Physical chemistry and radiochemistry

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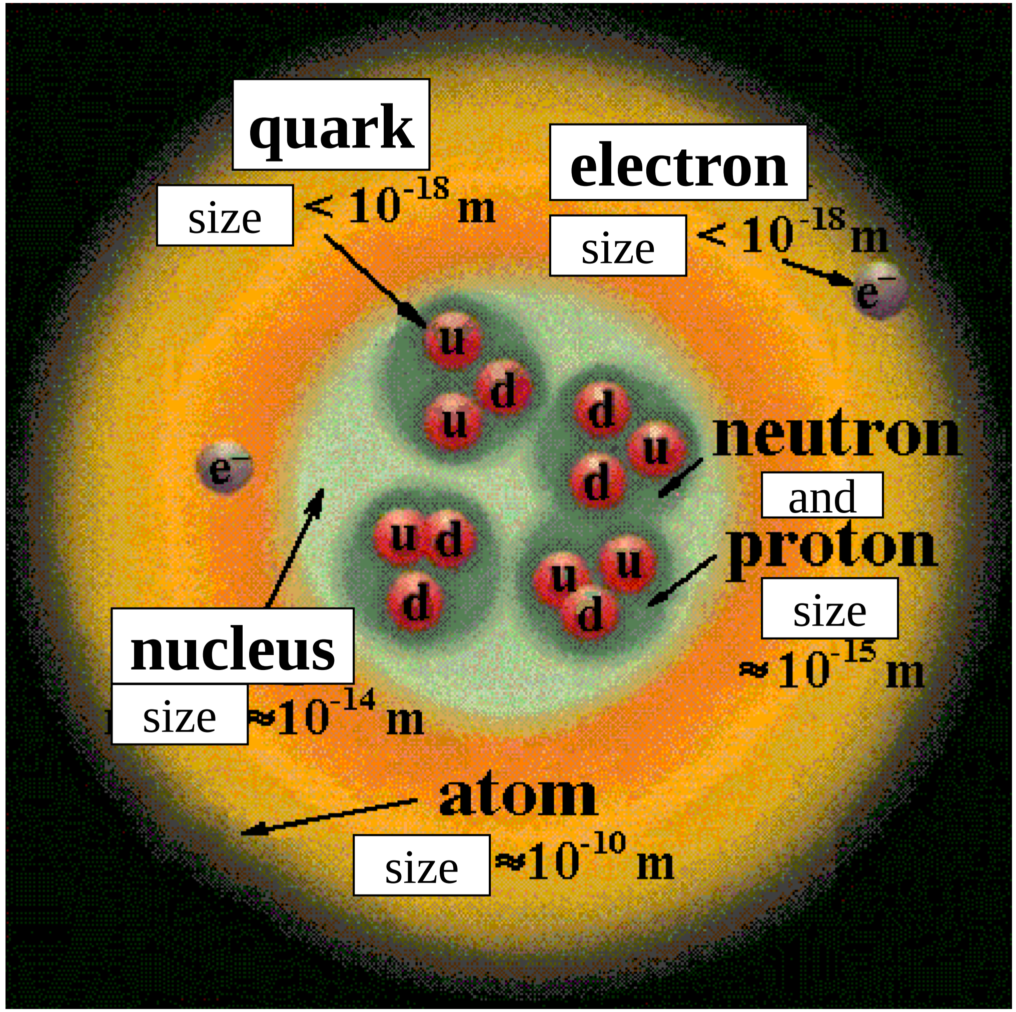
RADIOCHEMISTRY

- ✓ to understand the nuclear forces acting in the nucleus of the atoms
- ✓ the kinds and source of nuclear radiations
- ✓ interactions of nuclear radiation with the matter
- ✓ applications

Antoine Henri *Becquerel*
(1852 - 1908)

Maria *Skłodowska-Curie*
(1867 – 1934)

The nucleus



after http://astronomyonline.org/Science/Images/Mathematics/AtomicStructureSmall.jpg

$$\Delta E = mc^2$$

A=Z+N

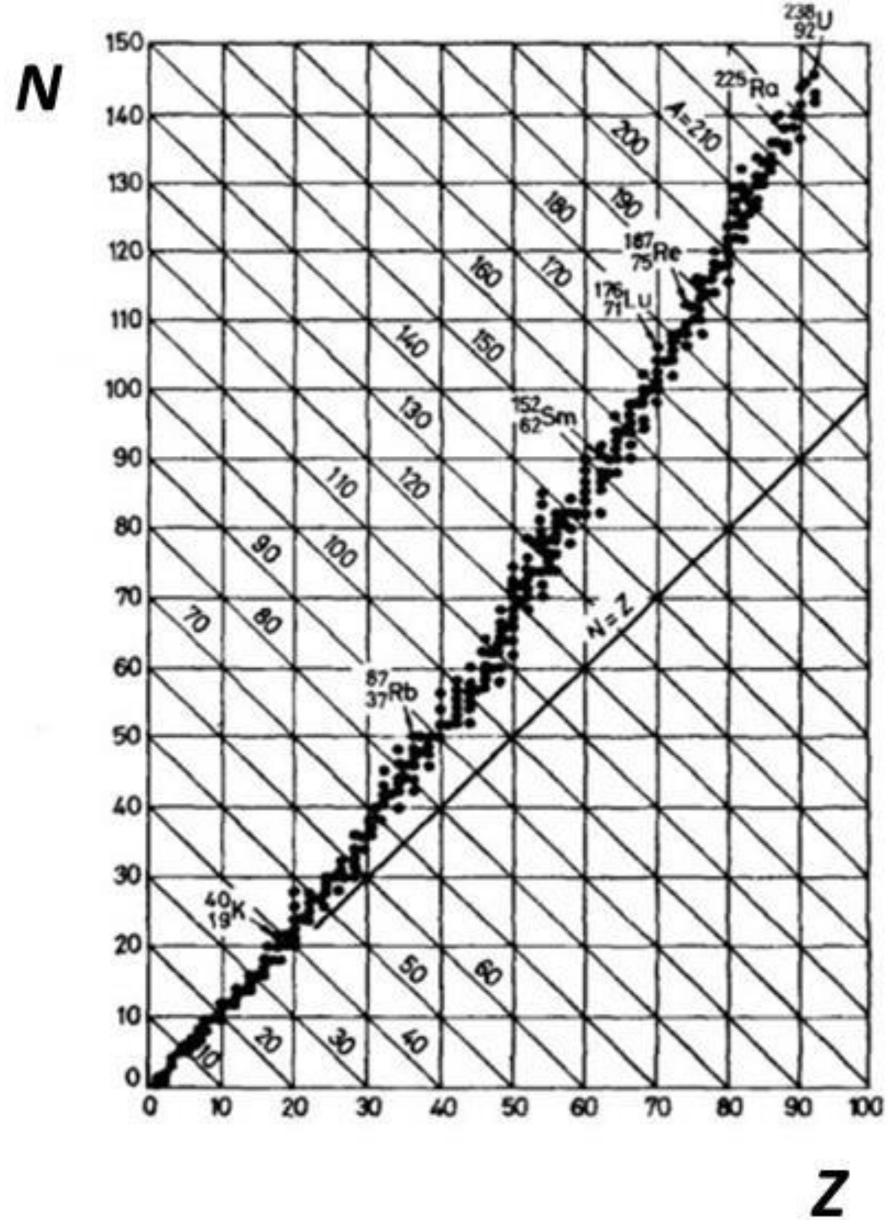
A: mass number
Z: atomic number

	m	E, MeV
p	1.6726×10^{-24}g	938.27
n	1.6749×10^{-24}g	939.55
e^-	9.109×10^{-28} g	0.51

Stable nuclides

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

$$A = Z + N$$

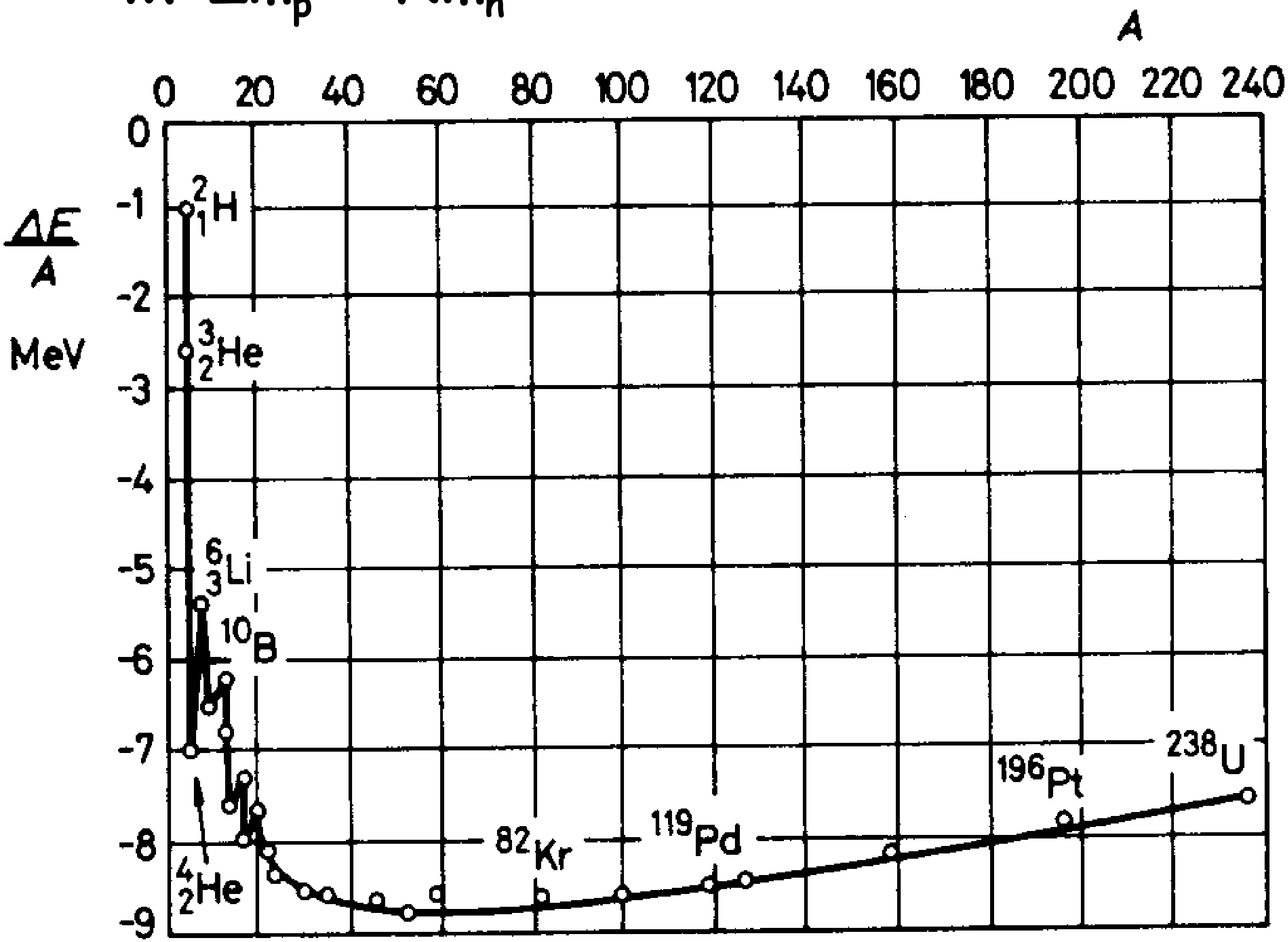


The role of the neutrons

Binding energy of the nucleus

$$\Delta E = \Delta mc^2$$

$$M < Zm_p + Nm_n$$



Classification of the nuclides

Isotope: identical Z

Isobar: identical A

Isotone: identical N

Isotope effect ¡ Radioactive isotope !

applications

- spectroscopies (resonance, MS)
- solvent (NMR, neutron scattering)
- enrichment of isotopes
- CSIA: compound specific isotope analysis

Negligible?

