Learning Objective

- To know how to use half-lives to describe the rates of first-order reactions.

Half-Lives

Another approach to describing reaction rates is based on the time required for the concentration of a reactant to decrease to one-half its initial value. This period of time is called the half-life of a reaction. The period of time it takes for the concentration of a reactant to decrease to one-half its initial value of the reaction, written as $t_{1/2}$. Thus the half-life of a reaction is the time required for the reactant concentration to decrease from $[A]_0$ to $[A]_0/2$. If two reactions have the same order, the faster reaction will have a shorter half-life, and the slower reaction will have a longer half-life.

The half-life of a first-order reaction under a given set of reaction conditions is a constant. This is not true for zeroth- and second-order reactions. The half-life of a first-order reaction is independent of the concentration of the reactants. This becomes evident when we rearrange the integrated rate law for a first-order reaction (Equation 13.5.1) to produce the following equation:

$$\ln \frac{[A]_0}{[A]} = kt \tag{13.5.1}$$

Substituting $[A]_0/2$ for $[A]$ and $t_{1/2}$ for $t$ (to indicate a half-life) into Equation 13.5.1 gives

$$\ln \frac{[A]_0}{[A]_0/2} = \ln 2 = kt_{1/2} \tag{13.5.2}$$

The natural logarithm of 2 (to three decimal places) is 0.693. Substituting this value into the equation, we obtain the expression for the half-life of a first-order reaction:

$$t_{1/2} = \frac{0.693}{k} \tag{13.5.3}$$
Thus, for a first-order reaction, each successive half-life is the same length of time, as shown in Figure 13.5.1, and is independent of [A].

Figure 13.5.1 The Half-Life of a First-Order Reaction This plot shows the concentration of the reactant in a first-order reaction as a function of time and identifies a series of half-lives, intervals in which the reactant concentration decreases by a factor of 2. In a first-order reaction, every half-life is the same length of time.

If we know the rate constant for a first-order reaction, then we can use half-lives to predict how much time is needed for the reaction to reach a certain percent completion.

<table>
<thead>
<tr>
<th>Number of Half-Lives</th>
<th>Percentage of Reactant Remaining</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \frac{100%}{2} = 50% )</td>
</tr>
<tr>
<td>2</td>
<td>( \frac{50%}{2} = 25% )</td>
</tr>
<tr>
<td>3</td>
<td>( \frac{25%}{2} = 12.5% )</td>
</tr>
<tr>
<td>( n )</td>
<td>( \left( \frac{100%}{2} \right)^n = \frac{1}{2^n} )</td>
</tr>
</tbody>
</table>

As you can see from this table, the amount of reactant left after \( n \) half-lives of a first-order reaction is \( \left( \frac{1}{2} \right)^n \) times the initial concentration.

Note the Pattern

For a first-order reaction, the concentration of the reactant decreases by a constant with each half-life and is independent of [A].
Example 13.5.1

The anticancer drug cisplatin hydrolyzes in water with a rate constant of $1.5 \times 10^{-3}$ min$^{-1}$ at pH 7.0 and 25°C. Calculate the half-life for the hydrolysis reaction under these conditions. If a freshly prepared solution of cisplatin has a concentration of 0.053 M, what will be the concentration of cisplatin after 5 half-lives? after 10 half-lives? What is the percent completion of the reaction after 5 half-lives? after 10 half-lives?

**Given:** rate constant, initial concentration, and number of half-lives

**Asked for:** half-life, final concentrations, and percent completion

**Strategy:**

A Use Equation 13.5.3 to calculate the half-life of the reaction.

B Multiply the initial concentration by $1/2$ to the power corresponding to the number of half-lives to obtain the remaining concentrations after those half-lives.

C Subtract the remaining concentration from the initial concentration. Then divide by the initial concentration, multiplying the fraction by 100 to obtain the percent completion.

**Solution:**

A We can calculate the half-life of the reaction using Equation 13.5.3:

$$ t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.5 \times 10^{-3}\text{ min}^{-1}} = 4.6 \times 10^2\text{ min} $$

Thus it takes almost 8 h for half of the cisplatin to hydrolyze.

