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:

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

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.

### The Integral Representation

First, write the differential form of the rate law.

\[
\text{Rate} = -\frac{d[A]}{dt} = k[A] \label{2}
\]

Rearrange to give:

\[
\frac{d[A]}{[A]} = -k\,dt \label{3}
\]

Second, integrate both sides of the equation.

\[
\int_{[A]_o}^{[A]} \frac{1}{[A]} \,d[A] = -\int_{t_o}^{t} k\, dt \label{4a}
\]

\[
\int_{[A]_{o}}^{[A]} \frac{1}{[A]} d[A] = -\int_{t_o}^{t} k\, dt \label{4b}
\]

Recall from calculus that:

\[
\int \frac{1}{x} = \ln(x) \label{5}
\]

Upon integration,

\[
\ln[A] - \ln[A]_o = -kt \label{6}
\]

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

\[
\ln[A] = \ln[A]_o - kt \label{7}
\]

This can be rearranged to:

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

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

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

$$mx = -kt \quad \text{(10)}$$

and $y$-intercept $b$:

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

Now, recall from the laws of logarithms that

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

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:

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

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, $e$:

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

Simplifying gives the second form of the rate law:
\[ [A] = [A]_oe^{-kt}\] \hfill (17)

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 $-k$.

### 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 \(\left(\frac{1}{2}\right)^3\) of the initial concentration and hence three half lives \(\left(\frac{1}{2}\right)^3\) have elapsed during this reaction. Then use equation 18:

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

\[
\frac{0.375}{3} = e^{-k \cdot 36}
\]

\[
k = \frac{\ln \left(\frac{0.375}{3}\right)}{36} = 0.0578 \text{ min}^{-1}
\]

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.

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

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

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 \( \frac{[H_2O_2]_t}{[H_2O_2]_0} \) ratio \( \frac{[H_2O_2]_t}{[H_2O_2]_0} = e^{-kt} \)
   This is a simple plug and play application once you have identified this equation.
   \[ \frac{[H_2O_2]_t}{[H_2O_2]_0} = e^{-(6.40 \times 10^{-5} \, \text{s}^{-1}) (600 \, \text{s})} = 0.9629 \] So 100-96.3=3.71% of the hydrogen peroxide has decayed by 600 s.
5. Rearranging Eq. 17 to solve for the \( \frac{[H_2O_2]_t}{[H_2O_2]_0} \) ratio \( \frac{[H_2O_2]_t}{[H_2O_2]_0} = e^{-kt} \)
   This is a simple plug and play application once you have identified this equation.
   \[ \frac{[H_2O_2]_t}{[H_2O_2]_0} = e^{-(6.40 \times 10^{-5} \, \text{s}^{-1}) (450 \, \text{s})} = 0.9720 \] 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

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

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