Topic 5.3: Concentration Changes Over Time

Revision Notes · AP Chemistry

UNIT 5 · KINETICS

On ExamFitter.com: Topic 5.3 Quiz · Topic 5.3 Worksheet · Unit 5: All Topics · AP Chemistry Home

From a Rate at an Instant to a Concentration at a Time

A rate law such as rate = $k[A]^2$ gives the rate at one instant, calculated from the concentrations at that instant.

It does not directly answer the question an experiment usually asks: how much reactant remains after a given time?

The integrated rate law answers that question. It combines the rate law with time and gives [A]t, the concentration of A at time t, for a reaction of the form A → products.

There is one integrated law for each order. Each one is a straight line equation, y = mx + b, written in a different variable, and that is what makes the order testable from data.

The Three Integrated Rate Laws

For a zero order reaction, $[A]t = [A]_0 - kt$. A plot of [A] against time is a straight line with slope −k and intercept $[A]_0$, and k has units M s^{-1}.

For a first order reaction, $\ln[A]t = \ln[A]_0 - kt$. A plot of ln[A] against time is a straight line with slope −k and intercept $\ln[A]_0$, and k has units s^{-1}.

For a second order reaction, $1/[A]t = kt + 1/[A]_0$. A plot of 1/[A] against time is a straight line with slope +k and intercept $1/[A]_0$, and k has units M^{-1} s^{-1}.

The second order form above applies to a rate law rate = $k[A]^2$ in a single reactant. The slope of the 1/[A] plot is positive because 1/[A] grows as [A] falls.

In every case the intercept hands you the starting concentration, in the form that plot uses, and the slope hands you k, with its sign handled as above.

© 2026 ExamFitter.com · Free AP Chemistry revision notes

Identifying the Order: Which Plot Is Straight

Given concentration against time data, construct all three plots. Exactly one of them is straight, and which one it is gives the order.

A straight [A] plot means zero order, a straight ln[A] plot means first order, and a straight 1/[A] plot means second order.

The same test can be run on the numbers before anything is plotted. Over equal time intervals, a zero order reaction removes the same amount of A each interval.

A first order reaction removes the same fraction each interval, so ln[A] falls by the same amount each interval. A second order reaction adds the same amount to 1/[A] each interval.

If none of the three plots is straight, the reaction does not follow simple zero, first or second order kinetics in A alone, and none of these three laws applies.

Half-Life and How It Changes

The half-life, $t_{1/2}$, is the time taken for the concentration of a reactant to fall to half of its value at the start of that interval.

For zero order, $t_{1/2} = [A]_0 \div 2k$. For first order, $t_{1/2} = \ln 2 \div k = 0.693 \div k$. For second order, $t_{1/2} = 1 \div (k[A]_0)$.

Only the first order half-life is independent of concentration, because its expression contains no concentration term. It stays the same at every point in the reaction.

Successive half-lives show the difference. In a zero order reaction each half-life is half as long as the one before, because there is less reactant to consume at the same fixed rate.

In a second order reaction each half-life is twice as long as the one before, because the falling concentration slows the rate steeply. In a first order reaction every half-life is equal.

After n half-lives of a first order reaction, the fraction remaining is $(1/2)^n$. Two half-lives leave one quarter, so 75% consumed always means two half-lives, whatever k is.

Reaching 10% remaining is not a whole number of half-lives. It takes $\ln 10 \div k$, which is $\ln 10 \div \ln 2 \approx 3.32$ half-lives.

© 2026 ExamFitter.com · Free AP Chemistry revision notes

Worked Examples

Example 1: Order and k from a data table. The decomposition $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ is first order in N_2O_5. The measured concentrations are 0.800 M at 0 s, 0.400 M at 20 s, 0.200 M at 40 s and 0.100 M at 60 s. The corresponding ln[A] values are −0.223, −0.916, −1.609 and −2.303, falling by equal steps, which confirms first order. The slope of the ln[A] plot is $(-2.303 - (-0.223)) \div 60 = -0.0347\ s^{-1}$, so $k = 0.0347\ s^{-1}$. The half-life is $0.693 \div 0.0347 \approx 20$ s, exactly the halving interval visible in the table.

