Nuclear Chemistry

So far only impt. factor in rx's. has been the number & arrangement of e^-

- Nucleus didn't matter

Nuclear Reactions

- changes in matter that originate in the nucleus

Review

nucleus contains protons & neutrons

(protons & neutrons = nucleons)

Symbol

$$^{A}_{Z}X$$

- mass no. (p+n) → A
- atomic no. (p) → Z
- X ← chemical symbol

Diff. isotopes of an element are now impt. & are distinguished by mass no.

$^{121}_{51}Sb$ $^{123}_{51}Sb$

antimony-121 antimony-123

A nucleus can undergo change in several ways:

Some nuclei are unstable & spontaneously emit particles & electromagnetic radiation.

Radioactivity - The spontaneous emission from the nucleus of the atom

Radio isotope - Isotopes that are radio active

1) Radioactivity

3 common types : α β γ

2 less common

a) Alpha Particles, α^{2+} or α

helium-4 nucleus, ${}^{4}_{2}He^{2+}$ or ${}^{4}_{2}He$

- omit 2+ charge bec. nuclear rx's do not depend on chemical form

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

Note: Conservation of nucleons

$238 = 234 + 4$ mass

$92 = 90 + 2$ charge

Polonium-210 undergoes α-emisson.

What is the product nucleus?

b) Beta Particles, β (β^-)

high energy electrons $^{0}_{-1}e$ ($^{0}_{-1}\beta$)

superscript 0 - small mass compared to (other) nucleons

subscript -1 - neg. charge, opposite of proton

β emission has effect of converting a neutron into a proton

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

$$^{210}_{82}Pb \longrightarrow \, ^{210}_{83}Bi + \, ^{0}_{-1}e$$

Note: conservation of nucleons & charge

c) Gamma Rays, γ

Not particles - electromag. radiation of very short wavelength

$\sim 10^{-12}$ m

∴ γ - no mass, no charge

Accompanies other radioactive emission

- the energy given off when excited states of products convert to ground state

d) Positrons, ${}^{0}_{1}e$ (β^+)

same mass as an electron but positive charge

${}^{0}_{1}e$ - arrises from conversion of proton into a neutron

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

$${}^{23}_{12}Mg \longrightarrow {}^{23}_{11}Na + {}^{0}_{1}e$$

Positrons have very short lifetimes - collides w. an e^- & is annihilated, producing gamma rays

$${}^{0}_{1}e + {}^{0}_{-1}e \rightarrow 2\,{}^{0}_{0}\gamma$$

e) Electron Capture, EC

X-rays

Nucleus captures an inner-orbital e^-

- has effect of converting a proton to a neutron

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

$${}^{40}_{19}K + {}^{0}_{-1}e \longrightarrow {}^{40}_{18}Ar + \text{X-ray}$$

photon is emitted when another orbital e^- drops to the lower level, filling the vacancy.

	Helium nucleus	Proton	Neutron	Electron	Positron	Photon
symbol	$^{4}_{2}He$	$^{1}_{1}p$	$^{1}_{0}n$	$^{0}_{-1}e$	$^{0}_{1}e$	$^{0}_{0}\gamma$
mass	4	1	1	0	0	0
charge	2+	1+	0	1-	1+	0
particle	**alpha**			**beta**		**gamma**
effect of loss	mass down 4, atomic number down 2 2 n, 2 p ⟶			no mass Δ, at. number up 1 n ⟶ p *	no mass Δ, at. number down 1 p ⟶ n *	no mass Δ, no at. number change
occurs most often	elements above at. no. 83 (high mass, high at. no.)			belt above - above belt of stability (n>p)	below belt of stability (n ≅ p) *	burst of light from excited state

Mass of particle lower, Energy of particles higher, penetrating power greater ⟶ (Slingshot out of nucleus)

* If electron is captured, same effect as positron loss - occurs more often as at. number increases

2) Nuclear Stability

Which nuclei are radioactive & how do they decay?

