Nuclear Chemistry

Study material

http://www2.bakersfieldcollege.edu/wcooper/Handouts%202013/Chap_21_Nuclear%20Chem_3.pdf

Nuclear Chemistry

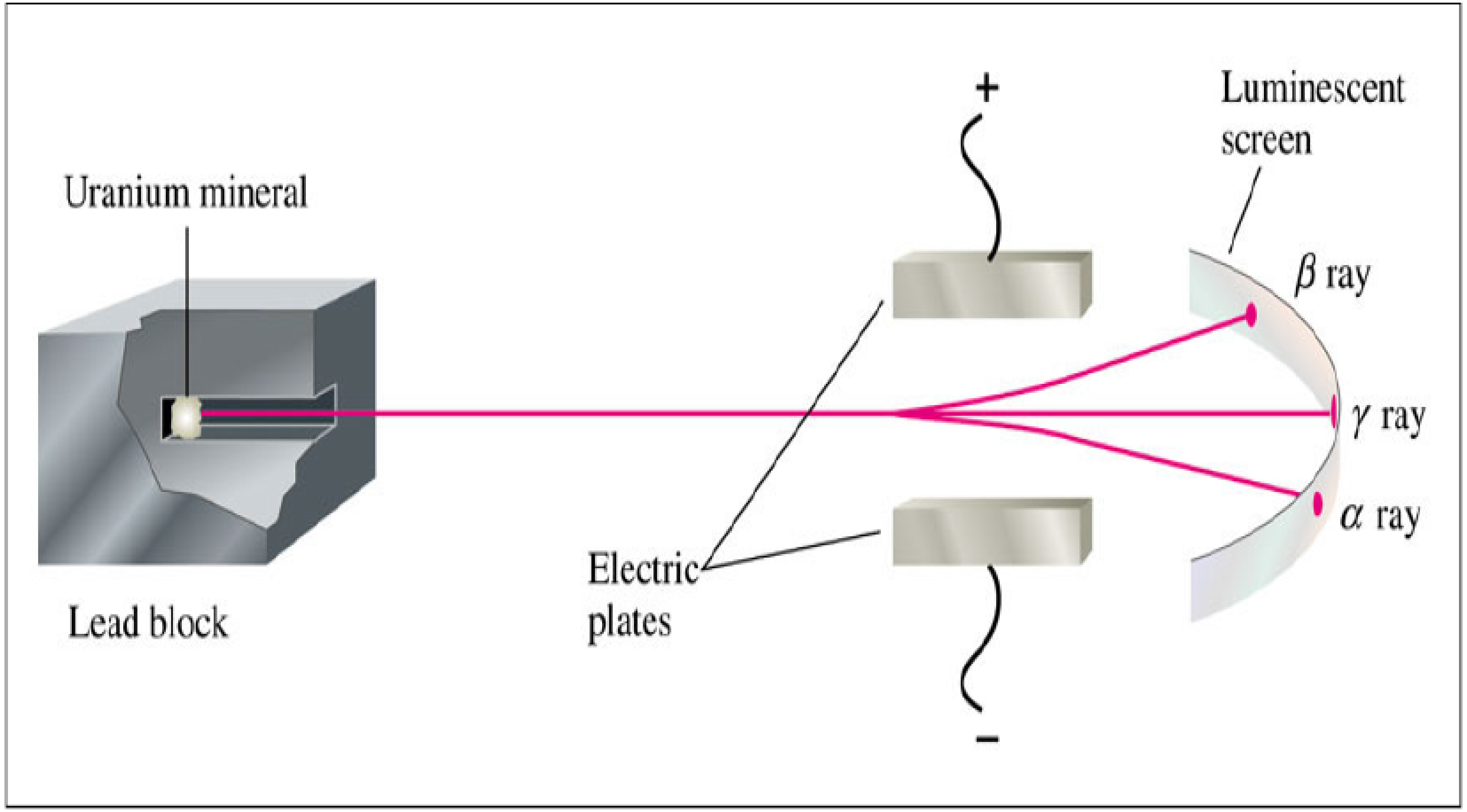
- In this chapter we will look at two types of **nuclear reactions**.
  - **Radioactive decay** is the process in which a nucleus spontaneously disintegrates, giving off radiation.
  - **Nuclear bombardment** reactions are those in which a nucleus is bombarded, or struck, by another nucleus or by a nuclear particle.

Radioactivity

- The phenomena of radioactivity was discovered by **Antoine Henri Becquerel** in 1896.
  - His work with uranium salts lead to the conclusion that the minerals gave off some sort of **radiation**.
  - This radiation was later shown to be separable by electric (and magnetic) fields into three types; **alpha** (α), **beta** (β), and **gamma** (γ) rays.

- **Alpha rays** bend away from a positive plate indicating they are positively charged.
- They are known to consist of **helium-4 nuclei** (nuclei with two protons and two neutrons).
- **Beta rays** bend in the opposite direction indicating they have a negative charge.
- They are known to consist of **high speed electrons**.
- **Gamma rays** are unaffected by electric and magnetic fields.
  - They have been shown to be a form of **electromagnetic radiation** similar to x rays, but higher in energy and shorter in wavelength.

Separation of Radiation From Radioactive Material (Uranium Mineral)



Nuclear Equations

- A **nuclear equation** is a symbolic representation of a nuclear reaction using nuclide symbols.
  - For example, the **nuclide symbol** for uranium-238 is $\mathbf{^{238}_{92}U}$
  - The radioactive decay of $\mathbf{^{238}_{92}U}$ by alpha-particle emission (loss of a $\mathbf{^{4}_{2}He}$ nucleus) is written

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

  - Reactant and product nuclei are represented in nuclear equations by their nuclide symbol.

- Other particles are given the following symbols.

Proton	${}^{1}_{1}\mathrm{H}$	or	${}^{1}_{1}\mathrm{p}$
Neutron	${}^{1}_{0}\mathrm{n}$		
Electron	${}^{0}_{-1}\beta$	or	${}^{0}_{-1}\mathrm{e}$
Positron	${}^{0}_{1}\beta$	or	${}^{0}_{1}\mathrm{e}$
Gamma photon	${}^{0}_{0}\gamma$		

- The total **charge is conserved** during a nuclear reaction.

- This means that the **sum of the subscripts for the products must equal the sum of the subscripts for the reactants**.

- The total **number of nucleons** is also conserved during a nuclear reaction.

- This means that the **sum of the <u>superscripts</u> for the products must equal the sum of the <u>superscripts</u> for the reactants**.

- Note that if all reactants and products but one are known in a nuclear equation, the identity of the missing nucleus (or particle) is easily obtained.

- This is illustrated in the next example.

A Problem To Consider

- Technetium-99 is a long-lived radioactive isotope of technetium. Each nucleus decays by emitting one beta particle. What is the product nucleus?
  - The nuclear equation is

$$^{99}_{43}\mathrm{Tc} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{-1}\beta$$

  - From the superscripts, you can write

$$99 = A + 0, \quad \text{or} \quad A = 99$$

- The nuclear equation is

$$^{99}_{43}\mathrm{Tc} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{-1}\beta$$

- Similarly, from the subscripts, you get

$$43 = Z - 1, \quad \text{or} \quad Z = 43 + 1 = 44$$

- Hence A = 99 and Z = 44, so the product is

$$^{99}_{44}\mathrm{Ru}$$

Nuclear Stability

- The existence of stable nuclei with more than one proton is due to the **nuclear force**.
  - The **nuclear force** is a strong force of attraction between nucleons that acts only at very short distances (about 10^{-15} m).
  - This force can **more than compensate** for the repulsion of electrical charges and thereby give a stable nucleus.

Nuclear Stability

- Several factors appear to contribute the stability of a nucleus.
  - The **shell model of the nucleus** is a nuclear model in which protons and neutrons exist in levels, or shells, analogous to the shell structure exhibited in electron configurations.
  - Experimentally, note that <u>nuclei with certain numbers of protons and neutrons</u> appear to be very stable.

- These numbers, called **magic numbers**, are the numbers of nuclear particles in a completed shell of protons or neutrons.

- Because nuclear forces differ from electrical forces, these numbers are not the same as those for electrons is atoms.

- For protons, the magic numbers are
  - **2, 8, 20, 28, 50, and 82**

- For neutrons, the magic numbers are
  - **2, 8, 20, 28, 50, 82, and 126**

- Evidence also points to the special stability of **pairs** of protons and **pairs** of neutrons.

- The table below lists the number of stable isotopes that have an even number of protons and an even number of neutrons.

