

Rate laws, orders and half-lives

AP Chemistry · Lesson

Quick answer: A rate law, $\text{rate} = k[A]^m[B]^n$, shows how reaction rate depends on reactant concentrations, with orders found by experiment. Integrated rate laws turn it into concentration against time: zero order is linear in $[A]$, first order in $\ln[A]$, second order in $1/[A]$. Half-life depends on k , and on $[A]_0$ except for first order.

Level: AP Chemistry · **Curriculum:** AP Chem Unit 5

What is a rate law?

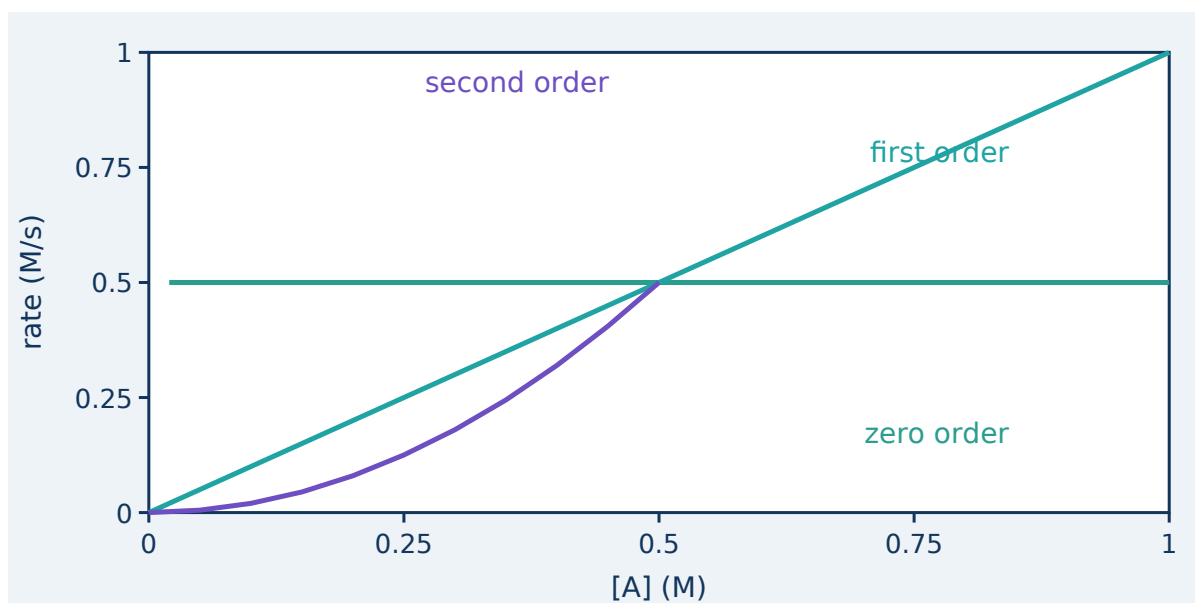
A rate law links the speed of a reaction to the concentrations of the reactants. For a reaction $A + B \rightarrow \text{products}$, experiments often give $\text{rate} = k[A]^m[B]^n$. The exponents m and n are the orders; they are found by experiment and are not read from the balanced equation.

Definition

The **order** in a reactant is the power of its concentration in the rate law. The **overall order** is the sum of the orders. The **rate constant** k depends on temperature and on the reaction, not on concentration.

The units of k follow from the order, because rate always has units of M s^{-1} .

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



The shape of rate against [A] shows the order: flat, straight or curved upwards.

How do you find the orders from initial rates?

Compare two experiments in which only one concentration changes. If doubling [A] doubles the rate, the order in A is 1; if it quadruples the rate, the order is 2; if the rate does not change, the order is 0.