B After 5 half-lives (about 38 h), the remaining concentration of cisplatin will be as follows:

$$ \frac{0.053\text{ M}}{2^5} = \frac{0.053\text{ M}}{32} = 0.0017\text{ M} $$

After 10 half-lives (77 h), the remaining concentration of cisplatin will be as follows:

$$ \frac{0.053\text{ M}}{2^{10}} = \frac{0.053\text{ M}}{1024} = 5.2 \times 10^{-5}\text{ M} $$

C The percent completion after 5 half-lives will be as follows:

$$ \text{percent completion} = \left( \frac{0.053\text{ M} - 0.0017\text{ M}}{0.53\text{ M}} \right) \times 100\% = 97\% $$

The percent completion after 10 half-lives will be as follows:

$$ \text{percent completion} = \left( \frac{0.053\text{ M} - 5.2 \times 10^{-5}\text{ M}}{0.53\text{ M}} \right) \times 100\% = 100\% $$

Thus a first-order chemical reaction is 97% complete after 5 half-lives and 100% complete after 10 half-lives.
Exercise

In Example 4 you found that ethyl chloride decomposes to ethylene and HCl in a first-order reaction that has a rate constant of $1.6 \times 10^{-6}$ s$^{-1}$ at 650°C. What is the half-life for the reaction under these conditions? If a flask that originally contains 0.077 M ethyl chloride is heated at 650°C, what is the concentration of ethyl chloride after 4 half-lives?

Answer: $4.3 \times 10^5$ s = 120 h = 5.0 days; $4.8 \times 10^{-3}$ M

Radioactive Decay Rates

As you learned in Chapter 1, radioactivity, or radioactive decay, is the emission of a particle or a photon that results from the spontaneous decomposition of the unstable nucleus of an atom. The rate of radioactive decay is an intrinsic property of each radioactive isotope that is independent of the chemical and physical form of the radioactive isotope. The rate is also independent of temperature. In this section, we will describe radioactive decay rates and how half-lives can be used to monitor radioactive decay processes.

In any sample of a given radioactive substance, the number of atoms of the radioactive isotope must decrease with time as their nuclei decay to nuclei of a more stable isotope. Using $N$ to represent the number of atoms of the radioactive isotope, we can define the rate of decay as the decrease in the number of a radioisotope’s nuclei per unit time:

$$A = -\frac{dN}{dt}$$  \hspace{1cm} (13.5.4)

Activity is usually measured in disintegrations per second (dps) or disintegrations per minute (dpm).

The activity of a sample is directly proportional to the number of atoms of the radioactive isotope in the sample:

$$A = kN$$  \hspace{1cm} (13.5.5)

Here, the symbol $k$ is the radioactive decay constant, which has units of inverse time (e.g., s$^{-1}$, yr$^{-1}$) and a characteristic value for each radioactive isotope. If we combine Equation 13.5.4 and Equation 13.5.5, we obtain the relationship between the number of decays per unit time and the number of atoms of the isotope in a sample:

$$-\frac{dN}{dt} = kN$$  \hspace{1cm} (13.5.6)

Equation 13.5.6 is the same as the equation for the reaction rate of a first-order reaction (Equation 13.3.2), except that it uses numbers of atoms instead of concentrations. In fact, radioactive decay is a first-order process and can be described in terms of either the differential rate law (Equation 13.5.7) or the integrated rate law:

$$N = N_0 e^{-kt}$$  \hspace{1cm} (13.5.7)

$$\ln \frac{N}{N_0} = -kt$$  \hspace{1cm} (13.5.8)

Because radioactive decay is a first-order process, the time required for half of the nuclei in any sample of a radioactive isotope to decay is a constant, called the half-life of the isotope. The half-life tells us how radioactive an isotope is (the
number of decays per unit time); thus it is the most commonly cited property of any radioisotope. For a given number of atoms, isotopes with shorter half-lives decay more rapidly, undergoing a greater number of radioactive decays per unit time than do isotopes with longer half-lives. The half-lives of several isotopes are listed in Table 13.5.1, along with some of their applications.

Table 13.5.1 Half-Lives and Applications of Some Radioactive Isotopes

<table>
<thead>
<tr>
<th>Radioactive Isotope</th>
<th>Half-Life</th>
<th>Typical Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrogen-3 (tritium)</td>
<td>12.32 yr</td>
<td>biochemical tracer</td>
</tr>
<tr>
<td>carbon-11</td>
<td>20.33 min</td>
<td>positron emission tomography (biomedical imaging)</td>
</tr>
<tr>
<td>carbon-14</td>
<td>$5.7 \times 10^3$ yr</td>
<td>dating of artifacts</td>
</tr>
<tr>
<td>sodium-24</td>
<td>14.951 h</td>
<td>cardiovascular system tracer</td>
</tr>
<tr>
<td>phosphorus-32</td>
<td>14.26 days</td>
<td>biochemical tracer</td>
</tr>
<tr>
<td>potassium-40</td>
<td>$1.248 \times 10^9$ yr</td>
<td>dating of rocks</td>
</tr>
<tr>
<td>iron-59</td>
<td>44.495 days</td>
<td>red blood cell lifetime tracer</td>
</tr>
<tr>
<td>cobalt-60</td>
<td>5.2712 yr</td>
<td>radiation therapy for cancer</td>
</tr>
<tr>
<td>technetium-99$m^*$</td>
<td>6.006 h</td>
<td>biomedical imaging</td>
</tr>
<tr>
<td>iodine-131</td>
<td>8.0207 days</td>
<td>thyroid studies tracer</td>
</tr>
<tr>
<td>radium-226</td>
<td>$1.600 \times 10^3$ yr</td>
<td>radiation therapy for cancer</td>
</tr>
<tr>
<td>uranium-238</td>
<td>$4.468 \times 10^9$ yr</td>
<td>dating of rocks and Earth's crust</td>
</tr>
<tr>
<td>americium-241</td>
<td>432.2 yr</td>
<td>smoke detectors</td>
</tr>
</tbody>
</table>

