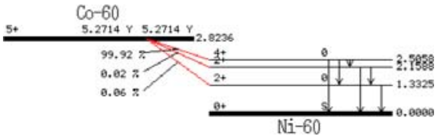
Nuclear Fuel Cycle 2013

Lecture 3: Basic Nuclear Chemistry, Part 2

Radioactive decay

N → Daughter + particle $t_{½}$ [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 → Daughter + particle λ [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

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

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

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

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

Radioactive equilibrium

Often the daughter is also radioactive:
Nuclide1 $(t_{½})_1$, λ_1→ Nuclide2 $(t_{½})_2$, λ_2 → Nuclide3

Nuclide1
$\downarrow t_{½,1}$
Nuclide2
$\downarrow t_{½,2}$
Nuclide3
(stable)

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

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

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

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

Radioactive equilibrium

Nuclide1 $(t_{½})_1$, λ_1→ Nuclide2 $(t_{½})_2$, λ_2 → 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

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

(since $A_i = N_i \lambda_i$)

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

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

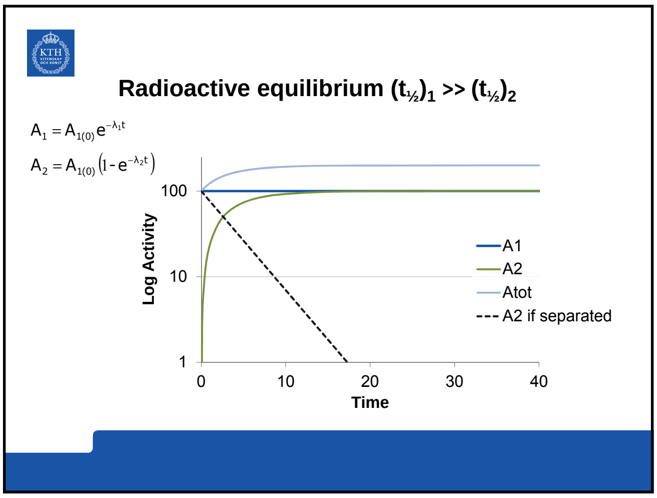
If $(t_{½})_1 >> (t_{½})_2$ then $\lambda_2 >> \lambda_1$ and the equilibrium can be simplified to

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

At equilibrium
$A_1 = A_2 = N_1\lambda_1 = N_2\lambda_2$ (= $N_3\lambda_3$ …)

Example:

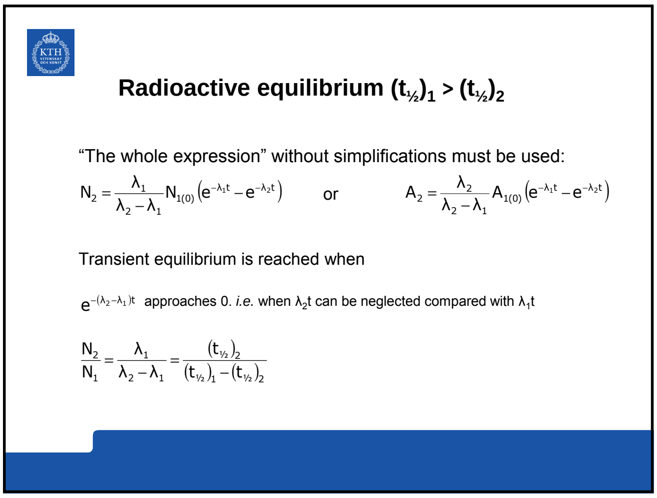
$$^{238}U \xrightarrow[\boxed{4.5\times10^{9}y}]{\alpha+2\beta} {}^{234}U \xrightarrow[2.5\times10^{5}y]{\alpha} {}^{230}Th \xrightarrow[7.5\times10^{4}y]{\alpha} {}^{226}Ra \xrightarrow[1.6\times10^{3}y]{4\alpha+2\beta} {}^{210}Pb \xrightarrow[22y]{2\beta+\alpha} {}^{206}Pb$$



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 $(t_{½})_1 > (t_{½})_2$

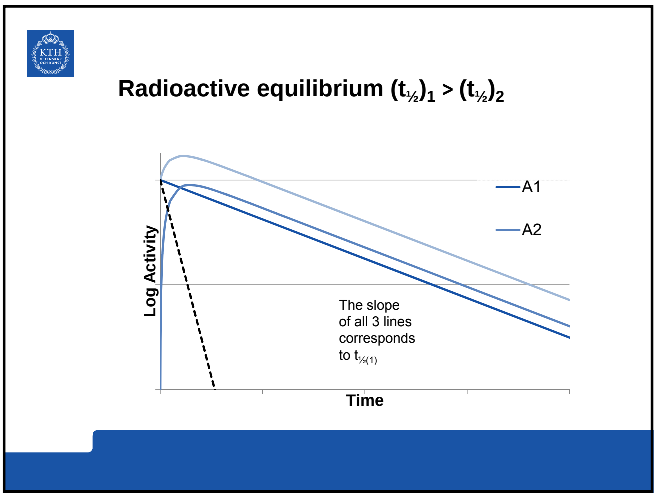
"The whole expression" without simplifications must be used:

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

Transient equilibrium is reached when

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

$$\frac{N_2}{N_1} = \frac{\lambda_1}{\lambda_2 - \lambda_1} = \frac{(t_{½})_2}{(t_{½})_1 - (t_{½})_2}$$



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

The slope of all 3 lines corresponds to $t_{½(1)}$

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

“The whole expression” without simplifications must be used:

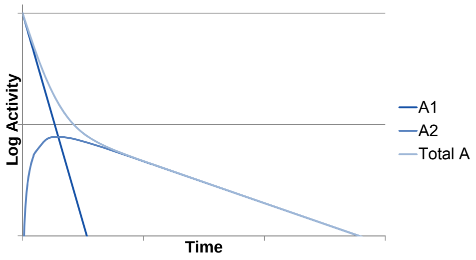
$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_{1(0)} \left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right) \quad \text{or} \quad A_2 = \frac{\lambda_2}{\lambda_2 - \lambda_1} A_{1(0)} \left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right)$$

Equilibrium is never reached,

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

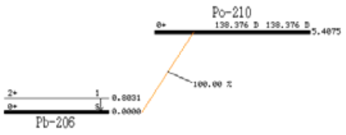
only the decay of the daughter is seen

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 that ^{210}Po can be extracted quantitatively)



^{210}Po production

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

^{210}Po production

Secular equilibrium: $A_1 = A_2 = N_1\lambda_1 = N_2\lambda_2$ (= $N_3\lambda_3$ …)
$N_{Po\text{-}210}\lambda_{Po\text{-}210} = N_{U\text{-}238}\lambda_{U\text{-}238}$

$$N_{Po-210} = \frac{1}{210}\times 6.022\times10^{23} = 2.87\times10^{21}\text{ atoms}$$

$t_{½,Po\text{-}210}$ = 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}

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

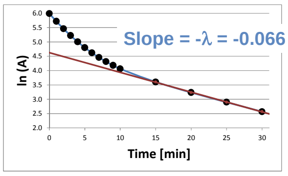
$$N_{U-238} = \frac{3.38\times10^{31}}{6.023\times10^{23}} = 5.61\times10^{7}\text{mol} \Rightarrow N_{U_3O_8} = \frac{5.61\times10^{7}}{3} = 1.87\times10^{7}\text{ mol}$$

= 15 750 tonnes U_3O_8 and 39 400 tonnes pitchblende

Example $(t_{½})_1 < (t_{½})_2$

A has a radioactive daughter and a stable grand-daughter
A → B → C(stable)
The total activity of this system has been measured. At t=0 the activity of B=0. Determine the half-life of B.

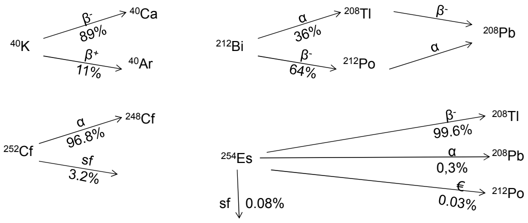
Time [min]	Tot A [Bq]	ln A [-]
0	400.0	5.99
1	304.4	5.72
2	235.4	5.46
3	185.4	5.22
4	148.7	5.00
5	121.7	4.80
6	101.6	4.62
7	86.3	4.46
8	74.6	4.31
9	65.5	4.18
10	58.2	4.06
15	36.7	3.60
20	25.4	3.24
25	18.1	2.90
30	13.0	2.56



$t_{½}$=ln(2)/0.066 = 10.5 min.