- labelling
- unorthodox organic synthesis routes

Radioactivity

Spontaneous transformation of the unstable nucleus.

The properties of the nucleus change in time and energy is released.

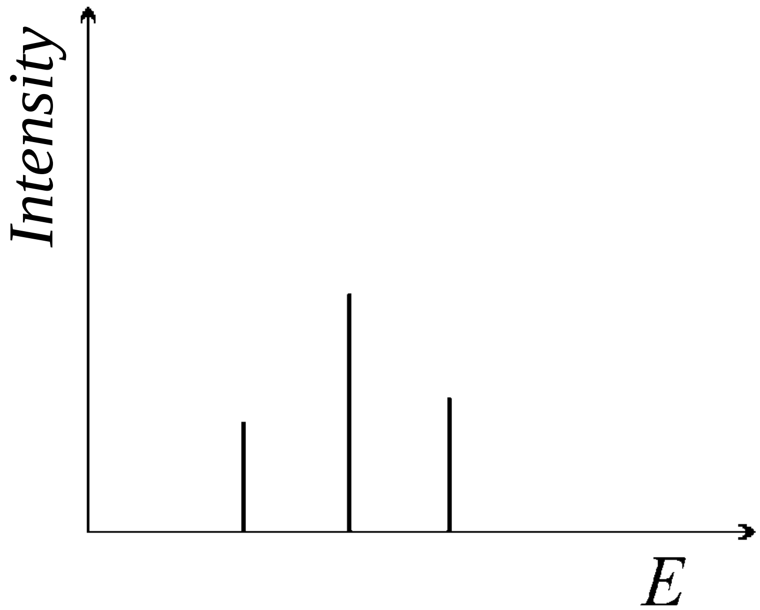
All the conservation laws are met.

Types of radioactive decay

Isomeric transition

$${}^{A*}_{Z}X \rightarrow {}^{A}_{Z}X + \gamma$$

$$\Delta E = h \cdot \nu$$



line spectrum

Examples

nuclide	$T_{1/2}$	E_{γ}, MeV
^{60m}Co	10.5 min	0.059
^{99m}Tc	6.0 h	0.143

Z	Nuclide	$T_{1/2}$	Way of decay	Particle energy, MeV	Gamma energy, MeV	η	Production	σ’	Daughter
27					2,02 11 % 2,60 16 % 2,99 1 % 3,25 12 % 3,47 1 %				
	^{57}Co	270 d	*E.X.*	100 %	0,014 6 % 0,122 88 % 0,136 10 %	83 % 1 % 1 %	^{56}Fe(*d*,*n*) ^{60}Ni(*p*,α)	0,9	
	^{58}Co	71,3 d	*E.X.* β⁺	85 % 0,47 15 %	0,81 100 % 1,62 0,5 % 0,51 (β⁺)		^{58}Ni(*n*,*p*)		
	^{60m}Co	10,5 min	*I*	100 %	0,059 0 %	≈100%	^{59}Co(*n*,γ)	19	^{60}Co
	^{60}Co	5,27 a	β⁻	0,31 ≈ 100 % 1,48 0,01 %	1,17 100 % 1,33 100 %		^{59}Co(*n*,γ)	37	
28	^{63}Ni	92 a	β⁻	0,067 100 %			^{62}Ni(*n*,γ)	0,77	
	^{65}Ni	2,521 h	β⁻	0,60 ≈ 23 % 1,01 ≈ 8 % 2,10 ≈ 69 %	0,37 5 % 1,11 13 % 1,49 18 %		^{64}Ni(*n*,γ)	0,016	
29	^{64}Cu	12,9 h	β⁻ β⁺ *E.X.*	0,57 38 % 0,66 19 % 43 %	0,51 (β⁺) 1,34 0,6 %		^{63}Cu(*n*,γ)	3,0	
	^{66}Cu	5,10 min	β⁻	0,76 < 0,2 % 1,59 ≈ 9 % 2,63 ≈ 91 %	0,83 0,2 % 1,04 9 %		^{65}Cu(*n*,γ)	0,56	

β - decays

β⁻-decay $$ {}^{A}_{Z}X \rightarrow {}^{\;\;A}_{Z+1}Y + \beta^{-} + \tilde{\nu} + [\gamma] $$

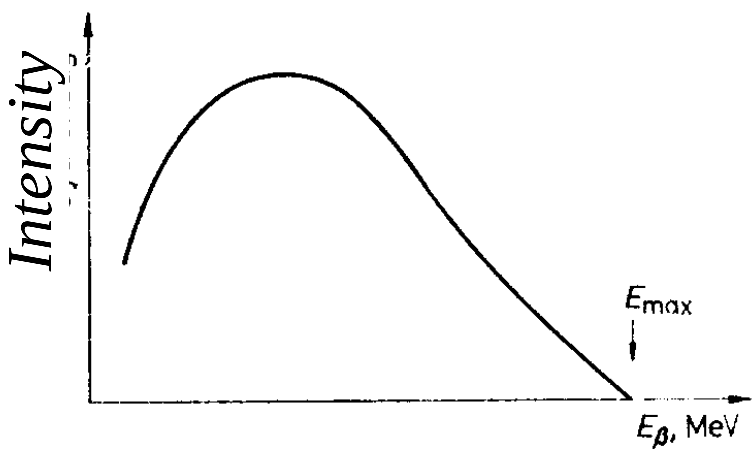
$$ n \rightarrow p + \beta^{-} + \tilde{\nu} $$ exothermic

β⁺-decay $$ {}^{A}_{Z}X \rightarrow {}^{\;\;A}_{Z-1}Y + \beta^{+} + \nu + [\gamma] $$

$$ p \rightarrow n + \beta^{+} + \nu $$ endothermic

Electron capture $$ e^{-} + {}^{A}_{Z}X \rightarrow {}^{\;\;A}_{Z-1}Y + \nu + [\gamma] $$

$$ e^{-} + p \rightarrow n + \nu $$ endothermic



common:
A= constant
ΔZ=±1
ν or $\tilde{\nu}$

Examples: pure β^- emitters

nuclide	Energia, MeV	$T_{1/2}$
^{3}H	0.018	12.26 y
^{14}C	0.159	5730 y
^{32}P	1.71	14.3 d
^{35}S	0.167	88 d
^{90}Sr	0.54	28.1 y
^{90}Y	2.25	64 h

Examples: mixed (β+γ) emitters

nuclide	$T_{1/2}$	β-energy, MeV	γ-energy, MeV
^{60}Co	5,27 a	0,31	1,17/1,33
^{131}I	8,07 d	0,61	0,36
^{137}Cs	30,23 a	0,51	0,662

Examples: positron emitters

nuklid	$T_{1/2}$	E_{β^+} MeV
^{11}C	20.3 min	0.97
^{13}N	9.97 min	1.2
^{15}O	124 s	1.7
^{18}F	109.7 min	0.064

Examples: EX (electron capture)

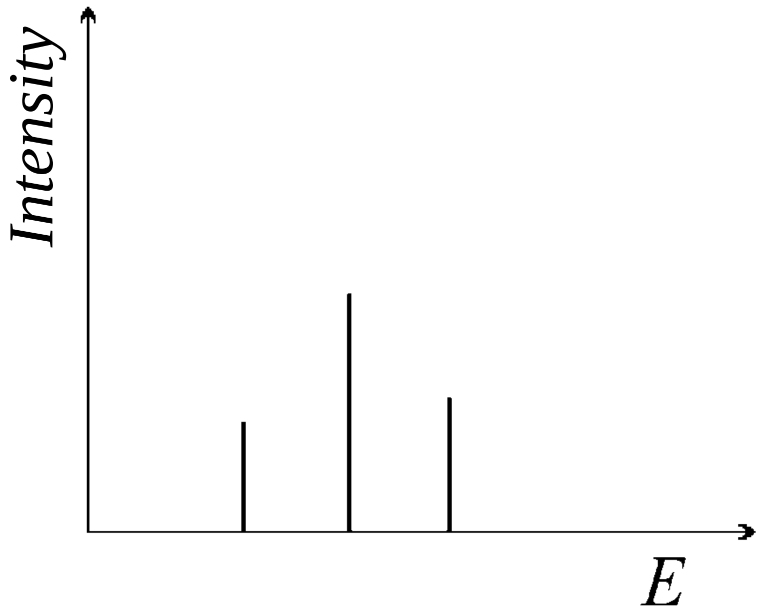
Nuclide	$T_{1/2}$	E_γ MeV
^{54}Mn	303 d	0.84
^{125}I	60 d	0.035

α-decay

α particle

$$ {}^{A}_{Z}X \rightarrow {}^{A-4}_{Z-2}Y + {}^{4}_{2}\mathrm{He}^{2+} + [\gamma] $$

4-9 MeV



line spectrum

Example: Alpha emitters

nuclide	$T_{1/2}$
^{235}U	7.1E8 a
^{226}Ra	1600 a
^{222}Rn	3.8 d

Gamma ray/radiation

Electromagnetic radiation, emmitted by the nucleus

Line spectrum

Isomeric transition ("escort" also)

Beta-radiations

e^- or e^+ radiation coming from the nucleus

Continuous spectrum

May be exclusive (but ν!)

