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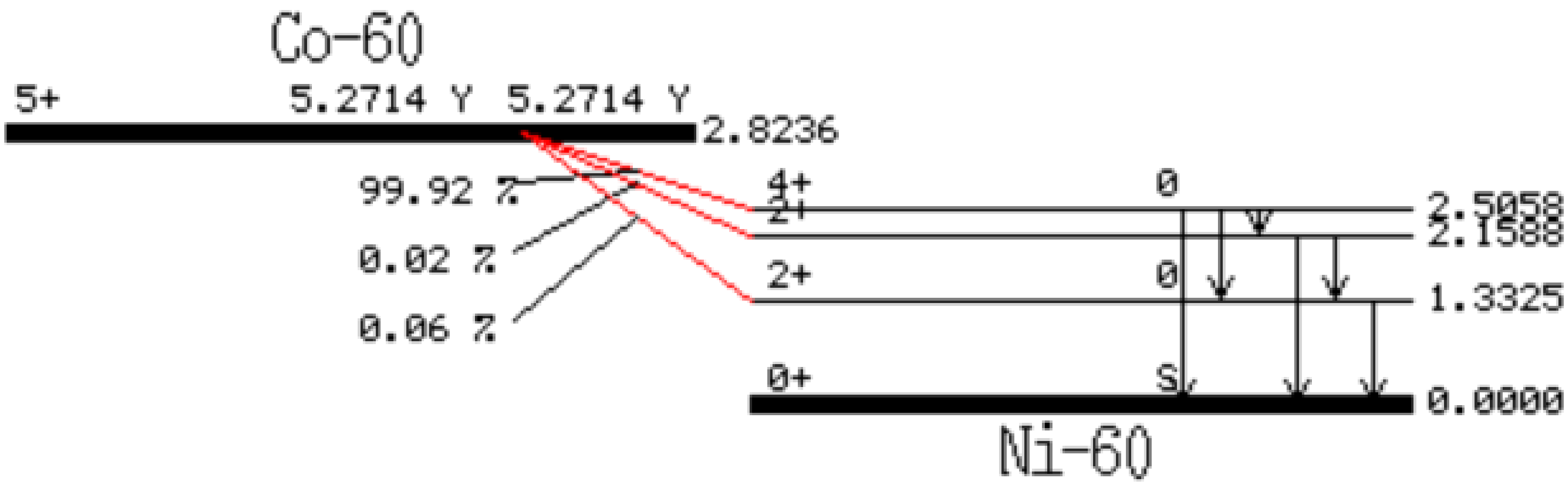
Nuclear Fuel Cycle 2011

Lecture 3: Basic Nuclear Chemistry, Part 2

Radioactive decay

N → Daughter + particle $t_{1/2}$ [s]

- The energy of the mother is higher than that of the daughter.
- The difference in energy is transferred
  - to the particle (as kinetic energy; velocity)
  - and often also to the daughter.
- The daughter loses the "remaining" energy in one or more γ-photons



Radioactive decay

$N \rightarrow$ Daughter + particle $\qquad \lambda\ [s^{-1}]$

The disappearance of N is a 1st order reaction with respect to N

$$A = -\frac{dN}{dt} = \lambda N$$

The Activity equals the rate of disappearance of N

$$-\int_{N_0}^{N} \frac{1}{N} dN = \int_0^t \lambda dt \Rightarrow \ln N - \ln N_0 = -\lambda t$$

$$N = N_0 e^{-\lambda t}$$

$$N = \frac{N_0}{2} \Longrightarrow t_{½} = \frac{\ln N_0 - \ln\left(\frac{N_0}{2}\right)}{\lambda} = \frac{\ln 2}{\lambda}$$

$$A = A_0 e^{-\lambda t} = A_0 e^{-\frac{\ln 2}{t_{½}} t}$$

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Radioactive equilibrium

Often the daughter is also radioactive:

Nuclide1 $(t_{½})_1$, $\lambda_1 \rightarrow$ Nuclide2 $(t_{½})_2$, $\lambda_2 \rightarrow$ Nuclide3

$$\frac{dN_2}{dt} = -\frac{dN_1}{dt} - \lambda_2 N_2 = \lambda_1 N_1 - \lambda_2 N_2$$

$$N_1 = N_{1(0)} e^{-\lambda_1 t}$$

$$\frac{dN_2}{dt} + \lambda_2 N_2 - \lambda_1 N_{1(0)} e^{-\lambda_1 t} = 0$$

$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_{1(0)} \left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right) + N_{2(0)} e^{-\lambda_2 t}$$

Radioactive equilibrium

Nuclide1 $(t_{½})_1$, $\lambda_1 \rightarrow$ Nuclide2 $(t_{½})_2$, $\lambda_2 \rightarrow$ Nuclide3

$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_{1(0)} \left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right) + N_{2(0)} e^{-\lambda_2 t}$$

Assuming that at t=0 a quantitative separation between Nuclide 1 and 2 has been achieved, then $N_{2(0)}=0$ and

$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_{1(0)} \left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right)$$

Expressed as radioactivity, this is

$$A_2 = \frac{\lambda_2}{\lambda_2 - \lambda_1} A_{1(0)} \left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right) \qquad \text{(since } A_i = N_i \lambda_i\text{)}$$

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Radioactive equilibrium $(t_{½})_1 >> (t_{½})_2$

$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_{1(0)} \left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right) + N_{2(0)} e^{-\lambda_2 t}$$

If $(t_{½})_1 >> (t_{½})_2$ then $\lambda_2 >> \lambda_1$ and the equilibrium can be simplified to

$$N_2 = \frac{\lambda_1}{\lambda_2} N_{1(0)} \left(1 - e^{-\lambda_2 t}\right) \qquad A_2 = A_{1(0)} \left(1 - e^{-\lambda_2 t}\right)$$

At equilibrium

$A_1 = A_2 = N_1\lambda_1 = N_2\lambda_2$ (= $N_3\lambda_3$ ...)