	Number of Stable Isotopes			
	157	52	50	5
Number of protons	**Even**	**Even**	**Odd**	**Odd**
Number of neutrons	**Even**	**Odd**	**Even**	**Odd**

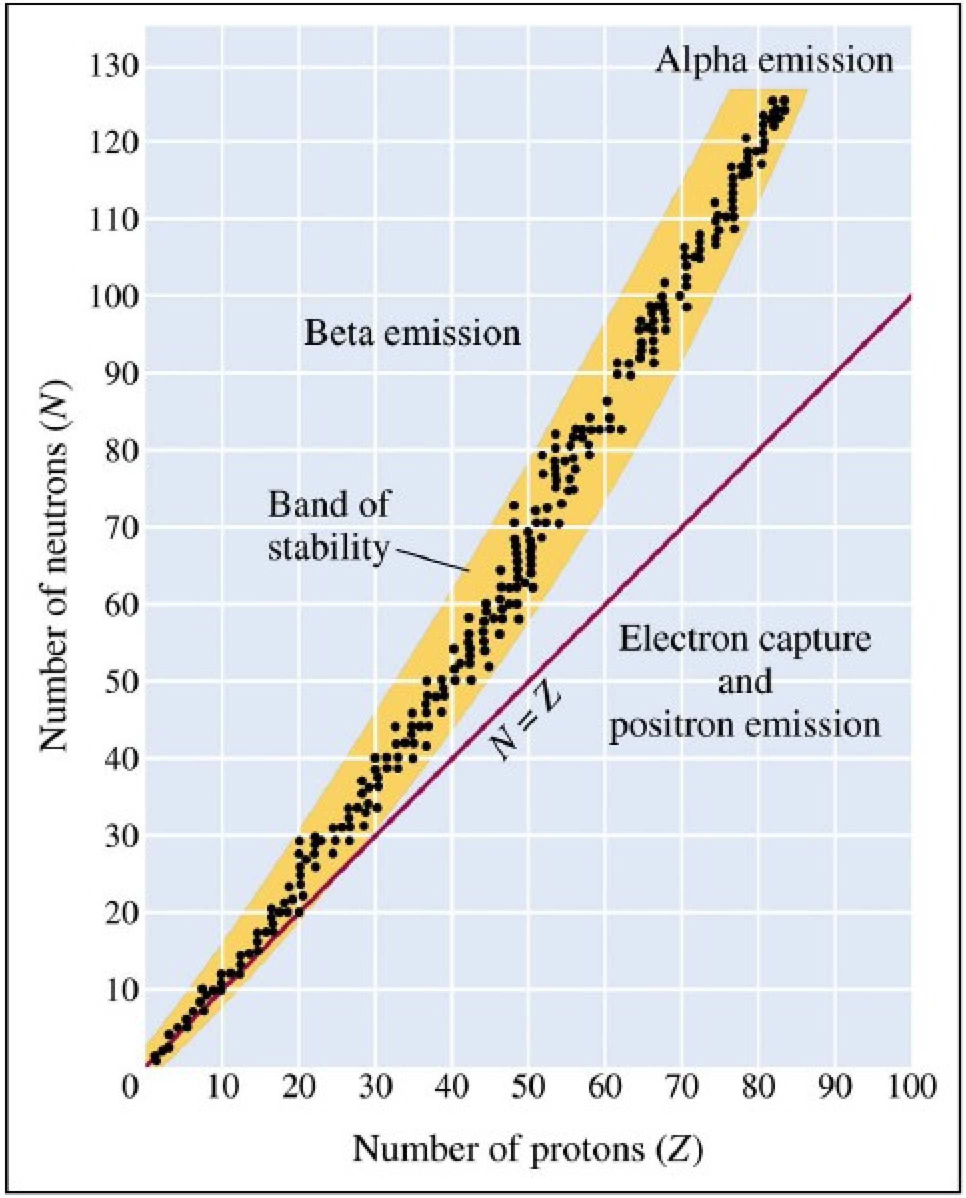
- Finally, when you plot each stable nuclide on a graph of protons vs. neutrons, these stable nuclei fall in a certain region, or **band**.

- The **band of stability** is the region in which stable nuclides lie in a plot of number of protons against number of neutrons.

- **No stable nuclides** are known with **atomic numbers greater than 83**.

- On the other hand, all elements with Z equal to 83 or less have one or more stable nuclides.

Band of Stability



Types of Radioactive Decay

- There are **six common types** of radioactive decay.
  - **1. Alpha emission** (abbreviated a): emission of a $^{4}_{2}\text{He}$ nucleus, or alpha particle, from an unstable nucleus.
    - An example is the radioactive decay of radium-226.

$$^{226}_{88}\text{Ra} \rightarrow {}^{222}_{86}\text{Rn} + {}^{4}_{2}\text{He}$$

- **2. Beta emission** (abbreviated β or β⁻): emission of a high speed electron from a stable nucleus.
- This is equivalent to the conversion of a neutron to a proton.

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

- **3. Positron emission** (abbreviated β^{+}): emission of a positron from an unstable nucleus.
- This is equivalent to the conversion of a proton to a neutron.

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

- **4. Electron capture** (abbreviated EC): the decay of an unstable nucleus by capturing, or picking up, an electron from an inner orbital of an atom.
- An example is the radioactive decay of potassium-40.

$$^{40}_{19}\mathrm{K} + ^{0}_{-1}\mathrm{e} \rightarrow ^{40}_{18}\mathrm{Ar}$$

- **5. Gamma emission** (abbreviated γ): emission from an excited nucleus of a gamma photon, corresponding to radiation with a wavelength of about 10^{-12} m.
- In many cases, radioactive decay produces a product nuclide in a **metastable** excited state.
- The excited state is unstable and emits a gamma photon and goes to a lower energy state.

- **4. Positron emission** (abbreviated β+): emission of a positron from an unstable nucleus.

- The radioactive decay of technetium-95 is an example of positron emission.

$${}^{95}_{43}\mathrm{Tc} \rightarrow {}^{95}_{42}\mathrm{Mo} + {}^{0}_{1}\mathrm{e}$$

- **5. Electron capture** (abbreviated EC): the decay of an unstable nucleus by capturing, or picking up, an electron from an inner orbital of an atom.

- In effect, a proton is changed to a neutron, as in positron emission.

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

- An example is metastable technetium-99.

$$^{99m}_{43}\mathrm{Tc} \rightarrow {}^{99}_{43}\mathrm{Tc} + {}^{0}_{0}\gamma$$

- **6. Spontaneous fission**: the spontaneous decay of an unstable nucleus in which a heavy nucleus of mass number greater than 89 splits into lighter nuclei and energy is released.

- For example, uranium-236 undergoes spontaneous fission.

$$^{236}_{92}\mathrm{U} \rightarrow {}^{96}_{39}\mathrm{Y} + {}^{136}_{53}\mathrm{I} + 4\,^{1}_{0}\mathrm{n}$$

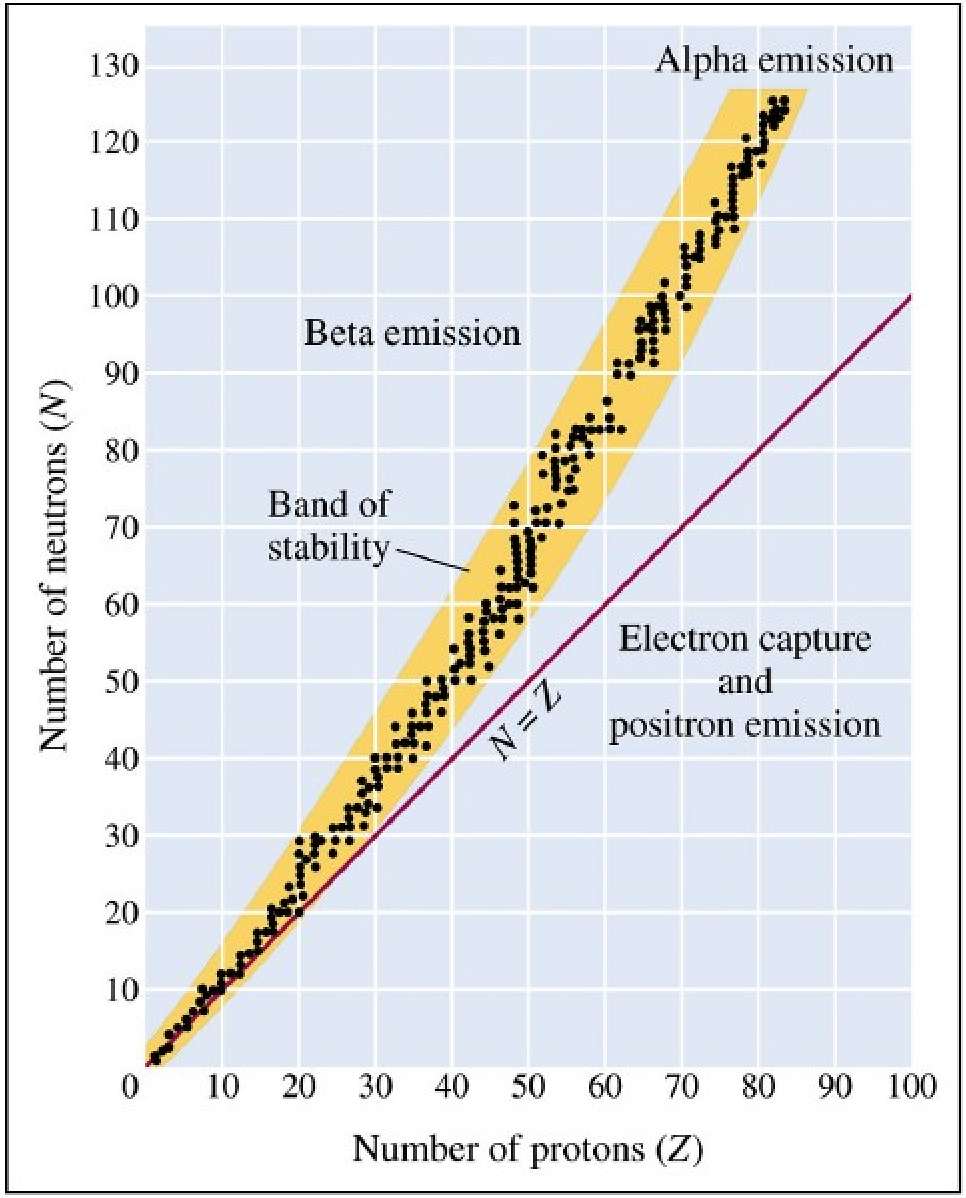
Predicting the Type of Radioactive Decay

- Nuclides **outside the band of stability** are generally **radioactive**.
  - Nuclides to the **left of the band** have more neutrons than that needed for a stable nucleus.
  - These nuclides tend to **decay by beta emission** because it reduces the neutron-to-proton ratio.

