A **first-order reaction** is a reaction that proceeds at a rate that depends *linearly* on only one reactant concentration.

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**The Differential Representation**

Differential rate laws are generally used to describe what is occurring on a molecular level during a reaction, whereas integrated rate laws are used for determining the reaction order and the value of the rate constant from experimental measurements. The differential equation describing first-order kinetics is given below:

\[
\text{Rate} = -\dfrac{d[A]}{dt} = k[A]^1 = k[A] \quad \text{(1)}
\]

The "rate" is the reaction rate (in units of molar/time) and \(k\) is the reaction rate coefficient (in units of 1/time). However, the units of \(k\) vary for non-first-order reactions. These differential equations are *separable*, which simplifies the solutions as demonstrated below.

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**The Integral Representation**

First, write the differential form of the rate law.

\[
\text{Rate} = -\dfrac{d[A]}{dt} = k[A] \quad \text{(2)}
\]

Rearrange to give:

\[
\dfrac{d[A]}{[A]} = -k\,dt \quad \text{(3)}
\]

Second, integrate both sides of the equation.

\[
\int_{[A]_o}^{[A]} \dfrac{d[A]}{[A]} = -\int_{t_o}^{t} k\, dt \quad \text{(4a)}
\]

\[
\int_{[A]_o}^{[A]} \dfrac{1}{[A]} d[A] = -\int_{t_o}^{t} k\, dt \quad \text{(4b)}
\]

Recall from calculus that:

\[
\int \dfrac{1}{x} = \ln(x) \quad \text{(5)}
\]

Upon integration,

\[
\ln[A] - \ln[A]_o = -kt \quad \text{(6)}
\]

Rearrange to solve for \([A]\) to obtain one form of the rate law:

\[
\ln[A] = \ln[A]_o - kt \quad \text{(7)}
\]

This can be rearranged to:

\[
\ln [A] = -kt + \ln [A]_o \quad \text{(8)}
\]
This can further be arranged into \( y = mx + b \) form:

\[
\ln [A] = -kt + \ln [A]_0 \tag{9}
\]

The equation is a straight line with slope \( m \):

\[
mx = -kt \tag{10}
\]

and \( y \)-intercept \( b \):

\[
b = \ln [A]_0 \tag{11}
\]

Now, recall from the laws of logarithms that

\[
\ln \left( \frac{[A]_t}{[A]_0} \right) = -kt \tag{12}
\]

where \([A]\) is the concentration at time \( t \) and \([A]_0\) is the concentration at time 0, and \((k)\) is the first-order rate constant.

Figure 1: Decay profiles for first-order reactions with large and small rate constants.

Because the logarithms of numbers do not have any units, the product \(-kt\) also lacks units. This concludes that unit of \( k \) in a first order of reaction must be time\(^{-1}\). Examples of time-1 include s\(^{-1}\) or min\(^{-1}\). Thus, the equation of a straight line is applicable:

\[
\ln [A] = -kt + \ln [A]_0 \tag{15}
\]

To test if it the reaction is a first-order reaction, plot the natural logarithm of a reactant concentration versus time and see whether the graph is linear. If the graph is linear and has a negative slope, the reaction must be a first-order reaction.

To create another form of the rate law, raise each side of the previous equation to the exponent, \( e \):

\[
large e^{\ln[A]} = e^{\ln[A]_0 - kt} \tag{16}
\]

Simplifying gives the second form of the rate law:
\[ [A] = [A]_o e^{-kt} \] 

The integrated forms of the rate law can be used to find the population of reactant at any time after the start of the reaction. Plotting \( \ln[A] \) with respect to time for a first-order reaction gives a straight line with the slope of the line equal to \(-k\). More information can be found in the article on rate laws.

This general relationship, in which a quantity changes at a rate that depends on its instantaneous value, is said to follow an exponential law. Exponential relations are widespread in science and in many other fields. Consumption of a chemical reactant or the decay of a radioactive isotope follow the exponential decay law. Its inverse, the law of exponential growth, describes the manner in which the money in a continuously-compounding bank account grows with time, or the population growth of a colony of reproducing organisms. The reason that the exponential function \( y = e^{x} \) so efficiently describes such changes is that \( \frac{dy}{dx} = e^{x} \); that is, \( e^{x} \) is its own derivative, making the rate of change of \( y \) identical to its value at any point.

### Graphing First-order Reactions

The following graphs represents concentration of reactants versus time for a first-order reaction.
Plotting $\ln[A]$ with respect to time for a first-order reaction gives a straight line with the slope of the line equal to $-k$.

<table>
<thead>
<tr>
<th>Time</th>
<th>First Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>40</td>
</tr>
<tr>
<td>1</td>
<td>35</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>15</td>
</tr>
</tbody>
</table>

Half-lives of first order reactions

The half-life ($t_{1/2}$) is a timescale on which the initial population is decreased by half of its original value, represented by the following equation.

$$[A] = \frac{1}{2} [A]_o$$

After a period of one half-life, $t = t_{1/2}$ and we can write

$$\frac{[A]_{1/2}}{[A]_o} = \frac{1}{2} = e^{-k t_{1/2}} \label{18}$$

Taking logarithms of both sides (remember that $\ln e^x = x$) yields

$$\ln 0.5 = -kt \label{19}$$

Solving for the half-life, we obtain the simple relation

$$t_{1/2} = \frac{\ln 2}{k} \approx \frac{0.693}{k} \label{20}$$

This indicates that the half-life of a first-order reaction is a constant.
Figure 2: Half lives graphically demonstrated for first-order reaction. Notice the the half-life is independent of initial concentration. This is not the case with other reaction orders.

Example 1: Estimated Rate Constants

The half-life of a first-order reaction was found to be 10 min at a certain temperature. What is its rate constant?