Example 2: A second order prediction. A → products is second order with $k = 0.50\ M^{-1}\ s^{-1}$ and $[A]_0 = 0.20$ M, so $1/[A]_0 = 5.0\ M^{-1}$. At t = 30 s, $1/[A]t = (0.50)(30) + 5.0 = 20\ M^{-1}$, giving [A]t = 0.050 M. The first half-life is $1 \div (k[A]_0) = 1 \div (0.50 \times 0.20) = 10$ s, yet reaching one quarter of $[A]_0$ takes 30 s rather than 20 s, because the second half-life, from 0.10 M to 0.050 M, lasts 20 s.

Example 3: A zero order prediction. A → products is zero order with $k = 0.040\ M\ s^{-1}$ and $[A]_0 = 1.20$ M. At t = 12 s, $[A]t = 1.20 - (0.040)(12) = 1.20 - 0.48 = 0.72$ M. The half-life is $[A]_0 \div 2k = 1.20 \div 0.080 = 15$ s. The same law reaches [A] = 0 at 30 s, and it cannot be used beyond that point, because a concentration cannot fall below zero.

Example 4: Time to a given fraction remaining. For a first order reaction with $k = 0.0231\ s^{-1}$, how long until only 10% of the reactant remains? Writing the law as $\ln([A]t \div [A]_0) = -kt$ with $[A]t \div [A]_0 = 0.100$ gives $t = \ln 10 \div k = 2.303 \div 0.0231 = 99.7$ s. Questions about a percentage remaining are always questions about the ratio $[A]t \div [A]_0$, so $[A]_0$ itself is never needed.

Traps That Cost Marks in Topic 5.3

Losing the sign of the slope. The [A] and ln[A] plots have slope −k, while the 1/[A] plot has slope +k. Reporting k itself as a negative number, or taking the slope of a 1/[A] plot as −k, are the two standard errors.

Reading $[A]_0$ straight off an ln[A] plot. The intercept of an ln[A] plot is $\ln[A]_0$, not $[A]_0$. The initial concentration is e raised to the intercept, so an intercept of −1.61 means $[A]_0 = 0.20$ M, not −1.61 M.

© 2026 ExamFitter.com · Free AP Chemistry revision notes

Assuming every half-life is constant. Only the first order half-life is constant. Applying 0.693 ÷ k to a zero or second order reaction gives a wrong time and usually the wrong units as well.

Swapping the half-life formulas. The zero order half-life is $[A]_0 \div 2k$ and the second order half-life is $1 \div (k[A]_0)$. They are not interchangeable, and each one depends on $[A]_0$ in a different way.

Confusing fraction consumed with fraction remaining. Consuming 75% leaves 25%, which is two half-lives for a first order reaction. Reading 75% as the fraction remaining turns the answer into a non whole number of half-lives and the wrong time.

Running a zero order law past zero. The equation $[A]t = [A]_0 - kt$ happily returns negative concentrations after the reactant is exhausted. Those values are meaningless: the law describes the reaction only while reactant remains.

Key Relationships to Remember

- Integrated rate laws: zero order $[A]t = [A]_0 - kt$; first order $\ln[A]t = \ln[A]_0 - kt$; second order $1/[A]t = kt + 1/[A]_0$
- Linear plots: [A] against t for zero order, ln[A] against t for first order, 1/[A] against t for second order
- Slopes and intercepts: slope $-k$ and intercept $[A]_0$ for zero order; slope $-k$ and intercept $\ln[A]_0$ for first order; slope $+k$ and intercept $1/[A]_0$ for second order
- Half-lives: zero order $t_{1/2} = [A]_0 \div 2k$; first order $t_{1/2} = 0.693 \div k$, independent of $[A]_0$; second order $t_{1/2} = 1 \div (k[A]_0)$
- Successive half-lives: each one halves for zero order, stays constant for first order, and doubles for second order
- After n half-lives of a first order reaction the fraction remaining is $(1/2)^n$; the time to reach a fraction f remaining is $\ln(1 \div f) \div k$
- Units of k: M s^{-1} for zero order, s^{-1} for first order, M^{-1} s^{-1} for second order

Continue Revising

Topic 5.3 Quiz: Concentration Changes Over Time

Topic 5.3 Worksheet

Unit 5: All Topics

© 2026 ExamFitter.com · Free AP Chemistry revision notes