May be escorted by gamma or characteristic X-rays

Alpha-radiation

$_{2}^{4}He^{2+}$ particles, emmitted by the nucleus

Linear spectrum

May be escorted by gamma radiation

Radioactivity

-Spontaneous decay

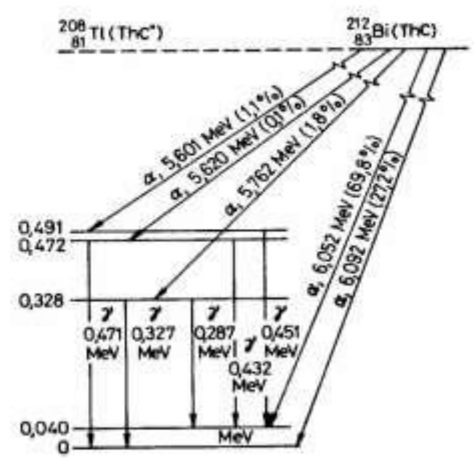
-Properties change in time
chemical identity
mass

-Energy is released		mass, MeV	typical energy, MeV
$h\nu$	from nucleus: gamma-ray	-	
e^-, e^+	from nucleus: beta-particle	0.51	
${}^{4}_{2}He^{2+}$	from nucleus: alpha-particle	~3700	4-9 MeV

Charge!

spontaneous fission

Occurs in nature!!!



Kinetics of the decay

Simple decay

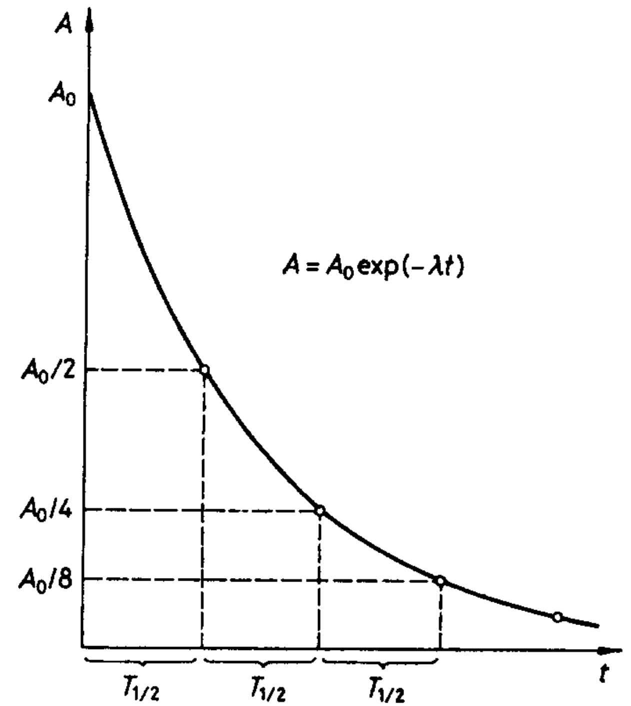
$$A \equiv -\frac{dN}{dt} = \lambda N$$

$$N = N_0 e^{-\lambda t} \qquad A = A_0 e^{-\lambda t}$$

$$T_{1/2} = \frac{\ln 2}{\lambda} \qquad [A] = \frac{1}{\text{time}}$$

$$\frac{1\ \text{decay}}{\text{second}} = 1\ \text{becquerel} = 1\ \text{Bq}$$

$$1\ \text{Ci} = 3.7\times 10^{10}\ \text{Bq}$$



I=kηA

Radiocarbon dating (or simply **carbon dating**)

radiometric dating technique based on the decay of ^{14}C to estimate the age of organic materials (wood, leather, etc.) up to 58,000 - 62,000 years.

Willard Libby, Nobel Prize in Chemistry (1949)

plant or animal alive : exchanging carbon with its surroundings → same proportion of $^{14}C/^{12}C$ as the biosphere.

Once it dies ^{14}C it contains decays, $^{14}C/^{12}C$ gradually reduce.

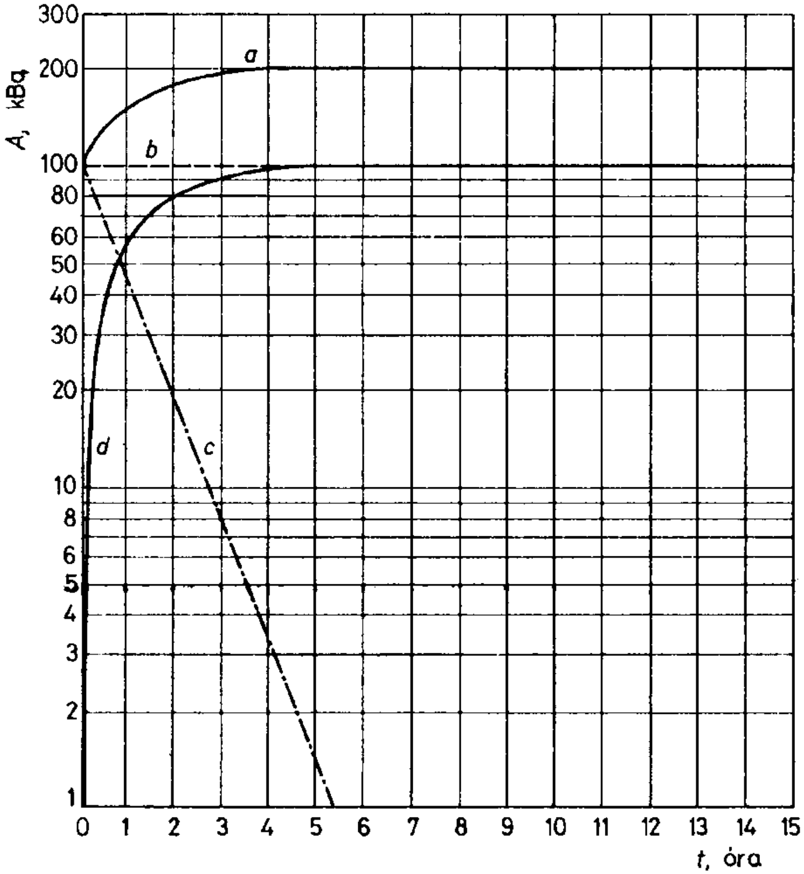
A mammoth was found in the Siberian permafrost. The ^{14}C content in the body was only 21 % of that found in living animals. Their $^{14}C/^{12}C$ ratio is 10^{-12}. How old is the mammoth ? The half-life of the radiocarbon is 5730 y.

Decay chains

$$X \xrightarrow[T_{1/2,X}]{\lambda_X} Y \xrightarrow[T_{1/2,Y}]{\lambda_Y} Z_{stable}$$

$$A_Y = \lambda_Y N_Y = A_{X,0} \frac{\lambda_Y}{\lambda_Y - \lambda_X} \left(e^{-\lambda_X t} - e^{-\lambda_Y t} \right)$$

relation *of* λ_A and λ_B ?



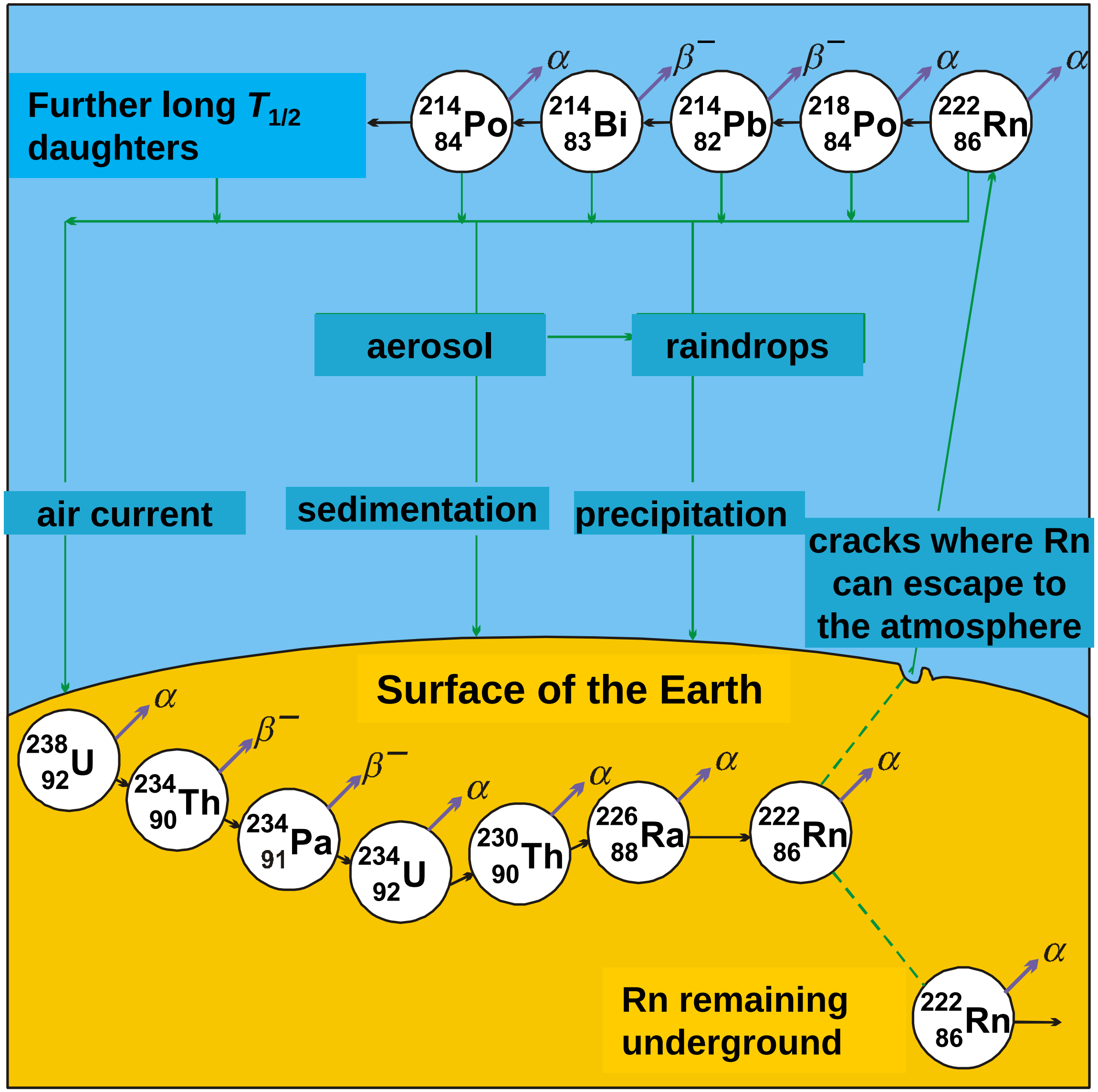
$T_{1/2,X} >> T_{1/2,Y}$

$T_{1/2,X} = 8 \cdot 10^7 h$

$T_{1/2,Y} = 0,8 h$

$$^{90}Sr \xrightarrow[28\,a]{\beta^-} {}^{90}Y \xrightarrow[64\,h]{\beta^-} {}^{90}Zr$$

$$^{226}_{88}\mathrm{Ra} \xrightarrow[1620\,\mathrm{a}]{\alpha} {}^{222}_{86}\mathrm{Rn} \xrightarrow[3{,}83\,\mathrm{d}]{\alpha} \ldots {}_{82}\mathrm{Pb}$$



When former Russian spy Alexander Litvinenko died from polonium-210 poisoning several years ago in London, it triggered a murder investigation that developed like a thriller.

