

Integrated Rate Laws and Reaction Mechanisms

How does concentration change with time, how do you find the order from data, and what is a reaction mechanism?

●●● Advanced

Kinetics

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Before you start: it helps to understand [Reaction Rates and Rate Laws](#).

What is it?

A rate law, such as $\text{rate} = k[A]^n$, tells you how fast a reaction goes **at one moment**. An **integrated rate law** tells you the **concentration at any time**. Each order gives a different equation, and each can be rearranged into a **straight line**:

Order	Integrated rate law	Straight-line plot	Slope	Half-life
0	$[A] = [A]_0 - kt$	$[A]$ against t	$-k$	$\frac{[A]_0}{2k}$
1	$\ln[A] = \ln[A]_0 - kt$	$\ln[A]$ against t	$-k$	$\frac{\ln 2}{k}$
2	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$	$1/[A]$ against t	$+k$	$\frac{1}{k[A]_0}$

🔑 KEY IDEA

To find the order from concentration–time data, plot $[A]$, $\ln[A]$ and $1/[A]$ against time. **Only one plot is a straight line**, and it tells you the order; its slope gives k . A **constant half-life** is the signature of a first-order reaction.

Why does it matter?

- **Medicine.** Drug levels in the blood usually fall by first-order kinetics, so doses are spaced by the drug's half-life.
- **Shelf life.** Manufacturers use integrated rate laws to predict how long medicines and foods stay within their limits.
- **Understanding reactions.** The rate law is a clue to the **mechanism**: the sequence of simple steps by which a reaction actually happens.

How does it work?

1. Using the integrated rate laws

Each equation links four quantities: $[A]_0$, $[A]$, k and t . Knowing any three, you can find the fourth. Make sure the units of k match the time unit, and that kt has the right units: no units for first order ($s^{-1} \times s$), M^{-1} for second order ($M^{-1} s^{-1} \times s$).

2. Half-lives

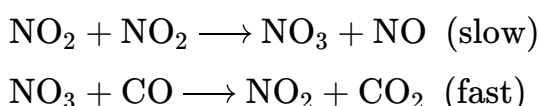
- **First order:** $t_{1/2} = \ln 2/k$, independent of concentration. Each half-life halves what is left, just like radioactive decay.
- **Second order:** $t_{1/2} = 1/(k[A]_0)$: each half-life is **twice** as long as the one before, because the concentration has halved.
- **Zero order:** $t_{1/2} = [A]_0/(2k)$: each half-life is **half** as long as the one before.

3. Reaction mechanisms

Most reactions happen in several **elementary steps**. For an elementary step (only), the rate law follows from how many particles collide: a step $A + B \longrightarrow$ has rate $= k[A][B]$.

- The **slowest** step is the **rate-determining step**: the overall reaction cannot go faster than it.
- A species made in one step and used up in a later one is an **intermediate**; it does not appear in the overall equation.
- A proposed mechanism must (1) add up to the overall equation and (2) give a rate law that matches experiment.

For $NO_2 + CO \longrightarrow NO + CO_2$, experiments give rate $= k[NO_2]^2$, with no CO. The accepted mechanism is:



The slow first step involves two NO_2 molecules, so rate $= k[NO_2]^2$; CO only appears in the fast step, so it does not affect the rate. NO_3 is the intermediate.

THINK OF IT LIKE THIS

A mechanism is like an assembly line. However fast the other workers are, the number of finished products per hour is set by the slowest worker (the rate-determining step). Speeding up a fast step changes nothing; speeding up the slow step speeds up everything.

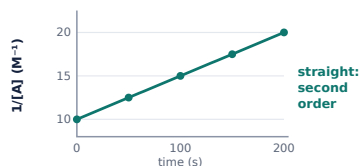
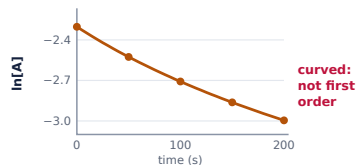
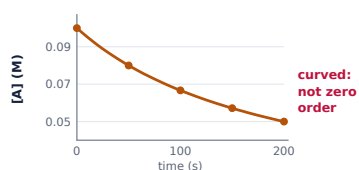
Q MORE PRECISELY

The integrated laws come from calculus: for first order, $-\frac{d[A]}{dt} = k[A]$ integrates to $\ln[A] = \ln[A]_0 - kt$. When a fast, reversible step comes **before** the slow step, the rate law can include species from that earlier step (the pre-equilibrium approach). A mechanism can never be proved, only supported: a mechanism that fits the data may still be replaced if new evidence appears.

Visualise it

Which plot is a straight line?

Same data, three ways: the straight one gives the order.

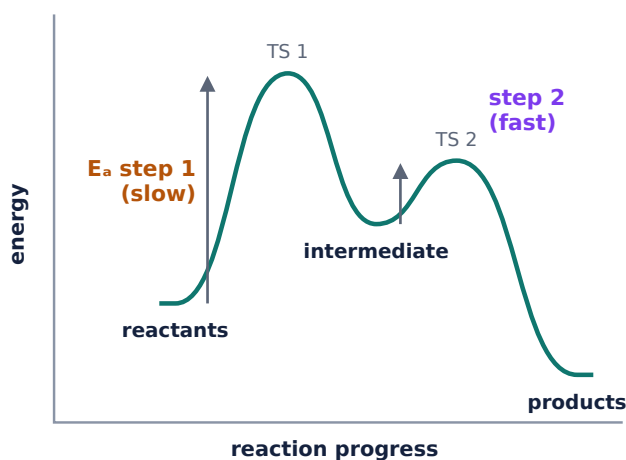


Slope of $1/[A]$ against $t = k = 0.0500 \text{ M}^{-1} \text{ s}^{-1}$.

