OWLBook: Chapter 24: Nuclear Chemistry

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**Section 24.1 Nuclear Reaction**

**Introductory Text**

Your study of chemistry to this point has been overwhelmingly based on the study of the electrons of atoms interact with other atoms to form everything around us. Strikingly absent from the conversation to this point has been the nucleus of the atom—it’s as if the nuclei are just along for the ride. We did discuss about how an atom gets its identity (the number of protons), and that there are isotopes of most elements (versions of an element with different masses due to more or less neutrons in the nucleus). We also talked about how 99.9+% of the mass of an atom but less than 0.00000000000001% of its total volume is due to the nucleus. Aside from that, the nucleus has been considered a constant throughout our study of chemistry. This is for a good reason: most of the time, nuclei are perfectly stable and do not change. This chapter explores the rest of the time, when nuclei do react and undergo change.

**Opening Exploration:** Penetrating Power of Radiation (new video-based module)

**24.1a Nuclear vs. Chemical Reactions**

In any normal chemical reaction, electrons move from one environment to another. Almost all reactions are accompanied by some energy being absorbed or released when those electrons move from one environment to another. In a nuclear reaction, parts of the nucleus change orientation or identity. These changes are also accompanied by an exchange of energy with the surroundings. This is similar to normal chemical systems but the scale of the energy exchanged is not. Most chemical reactions occur on the order of kJ/mol of reaction, for example propane, commonly used in bar-b-que-grills and for home heating, releases XXX kJ/mol when burned, or about X.X kJ/g. The reaction of Uranium-235, the fuel for the first nuclear explosion, released $1.95 \times 10^{10}$ kJ/mol or $8.31 \times 10^7$ kJ/g. This is 20,000x more energy per gram of reactant than what we consider a vigorous chemical explosion. Figure 24.XXX illustrates this difference, showing the relative amounts of water that can be boiled using a single gram of propane and a single gram of the most commonly used nuclear energy process, U-235 fission.

Figure 24.XXX Relative Amount of Water 1 g of Fuel can Boil

*pair of photos showing relative amount of water that can be boiled with 1 g of propane and 1 g U-235*
Another aspect of this energy difference is the types of electromagnetic radiation nuclear and chemical reactions emit. Just as the transition of electrons from one energy level to another in an atom is quantized and occurs with the transfer of a quantum of energy, nucleons exhibit a similar transition in the nucleus. When an excited state nucleus “relaxes” to the ground state, it too gives off a quantum of energy. When the electrons relaxed we could see some of those transitions as visible light because they were in the visible spectrum about 1 to 3 eV/photon. When the nucleus relaxes the transitions are on the order of MeV/photon or millions of electron volts per photon. We call these photons gamma rays.

Figure 24.XXX Electromagnetic Spectrum (taken from Chapter 6, highlight visible vs. gamma frequencies)

Quick Check
Roughly how much more energy is released when one mole of U-235 undergoes fission than when one mole of gasoline burns?

a) 10 times  b) 100 times  c) 1,000 times  d) 10,000 times  e) 100,000 times

ans: d

Section 24.1b Natural Radioactive Decay Reactions (reactions and penetrating power)

Alpha particle production: An α particle is a $^4_2\text{He}^{12}$ nucleus. Many nuclei that are particularly heavy, and all those beyond Bi on the periodic table undergo α emission. Every time a nucleus emits an α particle it loses two protons and two neutrons.

The heaviest stable element on the periodic table is $^{209}_{83}\text{Bi}$. Every isotope past $^{209}_{83}\text{Bi}$ on the periodic table is radioactive and can decay by alpha emission to lose mass and become stable. The alpha decay of uranium is shown below

$$^{238}_{92}\text{U} \rightarrow ^4_2\text{He}^{12} + ^{234}_{90}\text{Th} \quad \text{or} \quad ^{238}_{92}\text{U} \rightarrow ^{234}_{90}\text{Th}$$

Example Problem 24.1.1 Alpha Decay

Beta particle production: a β− particle is an electron. This electron is generated in the nucleus when a neutron is converted to a proton, $^0_\text{n} \rightarrow ^0_{-1}\text{β} + ^1_1\text{p}$. The mass number of the nucleus does not change in this process. An example of a beta emitter is $^{137}_{55}\text{Cs}$. Note the periodic table lists the average isotopic mass of naturally occurring Cs is 132.9amu. This gives us a clue that $^{137}_{55}\text{Cs}$ has too many neutrons to be stable.

$$^{137}_{55}\text{Cs} \rightarrow ^0_{-1}\text{β} + ^{137}_{56}\text{Ba}$$
Example Problem 24.1.2 Beta Decay

**Positron production:** a $\beta^+$ is an anti-electron. This is our first example of antimatter. An anti-electron has the same mass as an electron but carries exactly opposite charge to the electron, +1. Like beta particle production, positron production occurs in the nucleus to bring the balance of neutrons to protons closer to the center of the zone of stability. In the case of positron emission the nucleus contains too few neutrons for the number of protons. An example of a positron emitter is $^{22}_{11}$Na. Note the periodic table lists the average isotopic mass of naturally occurring Na as 22.99amu. Again, this gives us a clue that $^{22}_{11}$Na has too few neutrons to be stable. This would show up on the right side of figure xx-x.

$$^{22}_{11}{\text{Na}} \rightarrow ^0_{-1}\beta^+ + ^{22}_{10}{\text{Ne}}$$

In order for positron production to occur the energy difference between the parent and daughter nuclide must be in excess of 1.02MeV. This is due to the cost of producing antimatter, which also must obey $E=mc^2$.

