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General Chemístry Course Support

CHAPTER II : RODIOACTIVITY

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II. RADIOACTIVITY

II.1 Introduction :

In 1896, Antoine Becquerel discovered that a uranium-rich rock emits invisible rays that can darken a photographic plate in an enclosed container. Scientists offer three arguments for the nuclear origin of these rays. First, the effects of the radiation do not vary with chemical state; that is, whether the emitting material is in the form of an element or compound. Second, the radiation does not vary with changes in temperature or pressure—both factors that in sufficient degree can affect electrons in an atom. Third, the very large energy of the invisible rays (up to hundreds of eV) is not consistent with atomic electron transitions (only a few eV). Today, this radiation is explained by the conversion of mass into energy deep within the nucleus of an atom. The spontaneous emission of radiation from nuclei is called nuclear radioactivity (**Figure 2.1**).



Figure 2.1 The international ionizing radiation symbol is universally recognized as the warning symbol for nuclear radiation.

Early experiments revealed three types of nuclear "rays" or radiation: alpha (α) rays, beta (β) rays, and gamma (γ) rays. These three types of radiation are differentiated by their ability to penetrate matter. Alpha radiation is barely able to pass through a thin sheet of paper. Beta radiation can penetrate aluminum to a depth of about 3 mm, and gamma radiation can penetrate lead to a depth of 2 or more centimeters Figure 2.2



Figure 2.2 A comparison of the penetration depths of alpha (α), beta (β), and gamma (γ) radiation through various materials.

II.2 Types of Radioactive Decay

Ernest Rutherford's experiments involving the interaction of radiation with a magnetic or electric field (Figure 2.3) helped him determine that one type of radiation consisted of positively charged and relatively massive α particles; a second type was made up of negatively charged and much less massive β particles; and a third was uncharged electromagnetic waves, rays. We now know that particles are high-energy helium nuclei, particles are high-energy electrons, and γ radiation compose high-energy electromagnetic radiation. We classify different types of radioactive decay by the radiation produced.



Figure 2.3: Alpha particles, which are attracted to the negative plate and deflected by a relatively small amount, must be positively charged and relatively massive. Beta particles, which are attracted to the positive plate and deflected a relatively large amount, must be negatively charged and relatively light. Gamma rays, which are unaffected by the electric field, must be uncharged.

A diagram is shown. A gray box on the left side of the diagram labeled "Lead block" has a chamber hollowed out in the center in which a sample labeled "Radioactive substance" is placed. A blue beam is coming from the sample, out of the block, and passing through two horizontally placed plates that are labeled "Electrically charged plates." The top plate is labeled with a positive sign while the bottom plate is labeled with a negative sign. The beam is shown to break into three beams as it passes in between the plates; in order from top to bottom, they are red, labeled "beta rays," purple labeled "gamma rays" and green labeled "alpha rays."

The beams are shown to hit a vertical plate labeled "Photographic plate" on the far-right side of the diagram.

Alpha (a) decay is the emission of an α particle from the nucleus. For example, polonium-210 undergoes α decay:

Alpha decay occurs primarily in heavy nuclei (A > 200, Z > 83). Because the loss of an α particle gives a daughter nuclide with a mass number four units smaller and an atomic number two units smaller than those of the parent nuclide, the daughter nuclide has a larger n:p ratio than the parent nuclide. If the parent nuclide undergoing α decay lies below **the band of stability**, the daughter nuclide will lie closer to the band.

Beta (β) decay is the emission of an electron from a nucleus. Iodine-131 is an example of a nuclide that undergoes β decay:

$${}^{131}_{53}\mathrm{I} \longrightarrow {}^{0}_{-1}\mathrm{e} + {}^{131}_{54}\mathrm{X} \qquad \mathrm{or} \qquad {}^{131}_{53}\mathrm{I} \longrightarrow {}^{0}_{-1}\beta + {}^{131}_{54}\mathrm{Xe}$$

Beta decay, which can be thought of as the conversion of a neutron into a proton and a β particle, is observed in nuclides with a large n:p ratio. The beta particle (electron) emitted is from the atomic nucleus and is not one of the electrons surrounding the nucleus. Such nuclei lie above the band of stability. Emission of an electron does not change the mass number of the nuclide but does increase the number of its protons and decrease the number of its neutrons. Consequently, the n:p ratio is decreased, and the daughter nuclide lies closer to the band of stability than did the parent nuclide.

Gamma emission (γ emission) is observed when a nuclide is formed in an excited state and then decays to its ground state with the emission of a γ ray, a quantum of high-energy electromagnetic radiation. The presence of a nucleus in an excited state is often indicated by an asterisk (*). Cobalt-60 emits γ radiation and is used in many applications including cancer treatment:

$$^{60}_{27}\text{Co}^* \longrightarrow {}^{0}_{0}\gamma + {}^{60}_{27}\text{Co}$$

There is no change in mass number or atomic number during the emission of a γ ray unless the γ emission accompanies one of the other modes of decay.

Positron emission (β^+ decay) is the emission of a positron from the nucleus. Oxygen-15 is an example of a nuclide that undergoes positron emission:

$${}^{15}_{8}O \longrightarrow {}^{0}_{+1}e + {}^{15}_{7}N$$
 or ${}^{15}_{8}O \longrightarrow {}^{0}_{+1}\beta + {}^{15}_{7}N$

Positron emission is observed for nuclides in which the n:p ratio is low. These nuclides lie below the band of stability. Positron decay is the conversion of a proton into a neutron with the emission of a positron. The n:p ratio increases, and the daughter nuclide lies closer to the band of stability than did the parent nuclide.

Electron capture occurs when one of the inner electrons in an atom is captured by the atom's nucleus. For example, potassium-40 undergoes electron capture:

$$^{40}_{19}\text{K} + {}^{0}_{-1}\text{e} \longrightarrow {}^{40}_{18}\text{Ar}$$

Electron capture occurs when an inner shell electron combines with a proton and is converted into a neutron. The loss of an inner shell electron leaves a vacancy that will be filled by one of the outer electrons. As the outer electron drops into the vacancy, it will emit energy. In most cases, the energy emitted will be in the form of an X-ray. Like positron emission, electron capture occurs for "proton-rich" nuclei that lie below the band of stability. Electron capture has the same effect on the nucleus as does positron emission: The atomic number is decreased by one and the mass number does not change. This increases the n:p ratio, and the daughter nuclide lies closer to the band of stability than did the parent nuclide. Whether electron capture or positron emission occurs is difficult to predict. The choice is primarily due to kinetic factors, with the one requiring the smaller activation energy being the one more likely to occur. Figure 2.4 summarizes these types of decay, along with their equations and changes in atomic and mass numbers.

Туре	Nuclear equation	Representation	Change in mass/atomic numbers
Alpha decay	$\frac{4}{2}X$ $\frac{4}{2}He + \frac{4}{2} - \frac{4}{2}Y$		A: decrease by 4 Z: decrease by 2
Beta decay	$^{A}_{Z}X$ $^{0}_{-1}e + ^{A}_{Z+1}Y$		A: unchanged Z: increase by 1
Gamma decay	^Δ ₂ X ⁰ ₀ γ + ^Δ ₂ Υ	$\overbrace{\text{Excited nuclear state}}^{\checkmark} \bigvee_{\gamma} \bigvee_{\gamma}$	A: unchanged Z: unchanged
Positron emission	$^{A}_{Z}X$ $^{0}_{+1}e + ^{A}_{Y-1}Y$		A: unchanged Z: decrease by 1
Electron capture	$A_{Z}^{A}X = -1^{0}e + Y_{Y-1}^{A}Y$	X-ray v	A: unchanged Z: decrease by 1

Figure 2.4: This table summarizes the type, nuclear equation, representation, and any changes in the mass or atomic numbers for various types of decay.

II.3 Radioactive Decay Series

The naturally occurring radioactive isotopes of the heaviest elements fall into chains of successive disintegrations, or decays, and all the species in one chain constitute a radioactive family, or radioactive decay series. Three of these series include most of the naturally radioactive elements of the periodic table. They are the uranium series, the actinide series, and the thorium series. The neptunium series is a fourth series, which is no longer significant on the earth because of the short half-lives of the species involved. Each series is characterized by a parent (first member) that has a long half-life and a series of daughter nuclides that ultimately lead to a stable end-product—that is, a nuclide on the band of stability (Figure 2.5). In all three series, the end product is a stable isotope of lead. The neptunium series, previously thought to terminate with bismuth-209, terminates with thallium-205.



Figure 2.5: Uranium-238 undergoes a radioactive decay series consisting of 14 separate steps before producing stable lead-206. This series consists of eight α decays and six β decays.

II.4 Radioactive Half-Lives

Radioactive decay follows first-order kinetics. Since first-order reactions have already been covered in detail in the kinetics chapter, we will now apply those concepts to nuclear decay reactions. Each radioactive nuclide has a characteristic, constant half-life (t), the time required for half of the atoms in a sample to decay. An isotope's half-life allows us to determine how

long a sample of a useful isotope will be available, and how long a sample of an undesirable or dangerous isotope must be stored before it decays to a low-enough radiation level that is no longer a problem.

For example, cobalt-60, an isotope that emits gamma rays used to treat cancer, has a half-life of 5.27 years (Figure 3.6). In a given cobalt-60 source, since half of the nuclei ⁶⁰ Co decay every 5.27 years, both the amount of material and the intensity of the radiation emitted is cut in half every 5.27 years. (Note that for a given substance, the intensity of radiation that it produces is directly proportional to the rate of decay of the substance and the amount of the substance.) This is as expected for a process following first-order kinetics. Thus, a cobalt-60 source that is used for cancer treatment must be replaced regularly to continue to be effective.



Figure 2.6: For cobalt-60, which has a half-life of 5.27 years, 50% remains after 5.27 years (one half-life), 25% remains after 10.54 years (two half-lives), 12.5% remains after 15.81 years (three half-lives), and so on.

Since nuclear decay follows first-order kinetics, we can adapt the mathematical relationships used for first-order chemical reactions. We generally substitute the number of nuclei, N, for the concentration. If the rate is stated in nuclear decays per second, we refer to it as the activity of the radioactive sample. The rate for radioactive decay is: decay rate = λN With λ is the decay constant for the particular radioisotope.

II.5 Radioactive Decay Law

When an individual nucleus transforms into another with the emission of radiation, the nucleus is said to decay. Radioactive decay occurs for all nuclei with Z>82, and also for some unstable isotopes with Z<83.

The decay rate is proportional to the number of original (undecayed) nuclei N in a substance. The number of nuclei lost to decay, -dN in time interval dt, is written

$$-\frac{dN}{dt} = \lambda N$$

where λ is called the decay constant. (The minus sign indicates the number of original nuclei decreases over time.) In other words, the more nuclei available to decay, the more that do decay (in time dt). This equation can be rewritten as

$$rac{dN}{N} = -\lambda dt.$$

Integrating both sides of the equation, and defining N_0 to be the number of nuclei at t=0, we obtain

$$\int_{N_0}^N rac{dN'}{N} = -\int_0^t \lambda dt'.$$

This gives us

$$\ln rac{N}{N_0} = -\lambda t.$$

Taking the left and right sides of the equation as a power of e, we have the radioactive decay law.

II.5.1 RADIOACTIVE DECAY LAW

The total number N of radioactive nuclei remaining after time t is

$$N = N_0 e^{-\lambda t}$$

where λ is the decay constant for the particular nucleus.

The total number of nuclei drops very rapidly at first, and then more slowly (Figure 2.7).



Figure 2.7 A plot of the radioactive decay law demonstrates that the number of nuclei remaining in a decay sample drops dramatically during the first moments of decay.

The half-life $(T_{1/2})$ of a radioactive substance is defined as the time for half of the original nuclei to decay (or the time at which half of the original nuclei remain). The number of radioactive nuclei remaining after an integer (n) number of half-lives is therefore

$$N = rac{N_0}{2^n}$$

If the decay constant (λ) is large, the half-life is small, and vice versa. To determine the relationship between these quantities, note that when t=T_{1/2}, then N=N₀/2. Thus, Equation 10.10 can be rewritten as

$$rac{N_0}{2} = N_0 e^{-\lambda T_{1/2}}.$$

Dividing both sides by N₀ and taking the natural logarithm yields

$$\lnrac{1}{2}=\ln e^{-\lambda T_{1/2}}$$

which reduces to

$$\lambda = rac{0.693}{T_{1/2}}.$$

Thus, if we know the half-life $T_{1/2}$ of a radioactive substance, we can find its decay constant. The **lifetime** \overline{T} of a radioactive substance is defined as the average amount of time that a nucleus exists before decaying. The lifetime of a substance is just the reciprocal of the decay constant, written as

$$\overline{T} = \frac{1}{\lambda}.$$

The activity A is defined as the magnitude of the decay rate, or

$$A=-rac{dN}{dt}=\lambda N=\lambda N_0 e^{-\lambda t}.$$

The infinitesimal change dN in the time interval dt is negative because the number of parent (undecayed) particles is decreasing, so the activity (A) is positive. Defining the initial activity as $A_0=\lambda N_0$, we have

$$A = A_0 e^{-\lambda t}.$$

Thus, the activity A of a radioactive substance decreases exponentially with time (Figure 2.8).



Figure 2.8 (a) A plot of the activity as a function of time (b) If we measure the activity at different times, we can plot ln A versus t, and obtain a straight line.

EXAMPLE 1

Decay Constant and Activity of Strontium-90

The half-life of strontium-90, ${}^{90}_{38}Sr$, is 28.8 y. Find (a) its decay constant and (b) the initial activity of 1.00 g of the material.

Strategy

We can find the decay constant directly from. $\lambda = \frac{0.693}{T_{1/2}}$. To determine the activity, we first need to find the number of nuclei present.

Solution

a- The decay constant is found to be

$$\lambda = rac{0.693}{T_{1/2}} = \left(rac{0.693}{T_{1/2}}
ight) \left(rac{1 \ {
m yr}}{3.16 \ imes \ 10^7 \ {
m s}}
ight) = 7.61 \ imes \ 10^{-10} \ {
m s}^{-1}.$$

b- The atomic mass of ${}^{90}_{38}Sr$ is 89.91 g. Using Avogadro's number N_A=6.022×10²³ atoms/mol, we find the initial number of nuclei in 1.00 g of the material:

$$N_0 = rac{1.00 ext{ g}}{89.91 ext{ g}} (N_A) = 6.70 imes 10^{21} ext{ nuclei}$$

From this, we find that the activity A_0 at t=0 for 1.00 g of strontium-90 is $A_0=\lambda N_0$

= $(7.61 \times 10 - 10s^{-1})$ (6.70×10²¹nuclei)

 $=5.10 \times 10^{12}$ decays/s.

Expressing λ in terms of the half-life of the substance, we get

$$A = A_0 e^{-(0.693/T_{1/2})T_{1/2}} = A_0 e^{-0.693} = A_0/2.$$

Therefore, the activity is halved after one half-life. We can determine the decay constant λ by measuring the activity as a function of time. Taking the natural logarithm of the left and right sides of Equation 10.17, we get

$$\ln A = -\lambda t + \ln A_0.$$

This equation follows the linear form y=mx+b. If we plot ln A versus t, we expect a straight line with slope $-\lambda$ and y-intercept lnA₀ (Figure 10.10(b)). Activity A is expressed in units of becquerels (Bq), where one 1Bq=1decay per second. This quantity can also be expressed in decays per minute or decays per year. One of the most common units for activity is the curie (Ci), defined to be the activity of 1 g of ²²⁶Ra. The relationship between the Bq and Ci is

1Ci=3.70×10¹⁰Bq.

EXAMPLE 2

What is ¹⁴C Activity in Living Tissue?

Approximately 20% of the human body by mass is carbon. Calculate the activity due to ${}^{14}C$ in 1.00 kg of carbon found in a living organism. Express the activity in units of Bq and Ci.

Strategy

The activity of ¹⁴C is determined using the equation $A_0=\lambda N_0$, where λ is the decay constant and N_0 is the number of radioactive nuclei. The number of ¹⁴C nuclei in a 1.00-kg sample is determined in two steps. First, we determine the number of ¹²C nuclei using the concept of a mole. Second, we multiply this value by 1.3×10^{-12} (the known abundance of 14C in a carbon sample from a living organism) to determine the number of ¹⁴C nuclei in a living organism. The decay constant is determined from the known half-life of 14 C (available from Figure 10.4).

Solution

One mole of carbon has a mass of 12.0 g, since it is nearly pure ¹²C. Thus, the number of carbon nuclei in a kilogram is

$$N(^{12}\text{C}) = rac{6.02 \times 10^{23} \text{ mol}^{-1}}{12.0 \text{ g/mol}} \times (1000 \text{ g}) = 5.02 \times 10^{25}.$$

The number of ¹⁴C nuclei in 1 kg of carbon is therefore

 $N(^{14}C) = (5.02 \times 10^{25}) (1.3 \times 10^{-12}) = 6.52 \times 10^{13}.$

Now we can find the activity A by using the equation $A=0.693N/t_{1/2}$. Entering known values gives us

$$A = rac{0.693 \left(6.52 \ imes \ 10^{13}
ight)}{5730 \ ext{y}} = 7.89 \ imes \ 10^9 \ ext{y}^{-1}$$

or 7.89×10^9 decays per year. To convert this to the unit Bq, we simply convert years to seconds. Thus,

$$A = (7.89 \times 10^9 \text{ y}^{-1}) \frac{1.00 \text{ y}}{3.16 \times 10^7 \text{ s}} = 250 \text{ Bq},$$

or 250 decays per second. To express A in curies, we use the definition of a curie,

$$A = \frac{250 \text{ Bq}}{3.7 \times 10^{10} \text{ Bq/Ci}} = 6.76 \times 10^{-9} \text{ Ci.}$$

Thus, A=6.76 nCi.

Significance

Approximately 20% of the human body by weight is carbon. Hundreds of ¹⁴C decays take place in the human body every second. Carbon-14 and other naturally occurring radioactive substances in the body compose a person's background exposure to nuclear radiation. As we will see later in this chapter, this activity level is well below the maximum recommended dosages.

II.6 Radioactive Dating

Radioactive dating is a technique that uses naturally occurring radioactivity to determine the age of a material, such as a rock or an ancient artifact. The basic approach is to estimate the original number of nuclei in a material and the present number of nuclei in the material (after decay), and then use the known value of the decay constant λ and Equation 10.10 to calculate

the total time of the decay, t. An important method of radioactive dating is carbon-14 dating. Carbon-14 nuclei are produced when high-energy solar radiation strikes ¹⁴N nuclei in the upper atmosphere and subsequently decay with a half-life of 5730 years. Radioactive carbon has the same chemistry as stable carbon, so it combines with the ecosphere and eventually becomes part of every living organism. Carbon-14 has an abundance of 1.3 parts per trillion of normal carbon. Therefore, if you know the number of carbon nuclei in an object, you multiply that number by 1.3×10^{-12} to find the number of ¹⁴C nuclei in that object. When an organism dies, carbon exchange with the environment ceases, and ¹⁴C is not replenished as it decays. By comparing the abundance of ¹⁴C in an artifact, such as mummy wrappings, with the normal abundance in living tissue, it is possible to determine the mummy's age (or the time since the person's death). Carbon-14 dating can be used for biological tissues as old as 50,000 years, but is generally most accurate for younger samples, since the abundance of ¹⁴C nuclei in them is greater. Very old biological materials contain no ¹⁴C at all. The validity of carbon dating can be checked by other means, such as by historical knowledge or by tree-ring counting.

EXAMPLE 3

An Ancient Burial Cave

In an ancient burial cave, your team of archaeologists discovers ancient wood furniture. Only 80% of the original ¹⁴C remains in the wood. How old is the furniture?

Strategy

The problem statement implies that N/N₀=0.80. Therefore, the equation N=N₀e^{$-\lambda t$} can be used to find the product, λt . We know the half-life of ¹⁴C is 5730 y, so we also know the decay constant, and therefore the total decay time t.

Solution

Solving the equation $N=N_0e^{-\lambda t}$ for N/N_0 gives us

$$\frac{N}{N_0} = e^{-\lambda t}.$$

Thus, $0.80=e^{-\lambda t}$ Taking the natural logarithm of both sides of the equation yields $\ln 0.80=-\lambda t$, so that $-0.223=-\lambda t$.

Rearranging the equation to isolate t gives us

$$t = rac{0.223}{\lambda},$$

Where:

$$\lambda = rac{0.693}{t_{1/2}} = rac{0.693}{5730 \, \mathrm{y}}.$$

Combining this information yields

$$t = \frac{0.223}{\left(\frac{0.693}{5730 \text{ y}}\right)} = 1844 \text{ y}.$$

Significance

The furniture is almost 2000 years old—an impressive discovery. The typical uncertainty on carbon-14 dating is about 5%, so the furniture is anywhere between 1750 and 1950 years old. This date range must be confirmed by other evidence, such as historical records.