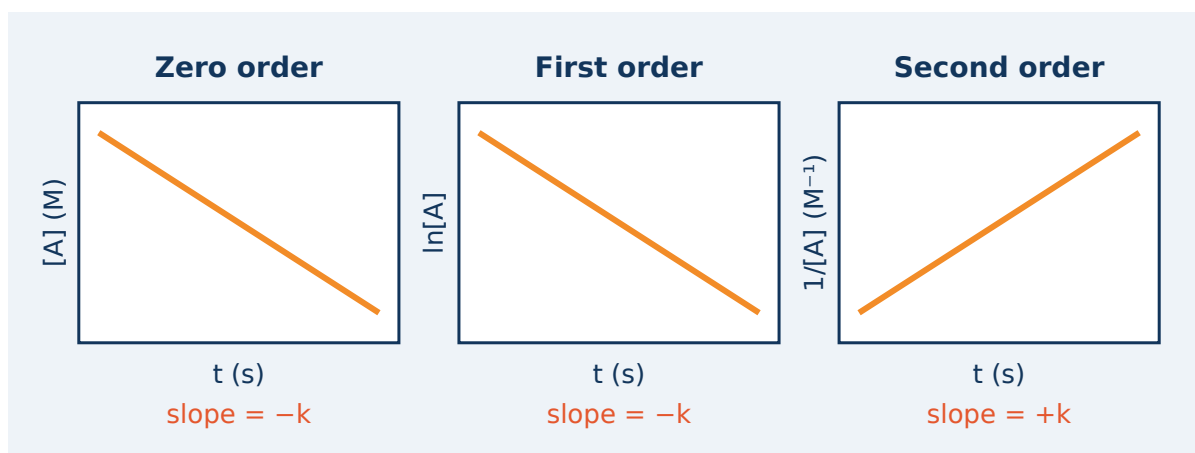
Worked example 1

Aarav in Pune measures initial rates for $A + B \rightarrow \text{products}$. Experiment 1: [A] = 0.10 M, [B] = 0.10 M, rate = 2.0×10^{-3} M/s. Experiment 2: [A] = 0.20 M, [B] = 0.10 M, rate = 8.0×10^{-3} M/s. Experiment 3: [A] = 0.10 M, [B] = 0.30 M, rate = 6.0×10^{-3} M/s.

Experiments 1 and 2: [A] doubles and the rate rises by 4 = 2^2 , so the order in A is 2.

Experiments 1 and 3: [B] triples and the rate triples, so the order in B is 1. Rate = $k[A]^2[B]$.

$k = \text{rate}/([A]^2[B]) = (2.0 \times 10^{-3})/((0.10)^2 \times 0.10) = 2.0 \text{ M}^{-2} \text{ s}^{-1}$.



Each order has one plot that gives a straight line; the slope gives k.

What are integrated rate laws?

An integrated rate law gives the concentration at any time. Each simple order has its own

equation and its own straight-line plot, which is how you decide the order from concentration–time data.

Integrated rate laws

Zero order: $[A] = [A]_0 - kt$, half-life $t_{1/2} = [A]_0/(2k)$.

First order: $\ln[A] = \ln[A]_0 - kt$, half-life $t_{1/2} = 0.693/k$.

Second order: $1/[A] = 1/[A]_0 + kt$, half-life $t_{1/2} = 1/(k[A]_0)$.

$[A]_0$ is the starting concentration (M), t is time (s), k is the rate constant with the units above.

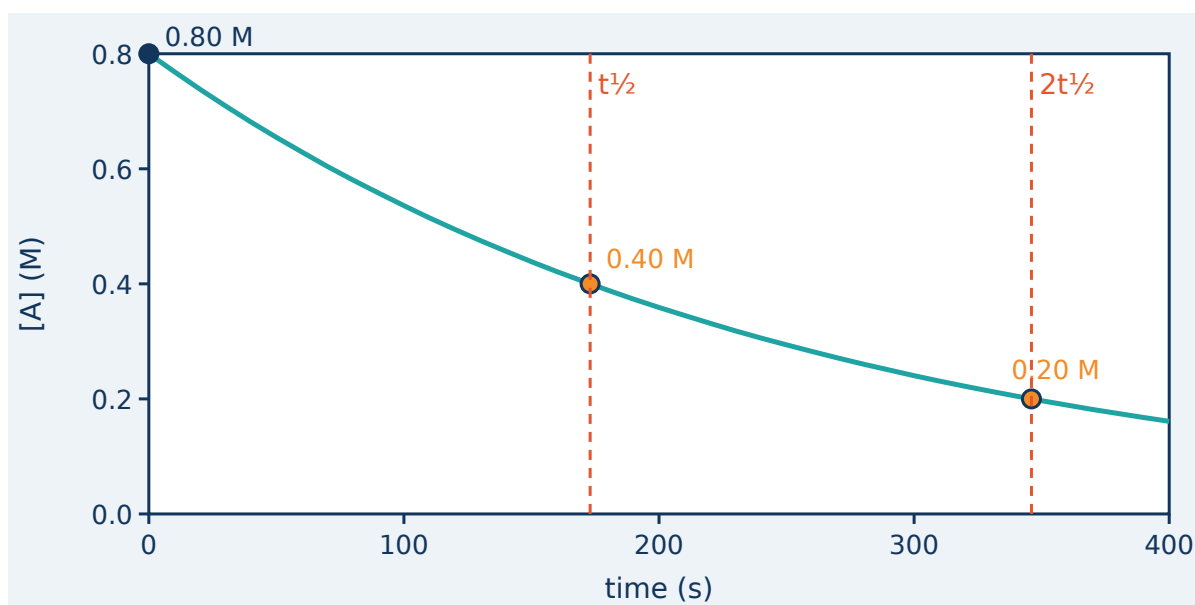
Order	Straight-line plot	Slope	Half-life as reaction proceeds
0	$[A]$ against t	$-k$	Gets shorter
1	$\ln[A]$ against t	$-k$	Constant
2	$1/[A]$ against t	$+k$	Gets longer

