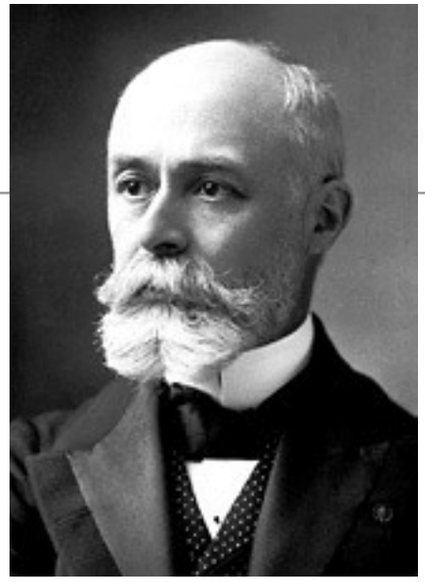
Chapter 21: Radioactivity and Nuclear Chemistry

Chem 102
Jussi Eloranta

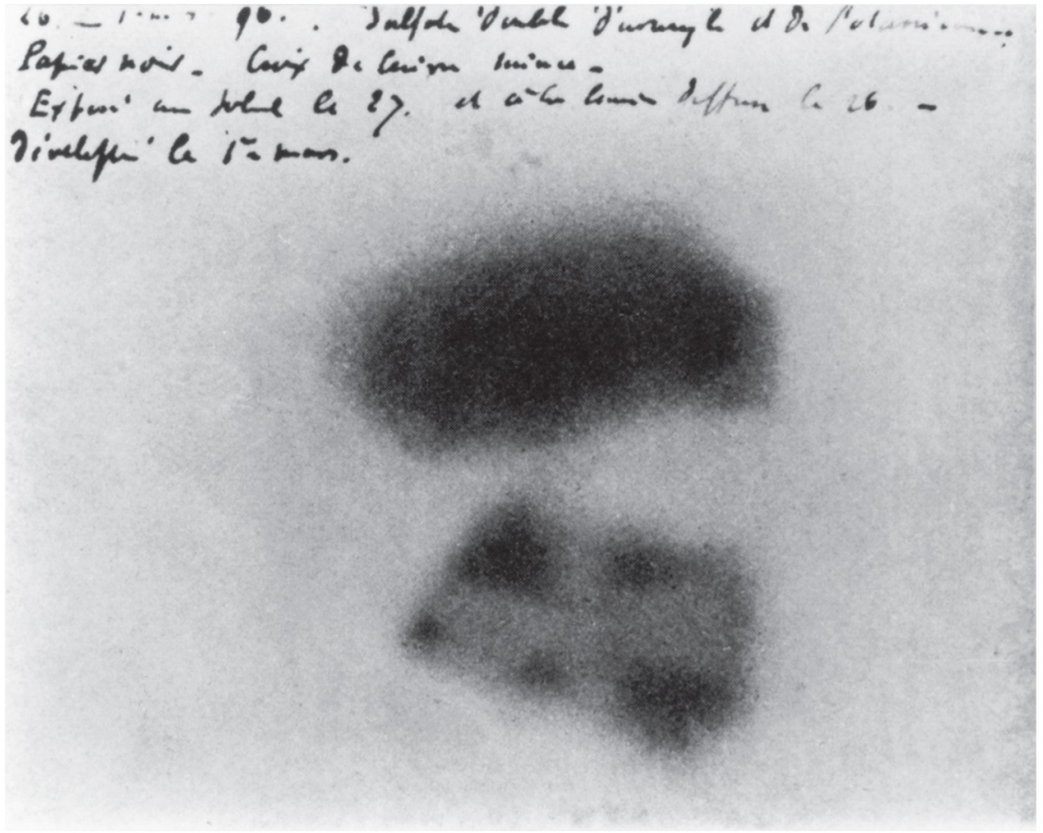
Discovery of radioactivity



- Discovered by Antoine-Henri Becquerel (1852-1908)

- SI unit of radioactivity is Bq

- Uranium-containing compound (potassium uranyl sulfate) was found to darken a photographic plate even though there was no light present



Radioactive materials

- Marie Curie (1867-1934)
- Two Nobel Prizes
  - Physics 1903 (with Pierre Curie and Henri Becquerel)
  - Chemistry 1911
- Discovered polonium (named after Poland; her home country) and radium





TABLE 20.4 Radiation Dose by Source for Persons Living in the United States

Source	Dose
Natural Radiation	
A 5-hour jet airplane ride	2.5 mrem/trip (0.5 mrem/hr at 39,000 feet) (whole body dose)
Cosmic radiation from outer space	27 mrem/yr (whole body dose)
Terrestrial radiation	28 mrem/yr (whole body dose)
Natural radionuclides in the body	35 mrem/yr (whole body dose)
Radon gas	200 mrem/yr (lung dose)
Diagnostic Medical Procedures	
Chest X-ray	8 mrem (whole body dose)
Dental X-rays (panoramic)	30 mrem (skin dose)
Dental X-rays (two bitewings)	80 mrem (skin dose)
Mammogram	138 mrem per image
Barium enema (X-ray portion only)	406 mrem (bone marrow dose)
Upper gastrointestinal tract test	244 mrem (X-ray portion only) (bone marrow dose)
Thallium heart scan	500 mrem (whole body dose)
Computed tomography (CT) head	200 mrem (whole body dose)
Computed tomography (CT) abdomen and pelvis	1000 mrem (whole body dose)
Consumer Products	
Building materials	3.5 mrem/yr (whole body dose)
Luminous watches (H-3 and Pm-147)	0.04–0.1 mrem/yr (whole body dose)
Tobacco products (to smokers of 30 cigarettes per day)	16,000 mrem/yr (bronchial epithelial dose)

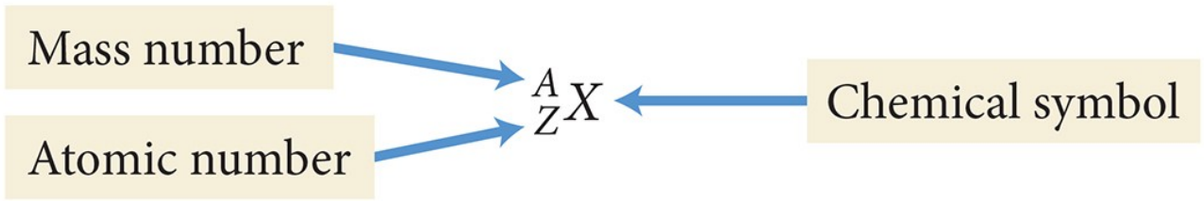
Source: Department of Health and Human Services, National Institutes of Health.

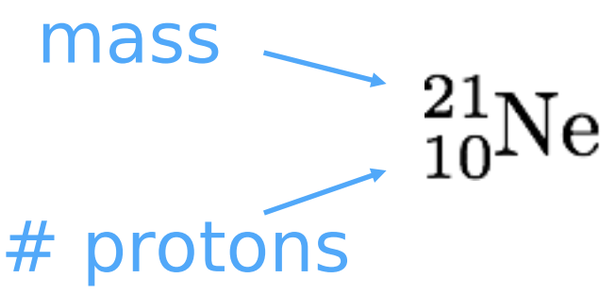
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rem: Roentgen equivalent man, absorbed dose of radiation
1 rem = 0.055% chance of eventually developing cancer
100 rem over short time causes acute radiation syndrome

Isotopes

Nucleus contains protons and neutrons:





Mass number (A) = the sum of the number of protons and number of neutrons in the nucleus

Atomic number (Z) = the number of protons in the nucleus

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- Number of neutrons: $N = A - Z$
- Proton $^{1}_{1}\mathrm{p}$
- Neutron $^{1}_{0}\mathrm{n}$
- Electron $^{0}_{-1}\mathrm{e}$

"nuclide": particular isotope

Nuclides and isotopes

- **Isotopes** have same atomic number (same number of protons) but a different number of neutrons (and different mass number):

  ^{20}Ne has 10 protons, 10 electrons, 10 neutrons

  ^{21}Ne has 10 protons, 10 electrons, 11 neutrons

- Sometimes written as Ne-20 and Ne-21
- Isotopes are sometimes called **nuclides**

Nuclear reactions

- Some isotopes are **stable**
- Others will undergo **radioactive decay**;

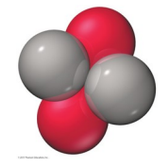
  half-life could be short (milliseconds) or long (billions of years)
- Elements can change from one to another!
- Equation for nuclear reactions:
  - Sum of the atomic numbers on both sides must be equal
  - Sum of mass numbers on both sides must be equal

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

Reactants	Products
Sum of mass numbers = 238	Sum of mass numbers = 234 + 4 = 238
Sum of atomic numbers = 92	Sum of atomic numbers = 90 + 2 = 92

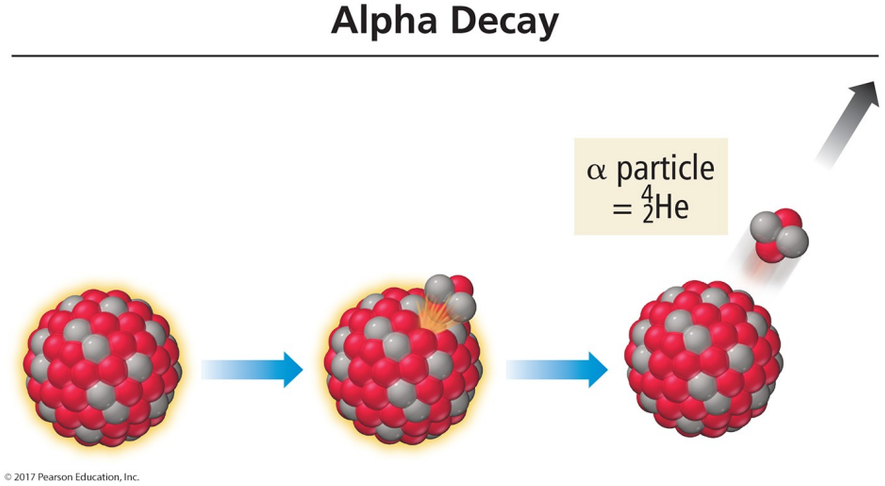
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Types of radiation: α (alpha) decay



α particle: Essentially the nucleus of a helium atom $^{4}_{2}\mathrm{He}$

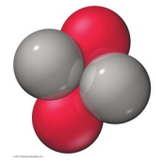
α particle can be emitted from the nucleus:



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

parent nuclide daughter nuclide

Types of radiation: α (alpha) decay





α particle: Essentially the nucleus of a helium atom $^{4}_{2}\mathrm{He}$

α particle can be emitted from the nucleus

- α particle is relatively massive (4 amu)
- Highest ionizing power;
  ability to ionize other molecules or atoms
- Lowest penetrating power:
  - ability to penetrate matter only slightly
  - can be stopped by a piece of paper, clothing
  - highly dangerous to ingest material that emits α particles

Example – Alpha decay

Write the nuclear equation for the alpha decay of Po-216.

We must deduce the identity of the daughter nuclide:

$$^{216}_{84}\text{Po} \rightarrow {}^{4}_{2}\text{He} + {}^{?}_{?}\text{??}$$

$A_{daughter} = 216 - 4 = 212$

$Z_{daughter} = 84 - 2 = 82$ (Pb)

Note that α emission **changes the identity** of the element!

$$^{216}_{84}\text{Po} \rightarrow {}^{4}_{2}\text{He} + {}^{212}_{82}\text{Pb}$$

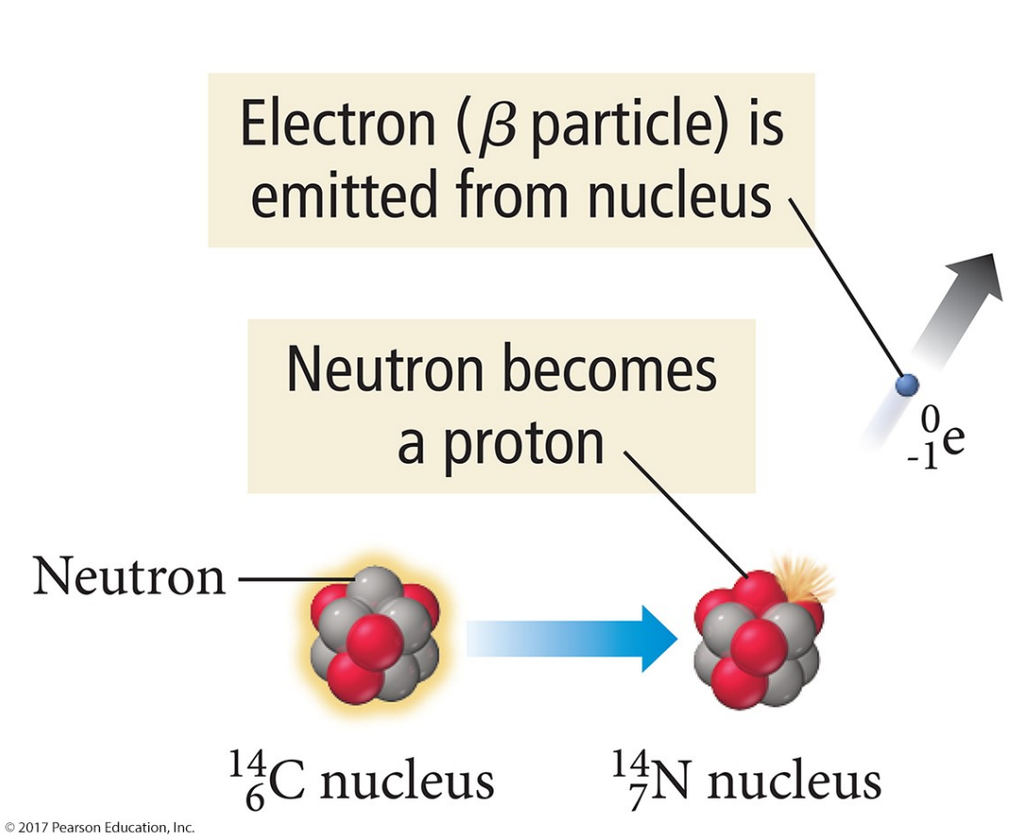
Types of radiation: β (beta) decay

β particle: Electron with high kinetic energy

β particle is emitted from the nucleus during the decay of a neutron into a proton

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

$$^{228}_{88}\mathrm{Ra} \longrightarrow {}^{228}_{89}\mathrm{Ac} + {}^{0}_{-1}\mathrm{e}$$



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Types of radiation: β (beta) decay

β particle: Electron with high kinetic energy

β particle is emitted from the nucleus as the decay of a neutron into a proton

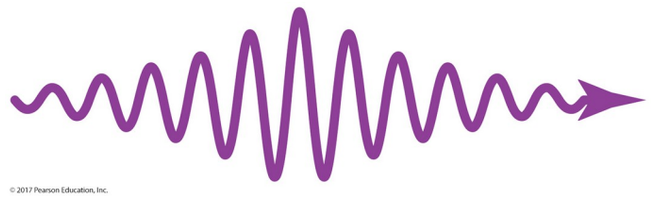
- β particle has relatively low mass
- low ionizing power
- high penetrating power;

    sheet of metal or thick wood can stop β particles

Types of radiation: γ (gamma) ray emission γ

γ ray is electromagnetic radiation (photon, not a particle)

$^{0}_{0}\gamma$



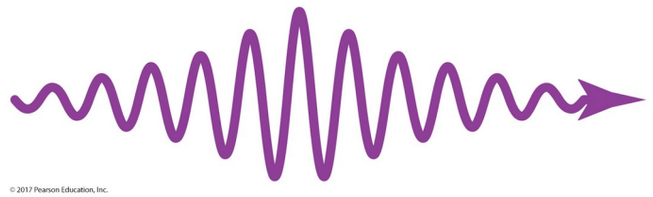
γ ray does not change the mass number or atomic number of the parent, but is often emitted together with α or β particles.

$$^{234}_{90}\text{Th} \rightarrow {}^{234}_{90}\text{Th} + {}^{0}_{0}\gamma$$

Types of radiation: γ (gamma) ray emission γ

γ ray is electromagnetic radiation (photon, not a particle)

$^{0}_{0}\gamma$



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- Lowest ionizing power
- Highest penetrating power; blocked by several inches of lead shielding or thick slabs of concrete
- Often emitted along with other particles

Positron emission

Positron is the antiparticle of the electron;

same mass as an electron, but opposite charge

- If a positron hits an electron, they annihilate each other and produce gamma rays
- **Examples:** proton converted to neutron and positron

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

or

$$ {}^{30}_{15}\mathrm{P} \longrightarrow {}^{30}_{14}\mathrm{Si} + {}^{0}_{+1}\mathrm{e} $$

- Application: Positron Emission Tomography (PET)

Electron capture

Electron capture is “opposite” of β emission.

Electron is absorbed by the nucleus:

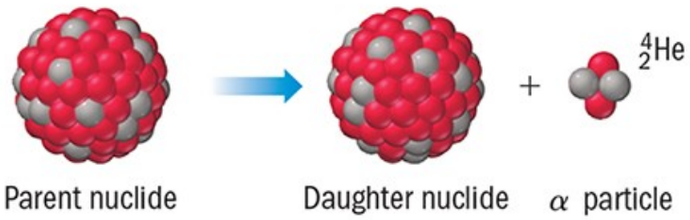
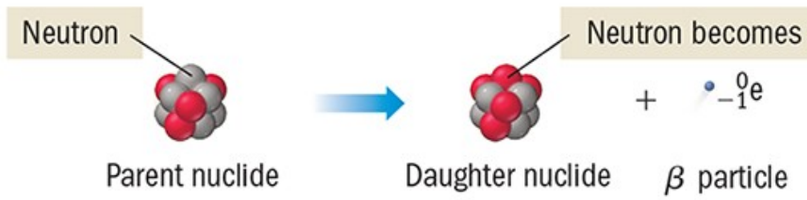
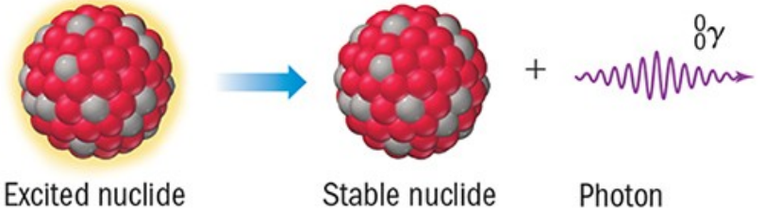
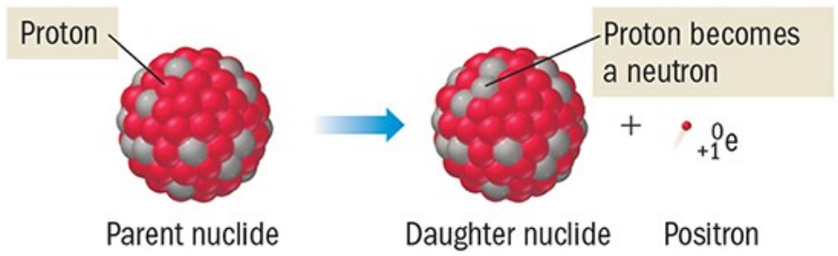
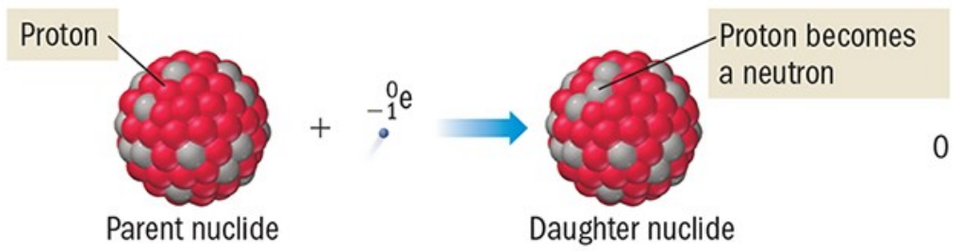
proton + electron → neutron:

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

or

$$ {}^{92}_{44}\mathrm{Ru} + {}^{0}_{-1}\mathrm{e} \longrightarrow {}^{92}_{43}\mathrm{Tc} $$

TABLE 20.1 Modes of Radioactive Decay

Decay Mode	Process	Change in: A	Z	N/Z*	Example
α		−4	−2	Increase	$^{238}_{92}U \longrightarrow {}^{234}_{90}Th + {}^{4}_{2}He$
β		0	+1	Decrease	$^{228}_{88}Ra \longrightarrow {}^{228}_{89}Ac + {}^{0}_{-1}e$
γ		0	0	None	$^{99m}_{43}Tc \longrightarrow {}^{99}_{43}Tc + {}^{0}_{0}\gamma$
Positron emission		0	−1	Increase	$^{30}_{15}P \longrightarrow {}^{30}_{14}Si + {}^{0}_{+1}e$
Electron capture		0	−1	Increase	$^{92}_{44}Ru + {}^{0}_{-1}e \longrightarrow {}^{92}_{43}Tc$

* Neutron-to-proton ratio

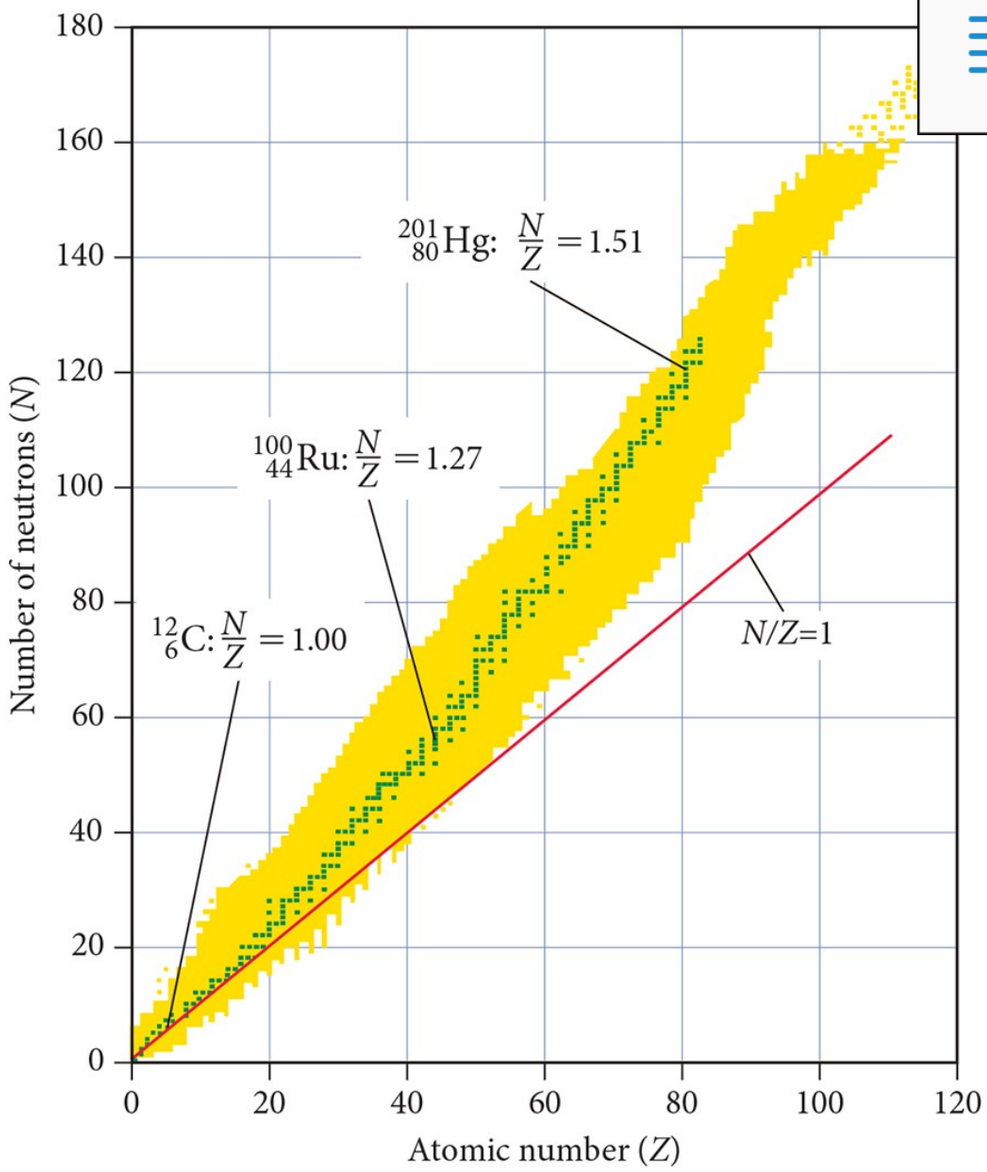
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Predicting radioactive decay

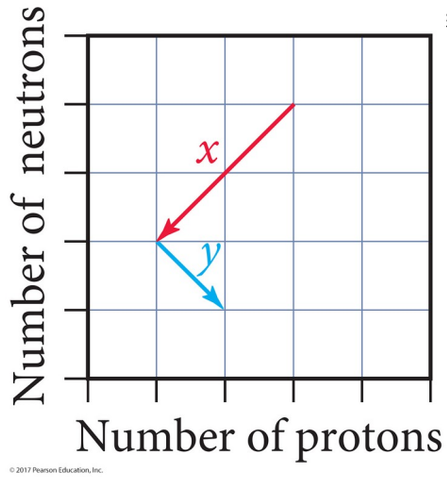
- It is not easy to predict what kind of radioactive decay an atom will undergo (if any)
- However, the larger the number of protons relative to neutrons, the more unstable the nucleus tends to be
- But protons repel each other!? What holds the nucleus together in the first place?
- The attractive short range **nuclear strong force** overcomes proton-proton repulsions (+ and + repel)
- Neutrons attract other protons and neutrons through the strong force and stabilize the nucleus because they add no repulsive forces

The Valley of Stability

- Can we predict the type of radioactivity produced from certain isotopes?
- Green dots are stable isotopes (non-radioactive)
- Above the green dots, isotopes tend to undergo *beta decay*
- Below the green dots, isotopes tend to undergo *positron emission or electron capture*
- $Z > 83$ (Bi) do not have stable isotopes



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x = α decay (He)
y = β decay (e)

Example

Is Mo-102 more likely to undergo β decay or positron emission?

Mo-102 has 42 protons and 60 neutrons, so $N / Z = 1.43$.

Based on the graph at this Z, we see that $N / Z \approx 1.3$. So the nuclide has too many neutrons. It will likely undergo beta decay, converting neutrons to protons.

Stability of nuclides

In addition to *N* / *Z*, the actual number of neutrons and protons affects stability:

Z	*N*	Number of nuclides
Even	Even	157
Even	Odd	53
Odd	Even	50
Odd	Odd	5

Most nuclides have an even number of neutrons and protons

Only few nuclides have odd number of neutrons and protons

Magic numbers

- Just as electrons occupy energy levels in an atom, **nucleons** (protons and neutrons) occupy energy levels in the nucleus.
- We already know certain numbers of electrons have special stability (2, 10, 18, 36, 54…; shell clousures).
- So certain numbers of protons or neutrons have special stability (*N* or *Z* = 2, 8, 20, 28, 50, 82, 126).
- These numbers are called **magic numbers** (at the time they seemed to be random).

