# How fast? The rate of chemical change

Reactivity 2.2 · SL and AHL

# Why does food last longer in a fridge?

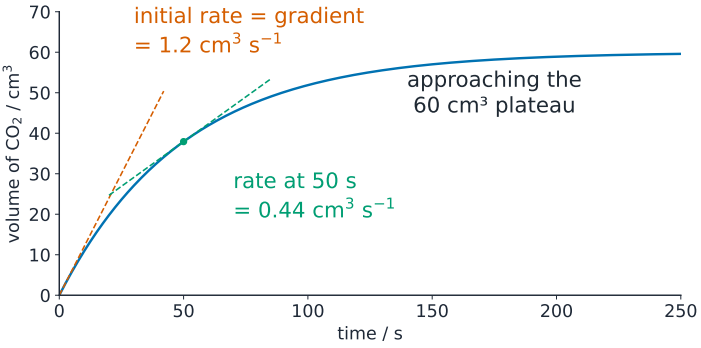
Temperature changes how fast a reaction goes.

- Cooling slows many deterioration reactions; storage life depends on the food and conditions.
- A firework burns in a second; iron rusts over months.
- This unit: measuring rate $\rightarrow$ collisions $\rightarrow$ controlled conditions.

# Following a reaction

| What changes | Method |
|---|---|
| gas given off | gas syringe, volume every 10 s |
| gas escapes | mass loss on a balance |
| colour | colorimeter |
| ions | conductivity or pH meter |
| precipitate | time for a cross to disappear |

# Reading a rate from a graph




The **initial rate** is the gradient at $t = 0$.

# Three conditions for reaction

- Particles must collide.
- With energy at least $E_a$, and the right orientation.

> **Activation energy** the minimum energy that colliding particles need for a reaction

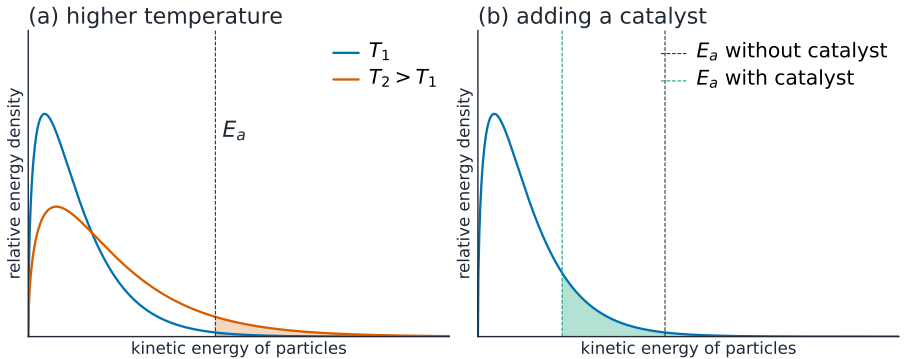
# Use kelvin for mean kinetic energy

1. **Compare.** Heat from 20 °C to 40 °C: temperatures are 293.15 K and 313.15 K.
2. **Mean energy.** Factor 313.15/293.15=1.068, an increase about 6.8%, rather than a doubling.
3. **Rate.** The high-energy tail changes too; this mean-energy ratio alone does not determine the rate factor.

## Decision

Temperature ratios for kinetic energy use kelvin.

# The Maxwell–Boltzmann distribution




Above-threshold energy is necessary; orientation and pathway still matter.

# Concentration, pressure and surface area

| Change | Why it is faster |
| --- | --- |
| higher concentration | more particles per $dm^3$ |
| compress the reactant gases | higher reactant concentration at fixed temperature |
| smaller pieces | more particles exposed |

# Check: why does temperature matter so much?

## Your turn

What is the main reason a higher temperature speeds up a reaction?

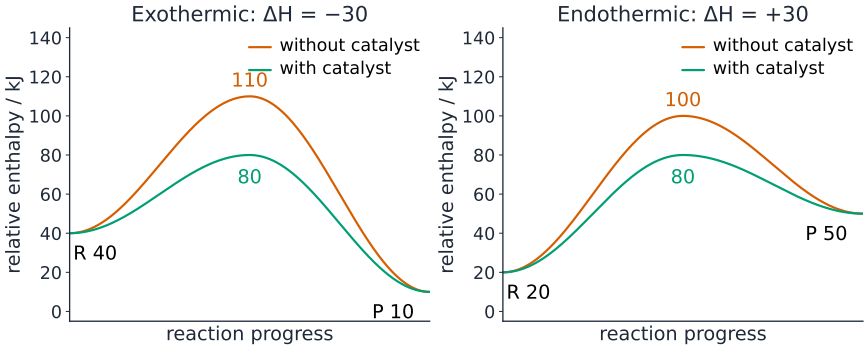
A. Particles collide a little more often.

