

Section 12.4

Integrated Rate Laws



Michael Stogsdill

Mott Community College

Learning Objectives



- Explain the form and function of an integrated rate law
- Perform integrated rate law calculations for zero-, first-, and second-order reactions
- Define half-life and carry out related calculations
- Identify the order of a reaction from concentration/time data

Integrated Rate Laws



- The **Integrated Rate Laws** relate the concentration of reactants and time.
- They can be used to determine the amount of reactant or product present after a period of time.
- They can also be used to estimate the time required for a reaction to proceed to a certain extent.
- They are derived using calculus, thus *integrated* (\int).

First-Order Reactions



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

- Where $[A]_t$ is the concentration of A at any time t, $[A]_0$ is the initial concentration of A, and k is the first-order rate constant.
- For mathematical convenience, this equation may be rearranged to other formats:

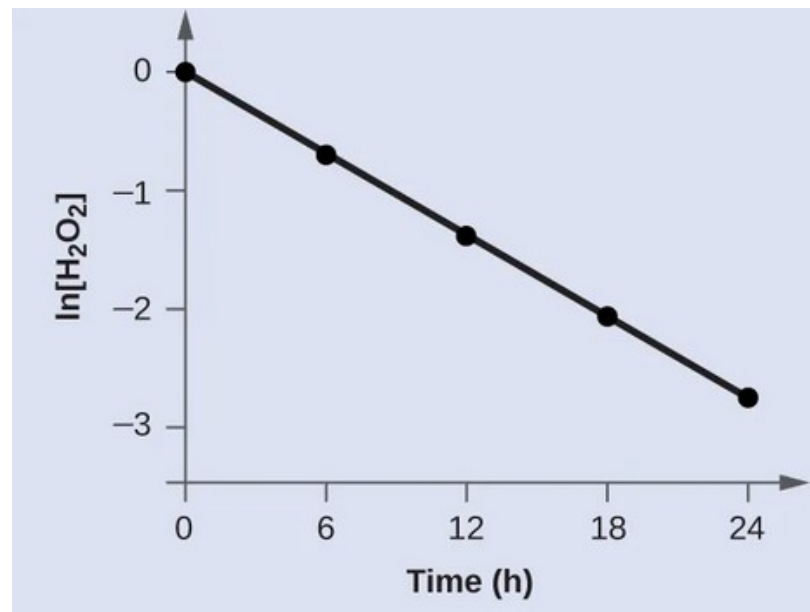
$$\ln \left(\frac{[A]_t}{[A]_0} \right) = -kt \quad \text{or} \quad \ln \left(\frac{[A]_0}{[A]_t} \right) = kt$$

$$\ln[A]_t = \ln[A]_0 - kt$$

Linear First-Order Integrated Rate Law



- A plot of $\ln[A]_t$ versus t for a first-order reaction is a straight line with a slope of $-k$ and a y-intercept of $\ln[A]_0$.
- If a set of rate data are plotted in this fashion but do not result in a straight line, the reaction is not first order in A.



$$\ln[A]_t = (-k)(t) + \ln[A]_0$$

$$y = mx + b$$

Second-Order Reactions



$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$
$$y = mx + b$$

- The integrated rate law for second-order reactions has the form of the equation of a straight line:
- A plot of $1/[A]_t$ versus t for a second-order reaction is a straight line with a slope of k and a y -intercept of $1/[A]_0$. If the plot is not a straight line, then the reaction is not second order.

Zero Order Reactions



- A zero-order reaction thus exhibits a constant reaction rate, regardless of the concentration of its reactant(s).

$$[A]_t = -kt + [A]_0$$

$$y = mx + b$$

- A plot of $[A]$ versus t for a zero-order reaction is a straight line with a slope of $-k$ and a y -intercept of $[A]_0$.

Half-Life of Reaction



- The **half-life of a reaction** ($t_{1/2}$) is the time required for one-half of a given amount of reactant to be consumed.
- In each succeeding half-life, half of the remaining concentration of the reactant is consumed.
- The equation for calculating the half life depends on the order of the reaction.

First-Order Half Life



$$\ln \frac{[A]_0}{[A]_t} = kt$$

$$t = \ln \frac{[A]_0}{[A]_t} \times \frac{1}{k}$$

$$t_{1/2} = \ln \frac{[A]_0}{\frac{1}{2}[A]_0} \times \frac{1}{k}$$

$$= \ln 2 \times \frac{1}{k} = 0.693 \times \frac{1}{k}$$

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

Second-Order Half Life



$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

$$\frac{1}{\frac{1}{2}[A]_0} - \frac{1}{[A]_0} = kt_{1/2}$$

$$\frac{2}{[A]_0} - \frac{1}{[A]_0} = kt_{1/2}$$

$$\frac{1}{[A]_0} = kt_{1/2}$$

$$t_{1/2} = \frac{1}{k[A]_0}$$

Zero-Order Half Life



$$[A] = -kt + [A]_0$$

$$\frac{[A]_0}{2} = -kt_{1/2} + [A]_0$$

$$kt_{1/2} = \frac{[A]_0}{2}$$

$$t_{1/2} = \frac{[A]_0}{2k}$$

Summary



	Zero-Order	First-Order	Second-Order
rate law	rate = k	rate = $k[A]$	rate = $k[A]^2$
units of rate constant	$M s^{-1}$	s^{-1}	$M^{-1} s^{-1}$
integrated rate law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \left(\frac{1}{[A]_0}\right)$
plot needed for linear fit of rate data	$[A]$ vs. t	$\ln[A]$ vs. t	$\frac{1}{[A]}$ vs. t
relationship between slope of linear plot and rate constant	$k = -\text{slope}$	$k = -\text{slope}$	$k = \text{slope}$
half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{[A]_0 k}$