Pearson

20.6: The Kinetics of Radioactive Decay and Radiometric Dating

Radioactivity is a natural component of our environment. The ground beneath you most likely contains radioactive atoms that emit radiation. The food you eat contains a residual quantity of radioactive atoms that are absorbed into your body fluids and incorporated into tissues. Small amounts of radiation from space make it through the atmosphere to constantly bombard Earth. Humans and other living organisms have evolved in this environment and have adapted to survive in it.

One reason for the radioactivity in our environment is the instability of all atomic nuclei beyond atomic number 83 (bismuth). Every element with more than 83 protons in its nucleus is unstable and therefore radioactive. In addition, some isotopes of elements with fewer than 83 protons are also unstable and radioactive. Radioactive nuclides *persist* in our environment because new ones are constantly being formed and because many of the existing ones decay only very slowly.

All radioactive nuclei decay via first-order kinetics, so the rate of decay in a particular sample is directly proportional to the number of nuclei present as indicated in this equation:

$$\text{rate} = kN$$

> You may find it useful to review the discussion of first-order kinetics in Section 14.4.

where N is the number of radioactive nuclei and k is the rate constant. Different radioactive nuclides decay into their daughter nuclides with different rate constants. Some nuclides decay quickly (large rate constant), while others decay slowly (small rate constant).

The time it takes for one-half of the parent nuclides in a radioactive sample to decay to the daughter nuclides is the *half-life* and is identical to the concept of half-life for chemical reactions that we discussed in Chapter 14. Thus, the relationship between the half-life of a nuclide and its rate constant is given by the same expression that we derived for a first-order reaction in Section 14.5:

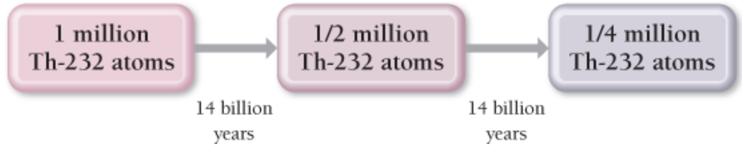
[20.1]

$$t_{1/2} = \frac{0.693}{k}$$

Nuclides that decay quickly have short half-lives and large rate constants—they are considered very active (many decay events per unit time). Nuclides that decay slowly have long half-lives and are less active (fewer decay events per unit time).

For example, thorium-232 is an alpha emitter with a half-life of 1.4×10^{10}years, or 14 billion years, so it is not particularly active. A sample of Th-232 containing 1 million atoms decays to $\frac{1}{2}$ million atoms in 14 billion years and then to $\frac{1}{4}$ million in another 14 billion years and so on. Notice that a radioactive sample does *not* decay to *zero* atoms in two half-lives—we can't add two half-lives together to get a "whole" life. The amount that remains after one half-life is always one-half of what was present at the start. The

The amount that remains after one half-life is always one-half of what was present at the start. The amount that remains after two half-lives is one-quarter of what was present at the start, and so on.



Some nuclides have very short half-lives. For example, radon-220 has a half-life of approximately 1 minute (Figure 20.9). A 1-million-atom sample of radon-220 decays to $\frac{1}{4}$ million radon-220 atoms in just 2 minutes and to approximately 1000 atoms in 10 minutes. Table 20.3 lists several nuclides and their half-lives.

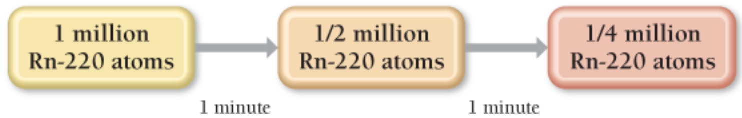


Figure 20.9 The Decay of Radon-220

Radon-220 decays with a half-life of approximately 1 minute.