Example:

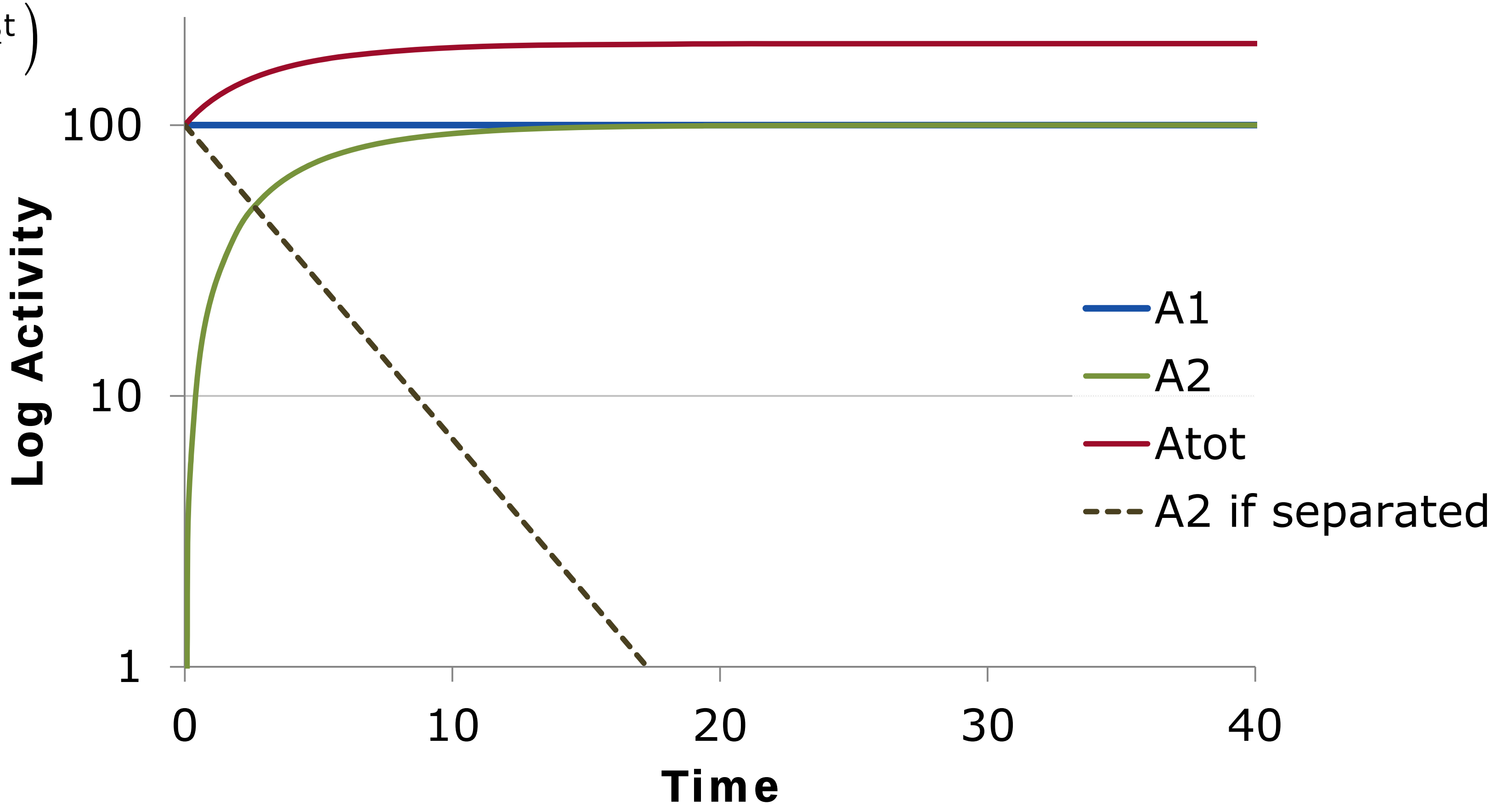
$$^{238}U \xrightarrow{\alpha + 2\beta} {}^{234}U \xrightarrow{\alpha} {}^{230}Th \xrightarrow{\alpha} {}^{226}Ra \xrightarrow{4\alpha + 2\beta} {}^{210}Pb \xrightarrow{2\beta + \alpha} {}^{206}Pb$$

4.5×10^9 y	2.5×10^5 y	7.5×10^4 y	1.6×10^3 y	22y

Radioactive equilibrium $(t_{½})_1 >> (t_{½})_2$

$$A_1 = A_{1(0)} e^{-\lambda_1 t}$$

$$A_2 = A_{1(0)} \left(1 - e^{-\lambda_2 t}\right)$$



Radioactive equilibrium $(t_{1/2})_1 > (t_{1/2})_2$

"The whole expression" with out simplifications must be used:

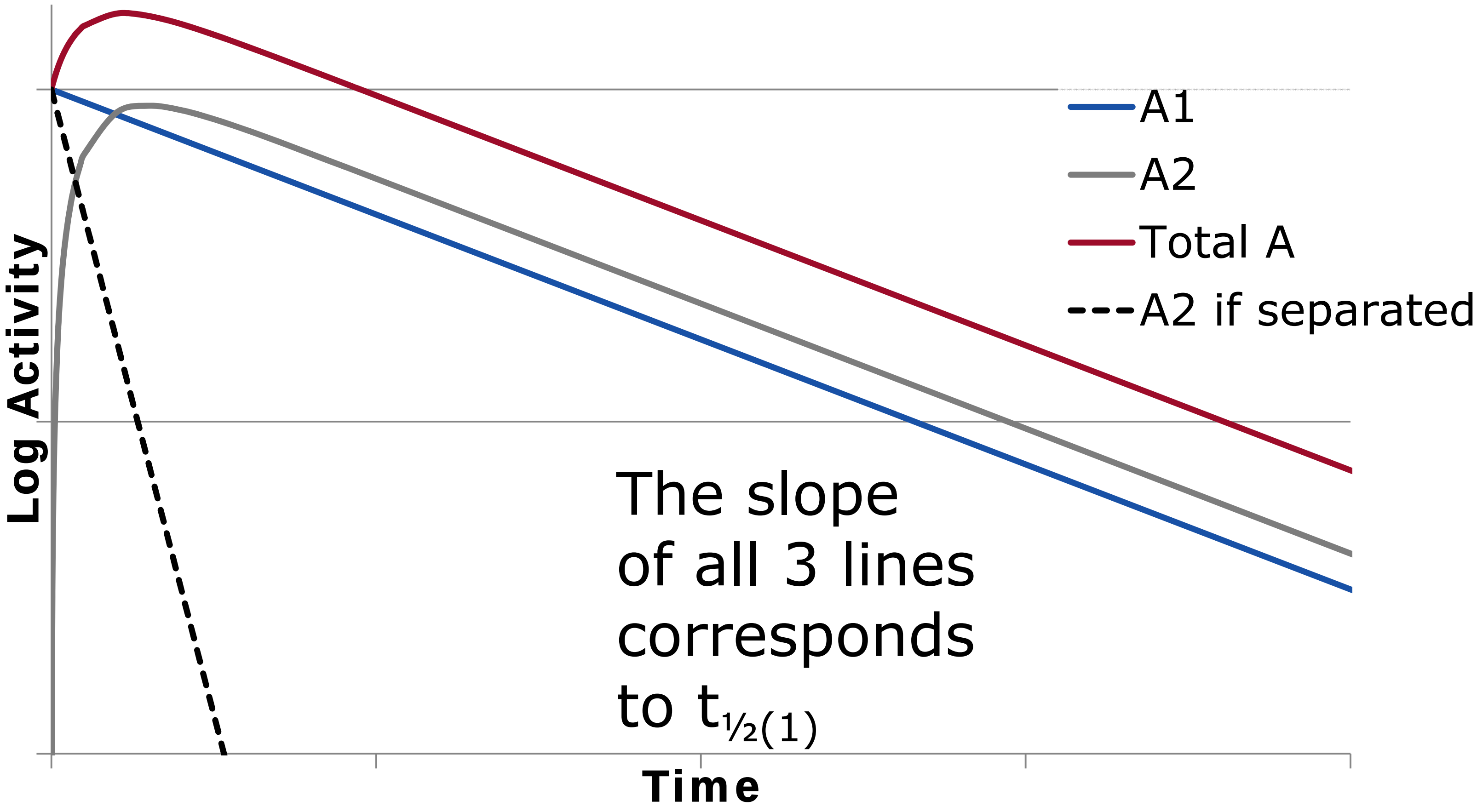
$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_{1(0)} \left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right) \qquad \text{or} \qquad A_2 = \frac{\lambda_2}{\lambda_2 - \lambda_1} A_{1(0)} \left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right)$$

Transient equilibrium is reached when

$e^{-(\lambda_2 - \lambda_1)t}$ approaches 0. *i.e.* when $\lambda_2 t$ can be neglected compared with $\lambda_1 t$

$$\frac{N_2}{N_1} = \frac{\lambda_1}{\lambda_2 - \lambda_1} = \frac{(t_{1/2})_2}{(t_{1/2})_1 - (t_{1/2})_2}$$

Radioactive equilibrium $(t_{½})_1 > (t_{½})_2$



Radioactive equilibrium $(t_{½})_1 < (t_{½})_2$

"The whole expression" with out simplifications must be used:

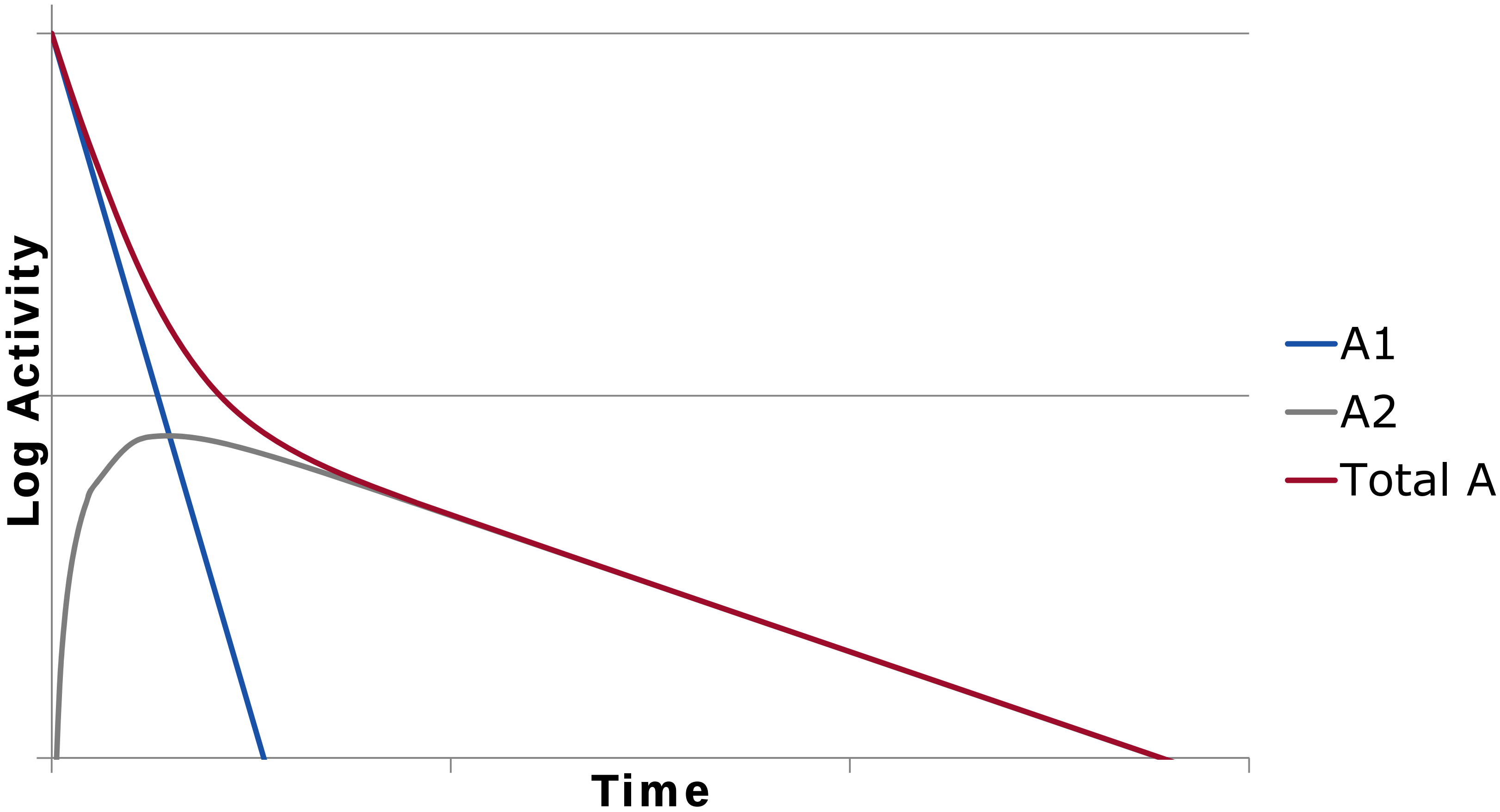
$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_{1(0)} \left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right) \quad \text{or} \quad A_2 = \frac{\lambda_2}{\lambda_2 - \lambda_1} A_{1(0)} \left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right)$$

Equilibrium is never reached,

but when $e^{-(\lambda 1-\lambda 2)t} << 1$,

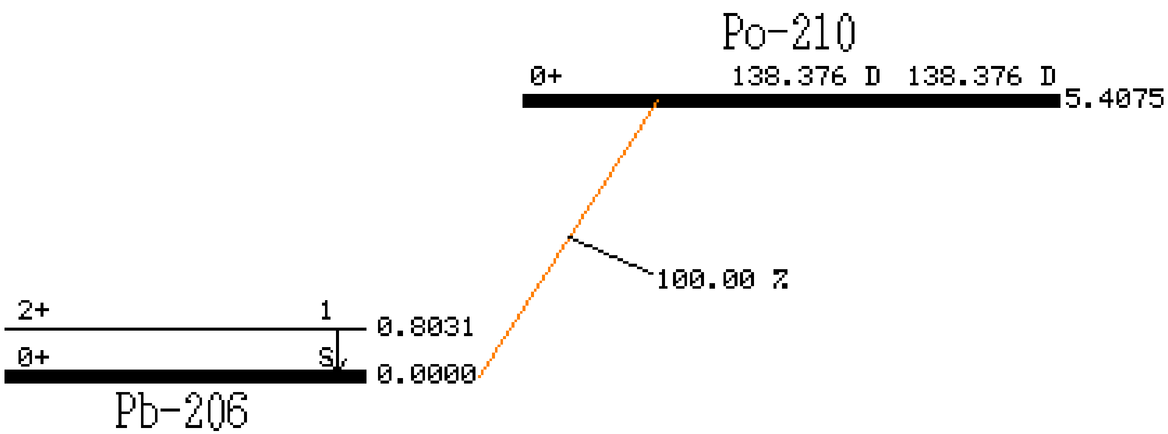
only the decay of the daughter is seen

Radioactive equilibrium $(t_{½})_1 < (t_{½})_2$



^{210}Po production

How much pitchblende containing 40% U_3O_8 is needed to produce 1 gram ^{210}Po?
(assuming ^{210}Po can be extracted quantitatively)