Predicting the Type of Radioactive Decay

- Nuclides **outside the band of stability** are generally **radioactive**.
  - In contrast, nuclides to the **right of the band** of stability have a neutron-to-proton ratio smaller than that needed for a stable nucleus.
  - These nuclides tend to **decay by positron emission or electron capture** because it increases the neutron to proton ratio.
  - In the very **heavy elements**, especially those with Z greater than 83, radioactive decay is often by **alpha emission**.

Band of Stability



A Problem To Consider

- Predict the expected type of radioactive decay for each of the following radioactive nuclides.

$^{47}_{20}\mathrm{Ca}$ $^{25}_{13}\mathrm{Al}$

  - The atomic weight of calcium is 40.1 amu, so you expect calcium-40 to be a stable isotope.
  - **Calcium-47** has a mass number greater than that of the stable isotope, so you would expect it to decay by **beta emission**.

$^{47}_{20}\mathrm{Ca}$ $^{25}_{13}\mathrm{Al}$

- The atomic weight of aluminum is 27.0 amu, so you expect aluminum-27 to be a stable isotope.

- **Aluminum-25** has a mass number less than that of the stable isotope, so you would expect it to decay by **positron emission or electron capture**.

Nuclear Bombardment Reactions

- In 1919, **Ernest Rutherford** discovered that it is possible to change the nucleus of one element into the nucleus of another element.
  - **Transmutation** is the change of one element to another by bombarding the nucleus of the element with nuclear particles or nuclei.

- Rutherford used a radioactive alpha source to bombard nitrogen nuclei.

$$^{14}_{7}\mathrm{N}+^{4}_{2}\mathrm{He}\rightarrow^{17}_{8}\mathrm{O}+^{1}_{1}\mathrm{H}$$

- He discovered that protons are ejected in the process.

- The British physicist **James Chadwick** suggested in 1932 that the radiation from beryllium consists of **neutral particles**, each with a mass approximately that of a proton.
  - Chadwick's suggestion led to the **discovery of the neutron**.

$$^{9}_{4}\mathrm{Be}+^{4}_{2}\mathrm{He}\rightarrow^{12}_{6}\mathrm{C}+^{1}_{0}\mathrm{n}$$

Nuclear Bombardment Reactions

- Nuclear bombardment reactions are often referred to by an **abbreviated notation**.
  - For example, the reaction

$$^{14}_{7}\mathrm{N} + ^{4}_{2}\mathrm{He} \rightarrow ^{17}_{8}\mathrm{O} + ^{1}_{1}\mathrm{H}$$

is abbreviated

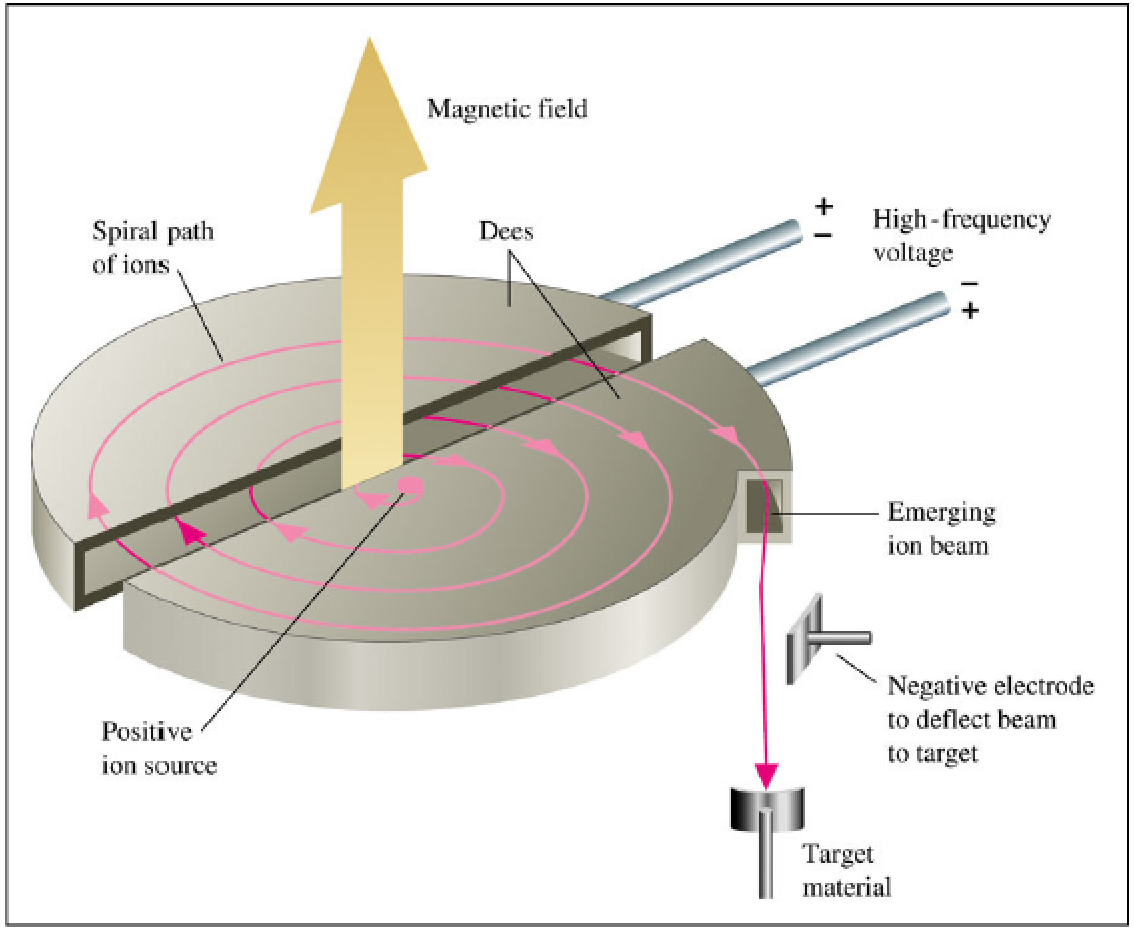
$$^{14}_{7}\mathrm{N}(\alpha,\mathrm{p})^{17}_{8}\mathrm{O}$$

Nuclear Bombardment Reactions

- Bombardment of heavy nuclei **require accelerated particles** for successful transmutation reactions.
  - A **particle accelerator** is a device used to accelerate electrons, protons, and alpha particles and other ions to very high speeds.
  - It is customary to measure the kinetic energy of these particles in units of **electron volts**.

$$1\,\mathrm{eV} = 1.602\times10^{-19}\ \mathrm{J}$$

- The following figure shows a diagram of a **cyclotron**, a type of particle accelerator consisting of two hollow, semicircular metal electrodes in which charged particles are accelerated in stages.



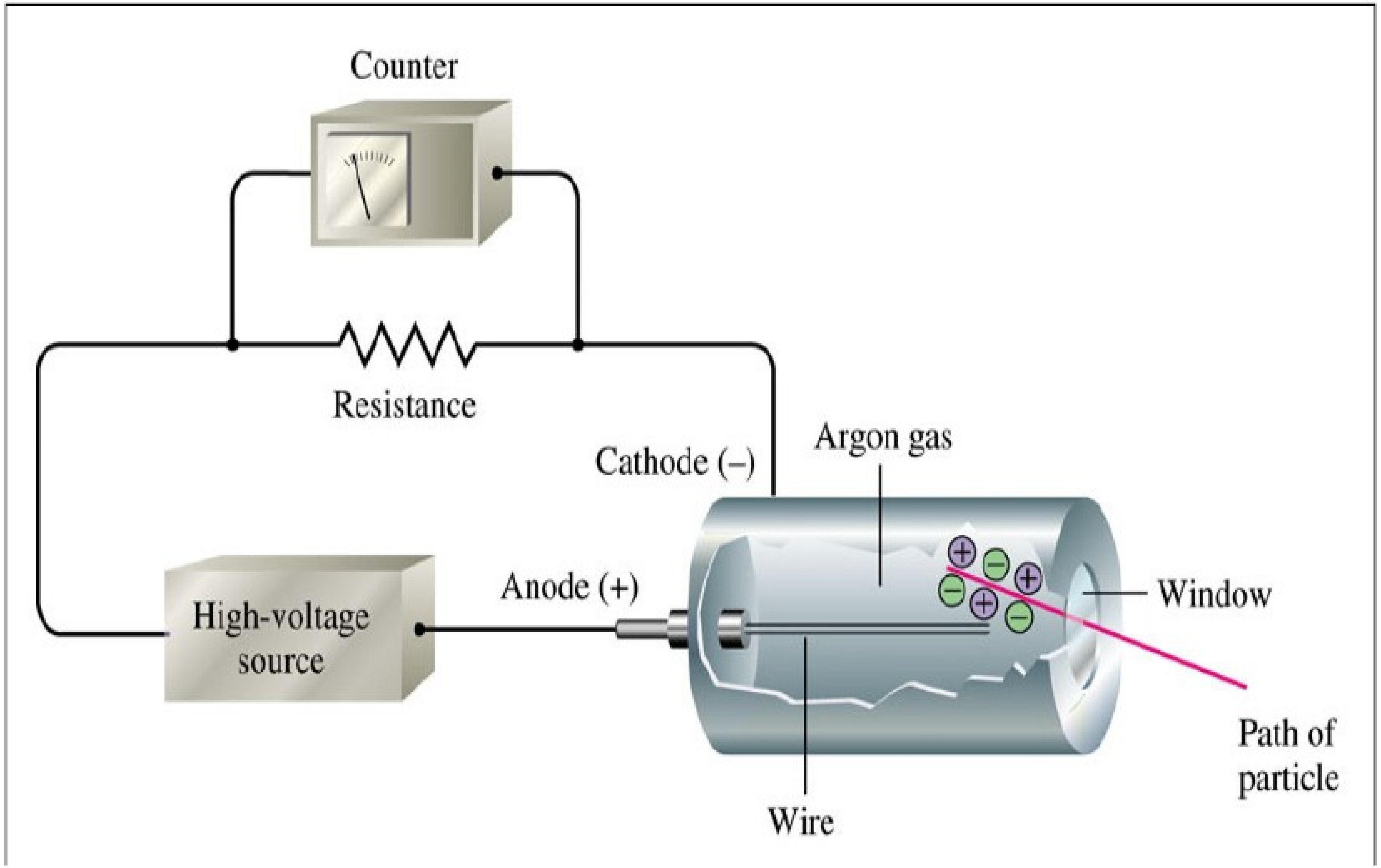
Transuranium Elements

- The **transuranium elements** are elements with atomic number greater than that of uranium (Z=92), the naturally occurring element of greatest Z.
  - The first transuranium element was produced at the University of California at Berkley in 1940 by **E. M. McMillan and P. H. Abelson**.
  - They produced an isotope of element 93, which they named **neptunium**.
  - Recent work has yielded other elements including the heaviest to date, 118.

