

# Orders & Calculations

[Rate equations](#)  
[Arrhenius & RDS](#)

In the previous 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, 1<sup>st</sup> and 2<sup>nd</sup> order. 0 order is easy to see as it is a straight line but 1<sup>st</sup> and 2<sup>nd</sup> 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

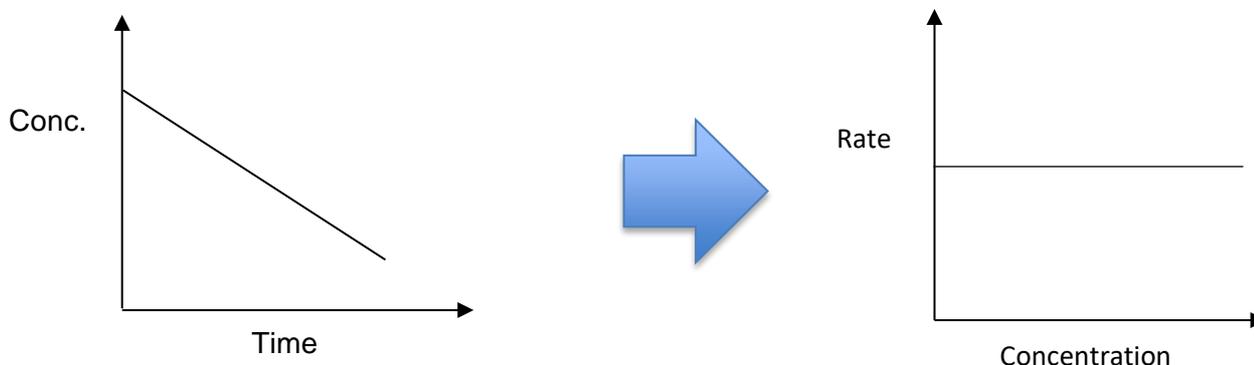
**zero order** is always a **horizontal line** as it has no affect on the rate.

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

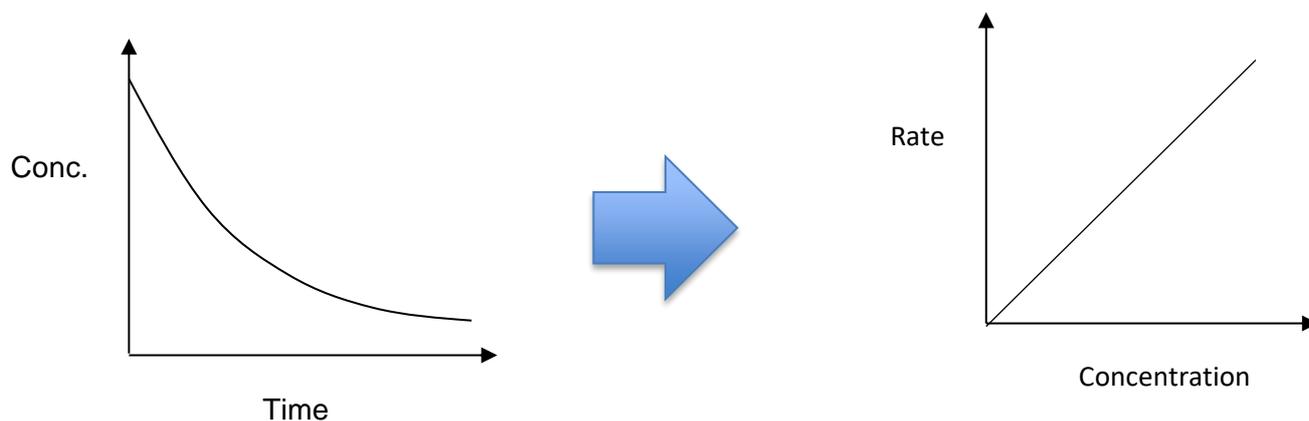
**2<sup>nd</sup> order** has a **curved shape** as it is a squared relationship.

- ✓ 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!