This positron does not live long in a world made of matter. When a positron comes in contact with an electron (its matter opposite) they annihilate each other generating pure energy. This energy is usually emitted in the form of two photons each having 0.511MeV of energy traveling in opposite directions to obey conservation laws.

**Electron capture:** One of the few instances where orbital electrons are involved in a nuclear reaction is in electron capture. Electron capture occurs when a nucleus has too few neutrons for the number of protons present. An example of this decay mode is shown below:

$$^{83}_{37}\text{Rb} + ^0_{-1}e^- \rightarrow ^{83}_{36}\text{Kr}$$

The result of this reaction is similar to that of positron production, both reactions result in the parent nuclei converting one proton to a neutron, thereby increasing nuclear stability. One main difference is that in electron capture the reaction can occur with less than 1.02MeV of energy in the transition between the parent and the daughter as no antimatter is created. For reactions that do have the necessary energy to create positrons they may still decay by electron capture. Most nuclei that have too few neutrons to be stable decay by a mixture of positron production and electron capture. As electron capture decay requires the capture of an orbital electron, nuclei with higher $Z$ (and therefore also larger #’s of electrons) have increasing proportions of electron capture decay over positron emission. This decay mode is also one of the few decay modes that are influenced by temperature or electronic environment of the nucleus (due to it’s reliance on capturing the electron). What would be the most likely electron captured by the nucleus? This capture leaves a vacancy in an electron orbital that gets filled by an outer orbital electron. When this occurs an x-ray photon is emitted.

Example Problem 24.1.3 Positron Emission and Electron Capture

**Gamma ray production:** Gamma ray production occurs when a nucleus is in an excited energetic state. This is most often the case following another nuclear event such as one of the decay modes discussed
above. When a nucleus is excited it can release energy by emitting a photon. When Cs-137 decays, it initially forms a metastable nucleon of Ba-137.

\[
^{137}_{55}\text{Cs} \rightarrow ^{0}_{-1}\beta + ^{137}_{56}\text{Ba}
\]

The \( m \) in the notation of the excited state of barium refers to metastable. This metastable, excited-state isotope decays to the ground state isotope by releasing a high-energy gamma ray.

\[
^{137m}_{56}\text{Ba} \rightarrow ^{137}_{56}\text{Ba} + ^{0}_{0}\gamma
\]

Many nuclear reactions produce excited state daughters that decay to the ground state by gamma ray production. Note in gamma ray production neither the mass number nor atomic number change from reactant to product, as this is solely a release of energy in the form of a photon.

**Shielding and penetration power:** alpha particles, beta particles and gamma rays are the most common forms of ionizing radiation and they all interact with matter a little differently. Alpha particles are the most massive and highly charged. As such they interact strongly with matter penetrating a couple inches of air easily stopped by a sheet of paper. Beta particles as you recall are fast moving electrons, much less massive than the alpha particle and have a negative charge. They also interact with matter but can penetrate much deeper depending on their kinetic energy. Beta particles can travel a few feet in air but can be stopped by a few millimeters of plastic or aluminum. Gamma rays are high-energy photons like x-rays and have no charge. They only weakly interact with matter and can travel great distances in air. High-density materials such as lead are used to shield gamma sources, sometimes requiring many centimeters thick to reduce exposure to safe levels.

**Section 24.1c Balancing Nuclear Reactions**

Chemical reactions are, by definition, balanced. All the matter present in the reactants is present in the products. Because normal chemical processes do not involve changes in any nuclei, and because the nucleus defines each element, a balanced chemical equation must have the same number of atoms of each element present. Not so for nuclear processes. Balancing a nuclear reaction equation involves balancing the mass and the charge of the species present.

Many nuclear reactions involve antimatter or particles with a mass number of zero. Their treatment in equation balancing is summarized in Table 24.1.

<table>
<thead>
<tr>
<th>Particle</th>
<th>Symbol</th>
<th>Mass number</th>
<th>Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proton</td>
<td>p</td>
<td>1</td>
<td>1+</td>
</tr>
<tr>
<td>Neutron</td>
<td>n</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Electron</td>
<td>e⁻</td>
<td>0</td>
<td>1⁻</td>
</tr>
<tr>
<td>Alpha</td>
<td>α</td>
<td>4</td>
<td>2⁺</td>
</tr>
<tr>
<td>Beta</td>
<td>β⁻</td>
<td>0</td>
<td>1⁻</td>
</tr>
<tr>
<td>Positron</td>
<td>β⁺</td>
<td>0</td>
<td>1⁺</td>
</tr>
</tbody>
</table>

**Example Problem 24.1.4**
Section 24.2 Nucleosynthesis of the Elements

Introductory Text

Look around. At anything. All the matter you see is made of atoms. The diversity of materials about us comes about because of the variety of about a hundred different chemical elements and the innumerable ways they can combine. We have discussed at length the ways atoms combine to form different compounds, but how do those hundred or so different elements come to exist in the first place? The answer: they are made inside stars! The universe was initially composed of almost only hydrogen-1 atoms: a single proton-electron pair. Almost all the other elements come into being starting with just hydrogen through a variety of processes called stellar nucleosynthesis.

