

Rates of Reaction (A2)

Rate of reaction is the rate of change of amount or concentration of a reactant or product. Units are often $\text{mol dm}^{-3}\text{s}^{-1}$.

For the reaction: $A + B \rightarrow C$

the rate of reaction is related to [A] and [B], where [] denotes "concentration of".

$$\text{Rate equation: Rate} = k[A]^m[B]^n$$

Order of reaction

m and n are 0, 1 or 2 and are found **experimentally**, not from the balanced equation for a reaction.

m is the **order of reaction** with respect to A and n is the order with respect to B.

$$\text{Overall order of reaction} = m + n$$

"The order of a reaction with respect to a given reactant is the power of that reactant's concentration in the experimentally determined rate equation.

The overall order of the reaction is the sum of the powers of the concentration terms in the experimentally determined rate equation."

Rate constant is k in the rate equation. It is constant for a particular reaction at a given temperature.

Half-life of a reaction is the time taken for the mass or concentration of a reactant to fall to half its initial value.

Rate-determining step is the slowest step in a mechanism which determines the overall rate of the reaction.

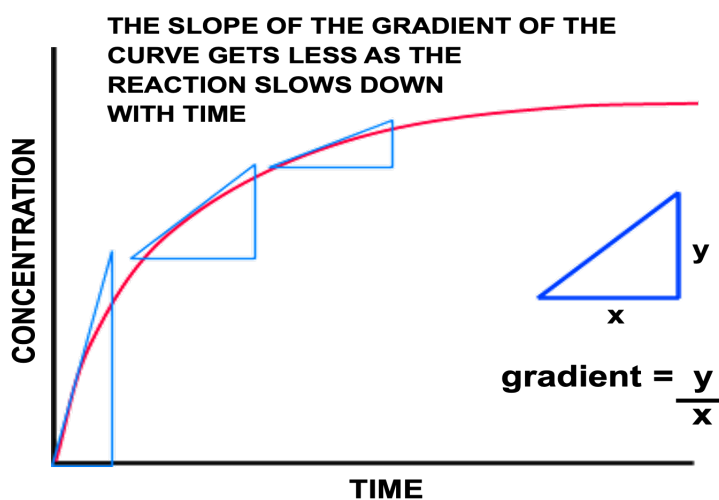
Use of a concentration-time graphs

In a **continuous rates experiment** one batch of chemicals is mixed and the concentration of one chemical is recorded over a period of time.

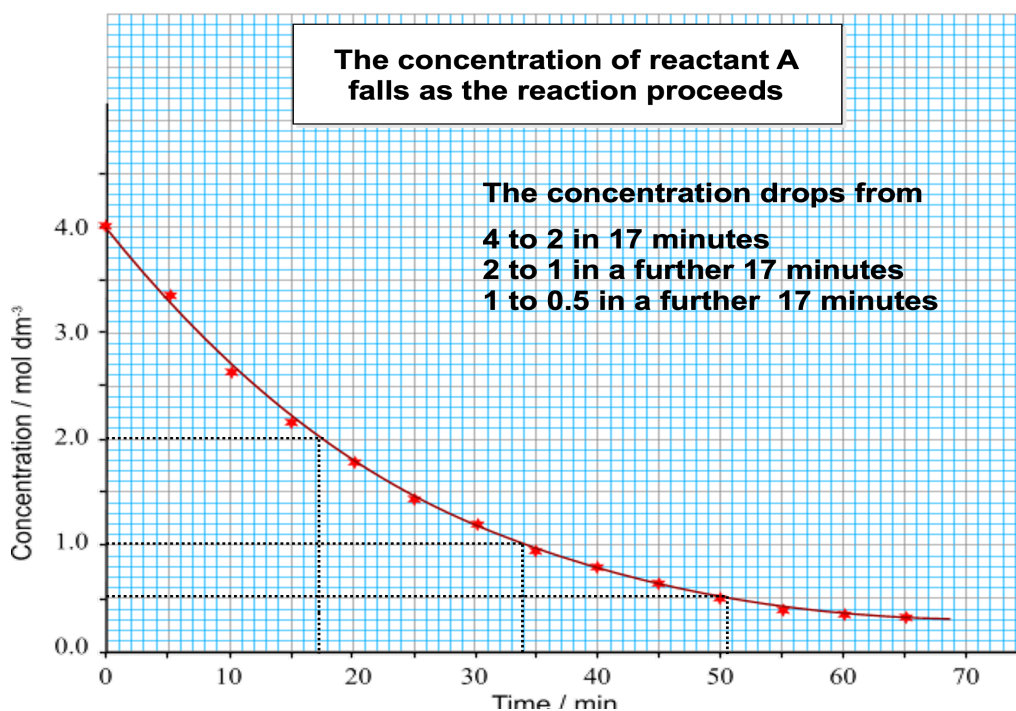
- To deduce the rate of a reaction

A concentration-time graph is plotted and tangents to the curve are drawn at several points.