Observations

1. Largest stable nucleus is $^{209}_{83}Bi$

   Nuclei w $Z > 83$ (& $A > 209$) tend to undergo α emission.

   Reduces A by 4 & Z by 2

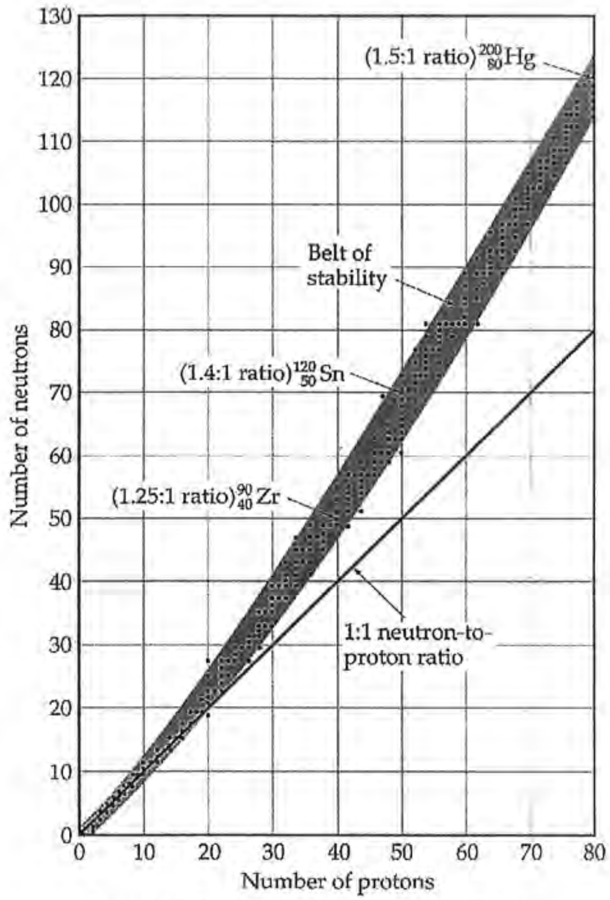
2. Nuclei w. 2, 8, 20, 50, 82 or 126 (for n) protons or neutrons are more stable

   - not radioactive

   "magic numbers"

   - closed nuclear shells

Trends of nuclear stability



1. Isotopes with 2, 8, 20, 28, 50, or 82 protons and/or 0, 2, 8, 20, 28, 50, 82, or 126 neutrons:

- Suggests that nuclei, like electrons reside in orbitals
- Examples of "extra" stable isotopes: ^{208}Pb, ^{118}Sn, ^{4}He

2. Nuclei with even #n and/or #p tend to be stable:

Number of Stable Isotopes	Protons	Neutrons
157	Even	Even
53	Even	Odd
50	Odd	Even
5	Odd	Odd

3. Rate of radioactive decay is NOT affected by:

- Temperature
- Pressure
- Physical state
- Chemical state (i.e. elemental ^{235}U and $^{235}UF_6$ decay at same rate)

3. Stability can be correlated w. neutron/proton ratio

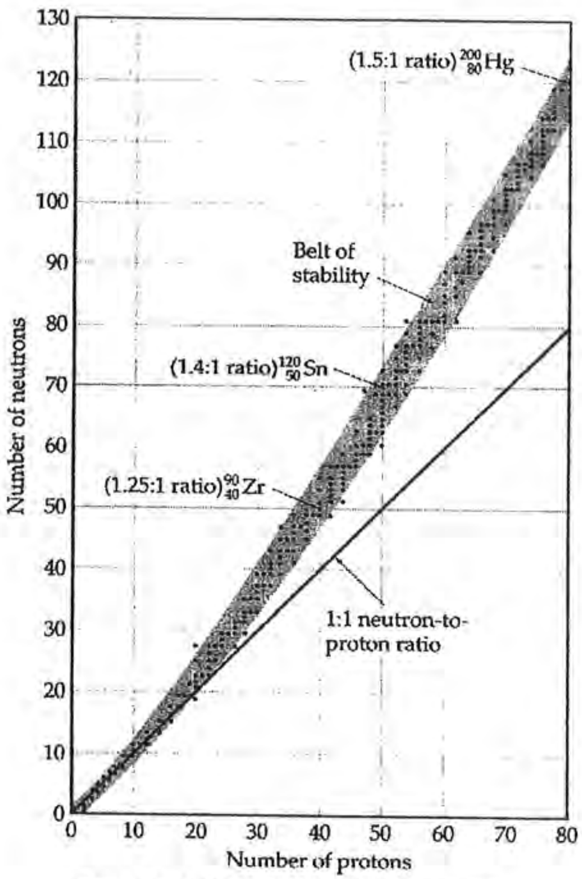
For light elements find $n/p \cong 1$

Heavier elements contain more neutrons than protons

$^{209}_{83}Bi$ $\quad n/p = 1.5$

Nuclei that lie outside this <u>zone of stability</u> undergo nuclear transformations that bring them into or closer to this zone

"Belt" of stable isotopes



Typical radioactive decay patterns:

1. Isotopes with #n:#p > belt are radioactive:
- Tend to undergo beta decay (emission)
- Results in increase in #p due to decay of neutron
- Ex: $^{14}C \rightarrow {}^{14}N + e^-$

2. Isotopes with #n:#p < belt are radioactive:
- Tend to undergo e^- capture or positron emission
- Results in increase in #n due to loss of proton
- Ex: $^{118}Xe \rightarrow {}^{118}I + {}^{0}e$

3. All isotopes with ≥ 84 protons are radioactive:
- Tend to undergo alpha decay (emission)
- May lead to isotopes of cases 1 and 2
- Ultimately, a stable isotope is obtained and the decay stops

A nucleus w. too high n/p ratio (to left + above line) can lower ratio by emitting β particle.

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

$$ {}^{14}_{6}C \longrightarrow {}^{14}_{7}N + {}^{0}_{-1}e $$

n/p = 1.3 n/p = 1

light, n/p should be ≈ 1

$^{14}_{7}N$ ⇒ one of the 5 stable odd-odd.

lose n, gain p
- move closer to stability zone

A nucleus w. too low n/p ratio (to rt. + below line) needs opposite process.