Worked example 2

Chiamaka in Lagos studies a first-order decomposition with $k = 4.0 \times 10^{-3} \text{ s}^{-1}$ and $[A]_0 = 0.80 \text{ M}$. How long until $[A] = 0.20 \text{ M}$?

$t = \ln([A]_0/[A])/k = \ln(0.80/0.20)/(4.0 \times 10^{-3}) = 1.386/(4.0 \times 10^{-3}) = 3.5 \times 10^2 \text{ s}$.

Check: $t_{1/2} = 0.693/(4.0 \times 10^{-3}) = 173 \text{ s}$, and 0.80 M halves twice (0.40 M , then 0.20 M) in $2 \times 173 = 346 \text{ s}$.



First-order decay with $k = 4.0 \times 10^{-3} \text{ s}^{-1}$: every 173 s the concentration halves.

Worked example 3

A second-order reaction has $k = 0.50 \text{ M}^{-1} \text{ s}^{-1}$ and $[A]_0 = 0.20 \text{ M}$. Find the half-life.

$t_{1/2} = 1/(k[A]_0) = 1/(0.50 \times 0.20) = 10 \text{ s}$. If $[A]_0$ is halved to 0.10 M , $t_{1/2}$ doubles to 20 s .

Which mistakes do students make?

Common mistake

Never take the orders from the coefficients of the balanced equation. For $2 \text{NO}_2 \rightarrow 2 \text{NO} + \text{O}_2$ the coefficient 2 does not force a second-order rate law; only experiments, or a mechanism, can tell you. Also, do not treat the half-life of a zero- or second-order reaction as constant: only a first-order half-life is independent of concentration.

Lina's tip

Before any algebra, write the units of k . If they are s^{-1} , the reaction is first order; $\text{M}^{-1} \text{s}^{-1}$ means second order; M s^{-1} means zero order. It is a free check on your answer.

How do you choose the right plot?

Plot $[\text{A}]$, $\ln[\text{A}]$ and $1/[\text{A}]$ against time. The one that gives a straight line reveals the order, and its slope gives k (take the absolute value for the first two). A constant half-life in successive intervals is a quick sign of first order.

Key points to remember

- Rate = $k[\text{A}]^m[\text{B}]^n$; orders come from experiments, not from coefficients.
- Units of k : M s^{-1} (order 0), s^{-1} (order 1), $\text{M}^{-1} \text{s}^{-1}$ (order 2).
- First order: $\ln[\text{A}] = \ln[\text{A}]_0 - kt$ and $t_{1/2} = 0.693/k$, independent of $[\text{A}]_0$.
- Second order: $1/[\text{A}] = 1/[\text{A}]_0 + kt$ and $t_{1/2} = 1/(k[\text{A}]_0)$.
- Zero order: $[\text{A}] = [\text{A}]_0 - kt$ and $t_{1/2} = [\text{A}]_0/(2k)$.

Rate laws, orders and half-lives: frequently asked questions

How do you determine the order of a reaction?

Use the method of initial rates: change one concentration at a time and see how the rate responds. Or plot $[\text{A}]$, $\ln[\text{A}]$ and $1/[\text{A}]$ against time and see which is a straight line.

Why is the half-life of a first-order reaction constant?

Because $t_{1/2} = 0.693/k$ contains no concentration term. Whatever the starting amount, it takes the same time for half of it to react.

Can the rate law be written from the balanced equation?

Only for a single elementary step. For an overall reaction the rate law must be measured, because the reaction may proceed through several steps.

What does the rate constant depend on?

It depends on the reaction and on temperature (and on any catalyst), but not on concentration. Raising the temperature increases k .

How do you find k from a graph?

Take the slope of the straight-line plot. For zero and first order the slope is $-k$; for second order the plot of $1/[A]$ against t has slope $+k$.