

Kinetics A2 rate equations

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Rate Equations

The rate equation relates mathematically the rate of reaction to the concentration of the reactants.

For the following reaction, $aA + bB \rightarrow \text{products}$, the generalised rate equation is:

$$r = k[A]^m[B]^n$$

r is often used as symbol for rate

The unit of r is usually **mol dm⁻³ s⁻¹**

The square brackets **[A]** means the concentration of A (unit **mol dm⁻³**)

k is called the **rate constant**

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m, n are called **reaction orders**

Orders are usually integers 0,1,2

NOTE: the orders have *nothing* to do with the stoichiometric coefficients in the balanced equation. They are worked out experimentally

0 means the reaction is **zero order with respect to that reactant**

1 means first order

2 means second order

The total order for a reaction is worked out by adding all the individual orders together (m+n)

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THE RATE CONSTANT (k)

1. The units of k depend on the overall order of reaction

For a 1st order overall reaction the unit of k is s^{-1}

For a 2nd order overall reaction the unit of k is $mol^{-1}dm^3s^{-1}$

For a 3rd order overall reaction the unit of k is $mol^{-2}dm^6s^{-1}$

The unit of k must be worked out from the rate equation

2. The value of k is independent of concentration and time

3. The value refers to a specific temperature and it increases if we increase temperature

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Example

$$\text{Rate} = k[A][B]^0 \quad m = 1 \text{ and } n = 0$$

- reaction is first order in A and zero order in B
- overall order = $1 + 0 = 1$
- usually written: $\text{Rate} = k[A]$

Remember: the values of the reaction orders must be determined from experiment; they cannot be found by looking at the balanced reaction equation

Calculating units of k

1. Rearrange rate equation to give k as subject

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

2. Insert units and cancel

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

$$k = \text{s}^{-1}$$

key

Example: Write rate equation for reaction between A and B where A is 1st order and B is 2nd order.

$$r = k[A][B]^2 \quad \text{overall order is 3}$$

Calculate the unit of k

1. Rearrange rate equation to give k as subject

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

3. Simplify fraction

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

2. Insert units and cancel

$$k = \frac{\text{mol dm}^{-3} \text{s}^{-1}}{\text{mol dm}^{-3} \cdot (\text{mol dm}^{-3})^2}$$

$$\text{Unit of } k = \text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$$

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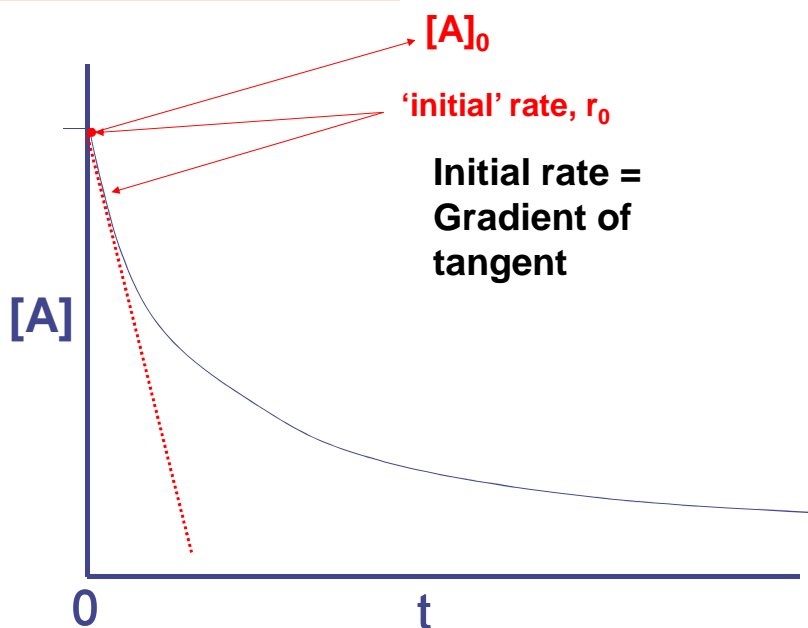
Initial Rate

The initial rate is the rate at the start of the reaction, where it is fastest. It is often obtained by taking the gradient of the conc vs time graph.

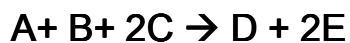
Normally to work out the rate equation we do a series of experiments where the initial concentrations of reactants are changed (one at a time) and measure the initial rate each time.

$$\text{rate} = \frac{\text{change in amount of substance}}{\text{time}}$$

Measuring Initial Rate



Using initial rate data



Experiment	[A] mol dm ⁻³	[B] mol dm ⁻³	[C] mol dm ⁻³	Rate mol dm ⁻³ s ⁻¹
1	0.1	0.5	0.25	0.1
2	0.2	0.5	0.25	0.2
3	0.1	1.0	0.25	0.4
4	0.1	0.5	0.5	0.1

Usually the experimental data is presented in tabular form.