$$p \rightarrow n$$

∴ either positron emission or electron capture

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

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

β^+ more common for lighter nuclei

$$^{20}_{11}Na \rightarrow {}^{20}_{10}Ne + {}^{0}_{1}e$$

$n/p = 0.82$ $\quad$ $n/p = 1$

E.C. more common for heavier nuclei

$$^{106}_{47}Ag + {}^{0}_{-1}e \rightarrow {}^{106}_{46}Pd$$

$n/p = 1.26$ $\quad$ $n/p = 1.30$

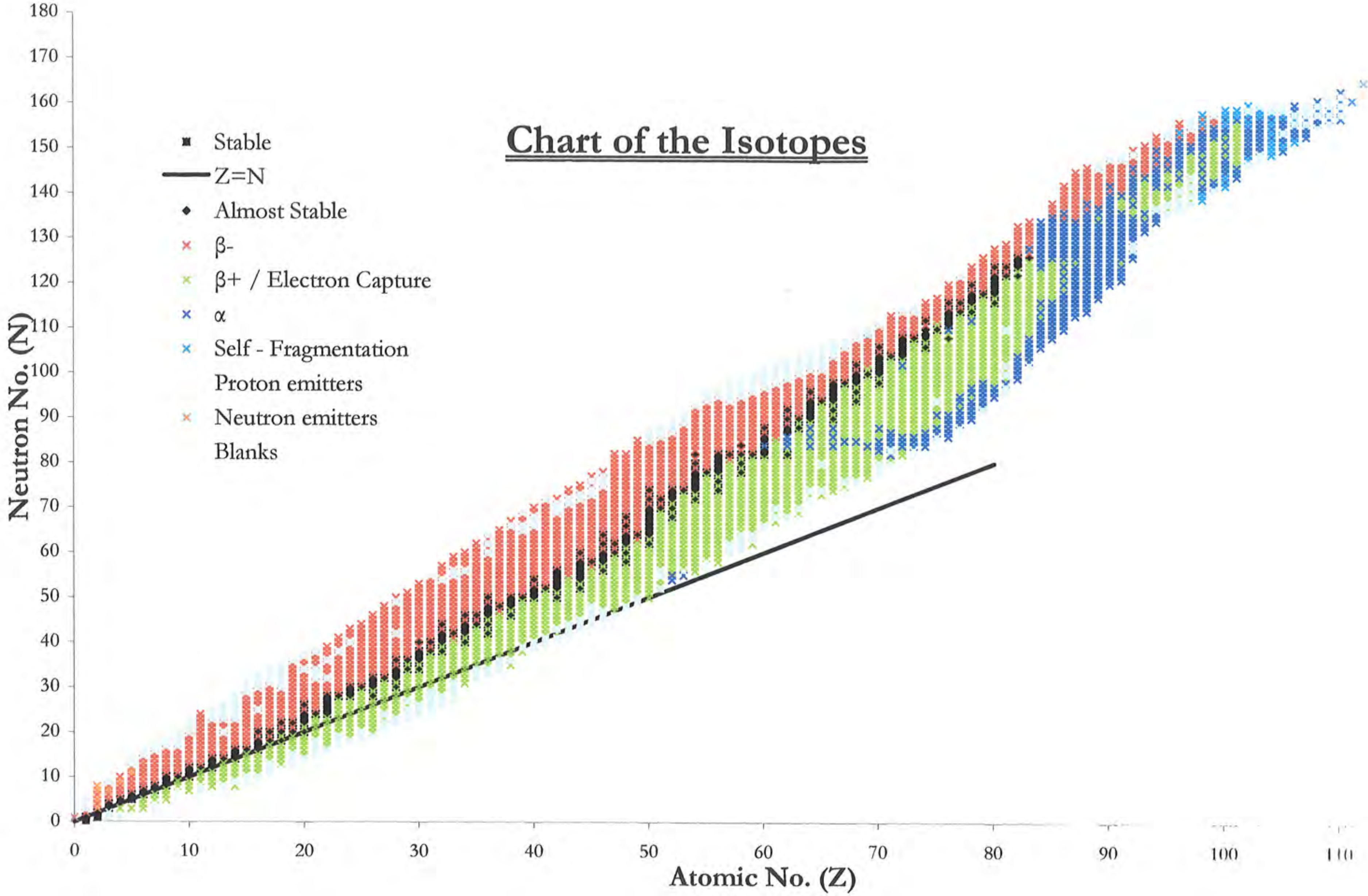


Chart of the Isotopes
Stable
Z=N
Almost Stable
β-
β+ / Electron Capture
α
Self - Fragmentation
Proton emitters
Neutron emitters
Blanks
Neutron No. (N)
Atomic No. (Z)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180

a) Radioactive Series or Nuclear Disintegration Series

Some nuclei cannot gain stability in a single step

∴ Series of emissions occur until a stable nucleus is achieved.