SOLUTION

Use Equation 20 that relates half life to rate constant for first order reactions:

$$k = \frac{0.693}{600 \; \text{s}} = 0.00115 \; \text{s}^{-1}$$

As a check, dimensional analysis can be used to confirm that this calculation generates the correct units of inverse time.

Notice that, for first-order reactions, the half-life is independent of the initial concentration of reactant, which is a unique aspect to first-order reactions. The practical implication of this is that it takes as much time for $[A]$ to decrease from 1 M to 0.5 M as it takes for $[A]$ to decrease from 0.1 M to 0.05 M. In addition, the rate constant and the half life of a first-order process are inversely related.
Example 2: Determining Half life

If 3.0 g of substance \( A \) decomposes for 36 minutes the mass of unreacted \( A \) remaining is found to be 0.375 g. What is the half life of this reaction if it follows *first-order* kinetics?

**SOLUTION**

There are two ways to approach this problem: The "simple inspection approach" and the "brute force approach"

**Approach #1: "The simple Inspection Approach"**

This approach is used when one can recognize that the final concentration of \( A \) is \( \left( \frac{1}{8} \right) \) of the initial concentration and hence three half lives \( \left( \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \right) \) have elapsed during this reaction. Then use equation 18:

\[
[t_{1/2}] = \frac{36 \text{ min}}{3} = 12 \text{ min}
\]

This approach works only when the final concentration is \( \left( \frac{1}{2} \right)^n \) that of the initial concentration, then \( n \) is the number of half lives that have elapsed. If this is not the case, then approach #2 can be used.

**Approach #2: "The brute force approach"**

This approach involves solving for \( k \) from the integral rate law equation (Eq. 12 or 17) and then relating \( k \) to the \( t_{1/2} \) via Equation 20.

\[
\frac{[A]_t}{[A]_o} = e^{-kt}
\]

\[
k = -\frac{\ln \frac{[A]_t}{[A]_o}}{t} = -\frac{\ln \frac{0.375 \text{ g}}{3 \text{ g}}}{36 \text{ min}} = 0.0578 \text{ min}^{-1}
\]

\[
k = -\frac{\ln \frac{[A]_t}{[A]_o}}{t} = -\frac{\ln \frac{0.375 \text{ g}}{3 \text{ g}}}{36 \text{ min}} = 0.0578 \text{ min}^{-1}
\]
\[ t_{1/2} = \frac{\ln(2)}{k} \approx \frac{0.693}{0.0578 \text{ min}^{-1}} \approx 12 \text{ min} \]

The first approach is considerably faster (if the number of half lives evolved is apparent).

**Practice Problems**

**Calculate the half-life of the reactions below:**

1. If 4.00 g A are allowed to decompose for 40 min, the mass of A remaining undecomposed is found to be 0.80 g.
2. If 8.00 g A are allowed to decompose for 34 min, the mass of A remaining undecomposed is found to be 0.70 g.
3. If 9.00 g A are allowed to decompose for 24 min, the mass of A remaining undecomposed is found to be 0.50 g.

**Determine the percent H\textsubscript{2}O\textsubscript{2} that decomposes in the time using** \( k = 6.40 \times 10^{-5} \text{ s}^{-1} \)

4. The time for the concentration to decompose is 600.0 s after the reaction begins. Use the value of \( k \) above.
5. The time for the concentration to decompose is 450 s after the reaction begins. Use the value of \( k \) above.

**Solutions**

Use the half life reaction that contains initial concentration and final concentration. Plug in the appropriate variables and solve to obtain:

1. 17.2 min
2. 9.67 min
3. 5.75 min
4. Rearranging Eq. 17 to solve for the \( \frac{[H\textsubscript{2}O\textsubscript{2}]}{[H\textsubscript{2}O\textsubscript{2}]} \) ratio
\( \frac{[H\textsubscript{2}O\textsubscript{2}]}{[H\textsubscript{2}O\textsubscript{2}]} = e^{-kt} \)

This is a simple plug and play application once you have identified this equation.
\( \frac{[H\textsubscript{2}O\textsubscript{2}]}{[H\textsubscript{2}O\textsubscript{2}]} = e^{-((6.40 \times 10^{-5} \text{ s}^{-1}) (600 \text{ s})} \)
\( \frac{[H\textsubscript{2}O\textsubscript{2}]}{[H\textsubscript{2}O\textsubscript{2}]} = 0.9629 \) So 100-96.3=3.71\% of the hydrogen peroxide has decayed by 600 s.
5. Rearranging Eq. 17 to solve for the \( \frac{[H\textsubscript{2}O\textsubscript{2}]}{[H\textsubscript{2}O\textsubscript{2}]} \) ratio
\( \frac{[H\textsubscript{2}O\textsubscript{2}]}{[H\textsubscript{2}O\textsubscript{2}]} = e^{-kt} \)

This is a simple plug and play application once you have identified this equation.
\( \frac{[H\textsubscript{2}O\textsubscript{2}]}{[H\textsubscript{2}O\textsubscript{2}]} = e^{-((6.40 \times 10^{-5} \text{ s}^{-1}) (450 \text{ s})} \)
\( \frac{[H\textsubscript{2}O\textsubscript{2}]}{[H\textsubscript{2}O\textsubscript{2}]} = 0.9720 \) So 100-96.3=2.8\% of the hydrogen peroxide has decayed by 450 s.

**Internal Links**

- [Reaction order](#)
- [Zero-order reactions](#)
- [Half-lives and Pharmacokinetics](#)
- [Second-order reactions](#)
References


Contributors

• Rachael Curtis (UCD), Cathy Nguyen (UCD)

• Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook