Reactor Chemistry

Radio Chemistry

Instruments for detecting ionizing radiation

Gas filled detectors

Gamma-spectrometer

Liquid scintillator

Gas filled detectors

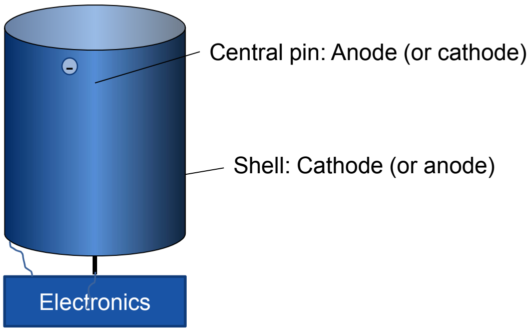
Principle for many of detectors
(GM counters for instance)

Radiation enters chamber

Ionizes gas in chamber

Ions travel towards
cathode/anode

=> Currency detected
by electronics



Central pin: Anode (or cathode)

Shell: Cathode (or anode)

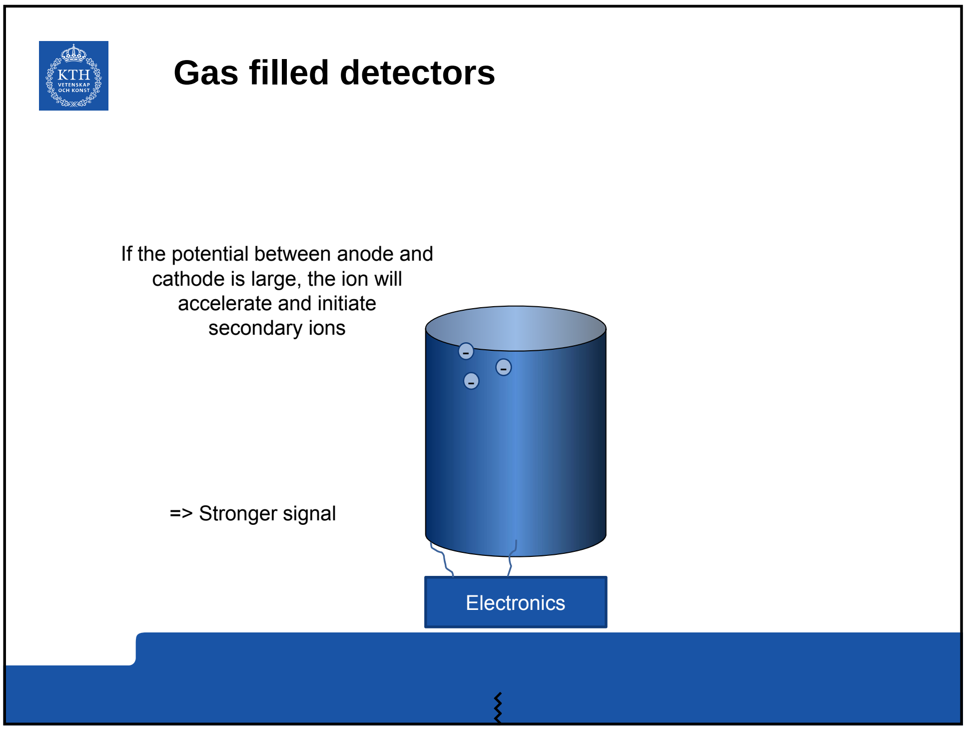
Gas filled detectors

Energy of α–particle is about 4 MeV

100 000 ionizations

The charge = $10^5 \times 1.602 \times 10^{-19}$ C ~ 10^{-14} A

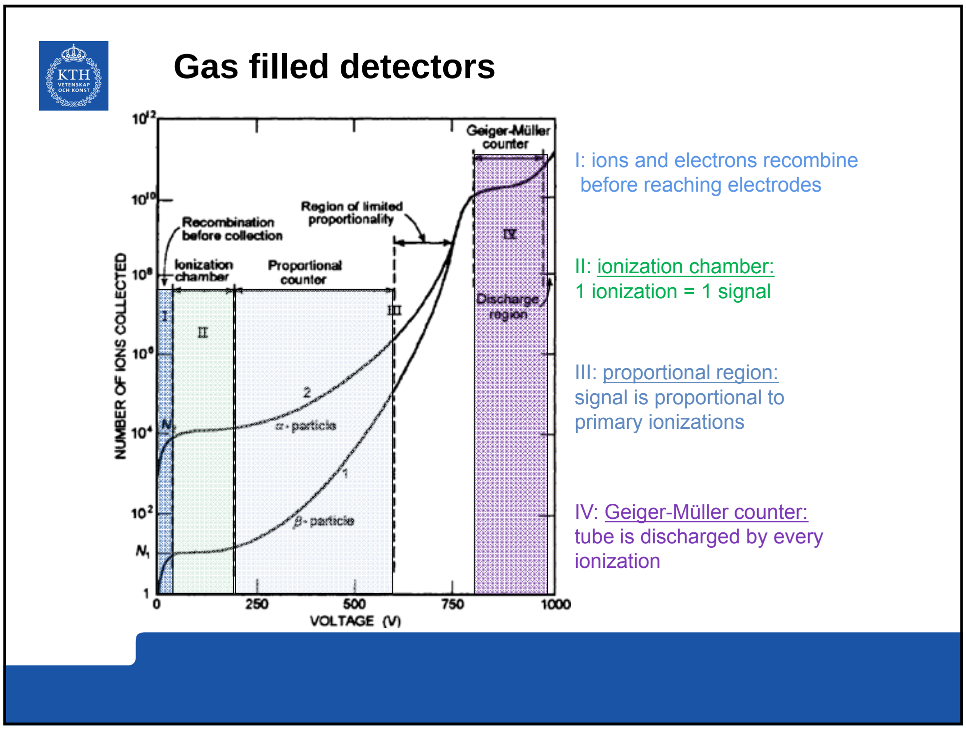
- The signal needs to be amplified greatly



Gas filled detectors

If the potential between anode and cathode is large, the ion will accelerate and initiate secondary ions

=> Stronger signal



Gas filled detectors

I: ions and electrons recombine before reaching electrodes

II: ionization chamber:
1 ionization = 1 signal

III: proportional region:
signal is proportional to primary ionizations

IV: Geiger-Müller counter:
tube is discharged by every ionization

γ-radiation

Gamma radiation has much longer range (lower LET) and will travel through air-filled detector with very few interactions.

Use denser material in detector:
Semiconductor

- When ionizing radiation interacts with the semiconductor an electron is excited to the conducting band.
  The electron then travels towards the anode.
- Gamma spectrometer (or Multichannel analyzer)

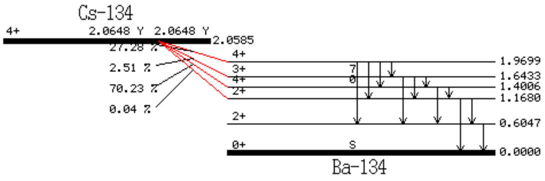
γ-counter

Almost every radioactive decay has quantified γ

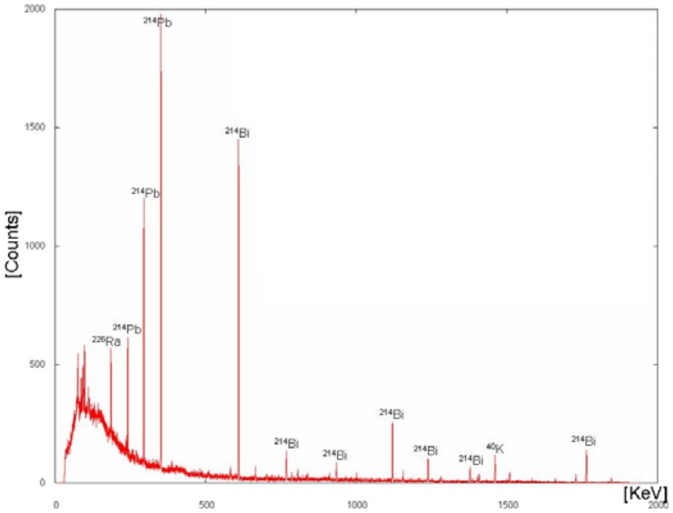
Cs-134 → Ba-134 + β^-

γ-Energy [keV]	Intensity [%]
232.6	0.0011
242.738	0.0272
326.589	0.0162
475.365	1.486
563.246	8.35
569.331	15.38
604.721	97.62
795.864	85.53
801.953	8.69
1038.610	0.988
1167.968	1.789
1365.185	3.014

Two distinct peaks

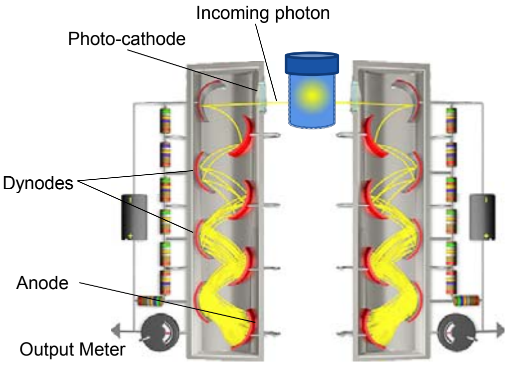


Example γ-spectrum (mineral sample)



Liquid scintillation

α/β^- radiation is absorbed by scintillation liquid
The energy is given back as light



Radio-chemical methods

Using radioactive tracers

Determine reaction mechanisms

Radiometric titration

Isotope dilution

Activation analysis

Why are radionuclides used?

- The exact same element is used, it has the same chemical and physical properties
- Radionuclides are independent of pressure, temperature, chemical and physical state
- Radionuclides are easy to detect and are measured with high precision

With radionuclides low amounts can be detected

$$A = N\lambda \quad \Longleftrightarrow \quad n = \frac{A}{N_A}\frac{t_{1/2}}{\ln 2}$$

Assume that 1 Bq can be measured with sufficient accuracy:

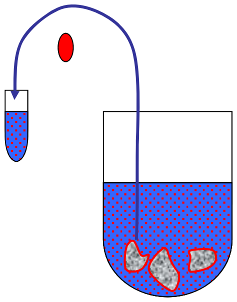
$t_{1/2}$	Number of atoms	mol
1 h	5 200	8.64×10^{-21}
1 d	125 000	2.08×10^{-19}
1 y	4.55×10^{7}	7.55×10^{-17}
10^{5} y	4.55×10^{12}	7.55×10^{-12}
10^{9} y	4.55×10^{16}	7.55×10^{-8}

Why are radionuclides used?

- The exact same element is used, it has the same chemical and physical properties
- Radionuclides are independent of pressure, temperature, chemical and physical state
- Radionuclides are easy to detect and are measured with high precision
- Does not affect the system (if activity is not too high)
- No interference of other elements
- Cheap (compared with for instance ICP-MS)

Example

Determination of Sr-distribution between granite and solution



Water

Add granite

Add tracer (Sr-90)

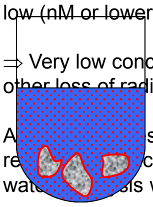
Wait for equilibrium

Take sample from solution

Sr-90 is a β^--emitter with
β_{max} at 550 keV
$t_{½}$ = 28.5 y

Example continued

Determination of distribution of cation between granite and solution



To be able to detect the radionuclide,
a reasonable concentration of radionuclide would be very low (nM or lower, depending on $t_{½}$)

⇒ Very low concentrations: any sorption to glass wall or other loss of radionuclide would have large impact

A [illegible] s more radionuclide to obtain a re [illegible] centration would cause significant wat [illegible] sis which would change the system

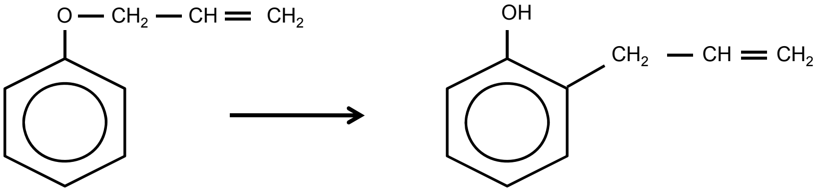
Example continued
Carrier

We need to add a carrier to our radioactive solution to ensure normal chemical behaviour and obtain reasonable concentrations.

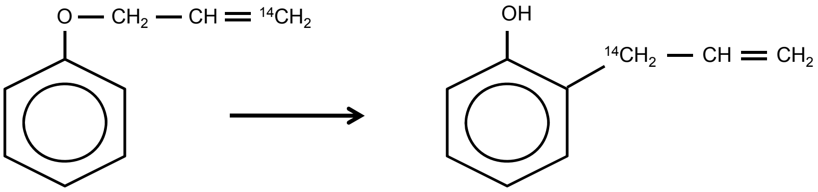
Working with radionuclides
Selecting radionuclide

- Has sufficient $t_{½}$ for the process to be studied to take place
- Same oxidation state as carrier (isotopic exchange)
- When very low activities are used the background has to be carefully attended
- Examine the nature of any radioactive daughters

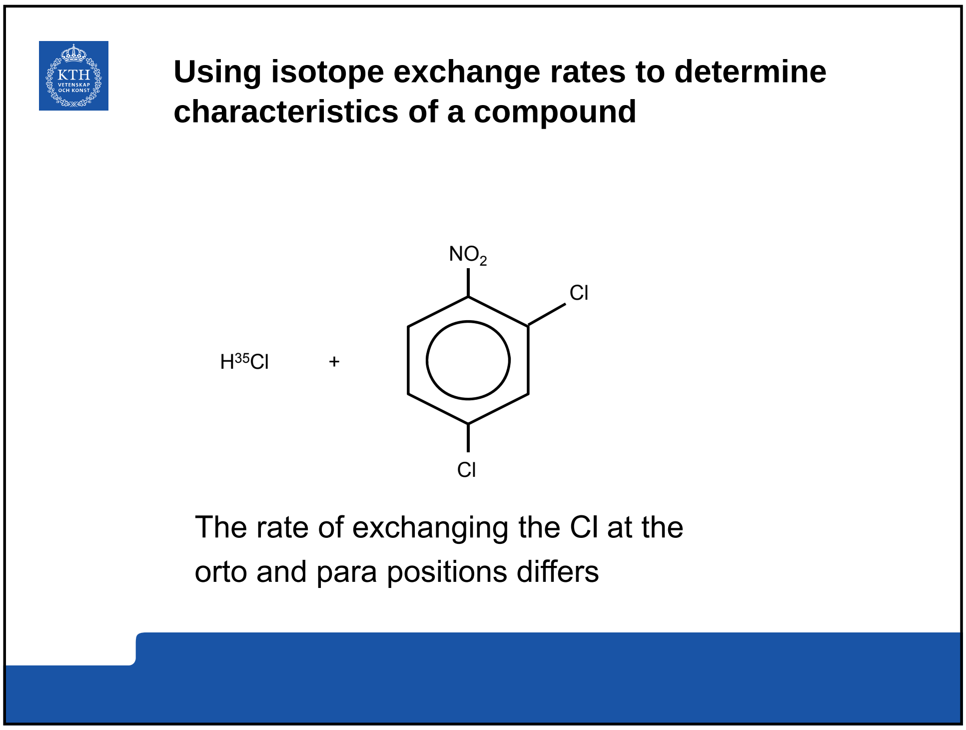
Determine reaction mechanisms
-For instance, the Claisen allyl rearrangement



Determine reaction mechanisms
-For instance, the Claisen allyl rearrangement



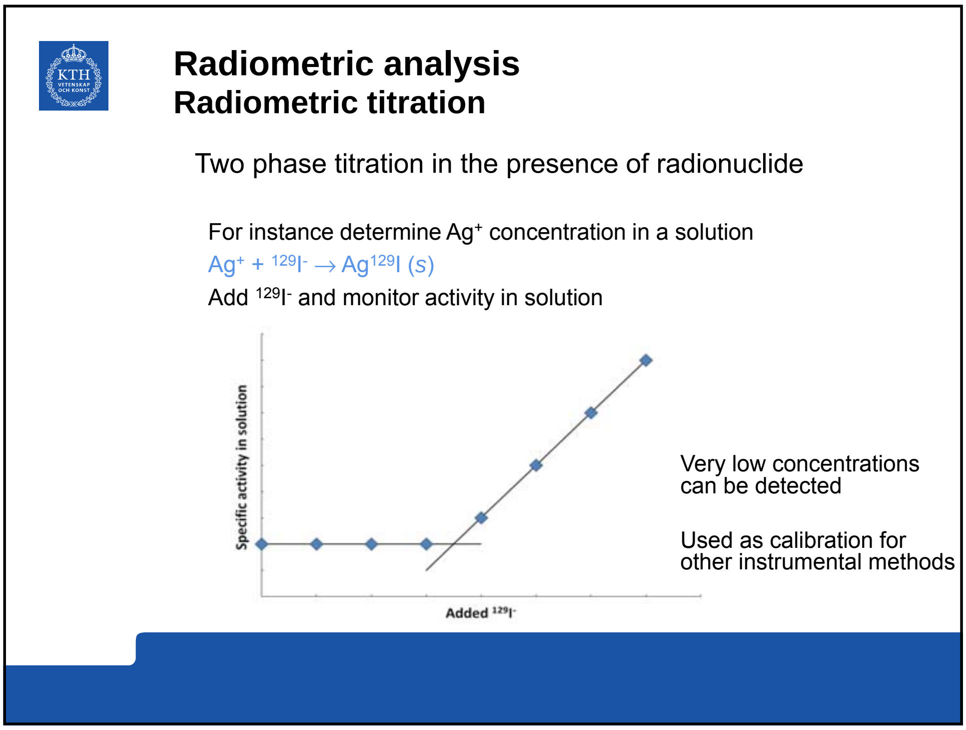
From decomposition products the mechanism can be determined



Using isotope exchange rates to determine characteristics of a compound

$H^{35}Cl$ +

The rate of exchanging the Cl at the orto and para positions differs



Radiometric analysis
Radiometric titration

Two phase titration in the presence of radionuclide

For instance determine Ag$^+$ concentration in a solution

$Ag^+ + {}^{129}I^- \rightarrow Ag^{129}I\ (s)$

Add $^{129}I^-$ and monitor activity in solution

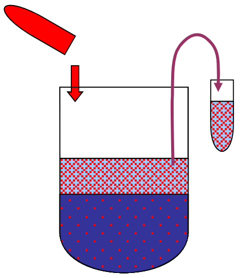
Very low concentrations can be detected

Used as calibration for other instrumental methods

Isotope dilution

Used when quantitative separation of one compound is not possible

Qualitative separation is needed, though



Take sample and measure

[illegible]

activity and mass

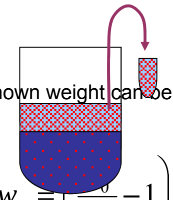
for [illegible] extraction

(Specific activity, S_m)

Isotope dilution

The specific activity is the same in the whole system.

$$S_m = S_{system} = \frac{\text{Total activity}}{\text{Total weight}} = \frac{w_0 S_0}{w_u + w_0}$$



And the unknown weight can be calculated from

$$w_u = \left(\frac{S_0}{S_m} - 1 \right) w_0$$

Take sample and measure
activity and mass
(Specific activity, S_m)

Isotope dilution

Applications

Determine

- The naphtalene concentration in tar
- Fatty acids in mixtures of natural fat
- Amino acids in biological material

Activation Analysis

By irradiating a sample with neutrons, a small amount of the atoms in the sample will take up a neutron and become radioactive.