Dual (triple) decay

Some radionuclides can decay in several ways. Examples:



Dual (triple, etc.) decay

For a dual decay, the decay law is written:

$$\begin{tikzcd}
 & B \\
A \arrow[ur, "\lambda_B"] \arrow[dr, "\lambda_C"'] & \\
 & C
\end{tikzcd}$$

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

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 $\lambda = \lambda_1 + \lambda_2 + \ldots \lambda_i = \sum_1^i \lambda_i$

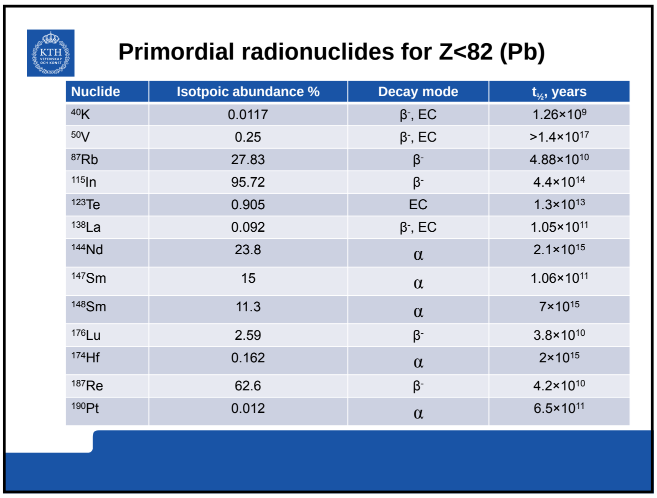
The partial half-lives are related $\frac{1}{(t_{½})} = \frac{1}{(t_{½})_1} + \frac{1}{(t_{½})_2} + \ldots \frac{1}{(t_{½})_i} = \sum_1^i \frac{1}{(t_{½})_i}$

Radionuclides in nature

Primordial ("original"):
$t_{½} > 10^8$ years

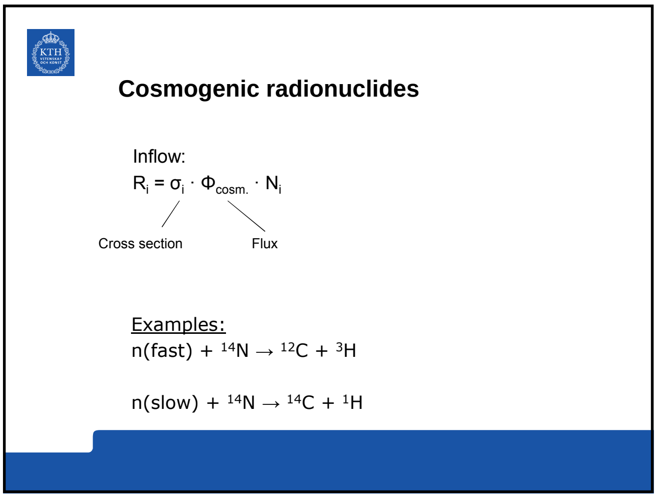
- Cosmogenic
  Cosmic radiation: γ-photons, mesons, neutrons, protons, α-particles, heavier particles

- Anthropogenic
  Fission products



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:

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

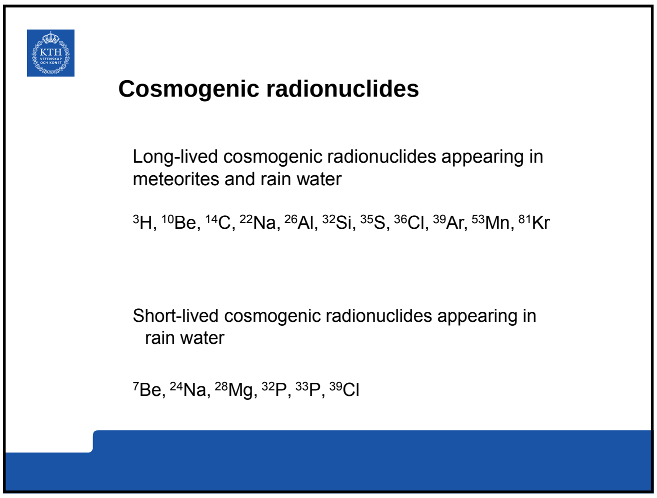
Cross section

Flux

Examples:

n(fast) + ^{14}N → ^{12}C + ^{3}H

n(slow) + ^{14}N → ^{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 $t_{½}$ should be in same order of magnitude
- Mother and daughter must be stuck in matrix