^{210}Po generates much heat as the atoms decay - it was used in Russian lunar landers to keep the craft's instruments warm at night.

^{210}Po is an α-emitter, that has a half-life of 138.4 days, E_α = 5.3 MeV

Interaction of the radiation with the matter

Particles/photons

I.		II.	III.
a	b		
p	e^+	n	γ
α	e^-		X

Partners

1. Electromagnetic field
2. Electron
3. Field of the nucleus
4. Nucleus

Mechanism	**Effect on radiation**	**Effect on matter**
A) Absorption	ΔI	E_{kin}, E^*
B) Coherent scattering (only the direction is altered))	ΔI	-
C) Incoherent scattering (also exchange of *E*)	ΔI, ΔE	
elastic (no excitation)		E_{kin}
inelastic		E_{kin}, E^*

1. Ionizing radiations

The first step of the ionizing radiation in the matter:

1. Neutral excitation

$$A + \text{radiation} \rightarrow A^* + \text{radiation}'$$

2. External ionization

$$A + \text{radiation} \rightarrow A^+ + e^- + \text{radiation}'$$

$$A_2 + \text{radiation} \rightarrow A^+ + A^- + \text{radiation}'$$

$$A_2 + \text{radiation} \rightarrow A_2^+ + e^- + \text{radiation}'$$

$$A_2 + \text{radiation} \rightarrow 2\,A\cdot + \text{radiation}'$$

3. Internal ionization

$$A + \text{radiation} \rightarrow A^{*+} + e^- + \text{radiation}'$$

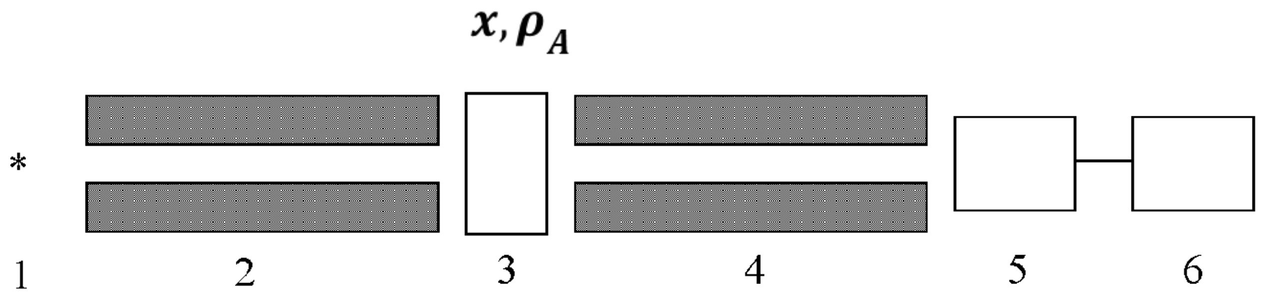
$$A^{*+} \rightarrow A^+ + X_{char}$$

$$A^{*+} \rightarrow A^{2+} + e^-_{Auger}$$

4. Bremsstrahlung (breaking radiation)

$$A + \text{radiation}^{\pm} \rightarrow A + X_b + \text{radiation}^{\pm\prime}$$

Quantitative description of the interaction



$$\nu = \sigma n x \rho_A$$

cross section

$$-dn = \sigma(E) n \rho_A dx$$

$$n = n_0 e^{-\sigma(E)\rho_A x}$$

$$I = \frac{n}{t}$$

$$I = I_0 e^{-\mu x}$$

linear absorption coefficient

$$I = I_0 e^{-\mu x} = I_0 e^{-\frac{\mu}{\rho} x \cdot \rho} = I_0 e^{-\mu_m d}$$

mass absorption coefficient

$$x_{1/2} = \frac{\ln 2}{\mu} \qquad d_{1/2} = \frac{\ln 2}{\mu_m}$$

α-radiation

Heavy, charged, high energy

With electrons: incoherent scattering

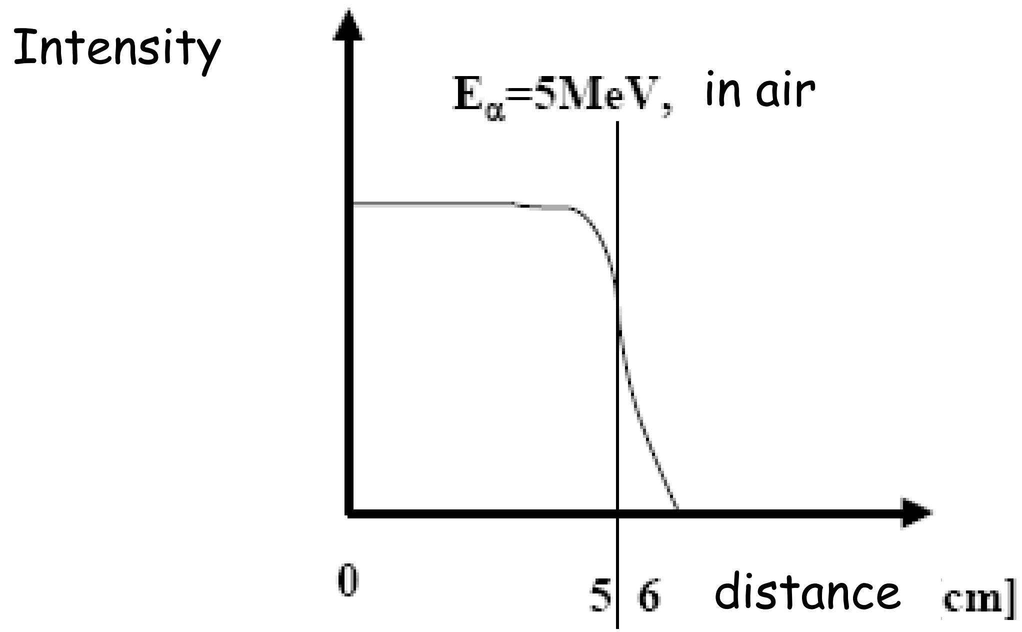
ionisation and excitation (50-50 %)

E and direction of the alpha particles is modified

With the nucleus: Rutherford-scattering

nuclear reaction (see later)

! Bremsstrahlung (continuous energy gamma radiation)!



β-radiation **small, charged, limited energy**

With electron: incoherent scattering

ionisation (external and internal)

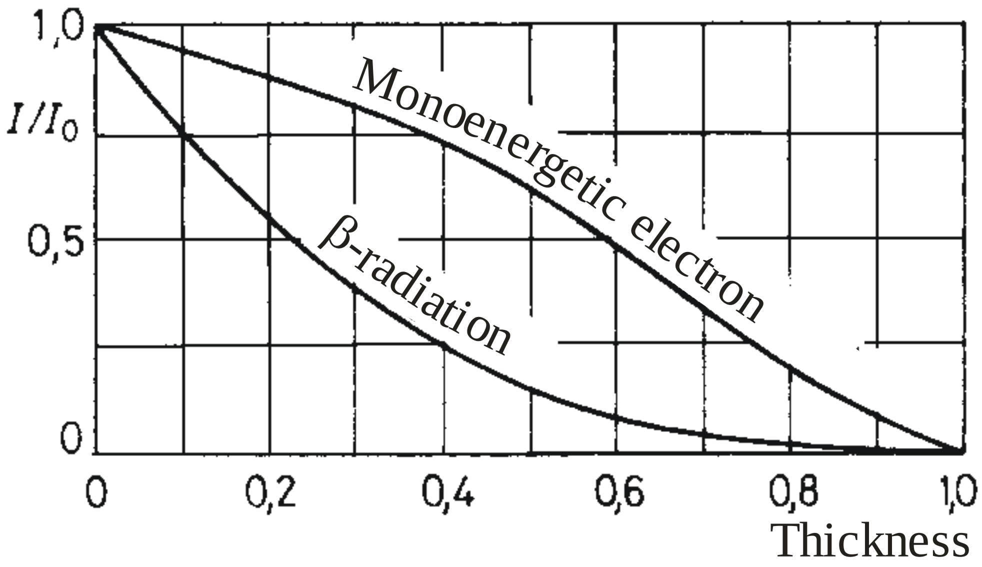
excitation

E and the direction of the radiation changes

$$\frac{\left(\frac{dE}{dx}\right)_r}{\left(\frac{dE}{dx}\right)_{ion}} = \frac{EZ}{800}$$

With the field of the nucleus: incoherent scattering

! Bremsstrahlung !



$$I = I_0 e^{-\mu' x} = I_0 e^{-\mu d}$$

Linear/mass absorption coefficient

Calculate the activity of 1 kg KCl. 0.012 % of the K atoms is radioactive ^{40}K. The half life of ^{40}K is $1.13 \cdot 10^9$ years.

We prepared a ^{35}S labelled protein at 12:00, 10 September 2014. The half life of the pure β^- emitter is 88 days. This sample was measured at noon on 26 September and the intensity was found 7000 imp/s. The overall effieciency of the measurement was 22 %. Calculate the activity of the sample in the time of synthesis.

