Chapter 21. Nuclear Chemistry

Common Student Misconceptions

- Initially, many students think that atoms of one element cannot be transformed into atoms of another element.
- Students often think that all radiation is man-made and harmful.
- Many students think that radioactivity is a man-made phenomenon.
- Students often think that the rate of radioactive decay depends on external conditions, such as *T* or *p*.
- Students often think that all isotopes of uranium are radioactive.

Teaching Tips

- This is new territory for students who have not taken advanced courses in physics.
- Radioactive decay processes are invariably first-order and therefore obey the rate law $\ln N_t/N_0 = -kt$ and the half-life expression $t_{1/2} = 0.693/k$, where k is the characteristic rate constant. Discussions of radionuclide half-lives may thus benefit from a short review of first-order kinetics from Chapter 14.

Lecture Outline

21.1 Radioactivity[1,2]

- **Nuclear reactions** involve changes in the atomic nuclei.
  - *Nuclear chemistry* is the study of nuclear reactions (their uses in chemistry and their impact on biological systems).
- When nuclei change spontaneously, emitting energy, they are said to be radioactive.
- Nuclear chemistry is the study of nuclear reactions and their uses and effects on biological systems.
- **Nucleons** are particles in the nucleus:
  - p^+: *proton*
  - n^0: *neutron*
  - *Atomic number* is the number of p^+.
  - *Mass number* is the number of $p^+ + n^0$.
    - The mass number is the total number of nucleons in the nucleus.
- *Isotopes* have the same number of p^+ but different numbers of n^0.
  - Different isotopes of the same element are distinguished by their mass numbers.
  - Different isotopes have different natural abundances.
  - Different isotopes of an element may be written using the name followed by the mass numbers:
    - Example: uranium-234

    They may also be written in a manner that shows the mass number as a superscript and the atomic number as a subscript:

$$^{234}_{92}\mathrm{U}$$

- A ***nuclide* is a nucleus containing a specified number of protons and neutrons.**
  - A **radionuclide** is a radioactive nucleus.
  - Atoms containing these nuclei are called **radioisotopes**.

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[1] "Radioactivity in the Classroom" from Further Readings
[2] "Identifying Students' Misconceptions about Nuclear Chemistry" from Further Readings

Nuclear Equations[3,4]

- Most nuclei are stable.
  - Radionuclides are unstable and spontaneously emit particles and/or electromagnetic radiation.
  - Example: Uranium-238 is radioactive.
    - It emits **alpha (α) particles**.
    - These are helium-4 particles.
      - A stream of these particles is called *alpha radiation*.
- When a nucleus spontaneously decomposes in this manner, we say it has decayed (*radioactive decay*).
  - *Nuclear equations* are used to represent this process.
    - In nuclear equations, the total number of nucleons is conserved.
    - We can represent the uranium-238 decay by the following nuclear equation:

$${}^{238}_{92}\text{U} \rightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\text{He}$$

    - The total number of protons and neutrons before a nuclear reaction must be the same as the total number of nucleons after the reaction.
    - If alpha particles are involved in the reaction, it may be described as **alpha decay**.

Types of Radioactive Decay[5,6,7,8,9]

- There are three types of radiation which we will consider:
  - α-Radiation is the loss of ${}^{4}_{2}\text{He}$ (**alpha particles**) from the nucleus.
  - β-Radiation is the loss of an electron from the nucleus.
    - These high-speed electrons are called **beta (β) particles**.
      - Example; iodine-131 undergoes decay by **beta emission**.
  - **Gamma (γ)**-Radiation is the loss of high-energy photons from the nucleus.
- Nucleons can undergo two other types of decay:
  - **positron emission**
    - A positron is a particle with the same mass as an electron but with the opposite sign.
  - **electron capture**
    - The nucleus captures an electron from the electron cloud surrounding the nucleus.
- Representations:
  - In nuclear chemistry, to ensure the conservation of nucleons we write all particles with their atomic and mass numbers: ${}^{4}_{2}\text{He}$ and ${}^{4}_{2}\alpha$ represent α-radiation.
- Nucleons can undergo decay. For example:
  - (β-emission) ${}^{1}_{0}\text{n} \rightarrow {}^{1}_{1}\text{p} + {}^{0}_{-1}\text{e}$
  - (electron capture) ${}^{1}_{1}\text{p} + {}^{0}_{-1}\text{e} \rightarrow {}^{1}_{0}\text{n}$

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[3] "Nuclear Chemistry: State of the Art for Teachers" from Further Readings
[4] "Radioactivity: A Natural Phenomenon" from Further Readings
[5] "Beta Decay Diagram" from Further Readings
[6] "Separation of Alpha, Beta, and Gamma Rays" Animation from Instructor's Resource CD/DVD
[7] "Scientists Honor Centennial of the Discovery of Radioactivity" from Further Readings
[8] "Radioactivity in Everyday Life" from Further Readings
[9] "Teaching Nuclear Science: A Cosmological Approach" from Further Readings

21.2 Patterns of Nuclear Stability[10]

Neutron-to-Proton Ratio[11]

- The proton has high mass and high charge.
- Therefore, the proton-proton repulsion is large.
- In the nucleus the protons are very close to each other.
- The cohesive forces in the nucleus are called *strong nuclear forces*.
  - Neutrons are involved with the strong nuclear force.
- As more protons are added (the nucleus gets heavier) the proton-proton repulsion gets larger.
  - Therefore, the heavier the nucleus, the more neutrons are required for stability.
- The *belt of stability* is the portion of a graph of (number of protons) vs. (number of neutrons) that contains all stable nuclei.
  - All nuclei with 84 or more protons are radioactive.
  - Nuclei above the belt of stability undergo β-emission.
    - When an ${}^{0}_{-1}e$ is lost; the number of neutrons decreases and the number of protons increases.
  - Nuclei below the belt of stability undergo β^{+}-emission or electron capture.
    - This results in the number of neutrons increasing and the number of protons decreasing.
  - Nuclei with atomic numbers greater than 83 usually undergo α-emission.
    - The number of protons and neutrons decreases (in steps of 2).

Radioactive Series[12,13]

- A nucleus usually undergoes more than one transition on its path to stability.
- The series of nuclear reactions that accompany this path is the **radioactive series**, or the **nuclear disintegration series**.

Further Observations[14]

- **Magic numbers** are 2, 8, 20, 28, 50, or 82 protons or 2, 8, 20, 28, 50, 82, or 126 neutrons.
  - Nuclei with a “magic number” of nucleons are more stable than nuclei that do not have the magic number of nucleons.
  - The magic numbers correspond to filled, closed-shell nucleon configurations.
- Nuclei with even numbers of protons and neutrons are more stable than nuclei with any odd numbers of nucleons.
  - The *shell model* of the nucleus rationalizes these observations.
    - The shell model of the nucleus is similar to the shell model for the atom.
  - Pairs of protons and neutrons in the nucleus are analogous to pairs of electrons in the atom.

21.3 Nuclear Transmutations[15]

- **Nuclear transmutations** are nuclear reactions resulting from the collisions between nuclei or between a nucleus and a neutron.
- For example, nuclear transmutations can occur using high-velocity α-particles:

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

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[10] “Teaching Aids for Nuclear Chemistry” from Further Readings
[11] Figure 21.2 from Transparency Pack
[12] “Uranium-238 Decay Series” Activity from Instructor’s Resource CD/DVD
[13] Figure 21.3 from Transparency Pack
[14] “Chemistry of the Heaviest Elements—One Atom at a Time” from Further Readings
[15] “Modeling Nuclear Decay: A Point of Integration between Chemistry and Mathematics” from Further Readings

Accelerating Charged Particles

- To overcome electrostatic forces, charged particles need to be accelerated before they react.
  - **Particle accelerators** (atom smashers, cyclotrons, synchnotrons) are used to accelerate particles using strong magnetic and electrostatic fields.
  - The Relativistic Heavy Ion Collider (RHIC) at Brookhaven National laboratory, the Tevatron at Fermilab and the Large Hadron Collider (LHC) are the largest particle accelerators in the world.

Reactions Involving Neutrons

- Most synthetic isotopes used in medicine and research are made using neutrons as projectiles.
- An example is the preparation of cobalt-60 for use in cancer radiation therapy.

Transuranium Elements[16]

- **Transuranium elements** follow uranium in the periodic table.

21.4 Rates of Radioactive Decay[17,18,19]

- Radioactive decay is a first-order process.
- Each isotope has a characteristic **half-life**.
  - Half-lives are not affected by temperature, pressure or chemical composition.
  - Natural radioisotopes tend to have longer half-lives than synthetic radioisotopes.
  - Half-lives range from fractions of a second to millions of years.
  - Naturally occurring radioisotopes can be used to determine the age of a sample.
    - This process is radiometric dating.

Radiometric Dating[20,21]

- The half-life of any particular nuclide is constant.
  - Thus, half –life may be used as a nuclear clock to determine the age of objects.
  - Dating of objects based on their isotopes and isotope abundances is called *radiometric dating*.
- Carbon-14 (^{14}C) is used to determine the ages of organic compounds by radiometric dating.
- For ^{14}C to be detected, the object must be less than 50,000 years old.
  - We assume that the ratio of ^{12}C to ^{14}C has been constant over time.
  - The half-life of ^{14}C is 5,715 years.
  - ^{14}C undergoes decay to ^{14}N via β-decay:

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

- Other dating methods are also used.
  - Uranium-lead dating has been used to estimate the age of the Earth at approximately 4.0-4.5 billion years.

Calculations Based on Half-life[22,23]

- Radioactive decay is a first-order process:

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[16] “Heavy Stuff” from Further Readings
[17] “Nucleogenesis! A Game with Natural Rules for Teaching Nuclear Synthesis and Decay” from Further Readings
[18] “First-Order Process” Animation from Instructor’s Resource CD/DVD
[19] “Radioactive Decay” Activity from Instructor’s Resource CD/DVD
[20] “Archaeological Dating” from Further Readings
[21] “Radioactive Dating: A Method for Geochronology” from Further Readings
[22] “California Earthquakes: Predicting the Next Big One Using Radiocarbon Dating” from Further Readings
[23] “Searching for Real Time” from Further Readings

$$\text{Rate} = kN$$

- If the activity of a sample at time = t is N_t, and the activity at time = 0 is N_0, then:

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

- The half-life of the sample is given by:

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

- In radioactive decay the constant, k, is called the *decay constant*.
- The rate of decay is called **activity** (disintegrations per unit time).

- There are several units used to express activity or radioactivity.
  - The **becquerel** (Bq) is the SI unit of radioactivity.
    - 1 Bq = 1 disintegration per second (dps).
  - The **Curie** (Ci) is an older, but still very widely used, unit of activity.
    - 1 Ci = 3.7×10^{10} disintegrations per second.

21.5 Detection of Radioactivity[24,25]

- Matter is ionized by radiation.
- A Geiger counter determines the amount of ionization by detecting an electric current.
  - A thin window is penetrated by the radiation and causes the ionization of Ar gas.
  - The ionized gas carries a charge, so current is produced.
    - The current pulse generated when the radiation enters is amplified and counted.
- Other methods are also used to detect radioactivity.
- One common method employs an instrument called a scintillation counter.
  - A substance called a *phosphor* is allowed to interact with radiation.
  - Light is produced when radiation strikes a suitable phosphor.
  - This light is detected and used to quantify the amount of radiation.

Radiotracers[26,27,28,29,30,31,32]

- Photosynthesis has been studied using ^{14}C:

$$6\ {}^{14}CO_2 + 6H_2O \xrightarrow[\text{chlorophyll}]{\text{sunlight}} {}^{14}C_6H_{12}O_6 + 6O_2$$

- The carbon dioxide is said to be ^{14}C labeled.
- The presence of ^{14}C in the intermediates or products of photosynthesis can be determined.
  - ^{14}C is detected as it moves from carbon dioxide to ultimately become incorporated into glucose.
    - Thus the path of the carbon atoms may be *traced*.
    - **Radiotracers** are used to follow an element through a chemical reaction.

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24 "How Radioactive Is Your Banana?" from Further Readings
25 "Development and Proliferation of Radioimmunoassay Technology" from Further Readings
26 "Radioactivity in the Service of Many" from Further Readings
27 "Positron Emission Tomography Merges Chemistry with Biological Imaging" from Further Readings
28 "PET Practice" from Further Readings
29 "Visualizing the Mind" from Further Readings
30 "Nuclear Medicine and Positron Emission Tomography: An Overview" from Further Readings
31 "Special Agents" from Further Readings
32 "The Role of Chemistry in Positron Emission Tomography" from Further Readings

21.6 Energy Changes in Nuclear Reactions

- Einstein showed that mass and energy are proportional:

$$E = mc^2$$

  - If a system loses mass, it loses energy (exothermic).
  - If a system gains mass, it gains energy (endothermic).
- Since c^2 is a large number, small changes in mass cause large changes in energy.
- Mass and energy changes in nuclear reactions are much greater than in chemical reactions.
- Consider:

$$^{238}_{92}\text{U} \rightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\text{He}$$

- For 1 mol of $^{238}_{92}\text{U}$, the masses are:

$$238.0003\text{ g} \rightarrow 233.9942\text{ g} + 4.0015\text{ g}.$$

  - The change in mass during the reaction is:

$$233.9942\text{ g} + 4.0015\text{ g} - 238.0003\text{ g} = -0.0046\text{ g}$$

  - The process is exothermic because the system has lost mass.

$$\Delta E = \Delta\left(mc^2\right) = c^2(\Delta m)$$

$$\Delta E = \left(2.9979\times10^8\text{ m/s}\right)^2(-0.0046\text{ g})\left(\frac{1\text{ kg}}{1000\text{ g}}\right)$$

$$\Delta E = -4.1\times10^{11}\,\frac{\text{kg m}^2}{\text{s}^2} = -4.1\times10^{11}\text{ J}$$

- To calculate the energy change per mole of ^{238}U :

Nuclear Binding Energies[33]

- The mass of a nucleus is less than the mass of its nucleons.
  - **Mass defect** is the difference between the mass of a nucleus and the masses of its nucleons.
  - **Nuclear binding energy** is the energy required to separate a nucleus into its nucleons.
  - Since $E = mc^2$, the binding energy is related to the mass defect.
- The larger the binding energy, the more likely a nucleus is to decompose.
- Heavy nuclei gain stability by splitting into smaller nuclei.
  - They give off energy if fragmented into two mid-sized nuclei.
  - This reaction is called **fission**.
- Very light nuclei are combined or fused together to form more massive nuclei.
  - Energy is released from this nuclear **fusion**.

21.7 Nuclear Power: Fission[34,35]

- Nuclear power plants and most forms of nuclear weapons utilize nuclear fission.
- Splitting of heavy nuclei is exothermic for large mass numbers.
- Consider a neutron bombarding a ^{235}U nucleus.
  - The heavy ^{235}U nucleus can split in several different ways such as:

$$^{1}_{0}\text{n} + {}^{235}_{92}\text{U} \rightarrow {}^{142}_{56}\text{Ba} + {}^{91}_{36}\text{Kr} + 3\,{}^{1}_{0}\text{n}$$

  - For every ^{235}U fission, an average of 2.4 neutrons are produced.

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[33] Figure 21.12 from Transparency Pack
[34] "Enriching Uranium" from Further Readings
[35] Figure 21.15 from Transparency Pack

    - Each neutron produced can cause the fission of another ^{235}U nucleus.
  - The number of fissions and the resulting energy increase rapidly.
  - Reactions that multiply this way are called **chain reactions**.
- Without controls, an explosion results.
  - Consider the fission of a nucleus that results in the production of neutrons.
  - Each neutron can cause another fission.
  - Eventually, a chain reaction forms.
  - A minimum mass of fissionable material is required for a chain reaction (or neutrons will escape before they can cause another fission).
    - This is called a **critical mass**.
  - When enough material is present for a chain reaction, we have a critical mass.
  - If the mass is lower than the critical mass (subcritical mass), the neutrons escape and a chain reaction does not occur.
  - At the critical mass, one neutron from each fission is effective in causing another fission.
  - Any mass over the critical mass is called **supercritical mass**.
- Critical mass for ^{235}U is about 1 kg.

Nuclear Reactors[36,37,38,39]

- Use fission as a power source.
- Use a subcritical mass of ^{235}U (^{238}U is enriched with about 3% ^{235}U).
- *Fuel elements* contain enriched $^{235}UO_2$ pellets are encased in Zr or stainless steel tubes.
- *Control rods* are composed of Cd or B, which absorb neutrons.
  - They help to regulate the flux of neutrons.
- *Moderators* are inserted to slow down the neutrons to make them more easily captured.
- A *containment shell* surrounds the reactor as an added safety precaution.
- Heat produced in the reactor core is removed by a *primary coolant.*
  - Water acts as both moderator and primary coolant in a *pressurized water reactor*.
- Much of the heat is transferred to a *secondary coolant.*
  - The secondary coolant is converted to high-pressure steam and is used to drive a turbine to generate electricity.
- About 2/3 of commercial reactors are pressurized water reactors.
  - Variations on the basic design include:
    - *Boiling water reactors*: generates steam by boiling the primary coolant (no secondary coolant is needed).
    - *Heavy water reactor*: used D_2O as moderator and primary coolant.
    - *Gas-cooled reactors*: used a gas such as CO_2 as primary coolant and graphite as moderator.
    - *High-temperature pebble-bed reactor*: not yet in commercial use.

Nuclear Waste

- Fission products accumulate as a reactor operates.
  - These reduce the reactor efficiency.
  - Commercial reactors are stopped periodically to replace or reprocess the fuel elements.
  - Transportation of the radioactive fuel rods using the nation's roads has met intense opposition.
  - Spent rods are stored at the reactor sites but the fuel is reprocessed outside of the country.
- Storage and disposal of radioactive wastes from such reactions is not a simple problem.
  - The fission products are extremely radioactive.

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[36] Figure 21.19 from Transparency Pack
[37] "Nuclear Power for the Future" from Further Readings
[38] "Lise Meitner and the Discovery of Nuclear Fission" from Further Readings
[39] "Aspects of Nuclear Waste Disposal of Use in Teaching Basic Chemistry" from Further Readings

- The potential for environmental contamination by long-lived isotopes is a serious consideration.
- *Fast breeder reactors* may represent a method of getting more power out of existing uranium sources and potentially reducing radioactive waste.
- The material separated from the uranium and plutonium during reprocessing is less radioactive than waste from other reactors.

21.8 Nuclear Power: Fusion[40,41]

- Light nuclei can fuse to form heavier nuclei.
  - Most reactions in the Sun are fusion reactions.
- Fusion products are not usually radioactive, so fusion is a good energy source.
- Also, the hydrogen required for the reaction can easily be supplied by seawater.
  - However, high energies are required to overcome repulsion between nuclei before the reaction can occur.
  - High energies are achieved by high temperatures, the reactions are known as **thermonuclear reactions**.
- Fusion of tritium and deuterium requires a temperature of about 40,000,000 K:

$$^{2}_{1}H + ^{3}_{1}H \rightarrow ^{4}_{2}He + ^{1}_{0}n$$

  - These temperatures can be achieved in a nuclear bomb, or a *tokamak*.
  - A tokamak is a magnetic bottle; strong magnetic fields contain a high-temperature plasma, so the plasma does not come into contact with the walls. (No known material can survive the temperatures required for fusion.)
  - To date, temperatures of about 100,000,000 K have been achieved in a tokamak.
- Research continues.

FORWARD REFERENCES

- Hydrogen as a fuel used by the Sun and other stars to produce energy will be mentioned in Chapter 22 (section 22.2).

21.9 Radiation in the Environment and Living Systems

- **Ionizing radiation** involves ionization that occurs when radiation removes an electron from an atom or molecule.
  - This is generally more harmful to biological systems than **nonionizing radiation**.
    - Radiation absorbed by tissue causes excitation (nonionizing radiation) or ionization (ionizing radiation).
- Most ionizing radiation interacts with water in tissues to form H_2O^+.
  - The H_2O^+ ions react with water to produce H_3O^+ and OH.
  - OH has one unpaired electron.
    - It is called the *hydroxy radical*.
    - The unpaired electron is shown by writing the species with a single dot: $\bullet OH$
    - This is an example of a **free radical**, a substance with unpaired electrons.
    - Free radicals generally undergo chain reactions.
    - They are capable of causing substantial damage in biological tissues.
- The penetrating power of radiation is a function of the mass of the radiation.
  - Therefore, γ-radiation (zero mass) penetrates much further than β-radiation, which penetrates much further than α-radiation.

Radiation Doses

- Absorbed radiation is measured in:

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[40] "Fusion—A Potential Power Source" from Further Readings
[41] "Uranium to Electricity: The Chemistry of the Nuclear Fuel Cycle" from Further Readings

- **Gray**: 1 Gy is the SI unit for absorption of 1 J of energy per kg of tissue.
- **Rad** is the *r*adiation *a*bsorbed *d*ose.
  - One rad is the absorption of 10^{-2} J of radiation per kg of tissue.
  - The rad is the unit most often used in medicine.
- One gray is equivalent to 100 rads.

- Because not all forms of radiation have the same effect, we correct for the differences using the RBE (*relative biological effectiveness*).
  - The RBE is about 1 for β- and γ-radiation and 10 for α-radiation.
  - A **rem** (*r*oentgen *e*quivalent for *m*an) = (rads) x (RBE).
  - The SI unit for effective dosage is the Sievert (1Sv = 1Gy = 100 rem).
    - The rem is the unit of radiation damage usually used in medicine.
- The average annual exposure to all natural sources of ionizing radiation (*background radiation)* is about 360 mrem.

Radon[42]

- The nucleus is $^{222}_{86}\text{Rn}$ which is a decay product of $^{238}_{92}\text{U}$
- Radon exposure accounts for more than half of the 360 mrem annual exposure to ionizing radiation.
- Rn is a noble gas; it is extremely stable.
  - Therefore, it is inhaled and exhaled without any chemical reactions occurring.
  - The half-life of $^{222}_{86}\text{Rn}$ is 3.82 days.
  - It decays as follows:

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

- The α-particles produced have a high RBE.
  - Therefore, inhaled Rn is thought to be a cause of lung cancer.
- The situation is complicated because $^{218}_{84}\text{Po}$ has a short half-life (3.11 min) also:

$$^{218}_{84}\text{Po} \rightarrow {}^{214}_{82}\text{Pb} + {}^{4}_{2}\text{He}$$

  - The $^{218}_{84}\text{Po}$ gets trapped in the lungs, where it continually produces α-particles.
- The EPA recommends $^{222}_{86}\text{Rn}$ levels in homes be kept below 4 pCi per liter of air.
  - Radon testing kits are readily available in many areas of the country.

FORWARD REFERENCES

- Group 8A elements will be the subject of section 22.3 in Chapter 22.

[42] "How Much Radon Is Too Much?" from Further Readings

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