24.2a Hydrogen Burning (regular and catalytic)

Nuclear synthesis happens in stars because that is where the temperature is high enough to bring two positively charged nuclei close enough together so that the strong nuclear force can take hold. The most important process that occurs in our sun and other normal stars is:

\[
\begin{align*}
\text{\textsuperscript{1}}\text{H} + \text{\textsuperscript{1}}\text{H} & \rightarrow \text{\textsuperscript{2}}\text{H} + \text{\textsuperscript{0}}\text{e}^+ + \nu \\
\text{\textsuperscript{2}}\text{H} + \text{\textsuperscript{1}}\text{H} & \rightarrow \text{\textsuperscript{3}}\text{He} + \gamma \\
\text{\textsuperscript{3}}\text{He} + \text{\textsuperscript{3}}\text{He} & \rightarrow \text{\textsuperscript{4}}\text{He} + 2\text{\textsuperscript{1}}\text{H}
\end{align*}
\]

This process is called hydrogen burning and occurs in young stars. The overall process is:

\[
\text{\textsuperscript{4}}\text{He} \rightarrow \text{\textsuperscript{1}}\text{H} + 2\text{\textsuperscript{1}}\text{H} + \text{\textsuperscript{0}}\text{e} + 2\nu
\]

In stars that contain the elements N, C and O, catalytic cycles can also lead to hydrogen burning. The
“CNO-I cycle” below is an example of this.

\[
{^{12}}_6C + {^1}_1H \rightarrow {^{13}}_7N + \gamma + 1.95 \text{ MeV} \\
{^{13}}_7N \rightarrow {^{12}}_6C + e^++\nu_e + 2.22 \text{ MeV} \\
{^{13}}_6C + {^1}_1H \rightarrow {^{14}}_7N + \gamma + 7.54 \text{ MeV} \\
{^{14}}_7N + {^1}_1H \rightarrow {^{15}}_8O + \gamma + 7.35 \text{ MeV} \\
{^{15}}_8O \rightarrow {^{15}}_7N + e^++\nu_e + 2.75 \text{ MeV} \\
{^{15}}_7N + {^1}_1H \rightarrow {^{12}}_6C + {^4}_2He + 4.96 \text{ MeV}
\]

These two things are taken from Wikopedia and need checking-bv

**24.2b Other Fusion Reactions**

As a star gets older the fraction of increases and helium burning begins.

\[
{^4}_2He + {^4}_2He \rightarrow {^8}_4Be \\
{^8}_4Be + {^4}_2He \rightarrow {^{12}}_6C
\]

The first reaction is a fast equilibrium generating \(^4_2\text{Be}\), a small fraction of this fuses with another \(^4_2\text{He}\) to form \(^{12}_6\text{C}\), a stable isotope. This kind of fusion reaction continues to occur, first by further addition of \(\text{He}\) nuclei (helium burning) and then even larger nuclei.

\[
{^{12}}_6C + 4 \rightarrow {^{16}}_8O + \gamma \\
{^{16}}_8O + 4 \rightarrow {^{20}}_{10}\text{Ne} + \gamma
\]
The rate at which these fusion reactions occur depends on the ability of the colliding nuclei to overcome electrostatic repulsions in order to get close enough for the strong nuclear force to take hold. This electrostatic-based activation energy increases with increasing nuclear charge, so the larger the nuclei, the higher the temperature at which the star must be in order for them to collide in a successful fusion event. For example, hydrogen burning occurs at temperature exceeding $XXXX \text{ K}$, but helium burning requires temperatures above $YYYY \text{ K}$.

### 24.2c Neutron Addition-Beta Decay

Fusion of positively charged nuclei is responsible for formation of elements up through about calcium, $Z = 20$. Beyond that the nuclei are just too highly charged to bring them together close enough to initiate strong-force nuclear bonds. So, how are all the rest of the elements formed? They are formed by a succession of neutron additions followed by radioactive beta decay reactions. Recall that beta decay essentially converts a nuclear neutron into a proton, increasing the atomic number by one. Inside stars, nuclei absorb neutrons released in other reactions. Because neutrons have no charge, there is no electrostatic barrier to this event. When enough neutrons have been added to make the nucleus unstable, it undergoes a beta decay. This creates the next element on the periodic table. That nucleus begins to absorb neutrons, which continues the process to eventually create all the elements with $Z > 20$. A small portion of this is shown in Figure 24.XXX.

\[
\begin{align*}
\text{Cu} & \rightarrow \text{Cu} \\
\text{Cu} & \rightarrow \text{Zn} + \text{B}^{-} \\
\text{Zn} & \rightarrow \text{Zn} \\
\text{Zn} & \rightarrow \text{Zn} \\
\text{Zn} & \rightarrow \text{Ga} + \text{B}^{-} \\
\text{Ga} & \rightarrow \text{Ge} + \text{B}^{-}
\end{align*}
\]

This process is also used to create many of the transuranic elements, all of which do not exist in nature but are synthesized. The reactions used to synthesize Pu and Am are shown here.
Section 24.3 Nuclear Stability

In practical terms nuclei are categorized very simply in terms of stability: stable and radioactive. That is, does the nucleus spontaneously decay, or does it not. This stability is kinetically-based, not thermodynamically. That is, not all “stable” nuclei are equally stable. The stability of a nucleus is essentially like bond energy between two bonded elements: how much lower in energy is the system with those protons and neutrons near each other in a nucleus than they would be if all separated?

