

RATE EQUATIONS PART 1

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RATE EQUATIONS

Rate of reaction = how fast the amount of product increases (or amount of reactant decreases)

For a reaction $A + B \rightarrow C$ the **rate equation** is $\text{rate} = k[A]^m[B]^n$ (m and n can be 0, 1 or 2)

The **order** of this reaction is m with respect to A and n with respect to B ; the **overall order** is $m + n$

The **rate constant** is k in the equation – it has a constant value at constant temperature

Half-life is the time taken for the amount of a reactant to decrease by one half

If a reaction happens in a series of steps, the **slowest** step is called the **rate-determining step**

WORKING OUT AND USING THE RATE EQUATION

You can use **initial rates** data to work out the order of a reaction and the rate constant (k). You need to carefully pick pairs of data in which the concentration of one reactant changes and look at how this affects the rate.

- Changing concentration with no effect on rate: **zero order**
- Concentration changes and rate changes by the **same factor** (e.g. $\times 2$ for both): **first order**
- Rate changes by the **square of the factor** concentration changes by (e.g. concentration $\times 2$ and rate $\times 4$, or concentration $\times 3$ and rate $\times 9$): **second order**

Example: chloromethane reacts with hydroxide ions to form methanol: $\text{CH}_3\text{Cl} + \text{OH}^- \rightarrow \text{CH}_3\text{OH} + \text{Cl}^-$

The reaction was performed with different initial concentrations of reactants, and the initial rate was measured. Use the data to write a rate equation for this reaction and work out the value of the rate constant, k .

$[\text{CH}_3\text{Cl}]$ / mol dm^{-3}	$[\text{OH}^-]$ / mol dm^{-3}	Initial rate / $\text{mol dm}^{-3} \text{s}^{-1}$	
0.020	0.10	1.0×10^{-4}	$[\text{CH}_3\text{Cl}]$ doubles ($[\text{OH}^-]$ remains constant), initial rate doubles – this means the reaction is first order with respect to CH_3Cl
0.040	0.10	2.0×10^{-4}	
0.020	0.20	2.0×10^{-4}	$[\text{OH}^-]$ doubles ($[\text{CH}_3\text{Cl}]$ remains constant), initial rate doubles – this means the reaction is first order with respect to OH^-

The rate equation is $\text{rate} = k[\text{CH}_3\text{Cl}]^m[\text{OH}^-]^n$

From the data above, we can tell that $m = 1$ and $n = 1$

$$\text{Rate} = k[\text{CH}_3\text{Cl}][\text{OH}^-] \quad \text{so } k = \frac{\text{rate}}{[\text{CH}_3\text{Cl}][\text{OH}^-]} = \frac{1.0 \times 10^{-4}}{0.020 \times 0.10} = 5.0 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

We can now work out the rate for any concentrations – e.g. if $[\text{CH}_3\text{Cl}] = 0.080 \text{ mol dm}^{-3}$ and $[\text{OH}^-] = 0.50 \text{ mol dm}^{-3}$

$$\text{Rate} = k[\text{CH}_3\text{Cl}][\text{OH}^-] = 5.0 \times 10^{-4} \times 0.080 \times 0.50 = 2.0 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$$

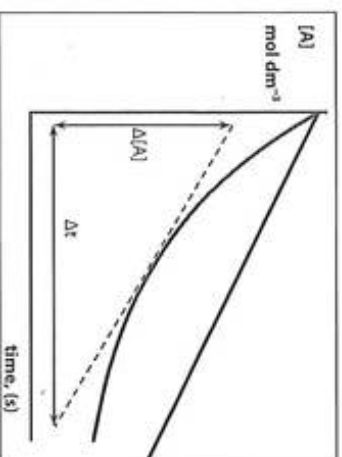
EXAM TIP

Units depend on the order. Don't try to memorise them – work them out every time.

WORKING OUT ORDERS FROM GRAPHS

1 Concentration–time graphs

For the reaction $A \rightarrow B$, the concentration of A decreases as the reaction progresses – but the shape of the graph of $[A]$ against time tells you the **order** of the reaction with respect to A



Straight line means **zero order**
Rate = gradient = k (constant)

Curve means **first or second order**
Rate = gradient = $k[A]$ or $k[A]^2$

EXAM TIP
The rate at any point is the gradient of the tangent at that point
 $\text{rate} = \Delta[A]/\Delta t$

$[A]$ can be continuously measured using techniques such as colorimetry

First and second order can be distinguished by measuring successive **half-lives** (time taken for $[A]$ to halve). If the half-life, $t_{1/2}$, is **constant**, then the graph represents a **first-order** reaction.

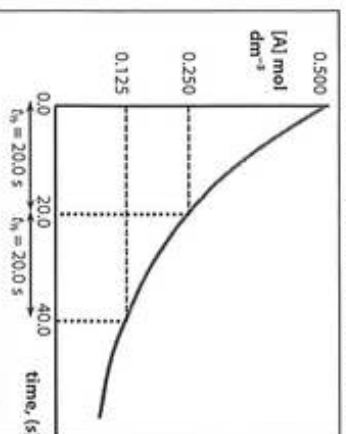
Calculating the rate constant, k

The time for $[A]$ to fall from $0.500 \text{ mol dm}^{-3}$ to $0.250 \text{ mol dm}^{-3}$ is 20.0 s
The time for $[A]$ to fall from $0.250 \text{ mol dm}^{-3}$ to $0.125 \text{ mol dm}^{-3}$ is 20.0 s

i.e. $t_{1/2} = 20.0 \text{ s}$ and is constant (so this reaction is first order)

For first-order reactions, the rate constant can be calculated using the formula: $k = \frac{\ln 2}{t_{1/2}}$

$$\text{In this case: } k = \frac{\ln 2}{20.0} = \frac{0.693}{20.0} = 0.0347 \text{ s}^{-1}$$



Finding the initial rate

Very early in the reaction, the graphs of first- and second-order reactions are approximately straight lines.

Initial concentration–time data (e.g. from timing the production of a small fraction of total amount of product) can be used to calculate the **initial rate**.

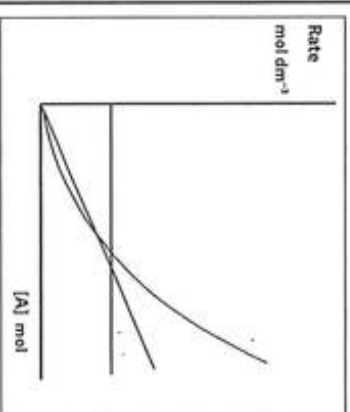
e.g. the concentration of product increases from 0 to $0.030 \text{ mol dm}^{-3}$ in 12 s , the initial rate is $0.030 / 12 = 2.5 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$.

For fast reactions this may require sophisticated techniques to time very short periods.

The initial rate can also be determined by measuring the gradient at the start of a concentration–time graph.

Rate–concentration graphs

For the reaction $A \rightarrow B$, the shape of the graph of rate vs $[A]$ tells you the **order** of the reaction with respect to A . For zero- and first-order reactions, you can work out the rate constant, k , from the graph.



Curved line (gradient changes) means **second order**
Rate = $k[A]^2$

Straight line with **gradient** > 0 means **first order**
Rate = $k[A]$
Rate constant, k = gradient
Horizontal line (gradient = 0) means **zero order**
Rate = k (i.e. $[A]$ has no effect)

This may be produced by measuring the initial rate several times with different initial concentrations of A