Radioactive decay series

- All atoms with $Z > 83$ (Bi) are radioactive - no stable isotopes.
- All decay by one or more α or β (sometimes γ) emission steps.
- Heaviest naturally occurring isotope is U-238 ($Z = 92$):

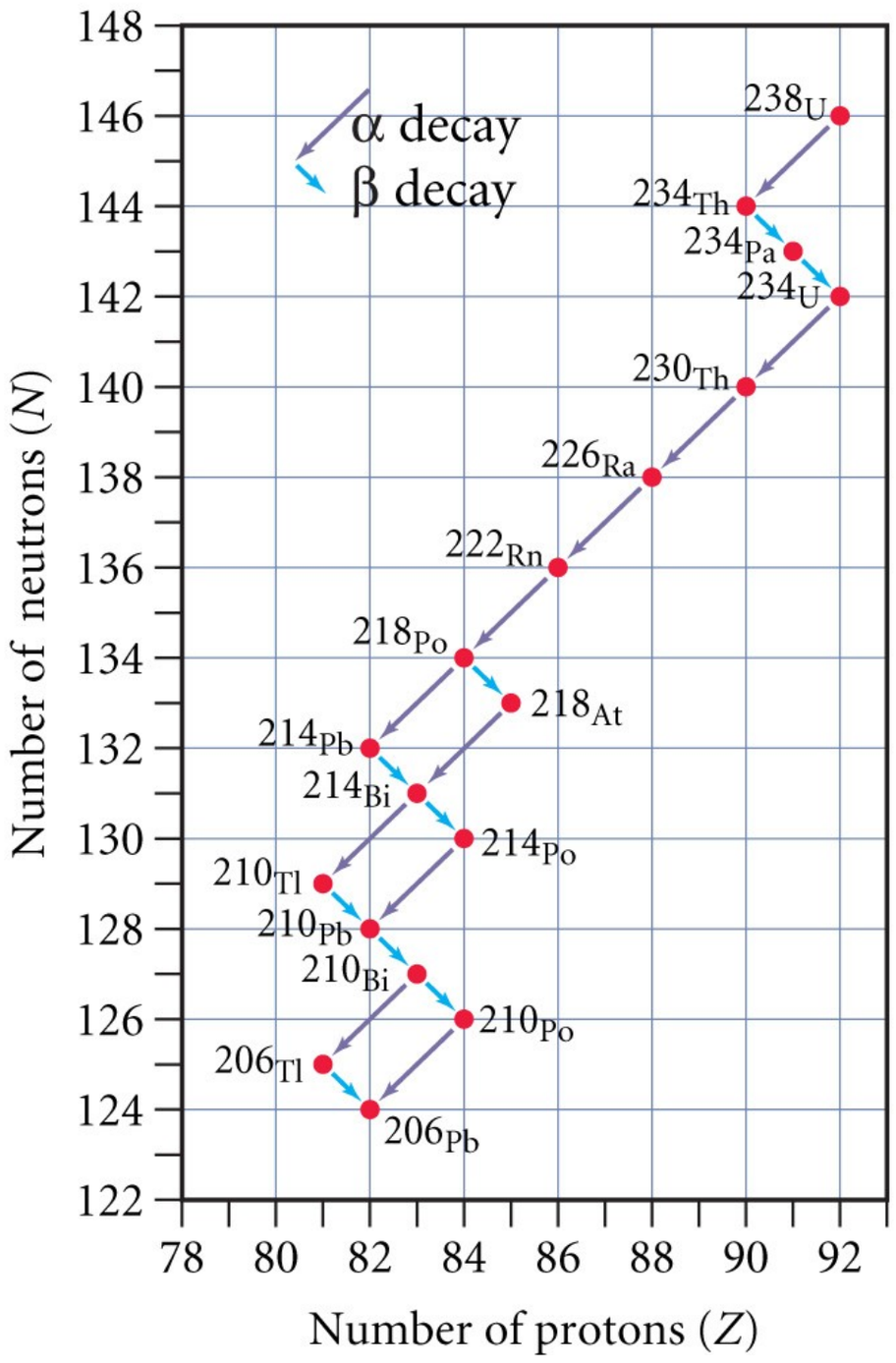
$$^{238}_{92}\mathrm{U} \rightarrow {}^{234}_{90}\mathrm{Th} + {}^{4}_{2}\mathrm{He} \qquad \alpha \text{ decay}$$

But the daughter Th-234 is radioactive too:

$$^{234}_{90}\mathrm{Th} \rightarrow {}^{234}_{91}\mathrm{Pa} + {}^{0}_{-1}\mathrm{e} \qquad \beta \text{ decay}$$

Radioactive decay series

- Radioactive decay occurs until a stable isotope is reached (where $Z \leq 83$)
- The steps are shown in a **radioactive decay series:** evolution of N vs. Z
- The one for U-238 ends at Pb-206
- The arrows indicate the type of decay