In order to calculate the order for a particular reactant it is necessary to compare two experiments where **only that reactant** is being changed

For example: For reactant A compare between experiments 1 and 2

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How to work out order

Experiment	[A] mol dm ⁻³	[B] mol dm ⁻³	[C] mol dm ⁻³	Rate mol dm ⁻³ s ⁻¹
1	0.1	0.5	0.25	0.1
2	0.2	0.5	0.25	0.2
3	0.1	1.0	0.25	0.4
4	0.1	0.5	0.5	0.1

If conc is doubled and rate stays the same: order= 0

If conc is doubled and rate doubles: order= 1

If conc is doubled and rate quadruples : order= 2

For reactant A as the concentration doubles so does the reaction rate. Therefore the order with respect to reactant A is first order

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Experiment	[A] mol dm ⁻³	[B] mol dm ⁻³	[C] mol dm ⁻³	Rate mol dm ⁻³ s ⁻¹
1	0.1	0.5	0.25	0.1
2	0.2	0.5	0.25	0.2
3	0.1	1.0	0.25	0.4
4	0.1	0.5	0.5	0.1

What is the order with respect to B?

Comparing between experiments 1 and 3 :

As the concentration of B doubles the rate quadruples.

Therefore the order with respect to B is 2nd order

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Experiment	[A] mol dm ⁻³	[B] mol dm ⁻³	[C] mol dm ⁻³	Rate mol dm ⁻³ s ⁻¹
1	0.1	0.5	0.25	0.1
2	0.2	0.5	0.25	0.2
3	0.1	1.0	0.25	0.4
4	0.1	0.5	0.5	0.1

What is the order with respect to C?

Comparing between experiments 1 and 4 :

As the concentration of C doubles the rate stays the same.

Therefore the order with respect to C is zero order

The overall rate equation is $r = k [A] [B]^2$

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Working out orders when two reactants are changed

In most questions it is possible to compare between two experiments where only one reactant has its initial concentration changed. If, however, both reactants are changed then the effect of both individual changes are multiplied together.

Experiment	Initial concentration of X/mol dm ⁻³	Initial concentration of Y/mol dm ⁻³	Initial rate/mol dm ⁻³ s ⁻¹
1	0.05	0.1	0.15 x 10 ⁻⁶
2	0.10	0.1	0.30 x 10 ⁻⁶
3	0.20	0.2	2.40 x 10 ⁻⁶

Comparing between experiments 1 and 2 :

As the concentration of X doubles the rate doubles.

Therefore the order with respect to X is 1st order

Working out orders when two reactants are changed

Experiment	Initial concentration of X/mol dm ⁻³	Initial concentration of Y/mol dm ⁻³	Initial rate/mol dm ⁻³ s ⁻¹
1	0.05	0.1	0.15 x 10 ⁻⁶
2	0.10	0.1	0.30 x 10 ⁻⁶
3	0.20	0.2	2.40 x 10 ⁻⁶

It is not possible to compare two experiment where only Y changes

Comparing between experiments 2 and 3 :

Both X and Y double and the rate goes up by 8

We know X is first order so that will have doubled rate

The effect of Y, therefore, on rate is to have quadrupled it.

Y must be second order

Calculating a value for k

Experiment	[A] mol dm ⁻³	[B] mol dm ⁻³	[C] mol dm ⁻³	Rate mol dm ⁻³ s ⁻¹
1	0.1	0.5	0.25	0.1
2	0.2	0.5	0.25	0.2
3	0.1	1.0	0.25	0.4
4	0.1	0.5	0.5	0.1

Choose any one of the experiments and put the values into the rate equation that has been rearranged to give k

$$r = k [A] [B]^2$$

$$k = \frac{r}{[A] [B]^2}$$

$$k = \frac{0.4}{0.1 \times 1.0^2}$$

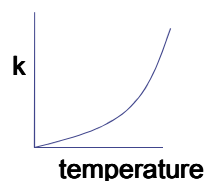
$$k = 4.0 \text{ mol}^{-2}\text{dm}^6\text{s}^{-1}$$

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Remember k is the same for all experiments done at the same temperature.

Increasing the temperature increases the value of the rate constant k

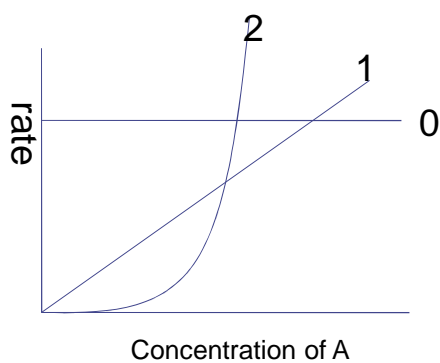
Increasing temperature increases the rate constant k. The relationship is given by the Arrhenius equation $k = Ae^{-E_a/RT}$ where A is a constant R is gas constant and E_a is activation energy.



You do not need to learn or use the Arrhenius equation but be aware that the relationship between k and Temperature is not directly proportional but is shown on the graph to the right

Rate vs concentration graphs for different orders

Initial rate data can also be used graphically to work out orders.



For zero order

$$r = k[A]^0 = k$$

For first order

$$r = k[A]^1$$

For second order

$$r = k[A]^2$$