

Orders, rate constants and activation energy

Chemistry grades 11-12 (A Level · IB · Class 11-12) · Lesson

Quick answer: A rate equation, $\text{rate} = k[A]^m[B]^n$, shows how concentration controls reaction speed; orders come from experiments, not from the balanced equation. The rate constant k rises with temperature according to the Arrhenius equation, and the slowest step in a mechanism, the rate-determining step, fixes the form of the rate equation.

Level: Chemistry grades 11-12 (A Level · IB · Class 11-12) · **Curriculum:** IB R2.2

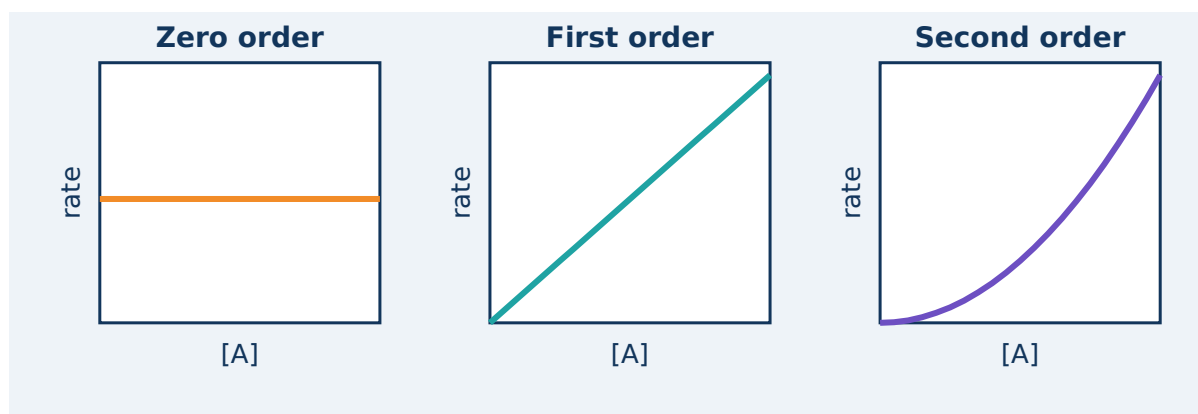
What is a rate equation?

Definition

A rate equation links the rate of a reaction to the concentrations of the reactants: $\text{rate} = k[A]^m[B]^n$. The exponents m and n are the orders of reaction with respect to A and B, the overall order is $m + n$, and k is the rate constant, which depends only on temperature (and catalyst).

Key law

Orders are found only by experiment. They are not the coefficients in the balanced equation. The rate equation of a reaction is also unrelated to its stoichiometry.



Rate against [A]: flat line (zero), straight line through the origin (first), upward curve (second).

Order in A	Rate against [A]	Doubling [A] changes the rate by	Units of k (overall)
0	constant	$\times 1$	$\text{mol dm}^{-3} \text{ s}^{-1}$
1	straight line through origin	$\times 2$	s^{-1}
2	curve upward	$\times 4$	$\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

How do you find the order from experimental data?

The initial-rates method changes one concentration at a time. If doubling [A] doubles the rate, the order is 1; if it quadruples the rate, the order is 2; if the rate is unchanged, the order is 0. Continuous monitoring gives the order from the shape of a concentration–time graph, as below.



Concentration against time for a first order and a zero order reaction.

Formula

First order half-life: $t_{1/2} = \ln 2 / k = 0.693 / k$

$t_{1/2}$ = half-life (s), k = rate constant (s^{-1}). The half-life of a first order reaction is constant; for zero order it falls as the concentration falls.

Worked example

For $A + B \rightarrow \text{products}$: experiment 1 has $[A] = 0.10$ and $[B] = 0.10 \text{ mol/dm}^3$ with rate $2.4 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$; experiment 2 has $[A] = 0.20$ and $[B] = 0.10$ with rate 4.8×10^{-4} ; experiment 3 has $[A] = 0.10$ and $[B] = 0.30$ with rate 2.16×10^{-3} .