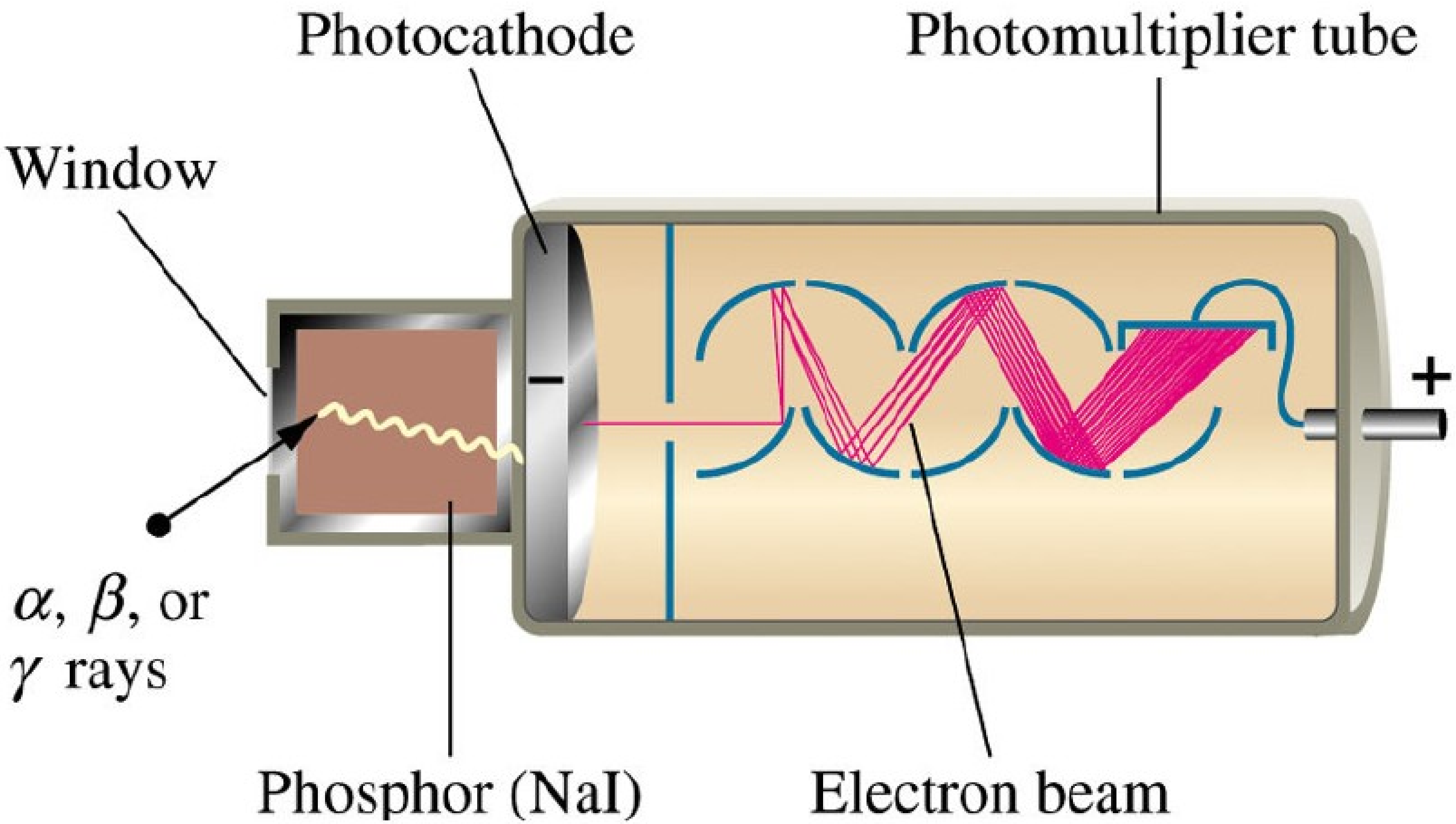
Radiations and Matter: Detection

- Two types of devices, **ionization counters** and **scintillation counters**, are used to count particles emitted from radioactive nuclei.
  - A **Geiger counter** a kind of ionization counter used to count particles emitted by radioactive nuclei, consists of a metal tube filled with gas, such as argon.

Geiger Counter



- A **scintillation counter** is a device that detects nuclear radiation from flashes of light generated in a material by the radiation.



Radiations and Matter: Detection

- The **activity of a radioactive source** is the number of nuclear disintegrations per unit time occurring in a radioactive material.
  - A **Curie (Ci)** is a unit of activity equal to 3.700 x 10^{10} disintegrations per second (dps).
  - A sample of technetium having an activity of 1.0 x 10^{-2} Ci is decaying at a rate of

$$(1.0\times10^{-2})\times(3.700\times10^{10}) = 3.7\times10^{8}\ \textbf{nuclei per second}$$

Biological Effects and Radiation Dosage

- To monitor the effect of nuclear radiations on biological tissue, it is necessary to have a **measure of radiation dosage**.
  - The **rad** (from radiation absorbed dose) is the dosage of radiation that deposits 1 x 10^{-2} J of energy per kilogram of tissue.
  - However, the biological effect of radiation depends not only on the energy deposited but also on the **type of radiation**.

- The **rem** is a unit of radiation dosage used to relate various kinds of radiation in terms of biological destruction.

- It equals the rad times a factor for the type of radiation, called the **relative biological effectiveness (RBE).**

$$\text{rems} = \text{rads} \times \text{RBE}$$

- Beta and gamma radiations have an RBE of about 1, where neutron radiation has an RBE about 5 and alpha radiation an RBE of about 10.

- A single dose of about 500 rems is fatal to most people.

Rate of Radioactive Decay

- The **rate of radioactive decay**, that is the number of disintegrations per unit time, is proportional to the number of radioactive nuclei in the sample.
  - You can express this rate mathematically as

$$\mathbf{Rate = kN_t}$$

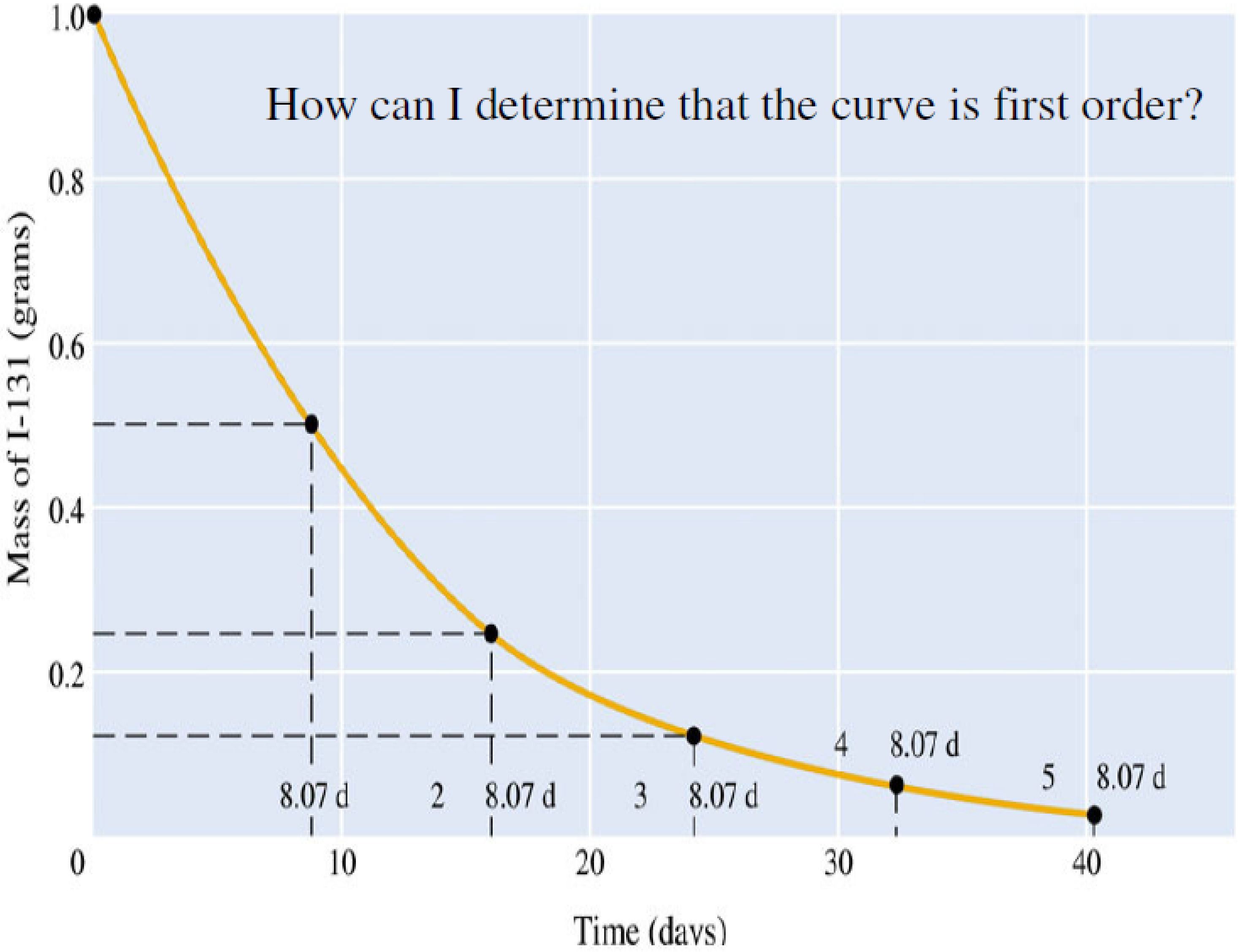
where $\mathbf{N_t}$ is the number of radioactive nuclei at time t, and **k** is the **radioactive decay constant**.

