

Reaction Rates and Rate Laws

How do you find the rate law and rate constant of a reaction?

●●○ Intermediate

Kinetics

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Before you start: it helps to understand [Molarity and Solution Stoichiometry](#) and [SI Units and Unit Conversions](#).

What is it?

Chemical kinetics is the study of how **fast** reactions happen. The **rate** of a reaction is the change in concentration of a reactant or product per unit time:

$$\text{rate} = -\frac{\Delta[\text{reactant}]}{\Delta t} = \frac{\Delta[\text{product}]}{\Delta t}$$

The minus sign makes the rate positive, because reactant concentrations decrease. Rates are usually given in **M/s** ($\text{mol L}^{-1} \text{s}^{-1}$).

🔑 KEY IDEA

A **rate law** links the rate to the concentrations: $\text{rate} = k[\text{A}]^m[\text{B}]^n$. The orders m and n must be found **by experiment**; they are not the coefficients of the balanced equation.

Why does it matter?

- **Industry and safety.** Chemists control rates to make products efficiently and to avoid runaway reactions.
- **Medicine.** Drug doses are spaced using the rate at which the body removes the drug (often a first-order half-life).
- **Mechanisms.** Rate laws give clues about the steps by which a reaction actually happens.

How does it work?

1. What changes the rate (collision theory)

Particles must **collide** with enough energy and the right orientation to react. A reaction is faster with:

- **higher concentration** (or pressure for gases): more frequent collisions;
- **higher temperature**: more frequent and, above all, more energetic collisions;

- **larger surface area** (smaller pieces of solid): more particles exposed;
- a **catalyst**: a lower-energy pathway (see Activation Energy and Catalysts).

2. Rates and stoichiometry

For $2\text{N}_2\text{O}_5(\text{g}) \longrightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$, NO_2 forms twice as fast as N_2O_5 disappears. To give one rate for the reaction, divide by the coefficients:

$$\begin{aligned}\text{rate} &= -\frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} \\ &= \frac{1}{4} \frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{\Delta[\text{O}_2]}{\Delta t}\end{aligned}$$

3. Rate laws and orders

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

- m is the **order with respect to A**; n is the order with respect to B; $m + n$ is the **overall order**.
- k is the **rate constant**. It is fixed at a given temperature and increases as the temperature rises.

Order in A	Doubling [A] multiplies the rate by
0	1 (no change)
1	2
2	4

4. Units of the rate constant

Because the rate is always in M/s, the units of k depend on the **overall order**:

Overall order	Rate law	Units of k
0	$\text{rate} = k$	M s^{-1}
1	$\text{rate} = k[\text{A}]$	s^{-1}
2	$\text{rate} = k[\text{A}]^2$ or $k[\text{A}][\text{B}]$	$\text{M}^{-1} \text{s}^{-1}$
3	$\text{rate} = k[\text{A}]^2[\text{B}]$	$\text{M}^{-2} \text{s}^{-1}$

5. First-order reactions and half-life

For a first-order reaction, the concentration falls **exponentially**:

$$[A]_t = [A]_0 e^{-kt}$$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

The **half-life**, $t_{1/2}$, is the time for the concentration to halve. For a first-order reaction it does **not** depend on the starting concentration, so every half-life is the same length.

∞ THINK OF IT LIKE THIS

A ticket queue at a stadium: open more gates (higher concentration of “gates”, or a catalyst) and people get through faster. A first-order half-life is like a sale where half of the remaining stock sells every hour: 100 items, then 50, then 25, then 12.5, with each halving taking the same time.

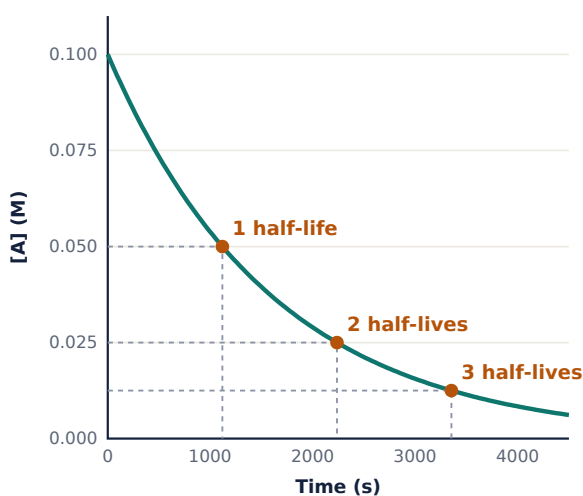
Q MORE PRECISELY

The rate measured over a time interval is an **average rate**; the **instantaneous rate** is the slope of the tangent to the concentration–time curve. The orders in a rate law reflect the reaction **mechanism** (its sequence of elementary steps), which is why they can’t be read from the overall equation. Second-order reactions have $t_{1/2} = \frac{1}{k[A]_0}$, which does depend on the starting concentration.