24.3a Isotopic Abundance

Neutron-Proton ratios
There are 263 naturally occurring nuclides. When we count up the number of protons and neutrons for each we find that 157 of them have an even number of both protons and neutrons, 52 have an even number of protons and odd number of neutrons, 50 have an even number of neutrons and odd number of protons, and only 4 have both an odd number of protons and neutrons. This suggests that pairing up
the protons and or neutrons increases the stability of a nucleus. There also seems to be certain magic numbers of protons or neutrons that are especially stable. These numbers are 2, 8, 20, 28, 50, 82, and 126. These magic numbers are analogous to the filling of electron energy levels in shell model of electron configuration. Some examples of “magic nuclei” are; \(^{39}\text{K}\), \(^{42}\text{Ca}\), and \(^{207}\text{Pb}\). Examples of “doubly magic” nuclei include; \(^{40}\text{Ca}\), and \(^{4}\text{He}\). Figure 19.1 shows a plot of all the known nuclides. Note that above atomic number 20 the stable nuclides have more neutrons than protons and this ratio increases as \(z\) increases. Further observation yields a step-like function to the plot due to the increased stability of the nucleus due to even numbers of nucleons. The area where the nuclides reside on this plot is called the “Zone of Stability”.

**Figure 19.1**
The zone of stability. The red dots indicate the nuclides that do not undergo radioactive decay. Note that as the number of protons in a nuclide increases, the neutron/proton ratio required for stability also increases.
24.3b Calculating Binding Energy

Mass Defect: As we look at atoms other than $^1_1\text{H}$ we notice that the mass of the atom is always less than the mass of the sum of the protons, neutrons and electrons that make it up. This is known as the mass deficiency or mass defect, $\Delta m$, and is equal to the difference of the sum of the masses of electrons, protons, and neutrons in the atom and the actual mass of the atom.

$$\Delta m = \text{(the sum of all } e^-, p^+, n^0) - \text{(actual mass of atom)}$$

Although this defect is rather small, it has a large effect on the stability of the atom. Remember part of Einstein’s “Theory of Relativity” states that matter and energy are equivalent. As such matter can be transformed into energy and energy into matter. This transformation occurs regularly in the sun and other stars as matter is converted into energy in a process called fusion. In addition we take advantage of this relationship when we split heavy nuclei to form more stable smaller nuclei in nuclear fission reactors to produce power.

Binding Energy: The binding energy of an atom is defined as the amount of energy that would be released if an atom were constructed from its individual components. An example would be:

$$8^1_1\text{H} + 8^0_0\text{n} \rightarrow ^{16}_8\text{O}$$

In order to calculate the change in energy for this reaction we recall $E=mc^2$. It follows then that;

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

Where $C$ is the speed of light in a vacuum (meters per second) and $\Delta m$ is the change in mass (products-reactants in kilograms). This gives energy in joules. Most nuclear reactions are expressed in units of
electron volt (eV) or million electron volt (MeV). The relationship is shown below.

\[
1 \text{eV} = 1.6021746 \times 10^{-19} \text{ J} \\
1 \text{MeV} = 1.6021746 \times 10^{-13} \text{ J}
\]

So by calculating the mass defect we can determine the binding energy of the nucleus. Notice we use the mass of the hydrogen atom that includes the mass of the electrons necessary to construct the atom.

**Example 24.3.XX**

What would the binding energy be for \(^{16}\text{O}\)?

\(^{16}\text{O}\) consists of 8 protons, 8 neutrons and 8 electrons. In order to calculate the binding energy we need to determine the mass defect (\(\Delta m\)). From table X we find the mass of the protons, neutrons and electrons. We use these masses to determine the calculated nuclear mass:

- protons: \(8 \times 1.0073\) amu
- electrons: \(8 \times 0.00054858\) amu
- neutrons: \(8 \times 1.0073\) amu

Calculated = 16.132 amu

\[\Delta m = 16.132 \text{ amu} - 15.995 \text{ amu} = 0.137 \text{ amu}\]

Since by definition 1 gram = \(6.022 \times 10^{23}\) amu, we can calculate the mass defect in kilograms:

\[
\frac{0.137 \text{ amu}}{\text{atom}} \times \frac{1 \text{ gram}}{6.022 \times 10^{23} \text{ amu}} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 2.275 \times 10^{-28} \text{ kg/atom}
\]