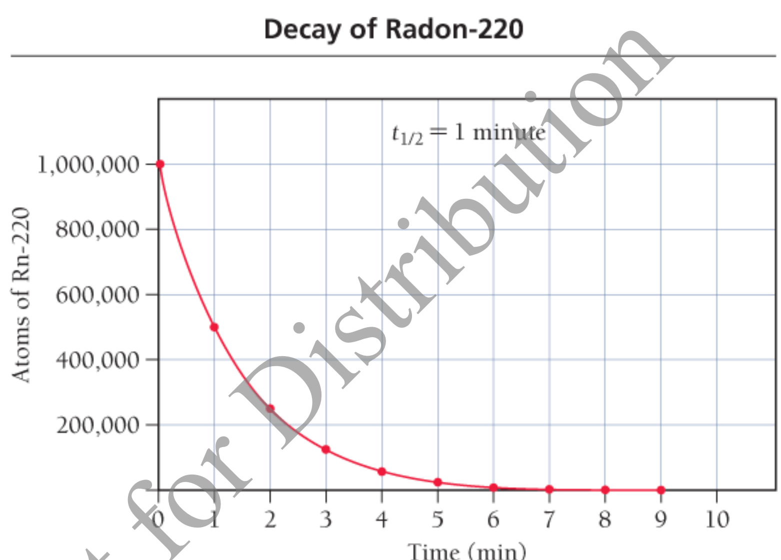


Table 20.3 Selected Nuclides and Their Half-Lives

Nuclide	Half-Life	Type of Decay
$^{232}_{90}Th$	1.4×10^{10} yr	alpha
$^{238}_{92}U$	4.5×10^{9} yr	alpha
$^{14}_{6}C$	5715 yr	beta
$^{220}_{86}Rn$	55.6 s	alpha
$^{219}_{90}Th$	1.05×10^{-6} s	alpha

Conceptual Connection 20.2 Half-Life

The Integrated Rate Law

Recall from Chapter 14 that for first-order chemical reactions, the concentration of a reactant as a function of time is given by the integrated rate law.

[20.2]

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

Because nuclear decay follows first-order kinetics, we can substitute the number of nuclei for concentration to arrive at the equation:

[20.3]

$$\ln\frac{N_t}{N_0} = -kt$$

where N_t is the number of radioactive nuclei at time t and N_0 is the initial number of radioactive nuclei. Example 20.4 demonstrates the use of this equation.

Example 20.4 Radioactive Decay Kinetics

Plutonium-236 is an alpha emitter with a half-life of 2.86 years. If a sample initially contains 1.35 mg of Pu-236, what mass of Pu-236 is present after 5.00 years?

SORT You are given the initial mass of Pu-236 in a sample and asked to find the mass after 5.00 years.

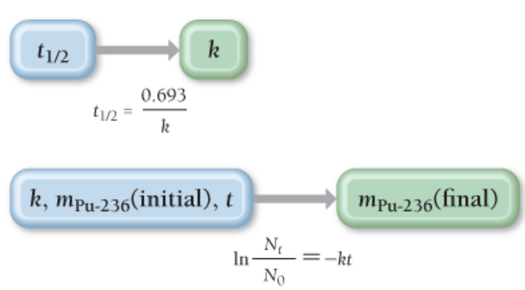
GIVEN:
$m_{\text{Pu-236}}\,(\text{initial}) = 1.35\ \text{mg};$
$t = 5.00\ \text{yr};\ t_{1/2} = 2.86\ \text{yr}$

FIND: $m_{\text{Pu-236}}\,(\text{final})$

STRATEGIZE Use the integrated rate law (Equation 20.3) to solve this problem. You can determine the value of the rate constant (k) from the half-life expression (Equation 20.1).

Use the value of the rate constant, the initial mass of Pu-236, and the time along with integrated rate law to find the final mass of Pu-236. Since the mass of the Pu-236 ($m_{\text{Pu-236}}$)is directly proportional to the number of atoms (N), and since the integrated rate law contains the ratio (N_t/N_0), you can substitute the initial and final masses.

CONCEPTUAL PLAN



SOLVE Follow the conceptual plan. Begin by determining the rate constant from the half-life.

Solve the integrated rate law for N_t and substitute the values of the rate constant, the initial mass of Pu-236, and the time into the solved equation. Calculate the final mass of Pu-236.

SOLUTION

$$\begin{aligned} t_{1/2} &= \frac{0.693}{k} \\ k &= \frac{0.693}{t_{1/2}} = \frac{0.693}{2.86\text{ yr}} \\ &= 0.24\underline{2}3/\text{yr} \end{aligned}$$

$$\begin{aligned} \ln\frac{N_t}{N_0} &= -kt \\ \frac{N_t}{N_0} &= e^{-kt} \\ N_t &= N_0 e^{-kt} \\ N_t &= 1.35\ \text{mg}\left[e^{-\left(0.24\underline{2}3/\cancel{\text{yr}}\right)\left(5.00\ \cancel{\text{yr}}\right)}\right] \\ N_t &= 0.402\text{ mg} \end{aligned}$$

CHECK The units of the answer (mg) are correct. The magnitude of the answer (0.402 mg) is about one-third of the original mass (1.35 mg), which seems reasonable given that the amount of time is between one and two half-lives. (One half-life would result in one-half of the original mass, and two half-lives would result in one-fourth of the original mass.)

FOR PRACTICE 20.4 How long will it take for the 1.35 mg sample of Pu-236 in Example 20.4 to decay to 0.100 mg?

Interactive Worked Example 20.4 **Radioactive Decay Kinetics**

Because radioactivity is a first-order process, the rate of decay is linearly proportional to the number of nuclei in the sample. Therefore, we can use the initial rate of decay (rate_0) and the rate of decay at time t (rate_t) in the integrated rate law.

$$\text{rate}_t = kN_t \qquad \text{rate}_0 = kN_0$$

$$\frac{N_t}{N_0} = \frac{\text{rate}_t/\cancel{k}}{\text{rate}_0/\cancel{k}} = \frac{\text{rate}_t}{\text{rate}_0}$$

Substituting into Equation 20.3, we get the following result:

[20.4]

$$\ln\frac{\text{rate}_t}{\text{rate}_0} = -kt$$

We can use Equation 20.4 to predict how the rate of decay of a radioactive sample will change with time or how much time has passed based on how the rate has changed (see Examples 20.5 and 20.6 later in this section).

Example 20.5 Using Radiocarbon Dating to Estimate Age

A skull believed to belong to an ancient human being has a carbon-14 decay rate of 4.50

disintegrations per minute per gram of carbon (4.50 dis/min · gC). If living organisms have a decay rate of 15.3 dis/min · gC, how old is the skull? (The decay rate is directly proportional to the amount of carbon-14 present.)

SORT You are given the current rate of decay for the skull and the assumed initial rate. You are asked to determine the age of the skull, which is the time that must have passed in order for the rate to have reached its current value.

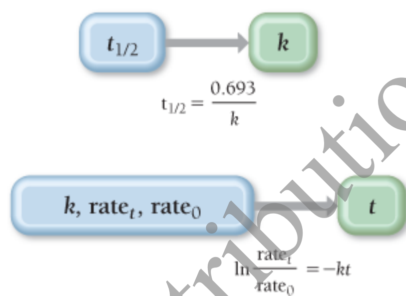
GIVEN:
$\text{rate}_t = 4.50 \text{ dis/min} \cdot \text{gC};$
$\text{rate}_0 = 15.3 \text{ dis/min} \cdot \text{gC};$

FIND: t

STRATEGIZE Use the expression for half-life (Equation 20.1) to find the rate constant (k) from the half-life for C-14, which is 5715 yr (Table 20.3).

Use the value of the rate constant and the initial and current rates to find t from the integrated rate law (Equation 20.4).

CONCEPTUAL PLAN



SOLVE Follow the conceptual plan. Begin by finding the rate constant from the half-life.

Substitute the rate constant and the initial and current rates into the integrated rate law and solve for t.