  - All radioactive decay follows **first order kinetics** as outlined in Chapter 14.
  - Therefore, the **half-life** of a radioactive sample is related only to the radioactive decay constant.

Rate of Radioactive Decay

- The **half-life, $t_{1/2}$** ,of a radioactive nucleus is the time required for one-half of the nuclei in a sample to decay.
  - The first-order relationship between $\mathbf{t_{1/2}}$ and the decay constant **k** is

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



How can I determine that the curve is first order?

A Problem To Consider

- The decay constant for the beta decay of technetium-99 is 1.0 x 10^{-13} s^{-1}. What is the half-life of this isotope in years?
  - Substitute the value of k into our half-life equation.

$$t_{½} = \frac{0.693}{1.0\times10^{-13}s^{-1}} = 6.9\times10^{12}\ s$$

  - Then convert from seconds to years.

$$6.9\times10^{12}\ s\times\frac{1\,min}{60\,sec}\times\frac{1\,h}{60\,min}\times\frac{1\,d}{24\,h}\times\frac{1\,y}{365\,d} = 2.2\times10^{5}\ y$$

Rate of Radioactive Decay

- Once you know the decay constant, you can calculate the **fraction of radioactive nuclei remaining** after a given period of time.
  - The first-order time-concentration equation is

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

A Problem To Consider

- Phosphorus-32 has a half-life of 14.3 days. What fraction of a sample of phosphorus-32 would remain after 5.5 days?
  - If we substitute k = 0.693/$t_{1/2}$ we get

$$\ln \frac{N_t}{N_o} = \frac{-0.693\,t}{t_{1/2}}$$

  - Substituting t = 5.5 d and $t_{1/2}$ = 14.3 d, you obtain

$$\ln \frac{N_t}{N_o} = \frac{-0.693\,(5.5\mathrm{d})}{(14.3\,\mathrm{d})} = -0.267$$

- Hence,

$$\textbf{Fraction nuclei remaining} = \frac{N_t}{N_o} = e^{-0.267} = 0.77$$

- A **radioactive tracer** is a very small amount of radioactive isotope added to a chemical, biological, or physical system to study the system.
  - A series of experiments using tracers was carried out in the 1950s by **Melvin Calvin** at the University of California at Berkley, to **discover the mechanism of photosynthesis in plants**.

Applications of Radioactive Isotopes

- Another example of radioactive tracers is **isotopic dilution**, a technique to determine the quantity of a substance in a mixture.
  - Human **blood volumes** are determined using the technique of isotopic dilution.
- **Neutron activation analysis** is an analysis of elements in a sample based on the conversion of stable isotopes to radioactive isotopes by bombarding a sample with neutrons.
  - Human hair samples are identified by neutron activation analysis.

Mass-Energy Calculations

- When nuclei decay, they form products of lower energy.
  - The **change of energy** is related to the **change in mass**, according to the mass-energy equivalence relation derived by Albert Einstein in 1905.
  - Energy and mass are equivalent and related by the equation

$$E = mc^2$$

Here c is the speed of light, 3.00×10^8 m/s.

Mass-Energy Calculations

- When nuclei decay, they form products of lower energy.
  - If a system **loses energy**, it must also **lose mass**.
  - Though mass loss in chemical reactions is small (10^{-12} kg), the mass changes in **nuclear reactions** are approximately a **million times larger.**
  - Consider the alpha decay of uranium-238 to thorium-234.

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

238.05078 234.04359 4.00260

  - We have written the atomic mass (in amu) beneath each nuclide symbol.

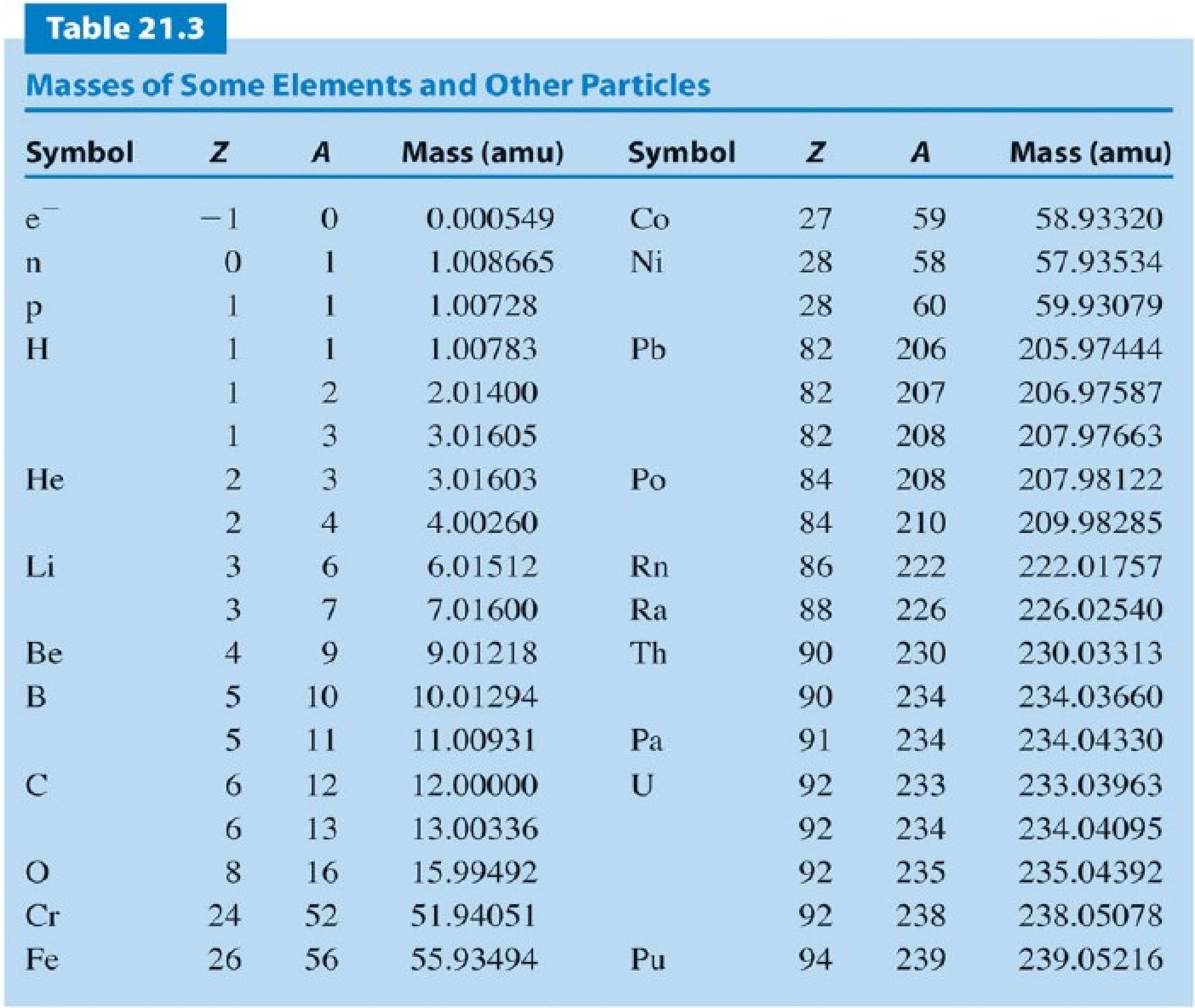


Table 21.3

Masses of Some Elements and Other Particles

Symbol	*Z*	*A*	Mass (amu)	Symbol	*Z*	*A*	Mass (amu)
e^-	−1	0	0.000549	Co	27	59	58.93320
n	0	1	1.008665	Ni	28	58	57.93534
p	1	1	1.00728		28	60	59.93079
H	1	1	1.00783	Pb	82	206	205.97444
	1	2	2.01400		82	207	206.97587
	1	3	3.01605		82	208	207.97663
He	2	3	3.01603	Po	84	208	207.98122
	2	4	4.00260		84	210	209.98285
Li	3	6	6.01512	Rn	86	222	222.01757
	3	7	7.01600	Ra	88	226	226.02540
Be	4	9	9.01218	Th	90	230	230.03313
B	5	10	10.01294		90	234	234.03660
	5	11	11.00931	Pa	91	234	234.04330
C	6	12	12.00000	U	92	233	233.03963
	6	13	13.00336		92	234	234.04095
O	8	16	15.99492		92	235	235.04392
Cr	24	52	51.94051		92	238	238.05078
Fe	26	56	55.93494	Pu	94	239	239.05216

- The change in mass for this reaction, in molar amounts is

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

238.05078 234.04359 4.00260

$$\Delta m = (234.04359 + 4.00260 - 238.05078) = -0.00459\ \mathrm{g}$$

- The energy change for 1 mol of uranium-238 is

$$\Delta E = \Delta mc^2 = (-4.59\times10^{-6}\ \mathrm{kg})\times(3.00\times10^{8}\ \mathrm{m/s})^2$$

$$\Delta E = -4.13\times10^{11}\ \mathrm{J} = \text{-}4.13\times10^{8}\ \mathrm{kJ}$$

Mass-Energy Calculations

- The equivalence of mass and energy explains the fact that **the mass of an atom is <u>always</u> less than the sum of the masses of its constituent particles.**
  - When nucleons come together to form a stable nucleus, energy is released.
  - According to Einstein's equation, there must be a **corresponding decrease in mass**.

