

Chemistry 3A

Introductory General Chemistry

S. M. Halloran



Fresno City College

- Discovery of Radioactivity
- Radioactivity Types: Alpha, Beta, Gamma
- Half-Life in Radioactivity
- Nuclear Chemistry: Purposeful Use of Radioactivity

Discovery of Radioactivity

- Roentgen learns that X-radiation can also expose photographic film
- Becquerel learn if fluorescent minerals can have same effect (no), but sees that one rock with uranium salt minerals fogged the photographic plate
- Marie & Pierre Curie determine that the element radium has even more radioactivity than uranium

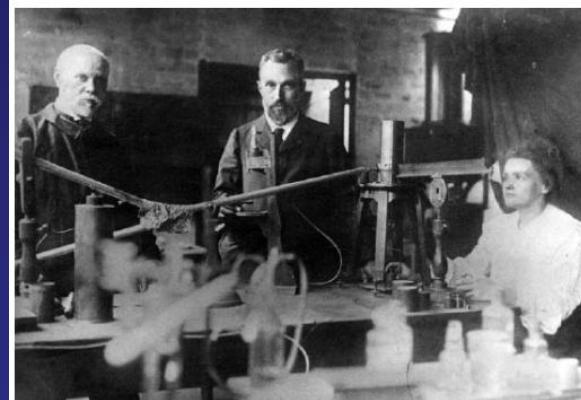


Figure 14.1.2: Marie Curie (right) and Pierre Curie (middle) with Henri Becquerel (left) shared the 1903 Nobel Prize.

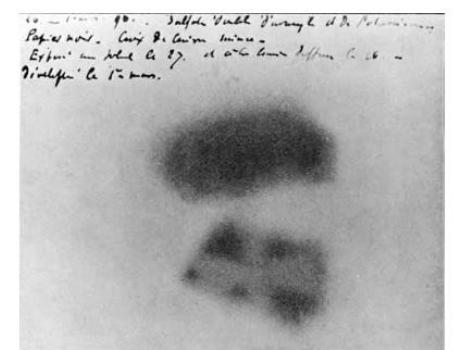


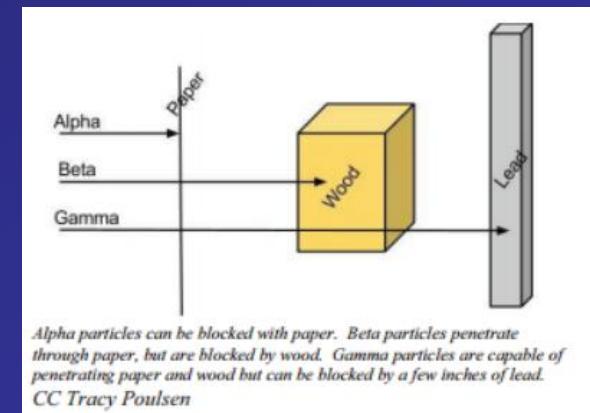
Figure 14.1.1: Image of Becquerel's photographic plate, which has been fogged by exposure to radiation from a uranium salt. The shadow of a metal Maltese Cross placed between the plate and the uranium salt is clearly visible (Public Domain).

Nuclear Binding Energy

- Except for ^1H nucleus, all atoms have multiple protons in a nucleus
- As like charges repel, something must keep protons held together in the nucleus. This is a force called **nuclear binding energy**
- This binding energy keeps nuclei stable. But too little binding energy can lead to natural radioactivity (nuclear disintegration)
- Scientists can force (smash) nuclei together to cause artificial radioactivity
- All kinds of radioactivity (nuclear disintegration) leads to energy release

Alpha, Beta, Gamma Radioactivity

- All nuclei with 84 and more protons are radioactive, and those with less have stable and unstable isotopes
- The decay of radioactive isotopes can be **alpha**, **beta**, and **gamma**
- The radiation of this nuclear disintegration can be damaging to atoms and the molecules/compounds of which they are part, and to cells and tissues in which these compounds exist
- The energy of the radiation can cause **ionization**, usually by knocking out electrons from atoms
- However, some radiation can be blocked, indicating some protection



Ionization versus Penetrating Power

- Generally there is a trade-off in ionizing power versus penetrating power
- **Alpha particles** have a large mass compared to beta particles & gamma rays, so they do not penetrate very much. But they have considerable ability to ionize and damage molecules/compounds
- **Beta particles** have far more penetrating power but less ionizing power
- **Gamma rays** have no mass, are most penetrating, but less ionizing compared to alpha and beta particles

Table 14.2.1 Comparison of Penetrating Power, Ionizing Power and Shielding of Alpha and Beta Particles, and Gamma Rays.

Particle	Symbol	Mass	Penetrating Power	Ionizing Power	Shielding
Alpha	α	4amu	Very Low	Very High	Paper Skin
Beta	β	1/2000amu	Intermediate	Intermediate	Aluminum
Gamma	γ	0 (energy only)	Very High	Very Low	2 inches lead

Alpha Decay

- Many isotopes of different elements show this type of **alpha particle** nuclear disintegration. Examples:
- $^{238}_{92}\text{U} \rightarrow ^4_2\text{He} + ^{234}_{90}\text{Th}$
- $^{230}_{90}\text{Th} \rightarrow ^4_2\text{He} + ^{226}_{88}\text{Ra}$
- Note the 2nd decay event is actually the product of the 1st decay event
- Recall that this notation is ^A_ZEl where **El** is the element, A = **mass number**, and Z = **atomic number**
- Note that **mass (A)** and **atomic (Z) number** is conserved on both sides of the decay arrow
- conservation: $238 = 4 + 234$, $92 = 2 + 90$

Beta Decay

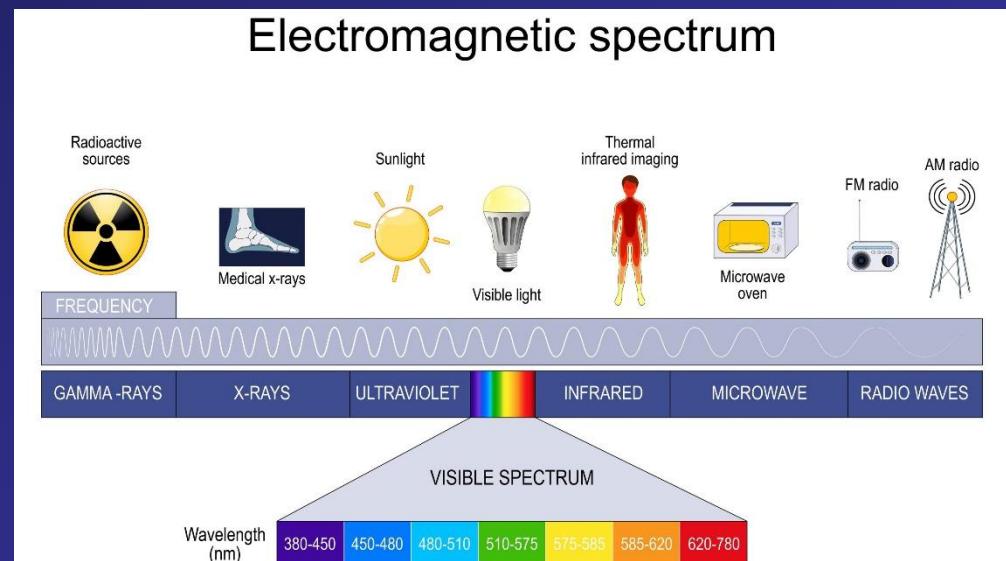
- In **beta particle** decay, a high energy electron is thrown out of nucleus
- How does an electron come from a nucleus? It is believed a neutron decays to a proton, which stays in the nucleus, and an electron is also spun out. Mass and charge are conserved! The element is converted to a new element
- $^{234}_{90}\text{Th} \rightarrow {}^0_{-1}\text{e} + {}^{234}_{91}\text{Pa}$ (mass & charged conserved always)
- Often ${}^0_{-1}\text{e}$ is symbolized as ${}^0_{-1}\beta$
- Note that thorium-234 can decay by alpha and beta particle paths

Gamma Radiation

- Alpha and beta decay are particles, having mass of a helium nucleus or at least an electron
- **Gamma rays** are photons, part of the same electromagnetic radiation spectrum as **visible light**, **ultraviolet**, **x-rays**, **infrared**, **microwave**, and **radio waves**
- In the alpha decay of U-238 process, this actually was accompanied by emission of two gamma rays of different energies:



- In fact, all nuclear decay reactions shown for alpha and beta decay include emitted gamma radiation



Summary

- All radioactivity involves significant energies
- Chemical bond energy releases are up to 10^3 kJ/mol
- But radioactivity is from 10^8 to 10^{10} kJ/mol, about a million times more energy

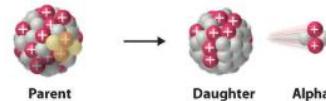
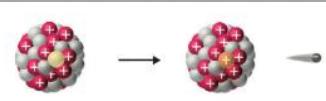
Decay Type	Radiation Emitted	Generic Equation	Model
Alpha decay	$\frac{4}{2} \alpha$	$\frac{A}{Z} X \longrightarrow \frac{A-4}{Z-2} X' + \frac{4}{2} \alpha$	
Beta decay	$\frac{0}{-1} \beta$	$\frac{A}{Z} X \longrightarrow \frac{A}{Z+1} X' + \frac{0}{-1} \beta$	
Gamma emission	$\frac{0}{0} \gamma$	$\frac{A}{Z} X^* \xrightarrow{\text{Relaxation}} \frac{A}{Z} X' + \frac{0}{0} \gamma$	

Figure 17.3.2: Three most common modes of nuclear decay.

“Nuclear Accounting”

- Mass is conserved: both atomic (Z) and mass (A) numbers must equal on both sides of the decay arrow
- Nuclear—not electron(ic)—charge is conserved in these equations. Generally the effect on electrons orbiting an atom involved in nuclear decay are not accounted for and the effect unknown. The nuclear charge effect is reflected in the changes of the atomic number (Z value), since Z is a direct count of the protons in a nucleus

A Series of Decay

- The U-238 isotope will actually undergo a series of decays as it progresses to an isotope that is stable
- A total of 14 decays will occur as U-238 decays to Pb-206.
- U-235 will decay to Pb-207
- Th-232 will end in Pb-208
- Billions/millions of years ago there may have been Radon naturally but it has all decayed.

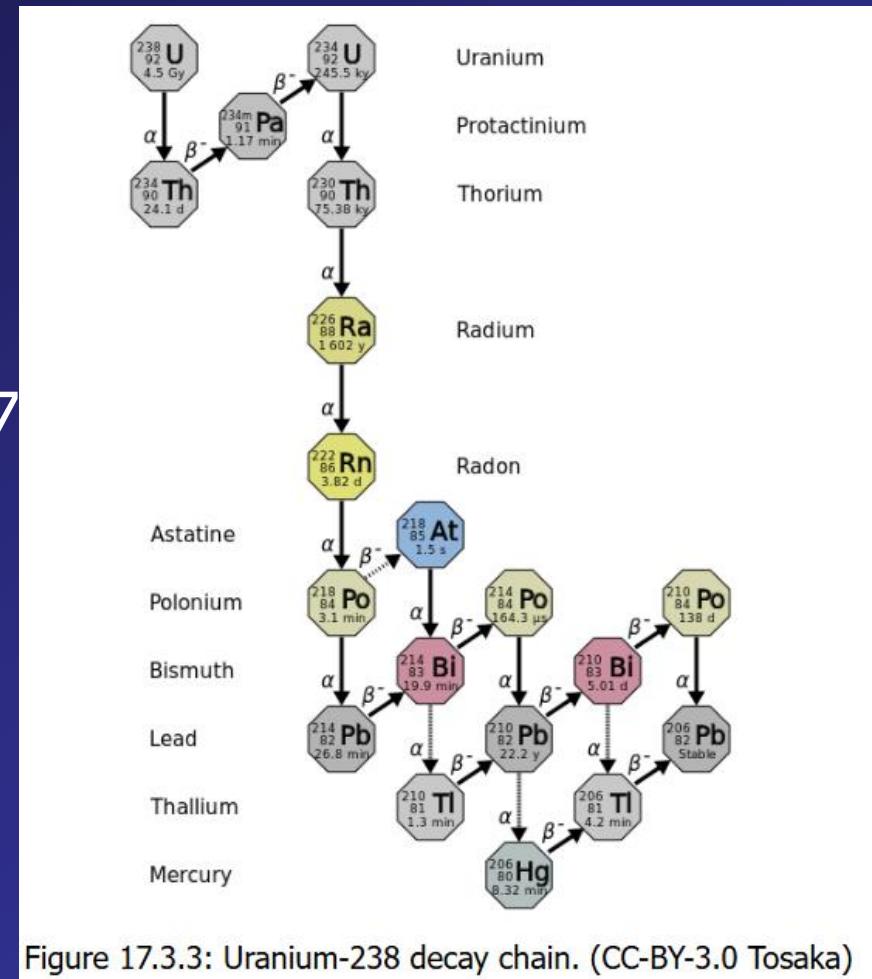


Figure 17.3.3: Uranium-238 decay chain. (CC-BY-3.0 Tosaka)

Half-Life

- Amount of radioactivity as it decays clearly decreases with time
- Period of time for that amount of radioactivity to decrease by half (50%) is called the **half-life**
- Half-life is symbolized by $t_{1/2}$.
- Half-lives for many isotopes can range from nanoseconds to billions of years

Period Range	Approximate Value	Example Isotope	Use/Context
Extremely Short	Nanoseconds (10^{-9} s)	Polonium-212 (299 ns)	Part of the uranium decay series.
Seconds/ Minutes	Seconds (10^{-2} to 10^3 s)	Oxygen-15 (\approx 2 minutes)	Used in Positron Emission Tomography (PET) scans.
Hours/Days	hours to days (10^3 to 10^6 s)	Technetium-99m (\approx 6 hours)	Most widely used medical diagnostic isotope.
Years/ Centuries	years to centuries (10^7 to 10^{10} s)	Cesium-137 (\approx 30 years)	Nuclear fallout/waste.
Geological Time	thousands to billions of years (10^{11} to 10^{17} s)	Carbon-14 (\approx 5,730 years)	Used for carbon dating.
Primordial	billions of years (10^{17} s +)	Uranium-238 (\approx 4.5 billion years)	Used for geological dating of Earth rocks.

Half-Life

- Cobalt-60 has a half-life of 5.27 y
- If at time $t = 0$, there is 10 g cobalt-60, at time $t = 5.27$ y, there will be 5 g. At time $t = 10.54$ y, there will be 2.5 g
- At $t = 15.81$ y, now 1.25 g, and at $t = 21.08$ y, which is 5 half-lives, the amount remaining is now 0.625 g
- It follows a curve:

Table 14.3.1 Half-Lives of Various Isotopes	
Isotope	Half-Life
^3H	12.3 y
^{14}C	5730 y
^{40}K	1.26×10^9 y
^{51}Cr	27.70 d
^{90}Sr	29.1 y
^{131}I	8.04 d
^{222}Rn	3.823 d
^{235}U	7.04×10^8 y
^{238}U	4.47×10^9 y
^{241}Am	432.7 y
^{248}Bk	23.7 h
^{260}Sg	4 ms

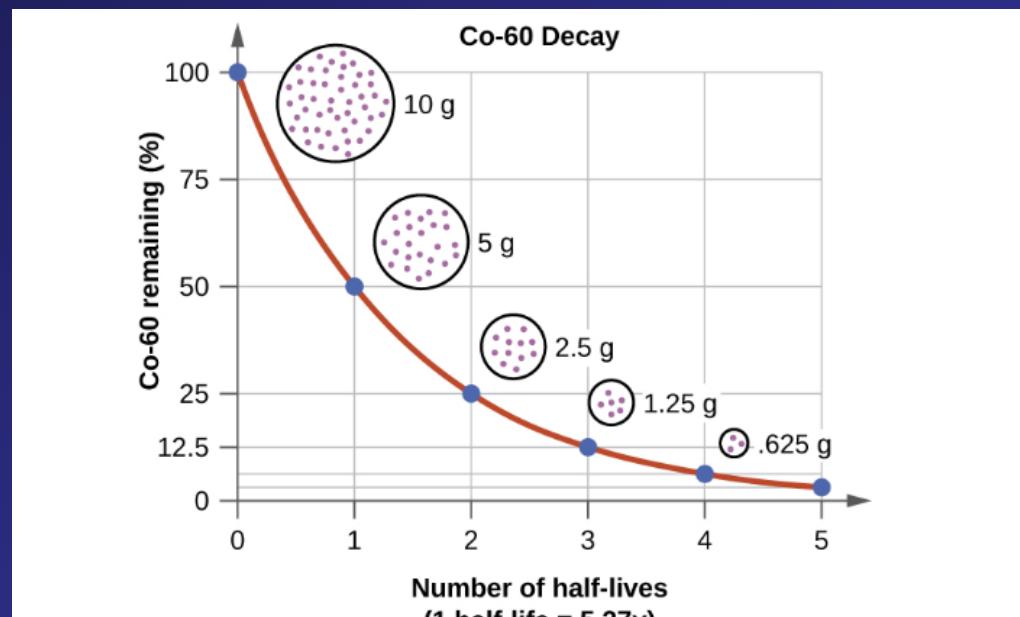
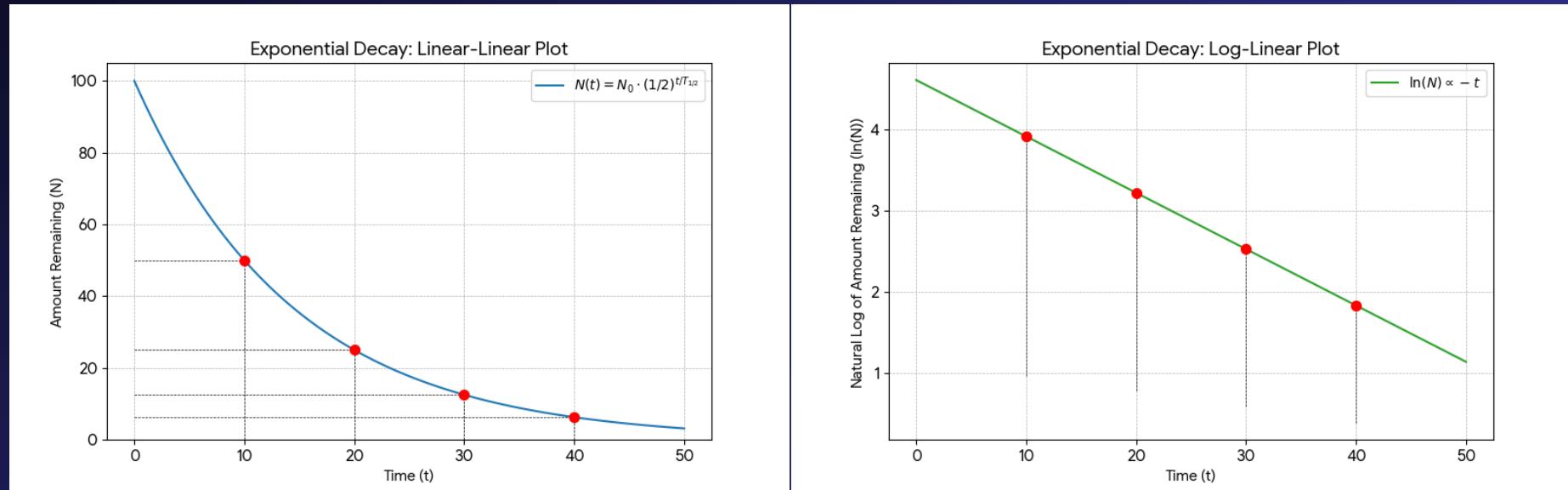


Figure 14.3.1: For cobalt-60, which has a half-life of 5.27 years, 50% remains after 5.27 years (one half-life), 25% remains after 10.54 years (two half-lives), 12.5% remains after 15.81 years (three half-lives), and so on.

Half-Life

- The math involving first-order (only one reactant) process that is radioactive decay is so important it must be understood graphically



- Flourine-20 has $t_{1/2} = 11.0$ s. If initial sample is 5.00 g of fluorine-20, how much is left after 44.0 s?
- $A = 5.00 \text{ g} \times \left(\frac{1}{2}\right)^4 = 5.00 \text{ g} \times \left(\frac{1}{16}\right) = 0.313 \text{ g}$

Detecting Radioactivity

- Because alpha, beta, and gamma radiation is ionizing, instruments like a Geiger-Muller tube can be constructed to detect ionizations of gases in the instrument as electric currents created to register counts and to hear the count as an audible “click”
- These counts occur without any identifiable source of radiation. This is called background radiation

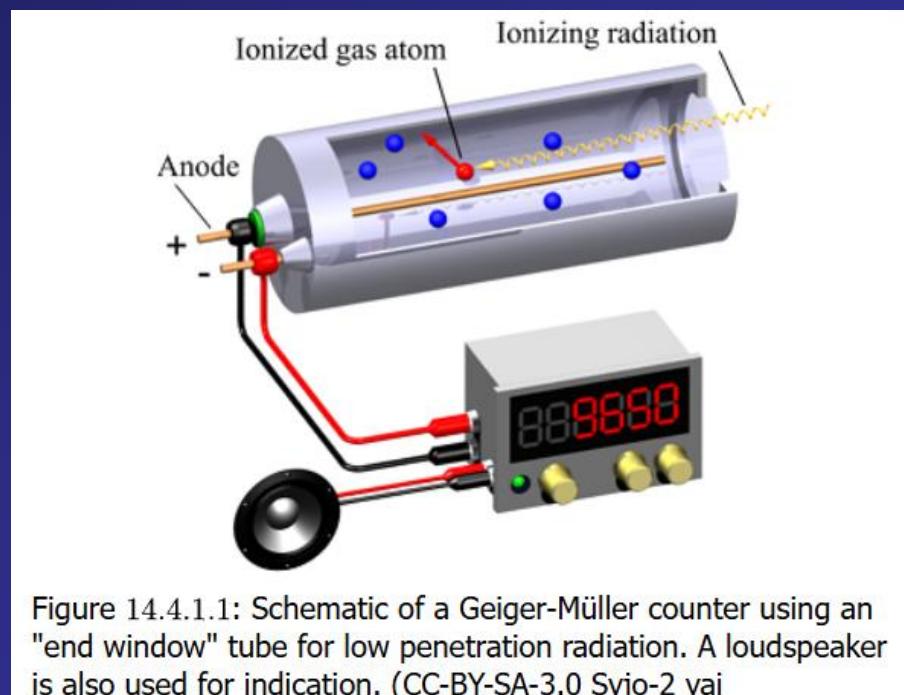
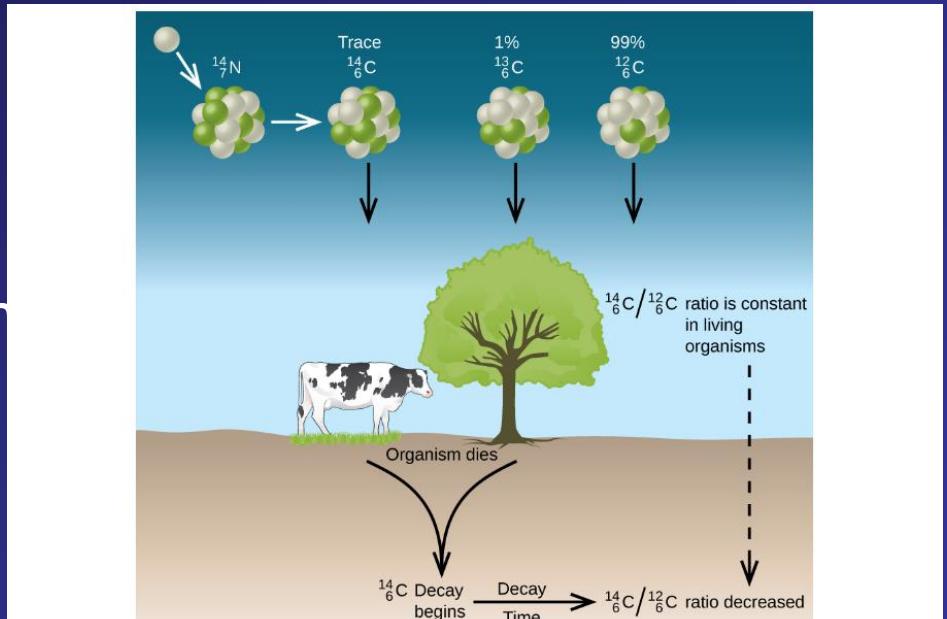


Figure 14.4.1.1: Schematic of a Geiger-Müller counter using an "end window" tube for low penetration radiation. A loudspeaker is also used for indication. (CC-BY-SA-3.0 Svjo-2 via

Radiometric Dating

- Radioisotopes can be used date object origin
- Carbon-14 in particular can be used to date things that were living organisms (radiocarbon or carbon-14 dating)
- Carbon-14:carbon-12 ratio can be used to determine how long ago an organism lived. Ratio is constant while organism is alive, but decreases after death



Figure

: Along with stable carbon-12, radioactive carbon-14 is taken in by plants and animals, and remains at a constant level within them while they are alive. After death, the C-14 decays and the C-14:C-12 ratio in the remains decreases. Comparing this ratio to the C-14:C-12 ratio in living organisms allows us to determine how long ago the organism lived (and died). (CC BY 4.0; OpenStax)

Atomic Fission & Fusion

- Fission reactions are when nuclei break up into two or more smaller nuclei

- In the fission reactor:



- Fusion reactions are when nuclei are brought together to form larger nuclei

- In the Sun:



- In fusion reactor:

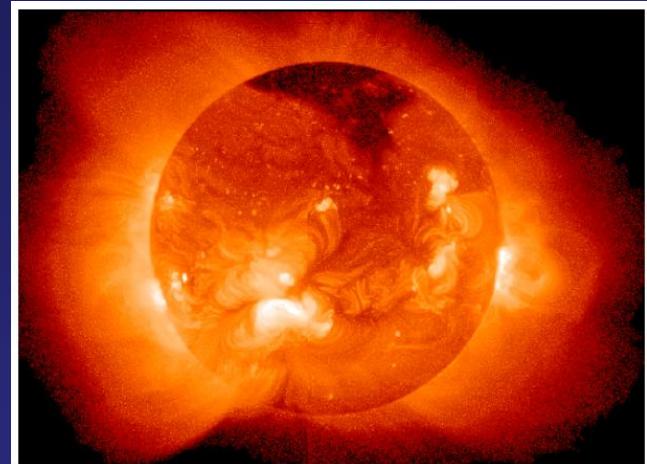


Figure 14.4.3.3: The energy that comes from the sun and other stars is produced by fusion. (Public Domain; NASA.)

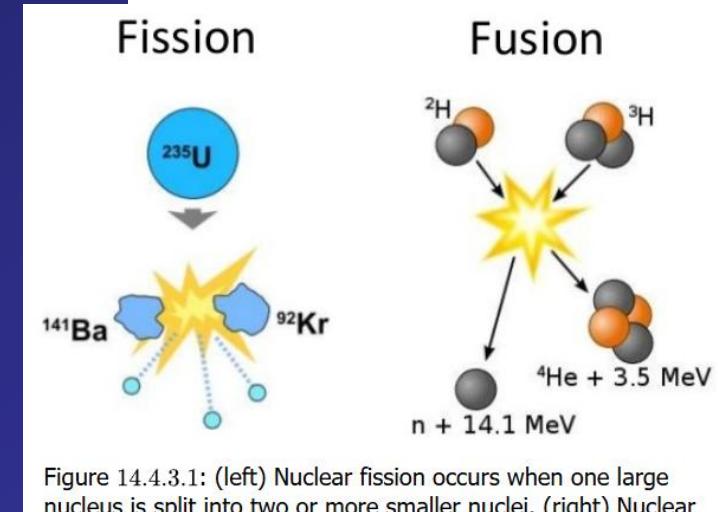


Figure 14.4.3.1: (left) Nuclear fission occurs when one large nucleus is split into two or more smaller nuclei. (right) Nuclear fusion happens when two small nuclei combine to make a larger nucleus.

Fission Chain Reaction

- Nuclear fission of U-235 is a self-sustaining chain reaction in which a neutron starts the process and yields three neutrons, any of which can strike another U-235 atom and continue with another fission
- Nuclear-based energy and usually low energy level radioisotopes have many constructive and useful applications, not just in weapons

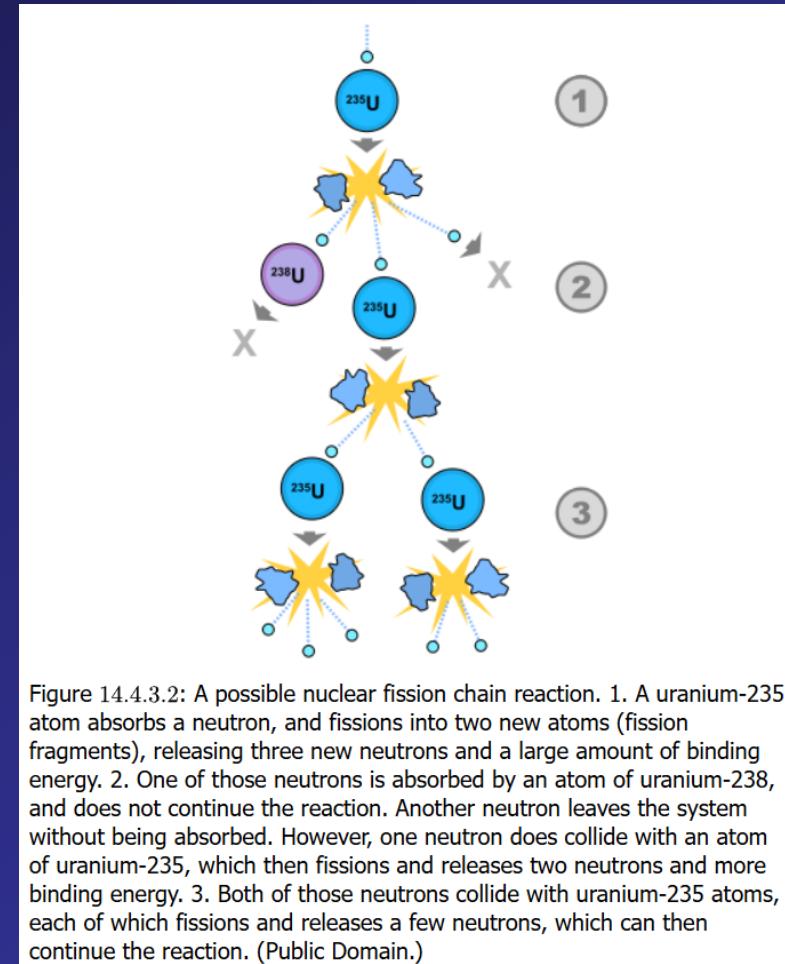


Figure 14.4.3.2: A possible nuclear fission chain reaction. 1. A uranium-235 atom absorbs a neutron, and fissions into two new atoms (fission fragments), releasing three new neutrons and a large amount of binding energy. 2. One of those neutrons is absorbed by an atom of uranium-238, and does not continue the reaction. Another neutron leaves the system without being absorbed. However, one neutron does collide with an atom of uranium-235, which then fissions and releases two neutrons and more binding energy. 3. Both of those neutrons collide with uranium-235 atoms, each of which fissions and releases a few neutrons, which can then continue the reaction. (Public Domain.)

Nuclear-Generated Electrical Energy

- 1831: Faraday shows that a coil of wire rotated/ moved in a magnetic field produced by permanent magnets generates an electric current (electrical energy) in the principle of electromagnetic induction
- Turbines are made of coiled wires within magnetic fields (permanent magnets) attached to a shaft with fins/blades: water that flows by falling (force of gravity) through hydroelectric dam penstocks
- Similar turbines are in nuclear power plants: nuclear energy heats water that turns into steam that makes the turbines turn to generate the electricity to power the grid

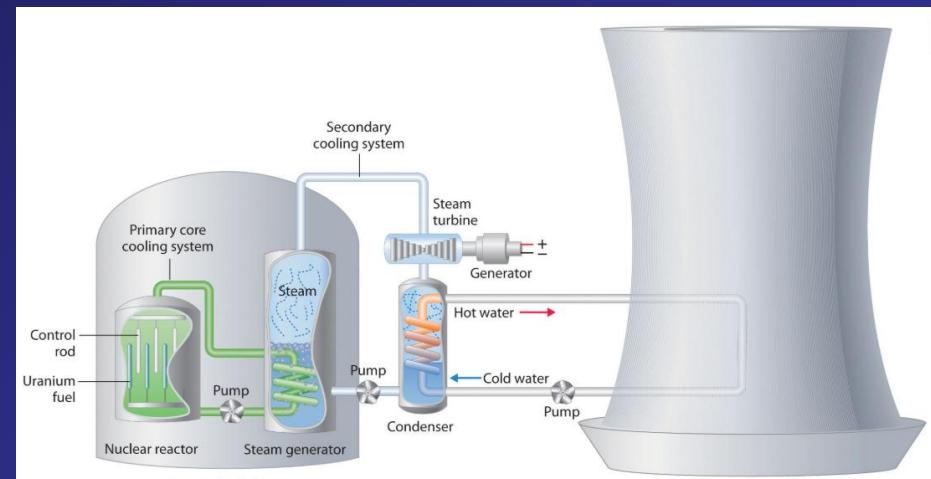
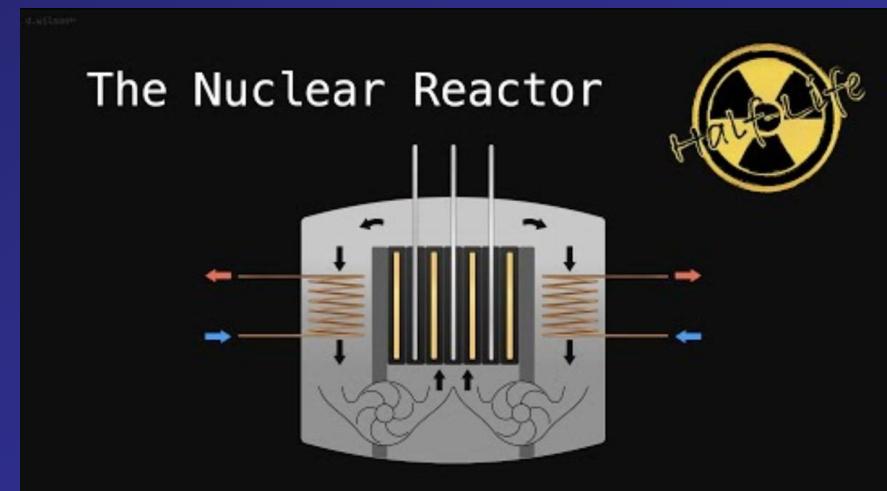


Figure 14.4.4.1: A Light-Water Nuclear Fission Reactor for the Production of Electric Power. The fuel rods are made of a corrosion-resistant alloy that encases the partially enriched uranium fuel; controlled fission of ^{235}U in the fuel produces heat. Water surrounds the fuel rods and moderates the kinetic energy of the neutrons, slowing them to increase the probability that they will induce fission. Control rods that contain elements such as boron, cadmium, or hafnium—which are very effective at absorbing neutrons—are used to control the rate of the fission reaction. A heat exchanger is used to boil water in a secondary cooling system, creating steam to drive the turbine and produce electricity. The large hyperbolic cooling tower, which is the most visible portion of the facility, condenses the steam in the secondary cooling circuit; it is often located at some distance from the actual reactor.

Elements of Controlling Fission

- Naturally occurring uranium is 99% U-238, <1% U-235 isotopes
- ^{235}U is what is needed for fission: the uranium ore is processed to achieve 3-5% ^{235}U enrichment. ^{235}U oxide is produced and its pellets packed into fuel rods
- Design of the reactor includes control rods to absorb neutrons to prevent uncontrolled chain reactions and especially to prevent nuclear explosions that result from radioactive materials reaching critical mass (as occurs in weapons)

- Trivia: A 1000 MWe reactor will consume about 27 tons (24,500 kg) enriched uranium annually, although this is only 1240 kg of fissionable ^{235}U mass (3.4 kg/day). One kilogram 235 can generate energy of 1500 tonnes of coal. Energy transduction is 1000 MWe for 3000 MWt, meaning it is only a third efficient



Fusion

- The sun provides energy through a fusion reaction of hydrogen (^1H) nuclei sustained by millions of degrees of heat energy
- Humans are trying to develop a sustained fusion reaction with considerable effort to harness it with

the potential of an output of energy well beyond the input of energy/cost to produce it

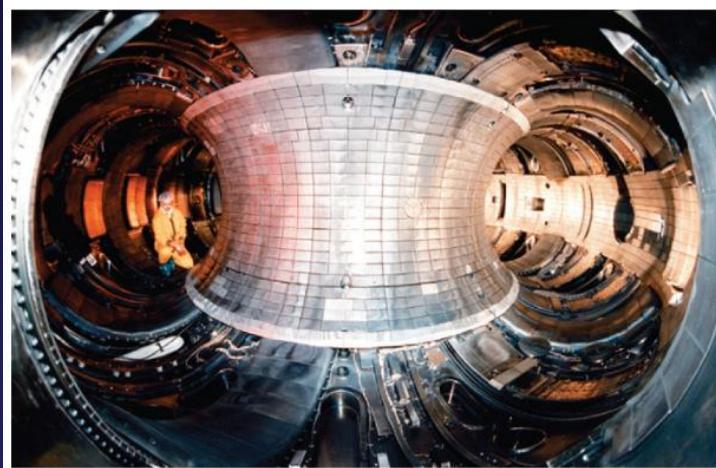
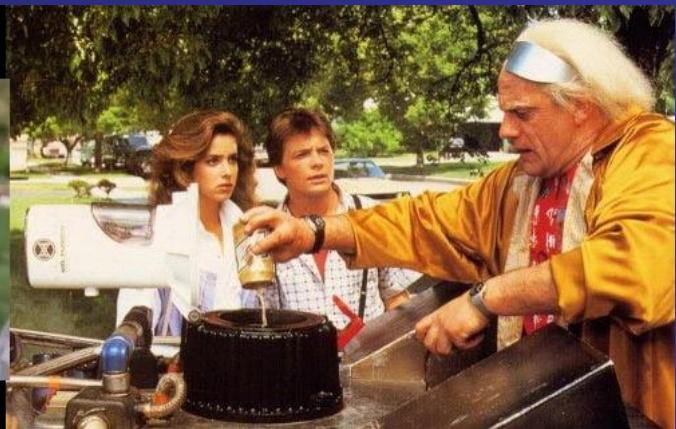


Figure 14.4.4.2: A Possible Design for a Nuclear Fusion Reactor. The extraordinarily high temperatures needed to initiate a nuclear fusion reaction would immediately destroy a container made of any known material. One way to avoid contact with the container walls is to use a high-energy plasma as the fuel. Because plasma is essentially a gas composed of ionized particles, it can be confined using a strong magnetic field shaped like a torus (a hollow donut).



Radiation Affecting Life

- Unstable nuclei of atoms can produce radiation in form of particles (alpha, beta) or electromagnetic radiation (gamma rays)
- The energy can produce high heat and break chemical bonds of biologically important molecules that can affect cells and tissues containing these damaged molecules
- Even without a lot of heat energy, radiative energy of low level might damage DNA responsible for making sure cells code correctly for proteins. The disruption could lead to a cell losing its control to replicate, leading to sporadic cancerous tumors

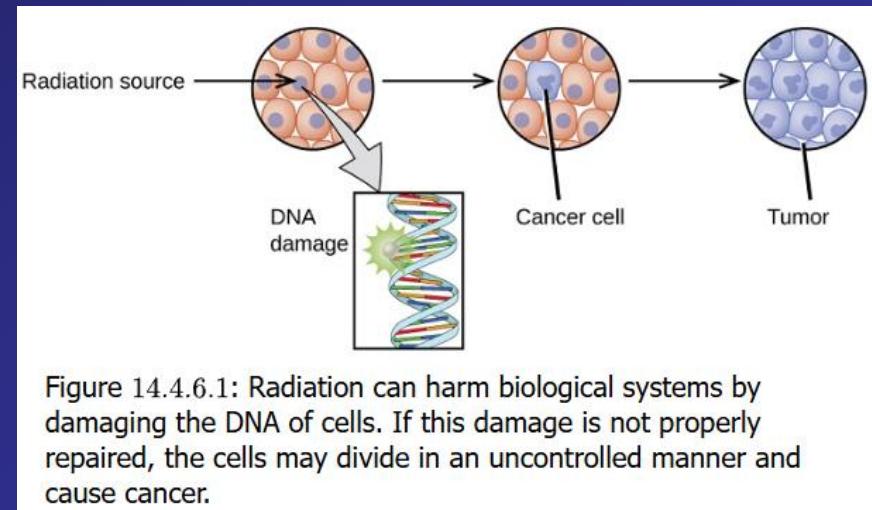


Figure 14.4.6.1: Radiation can harm biological systems by damaging the DNA of cells. If this damage is not properly repaired, the cells may divide in an uncontrolled manner and cause cancer.

Ionizing Radiation

- The electromagnetic spectrum is made up of nonionizing radiation (radio, microwaves, infrared, visible light) and ionizing radiation (ultraviolet, X- and gamma radiation, and the particles)
- Ionizing radiation has the effect of breaking chemical bonds that should not be broken, disrupting the structure and function of biomolecules
- A direct effect would be radiation damaging biomolecules directly
- An indirect effect would be to create a damaging form of a water (H_2O) molecule and it interacting with a biomolecule

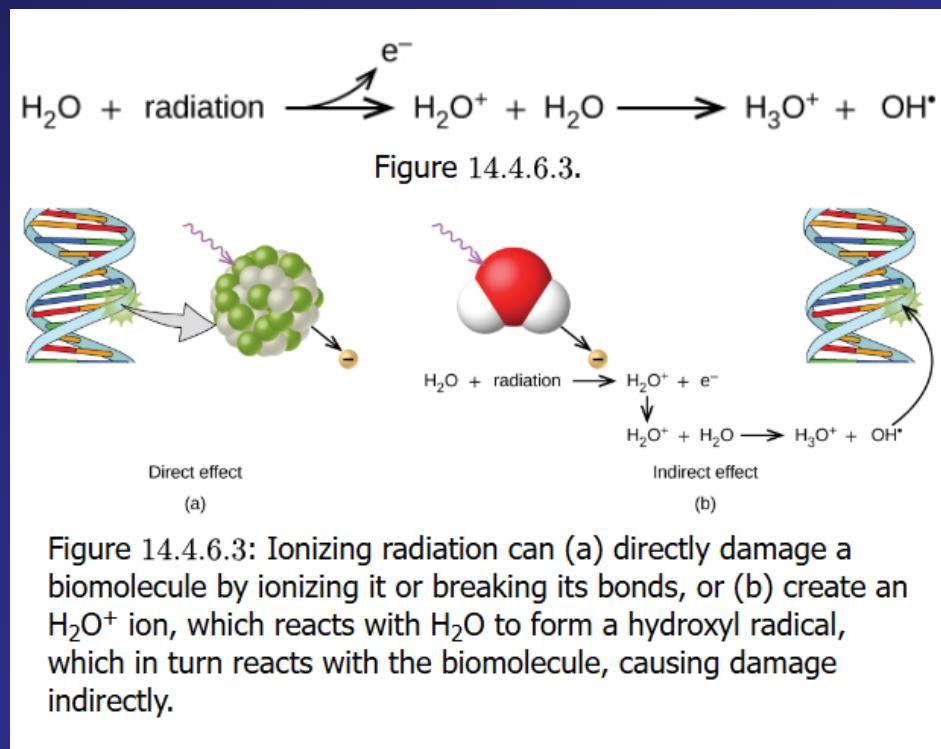
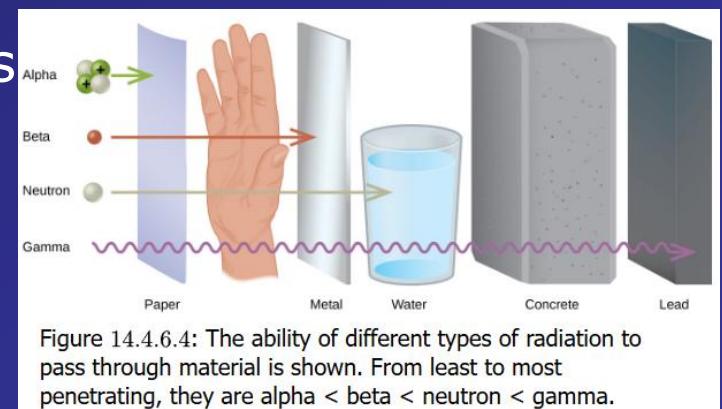


Figure 14.4.6.3: Ionizing radiation can (a) directly damage a biomolecule by ionizing it or breaking its bonds, or (b) create an H_2O^+ ion, which reacts with H_2O to form a hydroxyl radical, which in turn reacts with the biomolecule, causing damage indirectly.

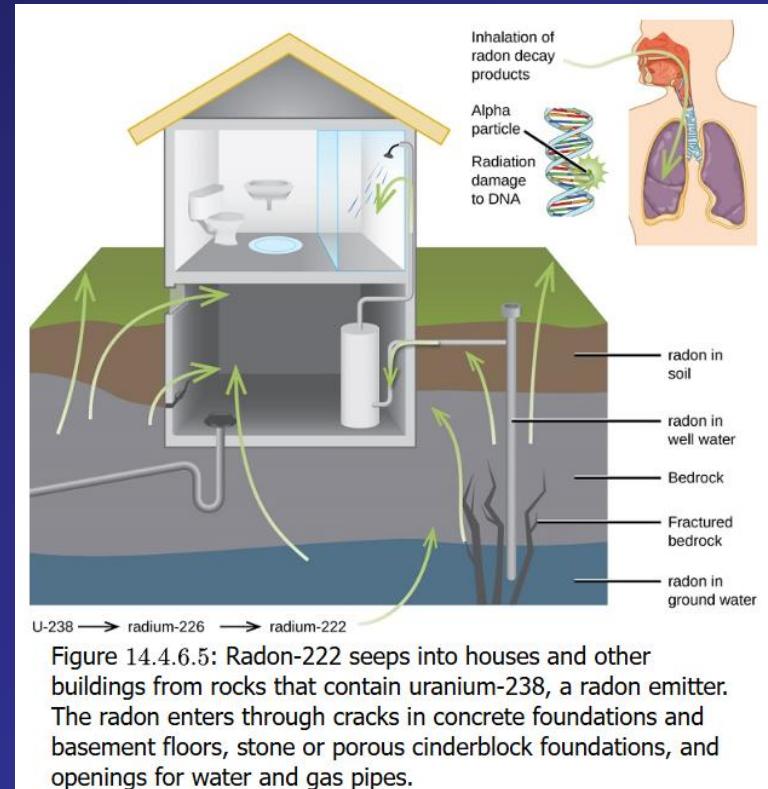
Radiation Exposure Biological Effects

- Radiation can cause damage to cells which could become cancer cells that limit harm to individual
- Could also damage DNA of germline (“reproductive”) cells that lead to genetic disease in next generation (children)
- Alpha particles are more powerful as ionizing radiation but are so big they travel only a short distance, so they do more damage if ingested & not if outside the body
- Beta particles can pass through tissues, but are less ionizing than alpha particles. A thin sheet of metal or a few centimeters of Plexiglas (transparent) will stop beta whose radioisotopes are used in experimental research laboratories
- Gamma radiation usually requires thick lead. Experimental scientists only use “low energy” gamma isotopes and limit their exposure



Radon (Rn-222)

- The alpha emitter Rn-222 is produced naturally when ^{238}U in soil and rocks decays
- It is a gas but a dense one that can accumulate in basements and lower floors of homes, being concentrated at levels that are 3 times higher than in outside air. 1 in 6 houses have levels so high they need special treatment
- Radon can significantly increase risk of lung cancer
- This cancer in nonsmokers attributable to radon & results in 20,000 US deaths annually



Detecting Radioactivity

- Devices and systems detecting all forms of radiation exist
- The Geiger-Müller tube detects electromagnetic (gamma, etc) radiation with gas particles in a chamber ionizing. This device mentioned in previous slide
- Scintillation counting systems put the radioisotope in an organic solvent with compounds that fluoresce when the decay event occurs: the fluorescence triggers a photodetector
- Dosimeters make use of various technologies, from exposure of photographic film, to electronic registers, quartz fiber, and thermoluminescent.

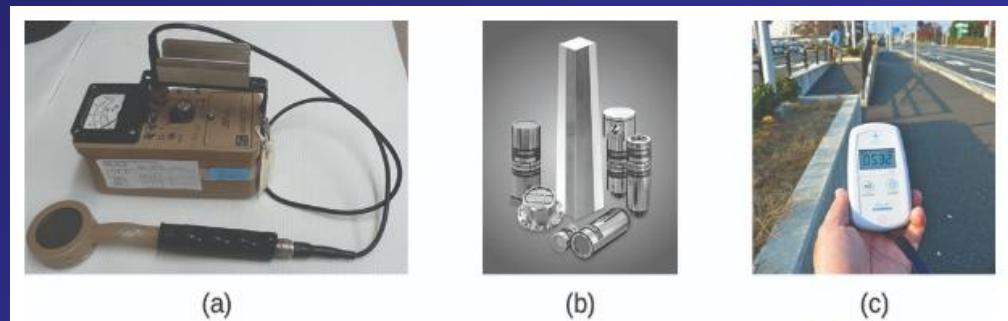


Figure 14.4.6.6: Devices such as (a) Geiger counters, (b) scintillators, and (c) dosimeters can be used to measure radiation. (Credit c: modification of work by "osaMu"/Wikimedia commons.)

Measuring Radioactivity

- The **becquerel** (Bq) is SI unit, representing **1 disintegration per second** (dps)
- The **curie** (Ci) is 3.7×10^{10} dps (37 billion dps). Scientists working with radioisotopes in research usually use **microcurie** (μ Ci) amounts
- Doses of radiation to measure exposure use the **gray** (Gy). This is **1 J energy per kilogram tissue**. The **rad** is **1/100th** of a Gy
- The **sievert** (Sv) is the SI unit for determining damage to tissue: it takes into account both the **energy** (in Gy) and **relative biological effectiveness (RBE)** of radiation exposure.
- The roentgen equivalent for man (rem) is used to indicate damage & exposure in people.
 $100 \text{ rem} = 1 \text{ Sv}$

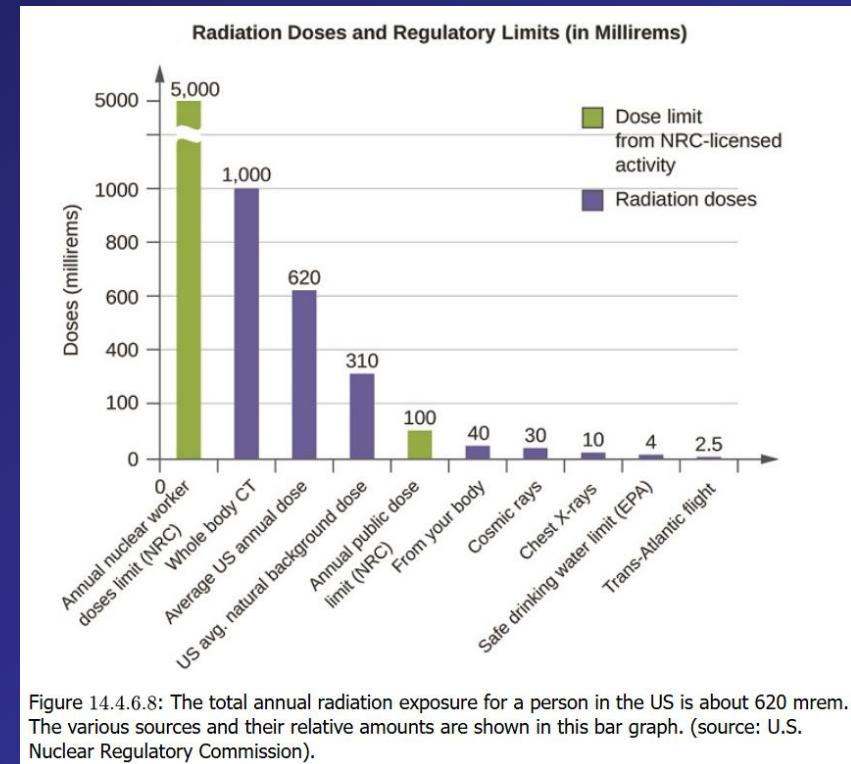
Table 14.4.6.1: Units Used for Measuring Radiation			
Measurement Purpose	Unit	Quantity Measured	Description
<i>activity of source</i>	becquerel (Bq)	radioactive decays or emissions	amount of sample that undergoes 1 decay/second
	curie (Ci)		amount of sample that undergoes 3.7×10^{10} decays/second
<i>absorbed dose</i>	gray (Gy)	energy absorbed per kg of tissue	$1 \text{ Gy} = 1 \text{ J/kg tissue}$
	radiation absorbed dose (rad)		$1 \text{ rad} = 0.01 \text{ J/kg tissue}$
<i>biologically effective dose</i>	sievert (Sv)	tissue damage	$\text{Sv} = \text{RBE} \times \text{Gy}$
	roentgen equivalent for man (rem)		$\text{Rem} = \text{RBE} \times \text{rad}$

Long-Term Radiation Exposure

- Multiple factors determine how damaging radiation can be: type, energy, distance from radiation, time of exposure
- Tens of rems can cause noticeable symptoms and illness. A 500 rem dose could lead to death (50% probability within 30 days). The effects can be cumulative over a lifetime

Table 14.4.6.2: Health Effects of Radiation

Exposure (rem)	Health Effect	Time to Onset (Without Treatment)
5–10	changes in blood chemistry	—
50	nausea	hours
55	fatigue	—
70	vomiting	—
75	hair loss	2–3 weeks
90	diarrhea	—
100	hemorrhage	—
400	possible death	within 2 months
1000	destruction of intestinal lining	—
	internal bleeding	—
	death	1–2 weeks
2000	damage to central nervous system	—
	loss of consciousness	minutes
	death	hours to days



Nuclear Medicine

- The thyroid gland produces iodine-containing hormones that regulate metabolism. The gland can be subject to diseases and disorders, like goiter and cancers
- Iodine-131 (^{131}I) is an isotope useful in diagnosis, including gland imaging, and particularly at the right levels in therapy by killing gland cells that become overactive (hyperthyroidism) and restoring health
- Of interest is that patients being treated with I-131 and who may travel by air may have to carry a special notice indicating to travel security officials their treatment, since half-life of isotope is about a week and they may trigger radiation detectors

Positron Emission Tomography (PET)

- Beta (β^-) particles are high speed electrons emitted when nuclei with too many neutrons to protons decay:



- Positrons (β^+) are high speed positive electrons emitted when nuclei with too many protons to neutrons decay:



- The isotopes have very short half-lives (in minutes) but are useful in many studies

Isotope	Half-Life	Common Chemical Form	Primary Medical Purpose
Fluorine-18	109.8 minutes	F-18 Fluorodeoxyglucose (FDG)	Oncology (Cancer): Identifies tumors and metastases by measuring glucose metabolism (cancer cells consume glucose rapidly). Neurology: Maps brain activity and detects dementia (e.g., Alzheimer's).
Carbon-11	20.4 minutes	C-11 Methionine, C-11 Raclopride	Neurology: Used for imaging neurotransmitter systems, receptors, and brain tumors. Its very short half-life requires an on-site cyclotron.
Oxygen-15	2.0 minutes	O-15 Water, O-15 Butanol	Perfusion/Blood Flow: Measures cerebral blood flow. Due to its extremely short half-life, it requires production and delivery next to the scanning room.
Nitrogen-13	9.9 minutes	N-13 Ammonia	Cardiology: Assesses myocardial (heart muscle) perfusion and viability to check for coronary artery disease.

External Beam Therapy (EBT)

- This concept of targeting diseased—such as cancerous—tissues with a focused destructive radiation beam narrowed at tumors and cancer cells has made gains with the use of technologies such as computed tomography (CT) that can map the diseased areas three-dimensionally
- Cancers of the head and neck, breast, colorectal region, the lungs, and prostate are part of the overall plans for management of therapy that incorporate radiation use



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