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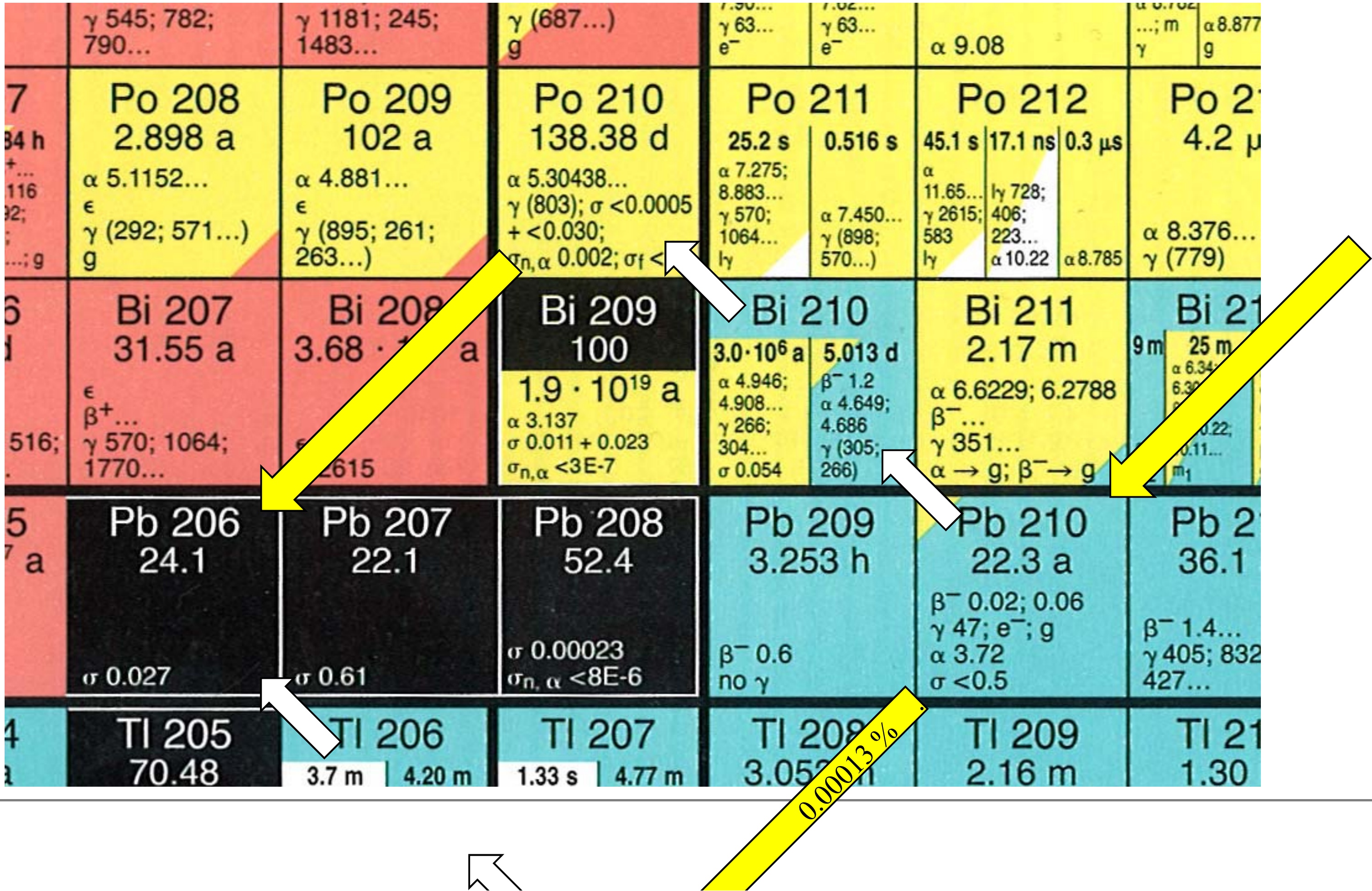


^{210}Po production

Secular equilibrium: $A_1 = A_2 = N_1\lambda_1 = N_2\lambda_2$ (= $N_3\lambda_3$ ...)

$N_{Po\text{-}210}\lambda_{Po\text{-}210} = N_{U\text{-}238}\lambda_{U\text{-}238}$

$$N_{Po-210} = \frac{1}{210} \times 6.022 \times 10^{23} = 2.87 \times 10^{21} \text{ atoms}$$

$t_{½,Po\text{-}210}$ = 138.38 d => $\lambda_{Po\text{-}210}$ = ln2/138.38 = 5.01×10^{-3} d^{-1}