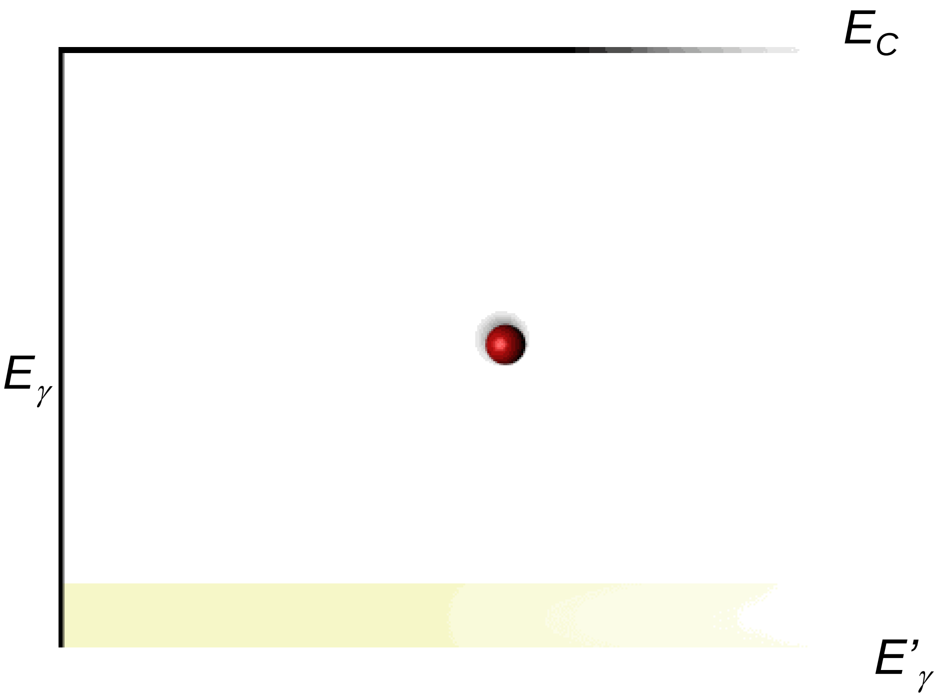
The linear absorption coefficient of gamma radiation of 660 keV in aluminum is 3,4 cm^{-1}. Calculate the half thickness. How efficiently will attenuate this radiation an 10 cm aluminum wall ?

γ-radiation

electromagnetic radiation

1. Compton-scattering

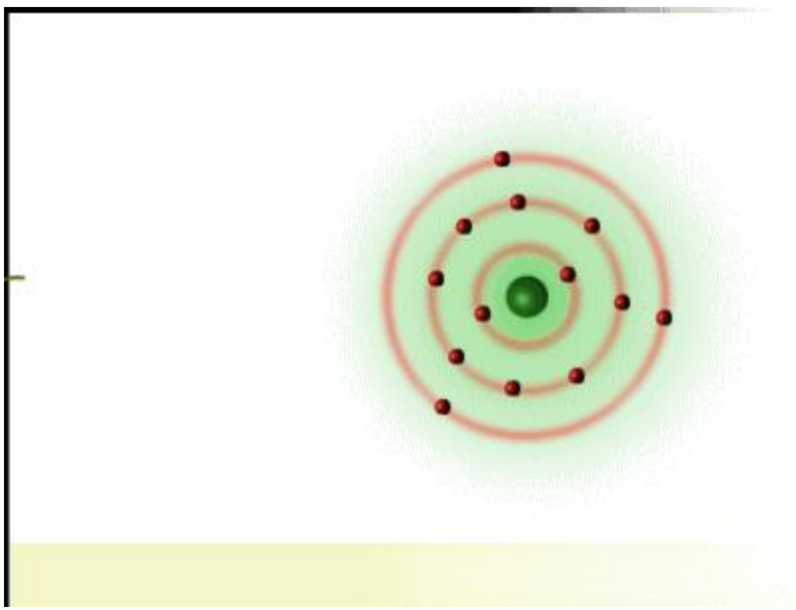
Elastic collision of the photon with an electron



$$\mu_C = \frac{\mu'_C}{\rho} = \sigma_C \frac{\rho_A}{\rho} = \sigma_C \frac{N_A Z}{A}$$

$$\sigma_C = \sigma_s + \sigma_a$$

2. Photoelectric effect



$$A + \gamma \longrightarrow A^{*+} + e_f^-$$

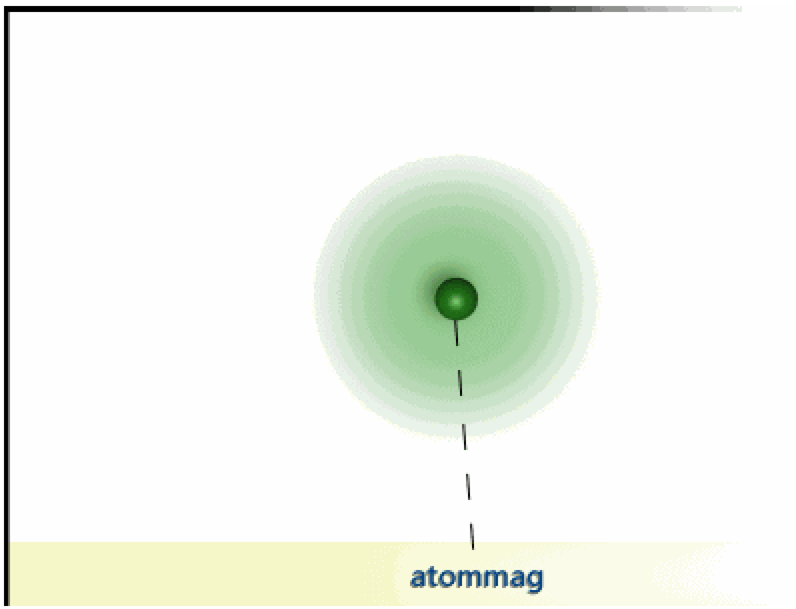
$$A^{*+} \longrightarrow A^{+} + X_k$$

$$A^{*+} \longrightarrow A^{2+} + e_A^-$$

$$\sigma_f \approx \text{konst.} \frac{Z^n}{(h\nu)^3}$$

$n(E)$=4 - 5

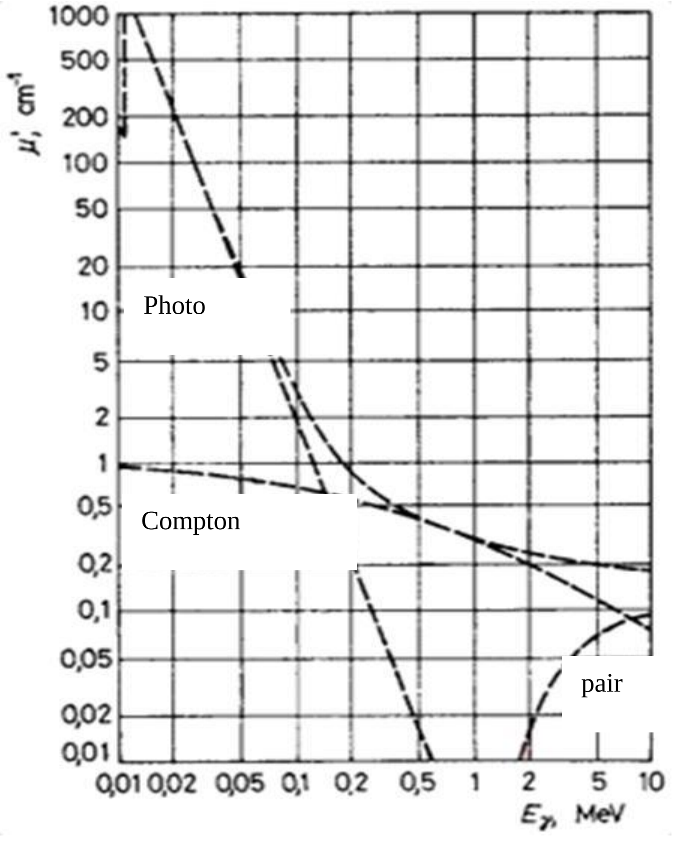
3. Pair production

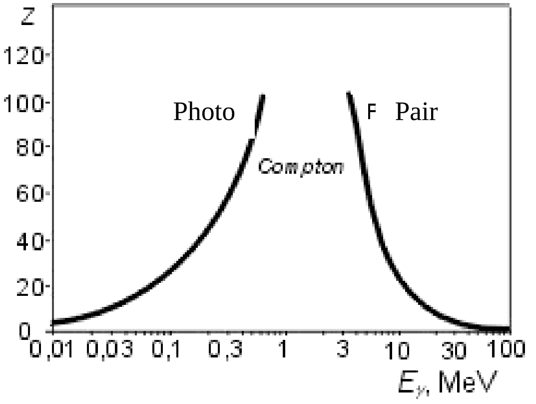


$$\sigma_p = K\left(E_\gamma - 1{,}02\right)^{2{,}2} Z^2$$

$$I = I_0 e^{-\mu d} = I_0 e^{-(\mu_C + \mu_f + \mu_p)d}$$

Germanium





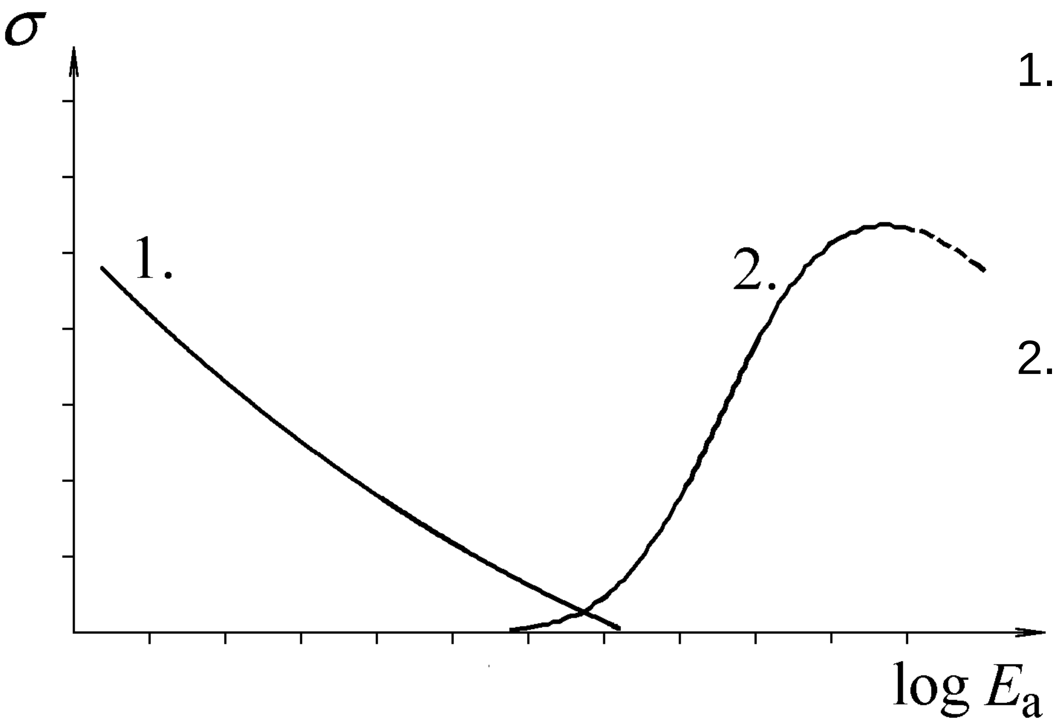
2. Nuclear reactions

Cross section (~probability)

