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

**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:

\[
\text{Rate} = -\frac{d[A]}{dt} = k[A]^1 = k[A]
\]  

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.

**The Integral Representation**

First, write the differential form of the rate law.

\[
\text{Rate} = -\frac{d[A]}{dt} = k[A]
\]

Rearrange to give:

\[
\frac{d[A]}{[A]} = -k\,dt
\]

Second, integrate both sides of the equation.

\[
\int_{[A]_o}^{[A]} \frac{d[A]}{[A]} = -\int_{t_o}^{t} k\, dt
\]

Recall from calculus that:

\[
\int \frac{1}{x} = \ln(x)
\]

Upon integration,

\[
\ln[A] - \ln[A]_o = -kt
\]

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

\[
\ln[A] = \ln[A]_o - kt
\]

This can be rearranged to:

\[
\ln [A] = -kt + \ln [A]_o
\]
This can further be arranged into $y = mx + b$ form:

$$\ln [A] = -kt + \ln [A]_o \quad (9)$$

The equation is a straight line with slope $m$:

$$mx = -kt \quad (10)$$

and y-intercept $b$:

$$b = \ln [A]_o \quad (11)$$

Now, recall from the laws of logarithms that

$$\ln \left(\frac{[A]_t}{[A]_o}\right) = -kt \quad (12)$$

where $[A]$ is the concentration at time $t$ and $[A]_o$ 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:

$$\ln [A] = -kt + \ln [A]_o \quad (15)$$

To test if 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, $e$:

$$\large e^{\ln [A]} = e^{\ln [A]_o - kt} \quad (16)$$

Simplifying gives the second form of the rate law:
\[ [A] = [A]_0 e^{-kt} \]  

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

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

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 \(\dfrac{1}{8}\) of the initial concentration and hence three half lives \(\left(\dfrac{1}{2} \times \dfrac{1}{2} \times \dfrac{1}{2}\right)\) have elapsed during this reaction. Then use equation 18:

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

This approach works only when the final concentration is \(\left(\dfrac{1}{2}\right)^n\) 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.

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

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

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$_2$O$_2$ 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 \( \left[\text{H}_2\text{O}_2\right]_t/\left[\text{H}_2\text{O}_2\right]_0 \) ratio \( \left[\text{H}_2\text{O}_2\right]_t/\left[\text{H}_2\text{O}_2\right]_0 = e^{-(kt)} \)
   This is a simple plug and play application once you have identified this equation.
   \[
   \left[\text{H}_2\text{O}_2\right]_t/\left[\text{H}_2\text{O}_2\right]_0 = e^{-(6.40 \times 10^{-5} \text{ s}^{-1}) (600 \text{ s})} = 0.9629
   \]
   So 100-96.3 = 3.71% of the hydrogen peroxide has decayed by 600 s.
5. Rearranging Eq. 17 to solve for the \( \left[\text{H}_2\text{O}_2\right]_t/\left[\text{H}_2\text{O}_2\right]_0 \) ratio \( \left[\text{H}_2\text{O}_2\right]_t/\left[\text{H}_2\text{O}_2\right]_0 = e^{-(kt)} \)
   This is a simple plug and play application once you have identified this equation.
   \[
   \left[\text{H}_2\text{O}_2\right]_t/\left[\text{H}_2\text{O}_2\right]_0 = e^{-(6.40 \times 10^{-5} \text{ s}^{-1}) (450 \text{ s})} = 0.9720
   \]
   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 and Attributions

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

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