$\lambda_{U\text{-}238}$ = ln2/(4.5×10^{9}*365) = 4.25×10^{-13} d^{-1}

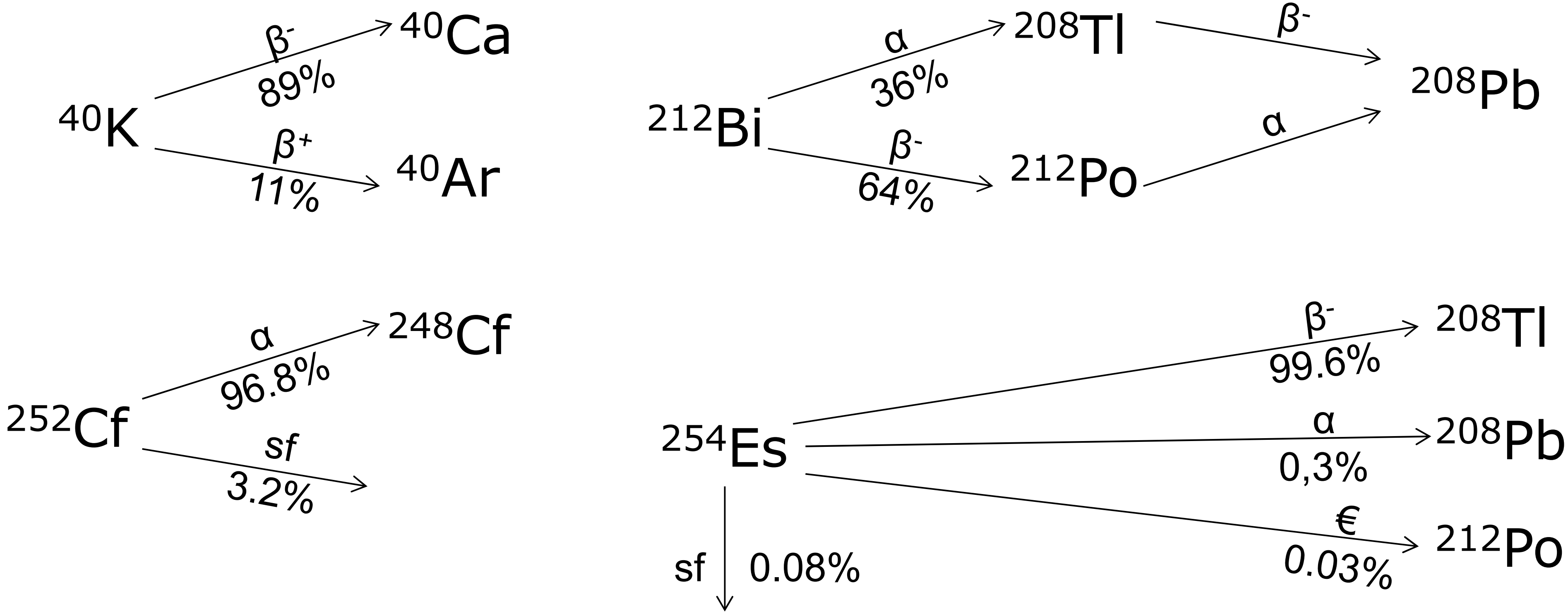
$$N_{U-238} = \frac{2.87\times10^{21}\times5.01\times10^{-3}}{4.25\times10^{-13}} = 3.38\times10^{31} \text{ atoms}$$

$$N_{U-238} = \frac{3.38\times10^{31}}{6.023\times10^{23}} = 5.61\times10^{7}\,\text{mol} \Rightarrow N_{U_3O_8} = \frac{5.61\times10^{7}}{3} = 1.87\times10^{7} \text{ mol}$$

= 15 750 tonnes U_3O_8 and 39 400 tonnes pitchblende

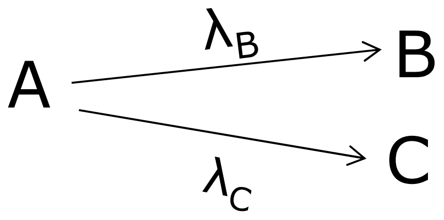
Dual (triple) decay

Some radionuclides can decay in several ways. Examples:



Dual (triple, etc.) decay

For a dual decay, the decay law is written:



$$-\frac{dN_A}{dt} = (\lambda_B + \lambda_C)N_A$$

The formation of B and C can be expressed as

$$\frac{dN_B}{dt} = \lambda_B N_A \quad \text{and} \quad \frac{dN_C}{dt} = \lambda_C N_A$$

The decay constant can be written $\lambda = \lambda_1 + \lambda_2 + \ldots \lambda_i = \sum_1^i \lambda_i$

The partial half-lives are related $\frac{1}{(t_{1/2})} = \frac{1}{(t_{1/2})_1} + \frac{1}{(t_{1/2})_2} + \ldots \frac{1}{(t_{1/2})_i} = \sum_1^i \frac{1}{(t_{1/2})_i}$

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Radionuclides in nature

- Primordial (“original”):
  $t_{½} > 10^8$ years

- Cosmogenic
  Cosmic radiation: γ-photons, mesons, neutrons, protons, α-particles, heavier particles

- Anthropogenic
  Fission products

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Primordial radionuclides for Z<82 (Pb)

Nuclide	Isotpoic abundance %	Decay mode	$t_{½}$, years
^{40}K	0.0117	β^-, EC	1.26×10^{9}
^{50}V	0.25	β^-, EC	$>1.4\times10^{17}$
^{87}Rb	27.83	β^-	4.88×10^{10}
^{115}In	95.72	β^-	4.4×10^{14}
^{123}Te	0.905	EC	1.3×10^{13}
^{138}La	0.092	β^-, EC	1.05×10^{11}
^{144}Nd	23.8	α	2.1×10^{15}
^{147}Sm	15	α	1.06×10^{11}
^{148}Sm	11.3	α	7×10^{15}
^{176}Lu	2.59	β^-	3.8×10^{10}
^{174}Hf	0.162	α	2×10^{15}
^{187}Re	62.6	β^-	4.2×10^{10}
^{190}Pt	0.012	α	6.5×10^{11}