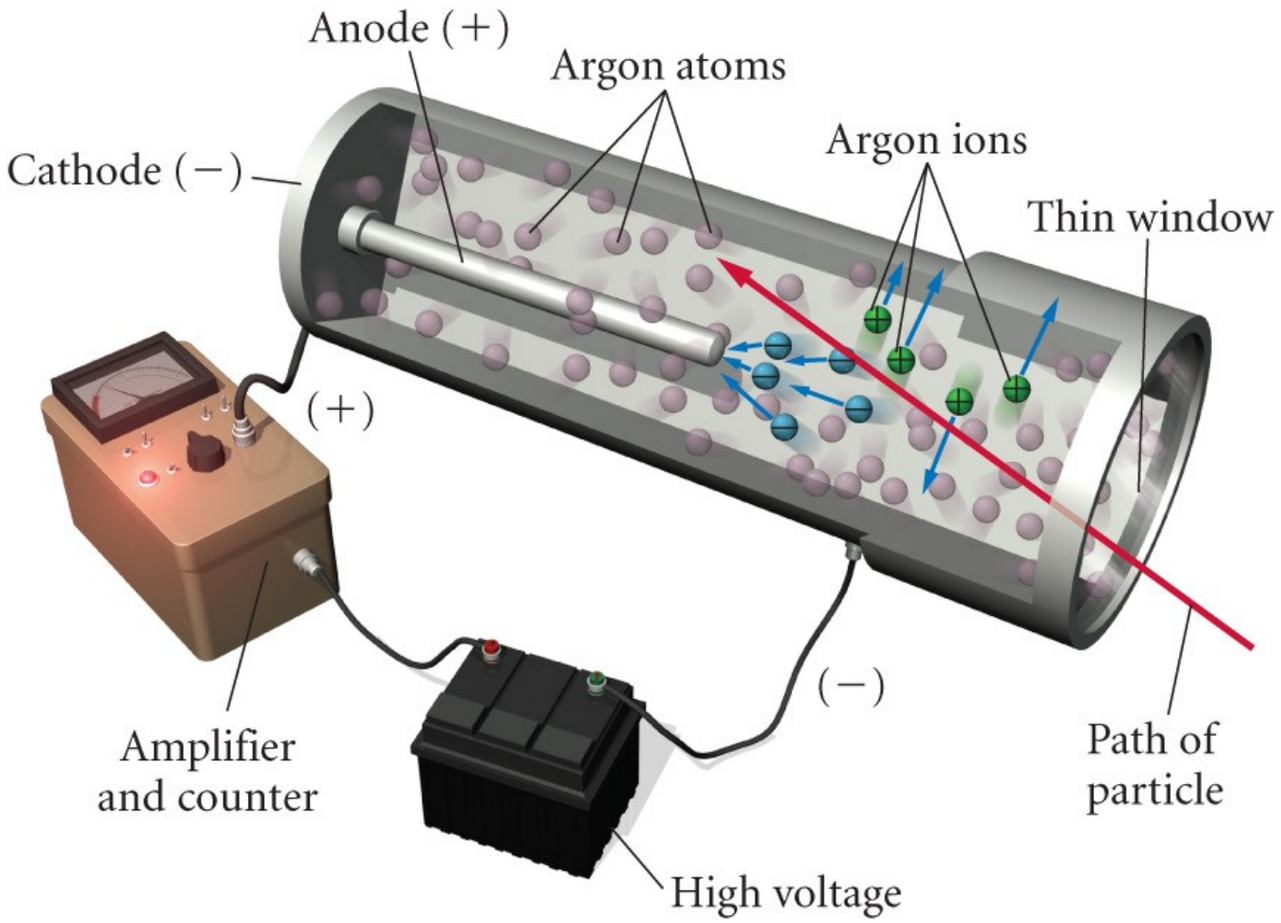
Detecting radioactivity

- The simplest detectors are **film-badge dosimeters**
- A piece of light-tight photographic film becomes darker when exposed to radiation
- They are **cumulative detectors** that continue to darken with each exposure
- They only detect radiation exposure when processed



Detecting radioactivity

When ionizing radiation enters a **Geiger-Müller tube**, Ar ions are created and collected.



A real time reading is obtained



A ‘click’ is an ion created by a radioactive particle

Kinetics of radioactive decay

- Radioactivity is a natural part of our environment:
  - Our food is naturally radioactive (weak)
  - The human body is naturally radioactive (weak)
- The Earth is 4.6 billion years old but radioactivity persists
  - Why?
    - Some elements have very long time for decay (half-life)
    - New radioactive elements are being created by cosmic ray bombardment from space
- Remember, <u>all</u> $Z > 83$ (Bi) will undergo radioactive decay
- Many nuclides with $Z < 83$ will also undergo decay

Kinetics of radioactive decay

- All radioactive decay is **first order** ("first order kinetics"):

$$\text{Rate} = k \cdot N$$

where N is the number of radioactive nuclei and k is the rate constant (1/s, 1/year etc.).

- Most often, the rate constant is converted to a **half-life** $t_{1/2}$ in the usual way:

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

- Elements with long half-lives decay slowly (i.e., remain long times in the environment)

Kinetics of radioactive decay

To calculate how many radioactive nuclei remain after a given period of time, N_t, we use the **integrated first-order rate law**:

$$\ln\left(\frac{N_t}{N_0}\right) = -kt$$

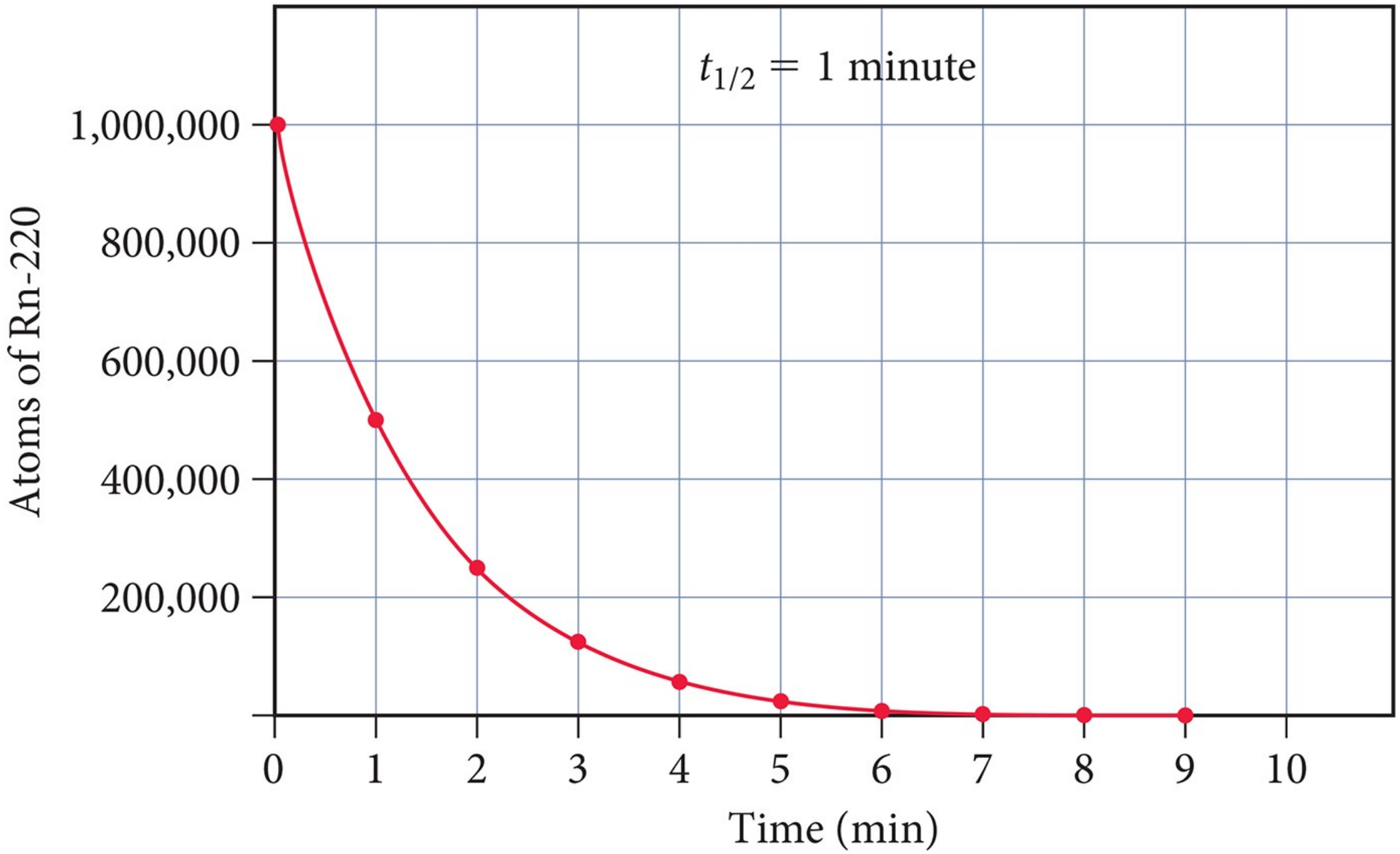
Initial number of radioactive nuclei

TABLE 19.3 Selected Nuclides and Their Half-Lives

Nuclide	Half-life	Type of Decay
$^{232}_{90}\mathrm{Th}$	1.4×10^{10} yr	Alpha
$^{238}_{92}\mathrm{U}$	4.5×10^{9} yr	Alpha
$^{14}_{6}\mathrm{C}$	5730 yr	Beta
$^{220}_{86}\mathrm{Rn}$	55.6 s	Alpha
$^{219}_{90}\mathrm{Th}$	1.05×10^{-6} s	Alpha

Two nuclides with the same Z may have very different $t_{1/2}$

Example: Decay of Radon-220



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Example

What mass of C-14 ($t_{1/2}$ = 5730 years) remains after 10,000 years if the initial mass was 145 mg?

Using the integrated rate law:

$$k = \frac{0.693}{t_{1/2}} = 1.209 \times 10^{-4}/\text{yr}$$

Note mg is proportional to *N*

$$\ln\left(\frac{N_t}{N_0}\right) = -kt \Rightarrow \frac{N_t}{N_0} = e^{-kt}$$

$$N_t = N_0 e^{-kt} = 145\ \text{mg} \times e^{-1.206\times10^{-4}/\text{yr}\times10{,}000\ \text{yr}}$$

$$= 43.4\ \text{mg}$$

Radiocarbon dating ("determining age")

- Upper atmosphere: $^{14}_{7}\mathrm{N} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{H}$

- Carbon-14 is in equilibrium, it is incorporated into CO_2

$^{14}CO_2$ → plants → herbivores → carnivores

$$^{14}_{6}\mathrm{C} \longrightarrow {}^{14}_{7}\mathrm{N} + {}^{0}_{-1}\mathrm{e} \quad t_{1/2} = 5730\ yr$$

- ^{14}C amount in *living* organisms is constant (^{12}C is the most stable natural isotope)



Radiocarbon dating

- Once the organism dies, ^{14}C begins decaying
- The ratio of C-14 to C-12 can be used to measure the time since death:

After one half-life: C-14 to C-12 ratio is 50% of the original

After two half-lives: C-14 to C-12 ratio is 25% of the original

...ETC...

Example

A scroll has a C-14 (k = 1.209x10^{-4} / yr) β decay rate of 9.05 emission events per gram per minute. If a new scroll has a decay rate of 12.04 emission events per gram per minute, how old is the scroll?

$$\ln\left(\frac{N_t}{N_0}\right) = -kt \Rightarrow t = -\ln\left(\frac{N_t}{N_0}\right)/k$$

$$t = \frac{\ln\left(\frac{9.05 \cancel{/\text{g min}}}{12.04 \cancel{/\text{g min}}}\right)}{-1.209 \times 10^{-4}/\text{yr}} = 2360 \text{ yr}$$

Note: decay rate proportional to *N* for first order

Example

dis/min g = disintegrations per minute per gram of carbon (decay rate)

The β decay rate of ^{14}C in living organisms is 15.3 dis/(min g). An old human skull has a decay rate of 4.50 dis/(min g). How old is the skull? The half-life of ^{14}C is 5730 years.

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730\ \text{yrs}} = 1.21 \times 10^{-4} \frac{1}{\text{yrs}}$$

$$\ln\left(\frac{rate_t}{rate_0}\right) = -kt \Rightarrow t = -\ln\left(\frac{rate_t}{rate_0}\right)/k$$

$rate_t \sim N_t$

$$= -\ln\left(\frac{4.50\ \text{dis/min gC}}{15.3\ \text{dis/min gC}}\right)/(1.21 \times 10^{-4} 1/\text{yrs}) = 10,000\ \text{yrs}$$