B. A much larger fraction of collisions has energy at least $E_a$.

C. The activation energy falls.

D. The enthalpy change becomes more negative.

# Catalysts




A **catalyst** does not change $\Delta H$ or the equilibrium position.

# Distinguish a mean from a tangent gradient

1. **Invented interval.** Gas rises from 10.0 to 34.0 $cm^3$ between 20 and 60 s: $(34-10)/(60-20)=0.600$ $cm^3/s$.
2. **Invented tangent.** Points on the **tangent**: (30 s,22 $cm^3$) and (70 s,46 $cm^3$). Gradient$=(46-22)/(70-30)=0.600$ $cm^3/s$.
3. **Interpret.** A secant averages an interval; a tangent estimates one instant. These two values happen to coincide.

## Decision

Use points on the tangent, rather than two arbitrary curve points.

# A coefficient changes the species disappearance rate

1. **Equation.** 2A $\rightarrow$ B at fixed volume; [A] falls by 0.030 mol/dm$^3$ over 5.0 s.
2. **A disappearance.** $0.030/5.0 = 0.0060$ mol/dm$^3$/s.
3. **B formation.** Divide by two: 0.0030 mol/dm$^3$/s, also the coefficient-normalized reaction rate.

## Decision

State which species and rate convention the data use.

# A plateau needs an explanation

## Possible chemistry

Limiting reagent exhausted in a complete reaction.

Dynamic equilibrium with equal forward and reverse rates.

## Possible measurement limit

Leaks, sensor saturation or a change smaller than resolution.

The curve records net measured change.

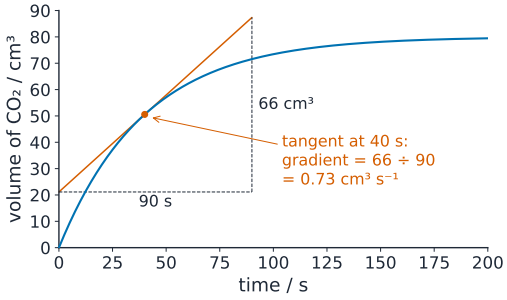
# A fixed threshold makes 1/t an approximate proxy

1. **Comparable trials.** Cross-disappearance times are 40 s and 25 s; use the same optical path and threshold.
2. **Relative factor.** $(1/25)/(1/40)=1.6$: the second trial has a 1.6-fold proxy rate.
3. **Limitation.** Changed threshold, path length or subjective timing breaks the comparison.

## Decision

This proxy does not directly give an instantaneous concentration rate.

# Rate from a tangent




Rate $\approx 0.73$ $cm^3$ $s^{-1}$

# Four ways to follow a rate

**gas syringe**: gas-tight joints, fit at once (early gas is fastest)

**mass loss**: gas must escape; account for evaporation and spray

**colorimeter**: calibrate; fixed wavelength, path, working range

**pH or conductivity**: pH is logarithmic; all ions conduct

change one factor, control the rest, repeat to estimate variability

Each has its own caveat

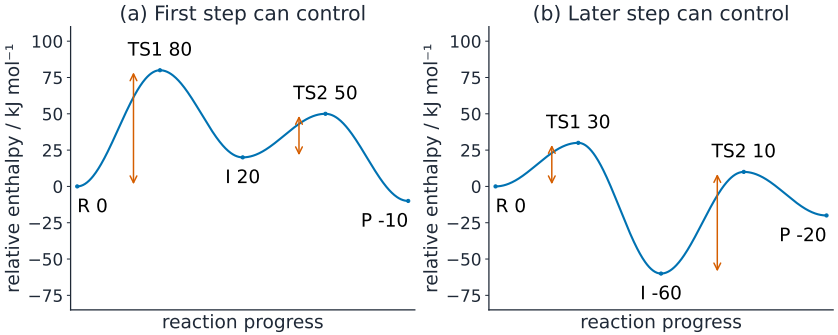
# Read the endothermic barriers in both directions

1. **Invented levels.** Reactants 20, products 50 and uncatalysed peak 100 kJ per reaction amount.
2. **Differences.** $\Delta H = +30$; forward Ea=80 and reverse Ea=50 kJ.
3. **Catalysed peak 80.** Forward Ea=60, reverse Ea=30; $\Delta H$ remains +30 kJ.