Cosmogenic radionuclides

Inflow:

$$R_i = \sigma_i \cdot \Phi_{cosm.} \cdot N_i$$

Cross section — Flux

<u>Examples:</u>

$$n(\text{fast}) + {}^{14}N \rightarrow {}^{12}C + {}^{3}H$$

$$n(\text{slow}) + {}^{14}N \rightarrow {}^{14}C + {}^{1}H$$

Cosmogenic radionuclides

Long-lived cosmogenic radionuclides appearing in meteorites and rain water

^{3}H, ^{10}Be, ^{14}C, ^{22}Na, ^{26}Al, ^{32}Si, ^{35}S, ^{36}Cl, ^{39}Ar, ^{53}Mn, ^{81}Kr

Short-lived cosmogenic radionuclides appearing in rain water

^{7}Be, ^{24}Na, ^{28}Mg, ^{32}P, ^{33}P, ^{39}Cl

Radiometric dating -Accumulation

- Determine age of geologic samples

Decay of mother nuclide: $A = A_0 e^{-\lambda t}$

Build up of daughter: $B = A_0(1-e^{-\lambda t})$

$$\Rightarrow t = \frac{\ln\left(1 + B/A\right)}{\lambda}$$

- t and t½ should be in same order of magnitude
- Mother and daughter must be stuck in matrix

Radiometric dating

- Th-serie: $^{232}Th\ (t_{½}=1.41\times10^{10}y)\xrightarrow{6\alpha,4\beta^-}{}^{208}Pb$
- Np-serie: $^{237}Np\ (t_{½}=2.1\times10^{6}y)\xrightarrow{7\alpha,4\beta^-}{}^{209}Bi$
- U-series: $^{238}U\ (t_{½}=4.5\times10^{9}y)\xrightarrow{8\alpha,6\beta^-}{}^{206}Pb$

  $^{235}U\ (t_{½}=7.08\times10^{8}y)\xrightarrow{7\alpha,4\beta^-}{}^{207}Pb$

^{206}Pb, ^{207}Pb and ^{208}Pb are of radiogenic origin while ^{204}Pb is not.

U and Th containing minerals can be dated by measuring the ratio of Pb and mother nuclide.

Another way is to measure the Pb-ratio: $\frac{^{207}Pb}{^{206}Pb}=\frac{1}{138}\frac{e^{\lambda_{235}t}-1}{e^{\lambda_{238}t}-1}$

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Radiometric dating

- ^{87}Rb ($t_{½}=1.41\times10^{10}$y) → ^{87}Sr
- ^{40}K ($t_{½}=1.27\times10^{9}$y) → ^{40}Ar (most of the argon in the atmosphere has been created this way)
- ^{187}Re ($t_{½}=5\times10^{10}$y) → ^{187}Os

$^{87}Rb/^{87}Sr$ is the most reliable method of dating old minerals

The oldest material found in the Earth's crust are 3.5×10^{9}years
Metoritic stones have been dated 4.5×10^{9}years

An approximative age of our solar system (5.9×10^{9}years) can be calculated assuming that the ratio $^{235}U/^{238}U$ was 1

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U-238/U-235 = 1

$$N_{238} = N_{238}^{0} e^{-\lambda_{238} t} \Longrightarrow N_{238}^{0} = \frac{N_{238}}{e^{-\lambda_{238} t}}$$

$$N_{238}^{0} = N_{235}^{0} \Longrightarrow \frac{N_{238}}{e^{-\lambda_{238} t}} = \frac{N_{235}}{e^{-\lambda_{235} t}}$$

$$\frac{N_{238}}{N_{235}} = \frac{e^{-\lambda_{238} t}}{e^{-\lambda_{235} t}}$$

$$\ln\left(\frac{N_{238}}{N_{235}}\right) = (\lambda_{235} - \lambda_{238})\, t$$

$$t = \frac{\ln\left(\frac{N_{238}}{N_{235}}\right)}{\lambda_{235} - \lambda_{238}} = 5.9 \times 10^{9}\ \text{y}$$

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Radiocarbon dating

- The ^{14}C-method ($t_{½}$=5 736y) is by far the most used for determining the age of biologic material.

$$n(slow) + {}^{14}N \rightarrow {}^{14}C + {}^{1}H$$

- It is assumed that the neutron flux has been constant.
  => the production of ^{14}C has been constant
  => equilibrium between production and decay of ^{14}C
  => constant $^{14}CO_2$ in atmosphere

