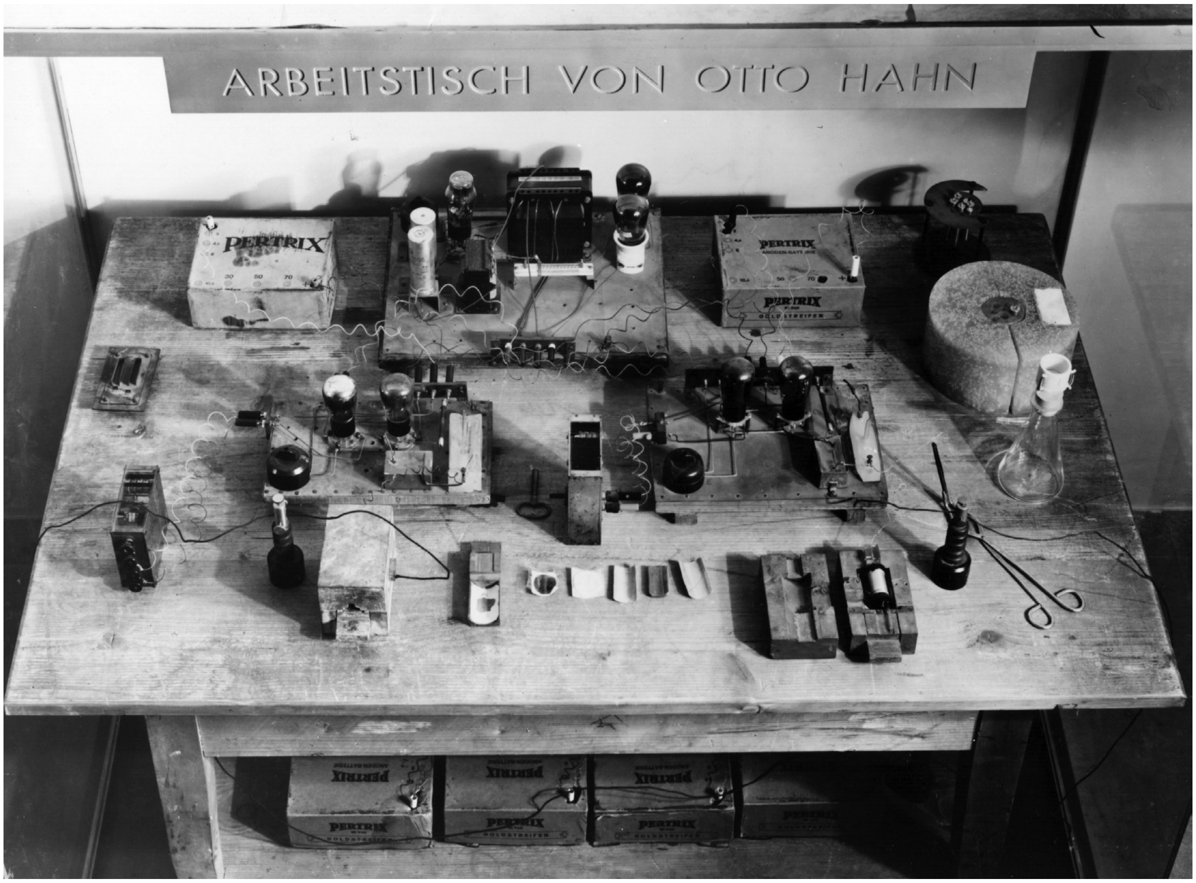
INTERCHAPTER O

Radiochemistry



In the autumn of 1938, the German nuclear physicist Otto Hahn and his student Fritz Strassmann discovered that when uranium-235 nuclei are bombarded with neutrons, they split into two roughly equal-sized fragments. The apparatus used by Hahn and Strassmann is shown here.

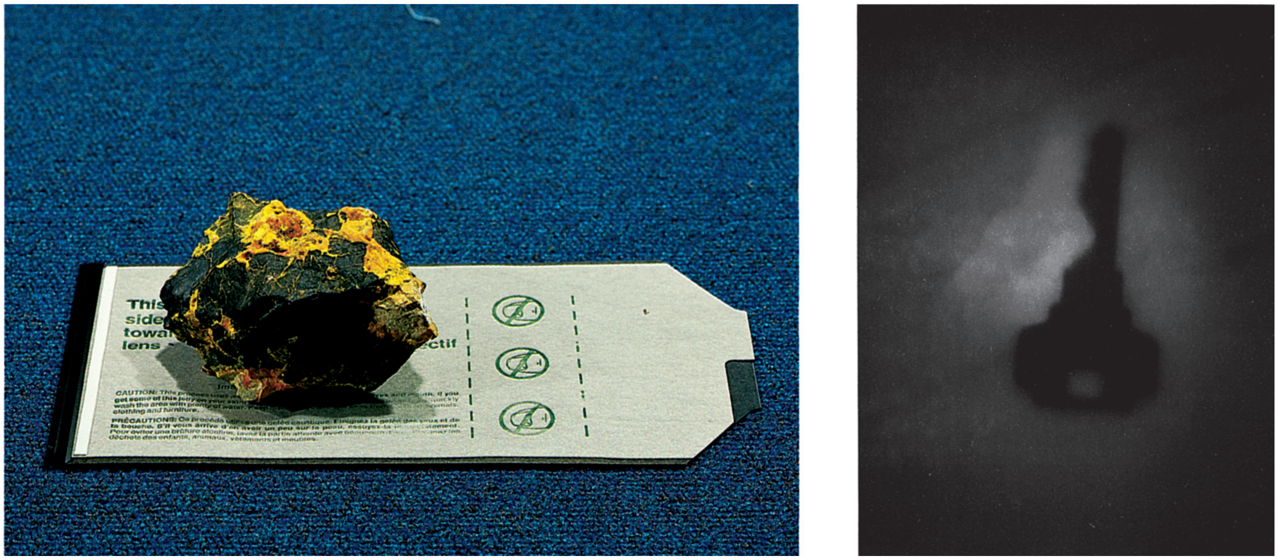


Figure O.1 (*left*) When a sample of $K_2UO_2(SO_4)_2(s)$ is placed on photographic film, which is wrapped in opaque paper, the radioactive emissions pass through the protective paper and cause the film to appear as if it had been exposed to light. (*right*) A metal key that was placed below the sample blocked the emissions, so we see the outline of the key on the developed film.

As we have seen in Chapters 2 and 17, many nuclei are unstable and spontaneously emit subatomic particles, a process called **radioactivity**. Radioactivity was discovered by the French scientist Henri Becquerel in 1896. He found that the compound potassium uranyl sulfate, $K_2UO_2(SO_4)_2(s)$, emitted radiation that penetrated heavy paper and caused the exposure of a photographic plate wrapped in the paper (Figure O.1). He was able to show that the uranium sample was the source of the emissions, which he called radioactivity. Shortly after Becquerel's discovery, Marie and Pierre Curie, working in Paris, discovered a number of other radioactive substances. The Curies and Becquerel shared the Nobel Prize in Physics in 1903, and Marie Curie received the Nobel Prize in Chemistry alone in 1911 for her research in radiochemistry. She is one of only four scientists to earn two Nobel Prizes in two different sciences. Later, the Curies' daughter Irène Joliot-Curie (Figure O.2) and her husband, Frédéric Joliot, produced the first artificial radioisotope, a process that has led to numerous applications in chemistry, biology, medicine, agriculture, geology, forensics, and engineering. The Joliot-Curies received the Nobel Prize in Chemistry in 1935 for their work on artificial radioisotopes. The study of the properties of radioisotopes and their applications is called **radiochemistry**, the topic of this Interchapter.

Figure O.2 Marie Curie with her daughter Irène. Both were pioneers in nuclear chemical research. Marie shared the 1903 Nobel Prize in Physics with her husband Pierre and Henri Becquerel, and she received the Nobel Prize in Chemistry singly in 1911. Irène Joliot-Curie shared the 1935 Nobel Prize in Chemistry with her husband, Frédéric Joliot.

O-1. There Are Several Types of Emissions from Radioactive Nuclei

All nuclei with more than 83 protons are radioactive. Radioactive isotopes (**radioisotopes**) can undergo change through a process called **nuclear decay**. Two common forms of nuclear decay are **α-decay** (the emission of a helium nucleus, denoted by $^{4}_{2}\mathrm{He}$) and **β-decay** (the emission of an electron, denoted by $^{0}_{-1}\mathrm{e}$). Also recall from Section 17-6 that such processes are described by nuclear equations. For example, radon-222 nuclei are radioactive and emit α-particles. The nuclear equation that describes this process is

$$^{222}_{86}\mathrm{Rn} \rightarrow {}^{218}_{84}\mathrm{Po} + {}^{4}_{2}\mathrm{H}$$

Notice that this nuclear equation is balanced because the total nuclear charge (given by the number of protons) and the total number of nucleons (given by the mass numbers) are the same on both sides.

An example of a β-emitter is carbon-14, which is used in radiocarbon dating (Section 17-7). The nuclear equation that describes this process is

$$^{14}_{6}\mathrm{C} \rightarrow {}^{14}_{7}\mathrm{N} + {}^{0}_{-1}\mathrm{e}$$

Note that the mass numbers do not change as a result of the emission of a β-particle, but that the atomic number increases by 1. Recall from Section 17-6 that the emission of a β-particle can be viewed as the result of the conversion of a neutron to a proton within the nucleus, as represented by $^{1}_{0}\mathrm{n} \rightarrow {}^{1}_{1}\mathrm{p} + {}^{0}_{-1}\mathrm{e}$, where $^{1}_{1}\mathrm{p}$ denotes a proton in the nucleus.

The emission of an α-particle or a β-particle frequently leaves the product nucleus in an excited state. The excited nucleus can relax to its ground state by emitting a photon, called a **gamma ray (γ-ray)**, whose frequency is given by the Planck equation (Chapter 4), $\Delta E = h\nu$, where ΔE is the energy difference between the excited state and the ground state of the nucleus. A gamma ray is a high-energy electromagnetic wave, similar to an X-ray. The emission of γ-rays causes no change in either the atomic number or the mass number of an element. Gamma-ray emission is analogous to an atom emitting a photon when an electron falls from an excited state to a lower energy state, as discussed in Chapter 4. We usually do not indicate γ-radiation in writing nuclear equations.

Several other types of radioactive emissions have been observed. For example, some nuclei emit a particle called a **positron**, which is a particle that has the same mass as an electron but a positive charge. The positron and other particles that have the same mass but the opposite charge of normal matter are referred to as **antimatter particles**. The symbol for a positron in nuclear equations is $^{0}_{+1}\mathrm{e}$. An example of a positron emission is given by the nuclear equation $^{38}_{19}\mathrm{K} \rightarrow {}^{38}_{18}\mathrm{Ar} + {}^{0}_{+1}\mathrm{e}$. The emission of a positron can be viewed as a result of the conversion of a proton to a neutron in the nucleus. The process can be represented as $^{1}_{1}\mathrm{p} \rightarrow {}^{1}_{0}\mathrm{n} + {}^{0}_{+1}\mathrm{e}$.

O-2. Mass Can Be Converted into Energy in a Nuclear Reaction

Positrons and other forms of antimatter typically exist for only a very short time. Positrons combine with electrons to annihilate each other. The reverse process, the production of a positron-electron pair out of energy, is shown in Figure O.3. When a particle, such as an electron, and its antiparticle, a positron,

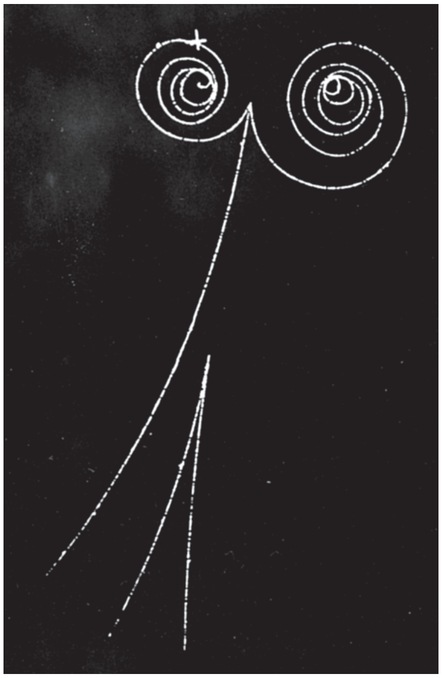


Figure O.3 An electron and a positron annihilate each other to produce two γ-ray photons. The reverse process also occurs; that is, a high-energy γ-ray photon can transform spontaneously into an electron and a positron, as seen in this photograph from a bubble chamber. Because it is uncharged, the photon leaves no track, but the electron and positron leave visible spiral tracks. An externally applied magnetic field causes the tracks to be spirals, and the opposite charges on the electron and positron cause them to spiral in opposite directions.

annihilate each other, their mass is converted into energy according to Einstein's famous formula

$$E = mc^2$$

where E is the energy, m is the mass, and c is the speed of light. Because we are referring to energy changes and mass changes, we write the above equation in the form

$$\Delta E = c^2 \, \Delta m$$

Using the fact that the speed of light is $3.00 \times 10^8\ \text{m·s}^{-1}$ and that the mass of an electron or a positron is 9.11×10^{-31} kg, we see that when an electron and a positron annihilate each other

$$\begin{aligned} \Delta E &= (2)(-9.11 \times 10^{-31}\ \text{kg})(3.00 \times 10^8\ \text{m·s}^{-1})^2 \\ &= -1.64 \times 10^{-13}\ \text{kg·m}^2\text{·s}^{-2} = -1.64 \times 10^{-13}\ \text{J} \end{aligned}$$

where we used the fact that $1\ \text{J} = 1\ \text{kg·m}^2\text{·s}^{-2}$. The resulting energy produced appears in the form of γ-ray photons.

While 1.64×10^{-13} J may not seem like a lot of energy, remember that this is the energy produced from a single positron-electron annihilation event. Consider the reaction described by the nuclear equation ${}^{6}_{3}\text{Li} + {}^{1}_{1}\text{H} \rightarrow {}^{3}_{2}\text{He} + {}^{4}_{2}\text{He}$. It turns out that the total mass of the products is slightly less than that of the reactants, $\Delta m = -4.3 \times 10^{-6}\ \text{kg·mol}^{-1}$. Thus, the energy released is equal to

$$\begin{aligned} \Delta E = \Delta mc^2 &= (-4.3 \times 10^{-6}\ \text{kg·mol}^{-1})(3.0 \times 10^8\ \text{m·s}^{-1})^2 \\ &= 3.9 \times 10^{11}\ \text{J·mol}^{-1} = -3.9 \times 10^8\ \text{kJ·mol}^{-1} \end{aligned}$$

This value of ΔE is typical for nuclear reactions. Values of ΔE for ordinary chemical reactions are on the order of 100 kJ·mol^{-1}, so we see that nuclear reactions involve energies a million times greater than chemical reactions (Figure O.4). This fact explains why enormous amounts of energy are produced by nuclear explosions and nuclear reactors, where a small amount of mass is converted to a large amount of energy.

You may be wondering why nuclear reactions don't satisfy the law of conservation of mass, but chemical reactions do. In fact, there are mass differences in chemical reactions also, but they are well below any measurable limit. For example, the mass difference corresponding to even $\Delta E = -5000\ \text{kJ·mol}^{-1}$, which is a value of ΔE for a very energetic chemical reaction, is

$$\begin{aligned} \Delta m = \frac{\Delta E}{c^2} &= \frac{-5.0 \times 10^6\ \text{J·mol}}{(3.0 \times 10^8\ \text{m·s}^{-1})^2} \\ &= -5.6 \times 10^{-11}\ \text{kg} = -5.6 \times 10^{-14}\ \text{g} \end{aligned}$$

Thus, chemical reactions obey the law of conservation of mass to an extremely high degree of accuracy. Both chemical reactions and nuclear reactions obey what we call the law of conservation of mass-energy because the total of mass and energy is rigorously conserved in both types of reactions.

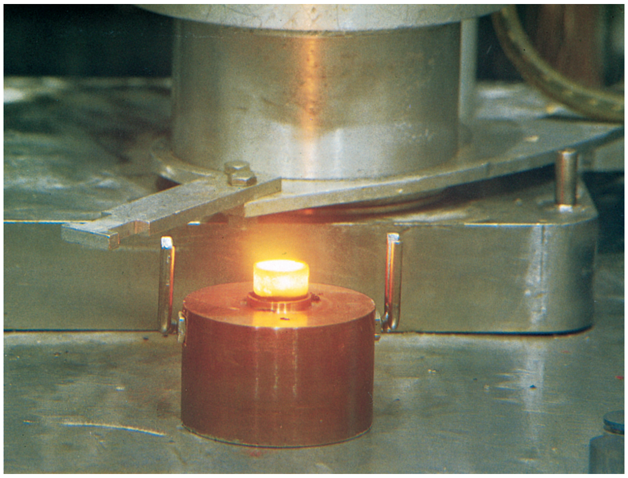


Figure O.4 A sample of the radioactive substance curium oxide glowing from the heat released during radioactive decay.

O-3. Emission from Radioactive Substances Can Be Detected by a Number of Means

There are a number of methods available to detect emissions from radioactive nuclei. The most common method is based on Becquerel's original observation that the emissions from radioactive substances affect photographic film in a manner similar to light. The difference is that the film can remain covered with a thin layer of opaque plastic that keeps out the visible light but permits the passage of the emissions from radioactive materials. This technique is used in the film badges worn by people who work with radioactive substances (Figure O.5). The extent of darkening of the developed film provides a quantitative measure of the degree of exposure of the film badge to radiation.

Gamma-ray and β-particle emissions can be detected rapidly and conveniently with a **Geiger counter** (Figure O.6). Figure O.7 shows a schematic

Figure O.5 Film badges, such as the one shown here, are worn by radiation workers and are routinely monitored to guard against accidental radiation exposure.

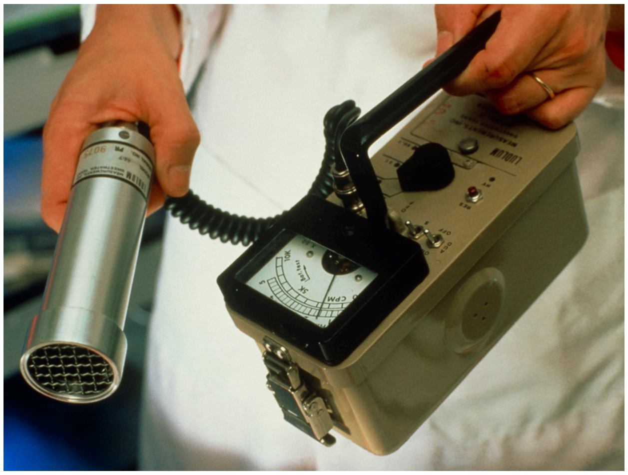


Figure O.6 A Geiger counter (see also Figure O.7).

diagram of a Geiger counter. A high voltage is continuously applied to electrodes in contact with a gas, producing an electric current. When β-particles or γ-rays from a radioactive source pass through the gas, they partially ionize it by knocking electrons out of the gas molecules or atoms. The ionization of the gas is detected as an increase in the electric current through the gas. The gas most commonly used in Geiger counters is argon, which is enclosed in a tube with a window that allows emissions from the radioactive source to enter the ionization chamber. The ionizing radiation from a single emission (say, a β-particle) produces a tiny burst of current between the electrodes. This increase in the current is amplified electronically and transmitted as an audible click by means of a speaker.

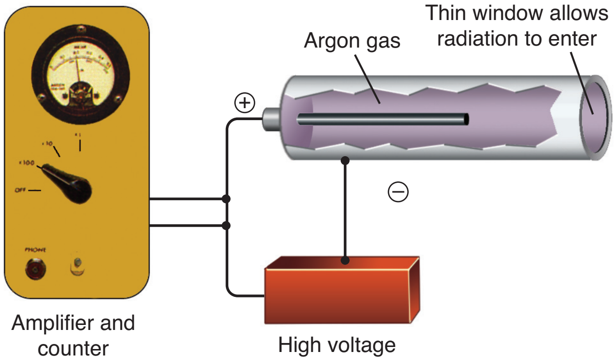


Figure O.7 Schematic diagram of a Geiger counter. Radiation that enters the thin window ionizes the argon gas in the chamber, and the ions produced carry current between the negative and positive electrodes. This current is detected by the amplifier and counter.

Radiation also is detected and measured by using **scintillation counters** (Figure O.8). Certain materials, such as $ZnS(s)$ and $NaI(s)$, when struck by radiation from radioactive materials, **fluoresce**; that is, they emit visible light. Electron excitations are produced by the radiation that strikes the fluorescent material. The fluorescence results from the emission of photons by excited electrons in the material as they decay back to their ground states. Scintillation counters are used extensively in nuclear chemistry and the health sciences. The fluorescence effect is also used in older (non-LCD) television sets and computer monitors; an electron gun fires electrons at fluorescent materials coating the inside surface of the screen.

The standard measure of the activity level of a radioactive substance is its **specific activity,** which is the number of nuclei that disintegrate per second per gram of the radioactive isotope. The specific activity of a radioisotope is related to its half-life, $t_{1/2}$, and its molar mass, M. To see what this relation is, let's start with the fact that radioactive decay is a first-order kinetic process, so that

$$\text{rate of decay} = kN$$

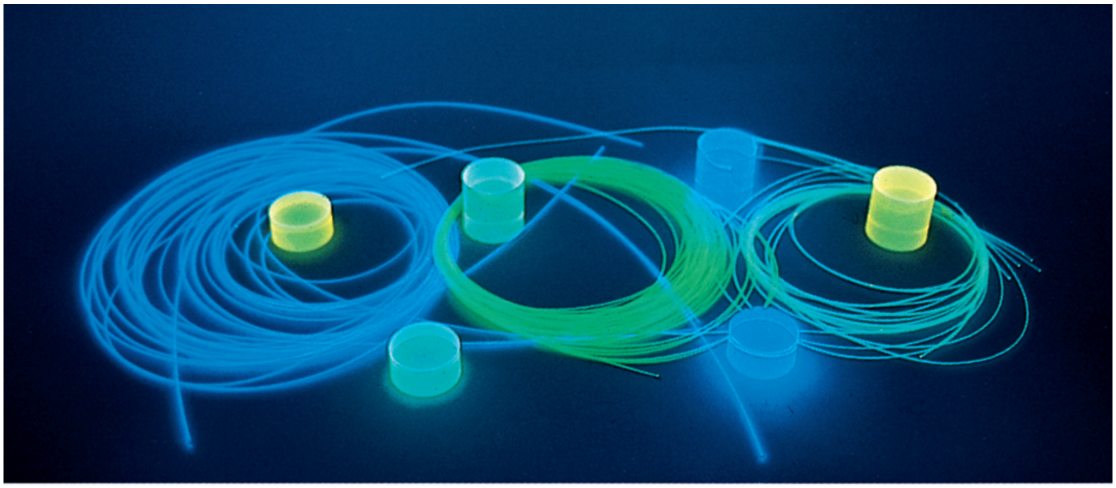


Figure O.8 Scintillators, like the ones shown here, emit a flash of light when a charged particle passes through them. The color of the light depends upon the type of material. Scintillating material may be formed into large blocks, sheets, or fine fibers.

where k is the first-order rate constant and N is the number of radioactive nuclei. The specific activity, therefore, is given by

$$\text{specific activity} = \frac{\text{rate of decay}}{\text{mass of the sample}} = \frac{kN}{m}$$

If we take one mole, for convenience, then N becomes Avogadro's number, N_A, and m becomes the molar mass, M, of the radioisotope. Thus, we can write

$$\text{specific activity} = \frac{kN_A}{M}$$

Finally, using the fact that $k = 0.0693/t_{1/2}$ for a first-order reaction, we have

$$\text{specific activity} = \frac{0.693N_A}{M\,t_{1/2}}$$

$$= \frac{4.17 \times 10^{23}\text{ disintegrations}}{M\,t_{1/2}}$$

Specific activity is inversely related to the half-life; the shorter the half-life, the greater the activity, and the longer the half-life, the less the activity. Because specific activity is defined as the number of disintegrations per second per gram, the value of $t_{1/2}$ in the above equation must be in seconds and the molar mass must be expressed in grams. As an example, let's calculate the specific activity of radium-226, which has a half-life of 1600 years. We first convert the half-life to seconds:

$$t_{1/2} = (1600\text{ yr})(365\text{ day}\cdot\text{yr}^{-1})(24\text{ h}\cdot\text{day}^{-1})(60\text{ min}\cdot\text{h}^{-1})(60\text{ s}\cdot\text{min}^{-1})$$
$$= 5.0 \times 10^{10}\text{ s}$$

The specific activity of radium-226 is thus

$$\text{specific activity} = \frac{4.17 \times 10^{23}\text{ disintegrations}}{(226\text{ g})(5.0 \times 10^{10}\text{ s})}$$
$$= 3.7 \times 10^{10}\text{ disintegrations}\cdot\text{s}^{-1}\cdot\text{g}^{-1}$$

The quantity 3.7×10^{10} disintegrations$\cdot$s^{-1} is called a **curie,** Ci, after Marie Curie. The SI unit of the rate of radioactive decay is a **becquerel** (Bq), which is defined as one disintegration per second: 1 Bq ≈ 27 pCi (picocuries).