Radiometric dating

Th-serie: ^{232}Th ($t_{½}$=1.41×10^{10}y) $\xrightarrow{6\alpha,4\beta^-}$ ^{208}Pb

Np-serie: ^{237}Np ($t_{½}$=2.1×10^{6}y) $\xrightarrow{7\alpha,4\beta^-}$ ^{209}Bi

U-series: ^{238}U ($t_{½}$=4.5×10^{9}y) $\xrightarrow{8\alpha,6\beta^-}$ ^{206}Pb

^{235}U ($t_{½}$=7.08×10^{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: $\frac{^{207}\mathrm{Pb}}{^{206}\mathrm{Pb}} = \frac{1}{138}\frac{e^{\lambda_{235}t}-1}{e^{\lambda_{238}t}-1}$

Radiometric dating

^{87}Rb ($t_{½}$=1.41×10^{10}y) → ^{87}Sr

^{40}K ($t_{½}$=1.27×10^{9}y) → ^{40}Ar (most of the argon in the atmosphere has been created this way)

^{187}Re ($t_{½}$=5×10^{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
Meteoritic stones have been dated 4.5×10^{9}years

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

U-238/U-235 = 1

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

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

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

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

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

Radiocarbon dating

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

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

- 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

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Example

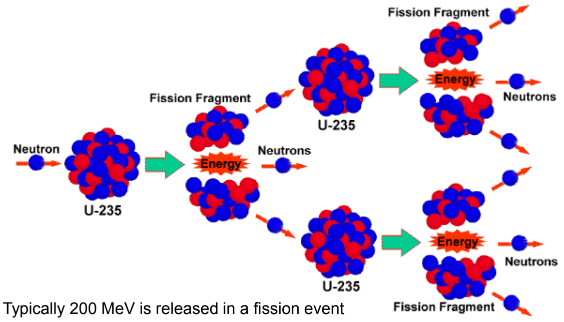
Before 1952 (when atmospheric nuclear bomb tests started) the specific activity of ^{14}C was ≈ 15 decays/min,g
(today it's closer to 20 dpm/g).

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

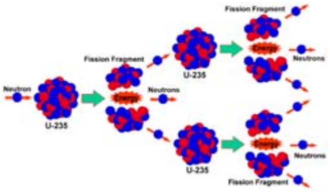
- Induced fission
  - When an isotope is struck by a fast neutron: ***fissionable***
  - When an isotope is struck by a thermal (slow) neutron: ***fissile***

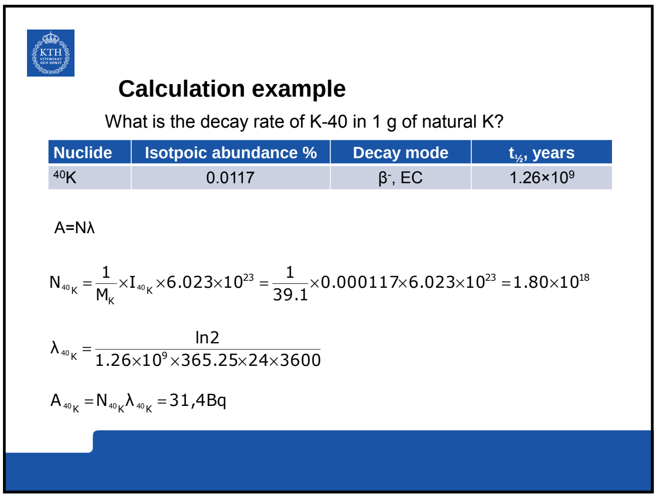
  (^{235}U and ^{239}Pu are fissionable and fissile)

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=Nλ

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

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

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