Mass-Energy Calculations

- The **binding energy** of a nucleus is the energy needed to break a nucleus into its individual protons and neutrons.
  - Thus the binding energy of the helium-4 nucleus is the energy change for the reaction

$$^{4}_{2}\mathrm{He} \rightarrow 2\,^{1}_{1}\mathrm{p} + 2\,^{1}_{0}\mathrm{n}$$

$$4.00260 \qquad 2(1.00728) \quad 2(1.008665) \quad \Delta m = 0.03040\ \mathrm{amu}$$

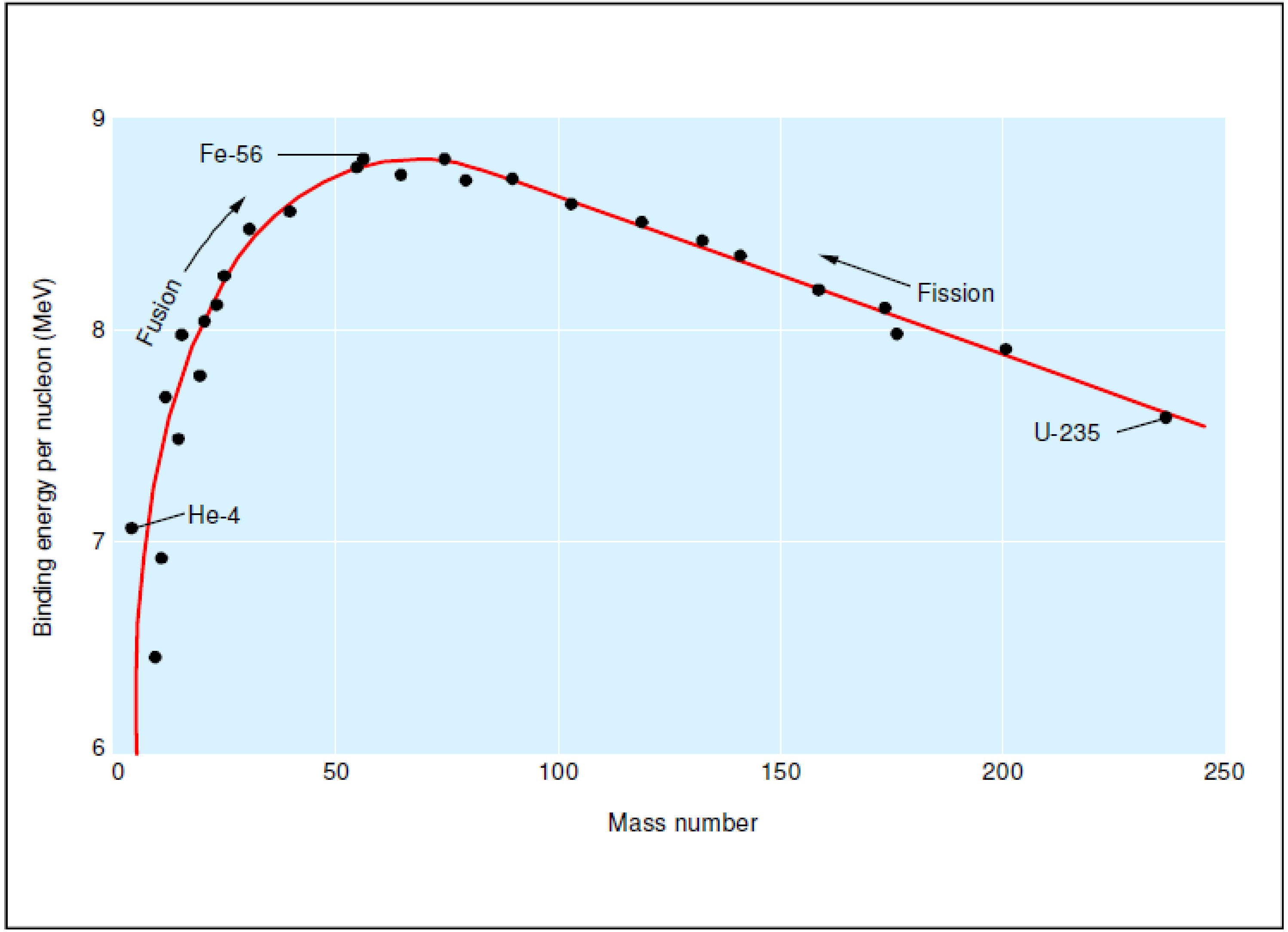
  - Both binding energy and the corresponding mass defect are reflections of the stability of the nucleus.

- Figure 20.16 shows the values of **binding energy per nucleon** plotted against the mass number for various nuclides.

- Note that nuclides **near mass number 50** have the largest binding energies per nucleon.

- For this reason, **heavy nuclei might be expected to split** to give lighter nuclei, while **light nuclei might be expected to combine** to form heavier nuclei.

Plot of binding energy per nucleon versus mass number

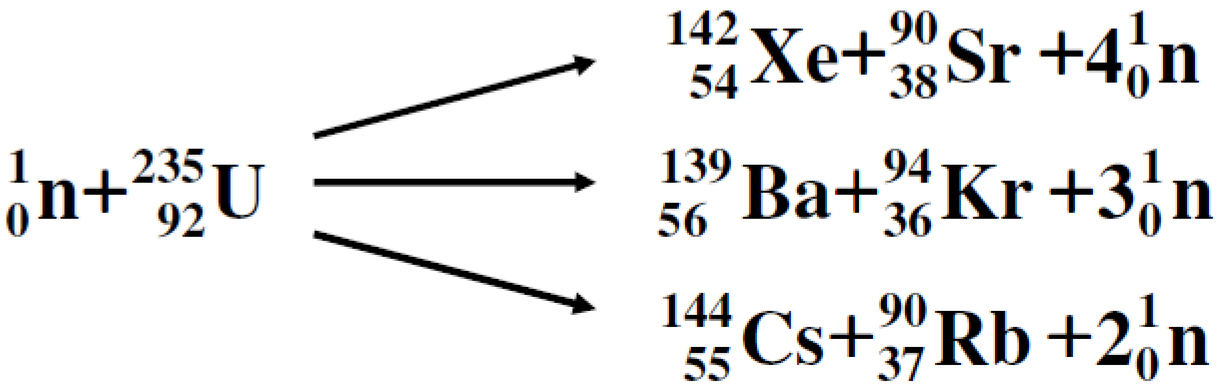


Nuclear Fission and Nuclear Fusion

- **Nuclear fission** is a nuclear reaction in which a heavy nucleus splits into lighter nuclei and energy is released.
  - For example, one of the possible mechanisms for the decay of californium-252 is

$$^{252}_{98}\mathrm{Cf} \rightarrow {}^{142}_{56}\mathrm{Ba} + {}^{106}_{42}\mathrm{Mo} + 4\,{}^{1}_{0}\mathrm{n}$$

- In some cases a nucleus can be induced to undergo fission by bombardment with neutrons.



$$^{1}_{0}n + ^{235}_{92}U \rightarrow ^{142}_{54}Xe + ^{90}_{38}Sr + 4\,^{1}_{0}n$$

$$^{1}_{0}n + ^{235}_{92}U \rightarrow ^{139}_{56}Ba + ^{94}_{36}Kr + 3\,^{1}_{0}n$$

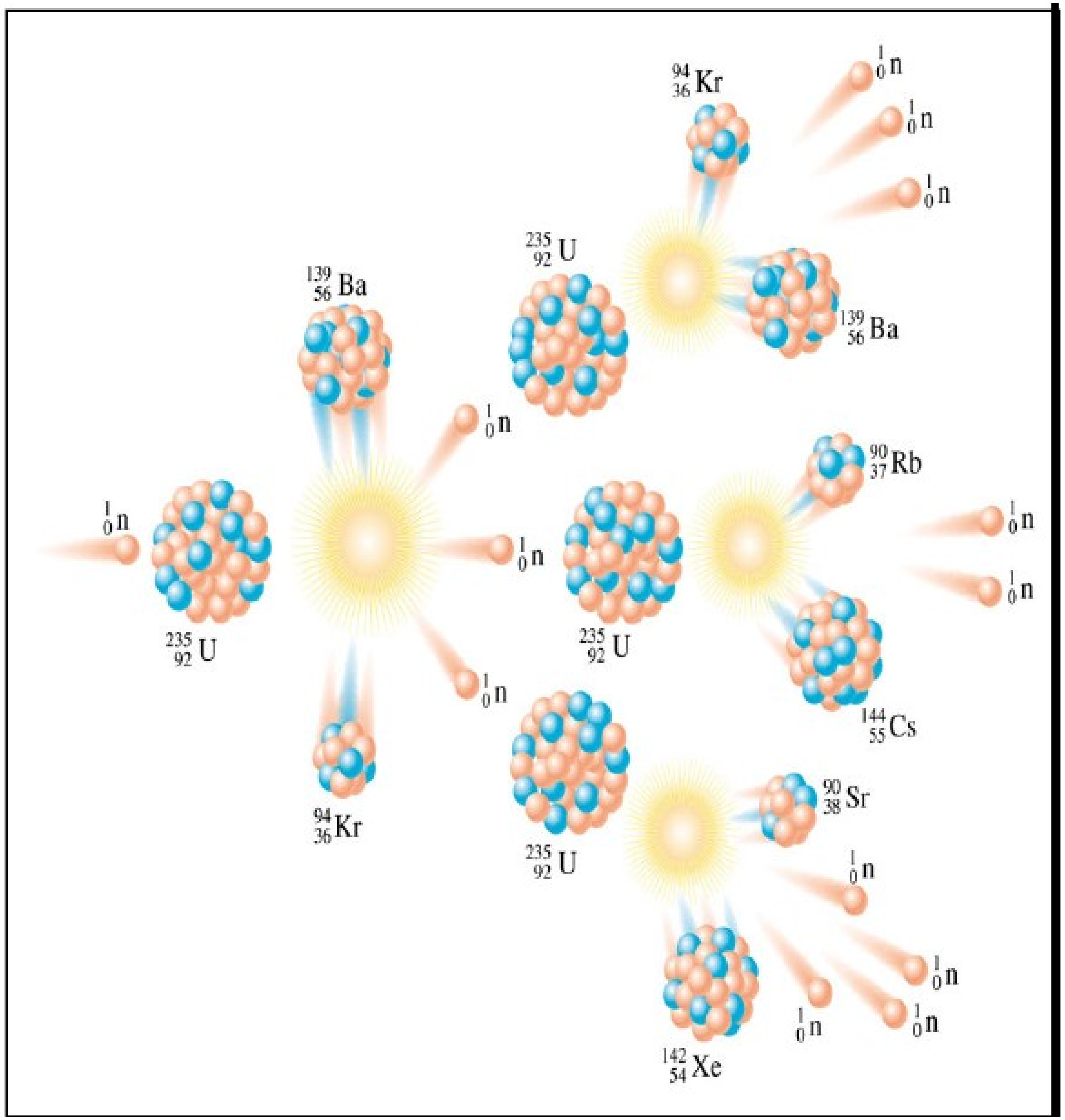
$$^{1}_{0}n + ^{235}_{92}U \rightarrow ^{144}_{55}Cs + ^{90}_{37}Rb + 2\,^{1}_{0}n$$

- When uranium-235 undergoes fission, **more neutrons are released** creating the possibility of a chain reaction.

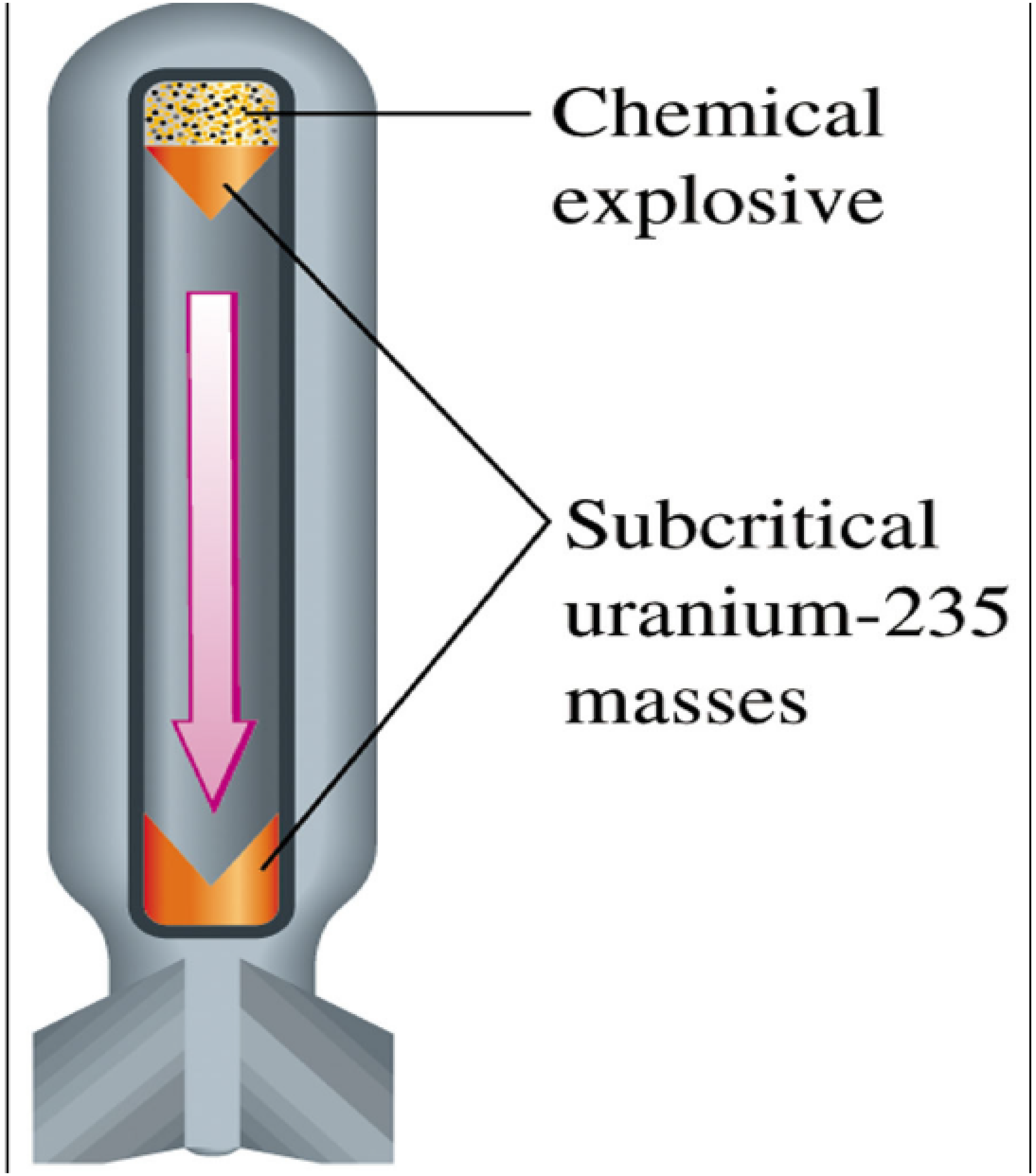
- A **chain reaction** is a self-sustaining series of nuclear fissions caused by the absorption of neutrons released from previous nuclear fissions.

- Figure shows how such a chain reaction occurs.

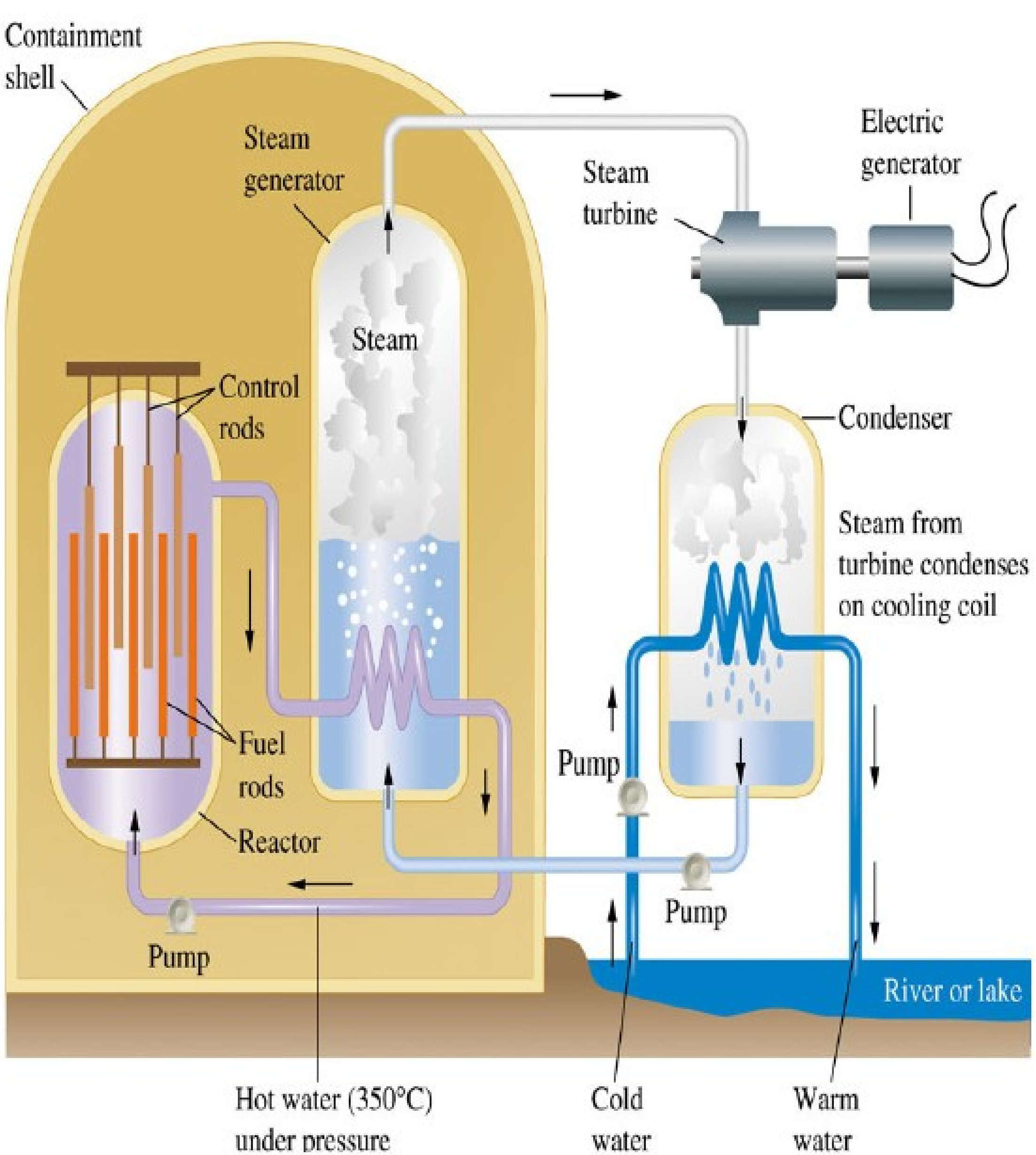
- To sustain a nuclear chain reaction you must achieve a **critical mass**, which is the smallest mass of fissionable material required for a chain reaction.

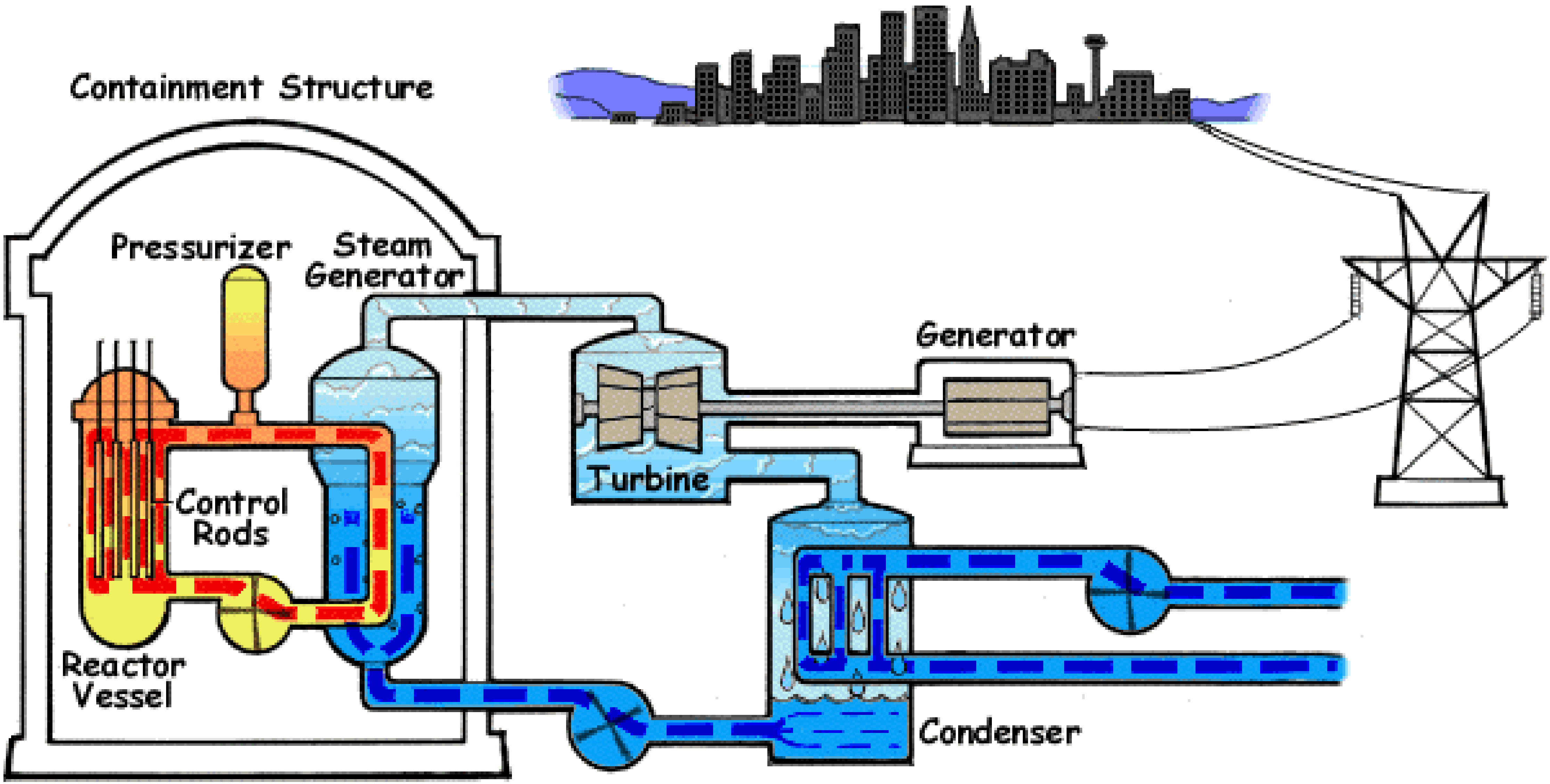


- A **supercritical mass** of fissionable material decays so rapidly as to cause a **nuclear explosion**



- A **nuclear fission reactor** is a device that permits a controlled chain reaction of nuclear fissions.




Containment Structure
Pressurizer
Steam Generator
Generator
Control Rods
Turbine
Reactor Vessel
Condenser

- **Nuclear fission** is a nuclear reaction in which a heavy nucleus splits into lighter nuclei and energy is released.
  - The **fuel rods** are the cylinders that contain fissionable material.
  - **Control rods** are cylinders composed of substances that absorb neutrons and can therefore slow the chain reaction.

Nuclear Fission and Nuclear Fusion

- **Nuclear fusion** is a nuclear reaction in which a light nuclei combine to give a stabler heavy nucleus plus possibly several neutrons, and energy is released.
  - An example of nuclear fusion is

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

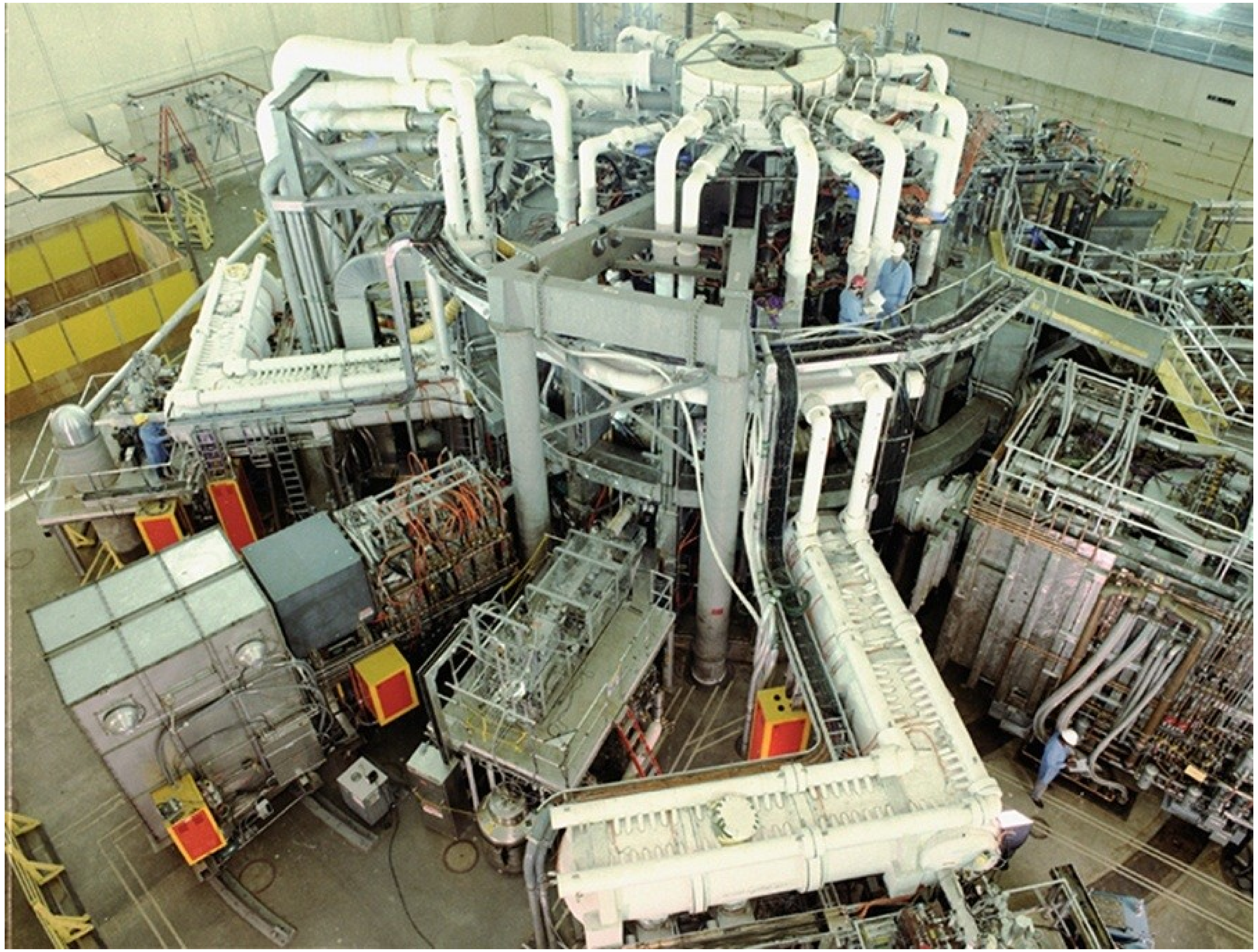
  - Such fusion reactions have been observed in the laboratory using particle accelerators.
  - **Sustainable fusion** reactions require temperatures of about **100 million °C**.

Nuclear Fission and Nuclear Fusion

- **Nuclear fusion** is a nuclear reaction in which a light nuclei combine to give a stabler heavy nucleus plus possibly several neutrons, and energy is released.
  - At these elevated temperature, a **plasma** resuts, that is, an electrically neutral gas of ions and electrons.
  - A **magnetic fusion reactor** uses a magnetic field to hold the plasma

The **Tokamak Fusion Test Reactor** (TFTR): an experimental tokamak built at Princeton Plasma Physics Laboratory (in Princeton, New Jersey) circa 1980.

http://en.wikipedia.org/wiki/Tokamak_Fusion_Test_Reactor



Operational Skills

- Writing a nuclear equation
- Deducing a product or reactant in a nuclear equation
- Predicting the relative stability of nuclides
- Predicting the type of radioactive decay
- Using the notation for a bombardment reaction
- Calculating the decay constant from the activity
- Relating the decay constant, half-life, and activity
- Determining the fraction of nuclei remaining after a specified time
- Applying the carbon-14 dating method
- Calculating the energy change for a nuclear reaction