$^{238}_{92}U \xrightarrow{\text{14 steps}} \alpha, \beta^-, \beta^-, \alpha \times 5, \beta^- \cdot \beta^-, \alpha, \beta^-, \beta^-, \alpha$

$\longrightarrow {}^{206}_{82}Pb$

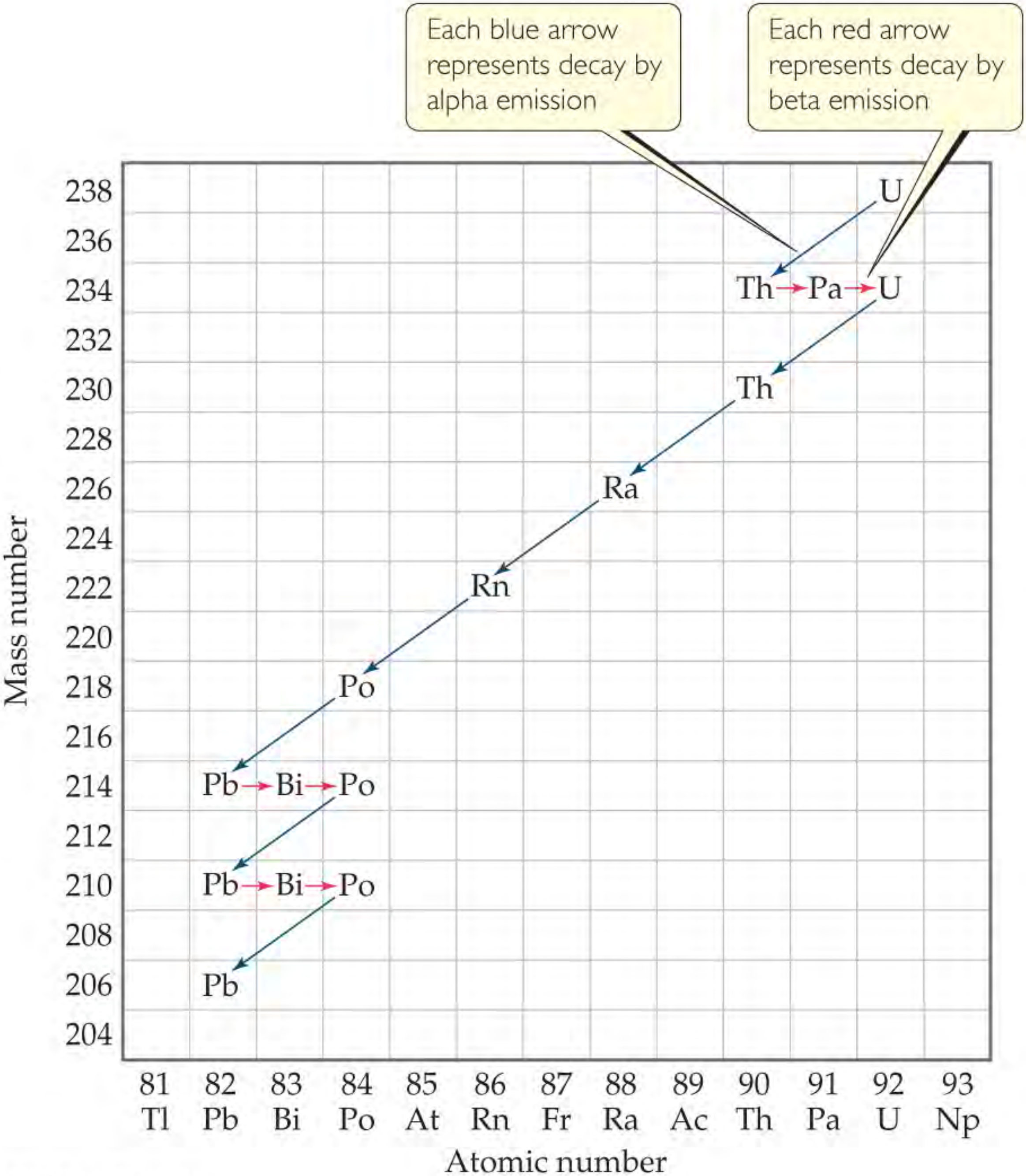
$8\alpha \Rightarrow$ A: -32, Z: -16

$6\beta \Rightarrow$ A: -0, Z: $+6$

$^{235}U \longrightarrow {}^{207}Pb$

$^{232}Th \longrightarrow {}^{208}Pb$

These 3 series occur in nature


Each blue arrow represents decay by alpha emission
Each red arrow represents decay by beta emission
U
Th
Pa
U
Th
Ra
Rn
Po
Pb
Bi
Po
Pb
Bi
Po
Pb
Mass number
238
236
234
232
230
228
226
224
222
220
218
216
214
212
210
208
206
204
81 Tl
82 Pb
83 Bi
84 Po
85 At
86 Rn
87 Fr
88 Ra
89 Ac
90 Th
91 Pa
92 U
93 Np
Atomic number

3) Artificial Transmutations

Conversion of 1 atom into another

Natural radioactivity (α & β) transforms one nucleus into another

Also, can be accomplished artificially