In reading about the use of uranium-238 in radiodating rocks in Chapter 17, you may have wondered how it is possible to determine a half-life as long as 4.47×10^9 years. The answer lies in our ability to count individual radioactive decay events and in the fact that Avogadro's number is enormous. There are 6.022×10^{23} uranium-238 nuclei in a sample that contains 238 grams of uranium-238. We can use the above equation to calculate the number of uranium-238 nuclei that disintegrate in 10.0 seconds in a sample that contains 2.00 mg of uranium-238.

The specific activity of uranium-238, which has a half-life of 4.47×10^9 years, is

$$\begin{pmatrix}\text{specific}\\ \text{activity}\end{pmatrix} = \frac{4.17 \times 10^{23}\ \text{disintegrations}}{(238\ \text{g})(4.47 \times 10^9\ \text{yr})(3.15 \times 10^7\ \text{s}\cdot\text{yr}^{-1})}$$
$$= 1.24 \times 10^4\ \text{disintegrations}\cdot\text{s}^{-1}\cdot\text{g}^{-1}$$

Thus, the number of disintegrations 2.00 mg of uranium-238 will undergo in 10.0 seconds is

$$(1.24 \times 10^4\ \text{disintegrations}\cdot\text{s}^{-1}\cdot\text{g}^{-1})(2.00 \times 10^{-3}\ \text{g})(10.0\ \text{s}) = 248\ \text{disintegrations}$$

Consequently, about 248 uranium-238 nuclei disintegrate in a 2.00-mg sample in only 10.0 seconds. It is easy with a modern radiocounting apparatus to measure such a large number of events in a 10.0-second interval. The half-life of uranium-238 can be measured by counting the number of disintegrations in a known mass of the radioisotope and then carrying out the reverse of the calculation just given with $t_{1/2}$ as the unknown, which is calculated from the measured specific activity.

O-4. Radioisotopes Can Be Produced in the Laboratory

Numerous radioactive decay reactions occur spontaneously in nature, changing one element into another and emitting particles in the process. In 1919, the New Zealand-born physicist Ernest Rutherford bombarded nitrogen with a beam of α-particles and was able to detect the reaction given by

$$^{14}_{7}\text{N} + ^{4}_{2}\text{He} \rightarrow ^{17}_{8}\text{O} + ^{1}_{1}\text{H}$$

where $^{1}_{1}\text{H}$ denotes a proton. Rutherford's experiment was the first laboratory synthesis of a nucleus. Following Rutherford's lead, hundreds of similar reactions have been carried out. The products of many of these reactions are radioactive isotopes that are not found in nature and therefore are called **artificial radioisotopes.** If these isotopes ever did exist in nature, they have long since disappeared, because their half-lives are so much shorter than the age of the earth.

Many of the radioisotopes produced have applications in numerous areas, including medicine, agriculture, and oil exploration. For example, iodine-131 is used to measure the activity of the thyroid gland, and iodine-123 is used to monitor brain activity (Figure O.9).

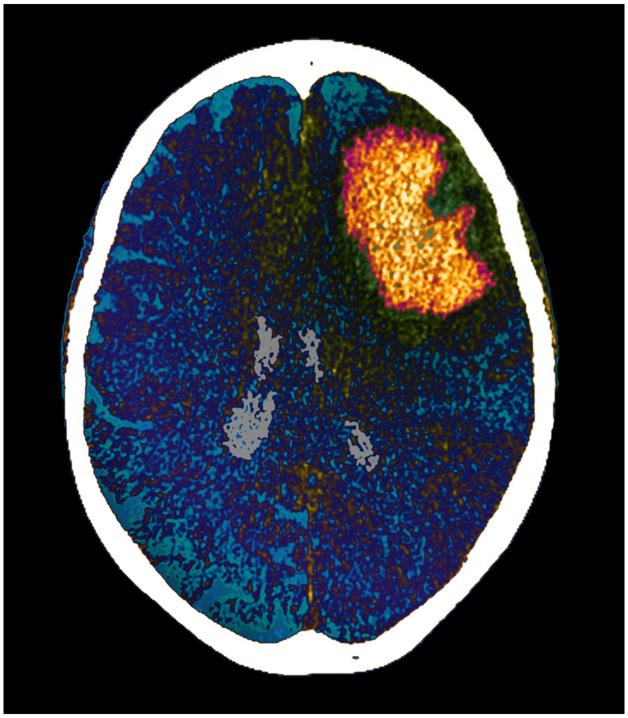


Figure O.9 CT scan using iodine-131 showing a brain hemorrhage.

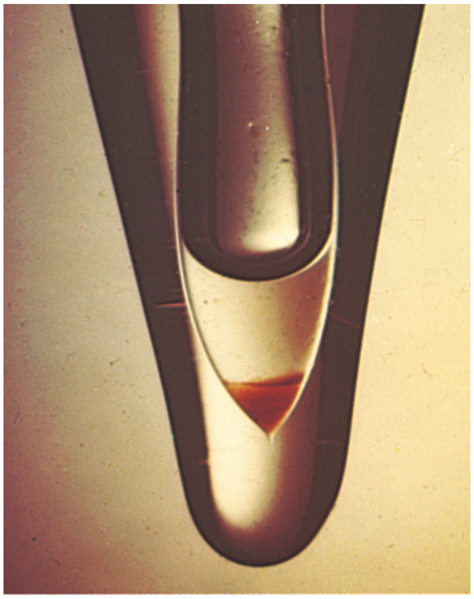


Figure O.10 The elements beyond uranium in the periodic table are called transuranium elements. With the exception of recently discovered traces of plutonium, these elements do not occur in nature but have been created in the laboratory. Shown here is the first visible sample of americium produced, with a mass of only a few micrograms.

