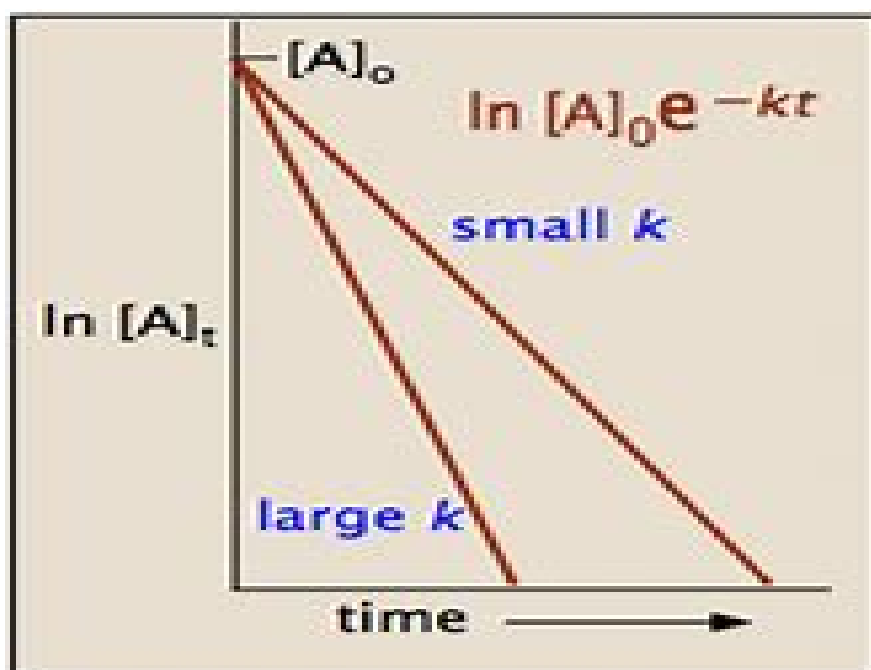


12.4.A - The Integrated Rate Law

Part 1: First Order



Integrated Rate Laws

So far our pursuit of rate laws has relied on reactant concentration driving the reaction. This focused on assessing the change in slope of a tangent line at different points along a reaction curve, which allowed us to derive a rate law.

In this two part section, we are going to look at how concentration changes with time.

First we will look only at first-order reactions, then we will look at second-order and zero-order reactions.



**First
Order**



First-Order Integrated Rate Law

Data for the integrated rate law consists of concentrations vs. time, rather than vs. initial rate.

Starting with our fundamental definition of rate, then employing integration (with calculus), we get the first order rate law:

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$$

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

Using logarithmic manipulation, this can also be shown in ratio form:

$$\ln\left(\frac{[A]_0}{[A]}\right) = kt$$

Is k the same?

First-Order Check

How can we determine if a data set is first-order?

The first-order rate law is in the form $y = mx + b$, and a plot of $\ln[A]$ (y-axis) vs. t (x-axis) should produce a linear graph with a slope of $-k$ and a y-intercept of $\ln[A]_0$.

Note: the slope is negative k , you will have to **remove** the negative sign to make k positive.

Making a simple data table of $\ln[A]$ should allow you to at-a-glance determine if it's first-order.

First-Order Example

A one-chemical decomposition reaction produced the following concentration vs. time data for chemical A:

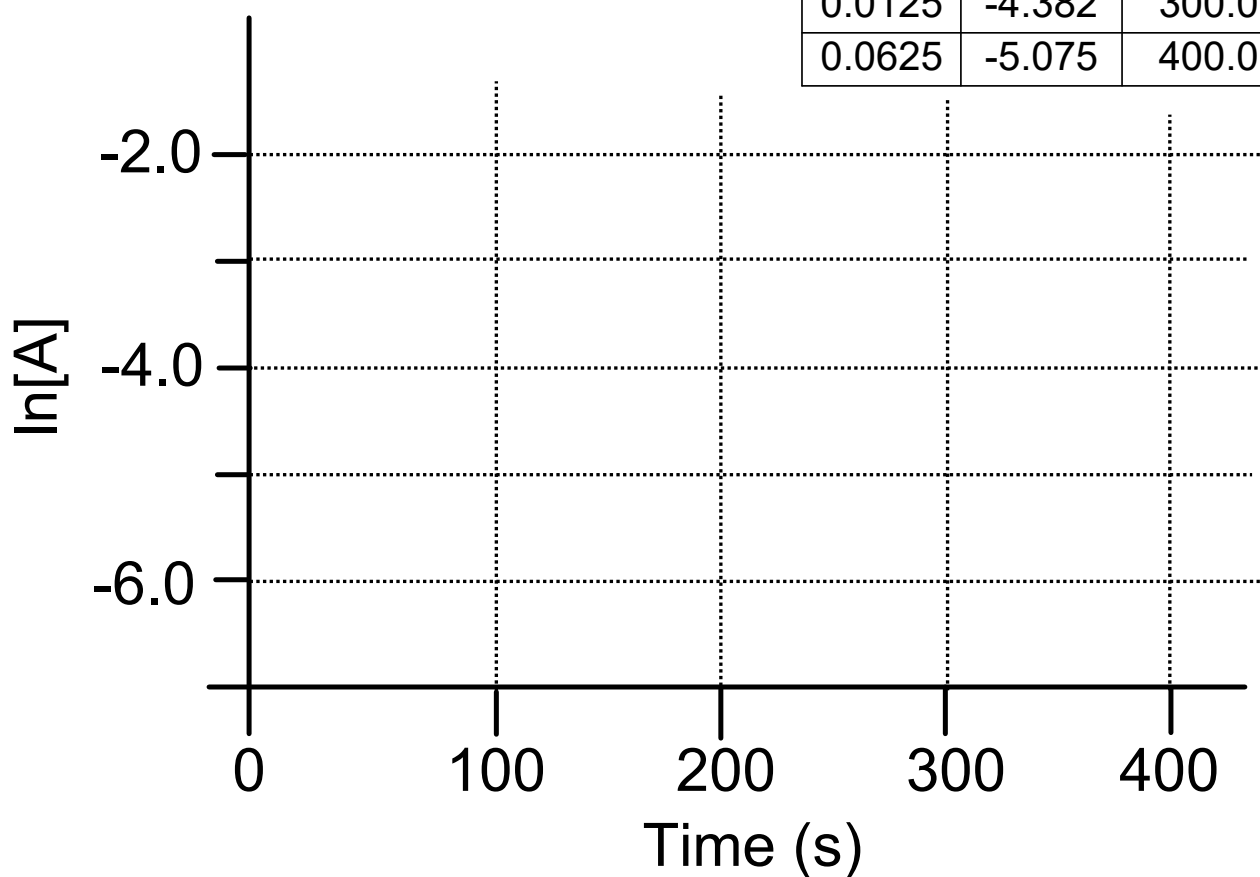
[A]	Time (s)
0.100	0.0
0.0707	50.0
0.0500	100.0
0.0250	200.0
0.0125	300.0
0.0625	400.0

1. Verify that the reaction is first-order.
2. Determine the rate constant k for the reaction.
3. Calculate [A] at time = 150 s into the reaction.

First-Order Example: Verification

1. To determine that the reaction is first-order, take the natural log of $[A]$, and plot it against time. If it's linear, then it's first order.