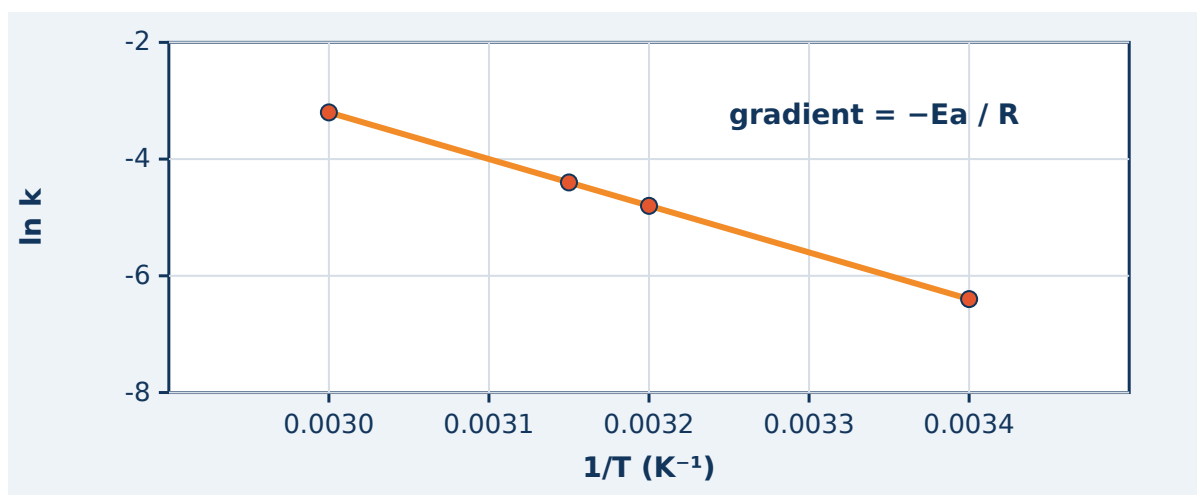
Doubling [A] doubles the rate, so the order in A is 1. Tripling [B] multiplies the rate by 9, so the order in B is 2. Rate = $k[A][B]^2$. Then $k = 2.4 \times 10^{-4} / (0.10 \times 0.10^2) = \mathbf{0.24 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}}$.

How does temperature change the rate constant?

Formula

Arrhenius: $k = A e^{-E_a/RT}$, so $\ln k = \ln A - E_a / (RT)$

k = rate constant, A = pre-exponential factor (same units as k), E_a = activation energy (J/mol), $R = 8.314 \text{ J/(mol K)}$, T = temperature (K). A graph of $\ln k$ against $1/T$ has gradient $-E_a/R$.



Arrhenius plot: a straight line with negative gradient $-E_a/R$.