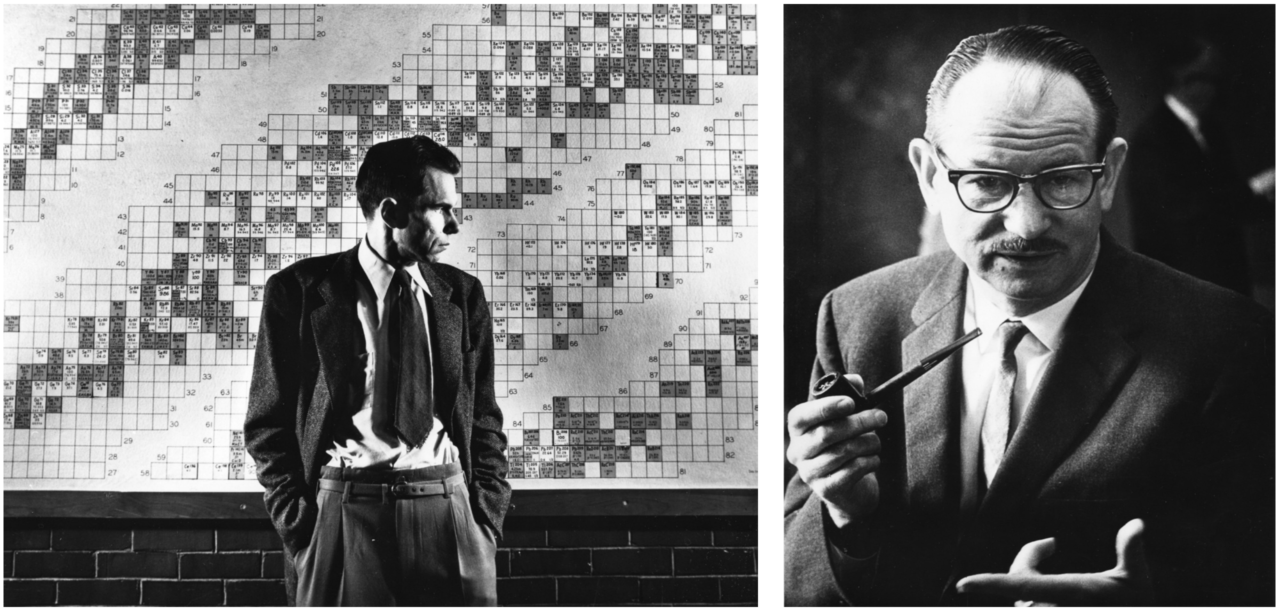


Figure O.11 Glenn T. Seaborg (*left*) and Edwin M. McMillan (*right*) shared the 1951 Nobel Prize in Chemistry for "their discoveries in the chemistry of the transuranium elements." The pair co-discovered ten of the transuranium elements.

A few of the many other radioisotopes that are used in medicine are sodium-24 (to follow blood circulation), technetium-99 (for brain, liver, and spleen tests), and phosphorus-32 (for treatment of leukemia).

Before the development of nuclear science, uranium lay at the end of the periodic table. Since the 1940s, most of the elements between $Z = 93$ and $Z = 116$ have been synthesized. Many of these elements were produced at the Lawrence Radiation Laboratory in Berkeley, California, as indicated by the names californium (98), berkelium (97), americium (95), and lawrencium (103) (Figure O.10). Many of these **transuranium elements** (Figure O.11) can be made in commercial quantities. For example, americium-241, an α- and β-emitter with a half-life of 432 years, is used in smoke detectors (Figure O.12).

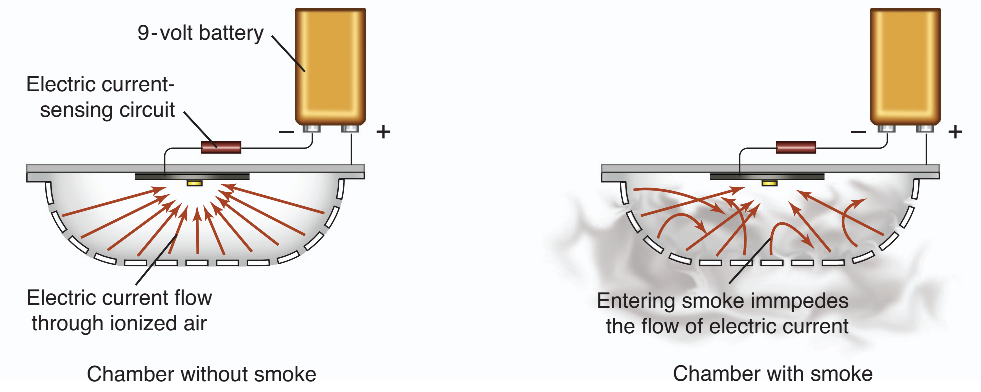


Figure O.12 Diagram of a home smoke detector. A small quantity of americium-241 ($t_{1/2}$ = 432 years) ionizes the air in the ionization chamber. An electric voltage is applied across the ionization chamber, and the ions in the air conduct an electric current that is constantly monitored electronically. When smoke particles pass through the ionization chamber, they impede the flow of electricity, which is detected by electronic circuitry. This reduction then triggers a horn alarm. A weak battery also produces a decreased current flow, which in some smoke detectors is signaled by an audible "beep."

O-5. Radioactive Elements Can Be Used as Tracers to Perform Sensitive Measurements

One of the most important applications of radioactive isotopes is their use as **tracers**, or labels, in chemical reactions. The use of radioactive tracers in chemistry was pioneered by George de Hevesy (Chapter 22 Frontispiece), who used radioactive isotopes to determine the solubility of sparingly soluble salts in the early 1900s. Because isotopes differ only in the number of neutrons in their nuclei, they undergo similar chemical reactions, and the isotopic composition of reactants will be the same as that of the products. For example, if AgBr(*s*) is precipitated from an NaBr(*aq*) solution by the addition of $AgNO_3(aq)$ in which the silver atoms consist of a small (trace) percentage of the radioisotope isotope silver-112 (a β-emitter), then the silver atoms in the AgBr(*s*) precipitate will consist of the same percentage of silver-112. For example, we might have

$$\mathrm{NaBr}(aq) + \underset{(0.001\%\ \mathrm{Ag\text{-}112})}{\mathrm{AgNO_3}(aq)} \rightarrow \mathrm{NaNO_3}(aq) + \underset{(0.001\%\ \mathrm{Ag\text{-}112})}{\mathrm{AgBr}(s)}$$

Thus, the isotopic composition of any element will remain the same throughout a chemical reaction. We can use this observation to determine the solubility of silver bromide. First we precipitate AgBr(*s*) with $AgNO_3(aq)$ containing a trace amount of silver-112 and measure its radioactivity. Suppose that we find an activity of $0.104\ \mu\mathrm{Ci{\cdot}mg^{-1}}$ of AgBr(*s*). This activity, which is a measure of the number of decay events per milligram of precipitate per second, is directly proportional to the amount of silver-112 in the precipitate.