Conventional equation

$^{10}B + \alpha \rightarrow$		$\rightarrow {}^{10}B + \alpha$
	$^{14}N^*$	$\rightarrow {}^{13}C + p$
$^{12}C + d \rightarrow$		$\rightarrow {}^{13}N + n$

Transition state



1. (n,γ)
   (n,f) ^{233}U, ^{235}U, ^{239}Pu, ^{241}Pu
   ^{10}B(n,α)
   ^{6}Li(n,α)

2. (γ,n)
   (n,2n)
   (n,α)
   (p,)
   (d,)

Tunnel effect

Kinetics of the nuclear reactions

$$\frac{dN^*}{dt} = \sigma_a N\phi - \lambda N^*$$

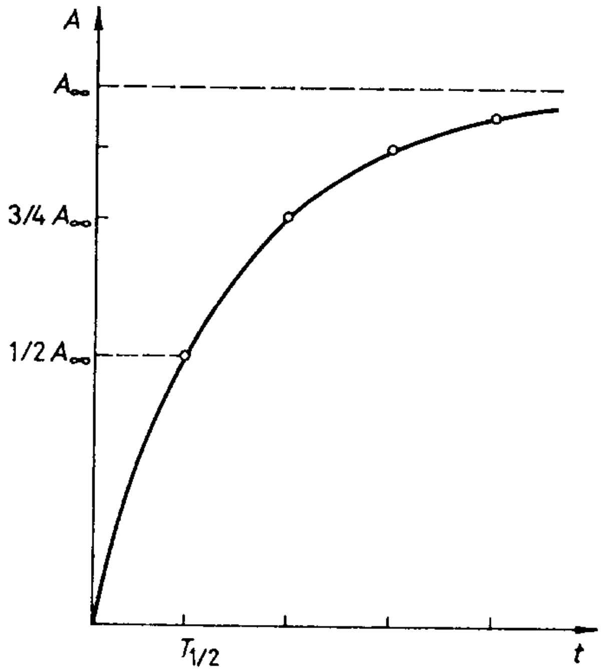
$$N^* = N^*_\infty\left[1-\exp(-\lambda t)\right]$$

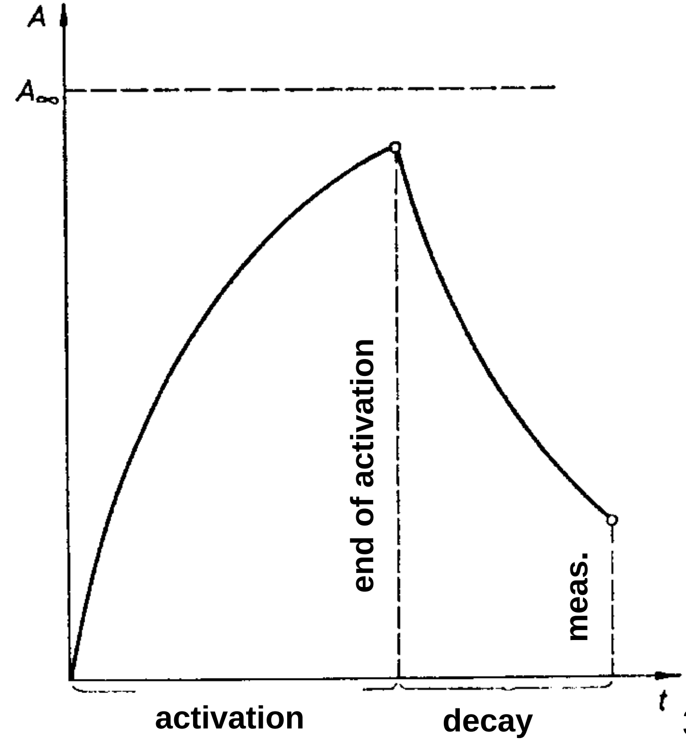
$$A = A_\infty\left[1-\exp(-\lambda t)\right]$$

$$A_\infty = \lambda N^*_\infty = \phi\sigma_a N$$

$$A' = \lambda N^* =$$

$$= A_\infty\left[1-\exp(-\lambda t)\right]\exp\left(-\lambda t_h\right)$$





We intend to obtain ^{65}Ni with neutron irradiation. Therefore, we expose 1 g of Ni (with a ^{64}Ni content of 91 %) to neutrons with a flux $\Phi=10^{12}$ 1/cm^{2}s. Thre cross section σ of the

$$^{64}Ni(n,\gamma)^{65}Ni$$

reaction is $1.55\cdot10^{-28}$ m^2. The half-life of ^{65}Ni is 2.52 h.

i) How long should the irradtiation last if we want to reach 80 % of the saturation activity?

ii) Estimate the ratio of the $^{64}Ni/^{65}Ni$ isotopes in the sample after being „cooled" for the same period as the activation lasted.

Interaction of neutrons with the matter

relatively heavy, no charge, energy ?

- elastic scattering

Table R8. The energy absorption efficiency of light elements

$(E_0 = 2\ \text{MeV}, E = kT)$

Element	$\Delta\bar{E}$, keV	n
^1H	1000	18
^2D	888	24
^4He	640	41
Be	360	50
C	284	111
Al	137	240

- inelastic scattering

Excited nucleus, hν

- neutron capture

(absorption): (n,?)

Due to the strong *E* dependence,

1. Slow			
a) cold		$E <$	0.025 eV
b) ***thermal***	0.025 eV	$< E <$	0.44 eV
c) resonance	0.44 eV	$< E <$	1000 eV
2. Medium	1 keV	$< E <$	500 keV
3. Fast	0.5 MeV	$< E <$	10 MeV
4. High energy	10 MeV	$< E <$	50 MeV
5. Super fast	50 MeV	$< E$	

Examples of practical relevance

(n,γ) $^{113}Cd(n,\gamma)^{114}Cd$ $\sigma = 6{,}31 \cdot 10^{-24}$ m^2

$^{135}Xe(n,\gamma)^{136}Xe$ $\sigma = 2{,}7 \cdot 10^{-22}\,m^2$,

$^{149}Sm(n,\gamma)^{150}Sm$ $\sigma = 6{,}6 \cdot 10^{-24}\,m^2$,

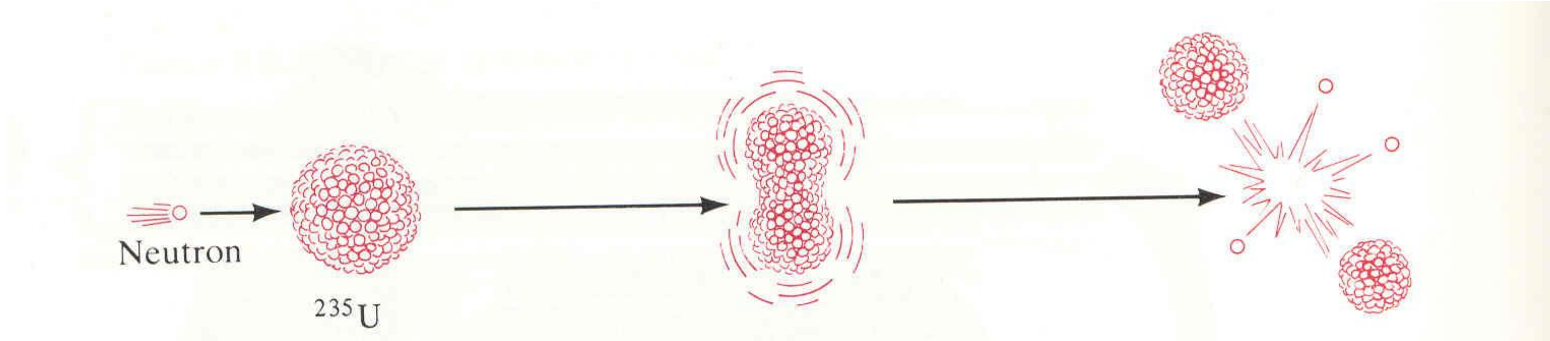
$^{157}Gd(n,\gamma)^{158}Gd$ $\sigma = 4{,}6 \cdot 10^{-23}\,m^2$,

(n,α) $^{10}B(n,\alpha)^{7}Li$ $\sigma = 3 \cdot 10^{-25}$ m^2

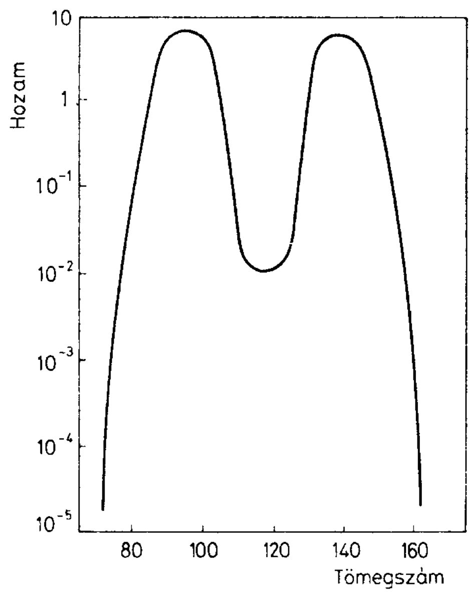
(n,f) fission

Fuel	Source of the fuel	Neutron energy needed
^{235}U	natural uranium	0.025 eV< $E_{neutron}$ < 0.44 eV (thermal)
^{233}U	from thorium with n absorption	0.025 eV< $E_{neutron}$ < 0.44 eV (thermal)
^{239}Pu	from ^{238}U with n absorption	0.025 eV< $E_{neutron}$ < 0.44 eV (thermal)
^{241}Pu	from ^{238}U with n absorption	0.025 eV< $E_{neutron}$ < 0.44 eV (thermal)
^{238}U	natural uranium	0.5 MeV< $E_{neutron}$ < 10 MeV (fast)
^{232}Pu	natural thorium	0.5 MeV< $E_{neutron}$ < 10 MeV (fast)

Fission (n,f)



$$^{235}U + n \xrightarrow{[^{236}U]} 3n + {}^{90}Kr + {}^{143}Ba \;\; +200 \text{ MeV}$$