Rutherford, 1919 : 1st successful artificial trans.

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

Represent conversion by listing, in order: target nucleus, bombarding particle, ejected particle, product nucleus

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

Other possible projectiles:
neutrons; deuterons, d (^2_1H); protons, p

In some cases product nucleus is unstable + decays.

a) Transuranium Elements

Follow U in periodic table
- prepared by bombardment tech. (not naturally occurring)

$$^{238}_{92}U + ^{2}_{1}H \longrightarrow ^{238}_{93}Np + 2\,^{1}_{0}n$$

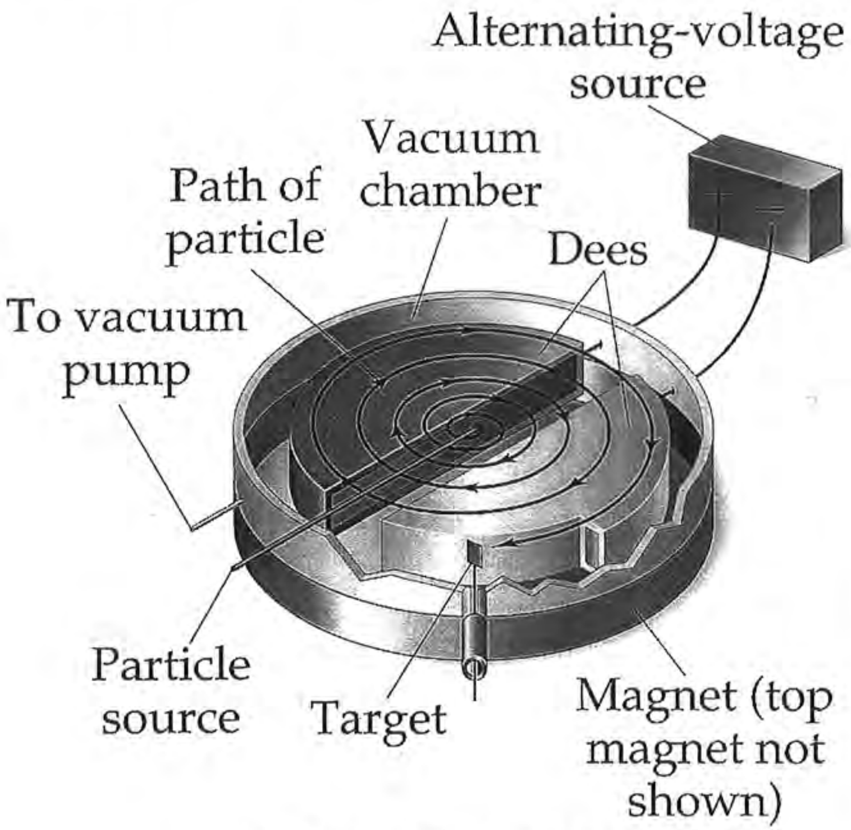
deuteron — neptunium

Target nucleus can be artificial so synthesis takes several steps

Nuclear reactions: "Atom smashers"

Ex. $^{14}N + {}^{4}He \rightarrow {}^{17}O + {}^{1}H$

Can take place in a "cyclotron":



Pb ions + protons $\rightarrow$???