*The $m$ denotes metastable, where an excited state nucleus decays to the ground state of the same isotope.

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Note the Pattern

Radioactive decay is a first-order process.

Radioisotope Dating Techniques

In our earlier discussion, we used the half-life of a first-order reaction to calculate how long the reaction had been occurring. Because nuclear decay reactions follow first-order kinetics and have a rate constant that is independent of temperature and the chemical or physical environment, we can perform similar calculations using the half-lives of
isotopes to estimate the ages of geological and archaeological artifacts. The techniques that have been developed for this application are known as radioisotope dating techniques.

The most common method for measuring the age of ancient objects is carbon-14 dating. The carbon-14 isotope, created continuously in the upper regions of Earth’s atmosphere by nuclear reactions initiated by energetic cosmic rays, reacts with atmospheric oxygen or ozone to form $^{14}\text{CO}_2$. As a result, the $\text{CO}_2$ that plants use as a carbon source for synthesizing organic compounds always includes a certain proportion of $^{14}\text{CO}_2$ molecules as well as nonradioactive $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$. Any animal that eats a plant ingests a mixture of organic compounds that contains approximately the same proportions of carbon isotopes as those in the atmosphere. When the animal or plant dies, the carbon-14 nuclei in its tissues decay to nitrogen-14 nuclei by a radioactive process known as beta decay, which releases low-energy electrons (β particles) that can be detected and measured:

$$^{14}\text{C} \rightarrow ^{14}\text{N} + \beta^{-} \tag{13.5.8}$$

The half-life for this reaction is $5700 \pm 30$ yr.

The $^{14}\text{C}/^{12}\text{C}$ ratio in living organisms is $1.3 \times 10^{-12}$, with a decay rate of 15 dpm/g of carbon (Figure 13.5.2). Comparing the disintegrations per minute per gram of carbon from an archaeological sample with those from a recently living sample enables scientists to estimate the age of the artifact, as illustrated in Example 11. Using this method implicitly assumes that the $^{14}\text{CO}_2/^{12}\text{CO}_2$ ratio in the atmosphere is constant, which is not strictly correct because the intensity of the cosmic ray flux varies somewhat. Moreover the method is not useful for samples that were alive after 1945 because of the relatively large amount of $^{14}\text{C}$ created by nuclear bomb explosions in the atmosphere. Other methods, such as dating by counting tree-rings and comparing the tree-ring dates to the $^{14}\text{C}/^{12}\text{C}$ ratio in a ring, have been used to calibrate the dates obtained by radiocarbon dating. All radiocarbon dates reported are now corrected for minor changes in the $^{14}\text{CO}_2/^{12}\text{CO}_2$ ratio over time.

Figure 13.5.2 Radiocarbon Dating A plot of the specific activity of $^{14}\text{C}$ versus age for a number of archaeological samples shows an inverse linear relationship between $^{14}\text{C}$ content (a log scale) and age (a linear scale).
Example 13.5.2

In 1990, the remains of an apparently prehistoric man were found in a melting glacier in the Italian Alps. Analysis of the $^{14}$C content of samples of wood from his tools gave a decay rate of 8.0 dpm/g carbon. How long ago did the man die?

**Given:** isotope and final activity

**Asked for:** elapsed time

**Strategy:**

A Use [Equation 13.5.5](#) to calculate $N_0/N$. Then substitute the value for the half-life of $^{14}$C into [Equation 13.5.3](#) to find the rate constant for the reaction.

B Using the values obtained for $N_0/N$ and the rate constant, solve [Equation 13.5.7](#) to obtain the elapsed time.