SOLUTION

$$
\begin{aligned}
t_{1/2} &= \frac{0.693}{k} \\
k &= \frac{0.693}{t_{1/2}} = \frac{0.693}{5715 \text{ yr}} \\
&= 1.21\underline{2} \times 10^{-4}/\text{yr}
\end{aligned}
$$

$$\ln \frac{\text{rate}_t}{\text{rate}_0} = -kt$$

$$
\begin{aligned}
t &= -\frac{\ln \frac{\text{rate}_t}{\text{rate}_0}}{k} = -\frac{\ln \frac{4.50 \ \cancel{\text{dis/min} \cdot \text{gC}}}{15.3 \ \cancel{\text{dis/min} \cdot \text{gC}}}}{1.21\underline{2} \times 10^{-4}/\text{yr}} \\
&= 1.0 \times 10^{4} \text{ yr}
\end{aligned}
$$

CHECK The units of the answer (yr) are correct. The magnitude of the answer is about 10,000 years, which is a little less than two half-lives. This value is reasonable given that two half-lives would result in a decay rate of about 3.8 dis/min · gC.

FOR PRACTICE 20.5 A researcher claims that an ancient scroll originated from Greek scholars in about 500 B.C. A measure of its carbon-14 decay rate gives a value that is 89% of that found in living organisms. How old is the scroll, and could it be authentic?

Interactive Worked Example 20.5 **Radiocarbon Dating**

Example 20.6 Using Uranium/Lead Dating to Estimate Age

A meteor contains 0.556 g of Pb-206 to every 1.00 g of U-238. Assuming that the meteor did not contain any Pb-206 at the time of its formation, determine the age of the meteor. Uranium-238 decays to lead-206 with a half-life of 4.5 billion years.

SORT You are given the current masses of Pb-206 and U-238 in a rock and asked to find its age. You are also given the half-life of U-238.

GIVEN:
$m_{\text{U-238}} = 1.00\text{ g}; m_{\text{Pb-206}} = 0.556\text{ g};$
$t_{1/2} = 4.5 \times 10^9\text{ yr}$

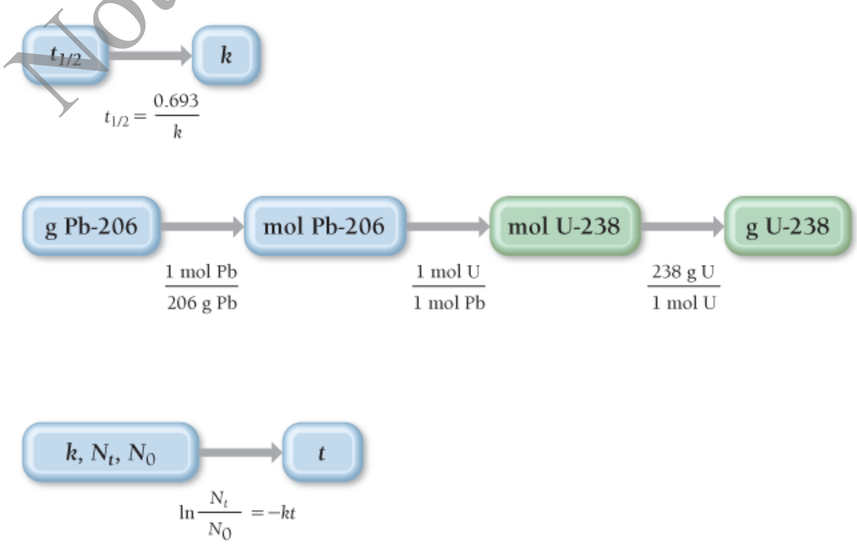
FIND: t

STRATEGIZE Use the integrated rate law (Equation 20.3) to solve this problem. To do so, you must first determine the value of the rate constant (k) from the half-life expression (Equation 20.1).

Before substituting into the integrated rate law, you need the ratio of the current amount of U-238 to the original amount (N_t/N_0). The current mass of uranium is 1.00 g. The initial mass includes the current mass (1.00 g) plus the mass that has decayed into lead-206, which you can determine from the current mass of Pb-206.

Use the value of the rate constant and the initial and current amounts of U-238 along with the integrated rate law to find t.

CONCEPTUAL PLAN



SOLVE Follow your plan. Begin by finding the rate constant from the half-life.

Determine the mass in grams of U-238 required to form the given mass of Pb-206.

Substitute the rate constant and the initial and current masses of U-238 into the integrated rate law and solve for t. (The initial mass of U-238 is the sum of the current mass and the mass that is required to form the given mass of Pb-206.)