So \(\Delta E = 2.275 \times 10^{-28} \frac{\text{kg}}{\text{atom}} \times \left( 2.998 \times 10^8 \frac{\text{meters}}{\text{second}} \right)^2 = 2.045 \times 10^{-11} \frac{\text{joules}}{\text{atom}}\)

or

\[\Delta E = 2.045 \times 10^{-11} \frac{\text{joules}}{\text{atom}} \times \frac{1 \text{ MeV}}{1.602 \times 10^{-13} \text{ joules}} = 127.6 \frac{\text{MeV}}{\text{atom}}\]

\[
\frac{\text{Binding Energy}}{\text{Nucleon}} = 127.6 \frac{\text{MeV}}{\text{atom}} \times \frac{1 \text{ atom}}{16 \text{ nucleons}} = 7.977 \frac{\text{MeV}}{\text{nucleon}}
\]

**24.3c Binding Energy Trends**

The binding energy per nucleon is an indication of the stability of the nucleus of an atom. We use the binding energy per nucleon to compare the stability of one nucleus vs. another. The greater the binding energy per nucleon the more stable the atom. \(^{56}\text{Fe}\) is the most stable nucleus as shown in figure xx.x with about 8.8 MeV/nucleon binding energy.
The stability of a nucleus is a sum of the attractive nuclear forces between all the nucleons (protons as well as neutrons) and repulsive electrostatic forces between like-charged protons. For elements lighter than Fe, addition of more protons and neutrons involves an increase in nuclear forces that is greater than the added repulsive electrostatic interactions. So, moving towards Fe leads to more stable nuclei. Moving past Fe towards heavier nuclei, the increase in repulsions outpaces increases in nuclear attractions. So, past Fe, nuclear stability decreases with increasing nuclear size.

You might wonder how elements past $^{56}$Fe are synthesized since it is a non-spontaneous process energetically speaking. Realize that as a star fuses lighter nuclei, a large excess of energy is released. It is this energy that fuels the synthesis of the heavy elements and the energy released in the explosion of a supernova is thought to generate substantial amounts of super-heavy elements like uranium and others.

If $^{56}$Fe is the most stable nucleus, then the universe would be more stable if all matter was composed of Fe atoms. Why, then, is the universe not composed of only iron?

**24.3d Predicting Radioactive Decay Paths**

The plot below is of all the known isotopes. They form a region called the band of stability, or the island of stability.
If an isotope lies below this curve, it has too few neutrons for the number of protons present. If it lies above the band, it has too many neutrons. When an isotope lies off the island, it will be radioactive and react to move towards the island. No one is ever voted off; only on. Nuclei are nice that way.

The common decay paths can be viewed in this way:
So, if an isotope is below, it will undergo either positron decay or electron capture. If it is above, it will undergo beta decay. If an isotope of a heavy element is to the upper right, it will often undergo alpha decay to move back towards the island.

**Section 24.4 Kinetics of Radioactive Decay**

**Section 24.4a Nuclear Decay Kinetics**

The decay of any radioactive nuclei is a random event much like an individual's lifespan; it is impossible to predict exactly how long a person will live and likewise when an atom will decay. By observing a large enough population it is possible to predict their average lifespan with reasonable certainty. This is the same method we employ in determining the decay rate of radioactive nuclei. Given a population of radioactive nuclei, say 1000, we observe 10 of these decay in one minute, if we double the number of nuclei we start with to 2000, then we would expect the number of decays in the first minute to be 20. This direct proportionality, as you recall from Chapter 14 is called first order kinetics. All nuclear decay processes obey first order kinetics. The integrated rate law for first order kinetics can be written as follows:

\[ N_t = N_i e^{-kt} \]

or (in \( y=mx+b \) form)

\[ \ln N_t = -kt + \ln N_i \]

Where \( N_i \) is the number of nuclei originally present at \( t=0 \) and \( k \) is the decay constant. This equation can be used to calculate the number of nuclei present at any time after \( t=0 \). To determine the exact number of radioactive nuclei in a sample is usually difficult so most calculations are based on the activity \( A \) of the sample. The activity is much easier to determine and is proportional to the number of nuclei present. We can observe the activity directly by using a radiation-detecting device. One of the most common devices for detecting radiation is the **Geiger counter**. The Geiger counter is useful in detecting most types of radiation and can be configured as a battery operated survey meter to scan areas for possible contamination by radioactive materials.

\[ A = -\frac{\Delta N}{\Delta t} = kN \]

The decay constant is related to the half-life of the reaction by:

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

**24.4b Radioactive Dating**
Radioactive Carbon Dating—this is copied from my version of Chapter 14; not sure what to do about it being repeated. -bv

Carbon exists as mostly $^{12}$C, with about 1% of $^{13}$C, and a very small fraction of radioactive $^{14}$C. It is formed in the upper atmosphere by reaction of $^{14}$N with high energy solar radiation. Because it is constantly decaying and being reformed in the upper atmosphere, there is a relatively constant concentration of $^{14}$C present as CO$_2$ in the atmosphere. That CO$_2$, like all CO$_2$, can be sequestered by photosynthesis to form plants. Those plants live their plant-like life, sometimes being eaten by animals, sometimes just dying. As a plant or animal lives it keeps exchanging C with the atmosphere, and the fraction of 14C in the plant or animal stays equal to that in the atmosphere.

Once the thing dies, however, its C content is “locked” and it no longer receives new $^{14}$C. Because the $^{14}$C is radioactive, the fraction of it present in the dead thing starts to decrease. If we compare the fraction present today with the fraction we presume to be the steady state $^{14}$C amount, we can estimate the time since death. This is shown in Figure 14.5.

The actual experiment involves measuring the 14C radioactivity from a sample. It is generally reported in units of counts per minute per gram of C. The half-life of 14C is 5730 years, and this technique is good for dating items as old as 50,000 years.

**Dating Rocks:**
This works the same as carbon dating, but uses isotopes that are much longer-lived. The experiment is done by determining \( \text{mol of parent}/(\text{mol parent} + \text{mol daughter}) \). Then

\[
\ln\left(\frac{\text{mol of parent}}{\text{mol parent} + \text{mol daughter}}\right) = -kt, \text{ solve for t.}
\]

Some important radioactive isotopes and the final stable daughter product are giving in this table:

<table>
<thead>
<tr>
<th>Parent Isotope</th>
<th>Stable Daughter Product</th>
<th>Currently Accepted Half-Life Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uranium-238</td>
<td>Lead-206</td>
<td>4.5 billion years</td>
</tr>
<tr>
<td>Uranium-235</td>
<td>Lead-207</td>
<td>704 million years</td>
</tr>
<tr>
<td>Thorium-232</td>
<td>Lead-208</td>
<td>14.0 billion years</td>
</tr>
<tr>
<td>Rubidium-87</td>
<td>Strontium-87</td>
<td>48.8 billion years</td>
</tr>
<tr>
<td>Potassium-40</td>
<td>Argon-40</td>
<td>1.25 billion years</td>
</tr>
<tr>
<td>Samarium-147</td>
<td>Neodymium-143</td>
<td>106 billion years</td>
</tr>
</tbody>
</table>

**24.4c Complex Decay Mechanisms**

**Natural Decay Series:** As we noted earlier, all nuclei heavier than bismuth decay by alpha emission. Those nuclei much heavier than that have to take multiple steps to get to a stable isotope. This series of steps is called a decay series. Below is the decay series of \(^{238}\text{U}\) to \(^{206}\text{Pb}\). Note the \(\beta\) decay adjusts the neutron to proton ratio in the nucleus bringing the daughter closer to the zone of stability.

![Figure 24.2](http://example.com/figure.png)

*Figure 24.2* The decay series from \(^{238}\text{U}\) to \(^{206}\text{Pb}\). Each nucleus in the series except \(^{206}\text{Pb}\) is radioactive, and the successive transformations (shown by the arrows) continue until \(^{206}\text{Pb}\) is finally formed. The horizontal red arrows indicate \(\beta\)-particle production (\(Z\) increases by 1 and \(A\) is unchanged). The diagonal blue arrows signify \(\alpha\)-particle production (both \(A\) and \(Z\) decrease).
Section 24.5 Nuclear Fission

Section 24.5a Fission Reactions, Power Plants and Bombs

**Spontaneous fission:** A number of very heavy radioactive nuclei decay by spontaneous fission. As the name suggests, this occurs when a parent nuclei cleaves into two smaller more stable nuclei. An example of spontaneous fission is shown in the following equation:

\[
^{252} \text{Cf} \rightarrow ^{141} \text{Ba} + ^{107} \text{Mo} + 4 \, ^1 \text{n}
\]

Nuclei that undergo spontaneous fission are used as neutron sources for a number of applications including the detection of trace materials in airline luggage screening equipment, and remote detection of moisture in grain storage units. Notice product nuclides of spontaneous fission have a very high neutron to proton ratio and undergo beta decay to increase their stability.

**Neutron induced fission:** As in spontaneous fission, the process of splitting heavy nuclei into smaller more stable nuclei is the same. In this case the fission event is initiated by the collision of a neutron into a heavy nuclei. An example is:

\[
^{235} \text{U} + ^1 \text{n} \rightarrow ^{141} \text{Ba} + ^{92} \text{Kr} + 3 \, ^1 \text{n}
\]

This is one example of many possible outcomes for the above reaction. Another example would be:

\[
^{235} \text{U} + ^1 \text{n} \rightarrow ^{140} \text{Xe} + ^{94} \text{Kr} + 2 \, ^1 \text{n}
\]

or

\[
^{235} \text{U} + ^1 \text{n} \rightarrow ^{135} \text{Sn} + ^{99} \text{Mo} + 2 \, ^1 \text{n}
\]

Notice the fission fragments in all the examples are asymmetric in size. This is due to the stability of the daughter nuclei. The fragments gravitate toward forming nuclei with magic numbers of protons or neutrons. They also tend to form nuclei with paired neutrons or protons but this is not always the case. A graph showing the distribution or yield of fission products is shown in figure xx.x.

Notice all of these reactions also produce free neutrons. If these neutrons react with additional \(^{235} \text{U}\) a chain reaction can occur. For a chain reaction to continue, a critical mass of material is necessary. (see figure xx.x).

**use new animations**

Neutron induced fission is the reaction utilized in all nuclear power plants. This is also the reaction exploited in nuclear weapons. The two most common isotopes susceptible to neutron-induced fission are \(^{235} \text{U}\), and \(^{239} \text{Pu}\).

Section 24.5b Production of Uranium Nuclear Fuel and Bombs
\(^{235}\)U is naturally occurring, accounting for about 0.72% atomic abundance, nearly all the rest is \(^{238}\)U. \(^{238}\)U is not fissile and cannot sustain a nuclear chain reaction. In order for nuclear power plants in the United States to produce a sustained nuclear chain reaction, the uranium ore is enriched to a level of about 3% \(^{235}\)U. Nuclear weapons require a much higher enrichment, in excess of 90% due to the need for supercritical explosive kinetics.

The process of producing enriched U-235 nuclear fuel is outlined here:

U ore contains small amounts of UO\(_2\) and UO\(_3\).

**Step 1. Oxidize UO\(_2\) to UO\(_3\)**

\[
\text{UO}_2 (s) + 2 \text{H}^+ (aq) \rightarrow \text{UO}_3^{2+} (\text{solid salt}) + \text{H}_2\text{O}(l)
\]

**Step 2. Solubilize U by reacting with H\(_2\)SO\(_4\)**

\[
\text{UO}_2^{2+} (\text{solid salt}) + 3 \text{SO}_4^{2-} (aq) \rightarrow \text{UO}_3 (\text{SO}_4)^{3-} (aq)
\]

**Step 3. Convert leached U into pure UO\(_3\).**

\[
2 \text{R}_3\text{N} + \text{H}_2\text{SO}_4 \rightarrow (\text{R}_3\text{NH})_2\text{SO}_4
\]

\[
2 (\text{R}_3\text{NH})_2\text{SO}_4 + \text{UO}_3 (\text{aq}) \rightarrow (\text{R}_3\text{NH})_2\text{UO}_3 (\text{aq}) + 2\text{SO}_4^{2-} (aq)
\]

\[
(\text{R}_3\text{NH})_2\text{UO}_3 (\text{aq}) + 2(\text{NH}_4)_2\text{SO}_4 \rightarrow 4\text{R}_3\text{N} + (\text{NH}_4)_2\text{UO}_3 (\text{aq}) + 2\text{H}_2\text{O}(l)
\]

\[
2\text{NH}_4 + 2\text{UO}_3 (\text{aq}) \rightarrow (\text{NH}_4)_2\text{UO}_3 (s) + 4\text{SO}_4^{2-} (aq)
\]

\[
(\text{NH}_4)_2\text{UO}_3 (s) \rightarrow \text{UO}_3 (s) + \text{H}_2\text{O}(l) + \text{NH}_3 (g)
\]

UO\(_3\) is then reacted to make pure UO\(_3\).

**Key:** \(\text{UO}_3\) formed is pure.

**Step 4. Convert UO\(_3\) into UF\(_6\)**

\[
\text{UO}_3 (s) + \text{H} (g) \rightarrow \text{UO}_2 (s) + \text{H}_2\text{O}(l)
\]

\[
\text{UO}_2 (s) + 4\text{HF}(g) \rightarrow \text{UF}_6 (s) + 2\text{H}_2\text{O}(l)
\]

\[
\text{UF}_6 (s) + \text{F} (g) \rightarrow \text{UF}_6 (l \text{ or g})
\]
Key: UF$_6$ has a boiling point near 50°C.

Useful nuclear fuel needs a U-235 content around 4%, but natural uranium ore has only 0.7% U-235. The uranium must be “enriched” by increasing the percentage of U-235. The idea is not to turn U-238 into U-235 (we can’t do that) but instead to take a mixture of the two and selectively discard U-238.

There is no exploitable difference in chemical properties between compounds of U-235 and U-238. The only difference is their masses. So, that is used. Separation of molecules by nature of their masses must be done in the gas phase. So, the U is converted into (nonpolar) UF$_6$, which has a boiling point near 50°C and can easily be used in the gas phase.

Gaseous UF$_6$ was originally enriched using a diffusion process but the best method today is to use a gas centrifuge. It is the components for these centrifuges that nuclear inspectors look for when doing searches of suspected secret nuclear installations. The uranium is easy to hide; the giant machines needed to enrich the uranium are not.

**Efficiencies:**
diffusion = 1.002/stage

\[
\text{Final Fraction} = 0.7 \times (1.002) \quad \#\text{cycles}
\]

gas centrifuge: 1.2/stage

\[
\text{Final Fraction} = 0.7 \times (1.2) \quad \#\text{cycles}
\]

Example Problem:
If an enrichment process has an efficiency of 1.002, how many enrichment cycles will be needed to enrich a sample from 0.7% U-235 to 4.0% U-235?

What if the enrichment efficiency is 1.20?

An atomic bomb requires 90% U-235 enrichment. How many cycles for that?

Section 24.5c Production of Plutonium Nuclear Fuel and Bombs

$^{239}\text{Pu}$ is not a naturally occurring element. It can be synthesized by the reaction of neutrons with $^{238}\text{U}$ in a breeder reactor. In a breeder reactor heat is generated as in a normal nuclear power plant but in addition, excess neutrons from the fission reaction are allowed to react with $^{238}\text{U}$ as follows:

$$^{238}\text{U} + \frac{1}{0}n \rightarrow ^{239}\text{Np} + ^{0}_{-1}\beta^{-}$$

$$^{239}\text{Np} \rightarrow ^{239}\text{Pu} + ^{0}_{-1}\beta^{-}$$

This reaction generates more fissile fuel than it consumes and is a potential source for much needed energy without the downside of creating greenhouse gasses. Safety is a concern however due to the potential ability to use $^{239}\text{Pu}$ for a nuclear weapon. Additional concerns of handling and storing radioactive waste generated from spent fuel are limiting the development of this energy source.

Section 24.5d How a Nuclear Powerplant Works

Do we even want this?

![Diagram of a nuclear powerplant]

I like the idea of the control rods; that’s worth pointing out:
\[
\frac{1}{3}\text{B} + \frac{1}{6}\text{Li} \rightarrow \frac{2}{3}\text{Li} + \frac{4}{2}\alpha
\]

**Section 24.6 Important Uses of Radioactivity**

**Section 24.6a Smoke Detectors**

An example of an alpha emitter used in most smoke detectors is \(^{241}\text{Am} \).\(^{241}\text{Am} \rightarrow \frac{4}{2}\text{He}^{+2} + \frac{237}{93}\text{Np} \)

This reaction is used as a source of ionizing radiation to detect the presence of smoke in air.

**Section 24.6b Food irradiation**

One additional application of the use of ionizing radiation is as a food preservative. For the same reasons as described above, organisms that contaminate foods can be killed by exposure to ionizing radiation. Many foods utilize this method. This reduces the need for chemical preservatives and improves shelf life. Public perception of this technique has been an issue as some mistakenly worry that the food becomes radioactive when exposed to ionizing radiation. Others worry that the food quality is degraded by the exposure. One fact is that food spoilage is dramatically reduced using this method.

**Section 24.6c Nuclear Medicine**

Positron emitters are used in the medical imaging technique called **Positron Emission Tomography** or **PET** scans. In this application, a positron-emitting isotope chemically bound to a tracer molecule is injected into a patient. The photons emitted from the annihilation events are recorded with a position sensitive detector. A computer can then create an image of where the tracer molecules deposited in the body. This technique is widely used for brain scans.
Another example of a beta emitter is $^{131}_{53}\text{I}$. Again note that the average mass on the periodic table is 126.9. $^{131}_{53}\text{I}$ is used as a treatment for hyperthyroidism. The high energy $\beta^-$ particles emitted from the radioactive iodine cause the thyroid to shrink and reduce its hormone output.

$$^{131}_{53}\text{I} \rightarrow _{-1}^0\beta + ^{131}_{54}\text{Xe}$$

**Section 24.6d. Radioactivity and DNA Damage**

At first this may seem like a strange heading for a topic in nuclear chemistry but it makes sense to group these topics together as they are all related by the effect ionizing radiation has on organisms. High-energy particles emitted from radioactive sources are called ionizing radiation because of their ability to eject electrons from elements or molecules thereby creating ions and free radicals. You have probably heard of free radicals and their potential impact on our health. When these events occur in a biological system many things can result. Damage to the DNA in a cell is the most concerning issue in exposure to radiation (see figure xx.x). This damage can lead to a few different outcomes. The first is DNA can actually repair itself if the damage is not too great. One of the beautiful aspects of DNA is that it keeps a backup copy of the information contained so if one strand is damaged the cell can use the other strand as a template to repair the damage. If the damage is repaired improperly a mutation occurs. If this mutation propagates as the cell divides, it can lead to possible medical issues including cancer. If the cell cannot repair the damage it can lead to cell death. We are exposed to ionizing radiation every day of our lives. Many of the atoms that make up our body are naturally radioactive. In addition, everything we eat and all the matter that surrounds us emits low levels of ionizing radiation. Medical x-rays and other nuclear medicine procedures like PET scans expose us to ionizing radiation. The sun emits ionizing cosmic rays...it is impossible to escape ionizing radiation. One interesting fact is that during cell mitosis the cell is the most susceptible to irreparable damage by ionizing radiation. This is due to the fact that the DNA strands separate at this time to duplicate the genetic information. If that single strand is damaged it usually results in cell death. We take advantage of this fact when we treat cancer with radiation treatments. Because cancer is unmitigated cell division, those cells are much more susceptible to ionizing radiation than normal cells (Yes it seems ironic that cancer could be caused by radiation and we use radiation to cure it).

**FIGURE 20.12**

Examples of damage to DNA from nuclear radiation. Damaged DNA can prevent cells from properly functioning and increase the likelihood of tumors.

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24.6e The Problem with Radon

Here is the decay path of natural uranium.
The parent uranium is mostly deep underground and its radiation is also deep underground where it can’t hurt us. All the elements along the way form solid compounds, so they, too, stay safely underground. But, one daughter product, Rn-222, is a gas and it seems out of the ground and into basements. If you breath it in, it might decay while in your lungs. If so, you get that radiation, but you also then have the daughter products that are formed stay in your body because they are no longer in the gas phase.