

2.1.1: First-Order Reactions

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:

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]^1 = k[A] \quad (2.1.1.1)$$

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.

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

Rearrange to give:

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

Second, integrate both sides of the equation.

$$\int_{[A]_o}^{[A]} \frac{d[A]}{[A]} = -\int_{t_o}^t k dt$$
$$\int_{[A]_o}^{[A]} \frac{1}{[A]} d[A] = -\int_{t_o}^t k dt$$

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:

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

The equation is a straight line with slope m :

$$mx = -kt$$

and y-intercept b :

$$b = \ln[A]_o$$

Now, recall from [the laws of logarithms](#) that

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

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.

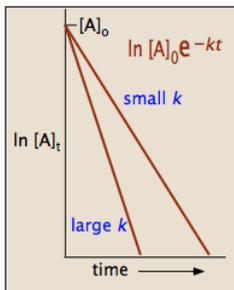


Figure 2.1.1.1: Decay profiles for first-order reactions with large and small rate constants. (CC BY; Stephen Lower)

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:

$$\ln[A] = -kt + \ln[A]_o. \quad (2.1.1.2)$$

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 :

$$e^{\ln[A]} = e^{\ln[A]_o - kt} \quad (2.1.1.3)$$

Simplifying gives the second form of the rate law:

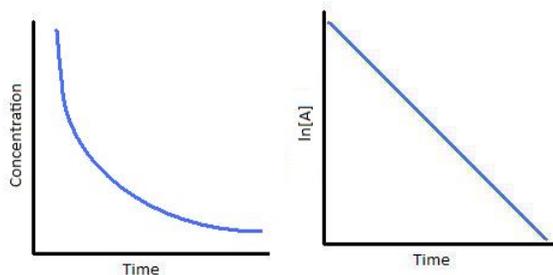
$$[A] = [A]_o e^{-kt} \quad (2.1.1.4)$$

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](#).

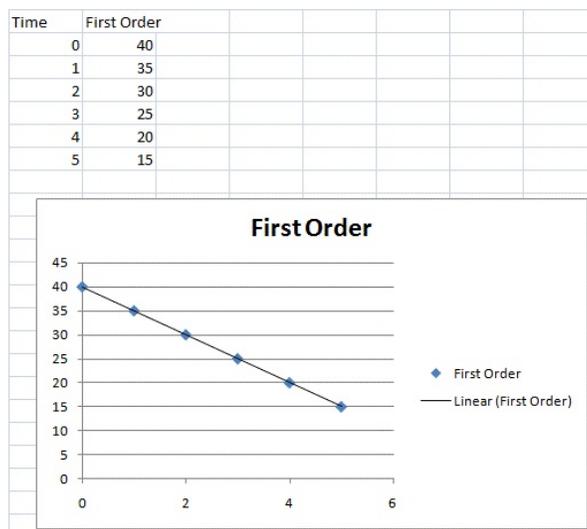
This general relationship, in which a quantity changes at a rate that depends on its instantaneous value, is said to follow an exponential law. Exponential relations are widespread in science and in many other fields. Consumption of a chemical reactant or the decay of a radioactive isotope follow the 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 $dy/dx = e^x$; 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

$$\frac{[A]_{1/2}}{[A]_o} = \frac{1}{2} = e^{-k t_{1/2}} \quad (2.1.1.5)$$

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

$$\ln 0.5 = -kt \quad (2.1.1.6)$$

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

$$t_{1/2} = \frac{\ln 2}{k} \approx \frac{0.693}{k} \quad (2.1.1.7)$$

This indicates that the half-life of a first-order reaction is a constant.

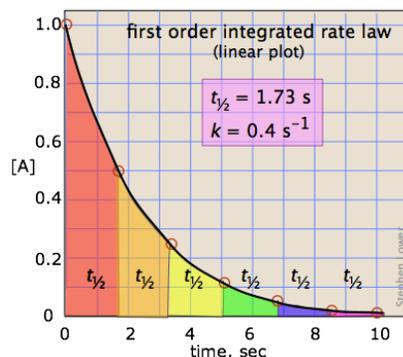


Figure 2.1.1.2: Half lives graphically demonstrated for first-order reaction. Notice the the half-life is independent of initial concentration. This is not the case with other reaction orders. (CC BY; Stephen Lower)

✓ 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?

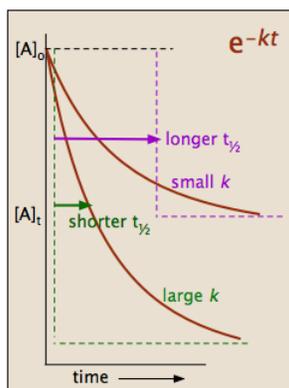
Solution

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 2.1.1.1: 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 $\frac{1}{8}$ of the initial concentration and hence three half lives ($\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2}$) have elapsed during this reaction.

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

This approach works only when the final concentration is $(\frac{1}{2})^n$ 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 2.1.1.4) and then relating *k* to the $t_{1/2}$ via Equation 2.1.1.7.

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

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

$$= -\frac{\ln \frac{0.375 \text{ g}}{3 \text{ g}}}{36 \text{ min}}$$

$$= 0.0578 \text{ min}^{-1}$$

Therefore, via Equation 2.1.1.7

$$t_{1/2} = \frac{\ln 2}{k} \approx \frac{0.693}{0.0578 \text{ min}^{-1}} \approx 12 \text{ min}$$

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

? Exercise 2.1.1.2a

Calculate the half-life of the reactions below:

- 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.
- 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.
- 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.

Answer

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

- 17.2 min
- 9.67 min
- 5.75 min

? Exercise 2.1.1.2b

Determine the percent H_2O_2 that decomposes in the time using $k = 6.40 \times 10^{-5} \text{ s}^{-1}$

- The time for the concentration to decompose is 600.0 s after the reaction begins.
- The time for the concentration to decompose is 450 s after the reaction begins.

Answer

- Rearranging Eq. 17 to solve for the $[\text{H}_2\text{O}_2]_t/[\text{H}_2\text{O}_2]_0$ ratio

$$\frac{[\text{H}_2\text{O}_2]_t}{[\text{H}_2\text{O}_2]_0} = e^{-kt}$$

This is a simple plug and play application once you have identified this equation.

$$\frac{[\text{H}_2\text{O}_2]_{t=600 \text{ s}}}{[\text{H}_2\text{O}_2]_0} = e^{-(6.40 \times 10^{-5} \text{ s}^{-1})(600 \text{ s})}$$

$$\frac{[\text{H}_2\text{O}_2]_{t=600 \text{ s}}}{[\text{H}_2\text{O}_2]_0} = 0.9629$$

So 100-96.3=3.71% of the hydrogen peroxide has decayed by 600 s.

- Rearranging Eq. 17 to solve for the $[\text{H}_2\text{O}_2]_t/[\text{H}_2\text{O}_2]_0$ 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.

$$\frac{[H_2O_2]_{t=450 \text{ s}}}{[H_2O_2]_0} = e^{-(6.40 \times 10^{-5} \text{ s}^{-1})(450 \text{ s})}$$

$$\frac{[H_2O_2]_{t=450 \text{ s}}}{[H_2O_2]_0} = 0.9720$$

So $100 - 97.2 = 2.8\%$ of the hydrogen peroxide has decayed by 450 s.

References

1. Petrucci, Ralph H. General Chemistry: Principles and Modern Applications 9th Ed. New Jersey: Pearson Education Inc. 2007.

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