Visualise it

A first-order reaction halves at equal intervals

$$[A]_0 = 0.100 \text{ M}, k = 6.20 \times 10^{-4} \text{ s}^{-1}, t_{1/2} = 1.12 \times 10^3 \text{ s}$$



$$0.100 \text{ M} \rightarrow 0.050 \text{ M} \rightarrow 0.025 \text{ M} \rightarrow 0.0125 \text{ M}, \text{ each taking } 1.12 \times 10^3 \text{ s}$$

In a first-order reaction every half-life is the same length.

Worked example

WORKED EXAMPLE: Average rate

Question: In $2 \text{H}_2\text{O}_2 \longrightarrow 2 \text{H}_2\text{O} + \text{O}_2$, $[\text{H}_2\text{O}_2]$ falls from 0.500 M to 0.400 M in 60.0 s. Find the average rate of disappearance of H_2O_2 and the average rate of the reaction.

Step 1 Rate of disappearance of H_2O_2 :

$$\begin{aligned} & - \frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t} \\ &= - \frac{0.400 \text{ M} - 0.500 \text{ M}}{60.0 \text{ s}} \\ &= 1.67 \times 10^{-3} \text{ M/s} \end{aligned}$$

Step 2

Rate of reaction (divide by the coefficient 2): $\frac{1.67 \times 10^{-3} \text{ M/s}}{2} = 8.33 \times 10^{-4} \text{ M/s}$

 WORKED EXAMPLE: The method of initial rates

Question: For $A + B \longrightarrow$ products:

Experiment	[A]	[B]	Initial rate
1	0.10 M	0.10 M	2.0×10^{-3} M/s
2	0.20 M	0.10 M	8.0×10^{-3} M/s
3	0.10 M	0.20 M	4.0×10^{-3} M/s

Find the rate law and k , with units.

Step 1 Experiments 1 $\rightarrow$ 2: [A] doubles, [B] constant; the rate is multiplied by $\frac{8.0 \times 10^{-3} \text{ M/s}}{2.0 \times 10^{-3} \text{ M/s}} = 4$, so the order in A is **2**.

Step 2 Experiments 1 $\rightarrow$ 3: [B] doubles; the rate is multiplied by 2, so the order in B is **1**.

Step 3 Rate law: **rate** = $k[A]^2[B]$ (third order overall).

Step 4 From experiment 1:

$$\begin{aligned}k &= \frac{\text{rate}}{[A]^2[B]} \\&= \frac{2.0 \times 10^{-3} \text{ M s}^{-1}}{(0.10 \text{ M})^2(0.10 \text{ M})} \\&= 2.0 \text{ M}^{-2} \text{ s}^{-1}\end{aligned}$$

The units follow from $\text{M s}^{-1} \div \text{M}^3 = \text{M}^{-2} \text{ s}^{-1}$.

 WORKED EXAMPLE: Half-life

Question: A first-order decomposition has $k = 6.20 \times 10^{-4} \text{ s}^{-1}$. Find its half-life.

$$\begin{aligned}t_{1/2} &= \frac{0.693}{6.20 \times 10^{-4} \text{ s}^{-1}} \\&= 1.12 \times 10^3 \text{ s}\end{aligned}$$

That is $1.12 \times 10^3 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} = 18.6 \text{ min}$.

Common mistake

COMMON MISTAKE: Taking orders from the balanced equation

For $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$ the rate law happens to be $\text{rate} = k[\text{NO}]^2[\text{O}_2]$, but that is an experimental result. Many reactions have orders that differ from their coefficients, so always use data.

COMMON MISTAKE: Giving every k the same units

k for a first-order reaction is in s^{-1} , but for a second-order reaction it is in $\text{M}^{-1} \text{s}^{-1}$. Work out the units from the rate law every time.

COMMON MISTAKE: Thinking every half-life doubles the time to finish

After 2 half-lives, $\frac{1}{4}$ of the reactant remains, not none. A first-order reaction never quite reaches zero.

NOTATION NOTE

- M/s , M s^{-1} and $\text{mol L}^{-1} \text{s}^{-1}$ mean the same thing.
- “ln” is the natural logarithm (base e); $\ln 2 = 0.693$.
- $[\text{A}]_0$ is the initial concentration; $[\text{A}]_t$ is the concentration at time t .

Remember this

REMEMBER THIS

- Rate = change in concentration $\div$ time (M/s); divide by coefficients for one reaction rate.
- Rate = $k[\text{A}]^m[\text{B}]^n$; orders come from experiments (method of initial rates).
- Units of k : zero order M s^{-1} ; first s^{-1} ; second $\text{M}^{-1} \text{s}^{-1}$; third $\text{M}^{-2} \text{s}^{-1}$.
- First order: $t_{1/2} = 0.693/k$, independent of starting concentration.

References

1. Brown, T. L.; LeMay, H. E., Jr.; Bursten, B. E.; Murphy, C. J.; Woodward, P. M.; Stoltzfus, M. W. Chemistry: The Central Science, 15th ed.; Pearson, 2022.

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