Nuclear Chemistry

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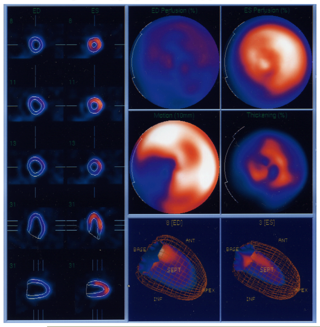

Pictures of human heart before and after stress using gamma rays from radioactive Tc-99m

Syllabus Learning Outcomes : 14

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Review Atomic Composition

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Particle	Mass (amu)	Charge
Proton	1.007	+1
Neutron	1.009	0
Electron	0.0005	-1

Review Isotopes

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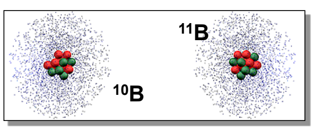
- **Atoms of the same element (same Z) but different mass number (A).**
- **Boron-10 (^{10}B) has 5 p and 5 n: $^{10}_{5}B$**
- **Boron-11 (^{11}B) has 5 p and 6 n: $^{11}_{5}B$**



Review Isotopes

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Isotope	Protons	Neutrons
carbon-12	6	6
carbon-13	6	7
carbon-14	6	8

Radioactivity and Nuclear Equations

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- *Radioactivity* is the spontaneous change of the nuclei of certain atoms, accompanied by the emission of subatomic particles and/or high-frequency electromagnetic radiation.
- A nucleus with a specified number of protons and neutrons is a ***nuclide***.
- Together, protons and neutrons are called ***nucleons***.
- In writing a nuclear equation, *the two sides of the equation must have the same totals of atomic numbers and mass numbers*.
- That is, each side must have the same number of nucleons, and the sum of atomic numbers must be the same on both sides.

Radioactivity

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- **One of the pieces of evidence for the fact that atoms are made of smaller particles came from the work of Marie Curie (1876-1934).**
- **She discovered radioactivity, the spontaneous disintegration of some elements into smaller pieces.**

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Types of Radiation

Table 23.1 Characteristics of α, β, and γ Radiation

Name	Symbols	Charge	Mass (g/particle)
Alpha	${}^{4}_{2}He$, ${}^{4}_{2}\alpha$	2+	6.65×10^{-24}
Beta	${}^{0}_{-1}e$, ${}^{0}_{-1}\beta$	1−	9.11×10^{-28}
Gamma	γ	0	0

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Types of Radioactive Decay

- ***Alpha (α) particle***: two protons and two neutrons (positive charge).
- ***Beta (β^-) particle***: high-energy electron (from the *nucleus*, not from the electron cloud).
- ***Gamma (γ) rays***: highly penetrating form of electromagnetic radiation with no charge.
- ***Positron***: (β^+) an emitted positron has same mass as an electron but its charge is 1+.
- In ***electron capture (EC)*** a nucleus absorbs an electron from an inner shell of the atom; an X ray is released.
- Many radionuclides undergo one specific type of decay, though some can undergo two or more types.

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Summary of Decay Types

		Changes in nucleus	
Mode of decay	**Radiation emitted**	**Atomic number**	**Mass number**
Alpha emission (α)	${}^{4}_{2}He$	−2	−4
Beta emission (β^-)	${}^{0}_{-1}e$	+1	0
Gamma emission (γ)	${}^{0}_{0}\gamma$	0	0
Positron emission (β^+)	${}^{0}_{1}e$	−1	0
Electron capture (EC)	X rays	−1	0

Example: a nucleus that emits a beta particle *increases* in atomic number by one, while mass number remains unchanged.

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Summary of Decay Types

Decay Mode	Symbol	Mass	Charge
Alpha particles	${}^{4}_{2}\alpha$	4	2
Beta particles	${}^{0}_{-1}\beta$	0	-1
Gamma rays	${}^{0}_{0}\gamma$	0	0
Positron	${}^{0}_{+1}\beta$	0	+1
Electron capture*	${}^{0}_{-1}e$	0	-1

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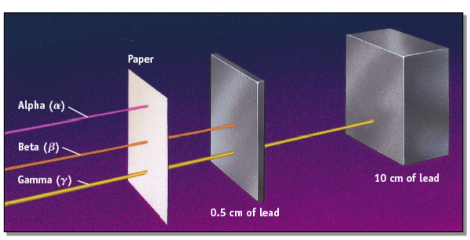
Radiation's Penetrating Ability



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Effects of Radiation

Table 23.4 Effects of a Single Dose of Radiation

Dose (rem)	Effect
0–25	No effect observed
26–50	Small decrease in white blood cell count
51–100	Significant decrease in white blood cell count, lesions
101–200	Loss of hair, nausea
201–500	Hemorrhaging, ulcers, death in 50% of population
500	Death

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Nuclear Reactions

- **Ernest Rutherford found Ra forms Rn gas when emitting an alpha particle.**
- **1902—Rutherford and Soddy proposed radioactivity is the result of the natural change of the isotope of one element into an isotope of a different element.**

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Nuclear Reactions: Alpha Emission

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

radium-226 ⟶ α particle + radon-222

Mass number: (protons + neutrons)	226	=	4	+	222
Atomic number: (protons)	88	=	2	+	86

Note that mass number (A) goes down by 4 and atomic number (Z) goes down by 2.

Nucleons are rearranged but conserved

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Nuclear Reactions: Alpha Emission

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

radium-226 alpha particle + radon-222

A:	226	=	4	+	222
Z:	88	=	2	+	86

Note that mass number (A) goes down by 4 and atomic number (Z) goes down by 2.

Nucleons are rearranged but conserved

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Nuclear Reactions: Beta Emission

$$^{239}_{92}\text{U} \longrightarrow {}^{0}_{-1}\beta + {}^{239}_{93}\text{Np}$$

uranium-239 ⟶ β particle + neptunium-239

Mass number: (protons + neutrons)	239	=	0	+	239
Atomic number: (protons)	92	=	−1	+	93

Note that mass number (A) is unchanged and atomic number (Z) goes up by 1.

How does this happen?

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

neutron electron proton

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Nuclear Reactions: Beta Emission

$$^{239}_{92}\text{U} \longrightarrow {}^{0}_{-1}\beta + {}^{239}_{93}\text{Np}$$

Uranium-239 beta particle + neptunium-239

A:	239	=	0	+	239
Z:	92	=	-1	+	93

Note that mass number (A) is unchanged and atomic number (Z) goes up by 1.

How does this happen? $^{1}_{0}\text{n} \longrightarrow {}^{0}_{-1}\text{e} + {}^{1}_{1}\text{p}$

neutron electron proton

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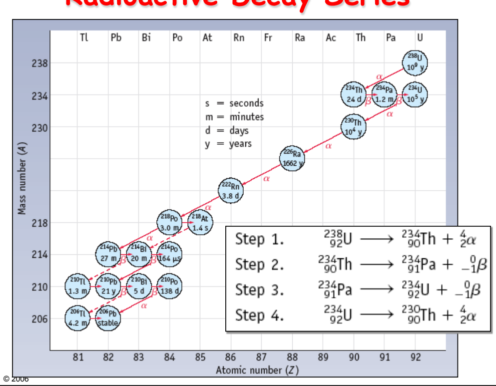
Radioactive Decay Series



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Nuclear Reactions

Positron ($^{0}_{+1}\beta$) emission: a positive electron

	$^{207}_{84}Po$	$\longrightarrow$	$^{0}_{+1}\beta$	+	$^{207}_{83}Bi$
	polonium-207	$\longrightarrow$	positron	+	bismuth-207
Mass number: (protons + neutrons)	207	=	0	+	207
Atomic number: (protons)	84	=	+1	+	83

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

K-capture: the capture of an electron from the first or K shell

	$^{7}_{4}Be$	+	$^{0}_{-1}e$	$\longrightarrow$	$^{7}_{3}Li$
	beryllium-7	+	electron	$\longrightarrow$	lithium-7
Mass number: (protons + neutrons)	7	+	0	=	7
Atomic number: (protons)	4	+	−1	=	3

An electron and proton combine to form a neutron.
$^{0}_{-1}e + {}^{1}_{1}p \rightarrow {}^{1}_{0}n$

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Ionizing Radiation and Living Matter

- Naturally occurring ionizing radiation is all around us.
- The dose received varies somewhat with where we live. It is slightly greater, for example, at higher elevations.
- Human activities have added to our exposure to radiation. However …
- … about two-thirds of the average radiation exposure comes from natural background radiation. Most of the remainder comes from medical procedures.
- Most medical procedures that involve radiation produce a rather low exposure.
- Damaging biological effects from ionizing radiation result from ionizing biological molecules, causing cumulative mutation and destruction.

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Origin of the Elements

- **The Big Bang Theory**
- **In the first moments there were only 2 elements — hydrogen and helium**

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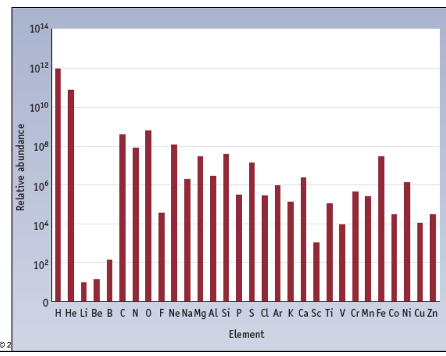
Element Abundance



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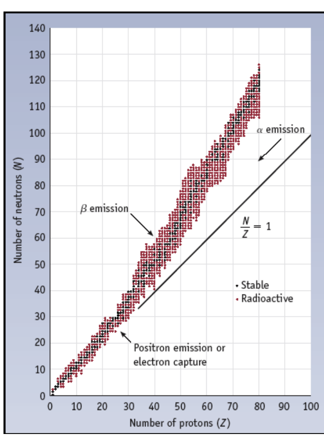

Stability of Nuclei

CD-ROM Screens 23.3 and 23.4

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Stability of Nuclei

Screens 23.3 and 23.4

- **H is most abundant element in the universe.**
  - **88.6% of all atoms**
  - **He is 11.3% of all atoms**
  - **H + He = 99.9% of all atom & 99% of mass of the universe.**
- **This tells us about the origin of the elements, and so does the existence of isotopes.**

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Isotopes

- **Hydrogen:**
  - $^{1}_{1}H$, protium
  - $^{2}_{1}H$, deuterium
  - $^{3}_{1}H$, tritium (radioactive)
- **Helium, $^{4}_{2}He$**
- **Lithium, $^{6}_{3}Li$ and $^{7}_{3}Li$**
- **Boron, $^{10}_{5}B$ and $^{11}_{5}B$**

- **Iron**
  - $^{54}_{26}Fe$, 5.82% abundant
  - $^{56}_{26}Fe$, 91.66% abundant
  - $^{57}_{26}Fe$, 2.19% abundant
  - $^{58}_{26}Fe$, 0.33% abundant

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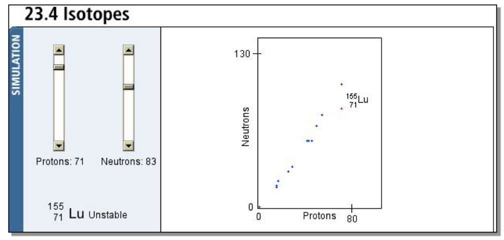
Simulation —Stability of Isotopes

Chem Now Screen 23.4



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Isotopes

- Hydrogen:
  - $^{1}_{1}H$, protium
  - $^{2}_{1}H$, deuterium
  - $^{3}_{1}H$, tritium (radioactive)
- Helium, $^{4}_{2}He$
- Lithium, $^{6}_{3}Li$ and $^{7}_{3}Li$
- Boron, $^{10}_{5}B$ and $^{11}_{5}B$

- **Except for $^{1}_{1}H$ the mass number is always at least 2 x atomic number.**
- **Repulsive forces between protons must be moderated by neutrons.**

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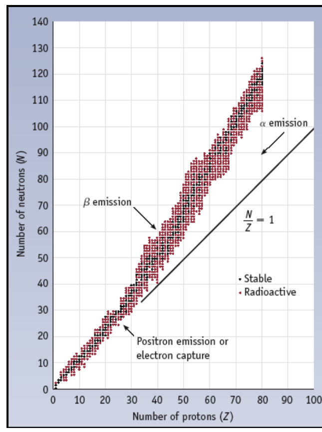

Stability of Nuclei

- **Heaviest naturally occurring non-radioactive isotope is ^{209}Bi with 83 protons and 126 neutrons**
- **There are 83 x 126 = 10,458 possible isotopes; few actually exist**

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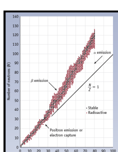
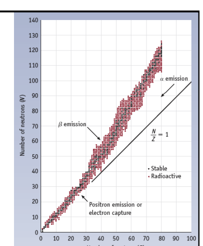


Stability of Nuclei

- **Up to Z = 20 (Ca), n ≈ p**
- **Beyond Ca, n > p (A > 2 Z)**
- **Above Bi (Z=83) all isotopes are radioactive, the heavier the nucleus the greater the decay rate.**
- **Above Ca:**
  - **Elements with EVEN Z have more isotopes**
  - **Isotopes with an EVEN number of neutrons tend to be more stable.**

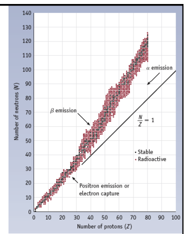
Stability of Nuclei



- **Out of > 300 stable isotopes:**

Z \ N	Even	Odd	
Even	157	52	→ $^{31}_{15}P$
Odd	50	5	→ $^{2}_{1}H$, $^{6}_{3}Li$, $^{10}_{5}B$, $^{14}_{7}N$, $^{180}_{73}Ta$
	↓ $^{19}_{9}F$		

Stability of Nuclei



Z \ N	Even	Odd
Even	157	52
Odd	50	5

- Suggests some PAIRING of NUCLEONS
- There are "nuclear magic numbers"

2	He	28	Ni
8	O	50	Sn
20	Ca	82	Pb

Band of Stability and Radioactive Decay

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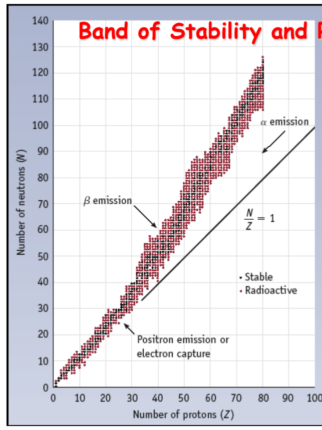

α emission reduces Z

$^{243}_{95}Am \dashrightarrow {}^{4}_{2}\alpha + {}^{239}_{93}Np$

β emission increases Z

$^{60}_{27}Co \dashrightarrow {}^{0}_{-1}\beta + {}^{60}_{28}Ni$

Isotopes with low n/p ratio, below band of stability decay, decay by positron emission or electron capture

$^{13}_{7}N \rightarrow {}^{13}_{6}C + {}^{0}_{+1}\beta$

Binding Energy, E_b

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E_b is the energy required to separate the nucleus of an atom into protons and neutrons.

For deuterium, $^{2}_{1}H$

$^{2}_{1}H \dashrightarrow {}^{1}_{1}p + {}^{1}_{0}n$ $E_b = 2.15 \times 10^8$ kJ/mol

E_b per nucleon = E_b/2 nucleons

= 1.08×10^8 kJ/mol nucleons

Calculate Binding Energy

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For deuterium, $^{2}_{1}H$: $^{2}_{1}H \dashrightarrow {}^{1}_{1}p + {}^{1}_{0}n$

Mass of $^{2}_{1}H$ = 2.01410 g/mol

Mass of proton = 1.007825 g/mol

Mass of neutron = 1.008665 g/mol

Δm = (mass protons + mass neutrons) – molar mass of isotope

Δm = 0.00239 g/mol = (1.007825 + 1.008665) – 2.01410

From Einstein's equation:

$E_b = (\Delta m)c^2 = 2.15 \times 10^8$ kJ/mol

E_b per nucleon = E_b/2 nucleons

= 1.08×10^8 kJ/mol nucleons

Binding Energy

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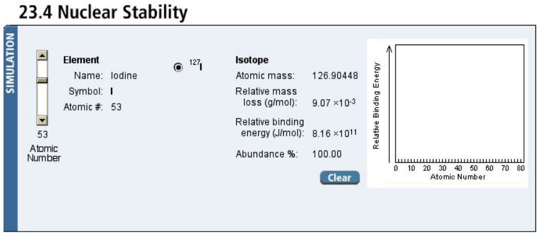
23.4 Nuclear Stability



Simulation of binding energy, ChemNow Screen 23.5

Binding Energy/Nucleon

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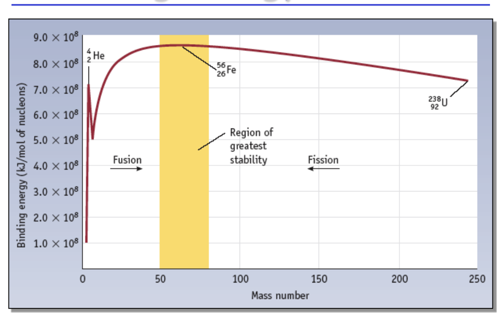

ChemNow Screen 23.5

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Half-Life

- **HALF-LIFE** is the time it takes for 1/2 a sample to disappear.
- **The rate of a nuclear transformation depends only on the "reactant" concentration.**
- **Concept of HALF-LIFE is especially useful for 1st order reactions.**

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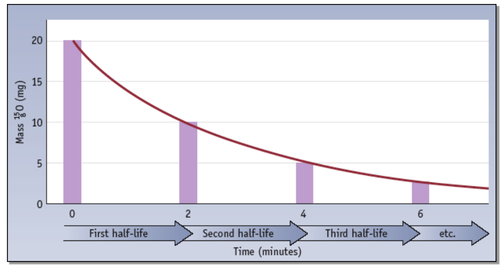
Half-Life



Decay of 20.0 mg of ^{15}O. What remains after 3 half-lives? After 5 half-lives? (half life from graph is 2 minutes)

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Kinetics of Radioactive Decay

Activity (A) = Disintegrations/time = (k)(N)

where N is the number of atoms

Decay is first order, and so

$\ln (A/A_o) = -kt$

The half-life of radioactive decay is

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

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Radiocarbon Dating

Radioactive C-14 is formed in the upper atmosphere by nuclear reactions initiated by neutrons in cosmic radiation

$$^{14}N + {}^{1}_{o}n \dashrightarrow {}^{14}C + {}^{1}H$$

The C-14 is oxidized to CO_2, which circulates through the biosphere.

When a plant dies, the C-14 is not replenished.

But the C-14 continues to decay with $t_{1/2}$ = 5730 years.

Activity of a sample can be used to date the sample.

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Radiocarbon Dating

- **Willard Libby (1908–1980)**

Libby received the 1960 Nobel Prize in chemistry for developing carbon-14 dating techniques. He is shown in this photo with the apparatus he used. Carbon-14 dating is widely used in fields such as anthropology.

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Artificial Nuclear Reactions

New elements or new isotopes of known elements are produced by bombarding an atom with a subatomic particle such as a proton or neutron -- or even a much heavier particle such as ^{4}He and ^{11}B.

Reactions using neutrons are called

n,γ reactions because a neutron is captured and a γ ray is usually emitted.

Radioisotopes used in medicine are often made by n,γ reactions.

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Artificial Nuclear Reactions

Example of a **n,γ reaction** is production of radioactive ^{31}P for use in studies of P uptake in the body.

$$^{31}_{15}P + {}^{1}_{0}n \dashrightarrow {}^{32}_{15}P + \gamma$$

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Transuranium Elements

Elements beyond 92 *(transuranium)* made starting with an **n,γ reaction**

$$^{238}_{92}U + {}^{1}_{0}n \dashrightarrow {}^{239}_{92}U + \gamma$$

$$^{239}_{92}U \dashrightarrow {}^{239}_{93}Np + {}^{0}_{-1}\beta$$

$$^{239}_{93}Np \dashrightarrow {}^{239}_{94}Pu + {}^{0}_{-1}\beta$$

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■ **Glenn T. Seaborg (1912–1999)** Seaborg figured out that thorium and the elements that followed it fit under the lanthanides in the periodic table. For this insight, he and Edwin McMillan shared the 1951 Nobel Prize in chemistry. Over a 21-year period, Seaborg and his colleagues synthesized 10 new transuranium elements (Pu through Lr). To honor Seaborg's scientific contributions, the name "seaborgium" was assigned to element 106. It marked the first time an element was named for a living person.

Transuranium Elements & Glenn Seaborg

$_{106}Sg$

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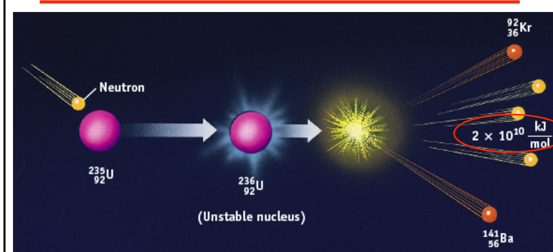
Nuclear Fission



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Nuclear Fission

Fission chain has three general steps:

1. *Initiation.* Reaction of a single atom starts the chain (e.g., ^{235}U + neutron)
2. *Propagation.* ^{236}U fission releases neutrons that initiate other fissions
3. *Termination.*

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■ **Lise Meitner (1878–1968)** Meitner's greatest contribution to 20th-century science was her explanation of the process of nuclear fission. She and her nephew, Otto Frisch, also a physicist, published a paper in 1939 that was the first to use the term "nuclear fission." Element number 109 is named meitnerium to honor Meitner's contributions. The leader of the team that discovered this element said that "She should be honored as the most significant woman scientist of [the 20th] century."

Nuclear Fission & Lise Meitner

$_{109}Mt$

Nuclear Fission & POWER

- Currently about 103 nuclear power plants in the U.S. and about 435 worldwide.
- 17% of the world's energy comes from nuclear.

Table 23.2 Percentage of Electricity Produced Using Nuclear Power Plants

Country (rank)	Total Power from Nuclear Energy (%)
1. France	75.0
2. Lithuania	73.1
3. Belgium	57.7
4. Bulgaria	47.1
5. Slovak Republic	47.0
6. Sweden	46.8
. . .	
19. United States	19.9
20. Russia	14.4
21. Canada	12.7

Source: *Chemical and Engineering News*, p. 42, Oct. 2, 2000.

Units for Measuring Radiation

Curie: 1 Ci = 3.7×10^{10} distintegrations/s

SI unit is the becquerel: 1 Bq = 1 dps

Rad: measures amount of energy absorbed

1 rad = 0.01 J absorbed/kg tissue

Rem: based on rad and type of radiation.

Quantifies biological tissue damage

Usually use "millirem"

Table 23.3 Radiation Exposure of an Individual for One Year from Natural and Artificial Sources

	Millirem/Year	Percentage
Natural Sources		
Cosmic radiation	50.0	25.8
The earth	47.0	24.2
Building materials	3.0	1.5
Inhaled from the air	5.0	2.6
Elements found naturally in human tissue	21.0	10.8
Subtotal	**126.0**	**64.9**
Medical Sources		
Diagnostic x-rays	50.0	25.8
Radiotherapy	10.0	5.2
Internal diagnosis	1.0	0.5
Subtotal	**61.0**	**31.5**
Other Artificial Sources		
Nuclear power industry	0.85	0.4
Luminous watch dials, TV tubes	2.0	1.0
Fallout from nuclear tests	4.0	2.1
Subtotal	**6.9**	3.5
Total	**193.9**	**99.9**

Nuclear Medicine: Imaging

Radioisotopes Used in Medical Diagnostic Procedures

Radioisotope	Half-Life (h)	Imaging
^{99m}Tc	6.0	Thyroid, brain, kidneys
^{201}Tl	73.0	Heart
^{123}I	13.2	Thyroid
^{67}Ga	78.2	Various tumors and abscesses
^{18}F	1.8	Brain, sites of metabolic activity

Nuclear Medicine: Imaging

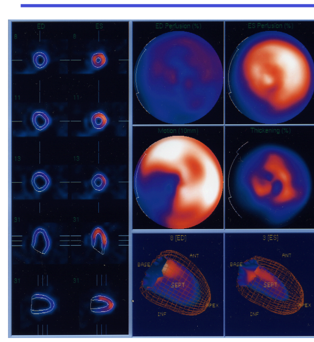
Technetium-99m is used in more than 85% of the diagnostic scans done in hospitals each year. Synthesized on-site from Mo-99.

$$^{99}_{42}Mo \dashrightarrow {}^{99m}_{43}Tc + {}^{0}_{-1}\beta$$

$^{99m}_{43}Tc$ decays to $^{99}_{43}Tc$ giving off γ ray.

Tc-99m concentrates in sites of high activity.

Nuclear Medicine: Imaging

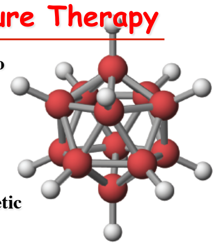


Imaging of a heart using Tc-99m before and after exercise.

BNCT

Boron Neutron Capture Therapy

- ^{10}B isotope (not ^{11}B) has the ability to capture slow neutrons
- In BNCT, tumor cells preferentially take up a boron compound, and subsequent irradiation by slow neutrons kills the cells via the energetic $^{10}B \rightarrow {}^{7}Li$ neutron capture reaction (that produces a photon and an alpha particle)
- $^{10}B + {}^{1}n \rightarrow {}^{7}Li + {}^{4}He + \text{photon}$



One of the compounds used in BNCT is $Na_2[B_{12}H_{12}]$. The structure of the $B_{12}H_{12}^{2-}$ anion is a regular polyhedron with 20 sides, called an icosahedron.

Food Irradiation

•Food can be irradiated with γ rays from ^{60}Co or ^{137}Cs.

•Irradiated milk has a shelf life of 3 mo. without refrigeration.

•USDA has approved irradiation of meats and eggs.