Nuclear Chemistry

• In this chapter we will look at two types of nuclear reactions.
  – Radioactive decay is the process in which a nucleus spontaneously disintegrates, giving off radiation.
  – Nuclear bombardment reactions are those in which a nucleus is bombarded, or struck, by another nucleus or by a nuclear particle.

Radioactivity

• The phenomena of radioactivity was discovered by Antoine Henri Becquerel in 1896.
  – His work with uranium salts lead to the conclusion that the minerals gave off some sort of radiation.
  – This radiation was later shown to be separable by electric (and magnetic) fields into three types; alpha (α), beta (β), and gamma (γ) rays.
– **Alpha rays** bend away from a positive plate indicating they are positively charged.
– They are known to consist of **helium-4 nuclei** (nuclei with two protons and two neutrons).
– **Beta rays** bend in the opposite direction indicating they have a negative charge.
– They are known to consist of **high speed electrons**.
– **Gamma rays** are unaffected by electric and magnetic fields. (See Figure 20.2)
  – They have been shown to be a form of **electromagnetic radiation** similar to x rays, but higher in energy and shorter in wavelength.

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**Figure 20.2: Separation of Radiation From Radioactive Material (Uranium Mineral)**

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**X-ray image of human organ.**

**Source:** CNRI/Photo Researchers
Nuclear Equations

- A **nuclear equation** is a symbolic representation of a nuclear reaction using nuclide symbols.
  - For example, the nuclide symbol for uranium-238 is $^{238}_{92}U$.
  - The radioactive decay of $^{238}_{92}U$ by alpha-particle emission (loss of a $^4_2He$ nucleus) is written $^{238}_{92}U \rightarrow ^{234}_{90}Th + ^4_2He$.
  - Reactant and product nuclei are represented in nuclear equations by their nuclide symbol.

- Other particles are given the following symbols.
  - Proton: $^1_1H$ or $^1_p$
  - Neutron: $^1_0n$
  - Electron: $^0_1e$ or $^1_e$
  - Positron: $^0_0e$ or $^1_e$
  - Gamma photon: $^0_0\gamma$

- The total **charge is conserved** during a nuclear reaction.
  - This means that the sum of the subscripts for the products must equal the sum of the subscripts for the reactants.
\begin{itemize}
  \item The total number of nucleons is also conserved during a nuclear reaction.
  \item This means that the sum of the superscripts for the products must equal the sum of the superscripts for the reactants.
  \item Note that if all reactants and products but one are known in a nuclear equation, the identity of the missing nucleus (or particle) is easily obtained.
  \item This is illustrated in the next example.
\end{itemize}

\textbf{A Problem To Consider}

\begin{itemize}
  \item Technetium-99 is a long-lived radioactive isotope of technetium. Each nucleus decays by emitting one beta particle. What is the product nucleus?
  \item The nuclear equation is
  \[
  ^{\text{99}}_{\text{43}}\text{Tc} \rightarrow ^{\text{A}}_{\text{Z}}\text{X} + ^{\text{0}}_{\text{-1}}\beta
  \]
  \item From the superscripts, you can write
  \[
  99 = A + 0, \quad \text{or} \quad A = 99
  \]
  \item The nuclear equation is
  \[
  ^{\text{99}}_{\text{43}}\text{Tc} \rightarrow ^{\text{A}}_{\text{Z}}\text{X} + ^{\text{0}}_{\text{-1}}\beta
  \]
  \item Similarly, from the subscripts, you get
  \[
  43 = Z - 1, \quad \text{or} \quad Z = 43 + 1 = 44
  \]
  \item Hence A = 99 and Z = 44, so the product is
  \[
  ^{\text{99}}_{\text{44}}\text{Ru}
  \]
\end{itemize}
Nuclear Stability

- The existence of stable nuclei with more than one proton is due to the **nuclear force**.
  - The **nuclear force** is a strong force of attraction between nucleons that acts only at very short distances (about $10^{-15}$ m).
  - This force can **more than compensate** for the repulsion of electrical charges and thereby give a stable nucleus.