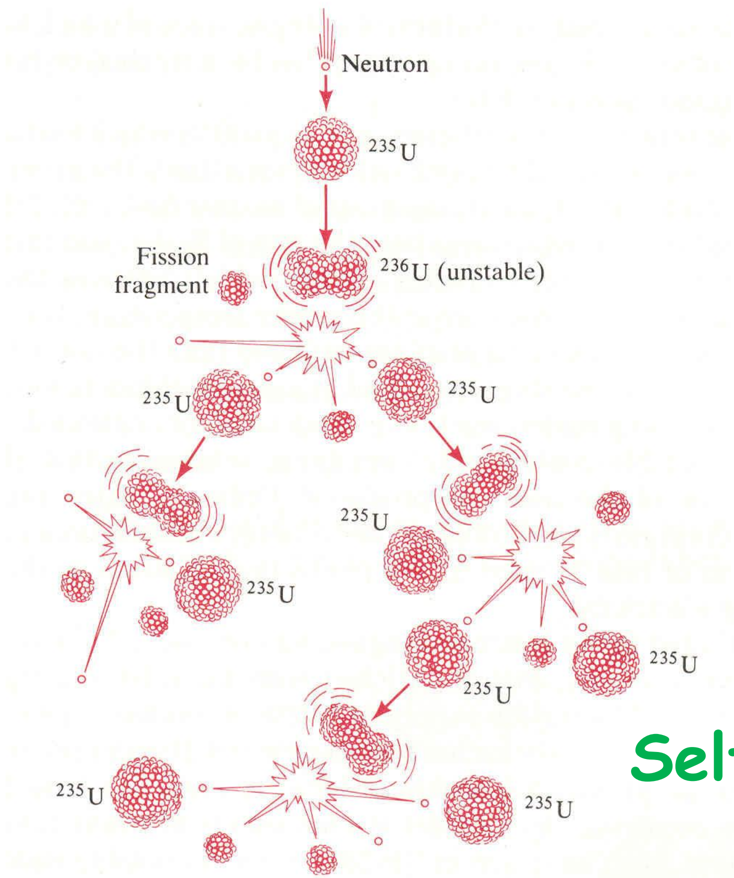


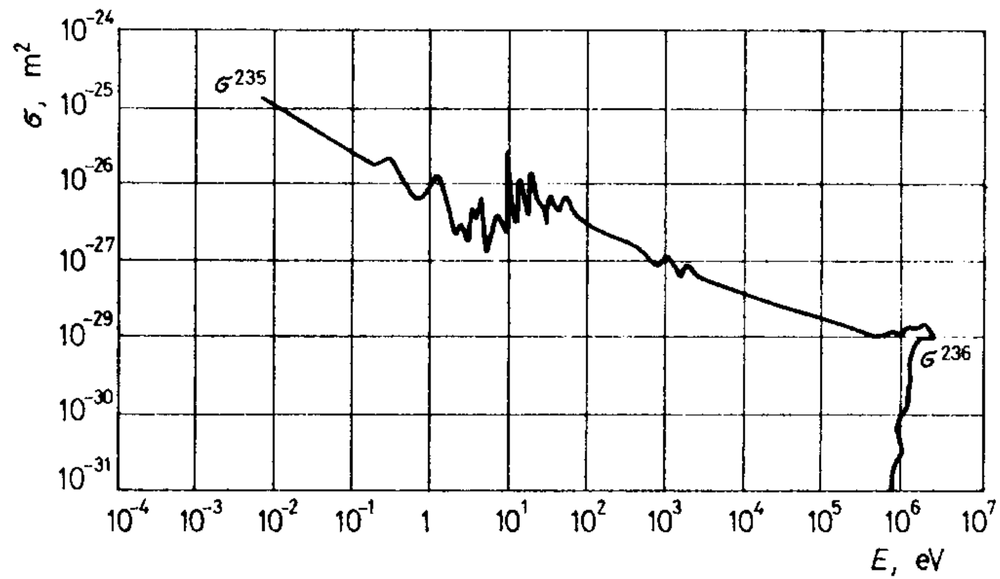
50 ways, 300 isotopes 35 elements

$$^{90}Kr \xrightarrow[33\text{ s}]{\beta^-} {}^{90}Rb \xrightarrow[2{,}7\text{ min}]{\beta^-} {}^{90}Sr \xrightarrow[28\text{a}]{\beta^-} {}^{90}Y \xrightarrow[64\text{h}]{\beta^-} {}^{90}Zr$$

Distribution 200 MeV

kinetic energy of fission products:	≈ 160 MeV
kinetic energy of the neutrons:	≈ 5 MeV
energy of the γ-rays:	≈ 5 MeV
energy of the secondary radioactive decay:	≈ 20 MeV
energy released at neutron capture:	≈ 10 MeV



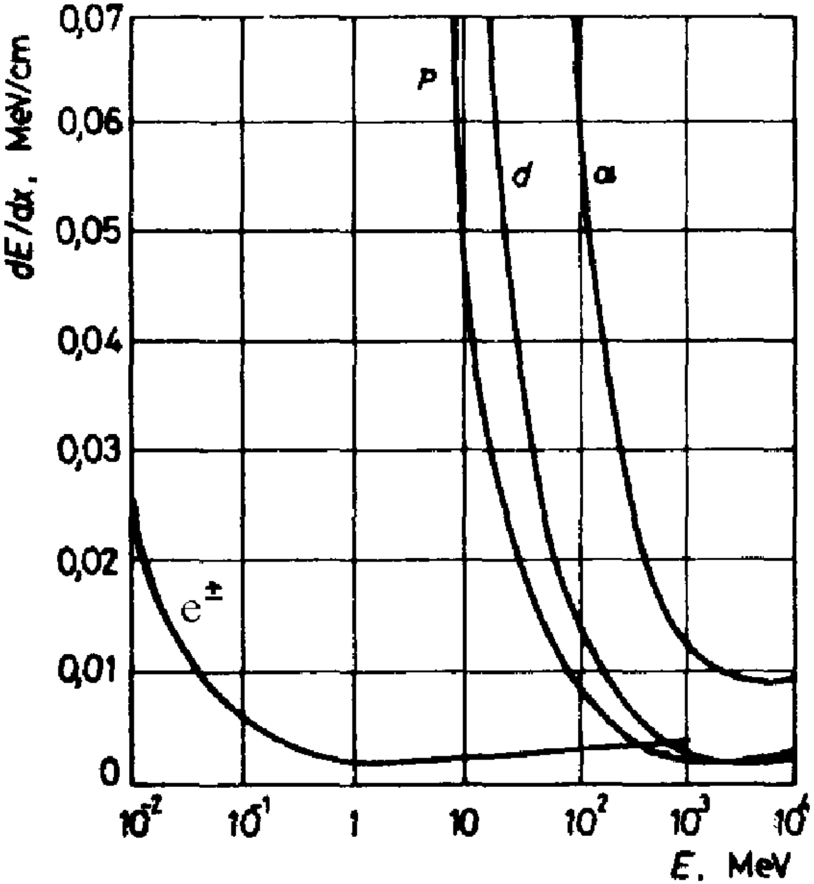


Self-sustaining chain reaction: control

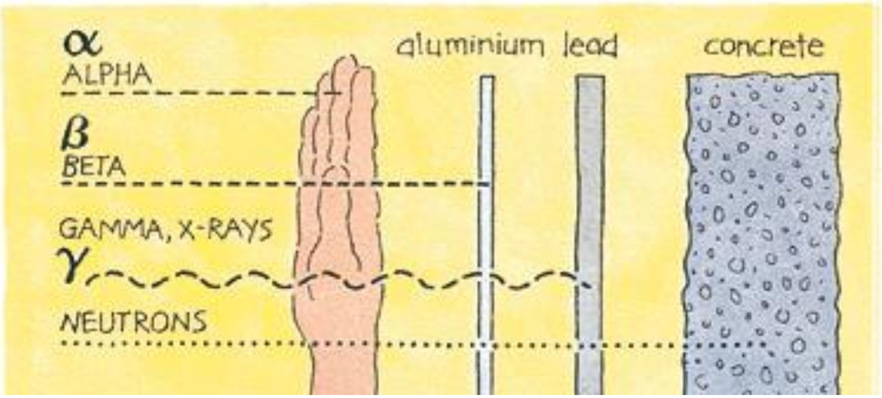
Detection of nuclear radiations

Interaction with matter: Linear energy transfer (LET)

air



Path



$$dE/dx \approx 1/v^2$$

The first step of the ionizing radiation in the matter:

1. Neutral excitation

   A + radiation → A^* + radiation'

2. External ionization

   A + radiation → A^+ + e^- + radiation'

   A_2 + radiation → A^+ + A^- + radiation'

   A_2 + radiation → A_2^+ + e^- + radiation'

   A_2 + radiation → 2 $A\cdot$ + radiation'

3. Internal ionization

   A + radiation → A^{*+} + e^- + radiation'

   A^{*+} → A^+ + X_{char}

   A^{*+} → A^{2+} + e^-_{Auger}

4. Bremsstrahlung (breaking radiation)

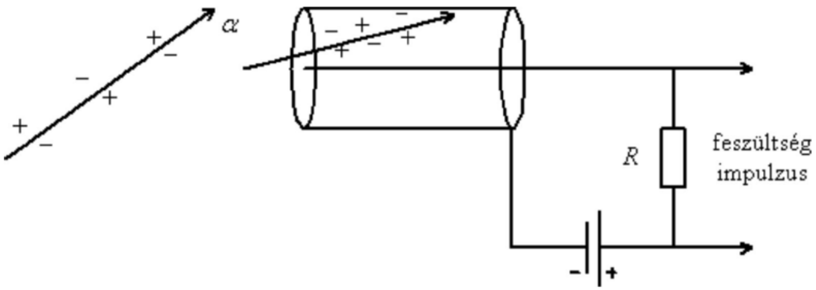
   A + radiation $^{\pm}$ → A + X_b + radiation $^{\pm}$'

FUNDAMETALS OF DETECTION

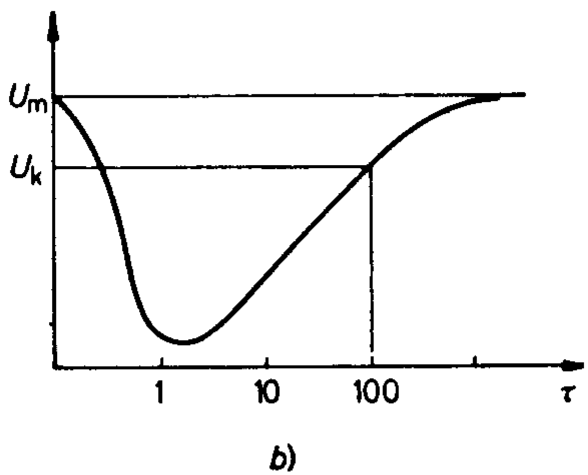
What do we want to know?

- yes/no
- type of radiation
- energy of radiation
- source
- activity ($I = k \eta A$)
- integral
  - real time evaluation
  - delayed evaluation
- rate

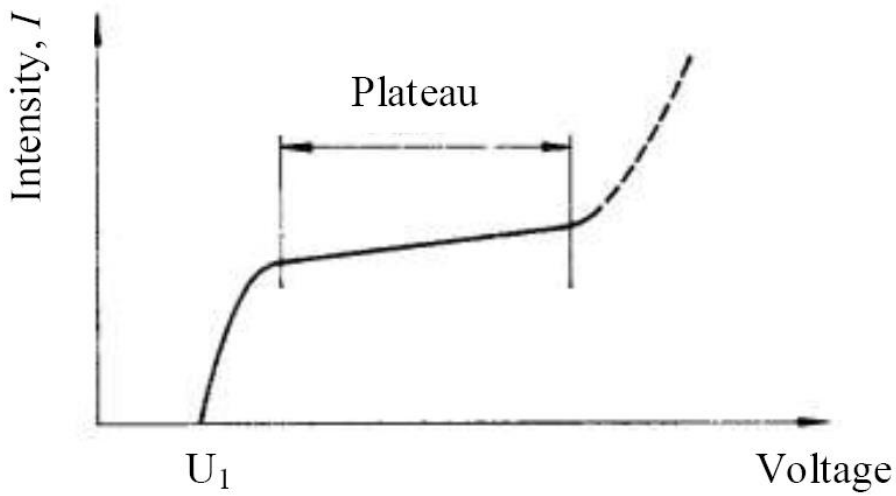
Geiger-Müller (GM) counter (gas ionisation detector)



Dead time



Characteristic curve



Semiconductor detectors

Typical semiconductors

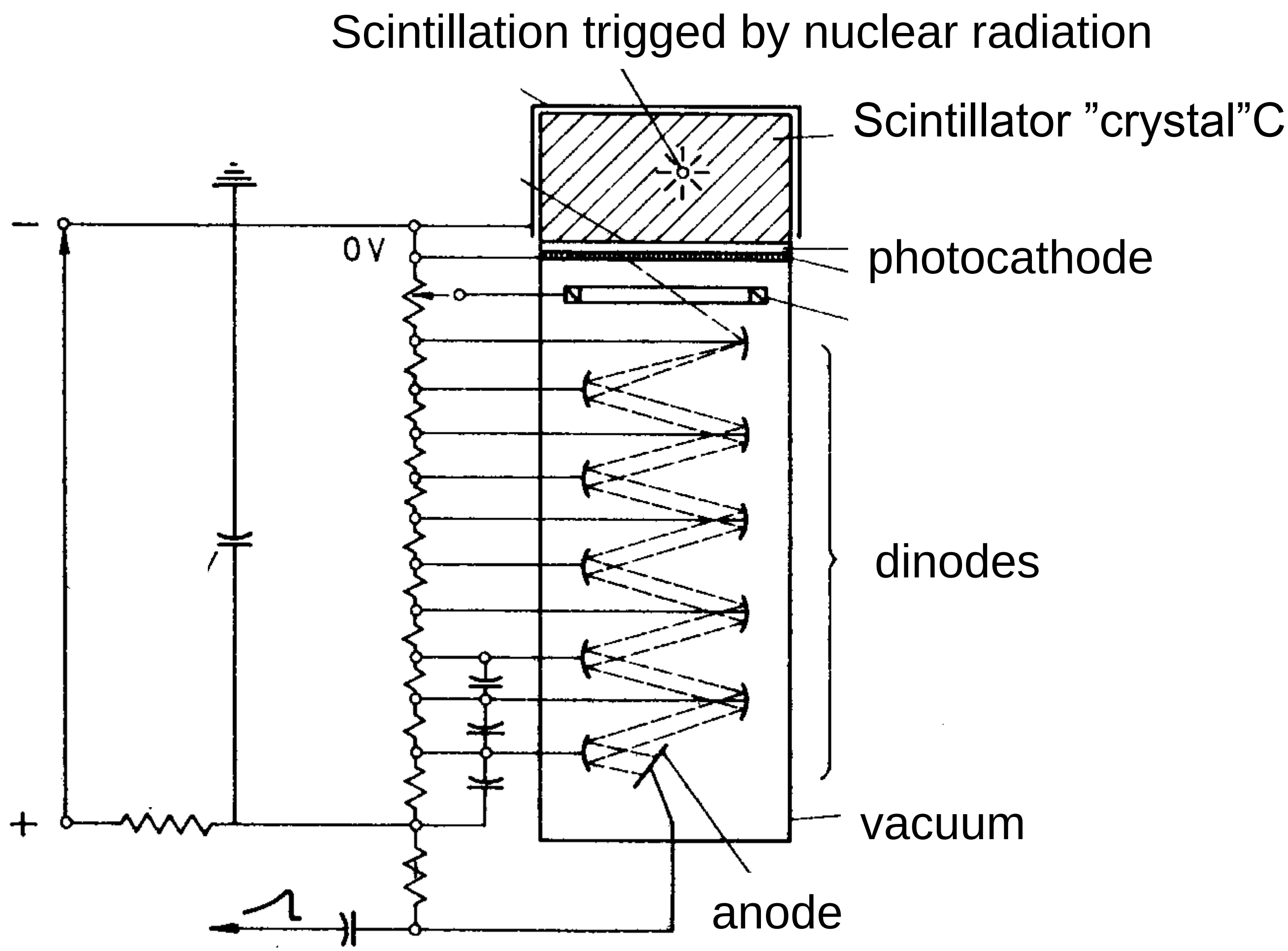
	Si	Ge	CdTe
Atomic number, *Z*	14	32	48 - 52
Energy gap, eV	1.12	0.74	1.47
Ionisation energy, eV	3.61	2.98	4.43

Ge(Li)

HPGe, Si(Li)

Scintillation detectors

Scintillator (material depends on the radiation) + photomultiplyer



Typical scintillation crystals

Depends on the type of radiation

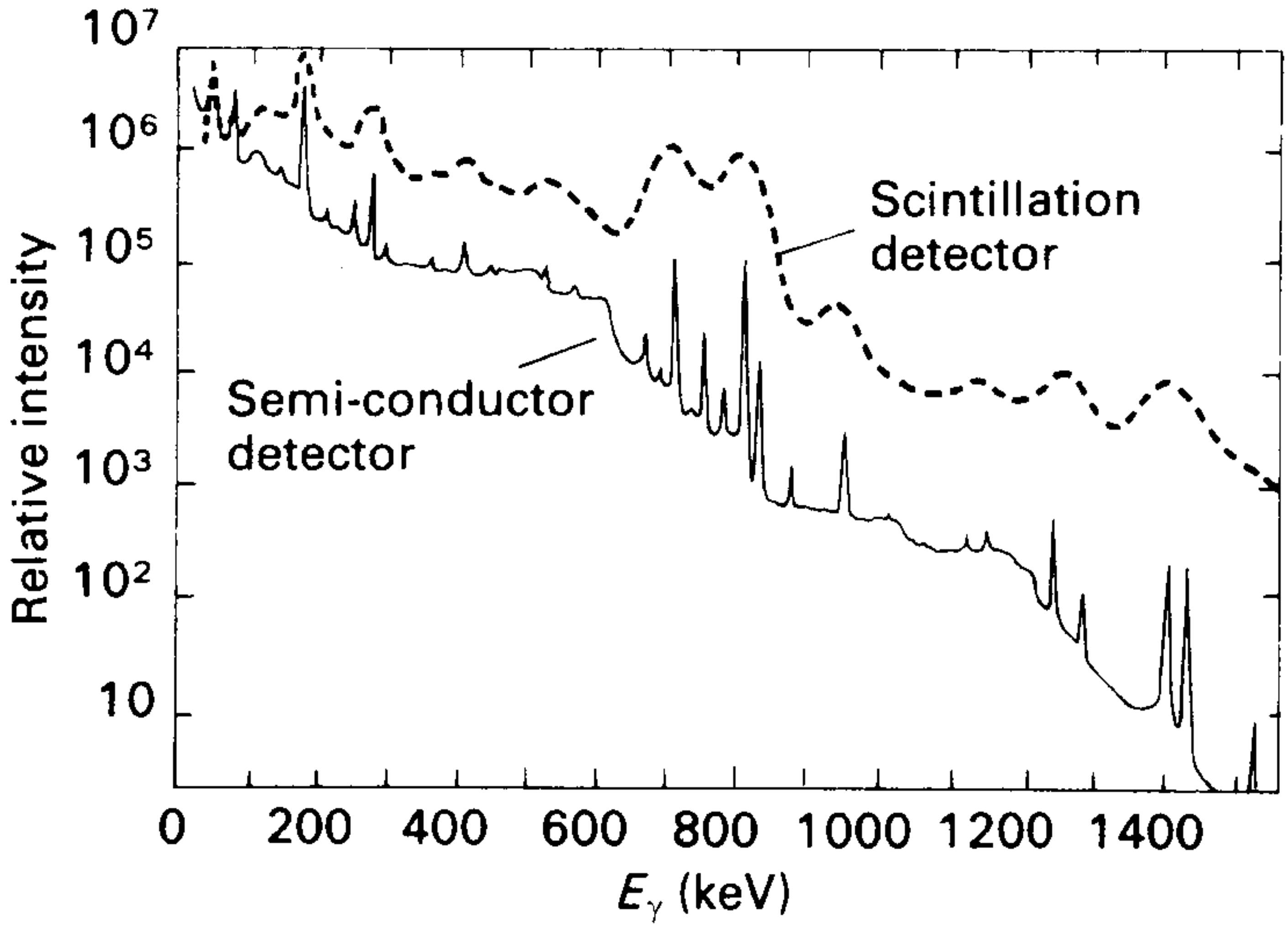
NaI(Tl)	gamma
Plastic	beta
ZnS	alpha

Liquid scintillation technique

for low *E* isotopes (^{3}H, ^{14}C)

scintillator and radioactive material dissolved in the same solution

Comparison of a scintillation and a semiconductor spectrum



Comparison of the features of the main detector types

Properties	GM counter	Scintillation detector	Semiconductor detector
Field of application	Primarily for particle radiation measurements	Measurements of any radioactive radiation types	Measurements of any radioactive radiation
Measurement efficiency	For particle radiation (α, β, n) near 100% for electromagnetic radiation 1 or 2%	Generally good	Generally good strongly temperature dependent at some types
Dead time	< 1 ms	<1 μs	<0.1 μs
Energy selectivity (qualitative identification of the radioactive source)	Non-selective	Selective	Very selective
Costs	Low	High, due to accessories	High
Other aspects	Limited but usually long life time	High counting rates	For drifted semiconductors, cooling required both for measurement an storage