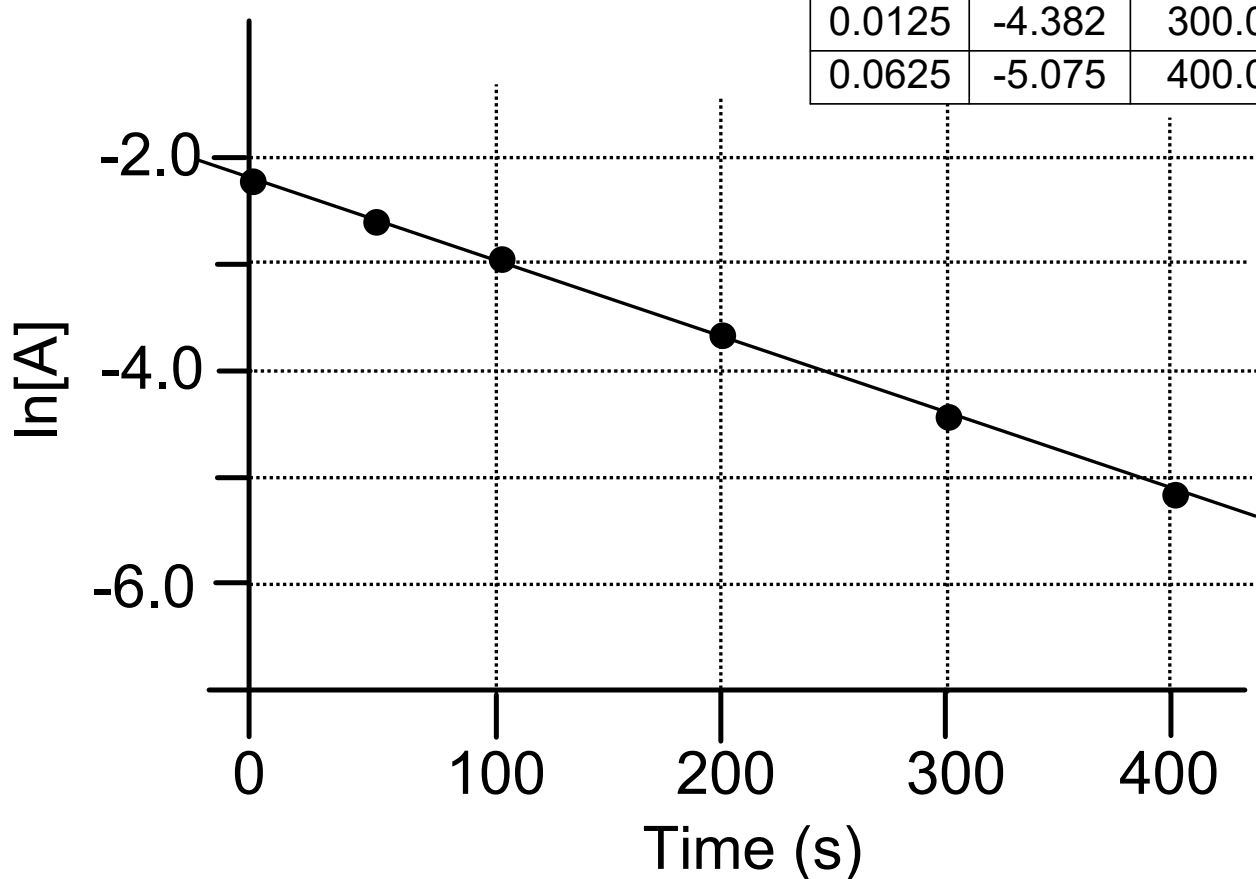
$[A]$	$\ln[A]$	Time (s)
0.1000	-2.303	0.0
0.0707	-2.649	50.0
0.0500	-2.996	100.0
0.0250	-3.689	200.0
0.0125	-4.382	300.0
0.0625	-5.075	400.0



First-Order Example: Verification

Looks linear to me.

[A]	ln[A]	Time (s)
0.1000	-2.303	0.0
0.0707	-2.649	50.0
0.0500	-2.996	100.0
0.0250	-3.689	200.0
0.0125	-4.382	300.0
0.0625	-5.075	400.0



First-Order Example: k

2. To find k , we can either

A. determine the slope of the line, or

B. use the integrated first-order rate law.

A. Slope of the line: the first and last points are on the line, so we can use them (rather than plugging values into a graphical analysis program):

$$\begin{aligned}k &= -(\text{slope}) = -\frac{\Delta y}{\Delta x} \\ &= -\frac{-5.075 - (-2.303)}{400.0 \text{ s}} = \boxed{6.93 \text{ E} - 3 \text{ s}^{-1}}\end{aligned}$$

First-Order Example: k

B. Using the ratio form of the Rate Law:

$$\ln\left(\frac{[A]_0}{[A]}\right) = kt$$

$$k = \frac{\ln\left(\frac{([A]_0)}{[A]}\right)}{t} = \frac{\ln\left(\frac{0.100 M}{0.00625 M}\right)}{400.0 s} = \boxed{6.93 E - 3 s^{-1}}$$

First-Order Example: $t = 150 \text{ s}$

3. Using the rate law and the k value just determined, we can calculate $[A]$ at time = 150 s:

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

$$\ln[A] = -6.93 \text{ E} - 3 \text{ s}^{-1} \cdot 150 \text{ s} + \ln[0.100] = -3.34$$

