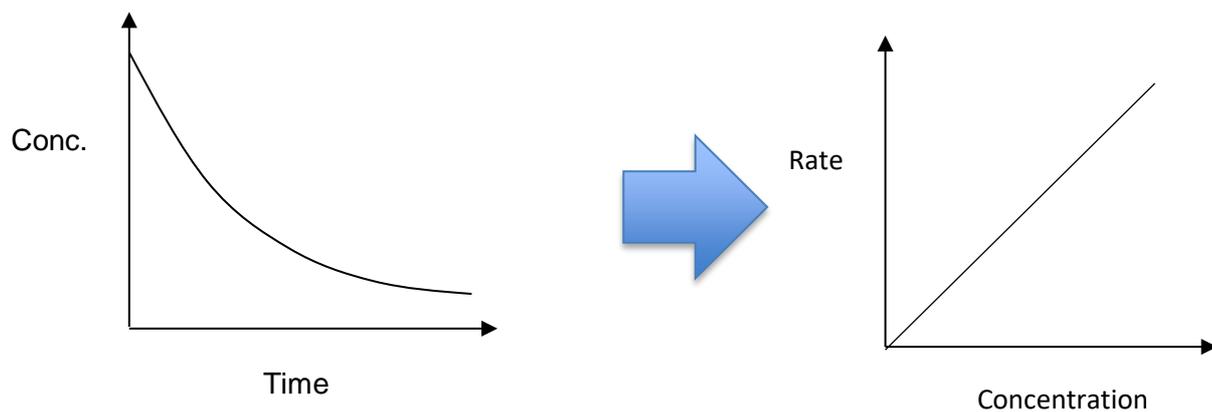
2nd order has a **curved shape** as it is a squared relationship.

- ✓ Just be careful with these graph types as students often get them mixed up. Remember that the concentrations of a reactant must decrease, therefore the curves always go downwards.
- ✓ Also note that concentration is on the y-axis on the left hand graphs but on the x-axis on the right hand graphs. Annoying or what!

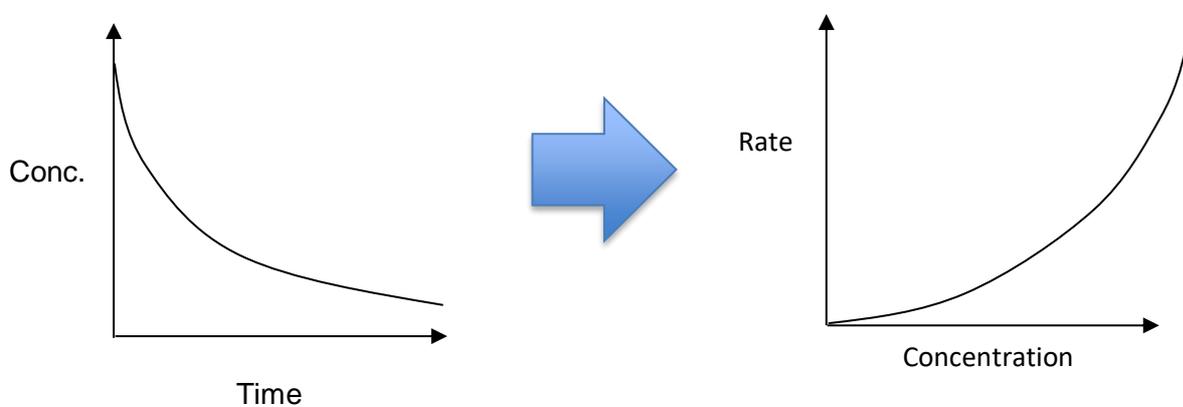
Zero order



1st order



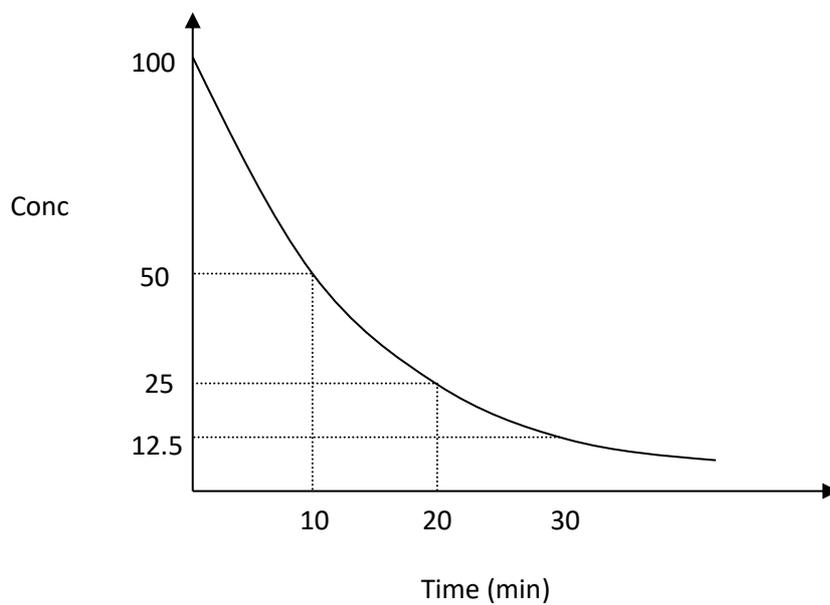
2nd order



Half-lives

the **time** it takes for the **concentration to half** is known as the half-life

From a concentration/time curve we can calculate the half-lives and work out the order.