We now let this precipitate come into equilibrium with 10.00 mL of water, take a one-milliliter sample, called an aliquot, of this solution, and then measure its activity. Suppose we find that the activity of the AgBr(*aq*) in this aliquot is $1.40 \times 10^{-5}\ \mu\mathrm{Ci{\cdot}mL^{-1}}$ of solution. Let's think of the activity of $0.104\ \mu\mathrm{Ci{\cdot}mg^{-1}}$ as being a direct measure of the number of silver-112 atoms (and hence a measure of all the silver atoms) in one milligram of the precipitate and the activity of $1.40 \times 10^{-5}\ \mu\mathrm{Ci{\cdot}mL^{-1}}$ as being a direct measure of the number of silver-112 atoms (and hence a measure of all the silver atoms) in one milliliter of solution. Then the ratio $1.40 \times 10^{-5}\ \mu\mathrm{Ci}/0.104\ \mu\mathrm{Ci} = 1.35 \times 10^{-4}$ is the fraction of the number of milligrams of AgBr(*s*) in one milliliter of solution. In terms of an equation, we have

$$\begin{pmatrix}\text{mass of AgBr per}\\ \text{milliliter of solution}\end{pmatrix} = \frac{1.40 \times 10^{-5}\ \mu\mathrm{Ci{\cdot}mL^{-1}}}{0.104\ \mu\mathrm{Ci{\cdot}mg^{-1}}}$$

$$= 1.35 \times 10^{-4}\ \mathrm{mg{\cdot}mL^{-1}}$$

which is equivalent to $1.35 \times 10^{-4}\ \mathrm{g{\cdot}L^{-1}}$ or 7.2×10^{-7} M. Note that we did not need to know the actual isotopic composition of the silver atoms. We simply needed to measure the activity of the AgBr(*s*) from the original solution and from the one-milliliter aliquot. This method allows for the determination of the solubility of a very sparingly soluble salt.

As another example, suppose we needed to determine the quantity of a particular component in a mixture, where no quantitative procedure for the isolation of this component is known. That is, we can isolate some, but not all, of the substance from the mixture, and so we cannot directly measure how much of the substance is in the mixture. In such a case the analysis may be made by the technique called **isotopic dilution**. Let m_u be the mass of the component in the mixture. We now add a known mass, m_1, of the compound containing a certain fraction of a radioisotope with a known activity, A_1, of radioactivity. After allowing the sample to come to equilibrium, some of the compound of interest is purified and isolated from the mixture, and its mass, m_2, and its activity, A_2, are measured. We can now set up the proportion

$$\frac{m_2}{m_u + m_1} = \frac{A_2}{A_1}$$

Solving for m_u gives

$$m_u = m_2\frac{A_1}{A_2} - m_1$$

Let's see how to apply this equation. A mixture is to be analyzed for penicillin. You add 10.0 mg of radioactively labeled penicillin of activity 4.05 μCi and allow the mixture to come to equilibrium. You then isolate and purify only 0.35 mg of crystalline penicillin from the mixture. Given that the activity of the purified penicillin is 0.0123 μCi, determine the penicillin content of the mixture. In this case, $A_1 = 4.05\ \mu\mathrm{Ci}$, $A_2 = 0.0123\ \mu\mathrm{Ci}$, $m_1 = 10.0$ mg, and $m_2 = 0.35$ mg, so

$$m_u = (0.35\ \mathrm{mg})\left(\frac{4.05\ \mu\mathrm{Ci}}{0.0123\ \mu\mathrm{Ci}}\right) - 10.0\ \mathrm{mg} = 110\ \mathrm{mg}$$

The applications of radioactive tracers are almost too numerous to list. They have been used in chemistry to determine equilibrium constants, reaction rates, and reaction mechanisms. They have been used in engineering to study the flow of liquids through pipes, the flow rates of rivers, the disposal of detergents in sewage systems, and the testing of leaks in sealed containers. The largest use of radionuclides is in the medical sciences.

O-6. Nuclear Chemistry Can Be Used to Detect Extremely Small Quantities of the Elements

One of the major uses of radioisotopes in chemistry is **neutron activation analysis,** which is the most sensitive, nondestructive method available for analyzing the elements in a sample. Because neutron activation analysis is capable of detecting as little as 10^{-12} grams of some elements, it is particularly useful for measuring trace quantities. In a neutron activation analysis, a sample is irradiated by a beam of neutrons. Various nuclei in the sample undergo nuclear reactions by absorbing neutrons. The product nuclei are usually radioactive and emit γ-rays. The energies of the γ-rays emitted by each radioisotope are characteristic of that radioisotope. Because each radioisotope emits γ-rays of only certain, well-defined energies, the frequencies of the γ-rays emitted by a sample after neutron irradiation, the so-called nuclear fingerprint, can be used to identify the elements present. The advantages of neutron activation analysis over more conventional analytical techniques are that the sample does not have to be pretreated, the method is nondestructive, many elements can be analyzed simultaneously, and the sensitivity is very great (Figure O.13).

Neutron activation analysis has numerous applications. For example, the authenticity of paintings and other artifacts can be established by determining the mineral content of the paint or other materials used. Prior to the twentieth century, each school of artists prepared its own paints from distinctive and individual recipes. The paint used in a painting in question is compared with the paint used in a painting known to be done by a specific artist. If the ingredients are the same, then the identity of the painter or, at least, the painter's studio, is verified. Another application of neutron activation analysis showed that Napoleon might have been poisoned by arsenic. When arsenic is ingested, it is concentrated in the hair. Analysis of several of Napoleon's hairs showed an abnormally large concentration of arsenic.

Neutron activation analysis is also used in criminal investigations. The basic idea is to match the distribution of elements in soil, paint, cosmetics, and so on found at the scene of a crime with those found with a criminal suspect. Neutron activation analysis of a wiping taken from a suspect's hand can reveal not only whether the person has fired a gun recently but also the type of ammunition used.

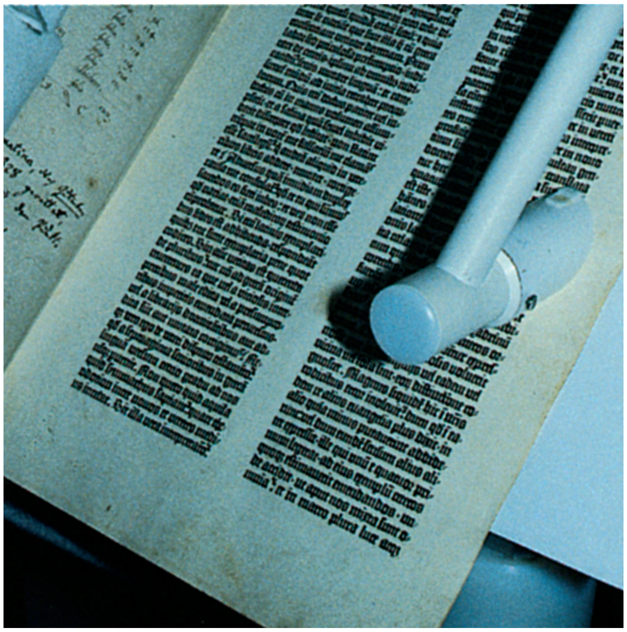


Figure O.13 Actual analysis of a page of the Gutenberg Bible (in progress). The operator can stand in complete safety next to the system because the low-energy charged particles cause little radiation when they stop.

