Chapter 20: Nuclear Chemistry

Key topics:
Nuclear reactions
Nuclear stability and decay
Radioactive decay

Nuclei and Nuclear Reactions

The nucleus of an atom can change because of

- radioactive decay (some nuclei are unstable)

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

- nuclear transmutation (nucleus collides with a particle)

$^{14}_{7}\mathrm{N} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{p}$ (nitrogen in atmosphere; neutrons from cosmic rays)

Notation:

mass number = number of protons and neutrons $\leftarrow {}^{14}_{6}\mathrm{C}$

atomic number = number of protons $\leftarrow$

Species often involved in nuclear reactions:

$\underbrace{{}^{1}_{1}\mathrm{H} \text{ or } {}^{1}_{1}\mathrm{p}}_{\text{proton}}$ $\underbrace{{}^{0}_{-1}e \text{ or } {}^{0}_{-1}\beta}_{\text{electron}}$ $\underbrace{{}^{0}_{+1}e \text{ or } {}^{0}_{+1}\beta}_{\text{positron}}$

$\underbrace{{}^{4}_{2}\alpha \text{ or } {}^{4}_{2}\mathrm{He}}_{\alpha \text{ particle}}$ $\underbrace{{}^{1}_{0}\mathrm{n}}_{\text{neutron}}$

What is the difference between representing an electron with *e* or β?

They are both electrons, but the notation tells us whether the electron comes from an orbital (usually a 1s atomic orbital) or from the nucleus (a neutron decays to yield a proton and an electron).

An α particle is identical to the ^{4}He nucleus.

TABLE 20.1 Comparison of Chemical Reactions and Nuclear Reactions

Chemical Reactions	Nuclear Reactions
1. Atoms are rearranged by the breaking and forming of chemical bonds.	1. Elements are converted to other elements (or isotopes).
2. Only electrons in atomic or molecular orbitals are involved in the reaction.	2. Protons, neutrons, electrons, and other subatomic particles such as α particles may be involved.
3. Reactions are accompanied by the absorption or release of relatively small amounts of energy.	3. Reactions are accompanied by the absorption or release of tremendous amounts of energy.
4. Rates of reaction are influenced by temperature, pressure, concentration, and catalysts.	4. Rates of reaction normally are not affected by temperature, pressure, or catalysts.

Balancing nuclear reactions

The mass numbers and the atomic numbers must balance.

e.g.,

$^{90}_{38}\mathrm{Sr}$ decays to what by emitting a β particle?

Answer:

$^{90}_{38}\mathrm{Sr} \rightarrow \mathrm{X} + {}^{0}_{-1}\beta$

so X must be $^{90}_{39}\mathrm{X}$ which is Yttrium $= {}^{90}_{39}\mathrm{Y}$

e.g.,
identify X in the following nuclear reaction $\quad {}^{222}_{86}\mathrm{Rn} \rightarrow \mathrm{X} + {}^{4}_{2}\alpha$
Answer:
X must be $\quad {}^{218}_{84}\mathrm{X}$ which is Polonium $= {}^{218}_{84}\mathrm{Po}$

Types of radiation

alpha (α) radiation: stream of α particles (helium nuclei)

- collide with air molecules to collect $2e^-$, becomes He
- stopped by a few inches of air, or a piece of paper
- cannot penetrate skin
- if an α emitter enters your lungs it can cause damage because it removes electrons from molecules in its path, leading to the formation of free radicals.

beta (β) radiation: stream of β particles (electrons)

- stopped by several feet of air, several millimeters of plastic, or an inch of wood
- can penetrate human skin to the “germinal layer”, where new skin cells are produced

gamma (γ) radiation: stream of γ particles (x-rays)

- very damaging
- hard to stop because they carry no charge
- used to sterilize food products and single-use medical supplies (syringes, catheters, gauze, etc)

Name	Charge	Symbol	Shield	Distance Traveled through air
alpha	positive	α	paper or clothing	2-4 cm
beta	negative	β	Heavy clothing, plastic	2-3 m
gamma	neutral	γ	lead, concrete	500 m