SOLUTION

$$\begin{aligned} t_{1/2} &= \frac{0.693}{k} \\ k &= \frac{0.693}{t_{1/2}} = \frac{0.693}{4.5 \times 10^9 \text{ yr}} \\ &= 1.5\underline{4} \times 10^{-10}/\text{yr} \end{aligned}$$

$$0.556 \cancel{\text{ g Pb-206}} \times \frac{1 \cancel{\text{ mol Pb-206}}}{206 \cancel{\text{ g Pb-206}}} \times \frac{1 \cancel{\text{ mol U-238}}}{1 \cancel{\text{ mol Pb-206}}} \times \frac{238 \text{ g U-238}}{1 \cancel{\text{ mol U-238}}} = 0.64\underline{2}4 \text{ g U-238}$$

$$\begin{aligned} \ln\frac{N_t}{N_0} &= -kt \\ t &= \frac{\ln\frac{N_t}{N_0}}{k} = -\frac{\ln\frac{1.00 \cancel{\text{ g}}}{1.00 \cancel{\text{ g}} + 0.64\underline{2}4 \cancel{\text{ g}}}}{1.5\underline{4} \times 10^{-10}/\text{yr}} \\ &= 3.2 \times 10^9 \text{ yr} \end{aligned}$$

CHECK The units of the answer (yr) are correct. The magnitude of the answer is about 3.2 billion years, which is less than one half-life. This value is reasonable given that less than half of the uranium in the meteor has decayed into lead.

FOR PRACTICE 20.6 A rock contains a Pb-206 to U-238 mass ratio of 0.145:1.00. Assuming that the rock did not contain any Pb-206 at the time of its formation, determine its age.

The radioactive isotopes in our environment and their predictable decay with time can therefore be used to estimate the age of rocks or artifacts containing those isotopes. The technique is known as **radiometric dating**, and here we examine two different types individually.

Conceptual Connection 20.3 Half-Life and the Amount of Radioactive Sample

Interactive

Radiocarbon Dating

Archaeologists, geologists, anthropologists, and other scientists use **radiocarbon dating**, a technique devised in 1949 by Willard Libby (1908–1980) at the University of Chicago, to estimate the ages of fossils and artifacts. For example, in 1947, young shepherds searching for a stray goat near the Dead Sea (east of Jerusalem) entered a cave and discovered ancient scrolls that had been stuffed into jars. These scrolls—now named the Dead Sea Scrolls—are 2000-year-old texts of the Hebrew Bible, predating other previously discovered manuscripts by almost a thousand years.

The Dead Sea Scrolls, like other ancient artifacts, contain a radioactive signature that reveals their age. This signature results from the presence of carbon-14 (which is radioactive) in the environment. Carbon-14 is constantly formed in the upper atmosphere by the neutron bombardment of nitrogen.

$$^{14}N + {}^{1}n \rightarrow {}^{14}C + {}^{1}H$$

$$^{14}_{7}\mathrm{N} + ^{1}_{0}\mathrm{n} \to ^{14}_{6}\mathrm{C} + ^{1}_{1}\mathrm{H}$$

The Dead Sea Scrolls are 2000-year-old biblical manuscripts. Their age was determined by radiocarbon dating.

After it forms, carbon-14 decays back to nitrogen by beta emission with a half-life of 5715 years.

$$^{14}_{6}\mathrm{C} \to ^{14}_{7}\mathrm{N} + ^{0}_{-1}\mathrm{e} \quad t_{1/2} = 5715 \text{ yr}$$

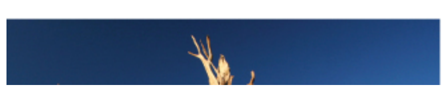
Libby received the Nobel Prize in 1960 for the development of radiocarbon dating.

The continuous formation of carbon-14 in the atmosphere and its continuous decay to nitrogen-14 produce a nearly constant equilibrium amount of atmospheric carbon-14. The atmospheric carbon-14 is oxidized to carbon dioxide and incorporated into plants by photosynthesis. The C-14 then makes its way up the food chain and ultimately into all living organisms. As a result, the tissues in all living plants, animals, and humans contain the same ratio of carbon-14 to carbon-12 $(^{14}\mathrm{C} : {}^{12}\mathrm{C})$as that found in the atmosphere. When a living organism dies, however, it stops incorporating new carbon-14 into its tissues. The $^{14}\mathrm{C} : {}^{12}\mathrm{C}$ratio then begins to decrease with a half-life of 5715 years.