TERMS YOU SHOULD KNOW

radioactivity	*O1*
radiochemistry	*O1*
radioisotope	*O2*
nuclear decay	*O2*
α-decay	*O2*
β-decay	*O2*
gamma ray (γ-ray)	*O2*
positron	*O2*
antimatter particle	*O2*
Geiger counter	*O3*
scintillation counter	*O4*
fluoresce	*O4*
specific activity	*O4*
curie (Ci)	*O5*
becquerel (Bq)	*O5*
artificial radioisotope	*O6*
transuranium elements	*O7*
tracer	*O8*
isotopic dilution	*O8*
neutron activation analysis	*O9*

QUESTIONS

O-1. A radioisotope is an α-emitter and forms protactinium-235. Name the radioisotope.

O-2. Fill in the missing symbols in the following nuclear equations:

(a) ${}^{214}_{82}\text{Pb} \rightarrow {}^{214}_{83}\text{Bi} + ?$

(b) ${}^{11}_{6}\text{C} \rightarrow ? + {}^{0}_{+1}\text{e}$

(c) $? \rightarrow {}^{97}_{41}\text{Nb} + {}^{0}_{-1}\text{e}$

O-3. Phosphorus-32 (a β-emitter) is used extensively as a radioactive tracer to assist in mapping chemical and biochemical reaction pathways. Write a balanced nuclear equation to describe the decay of phosphorus-32.

O-4. The energy released per second by the sun, which generates its energy release from nuclear reactions, is $1 \times 10^{26}\ \text{J}\cdot\text{s}^{-1}$. Calculate the corresponding loss in mass of the sun per second.

O-5. Marie Curie observed that 1.0 gram of pure radium-226 generates $104\ \text{J}\cdot\text{h}^{-1}$. Given that 1.0 gram of radium-226 has a disintegration rate of 3.7×10^{10} disintegrations$\cdot\text{s}^{-1}$, calculate the energy released in each disintegration. Compare this with what you calculate, given the equation

$$ {}^{226}_{88}\text{Ra} \rightarrow {}^{222}_{86}\text{Rn} + {}^{4}_{2}\text{He} $$

and the atomic masses ${}^{226}_{88}\text{Ra} = 226.025\,410$ u, ${}^{222}_{86}\text{Rn} = 222.017\,578$ u, and ${}^{4}_{2}\text{He} = 4.002\,602$ u.

O-6. The half-life of a positron is very short. It reacts with an electron, and the masses of both are converted to two γ-rays (Figure O.3):

$$ {}^{0}_{+1}\text{e} + {}^{0}_{-1}\text{e} \rightarrow 2\gamma $$

This reaction is called an annihilation reaction. Calculate the energy produced by the reaction between one electron and one positron. Assuming that the two γ-rays have the same frequency, calculate this frequency. Take the mass of an electron or positron to be 9.109×10^{-31} kg.

O-7. The half-life for iodine-131, which is used extensively in nuclear medicine, is 8.04 days. Iodine-131 decays by β-particle and γ-ray emission. Calculate the specific activity and the total number of β-particles emitted per second by a sample that contains 2.00 mg of iodine-131.

O-8. Fluorine-18 has a half-life of 110 min. Calculate the specific activity of fluorine-18 in units of curies per gram.

O-9. The radioisotope sulfur-35 is used extensively in biological and environmental studies. It is prepared in a cyclotron and is free of all other isotopes of sulfur. Its half-life is 87 days. Calculate the specific activity (in curies per gram) of a freshly prepared sample of sulfur-35.

O-10. The radioisotope iodine-128 (half-life 25 min) is used as a diagnostic tool for thyroid imaging. A typical dose is 100 μCi. Compute the number of grams of iodine-128 equivalent to 100 μCi.

O-11. The amount of oxygen dissolved in a sample of water can be measured by using the radioisotope thallium-204. Solid thallium reacts with oxygen according to the equation

$$4\,\mathrm{Tl}(s) + \mathrm{O_2}(aq) + 2\,\mathrm{H_2O}(l) \rightarrow 4\,\mathrm{Tl^+}(aq) + 4\,\mathrm{OH^-}(aq)$$

The amount of oxygen can be determined by measuring the radioactivity due to thallium-204 in the water sample. In one experiment we note that 10.0 mL of water is reacted with some thallium metal whose activity is 1.13×10^8 disintegrations·min^{-1}·mol^{-1}. The radioactivity of water is 563 disintegrations·min^{-1}. Calculate the concentration of oxygen in the sample.

O-12. Low concentrations of sulfate ion in aqueous samples can be measured by precipitating $\mathrm{SO_4^{2-}}(aq)$ with the radioisotope barium-131 in the form of $\mathrm{Ba^{2+}}(aq)$. The radioactivity of the precipitate, $\mathrm{BaSO_4}(s)$, is then measured. In one experiment, sulfate ion was precipitated with barium-131, whose activity is 7.6×10^7 disintegrations·min^{-1}·g^{-1}. The radioactivity of $\mathrm{BaSO_4}(s)$ precipitated from a 10.0-mL sample of the aqueous solution was 3270 disintegrations·min^{-1}. Calculate the concentration of $\mathrm{SO_4^{2-}}(aq)$ in the aqueous solution.

O-13. A 50.0-mL sample of a 0.075-M $\mathrm{Pb(NO_3)_2}(aq)$ solution is mixed with 50.0 mL of a 0.150-M $\mathrm{NaI}(aq)$ solution that has been labeled with the radioisotope iodine-131. The activity of the radioactive $\mathrm{NaI}(aq)$ solution is 20 000 disintegrations·min^{-1}·mL^{-1}. After precipitation, the mixture is filtered, and the supernatant liquid has an activity of 320 disintegrations·min^{-1}·mL^{-1}. Calculate the solubility-product constant of $\mathrm{PbI_2}(s)$.

O-14. In order to determine the amount of the amino acid threonine in a specific protein (see Interchapter T), a biochemist breaks down a 10.00-gram sample of the protein into its constituent amino acids. She then adds a 3.00-mg sample of carbon-14 labeled threonine with a specific activity of 3000 disintegrations per minute. Next she separates and purifies 60.0 milligrams of threonine from the mixture. The activity of the isolated sample is 1200 disintegrations per minute. How much threonine was present in the original sample?