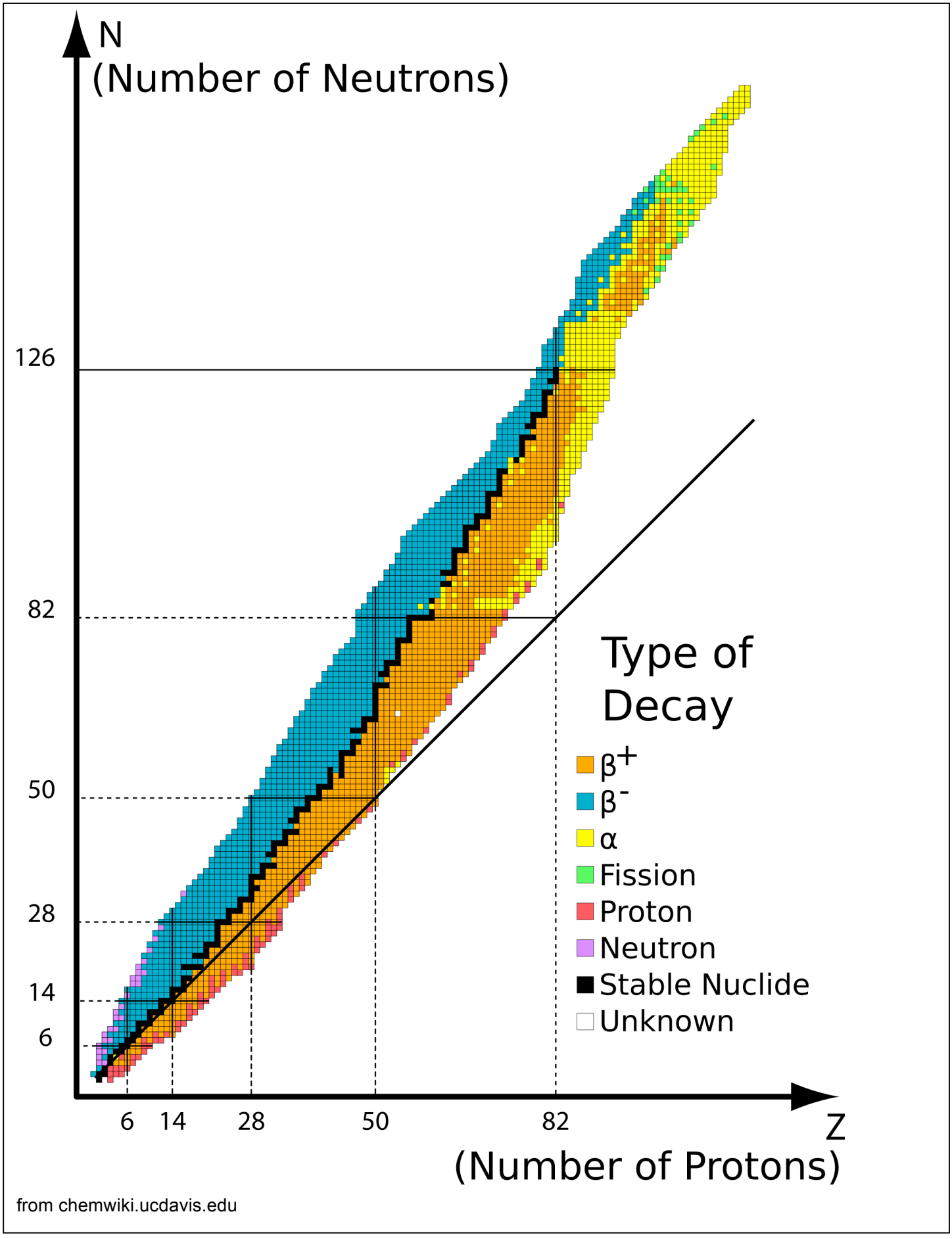
Nuclear Stability

- many stable nuclei contain 2, 8, 20, 50, 82, or 126 protons or neutrons (called *magic numbers*). For example, tin (Sn, Z = 50) has 10 stable isotopes!
- many more stable nuclei have even numbers of both protons and neutrons as opposed to odd numbers

TABLE 20.2 Number of Stable Isotopes with Even and Odd Numbers of Protons and Neutrons

Protons	Neutrons	Number of Stable Isotopes
Odd	Odd	4
Odd	Even	50
Even	Odd	53
Even	Even	164

- all isotopes of elements with Z > 83 are unstable (radioactive)
- all isotopes of technetium (Tc, Z = 43) and promethium (Pm, Z = 61) are unstable (radioactive)



from chemwiki.ucdavis.edu

For Z < 20: neutron / proton ratio close to 1 for stability

As Z increases, the neutron / proton ratio for stability increases

There is a “belt” or “band” of stability (zone with stable nuclei)

Above the band of stability:
- too many neutrons
- expect β particle radiation

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

$$^{1}_{0}\mathrm{n} \rightarrow {}^{1}_{1}\mathrm{p} + {}^{0}_{-1}\beta$$

Below the band of stability
- too many protons
- expect positron radiation or electron capture

$$^{38}_{19}\mathrm{K} \rightarrow {}^{38}_{18}\mathrm{Ar} + {}^{0}_{+1}\beta$$

$$^{37}_{18}\mathrm{Ar} + {}^{0}_{-1}e \rightarrow {}^{37}_{17}\mathrm{Cl}$$

$$^{1}_{1}\mathrm{p} \rightarrow {}^{1}_{0}\mathrm{n} + {}^{0}_{+1}\beta$$

$$^{1}_{1}\mathrm{p} + {}^{0}_{-1}e \rightarrow {}^{1}_{0}\mathrm{n}$$

Isotopes with Z > 83
- expect α radiation

Nuclear binding energy: Energy required to break the nucleus into its individual *nucleons* (protons and neutrons).

This is a quantitative measure of nuclear stability.

Shows up as a *mass defect*: the sum of the mass of the protons and neutrons is greater than the nucleus mass !!

e.g., Consider aluminum, which has 100% natural abundance of the $^{27}_{13}\mathrm{Al}$ isotope. There are 13 protons and 14 neutrons.

Proton mass = 1.00728 amu; neutron mass = 1.008665 amu
13 x 1.00728 amu + 14 x 1.008665 amu = 27.21595 amu.
(also 13 electrons = 13 x 0.00054858 amu = 0.00713 amu)

But an aluminum atom has a mass of 26.98154 amu.
The formation of $^{27}_{13}\mathrm{Al}$ is exothermic because the mass defect is released as energy. This energy is required to break up the nucleus into its separate protons and neutrons.

Mass defect: 27.21595 amu – 26.98154 amu = 0.23441 amu
We convert this to energy using Einstein's equation:

$$E = mc^2 = \frac{0.23441 \text{ amu}}{6.0221418 \times 10^{26} \text{ amu/kg}} \times (2.99792458 \times 10^8 \text{ m/s})^2$$
$$= 3.5 \times 10^{-11} \text{ J or, multiplying by Avogadro's number, } 2.1 \times 10^{10} \text{ kJ/mol}$$

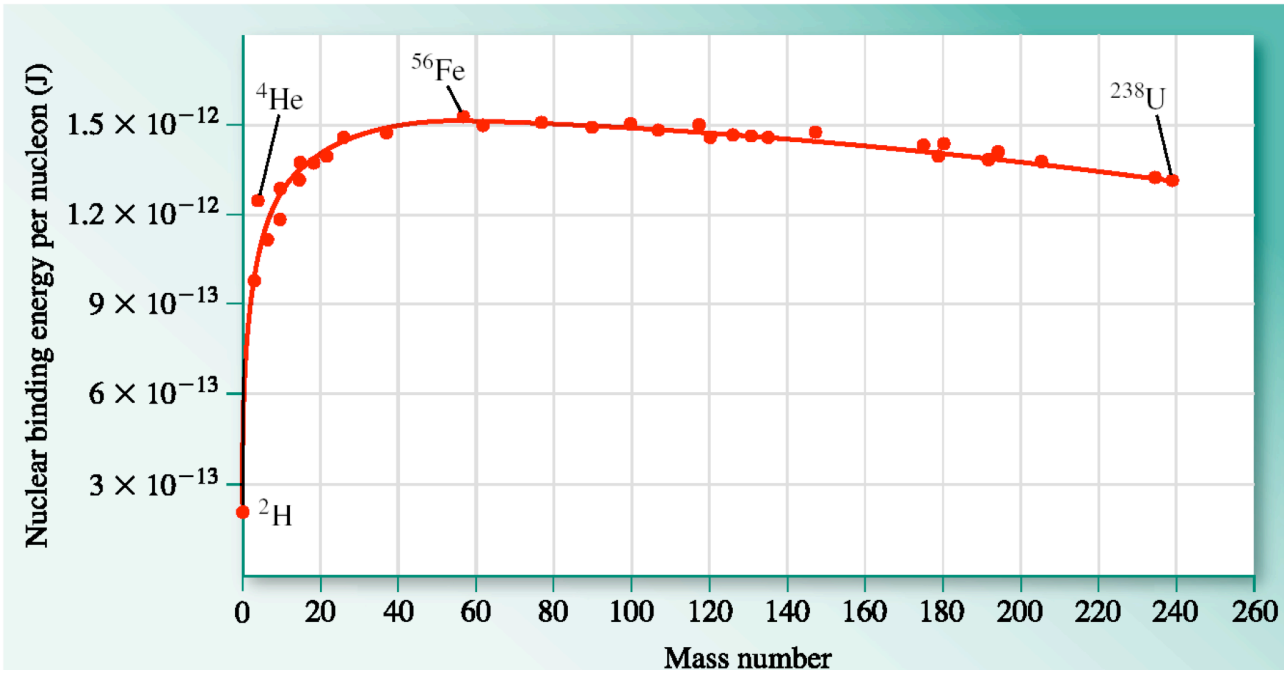
What should we compare to? The combustion of methane releases 890 kJ/mol of heat.

$$\frac{2.1 \times 10^{10} \text{ kJ/mol}}{890 \text{ kJ/mol}} = 2.37 \times 10^7$$

so about 24 million times more energy !!

This is the nuclear fusion process, which occurs naturally in the sun. It is considered a possible future energy source but there are still technical difficulties to obtain energy in this way.

$$\text{nuclear binding energy per nucleon} = \frac{\text{nuclear binding energy}}{\text{number of nucleons}}$$

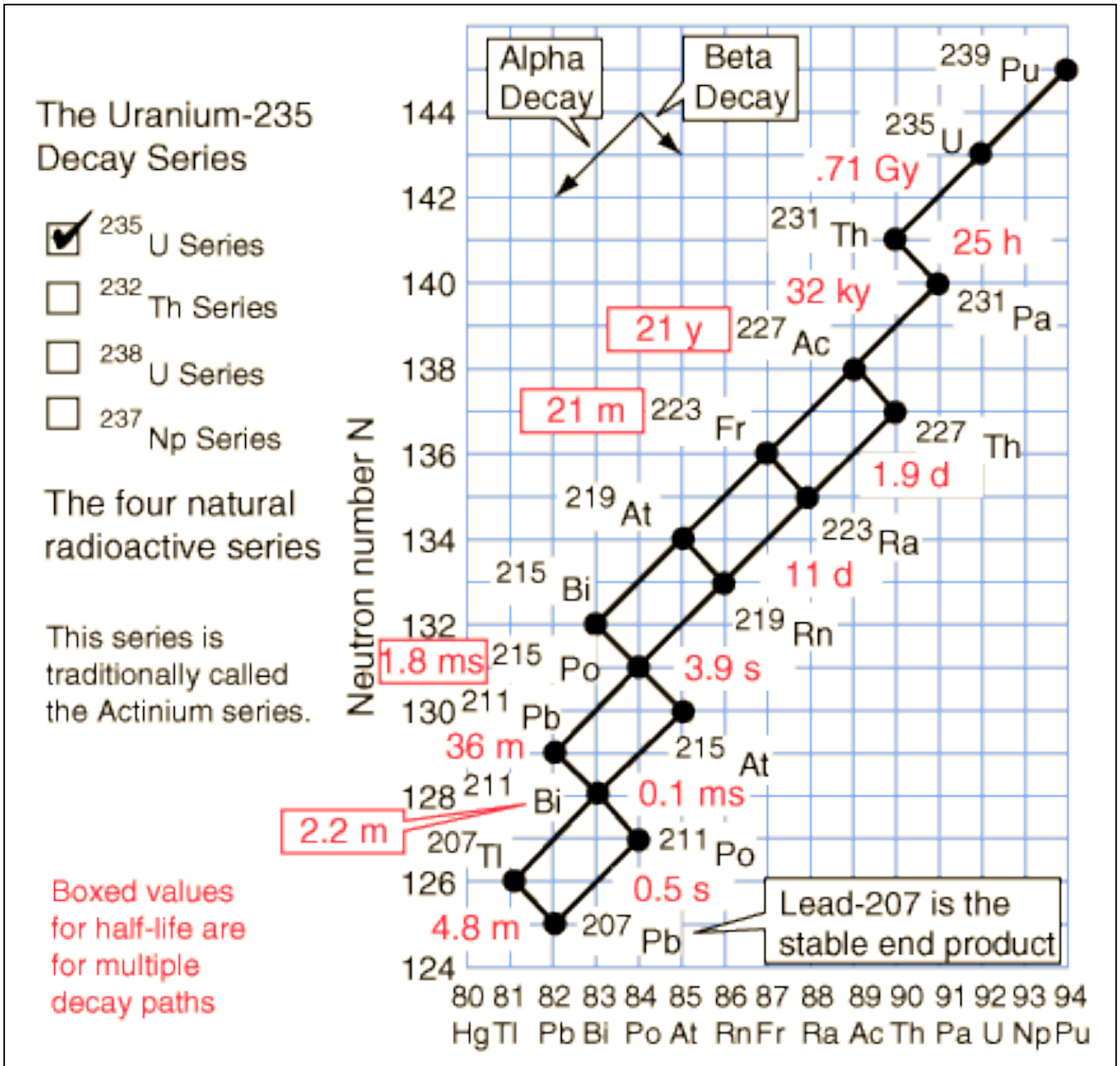


Natural Radioactivity

The disintegration of a radioactive nucleus is often the beginning of a *radioactive decay series*.
There are 4 naturally occurring series.