Since many artifacts, including the Dead Sea Scrolls, are made from materials that were once living—such as papyrus, wood, or other plant and animal derivatives—the $^{14}\mathrm{C} : {}^{12}\mathrm{C}$ratio in these artifacts indicates their age. For example, suppose an ancient artifact has a $^{14}\mathrm{C} : {}^{12}\mathrm{C}$ratio that is 25% of that found in living organisms. How old is the artifact? Since it contains one-quarter as much carbon-14 as a living organism, it must be two half-lives or 11,460 years old. The maximum age that we can estimate from carbon-14 dating is about 50,000 years—beyond that, the amount of carbon-14 becomes too low to measure accurately.

The accuracy of carbon-14 dating can be checked against objects whose ages are known from historical sources. These kinds of comparisons reveal that ages obtained from C-14 dating may deviate from the actual ages by up to about 5%. For a 6000-year-old object, that is a margin of error of about 300 years. The reason for the deviations is the variance of atmospheric C-14 levels over time.

In order to make C-14 dating more accurate, scientists have studied the carbon-14 content of western bristlecone pine trees, which can live up to 5000 years. Each tree trunk contains growth rings corresponding to each year of the tree's life, and the wood in each ring incorporates carbon derived from the carbon dioxide in the atmosphere at that time. The rings thus provide a record of the historical atmospheric carbon-14 content. In addition, the rings of living trees can be correlated with the rings of dead trees (if part of the lifetimes of the trees overlapped), allowing the record to be extended back about 11,000 years. Using the data from the bristlecone pine, we can correct the 5% deviations from historical dates. In this way, the known ages of bristlecone pine trees are used to calibrate C-14 dating, resulting in more accurate results.



Some western bristlecone pine trees live up to 5000 years; scientists can precisely determine the age of a tree by counting the annual rings in its trunk. The trees can therefore be used to calibrate the time scale for radiocarbon dating.

Each tree ring represents a year of growth, and the wood in that ring is a living record of the amount of C-14 present in the atmosphere during that year.

Uranium/Lead Dating

Radiocarbon dating can only measure the ages of objects that were once living and that are relatively young (<50,000 years). Other radiometric dating techniques can measure the ages of prehistoric objects that were never alive. The most dependable technique relies on the ratio of uranium-238 to lead-206 within igneous rocks (rocks of volcanic origin). This technique measures the time that has passed since the rock solidified (at which point the "radiometric clock" was reset).

Because U-238 decays into Pb-206 with a half-life of 4.5×10^9 years, the relative amounts of U-238 and Pb-206 in a uranium-containing rock reveal its age. For example, if a rock originally contained U-238 and currently contains equal amounts of U-238 and Pb-206, the rock is 4.5 billion years old, assuming that it did not contain any Pb-206 when it was formed. The latter assumption can be tested because the lead that results from the decay of uranium has a different isotopic composition than the lead that is deposited in rocks at the time of their formation. Example 20.6 shows how we can use the relative amounts of Pb-206 and U-238 in a rock to estimate its age.

The uranium/lead radiometric dating technique and other radiometric dating techniques (such as the decay of potassium-40 to argon-40) have been widely used to measure the ages of rocks on Earth and have produced highly consistent results. Rocks with ages greater than 3.5 billion years have been found on every continent. The oldest rocks have an age of approximately 4.0 billion years, establishing a lower limit for Earth's age (Earth must be at least as old as its oldest rocks). The ages of about 70 meteorites that have struck Earth have also been extensively studied and have been found to be about 4.5 billion years old. Since the meteorites were formed at the same time as our solar system (which includes Earth), the best estimate for Earth's age is about 4.5 billion years. That age is consistent with the estimated age of our universe—about 13.7 billion years.

> The age of the universe is estimated from its expansion rate, which is measured by examining changes in the wavelength of light from distant galaxies.