Plot the data three ways: the straight-line plot identifies the order, and its slope gives k .

A two-step mechanism

The step with the higher barrier is slow and sets the rate.



Step 1: $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$ (slow)

Step 2: $\text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2$ (fast). Rate = $k[\text{NO}_2]^2$

The step with the highest barrier is the rate-determining step; the intermediate sits in the valley between the two.

Worked example

WORKED EXAMPLE: First order: concentration and time

Question: A first-order reaction has $k = 2.50 \times 10^{-3} \text{ s}^{-1}$ and $[A]_0 = 0.500 \text{ M}$. Find (a) $[A]$ after 300. s (b) the time for $[A]$ to fall to 0.100 M (c) the half-life.

Step 1 (a) $\ln[A] = \ln(0.500) - (2.50 \times 10^{-3} \text{ s}^{-1})(300. \text{ s}) = -0.6931 - 0.750 = -1.443$, so $[A] = e^{-1.443} = \mathbf{0.236 \text{ M}}$

Step 2 (b) $t = \frac{\ln([A]_0/[A])}{k} = \frac{\ln(0.500 \text{ M}/0.100 \text{ M})}{2.50 \times 10^{-3} \text{ s}^{-1}} = \frac{1.609}{2.50 \times 10^{-3} \text{ s}^{-1}} = \mathbf{644 \text{ s}}$

Step 3 (c) $t_{1/2} = \frac{0.6931}{2.50 \times 10^{-3} \text{ s}^{-1}} = \mathbf{277 \text{ s}}$

WORKED EXAMPLE: Second order

Question: A second-order reaction has $k = 0.0400 \text{ M}^{-1} \text{ s}^{-1}$ and $[A]_0 = 0.200 \text{ M}$. Find $[A]$ after 100. s and the first half-life.

Step 1 $\frac{1}{[A]} = \frac{1}{0.200 \text{ M}} + (0.0400 \text{ M}^{-1} \text{ s}^{-1})(100. \text{ s}) = 5.00 \text{ M}^{-1} + 4.00 \text{ M}^{-1} = 9.00 \text{ M}^{-1}$

Step 2 $[A] = \frac{1}{9.00 \text{ M}^{-1}} = \mathbf{0.111 \text{ M}}$

Step 3 $t_{1/2} = \frac{1}{(0.0400 \text{ M}^{-1} \text{ s}^{-1})(0.200 \text{ M})} = \mathbf{125 \text{ s}}$

WORKED EXAMPLE: Finding the order from data

Question: $[A] = 0.100, 0.0800, 0.0667, 0.0571$ and 0.0500 M at $t = 0, 50, 100, 150$ and 200 s . Find the order and k .

Step 1 $\ln[A] = -2.303, -2.526, -2.708, -2.862, -2.996$: the differences shrink ($-0.223, -0.182, -0.154, -0.134$), so $\ln[A]$ is **not** linear: not first order.

Step 2 $1/[A] = 10.0, 12.5, 15.0, 17.5, 20.0 \text{ M}^{-1}$: it rises by exactly 2.5 M^{-1} every 50 s, a **straight line: second order**.

Step 3 $k = \text{slope} = \frac{2.5 \text{ M}^{-1}}{50 \text{ s}} = \mathbf{0.0500 \text{ M}^{-1} \text{ s}^{-1}}$

Common mistake

 **COMMON MISTAKE:** Using the first-order half-life for every reaction

$t_{1/2} = 0.693/k$ is only for **first-order** reactions. For second order the half-life depends on the starting concentration and grows as the reaction proceeds.

 **COMMON MISTAKE:** Writing a rate law from the overall equation

Orders come from experiment or from the **slow elementary step**, not from the coefficients of the overall equation. For $\text{NO}_2 + \text{CO} \longrightarrow \text{NO} + \text{CO}_2$, the rate law is $k[\text{NO}_2]^2$, not $k[\text{NO}_2][\text{CO}]$.

 **COMMON MISTAKE:** Mixing time units

If k is in s^{-1} , time must be in seconds. Convert minutes or hours first, or kt will be wrong by a factor of 60 or 3600.

 **NOTATION NOTE**

- $[\text{A}]_0$ is the initial concentration; $[\text{A}]$ or $[\text{A}]_t$ is the concentration at time t .
- “ln” is the natural logarithm (base e); $\ln 2 = 0.6931$.
- $\text{M}^{-1} \text{s}^{-1}$ can also be written $\text{L mol}^{-1} \text{s}^{-1}$.

Remember this

 **REMEMBER THIS**

- Zero order: $[\text{A}]$ linear in t . First order: $\ln[\text{A}]$ linear (slope $-k$). Second order: $1/[\text{A}]$ linear (slope $+k$).
- Half-lives: zero $[\text{A}]_0/2k$; first $\ln 2/k$ (constant); second $1/(k[\text{A}]_0)$.
- The slow step is rate-determining; intermediates are made then used up; a mechanism must add up to the overall equation and match the rate law.

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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