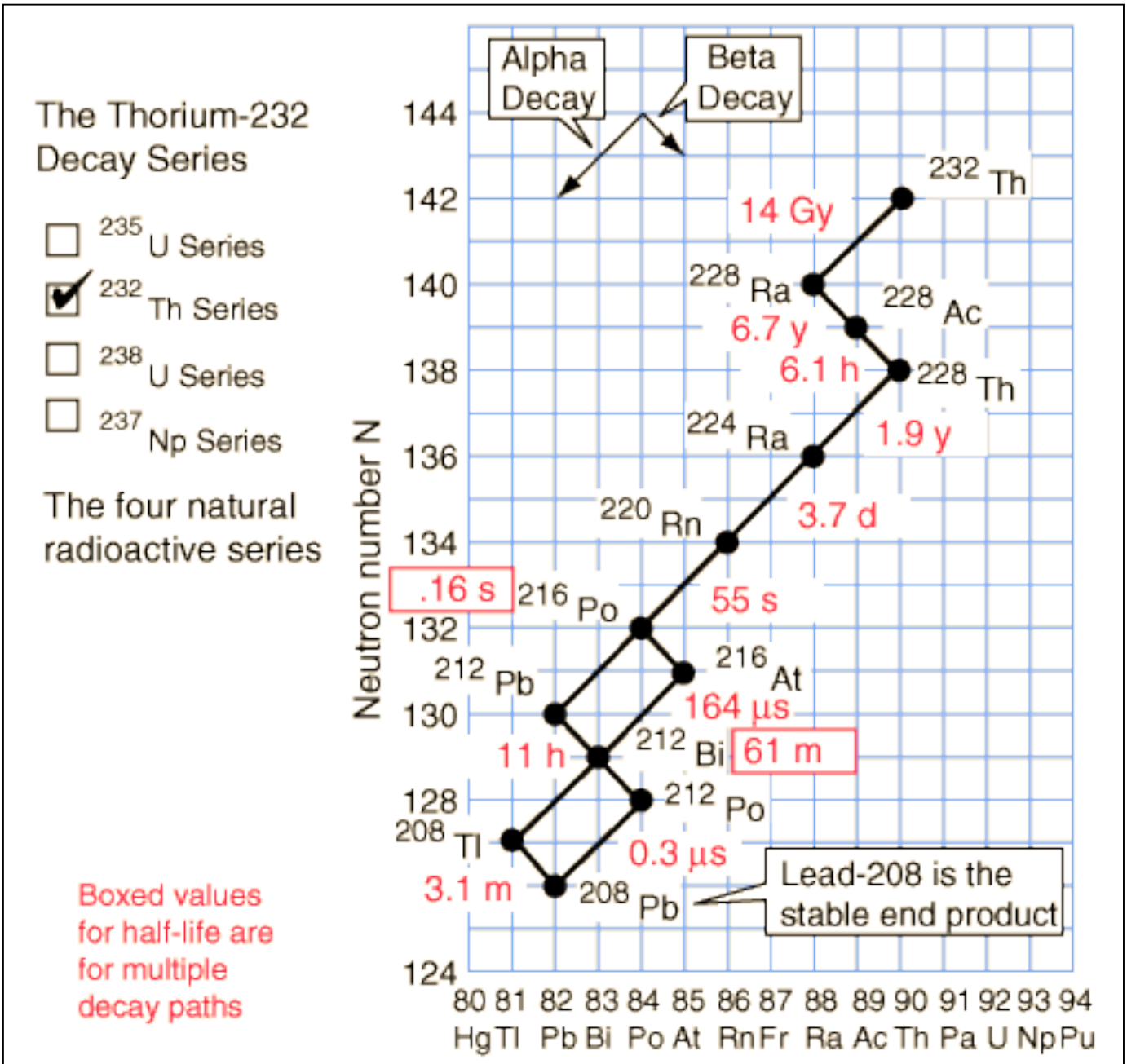
The series ends when a stable isotope is generated.

The beginning isotope is called the *parent* and the product isotope(s) are called the *daughter*(s).



from http://hyperphysics.phy-astr.gsu.edu

$1\mu s = 10^{-6}s$, $1\ ms = 10^{-3}s$, $1\ My = 10^{6}y$, $1\ Gy = 10^{9}y$



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Kinetics of radioactive decay

All radioactive decays obey first-order kinetics.

The Chapter 19 formula

$$\ln[\mathrm{A}]_t - \ln[\mathrm{A}]_0 = -kt \quad \text{or} \quad \ln\frac{[\mathrm{A}]_t}{[\mathrm{A}]_0} = -kt \quad \text{or} \quad [\mathrm{A}]_t = [\mathrm{A}]_0 e^{-kt}$$

becomes

$$\ln\frac{N_t}{N_0} = -kt \qquad \text{and} \qquad t_{1/2} = \frac{0.693}{k}$$

where N = number of radioactive nuclei

We can use this kinetics to date objects.

e.g., Carbon dating: (half life of carbon-14 = 5715 years)

carbon-14 is produced when atmospheric nitrogen is bombarded by cosmic rays

$$^{14}_{7}\mathrm{N} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{H}$$

and then the carbon-14 decays according to

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

A piece of linen cloth found at an ancient burial site is found to have a ^{14}C activity of 4.8 disintegrations per minute. Determine the age of the cloth. Assume that the carbon-14 activity of an equal mass of living flax (the plant from which linen is made) is 14.8 disintegrations per minute.