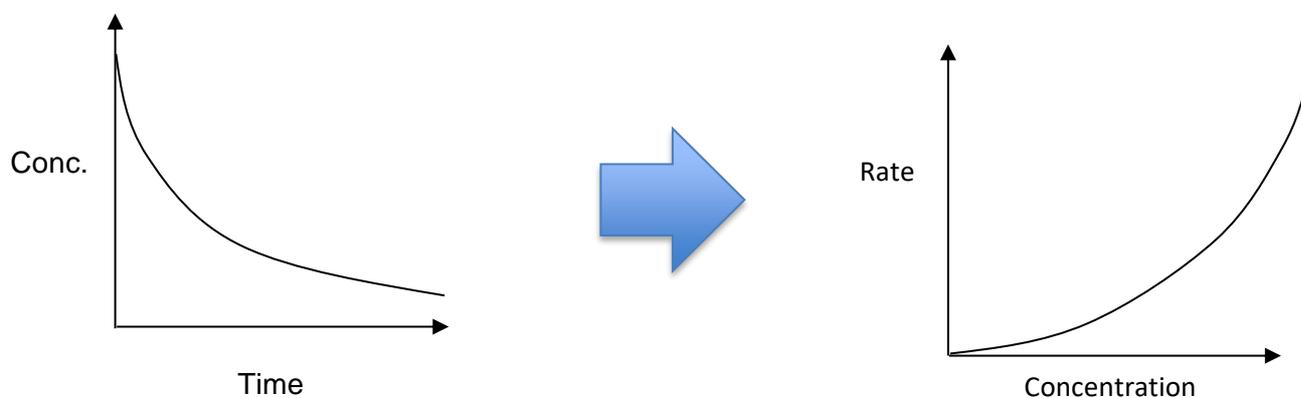
## Zero order



## 1<sup>st</sup> order



## 2<sup>nd</sup> order



## 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 <sup>-3</sup> )	Initial [B] (mol dm <sup>-3</sup> )	Initial rate (mol dm <sup>-3</sup> s <sup>-1</sup> )
1	$6 \times 10^{-3}$	$1 \times 10^{-3}$	$3.0 \times 10^{-3}$
2	$6 \times 10^{-3}$	$2 \times 10^{-3}$	$6.0 \times 10^{-3}$
3	$1 \times 10^{-3}$	$6 \times 10^{-3}$	$0.5 \times 10^{-3}$
4	$2 \times 10^{-3}$	$6 \times 10^{-3}$	$2.0 \times 10^{-3}$

## 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  $6 \times 10^{-3}$  and the [B] is doubled. We can also see that the rate has doubled due to this change in [B]. Therefore, B is 1<sup>st</sup> 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 2<sup>nd</sup> 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 <sup>-3</sup> )	Initial [B] (mol dm <sup>-3</sup> )	Initial rate (mol dm <sup>-3</sup> s <sup>-1</sup> )
1	0.12	0.26	$2.10 \times 10^{-4}$
2	0.36	0.26	$1.89 \times 10^{-3}$
3	0.72	0.13	$3.78 \times 10^{-3}$

**Experiments 1 and 2:** we must start here as it's the only option to can the [B] constant. The [A] has been **tripled** and the rate has gone up by a factor of **9**. Therefore A must be **2<sup>nd</sup> 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:** 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 2<sup>nd</sup> 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. We must also forget about the initial  $1.89 \times 10^{-3}$  value and use  **$7.56 \times 10^{-3}$**  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 **1<sup>st</sup> order**.

The rate equation is: **rate = k[A]<sup>2</sup>[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.

Experiment	Initial [A] / mol dm <sup>-3</sup>	Initial [B] / mol dm <sup>-3</sup>	Initial rate / mol dm <sup>-3</sup> s <sup>-1</sup>
1	$4.2 \times 10^{-3}$	$2.8 \times 10^{-3}$	$3.3 \times 10^{-5}$
2	$7.9 \times 10^{-3}$	$2.8 \times 10^{-3}$	
3		$5.6 \times 10^{-3}$	$1.8 \times 10^{-4}$

### Calculating k

We can calculate k by using the data from experiment 1 (any complete row in the table).

The rate equation was given as:

$$\text{rate} = k[\text{A}]^2$$

Therefore:

$$k = \text{rate}/[\text{A}]^2$$

$$k = 3.3 \times 10^{-5}/[4.2 \times 10^{-3}]^2$$

$$= 1.87$$

### 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. It's the same method that we used in the [equilibrium](#) topic:

Using the same example: **rate = k[A]<sup>2</sup>**, we have to rearrange it in terms of k:

$$k = \frac{\text{Rate}}{[\text{A}]^2}$$

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

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

We can cancel one of the mol dm<sup>-3</sup> on the bottom line with the mol dm<sup>-3</sup> on the top line.

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



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

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

- ✓ Remember mol dm<sup>-3</sup> is actually mol<sup>1</sup> dm<sup>-3</sup>, 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:

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

- ✓ Don't forget that the units of rate **must** have s<sup>-1</sup>. This **cannot** be cancelled and therefore it is impossible to get "no units".

Now that we have k, we can simply substitute into the rate equation to calculate the rate in experiment 2 and [A] in experiment 3:

Experiment	Initial [A] / mol dm <sup>-3</sup>	Initial [B] / mol dm <sup>-3</sup>	Initial rate / mol dm <sup>-3</sup> s <sup>-1</sup>
1	4.2 × 10 <sup>-3</sup>	2.8 × 10 <sup>-3</sup>	3.3 × 10 <sup>-5</sup>
2	7.9 × 10 <sup>-3</sup>	2.8 × 10 <sup>-3</sup>	1.2 × 10 <sup>-4</sup>
3	9.8 × 10 <sup>-3</sup>	5.6 × 10 <sup>-3</sup>	1.8 × 10 <sup>-4</sup>

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