## Decision

At the same temperature the thermal-energy distribution is unchanged.

# AHL: Mechanisms and the slow step




Measure each barrier from the state immediately before that peak.

# AHL: The rate equation

- Orders come from experiments, not the balanced equation.
- k applies to a specified pathway, medium and **catalyst**; positive-Ea Arrhenius k rises with T.

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

Units of $k$: first **order** $s^{-1}$, second order $dm^3\ mol^{-1}\ s^{-1}$

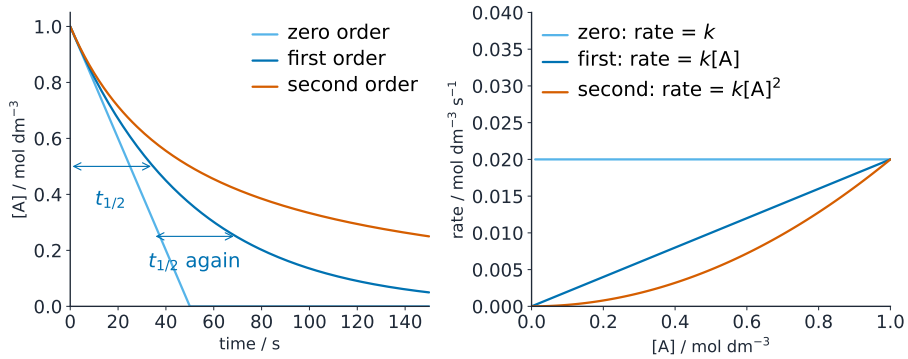
# AHL: Orders from initial rates

1. **[NO] ×2.** Invented data, concentrations in mol/dm$^3$ and rates in mol/dm$^3$/s: [NO] 0.10→0.20 at [$Br_2$] 0.10; rate 0.0012→0.0048: **order** 2.
2. **[$Br_2$] ×2.** At [NO] 0.10, [$Br_2$] 0.10→0.20; rate 0.0012→0.0024: order 1.
3. *k.* $1.2 \times 10^{-3}/(0.10^2 \times 0.10) = 1.2$ dm$^6$ mol$^{-2}$ s$^{-1}$

**Decision**

rate $= k[\mathrm{NO}]^2[\mathrm{Br_2}]$

# AHL: Graphs of each order




Straight [A]-time line: zero **order**. Constant **half-life**: first order.

# AHL: Matching a mechanism

## Step 1 (slow)

Supplied model: $NO_2 + CO \rightarrow NO + CO_2$, rate $= k[NO_2]^2$.

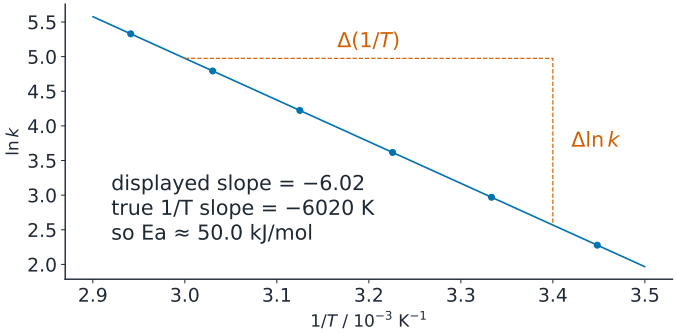
Proposed slow step: $2NO_2 \rightarrow NO_3 + NO$.

## Step 2 (fast)

$NO_3 + CO \rightarrow NO_2 + CO_2$.

$NO_3$ cancels as an **intermediate**; the summed equation and predicted law agree. This does not prove uniqueness.

# AHL: The Arrhenius equation




$\ln k$ against $1/T$ has gradient $-E_a/R$.