Large hadron collider at CERN

Another method of getting atoms of highest at. no.

- Bombardment using nuclei (projectile) of more massive elements than H, He

$^{10}_{5}B$ $^{12}_{6}C$ $^{14}_{7}N$

e.g. dubnium, $Z = 105$

$$^{249}_{98}Cf + ^{15}_{7}N \rightarrow ^{260}_{105}Da + 4\,^{1}_{0}n$$

4) Rates of Radioactive Decay

Rates are 1st order

- Depend only on amt. of material

Not affected by chemical form, temp., pressure

- property that is both useful and harmful

useful - dependable, constant source

harmful - can't get rid of it
- loses activity at its own rate

Recall from kinetics,

First-order rate law is,

$$\text{rate} = \frac{-d[A]}{dt} = k[A]$$

or

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

$$\ln \frac{N_t}{N_0} = -kt$$

$N \equiv$ # of nuclei of a particular radioisotope

If we know a rate (decay) constant, k, we can determine fraction remaining at any time

A very useful time is the

half-life

- the time req. for half the sample to decay

If time is $t_{1/2}$,

$$\ln \frac{\frac{1}{2}N_0}{N_0} = -k\,t_{1/2}$$

$$-0.693 = -k\,t_{1/2}$$

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

For ${}^{90}_{38}Sr$, $t_{1/2} = 28.8\,yr$

$$k = \frac{0.693}{t_{1/2}} = 2.41 \times 10^{-2}\,yr^{-1}$$

$$\frac{2.41 \times 10^{-2}}{yr} \times \frac{1\,yr}{365\,d} \times \frac{1\,d}{24\,hr} \times \frac{1\,hr}{3600\,s} = 7.63 \times 10^{-10}\,s^{-1}$$

Rates of decay are expressed in terms of **half-life**

- A constant for a given isotope

Anything from fractions of a second to billions of years

e.g. $\frac{1}{2}$-life of strontium-90 is 28.8 yr

$$^{90}_{38}Sr \longrightarrow \, ^{90}_{39}Y + \, ^{0}_{-1}e$$

After 28.8 yr, $\frac{1}{2}$ of sample $^{90}_{38}Sr$ has been converted to yttrium.

Another 28.8 yr (total of 57.6 yr) $\Rightarrow \frac{1}{4}$ original

^{90}Sr is possible product of nuclear fission of ^{235}U – used in nuclear weapons & reactors

Rates of radioactive decay

Radioactive decay follows first order kinetics:

$$\ln[A]_t - \ln[A]_0 = -kt$$

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

TABLE 21.4 The Half-lives and Type of Decay for Several Radioisotopes

	Isotope	Half-life (yr)	Type of Decay
Natural radioisotopes	$^{238}_{92}U$	4.5×10^9	Alpha
	$^{235}_{92}U$	7.0×10^8	Alpha
	$^{232}_{90}Th$	1.4×10^{10}	Alpha
	$^{40}_{19}K$	1.3×10^9	Beta
	$^{14}_{6}C$	5715	Beta
Synthetic radioisotopes	$^{239}_{94}Pu$	24,000	Alpha
	$^{137}_{55}Cs$	30	Beta
	$^{90}_{38}Sr$	28.8	Beta
	$^{131}_{53}I$	0.022	Beta

Radioactive decay rates are not affected by T, P, physical state, or compound state

1950's : Nuclear weapons testing in atm

- radioactive clouds containing ^{90}Sr which settled on grass & ingested by cows.

Shows up in milk - acts like Ca

$\Rightarrow$ incorporated in bone

β^- emitter for rest of life

($3\ t_{1/2}$'s = 87 yr)

β^- stopped by 4-10 mm of living cells

- Internal damage : bone cancer
leukemia