Kinetics

Rate equations, order and half-life, finding order from data and graphs, rate-determining steps and mechanisms, SN1 and SN2, the Arrhenius equation, and catalysts.

Rate equations

The **rate equation** links the rate to the concentrations of reactants. For $A + B \longrightarrow$ products:

$$\text{rate} = k[A]^m[B]^n$$

- The **order with respect to a substance** is the power to which its concentration is raised in the rate equation (0, 1 or 2).
- The **overall order** is the sum of the individual orders, $m + n$.
- k is the **rate constant**. It is constant at a given temperature and its units depend on the overall order.

Orders can only be found from **experiment**, never from the stoichiometric equation.

Order	Effect of doubling the concentration	Rate–concentration graph
0	No effect on the rate	Horizontal line
1	Rate doubles	Straight line through the origin
2	Rate quadruples	Curve (upward)

Units of k

Rearrange the rate equation and substitute units.

Overall order	Units of k
0	mol dm^{-3} s^{-1}
1	s^{-1}
2	dm^3 mol^{-1} s^{-1}
3	dm^6 mol^{-2} s^{-1}

Half-life

The **half-life**, $t_{1/2}$, is the time for the concentration of a reactant to halve. For a **first-order** reaction the half-life is **constant**, however much reactant remains, and

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

On a concentration–time graph, measure several successive half-lives. If they are equal, the reaction is first order.

Finding the order from data

Concentration–time graph

- A **straight line** with a constant negative gradient is **zero order** (rate does not change).
- A curve with a **constant half-life** is **first order**.
- Draw tangents at several concentrations to find rates; a plot of **rate against concentration** then gives the order (above).

Initial-rate method

Do separate experiments with different **initial concentrations** of one reagent, keeping the others fixed, and find the initial rate (from the gradient of the tangent at $t = 0$, or from $1/t$ in a clock reaction).

> **TRY IT**
>
> The initial rate doubles when $[A]$ doubles, and is unchanged when $[B]$ doubles. Another experiment shows that quadrupling $[C]$ gives a rate sixteen times as great. Write the rate equation.

Order in A is 1, in B is 0, in C is 2. Rate $= k[A][C]^2$.

Clock reactions

In an iodine clock reaction, the time t for the sudden appearance of a blue colour with starch is measured. The rate is proportional to $1/t$, a good approximation to the initial rate if only a small fraction of reactant has been used.

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Techniques for following a reaction

Technique	Used when
Titration	Take samples at intervals, **quench** to stop the reaction (e.g. add excess sodium hydrogencarbonate to an acid-catalysed reaction), titrate
Colorimetry	A reactant or product is coloured; a calibration curve relates absorbance to concentration
Mass change	A gas leaves the flask
Volume of gas	A gas is evolved (gas syringe)
Conductivity or pH	Ions are used up or formed

Rate-determining step and mechanism

The **rate-determining step** is the **slowest step** in a mechanism. The rate equation includes only species up to and including the rate-determining step. A species in the rate equation is in the rate-determining step (or in an earlier fast equilibrium step).

- An order of zero in a reactant means it takes part **after** the rate-determining step.
- A reaction that is first order overall with a two-step mechanism: the slow step involves one species.

> **TRY IT**
>
> The reaction $2NO + O_2 \rightarrow 2NO_2$ has rate $= k[NO]^2[O_2]$. Suggest what the rate-determining step involves.

It involves two molecules of NO and one of O_2 (three particles), such as a step in which these three collide, or a fast equilibrium to form N_2O_2 followed by a slow reaction of N_2O_2 with O_2.

Propanone and iodine

The acid-catalysed iodination of propanone, $CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + HI$, has rate $= k[CH_3COCH_3][H^+]$. The rate is **zero order in iodine**, so iodine is **not** involved in the rate-determining step. The slow step involves propanone and H^+ (forming an enol), and the iodine reacts later in a fast step. This is the basis of **Core Practical 9a**, in which the rate is followed by **titrating** samples (quenched with sodium hydrogencarbonate) against sodium thiosulfate. **Core Practical 9b** times an **iodine clock** reaction instead.

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SN1 and SN2

The rate equations for the hydrolysis of halogenoalkanes give evidence for the mechanisms.

	Tertiary halogenoalkane	**Primary halogenoalkane**
Rate equation	rate $= k[RBr]$ (first order)	rate $= k[RBr][OH^-]$ (second order)
Mechanism	**SN1**: slow ionisation to a carbocation, then fast attack by OH^-	**SN2**: one step, OH^- attacks as the bromide leaves
Intermediate	Carbocation (planar)	Transition state (five-coordinate)

(Secondary halogenoalkanes can react by both routes.)

In SN1 the nucleophile does not appear in the rate equation, because it is only involved after the rate-determining step. In SN2 both are in the slow step.

Activation energy and temperature

The **Arrhenius equation** relates the rate constant to temperature (it is given in exams if needed):

$$k = Ae^{-E_a/RT} \qquad \ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T}$$

A graph of $\ln k$ against $1/T$ is a **straight line** with gradient $-E_a/R$ (and intercept $\ln A$). So $E_a = -\text{gradient} \times R$, with $R = 8.31$ J K^{-1} mol^{-1} and T in kelvin, giving E_a in J mol^{-1}.

Core Practical 10 finds E_a by measuring the rate of a reaction (e.g. thiosulfate with acid, or magnesium with hydrochloric acid) at different temperatures.

NOTE

Temperature must be in kelvin, and convert E_a to kJ mol^{-1} by dividing by 1000. Keep the concentrations the same for each run.

Catalysts

- A **heterogeneous catalyst** is in a different phase from the reactants. In industrial gas reactions the **solid catalyst provides a surface**: reactant molecules are **adsorbed**, bonds weaken, reaction occurs and the products are **desorbed**.
- A **homogeneous catalyst** is in the same phase as the reactants and reacts via an intermediate.

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