**Solution:**

We know the initial activity from the isotope’s identity (15 dpm/g), the final activity (8.0 dpm/g), and the half-life, so we can use the integrated rate law for a first-order nuclear reaction ([Equation 13.5.7](#)) to calculate the elapsed time (the amount of time elapsed since the wood for the tools was cut and began to decay).

\[
\ln \frac{N}{N_0} = -kt
\]

\[
\ln \left( \frac{N_0}{N} \right) = kt
\]

A From [Equation 13.5.5](#), we know that $A = kN$. We can therefore use the initial and final activities ($A_0 = 15$ dpm and $A = 8.0$ dpm) to calculate $N_0/N$:

\[
\frac{A_0}{A} = \frac{N_0}{N} = \frac{15}{8.0}
\]

Now we need only calculate the rate constant for the reaction from its half-life (5730 yr) using [Equation 13.5.3](#):

\[
\frac{t_{1/2}}{0.693} = k
\]

This equation can be rearranged as follows:

\[
k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730 \text{ yr}} = 1.22 \times 10^{-4} \text{ yr}^{-1}
\]

B Substituting into the equation for $t$,

\[
t = \frac{\ln \left( \frac{N}{N_0} \right)}{k} = \frac{\ln \left( \frac{15}{8.0} \right)}{1.22 \times 10^{-4} \text{ yr}^{-1}} = 5.2 \times 10^3 \text{ yr}
\]

From our calculations, the man died 5200 yr ago.

Exercise
It is believed that humans first arrived in the Western Hemisphere during the last Ice Age, presumably by traveling over an exposed land bridge between Siberia and Alaska. Archaeologists have estimated that this occurred about 11,000 yr ago, but some argue that recent discoveries in several sites in North and South America suggest a much earlier arrival. Analysis of a sample of charcoal from a fire in one such site gave a $^{14}$C decay rate of 0.4 dpm/g of carbon. What is the approximate age of the sample?

**Answer:** 30,000 yr

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**Summary**

The **half-life** of a reaction is the time required for the reactant concentration to decrease to one-half its initial value. The half-life of a first-order reaction is a constant that is related to the rate constant for the reaction: $t_{1/2} = \frac{0.693}{k}$.

Radioactive decay reactions are first-order reactions. The **rate of decay**, or **activity**, of a sample of a radioactive substance is the decrease in the number of radioactive nuclei per unit time.

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### Key Takeaways

- The half-life of a first-order reaction is independent of the concentration of the reactants.
- The half-lives of radioactive isotopes can be used to date objects.

### Key Equations

#### Half-life of first-order reaction

\[ t_{1/2} = \frac{0.693}{k} \]

#### Radioactive decay

\[ A = kN \]

### Conceptual Problems

1. What do chemists mean by the **half-life** of a reaction?
2. If a sample of one isotope undergoes more disintegrations per second than the same number of atoms of another isotope, how do their half-lives compare?

### Numerical Problems

1. Half-lives for the reaction $A + B \rightarrow C$ were calculated at three values of $[A]_0$, and $[B]$ was the same in all cases. The data are listed in the following table:
Does this reaction follow first-order kinetics? On what do you base your answer?

2. Ethyl-2-nitrobenzoate (NO$_2$C$_6$H$_4$CO$_2$C$_2$H$_5$) hydrolyzes under basic conditions. A plot of [NO$_2$C$_6$H$_4$CO$_2$C$_2$H$_5$] versus t was used to calculate $t_{1/2}$, with the following results:

<table>
<thead>
<tr>
<th>[NO$_2$C$_6$H$_4$CO$_2$C$_2$H$_5$] (M/cm$^3$)</th>
<th>$t_{1/2}$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.050</td>
<td>240</td>
</tr>
<tr>
<td>0.040</td>
<td>300</td>
</tr>
<tr>
<td>0.030</td>
<td>400</td>
</tr>
</tbody>
</table>

Is this a first-order reaction? Explain your reasoning.

3. Azomethane (CH$_3$N$_2$CH$_3$) decomposes at 600 K to C$_2$H$_6$ and N$_2$. The decomposition is first order in azomethane. Calculate $t_{1/2}$ from the data in the following table:

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>P$_{Azomethane}$ (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.2 × 10$^{-2}$</td>
</tr>
<tr>
<td>2000</td>
<td>3.99 × 10$^{-2}$</td>
</tr>
<tr>
<td>4000</td>
<td>1.94 × 10$^{-2}$</td>
</tr>
</tbody>
</table>

How long will it take for the decomposition to be 99.9% complete?

4. The first-order decomposition of hydrogen peroxide has a half-life of 10.7 h at 20°C. What is the rate constant (expressed in s$^{-1}$) for this reaction? If you started with a solution that was 7.5 × 10$^{-3}$ M H$_2$O$_2$, what would be the initial rate of decomposition (M/s)? What would be the concentration of H$_2$O$_2$ after 3.3 h?

Answers

1. No; the reaction is second order in A because the half-life decreases with increasing reactant concentration according to $t_{1/2} = 1/k[A_0]$.
2. 
3. $t_{1/2} = 1.92 × 10^3$ s or 1920 s; 19100 s or 5.32 hrs.
4. 
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