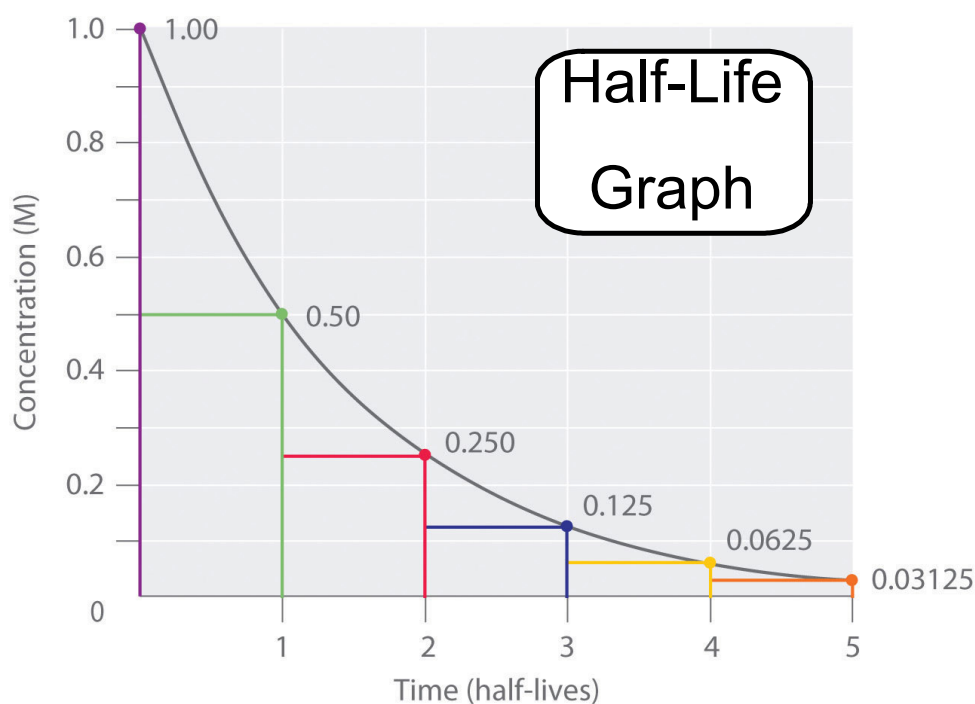
$$e^{\ln[A]} = e^{-3.34}$$

$$[A] = \boxed{0.0354 \text{ M}}$$

Reaction Half-Life.

A half-life is the time required for a reactant to reach half of its original concentration.

This is applicable to nuclear decay as well (to be studied later), where radioactive elements transmute into other elements at some measurable rate depending on the isotope.



Half-Life Math.

Once k is known, half life is easily obtained using the ratio form of the integrated rate law.

Setting $[A]_0 = 1$, and $[A] = 0.5$ (one half the original), we get:

$$\ln\left(\frac{[A]_0}{[A]}\right) = kt_{\frac{1}{2}}$$

$$\ln\left(\frac{1}{0.5}\right) = \ln 2 = 0.693 = kt_{\frac{1}{2}}$$

$t_{\frac{1}{2}} = \frac{0.693}{k}$	$t_{1/2} = \text{half life (s)}$ $k = \text{decay constant (s}^{-1}\text{)}$
-------------------------------------	---

More Half-Life Math.

Other possibly useful relations are:

A. Determine number of elapsed half-lives (n) during some time period:

$$n = \frac{\text{total time}}{\text{half - life}}$$

B. Divide initial sample concentration thusly:

$$[A] = \frac{[A]_0}{2^n}$$

Half-Life Example

4. What is the half life from the previous example?

$$t_{\frac{1}{2}} = \frac{0.693}{6.93 E - 3 s^{-1}} = 100 s$$

5. How much sample will be left after 425 seconds?

Note: you can use the rate law from earlier, but consider this as an alternative method.

$$n = \frac{\text{total time}}{\text{half - life}} = \frac{425}{100} = 4.25$$

$$[A] = \frac{[A]_0}{2^n} = \frac{0.100 M}{2^{4.25}} = \boxed{5.26 E - 3 M}$$

Homework

Read the rest of 12.4 in your Textbook

12.4.A Problems in your Booklet
Due Next Class