Nuclear Stability

- Several factors appear to contribute the stability of a nucleus.
  - The **shell model of the nucleus** is a nuclear model in which protons and neutrons exist in levels, or shells, analogous to the shell structure exhibited in electron configurations.
  - Experimentally, note that **nuclei with certain numbers of protons and neutrons** appear to be very stable.

- These numbers, called **magic numbers**, are the numbers of nuclear particles in a completed shell of protons or neutrons.
  - Because nuclear forces differ from electrical forces, these numbers are not the same as those for electrons in atoms.
  - For protons, the magic numbers are
    - 2, 8, 20, 28, 50, and 82
  - For neutrons, the magic numbers are
    - 2, 8, 20, 28, 50, 82, and 126
Evidence also points to the special stability of pairs of protons and pairs of neutrons.

The table below (Table 21.1) lists the number of stable isotopes that have an even number of protons and an even number of neutrons.

<table>
<thead>
<tr>
<th>Number of Stable Isotopes</th>
<th>157</th>
<th>52</th>
<th>50</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of protons</td>
<td>Even</td>
<td>Even</td>
<td>Odd</td>
<td>Odd</td>
</tr>
<tr>
<td>Number of neutrons</td>
<td>Even</td>
<td>Odd</td>
<td>Even</td>
<td>Odd</td>
</tr>
</tbody>
</table>

Finally, when you plot each stable nuclide on a graph of protons vs. neutrons, these stable nuclei fall in a certain region, or band.

The band of stability is the region in which stable nuclides lie in a plot of number of protons against number of neutrons. (see Figure 20.3)

No stable nuclides are known with atomic numbers greater than 83.

On the other hand, all elements with Z equal to 83 or less have one or more stable nuclides.

Figure 20.3: Band of Stability
Types of Radioactive Decay

- There are six common types of radioactive decay.
  
  1. Alpha emission (abbreviated α): emission of a \(^4\text{He}\) nucleus, or alpha particle, from an unstable nucleus.

  - An example is the radioactive decay of radium-226.

    \[
    ^{226}\text{Ra} \rightarrow ^{222}\text{Rn} + ^{+4}\text{He}
    \]

  2. Beta emission (abbreviated β or \(\beta\)): emission of a high speed electron from a stable nucleus.

  - This is equivalent to the conversion of a neutron to a proton.

    \[
    _{0}\text{n} \rightarrow _{1}\text{p} + ^{0}_{-1}\text{e}
    \]

  3. Positron emission (abbreviated \(\beta^+\)): emission of a positron from an unstable nucleus.

  - This is equivalent to the conversion of a proton to a neutron.

    \[
    _{1}\text{p} \rightarrow _{0}\text{n} + ^{0}_{+1}\text{e}
    \]

- Positron emission (abbreviated \(\beta^+\)): emission of a positron from an unstable nucleus.

  - The radioactive decay of technetium-95 is an example of positron emission.

    \[
    ^{95}\text{Tc} \rightarrow ^{95}\text{Mo} + ^{0}_{+1}\text{e}
    \]

- Electron capture (abbreviated EC): the decay of an unstable nucleus by capturing, or picking up, an electron from an inner orbital of an atom.

  - In effect, a proton is changed to a neutron, as in positron emission.

    \[
    _{1}\text{p} + ^{0}_{-1}\text{e} \rightarrow _{0}\text{n}
    \]
4. **Electron capture** (abbreviated EC): the decay of an unstable nucleus by capturing, or picking up, an electron from an inner orbital of an atom.

   - An example is the radioactive decay of potassium-40.
     \[ ^{40}_{19}\text{K} + ^0_0e \rightarrow ^{40}_{18}\text{Ar} \]

5. **Gamma emission** (abbreviated \(\gamma\)): emission from an excited nucleus of a gamma photon, corresponding to radiation with a wavelength of about \(10^{-12}\) m.

   - In many cases, radioactive decay produces a product nuclide in a **metastable** excited state.
   - The excited state is unstable and emits a gamma photon and goes to a lower energy state.

   - An example is metastable technetium-99.
     \[ ^{99}_{43}\text{Tc} \rightarrow ^{99}_{43}\text{Tc} + ^0_0\gamma \]

6. **Spontaneous fission**: the spontaneous decay of an unstable nucleus in which a heavy nucleus of mass number greater than 89 splits into lighter nuclei and energy is released.

   - For example, uranium-236 undergoes spontaneous fission.
     \[ ^{236}_{92}\text{U} \rightarrow ^{96}_{39}\text{Y} + ^{136}_{53}\text{I} + ^4_0n \]

---

**Predicting the Type of Radioactive Decay**

- **Nuclides** outside the band of stability are generally **radioactive**.
  - Nuclides to the **left of the band** have more neutrons than that needed for a stable nucleus.
  - These nuclides tend to **decay by beta emission** because it reduces the neutron-to-proton ratio.
Predicting the Type of Radioactive Decay

- Nuclides outside the band of stability (Figure 20.3) are generally radioactive.
  - In contrast, nuclides to the right of the band of stability have a neutron-to-proton ratio smaller than that needed for a stable nucleus.
  - These nuclides tend to decay by positron emission or electron capture because it increases the neutron to proton ratio.
  - In the very heavy elements, especially those with Z greater than 83, radioactive decay is often by alpha emission.

Figure 20.3: Band of Stability

A Problem To Consider

- Predict the expected type of radioactive decay for each of the following radioactive nuclides.

\[ {}_{20}^{47}\text{Ca} \quad {}_{13}^{25}\text{Al} \]

  - The atomic weight of calcium is 40.1 amu, so you expect calcium-40 to be a stable isotope.
  - Calcium-47 has a mass number greater than that of the stable isotope, so you would expect it to decay by beta emission.
The atomic weight of aluminum is 27.0 amu, so you expect aluminum-27 to be a stable isotope.

- Aluminum-25 has a mass number less than that of the stable isotope, so you would expect it to decay by positron emission or electron capture.

**Nuclear Bombardment Reactions**

- In 1919, Ernest Rutherford discovered that it is possible to change the nucleus of one element into the nucleus of another element.
  - Transmutation is the change of one element to another by bombarding the nucleus of the element with nuclear particles or nuclei.

Rutherford used a radioactive alpha source to bombard nitrogen nuclei.

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

- He discovered that protons are ejected in the process.

- The British physicist James Chadwick suggested in 1932 that the radiation from beryllium consists of neutral particles, each with a mass approximately that of a proton.
  - Chadwick’s suggestion led to the discovery of the neutron.

\[
^{8}_{4}\text{Be} + ^{4}_{2}\text{He} \rightarrow ^{12}_{6}\text{C} + ^{1}_{0}\text{n}
\]
Nuclear Bombardment Reactions

- Nuclear bombardment reactions are often referred to by an **abbreviated notation**.
  - For example, the reaction
  \[ ^{14}_7 N + ^2_4 He \rightarrow ^{17}_8 O + ^1_2 H \]
  is abbreviated
  \[ ^{14}_7 N(\alpha, p)^{17}_8 O \]

Nuclear Bombardment Reactions

- Bombardment of heavy nuclei **require accelerated particles** for successful transmutation reactions.
  - A **particle accelerator** is a device used to accelerate electrons, protons, and alpha particles and other ions to very high speeds.
  - It is customary to measure the kinetic energy of these particles in units of **electron volts**.
    \[ 1 \text{ eV} = 1.602 \times 10^{-19} \text{ J} \]

- Figure 20.5 shows a diagram of a **cyclotron**, a type of particle accelerator consisting of two hollow, semicircular metal electrodes in which charged particles are accelerated in stages.
Transuranium Elements

• The transuranium elements are elements with atomic number greater than that of uranium (Z=92), the naturally occurring element of greatest Z.
  – The first transuranium element was produced at the University of California at Berkeley in 1940 by E. M. McMillan and P. H. Abelson.
  – They produced an isotope of element 93, which they named neptunium.
  – Recent work (described in the essay at the end of Section 1.5) has yielded other elements including the heaviest to date, 118.

Radiations and Matter: Detection

• Two types of devices, ionization counters and scintillation counters, are used to count particles emitted from radioactive nuclei.
  – A Geiger counter (Figure 20.9), a kind of ionization counter used to count particles emitted by radioactive nuclei, consists of a metal tube filled with gas, such as argon.
A scintillation counter (Figure 21.10) is a device that detects nuclear radiation from flashes of light generated in a material by the radiation.

Radiations and Matter: Detection

• The **activity of a radioactive source** is the number of nuclear disintegrations per unit time occurring in a radioactive material.
  
  – A **Curie (Ci)** is a unit of activity equal to $3.700 \times 10^{10}$ disintegrations per second (dps).
  
  – A sample of technetium having an activity of $1.0 \times 10^{-2}$ Ci is decaying at a rate of

$$
(1.0 \times 10^{-2}) \times (3.700 \times 10^{10}) = 3.7 \times 10^{8} \text{ nuclei per second}
$$

Biological Effects and Radiation Dosage

• To monitor the effect of nuclear radiations on biological tissue, it is necessary to have a **measure of radiation dosage**.
  
  – The **rad** (from radiation absorbed dose) is the dosage of radiation that deposits $1 \times 10^{-2}$ J of energy per kilogram of tissue.
  
  – However, the biological effect of radiation not only on the energy deposited but also on the **type of radiation**.
The rem is a unit of radiation dosage used to relate various kinds of radiation in terms of biological destruction.

- It equals the rad times a factor for the type of radiation, called the relative biological effectiveness (RBE).

\[ \text{rems} = \text{rads} \times \text{RBE} \]

- Beta and gamma radiations have an RBE of about 1, where neutron radiation has an RBE about 5 and alpha radiation an RBE of about 10.

- A single dose of about 500 rems is fatal to most people.

Rate of Radioactive Decay

- The rate of radioactive decay, that is the number of disintegrations per unit time, is proportional to the number of radioactive nuclei in the sample.

- You can express this rate mathematically as

\[ \text{Rate} = kN_t \]

where \( N_t \) is the number of radioactive nuclei at time \( t \), and \( k \) is the radioactive decay constant.

- All radioactive decay follows first order kinetics as outlined in Chapter 14.

- Therefore, the half-life of a radioactive sample is related only to the radioactive decay constant.

Rate of Radioactive Decay

- The half-life, \( t_{1/2} \), of a radioactive nucleus is the time required for one-half of the nuclei in a sample to decay. (see Figure 20.11)

- The first-order relationship between \( t_{1/2} \) and the decay constant \( k \) is

\[ t_{1/2} = \frac{0.693}{k} \]
A Problem To Consider
• The decay constant for the beta decay of technetium-99 is $1.0 \times 10^{-13} \text{ s}^{-1}$. What is the half-life of this isotope in years?
  - Substitute the value of $k$ into our half-life equation.
  $$t_{1/2} = \frac{0.693}{1.0 \times 10^{-13} \text{ s}^{-1}} = 6.9 \times 10^{12} \text{ s}$$
  - Then convert from seconds to years.
  $$6.9 \times 10^{12} \text{ s} \times \frac{1 \text{ min}}{60 \text{ sec}} \times \frac{1 \text{ h}}{60 \text{ min}} \times \frac{1 \text{ d}}{24 \text{ h}} \times \frac{1 \text{ y}}{365 \text{ d}} = 2.2 \times 10^8 \text{ y}$$

Rate of Radioactive Decay
• Once you know the decay constant, you can calculate the fraction of radioactive nuclei remaining after a given period of time.
  - The first-order time-concentration equation is
  $$\ln \frac{N_t}{N_0} = -kt$$
A Problem To Consider

- Phosphorus-32 has a half-life of 14.3 days. What fraction of a sample of phosphorus-32 would remain after 5.5 days?
  - If we substitute $k = \frac{0.693}{t_{\frac{1}{2}}}$ we get
    \[
    \ln \frac{N_t}{N_0} = - \frac{0.693}{t_{\frac{1}{2}}} t
    \]
  - Substituting $t = 5.5$ d and $t_{\frac{1}{2}} = 14.3$ d, you obtain
    \[
    \ln \frac{N_t}{N_0} = \frac{-0.693 (5.5 \text{ d})}{(14.3 \text{ d})} = -0.267
    \]
  - Hence,
    \[
    \text{Fraction nuclei remaining} = \frac{N_t}{N_0} = e^{-0.267} = 0.77
    \]

- A radioactive tracer is a very small amount of radioactive isotope added to a chemical, biological, or physical system to study the system.
  - A series of experiments using tracers was carried out in the 1950s by Melvin Calvin at the University of California at Berkeley, to discover the mechanism of photosynthesis in plants.

Applications of Radioactive Isotopes

- Another example of radioactive tracers is isotopic dilution, a technique to determine the quantity of a substance in a mixture.
  - Human blood volumes are determined using the technique of isotopic dilution.

- Neutron activation analysis is an analysis of elements in a sample based on the conversion of stable isotopes to radioactive isotopes by bombarding a sample with neutrons.
  - Human hair samples are identified by neutron activation analysis.
Mass-Energy Calculations

- When nuclei decay, they form products of lower energy.
  - The change of energy is related to the change in mass, according to the mass-energy equivalence relation derived by Albert Einstein in 1905.
  - Energy and mass are equivalent and related by the equation
    \[ E = mc^2 \]
    Here \( c \) is the speed of light, \( 3.00 \times 10^8 \text{ m/s} \).

Mass-Energy Calculations

- When nuclei decay, they form products of lower energy.
  - If a system loses energy, it must also lose mass.
  - Though mass loss in chemical reactions is small (10^{-12} \text{ kg}), the mass changes in nuclear reactions are approximately a million times larger.
  - Consider the alpha decay of uranium-238 to thorium-234.
    \[ ^{238}\text{U} \rightarrow ^{234}\text{Th} + ^4\text{He} \]
    \[ ^{238.05078} \text{U} \rightarrow ^{234.04359} \text{Th} + ^4\text{He} \]
    - We have written the atomic mass (in amu) beneath each nuclide symbol. (see Table 21.3)

<table>
<thead>
<tr>
<th>Masses of Some Elements and Other Particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symbol</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>c</td>
</tr>
<tr>
<td>n</td>
</tr>
<tr>
<td>p</td>
</tr>
<tr>
<td>H</td>
</tr>
<tr>
<td>Li</td>
</tr>
<tr>
<td>Be</td>
</tr>
<tr>
<td>B</td>
</tr>
<tr>
<td>N</td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>O</td>
</tr>
<tr>
<td>Fe</td>
</tr>
</tbody>
</table>

(see Table 21.3)
\[ \text{The change in mass for this reaction, in molar amounts is} \]
\[ ^{238}\text{U} \rightarrow ^{234}\text{Th} + ^{4}\text{He} \]
\[ \Delta m = (234.04359 + 4.00260 - 238.05078) = -0.00459 \text{ g} \]

\[ \text{- The energy change for 1 mol of uranium-238 is} \]
\[ \Delta E = \Delta mc^2 = (-4.59 \times 10^{-6} \text{ kg}) \times (3.00 \times 10^8 \text{ m/s})^2 \]
\[ \Delta E = -4.13 \times 10^{11} \text{ J} = -4.13 \times 10^8 \text{ kJ} \]

\[ \text{Mass-Energy Calculations} \]
\[ \text{• The equivalence of mass and energy explains the fact that the mass of an atom is always less than the sum of the masses of its constituent particles.} \]
\[ \text{- When nucleons come together to form a stable nucleus, energy is released.} \]
\[ \text{- According to Einstein’s equation, there must be a corresponding decrease in mass.} \]

\[ \text{Mass-Energy Calculations} \]
\[ \text{• The binding energy of a nucleus is the energy needed to break a nucleus into its individual protons and neutrons.} \]
\[ ^{4}\text{He} \rightarrow ^{2}_{1}\text{p} + ^{2}_{0}\text{n} \]
\[ \Delta m = 0.03040 \text{ amu} \]
\[ \text{- Both binding energy and the corresponding mass defect are reflections of the stability of the nucleus.} \]
Figure 20.16 shows the values of binding energy per nucleon plotted against the mass number for various nuclides.

Note that nuclides near mass number 50 have the largest binding energies per nucleon.

For this reason, heavy nuclei might be expected to split to give lighter nuclei, while light nuclei might be expected to combine to form heavier nuclei.

Figure 201.16 Plot of binding energy per nucleon versus mass number

Nuclear Fission and Nuclear Fusion

- **Nuclear fission** is a nuclear reaction in which a heavy nucleus splits into lighter nuclei and energy is released. (See Animation: Nuclear Fission)

  - For example, one of the possible mechanisms for the decay of californium-252 is

\[
^{252}\text{Cf} \rightarrow ^{142}\text{Ba} + ^{106}\text{Mo} + ^{4}\text{n}
\]
In some cases a nucleus can be induced to undergo fission by bombardment with neutrons.

\[
{ }_{6}^{1}n + { }_{92}^{235}U \rightarrow { }_{54}^{142}Xe + { }_{38}^{90}Sr + { }_{0}^{1}n \\
{ }_{56}^{139}Ba + { }_{36}^{94}Kr + 3{ }_{0}^{1}n \\
{ }_{55}^{144}Cs + { }_{37}^{90}Rb + 2{ }_{0}^{1}n
\]

When uranium-235 undergoes fission, more neutrons are released creating the possibility of a chain reaction.

A chain reaction is a self-sustaining series of nuclear fissions caused by the absorption of neutrons released from previous nuclear fissions.

To sustain a nuclear chain reaction you must achieve a critical mass, which is the smallest mass of fissionable material required for a chain reaction.

A supercritical mass of fissionable material decays so rapidly as to cause a nuclear explosion.
A nuclear fission reactor is a device that permits a controlled chain reaction of nuclear fissions. (see Figure 20.19)

• Nuclear fission is a nuclear reaction in which a heavy nucleus splits into lighter nuclei and energy is released.
  - The fuel rods are the cylinders that contain fissionable material.
  - Control rods are cylinders composed of substances that absorb neutrons and can therefore slow the chain reaction.

Nuclear Fission and Nuclear Fusion

• Nuclear fusion is a nuclear reaction in which a light nuclei combine to give a stabler heavy nucleus plus possibly several neutrons, and energy is released. (See Animation: Nuclear Fusion)
  - An example of nuclear fusion is
    \[ ^1_1H + ^1_1H \rightarrow ^2_4He + ^0_1n \]
  - Such fusion reactions have been observed in the laboratory using particle accelerators.
  - Sustainable fusion reactions require temperatures of about 100 million °C.
Nuclear Fission and Nuclear Fusion

- **Nuclear fusion** is a nuclear reaction in which light nuclei combine to give a stabler heavy nucleus plus possibly several neutrons, and energy is released.
  - At these elevated temperature, a **plasma** results, that is, an electrically neutral gas of ions and electrons.
  - A magnetic fusion reactor uses a magnetic field to hold the plasma (see Figure 20.20).

Figure 20.20: Torus Fusion Reactor

Source: Princeton Plasma Physics Laboratory

Operational Skills

- Writing a nuclear equation
- Deducing a product or reactant in a nuclear equation
- Predicting the relative stability of nuclides
- Predicting the type of radioactive decay
- Using the notation for a bombardment reaction
- Calculating the decay constant from the activity
- Relating the decay constant, half-life, and activity
- Determining the fraction of nuclei remaining after a specified time
- Applying the carbon-14 dating method
- Calculating the energy change for a nuclear reaction