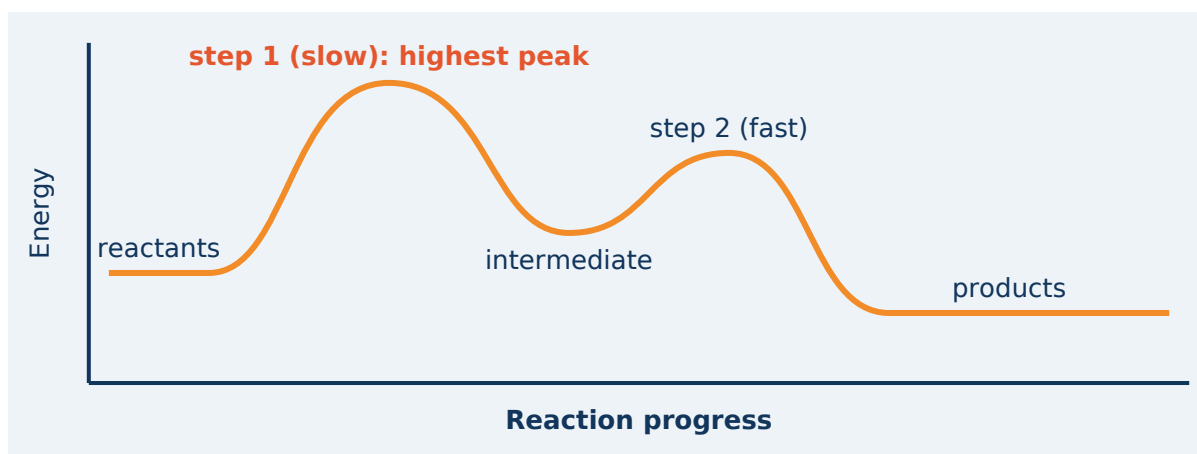
Worked example

A reaction has $k = 1.5 \times 10^{-3} \text{ s}^{-1}$ at 300 K and $1.2 \times 10^{-2} \text{ s}^{-1}$ at 320 K. Calculate E_a .

$\ln(k_2/k_1) = \ln 8 = 2.079$. $1/300 - 1/320 = 2.083 \times 10^{-4} \text{ K}^{-1}$. $E_a = 8.314 \times 2.079 / 2.083 \times 10^{-4} = 82\,980 \text{ J/mol} = \mathbf{83.0 \text{ kJ/mol}}$.

What is the rate-determining step?

Many reactions occur in several steps. The slowest step controls the overall rate and is the rate-determining step. Species in the rate equation appear in that step or in the equilibria before it. For example, the hydrolysis of $(\text{CH}_3)_3\text{CBr}$ by hydroxide has rate $= k[(\text{CH}_3)_3\text{CBr}]$. The slow step is $(\text{CH}_3)_3\text{CBr} \rightarrow (\text{CH}_3)_3\text{C}^+ + \text{Br}^-$, which involves no OH^- , and the fast step $(\text{CH}_3)_3\text{C}^+ + \text{OH}^- \rightarrow (\text{CH}_3)_3\text{COH}$ follows.



Two-step mechanism: the step with the highest peak is the slow, rate-determining step.

Common mistake

Do not write the rate equation from the balanced equation, and do not give k a fixed unit. The units of k depend on the overall order and must be worked out from the rate equation.

Lina's tip

To get the units of k , put the units into the rate equation, $\text{mol dm}^{-3} \text{ s}^{-1} = k \times (\text{mol}$

$\text{dm}^{-3})^{\text{order}}$, and solve for k .

Key points to remember

- Rate = $k[A]^m[B]^n$; overall order = $m + n$; orders are found experimentally.
- Units of k : zero order $\text{mol dm}^{-3} \text{s}^{-1}$, first order s^{-1} , second order $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$.
- First order half-life $t_{1/2} = 0.693 / k$ and is constant.
- Arrhenius: $\ln k = \ln A - E_a / RT$; gradient of $\ln k$ against $1/T$ is $-E_a/R$.
- The rate-determining step is the slowest step and sets the species in the rate equation.

Orders, rate constants and activation energy: frequently asked questions

What is the order of reaction?

The order with respect to a reactant is the power to which its concentration is raised in the rate equation. It tells you how the rate changes when that concentration changes and is found from experiments.

How do you find the units of the rate constant?

Substitute the units of rate and of each concentration into the rate equation and rearrange for k . For a first order reaction the units are s^{-1} , and for a second order reaction $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$.

What does the half-life tell you?

For a first order reaction the half-life is constant and equals 0.693 divided by k . If the half-life changes as the reaction proceeds, the reaction is not first order.

How do you find activation energy from a graph?

Plot $\ln k$ against $1/T$ for several temperatures. The gradient of the straight line equals $-E_a/R$, so $E_a = -\text{gradient} \times 8.314 \text{ J/(mol K)}$.

What is a rate-determining step?

It is the slowest step in a reaction mechanism and controls the overall rate. The reactants that appear in the rate equation take part in this step or in steps before it.