Solution:
First we find k:

$$k = \frac{0.693}{5715 \text{ yr}} = 1.21 \times 10^{-4} \text{ yr}^{-1}$$

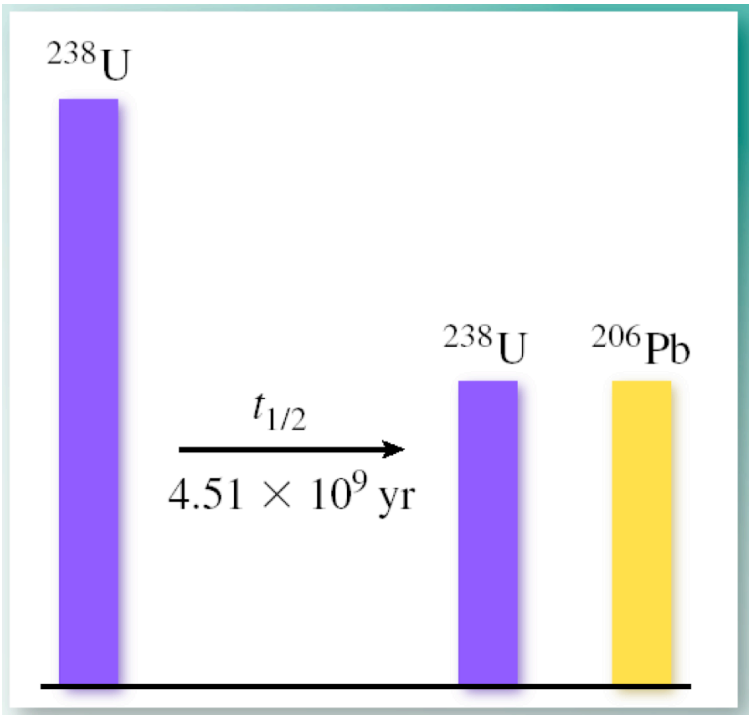
We use activity in place of the number of radioactive nuclei since the activity is proportional to the number of nuclei.

$$\ln \frac{^{14}\text{C activity in artifact}}{^{14}\text{C activity in living flax}} = -kt \qquad \Rightarrow \ln \frac{4.8}{14.8} = -kt$$

$$t = \frac{-1.126}{-1.21 \times 10^{-4} \text{ yr}^{-1}} = 9306 \text{ years old}$$

e.g., ^{238}U dating: (half life of uranium-238 = 4.51 x 10^9 years)

$$^{238}_{92}\text{U} \rightarrow \ ^{206}_{82}\text{Pb} + 8\ ^{4}_{2}\alpha + 6\ ^{0}_{-1}\beta$$



Used for determining the age of rocks.

After one half-life, we expect to find equal amounts of uranium and lead, namely

$$\text{mass ratio } \frac{^{206}_{82}\text{Pb}}{^{238}_{92}\text{U}} = \frac{206 \text{ g}/2}{238 \text{ g}/2} = 0.866$$

Ratios > 0.866 are older than 4.51 x 10^9 years.

Determine the age of a rock that contains 12.75 mg of ^{238}U and 1.19 mg of ^{206}Pb.

Solution:

$$1.19 \text{ mg } {}^{206}_{82}\text{Pb} \times \frac{238 \text{ mg } {}^{238}_{92}\text{U}}{206 \text{ mg } {}^{206}_{82}\text{Pb}} = 1.375 \text{ mg } {}^{238}_{92}\text{U}$$

Therefore the original mass of ^{238}U was 12.75 + 1.375 = 14.125 mg. The rate constant k = 1.54 x 10^{-10} yr^{-1}.

$$t = \left(\ln \frac{12.75}{14.125}\right) \frac{-1}{1.54 \times 10^{-10} \text{ yr}^{-1}} = 6.65 \times 10^{8} \text{ yr} = 665 \text{ million years}$$

Nuclear Transmutation involves the preparation of an isotope from the collision of two particles

e.g.,

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

$${}^{6}_{3}\text{Li} + {}^{1}_{0}\text{n} \rightarrow {}^{3}_{1}\text{H} + {}^{4}_{2}\alpha \qquad \text{tritium}$$

$${}^{242}_{96}\text{Cm} + {}^{4}_{2}\alpha \rightarrow {}^{245}_{98}\text{Cf} + {}^{1}_{0}\text{n} \qquad \text{californium}$$