- When organism dies it ceases to take in new ^{14}C-isotopes

Example

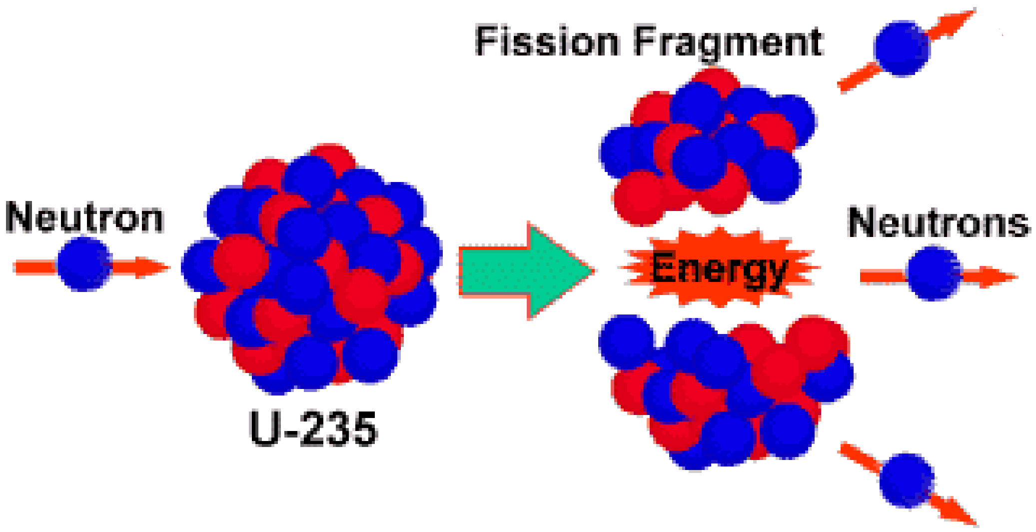
- Before 1952 (when atmospheric nuclear bomb tests started) the specific activity of ^{14}C was ≈ 15 decays/min,g
  (today it's closer to 20 dpm/g).

In a sample containing 250 mg carbon, 2480 C-14 decays occurred during 20 hours. How old is the sample? [$t_{½,C\text{-}14}$= 5 736y]

Specific activity = 2480/(20*60*0.25)= 8.267 dpm/g

$$A = A_0 e^{-\lambda t} \Rightarrow t = \frac{\ln\left(A_0 / A\right)}{\lambda} = \frac{\ln\left(15 / 8.267\right)}{\ln 2 / 5736} = 4930$$

Fission



Typically 200 MeV is released in a fission event

Fission

- Spontaneous fission

- Induced fission
  - When an isotope is struck by a fast neutron: *fissionable*
  - When an isotope is struck by a thermal (slow) neutron: *fissile*

  (^{235}U and ^{239}Pu are fissionable and fissile)

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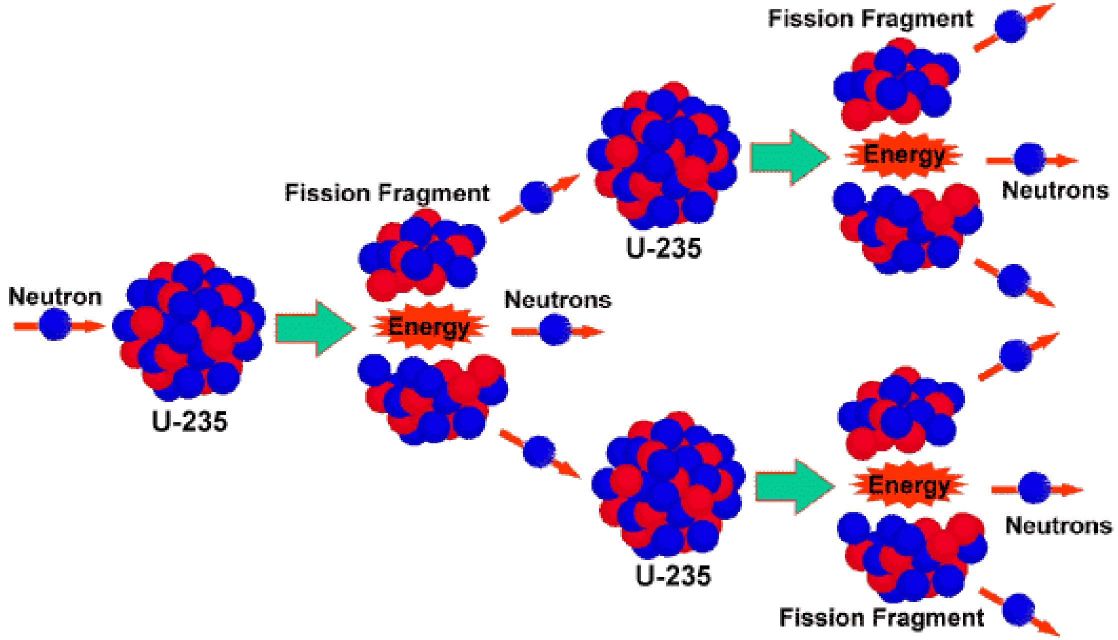
Nuclear chain reaction

- A nuclear chain reaction will take place if sufficient amount of neutrons are produced and captured.

- *Critical mass*: the smallest amount of fissile material needed for a sustained nuclear chain reaction



Calculation example

- What is the decay rate of K-40 in 1 g of natural K?

Nuclide	Isotpoic abundance %	Decay mode	$t_{½}$, years
^{40}K	0.0117	β^-, EC	1.26×10^9

$$A = N\lambda$$

$$N_{^{40}K} = \frac{1}{M_K} \times I_{^{40}K} \times 6.023 \times 10^{23} = \frac{1}{39.1} \times 0.000117 \times 6.023 \times 10^{23} = 1.80 \times 10^{18}$$

$$\lambda_{^{40}K} = \frac{\ln 2}{1.26 \times 10^9 \times 365.25 \times 24 \times 3600}$$

$$A_{^{40}K} = N_{^{40}K} \lambda_{^{40}K} = 31{,}4 \mathrm{Bq}$$