Working out the half-life

Pick a starting concentration. In the example above 50 was chosen. Draw a **horizontal line** from 50 to the curve. Then draw a **vertical line** from the curve to the x-axis to give a time value → **10 minutes**.

Do it again from a concentration of 25. Draw a horizontal line, then a vertical line → **20 minutes**.

The difference between these values is **10 minutes**, which is the half-life.

To get the order, two successive half-lives are required. So we half the concentration again to 12.5 and repeat the process → **30 mins**.

The difference in time between the 30 mins and 20 mins is also **10 mins**.

From this we can say that two successive half-lives are the **same**. This means it is 1st order.

1st order the reaction, the half-life is **constant**. 2nd order reaction it is **not constant**

✓ There is a very very high chance that the order will be 1st order in a half-life question.

A slightly strange calculation....

The rate constant, k , can be calculated from the half-life using the following equation:

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

$t_{1/2}$ = the half life of 1st order reaction

Calculations

Calculations usually involve working out the orders → rate equation and also a value for the rate constant, k .

They will do several experiments where the concentration of each reactant is varied to see how it affects the rate. The data is usually presented in a table:

Experiment	Initial [A] (mol dm ⁻³)	Initial [B] (mol dm ⁻³)	Initial rate (mol dm ⁻³ s ⁻¹)
1	6 x 10 ⁻³	1 x 10 ⁻³	3.0 x 10 ⁻³
2	6 x 10 ⁻³	2 x 10 ⁻³	6.0 x 10 ⁻³
3	1 x 10 ⁻³	6 x 10 ⁻³	0.5 x 10 ⁻³
4	2 x 10 ⁻³	6 x 10 ⁻³	2.0 x 10 ⁻³

Calculating the orders

The problem here is that there are two reactants, A and B. We must keep the concentration of one of them **constant** and vary the concentration of the other, so only one of them is affecting the rate.

Look at **experiments 1 and 2** in the table. The [A] is held constant at 6x10⁻³ and the [B] is doubled. We can also see that the rate has doubled due to this change in [B]. Therefore, B is 1st order (linear relationship).

Next, **experiments 3 and 4**. We can keep the [B] constant and double the [A]. We can see that the rate has increased by a **factor of 4**. Therefore, A is 2nd order (squared relationship).

Therefore, the rate equation is: **rate = k[A]²[B]**

More difficult example

To calculate the rate equation from the data in the table below we will use the same method as we did above. The additional problem is that we cannot keep the concentration of reactant A constant.

Experiment	Initial [A] (mol dm ⁻³)	Initial [B] (mol dm ⁻³)	Initial rate (mol dm ⁻³ s ⁻¹)
1	0.12	0.26	2.10 x 10 ⁻⁴
2	0.36	0.26	1.89 x 10 ⁻³
3	0.72	0.13	3.78 x 10 ⁻³

Experiments 1 and 2: we must start here as it's the only option to keep the [B] constant. The [A] has been **tripled** and the rate has gone up by a factor of **9**. Therefore A must be **2nd order**.

Next, we can pick either experiments 1 and 3 or 2 and 3 to work out the order of B. It doesn't matter which we choose as we can't keep [A] constant.

Experiments 2 and 3: the problem is the change in value for the rate is caused by **two changes** in concentration: A **and** B.

We **must** deal with A first as we know the order and see what it does to the rate. The [A] has been doubled. We know it is 2nd order, so it will cause the rate to increase by a factor of 4. We must multiply $1.89 \times 10^{-3} \times 4 \rightarrow 7.56 \times 10^{-3}$.

✓ At this point it is a good idea to actually write this new value in for the rate. The old value is irrelevant now.

This takes care of A and we can now forget about A and look at B. Use 7.56×10^{-3} as the starting point.

The [B] has been halved and the rate has also been halved: $7.56 \times 10^{-3} \rightarrow 3.78 \times 10^{-3}$. Therefore B must be **1st order**.

The rate equation is: **rate = k[A]²[B]**

Alternative questions

Sometimes they will give you the rate equation and leave a gap in the table. You might have to work out an initial rate or a concentration. There is a very easy way to do this.

They usually get you to calculate k, the rate constant, at some point. If you have k and the rate equation, you can simply put the values into the rate equation and rearrange to calculate anything you need.

The rate constant, k, is always calculated by simply putting numbers into the rate equation.

✓ You can work out these values without calculating k first. But it is a whole lot harder and can be confusing as you are working backwards. But it is worth being able to do it.

Units of k

Units of k are quite a big deal in these questions as they will change with each reaction, so you need to know how to work them out.

Example

If we have **rate = k[A][B]**, we have to rearrange it in terms of k:

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

We then input the units for rate, [A] and [B]. This gives:

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

We can cancel one of the mol dm⁻³ on the bottom line with the mol dm⁻³ on the top line. This leaves:

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

But we can't leave it like that as we need it all on the same line. By bringing mol dm^{-3} to the top line we need to **reverse the indices**.

Remember mol dm^{-3} is actually $\text{mol}^1 \text{dm}^{-3}$, we just usually don't write in the 1. But when it comes to the top line we need it as it becomes -1. The -3 then becomes 3, which gives:

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

- ✓ Don't forget that the units of rate have s^{-1} . This **cannot** be cancelled and therefore it is impossible to get "no units". Compare this with the units in the [equilibrium topic](#).