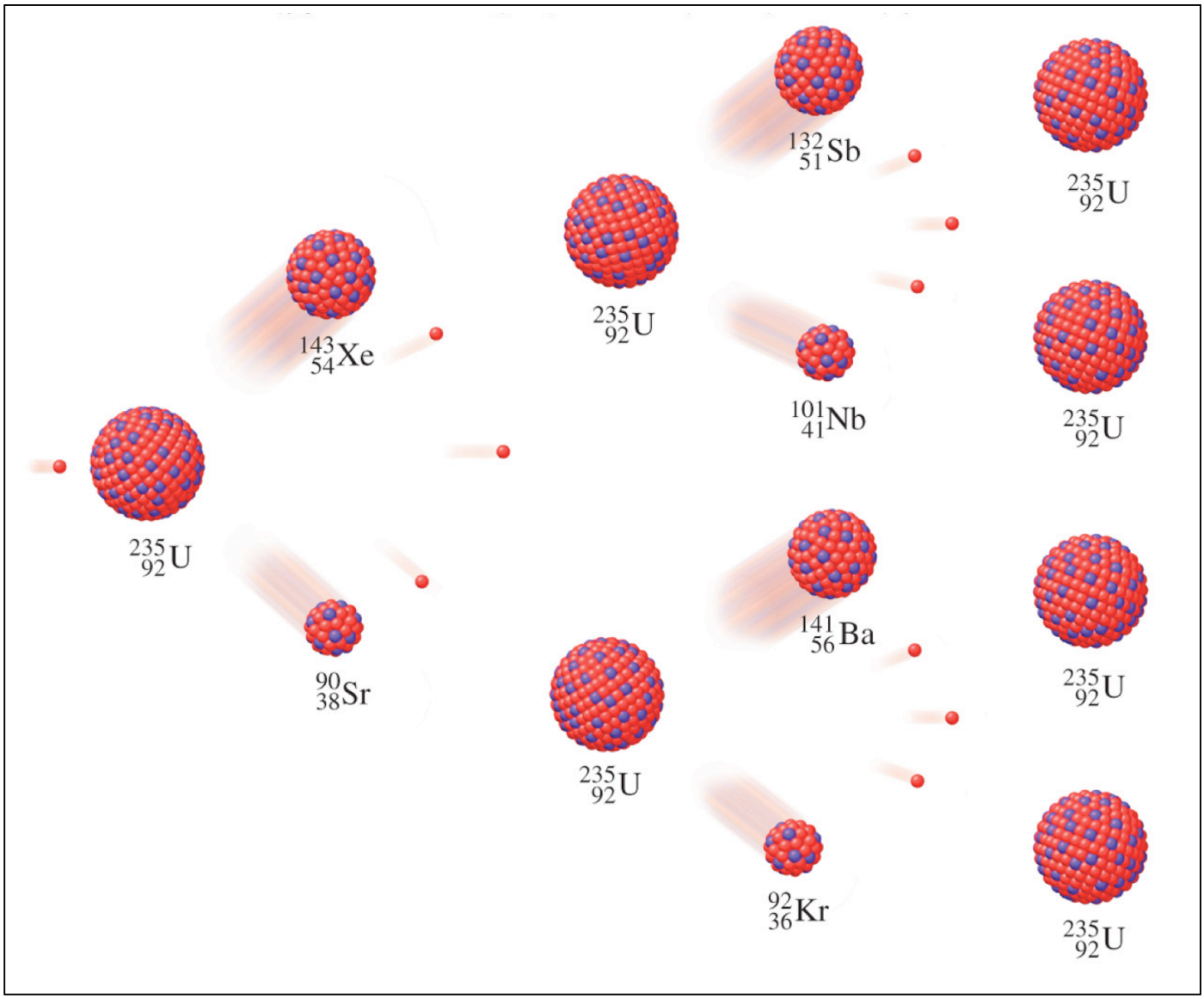
Cf is used in airport neutron-activation detectors of explosives.

It (any many other elements) is prepared using a particle accelerator.

Nuclear Fission is the process in which a heavy nucleus (mass number > 200) divides to form smaller nuclei and one or more neutrons.

For uranium, more neutrons are produced than captured.

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{90}_{38}\mathrm{Sr} + {}^{143}_{54}\mathrm{Xe} + 3\,{}^{1}_{0}\mathrm{n}$$

This can lead to a nuclear chain reaction:

- uncontrolled: atomic bomb
- controlled: nuclear reactor