# AHL: Two temperatures

1. **Ratio.** k doubles from 298 K to 308 K: $\ln(k_2/k_1)=\ln 2=0.693$.
2. **1/T.** $1/298 - 1/308 = 1.0895 \times 10^{-4}$ K$^{-1}$
3. **Solve.** $E_a = 8.31 \ln 2/(1/298 - 1/308) = 5.29 \times 10^4$ J/mol.

**Decision**

$E_a = 52.9$ kJ mol$^{-1}$

# AHL: Intermediate and transition state are different

## Intermediate

A species formed in one step and consumed later.

A local energy minimum, with a finite population.

## Transition state

A fleeting high-energy configuration on a pathway.

A peak, with a local barrier measured from its preceding state.

# AHL: Derive a law when the second step is slow

1. **Fast pre-equilibrium.** $A+B \rightleftharpoons I$ gives $[I]=K[A][B]$. Then $I+B \rightarrow P$ is slow.
2. **Substitute.** $r=k_2[I][B]=k_2K[A][B]^2$.
3. **Check.** Overall $A+2B \rightarrow P$. I cancels; slow-step **molecularity** 2, overall **order** 3.

**Decision**

This deduction requires the stated pre-equilibrium assumption.

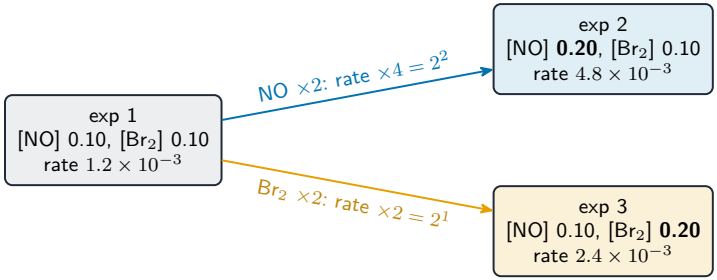
# AHL: Apply a constant first-order half-life

1. **Define the law.** $-\mathrm{d[A]/dt}=\mathrm{k[A]}$, with constant $\mathrm{k}=0.0231\ \mathrm{s}^{-1}$.
2. **Half-life.** $t_{½}=\ln 2/\mathrm{k}=0.693/0.0231=30.0$ s.
3. **Successive intervals.** [A] halves again in another 30.0 s under the same law and conditions.

## Decision

A different **order** or changing k need not give equal half-lives.

# Orders from initial rates




rate $= k[\mathrm{NO}]^2[\mathrm{Br_2}]$
third order overall
$k = 1.2$ dm$^6$ mol$^{-2}$ s$^{-1}$
(invented data)

> Rate $= k[\mathrm{NO}]^2[\mathrm{Br_2}]$

# The slow step sets the rate law

step 1: $NO_2 + NO_2 \rightarrow NO_3 + NO$ **slow** → rate $= k[NO_2]^2$

step 2: $NO_3 + CO \rightarrow NO_2 + CO_2$ **fast**

from the slow step's reactants, not the overall equation

overall: $NO_2 + CO \rightarrow NO + CO_2$

$NO_3$ is an intermediate: made in step 1, used in step 2

> Species in that step appear in the **rate equation**

# AHL: Recover Ea and A from a scaled axis

1. **Invented fit.** $\ln(k/s^{-1})=25.0-6.00x$, where $x=1000\ K/T$.
2. **Activation energy.** Convert the horizontal scale: $E_a=6.00\times1000\times8.31=49860\ J/mol=49.9\ kJ/mol$.
3. **Prefactor.** Intercept $\ln(A/s^{-1})=25.0$, so $A=e^{25}=7.20\times10^{10}\ s^{-1}$.

## Decision

The prefactor has the same units as k; keep k units consistent.

# Exam tips

> Keep equal area for the same particle count; the ideal tail approaches zero.

- Draw tangents long; read two far-apart points.
- Concentration changes collision frequency; temperature changes the energy fraction.
- AHL. Orders only come from experiments.
- AHL. $T$ in K, $E_a$ in J mol$^{-1}$.

# Check yourself

## Try these

Explain why powdered $CaCO_3$ reacts faster than lumps.

Sketch Maxwell–Boltzmann curves at two temperatures and explain the rise in rate.

Explain how a catalyst works, with an energy profile.

AHL. Find $E_a$ when $k$ goes from $3.0 \times 10^{-4}$ to $1.2 \times 10^{-3}$ $s^{-1}$ between 300 and 320 K.