Nuclear Chemistry

Nuclear Equations

- Nucleons: particles in the nucleus:
  - p^+: proton
  - n^0: neutron.
- Mass number: the number of $p^+ + n^0$.
- Atomic number: the number of p^+.
- Isotopes: have the same number of p^+ and different numbers of n^0.
- In nuclear equations, number of nucleons is conserved:

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

Nuclear Equations

- In the decay of ^{131}I an electron is emitted. For balancing purposes, we assign the electron an atomic number of -1.
- The total number of protons and neutrons before a nuclear reaction must be the same as the total number of nucleons after reaction.

Radioactivity

Types of Radioactive Decay

- There are three types of radiation which we consider:
  - α-Radiation is the loss of $^{4}_{2}He$ from the nucleus,
  - β-Radiation is the loss of an electron from the nucleus,
  - γ-Radiation is the loss of high-energy photon from the nucleus.
- In nuclear chemistry to ensure conservation of nucleons we write all particles with their atomic and mass numbers: $^{4}_{2}He$ and $^{4}_{2}\alpha$ represent α-radiation.

Types of Radioactive Decay

- Nucleons can undergo decay:

$$^{1}_{0}n \rightarrow {}^{1}_{1}p^+ + {}^{0}_{-1}e^- \text{ (}\beta\text{-emission)}$$

$$^{0}_{-1}e^- + {}^{0}_{1}e^+ \rightarrow 2{}^{0}_{0}\gamma \text{ (positron annihilation)}$$

$$^{1}_{0}p^+ \rightarrow {}^{1}_{0}n + {}^{0}_{1}e^+ \text{ (positron or } \beta^+\text{-emission)}$$

$$^{1}_{1}p^+ + {}^{0}_{-1}e^- \rightarrow {}^{1}_{0}n \text{ (electron capture)}$$

- A positron is a particle with the same mass as an electron but a positive charge.

Patterns of Nuclear Stability

Neutron-to-Proton Ratio

- 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. The heavier the nucleus, the more neutrons are required for stability.
- The belt of stability deviates from a 1:1 neutron to proton ratio for high atomic mass.

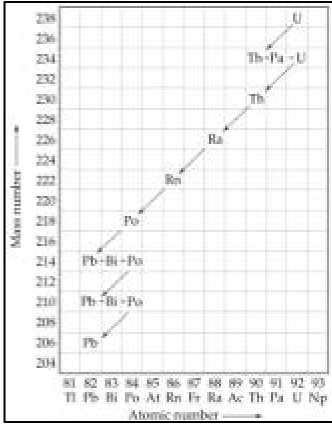
Patterns of Nuclear Stability

Neutron-to-Proton Ratio

- At Bi (83 protons) the belt of stability ends and all nuclei are unstable.
  - Nuclei above the belt of stability undergo β-emission. An electron is lost and the number of neutrons decreases, 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

- 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.
- Nuclei resulting from radioactive decay are called daughter nuclei.



Radioactive Series

For ^{238}U, the first decay is to ^{234}Th (α-decay). The ^{234}Th undergoes β-emission to ^{234}Pa and ^{234}U. ^{234}U undergoes α-decay (several times) to ^{230}Th, ^{226}Ra, ^{222}Rn, ^{218}Po, and ^{214}Pb. ^{214}Pb undergoes β-emission (twice) via ^{214}Bi to ^{214}Po which undergoes α-decay to ^{210}Pb. The ^{210}Pb undergoes β-emission to ^{210}Bi and ^{210}Po which decays (α) to the stable ^{206}Pb.

Patterns of Nuclear Stability

Further Observations

- Magic numbers are nuclei with 2, 8, 20, 28, 50, or 82 protons or 2, 8, 20, 28, 50, 82, or 126 neutrons.
- Nuclei with even numbers of protons and neutrons are more stable than nuclei with any odd 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.)
- The magic numbers correspond to filled, closed-shell nucleon configurations.

Nuclear Transmutations

Using Charged Particles

- Nuclear transmutations are the collision between nuclei.
- For example, nuclear transmutations can occur using high velocity α-particles:

$$^{14}_{7}\text{N} + {}^{4}_{2}\alpha \rightarrow {}^{17}_{8}\text{O} + {}^{1}_{1}\text{p}.$$

- The above reaction is written in short-hand notation:

$$^{14}_{7}\text{N}(\alpha,\text{p})^{17}_{8}\text{O}.$$

- To overcome electrostatic forces, charged particles need to be accelerated before they react.

Nuclear Transmutations

Using Charged Particles

- A cyclotron consists of D-shaped electrodes (dees) with a large, circular magnet above and below the chamber.
- Particles enter the vacuum chamber and are accelerated by making the dees alternatively positive and negative.
- The magnets above and below the dees keep the particles moving in a circular path.
- When the particles are moving at sufficient velocity they are allowed to escape the cyclotron and strike the target.

Rates of Radioactive Decay

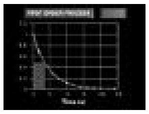
- ^{90}Sr has a half-life of 28.8 yr. If 10 g of sample is present at $t = 0$, then 5.0 g is present after 28.8 years, 2.5 g after 57.6 years, etc. ^{90}Sr decays as follows

$$^{90}_{38}\text{Sr} \rightarrow {}^{90}_{39}\text{Y} + {}^{0}_{-1}\text{e}$$

- 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.

Rates of Radioactive Decay

- Half-lives can range from fractions of a second to millions of years.
- Naturally occurring radioisotopes can be used to determine how old a sample is.
- This process is radioactive dating.



Rates of Radioactive Decay

Dating

- Carbon-14 is used to determine the ages of organic compounds because half-lives are constant.
- We assume the ratio of ^{12}C to ^{14}C has been constant over time.
- For us to detect ^{14}C the object must be less than 50,000 years old.
- The half-life of ^{14}C is 5,730 years.
- It undergoes decay to ^{14}N via β-emission:

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

Rates of Radioactive Decay

Calculations Based on Half Life

- Radioactive decay is a first order process:

$$\text{Rate} = kN$$

- In radioactive decay the constant, k, is the decay constant.
- The rate of decay is called activity (disintegrations per unit time).
- If N_0 is the initial number of nuclei and N_t is the number of nuclei at time t, then

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

Rates of Radioactive Decay

Calculations Based on Half Life

- With the definition of half-life (the time taken for $N_t = \frac{1}{2}N_0$), we obtain

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

Detection of Radioactivity

- Matter is ionized by radiation.
- 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 carried a charge and so current is produced.
- The current pulse generated when the radiation enters is amplified and counted.

Radiotracers

- Radiotracers are used to follow an element through a chemical reaction.
- 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.

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 (8.99×10^{16} m^2/s^2) small changes in mass cause large changes in energy.
- Mass and energy changed in nuclear reactions are much greater than chemical reactions.

Energy Changes in Nuclear Reactions

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

- for 1 mol of the masses are

  238.0003 g → 233.9942 g + 4.015 g.

- The change in mass during reaction is

  233.9942 g + 4.015 g - 238.0003 g = -0.0046 g.

- The process is exothermic because the system has lost mass.
- To calculate the energy change per mole of ${}^{238}_{92}\mathrm{U}$:

$$\begin{aligned}\Delta E &= \Delta\left(mc^2\right) = c^2 \Delta m \\ &= \left(2.9979 \times 10^8 \text{ m/s}^2\right)^2 \left(-0.0046 \times 10^{-3} \text{ kg}\right) \\ &= -4.1 \times 10^{11} \text{ J}\end{aligned}$$

Nuclear Binding Energies

- The mass of a nucleus is less than the mass of their nucleons.
- Mass defect is the difference in mass between the nucleus and the masses of nucleons.
- 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.

Energy Changes in Nuclear Reactions

Nuclear Binding Energies

- The larger the binding energy the more likely a nucleus will decompose.
- Average binding energy per nucleon increases to a maximum at mass number 50 - 60, and decreases afterwards.
- Fusion (bringing together nuclei) is exothermic for low mass numbers and fission (splitting of nuclei) is exothermic for high mass numbers.

Nuclear Fission

- Splitting of heavy nuclei is exothermic for large mass numbers.
- During fission, the incoming neutron must move slowly because it is absorbed by the nucleus,
- The heavy ${}^{235}\mathrm{U}$ nucleus can split into many different daughter nuclei, e.g.

$${}^{1}_{0}\mathrm{n} + {}^{238}_{92}\mathrm{U} \rightarrow {}^{142}_{56}\mathrm{Ba} + {}^{91}_{36}\mathrm{Kr} + 3{}^{1}_{0}\mathrm{n}$$

  releases 3.5×10^{-11} J per ${}^{235}\mathrm{U}$ nucleus.

Nuclear Fission

- For every ${}^{235}\mathrm{U}$ fission 2.4 neutrons are produced.
- Each neutron produced can cause the fission of another ${}^{235}\mathrm{U}$ nucleus.
- The number of fissions and the energy increase rapidly.
- Eventually, a chain reaction forms.
- Without controls, an explosion results.
- Consider the fission of a nucleus that results in daughter neutrons.

Nuclear Fission

- 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 escape before they cause another fission).
- When enough material is present for a chain reaction, we have critical mass.
- Below critical mass (subcritical mass) the neutrons escape and no chain reaction occurs.

Nuclear Fission

Nuclear Reactors

- Use fission as a power source.
- Use a subcritical mass of ^{235}U (enrich ^{238}U with about 3% ^{235}U).
- Enriched $^{235}UO_2$ pellets are encased in Zr or stainless steel rods.
- Control rods are composed of Cd or B, which absorb neutrons.

Nuclear Fusion

- Light nuclei can fuse to form heavier nuclei.
- Most reactions in the Sun are fusion.
- Fusion products are not usually radioactive, so fusion is a good energy source.
- Also, the hydrogen required for reaction can easily be supplied by seawater.
- However, high energies are required to overcome repulsion between nuclei before reaction can occur.

- High energies are achieved by high temperatures: the reactions are thermonuclear.
- Fusion of tritium and deuterium requires about 40,000,000K:

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

- These temperatures can be achieved in a nuclear bomb or a tokamak.

Biological Effects of Radiation

- The penetrating power of radiation is a function of mass.
- Therefore, γ-radiation (zero mass) penetrates much further than β-radiation, which penetrates much further than α-radiation.
- Radiation absorbed by tissue causes excitation (nonionizing radiation) or ionization (ionizing radiation).
- Ionizing radiation is much more harmful than nonionizing radiation.

Biological Effects of 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.
- Free radicals generally undergo chain reactions.