The gradient of the graph at a particular point gives the rate at that point.

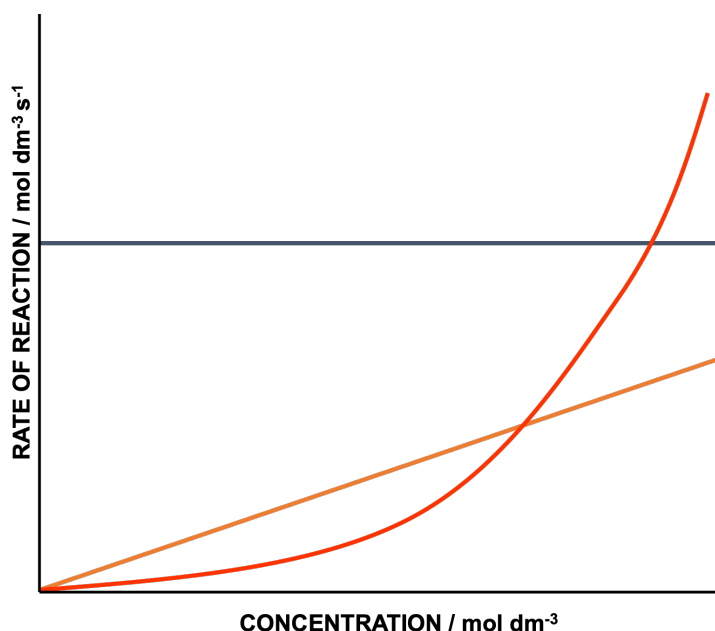


- **The half-life of a first-order reaction** is independent of concentration. It is obtained from a concentration-time graph by reading off the time taken for the concentration to fall to half its initial value. The half-life of a first order reaction is independent of the concentration.



Deducing, from a rate-concentration graph, the order (0,1 or 2) with respect to a reactant

NB For a zero order reaction, rate is independent of concentration.



SECOND ORDER – the rate is proportional to the square of the concentration. You get an upwardly sloping curve.

ZERO ORDER – the rate does not depend on the concentration. The line is parallel to the x axis.

FIRST ORDER – the rate is proportional to the concentration so you get a straight line of fixed gradient. The gradient of the line equals the rate constant for the reaction.

Initial rates method of obtaining order with respect to a reactant

The initial rate of reaction is measured for several batches of chemicals, using different concentrations. The concentration of each chemical is changed in turn whilst the others are fixed.

e.g. Deduce the order of reaction using the following results for the reaction between two gases, A and B;

Experiment	[A] (mol dm ⁻³)	[B] (mol dm ⁻³)	Initial rate (mol dm ⁻³ s ⁻¹)
1	0.15	0.15	1.0
2	0.30	0.15	4.0
3	0.15	0.30	2.0

1&2 [B] constant, [A] doubled, rate is x4 Reaction is second order wrt A.

1&3 [A] constant, [B] doubled, rate doubled. Reaction is first order wrt B.
Reaction is third order overall.

Constructing a rate equation for the above example:

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

Calculating a rate constant from a rate equation NB Take care with units.

$$\text{In the above example, } k = \frac{\text{Rate}}{[\text{A}]^2[\text{B}]} = \frac{1.0}{0.15^2 \times 0.15} = 296 \text{ mol}^{-2}\text{dm}^6\text{s}^{-1}$$

The effect of temperature change on a rate constant and the rate of a reaction

An increase of 10 degrees C approximately doubles the rate of reaction. Increasing temperature increases the value of k for a reaction.

Reaction mechanisms

The rate equation for a reaction may be obtained from the rate-determining step.

e.g. If RDS is $\text{A} + 2\text{B} \rightarrow \dots$ then reaction is first order wrt A and second order wrt B, i.e. the slowest step in the mechanism involves 1 molecule of A and 2 molecules of B.

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

Possible steps in a reaction mechanism must add up to the balanced equation for the reaction.

In the above example, if the balanced equation is: **$2\text{A} + 2\text{B} \rightarrow \text{C} + \text{D}$**

A possible mechanism is:

