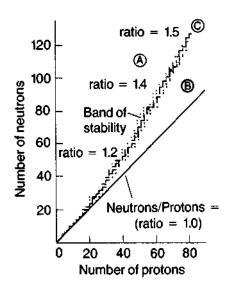
Nuclear Chemistry

Radioactivity and Half-Life

All elements with more than 82 protons have unstable nuclei (i.e. Bi and beyond!) and are said to be radioactive. This is because there are too many protons in too small a volume to be stable – the repulsive forces among the protons are too strong to allow such nuclei to exist. There are, however, certainly isotopes of elements smaller than 82 that are also unstable. Scientists view nuclear instability not only in terms of nuclear size but also due to nuclear binding energy and the ratio of neutrons to protons.

Neutron to Proton Ratio

One theory of nuclear structure assumes that nucleons exist in energy levels within the nucleus. In accord with this theory, it can be shown that the most stable nuclei, and hence nuclei in which nucleons occupy the lowest energy level, are those with certain neutron-proton combinations. This becomes apparent when the number of neutrons is plotted versus the number of protons for the known stable isotopes.

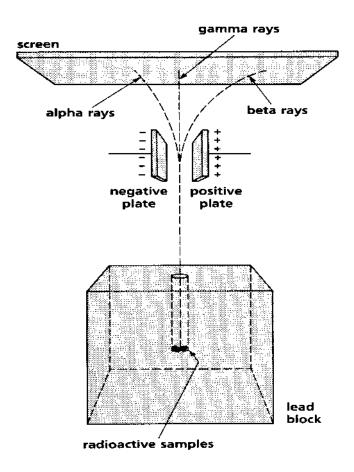


Several facts can be derived from analysis of the plot of the number of neutrons versus the number of protons.

- 1. Stable nuclei are confined to a narrow zone indicating that the neutron-to-proton ratio (n/p) required for stability is relatively restricted.
- 2. The n/p ratio of stable nuclei increases with an increase in the number of protons. The stable isotopes of elements 1 to 20 have a n/p ratio of 1 or greater, while stable isotopes of elements 21 to 82 have n/p ratios greater

- than 1. Thus, the greater the number of protons in a nucleus, the greater the number of neutrons per proton required to form a stable nucleus.
- 3. Elements with more than 83 protons can form no stable nuclei. Thus, no stable nucleus with more than 83 protons can form regardless of the number of neutrons. It appears that nuclear forces cannot permanently exceed repulsive forces when more than 83 protons are assembled.

Radioactive elements become stable by emitting particle radiation and high energy electromagnetic radiation. These occur as three basic types and they were discovered when a radioactive source (such as U-238) was placed in a lead container with a small opening. The radiation coming out of the opening was subjected to an electric field and it was shown that the radiation consisted of three types:



- Particles deflected toward the negative plate called alpha (α) particles
- Particles deflected toward the positive plate called beta (β) particles
- Electromagnetic waves unaffected by the plates called gamma (χ) waves

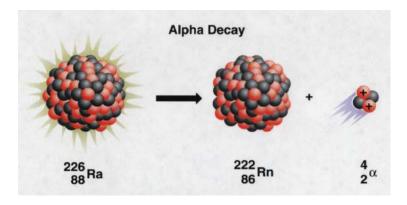
Types of Radiation

I. Alpha Decay

- Involves emission of a 2 proton-2 neutron unit from the nucleus; this unit is a helium nucleus
- Symbol is 4 He (α)
- Slow speed
- Poor penetrating power (can be stopped by sheet of paper)
- High ionizing capacity (when hitting an atom it can "knock off" an atom's valence electron causing it to become an ion

Example:
$${226 \text{Ra} \rightarrow {}^{4}\text{He} + {}^{222}\text{Rn} \atop 88} \atop 2}$$

note the mass number (P + N) decreases by 4 and the atomic number (P only) decreases by 2

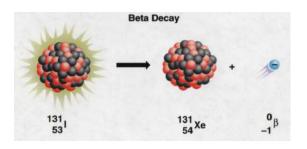


II. Beta Decay

- Involves emission of a high speed electron from the nucleus
- A neutron breaks down to a proton (which remains in the nucleus) and an electron which is ejected from the nucleus
- fairly high speed
- Moderate penetrating power (can be stopped by the thickness of your chemistry textbook
- Moderate ionizing capacity
- Symbol is ${}^{o}e(\beta)$

Example:
$${}^{214}\text{Pb} \rightarrow {}^{0}\text{e} + {}^{214}\text{Bi} \atop 82 \quad {}^{-1} \quad 83$$

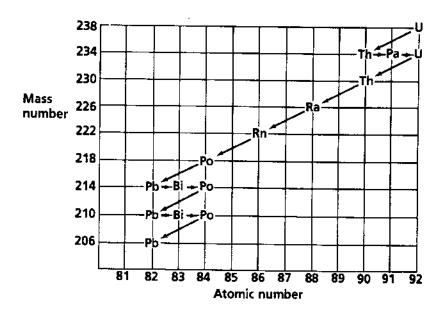
note the atomic number increases by 1 while the mass number stays the same



III. Gamma Radiation

- Travel at speed of light
- High penetrating power
- Very small ionizing capacity
- Emissions of gamma rays reduce the energy content of a nucleus without change in atomic or mass number
- Symbol is χ

Note the decay series of the isotope U-238 to the stable Pb-206 isotope. U-238 has a half-life of about 4.5×10^9 years (approximately the age of the earth). The ratio of U-238 to Pb-206 in a sample rock is used in geologic dating. The diagram below illustrates the decay series of uranium-238.



IV. Positron production

- Particle with same mass as an electron but opposite charge
- Has the effect of changing a proton to a neutron
- Results no change in mass number but a decrease of 1 in atomic number
- Symbol is ⁰e

Example:
$${}^{22}\text{Na} \rightarrow {}^{0}\text{e} + {}^{22}\text{Ne}$$
 ${}^{11} + {}^{1} = {}^{10}$

V. Electron Capture

- An inner-orbital electron is captured by the nucleus
- Does not occur often and is accompanied by gamma radiation

Example
$${}^{201}\text{Hg} + {}^{0}\text{e} \rightarrow {}^{201}\text{Au} + {}^{0}\lambda \atop 80 \quad {}^{-1} \quad {}^{79} \quad {}^{0}$$

The Regents reference table (Table O) below shows the notation and symbols used in nuclear chemistry. You should become very familiar with the notation and symbols.

Table O
Symbols Used in Nuclear Chemistry

Name	Notation	Symbol	
alpha particle	${}^4_2\text{He or } {}^4_2\alpha$	α	
beta particle (electron)	$_{-1}^{0}$ e or $_{-1}^{0}$ $\boldsymbol{\beta}$	β-	
gamma radiation	00γ	γ	
neutron	l ₀ n	n	
proton	H or Ip	p	
positron	0 or 0β	β+	

Problems

- 1. Write balanced nuclear equations for the following processes:
 - a) the decay of gold-198:

- b) the decay of uranium-235:
- c) the decay of phosphorous-32:
- d) the decay of potassium-37:
- e) the decay of francium-220

Half-Life

The half-life of an unstable isotope is the time required for one-half of the nuclei in a sample to decay:

$$X g \rightarrow 1/2X g \rightarrow 1/4X g \rightarrow 1/8X g \rightarrow 1/16X g \rightarrow etc$$

The half-life of a radioactive isotope is independent of temperature and pressure and the mass of the unstable element. The half-life is also characteristic of that particular isotope. The Regents reference table (Table N) lists the half-life and decay mode for selected nuclides.

Radiocarbon Dating

One of the best known radioactive isotopes is carbon-14. The half-life of carbon-14 is 5730 years. This radioactive isotope is produced in the Earth's atmosphere by the action of cosmic rays on ordinary atmospheric nitrogen (N-14). (Cosmic rays are streams of high-energy charged particles and neutrons from outer space that collide with atoms in the Earth's upper atmosphere.) This action results in the nitrogen-14 being converted to carbon-14. The reaction is as follows:

$${}^{14}N + {}^{1}n \rightarrow {}^{14}C + {}^{1}H$$

New atoms of C-14 are produced at the same rate that the isotope decays. Scientists assume that the production of C-14 has been essentially constant for a long time. After being produced by the cosmic rays, the C-14 is then oxidized in the atmosphere to form ¹⁴CO₂, which mixes with the ¹²CO₂ already present in the atmosphere. As a result, the atmosphere always contains a fixed ratio of ¹⁴CO₂ to ¹²CO₂.

What makes C-14 such an important isotope? The answer is in the way in which carbon dioxide is used by plants and animals. Carbon dioxide is an essential part of the process of photosynthesis in plants. Photosynthesis is the process by which green plants use the sun's energy to convert carbon dioxide and water into sugars and starches. The sugars and starches, in turn, are food for animals that eat the plants and exhale carbon dioxide. Because this cycle exposes plants and animals to a constant source of C-14, the amount of this isotope in living plants and animals is constant. The emission of beta particles is likewise constant as the isotope decays.

The incorporation of C-14 into plant and animal tissues stops once the organism dies. The emission of beta particles will then drop as the C-14 decays. After 5730 years the rate of beta emissions will have dropped to one half the rate in living organisms; after 11, 460 years the rate will have dropped to one quarter, and so forth. By determining the rate of beta emission from plant and animal remains or products – such as wooden objects, textiles, and leather – scientists can estimate the age of these objects. Such estimates are accurate up to about 7000 years and give a reasonable approximation up to 30, 000 years. (After this length of time, the rate of beta emissions is too slow to be measured reliably.)

Table N Selected Radioisotypes

Nuclide	Half-Life	Decay Mode	Nuclide Name	
¹⁹⁸ Au	2,69 d	β	gold-198	
14C	5730 y	β	earbon-I4	
³⁷ Ca	175 ms	β¹	calcium-37	
⁶⁰ Co	5.26 y	β-	cobalt-60	
$^{137}\mathrm{Cs}$	30.23 y	β-	cesium-137	
53 _{Fe}	8.51 min	β-	iron-53	
220Fr	27.5 s	α	francium-220	
3H	12.26 y	β-	hydrogen-3	
131I	8.07 d	β-	iodine-131	
³⁷ K	1.23 s	β.	potassium-37	
⁴² K	12.4 h	β-	potassium-42	
85Kr	10.76 y	β-	krypton-85	
16 _N	7.2 s	β	nitrogen-16	
¹⁹ Ne	17.2 s	β+	ncon-19	
32P	14.3 d	β-	phosphorus-32	
²³⁹ Pu	$2.44 \times 10^4 \text{ y}$	α	plutonium-239	
²²⁶ Ra	1600 y	α	radium-226	
²²² Rn	3.82 d	α	radon-222	
⁹⁰ Sг	28.1 y	β-	strontium-90	
⁹⁹ Tc	$2.13 \times 10^{5} \text{ y}$	β-	teclmetium-99	
²³² Th	$1.4 \times 10^{10} \mathrm{y}$	α	thorium-232	
233 _U	$1.62 \times 10^{5} \text{ y}$	α	uranium-233	
²³⁵ U	$7.1 \times 10^{8} \text{ y}$	α	uranium-235	
²³⁸ U	$4.51 \times 10^9 \text{ y}$	α	oranium-238	

 $\begin{aligned} & ms = milliseconds; \ s = seconds; \ min = minutes; \\ & h = bours; \ d = days; \ y = years \end{aligned}$

Half-Life Problems

Problem 1

A radioactive element has a half-life of 4 hours. What fraction of an original sample will remain at the end of 12 hours?

Problem 2

A sample original sa		has a mas	s of 1.0 gr	ram after	112 years.	Calculate the	mass of the
originar sa	impre.						

Problem 3

Exactly $1.0~{\rm g}$ of Na-24 decomposes by beta emission to $1/8~{\rm g}$ in 45 hours. Determine its half-life.

4. A sample of fossilized wood that, when alive, would have contained 24 g of carbon-14. It now contains 1.5 g of carbon-14. Determine the approximate age of the sample.

5. A 64 g sample of germanium-66 is left undisturbed for 12.5 hours. At the end of that period, only 2.0 g remain. Calculate the half-life of this material.

6. Cobalt-60 has a half-life of 5.26 years. If a pellet that has been in storage for 26.5 years contains 14.5 g of cobalt-60, determine the mass of this isotope that was present when the pellet was put into storage.

Nuclear Reactions

It was discovered that the mass of an atomic nucleus is less than the sum of the masses of individual protons and neutrons making up the nucleus. The mass which is lost is known as mass defect and the energy equivalent is known as the binding energy of the nucleus. Recall iron has the highest binding energy per nucleon.

- I. **Transmutations** conversion of one element to a different one.
 - a) natural alpha and beta decay
 - b) <u>artificial</u> involves "hitting" a nucleus with an alpha particle or bare proton in a particle accelerator. **Particle accelerators** use magnetic fields to accelerate charged particles (like protons, electrons and alpha particles but not neutrons) to near the speed of light before colliding them.

Example:
$${}^{14}N + {}^{4}He \rightarrow {}^{17}O + {}^{1}H$$

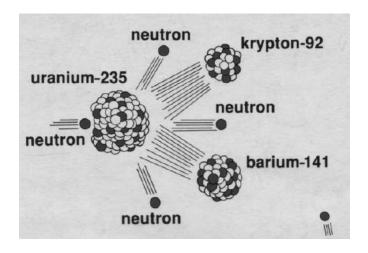
Note: the transuranic elements (those beyond uranium) are all man-made:

Example:
$${}^{238}U + {}^{1}n \rightarrow {}^{239}U \rightarrow {}^{239}Np + {}^{0}e \rightarrow {}^{239}Pu + {}^{0}e = {}^{92}0 + {}^{0}e = {}^{92}0 + {}^{0}e = {}^{1}e = {}^$$

II. Nuclear Fission

- splitting a large nucleus into smaller nuclei of similar size with release of energy
- there are two fissionable isotopes: U-235 and Pu-239

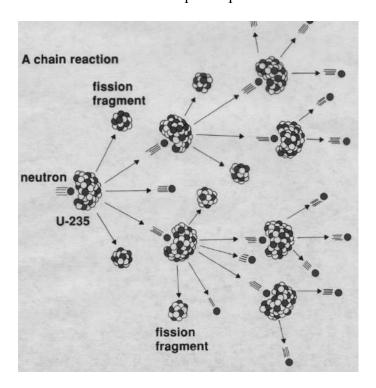
example:
$${}^{235}U + {}^{1}n \rightarrow {}^{139}Ba + {}^{94}Kr + 3 {}^{1}n \atop 92 \quad 0 \quad 56 \quad 36 \quad 0$$



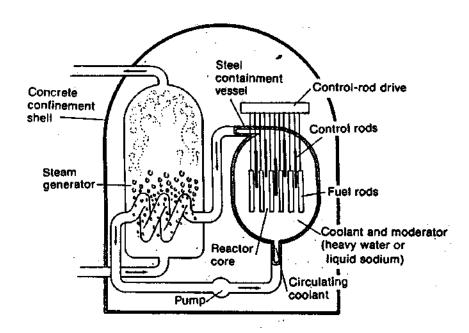
two factors of monumental consequence:

- the difference in mass between reactants and products indicated a significant mass lost this mass was converted to energy via $E = mc^2$
- the potential for a **chain reaction** a reaction that is self-sustaining that is, the reaction generates the means to trigger additional reactions. The amount of fissionable material that will support a chain reaction is termed the **critical mass**.

Uncontrolled fission reaction = atomic bomb Controlled fission reaction = nuclear power plants



Nuclear Fission Reactor



Main components:

Nuclear Fuel – Uranium-235 is the only naturally occurring isotope of uranium that will undergo fission. The percentage of U-235 in a pure sample of uranium is only 0.7% and this amount is insufficient to sustain a chain reaction. The U-235 is separated from pure uranium to produce "enriched" uranium (about 3% U-235). This mixture is used to produce uranium oxide for use as fuel in the reactor. Pellets of uranium oxide are packed in stainless steel tubes called **fuel rods**.

Moderators – used to slow down the neutrons produced as a result of fission reactions. The moderator functions to absorb some of the energy of the high kinetic energy neutrons to slow them down so they can be captured by the U-235 nuclei. Some common materials used for moderators include graphite, molten sodium, and heavy water (water containing a deuterium hydrogen).

Control Rods – function to control the rate of the fission reaction by <u>absorbing neutrons</u>. Substances such as cadmium or boron are very effective absorbers of neutrons. Control rods made from one of these substances are located side-by-side with the fuel rods in the reactor. By inserting and withdrawing these rods, the supply of neutrons can be regulated and, in cases of emergency, shut off completely.

Coolants – the primary coolant, which is often water at high pressure, is circulated around the reactor core where it absorbs the tremendous amount of heat generated by the fission reaction. Since the water is under pressure it reaches 300°C without boiling and is pumped into a steam generator. The steam generator contains water under normal pressure. The heat from the primary coolant is transferred to this water (secondary coolant) which causes it to form steam. The steam is then used to drive a

turbine which generates electricity. The primary coolant, now at a lower temperature, is pumped back into the reactor core and the cycle continues.

Shields – the core of a reactor is surrounded by a containment vessel in which the primary coolant circulates. The walls of this vessel are lined with thick steel slabs to reduce the flow of radiation from the core. The containment vessel, in turn, is surrounded by thick concrete blocks designed to protect personnel from radiation exposure.

Advantages: provides much needed energy

Disadvantages: radioactive waste

thermal pollution of river water possibility of mechanical/human error

Breeder Reactor – some control rods are replaced with rods containing U-238. The U-238 absorb neutrons and then decay to form fissionable Pu-239.

Nuclear Waste

When the fuel rods in fission reactors become "spent", they contain a mixture of highly radioactive isotopes. These include both the fission products and what remains of the nuclear fuel. Some of these fission products have very short half-lives (on the order of seconds) while others have half-lives of hundreds of thousands of years. All nuclear power plants currently store their spent fuel rods in holding tanks containing water. The water cools the rods and acts as a radiation shield. The spent fuel rods are held in these water "pools" for many years as they continue to generate heat.

In 1982 the U.S. Congress passed the Nuclear Waste Policy Act, which established a timetable for choosing and preparing sites for deep underground disposal of radioactive materials. The disposal plan calls for the incorporation of the spent nuclear fuel into blocks of borosilicate glass that will be packed in corrosion-resistant metal containers and then buried in deep, stable rock formations. In 1987 Congress amended the Nuclear Waste Policy Act to make Yucca Mountain in Nevada the primary potential site.

III. Nuclear Fusion

- two small nuclei (hydrogen) collide to form a bigger nucleus (He) the release of energy
- significant mass loss converted to energy
- no chain reaction; no critical mass
- fusion reactions are the source of the Sun's energy; millions of tons of matter (H) are converted to energy in the Sun every second

- in order for fusion reactions to occur, exceedingly high temperatures are needed (to overcome repulsive forces between protons); it is necessary to" confine" the plasma with electromagnets
- fusion bomb = uncontrolled fusion = hydrogen bomb

example:
$${}^{3}H + {}^{2}H \rightarrow {}^{4}He + 1n + ENERGY$$

Advantages of nuclear fusion:

- clean
- few radioactive products
- fuel inexhaustible (H in water in oceans)
- no possibility of reaction going out of control

Radioisotopes

Uses include as tracers (C-14), dating (C-14 and U-238/Pb-206 ratio), diagnosis of brain tumors (Tc) thyroid disease (I-131), etc.