The sample has been ”activated”

Advantages with NAA

- Highly sensitive
- Nondestructive
- Determination of elements in complex samples;

  - Environmental samples
  - Mineral samples
  - Archeological samples

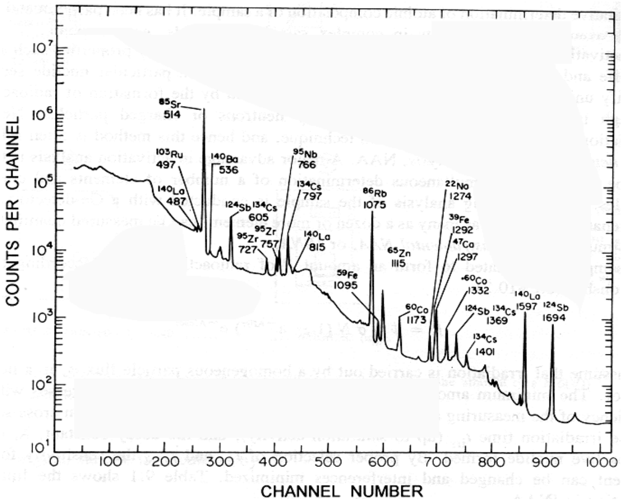
Example

Environmental history of waters in Sweden

1. Mussels were collected from rivers and lakes in Sweden.
   Mussels build shell thicker each year;
   The composition of the shell reflects the water chemistry.
2. Shells were sliced.
3. Sent to neutron irradiation source.
4. Sample was measured directly at arrival from reactor
   (short lived nuclides dominate spectrum).
5. Sample was measured 2 weeks after irradiation
   (short lived nuclides not present anymore).
6. Evaluation of the spectra.

Example

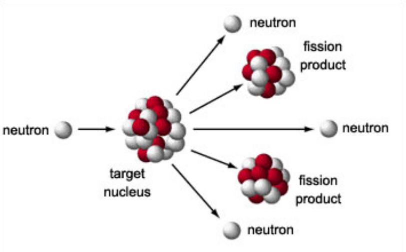
Environmental history of waters in Sweden



Reactor Chemistry

Reactor Concepts

Fission



Exotherm process for all nuclides with more than 130 nucleons (A>130)

Activation energy for A=130 is very high; 100 MeV
For A > 230 the activation energy is <10 MeV

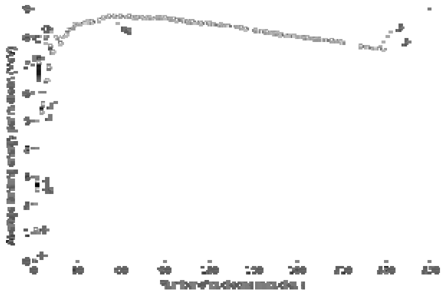
Fission with thermal (slow) neutrons is only possible for
(even, odd) or (odd, odd) nuclei with Z>90

Binding energy per nucleon

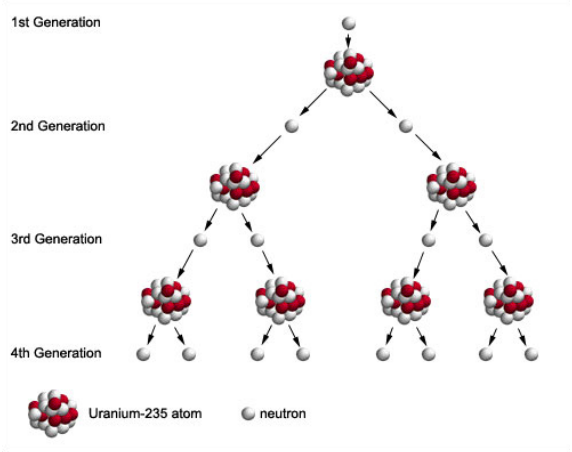
Average binding energy per nucleon (BE/A)

Fission exothermic for A > 60

Fusion exothermic for A < 60



Nuclear chain reaction



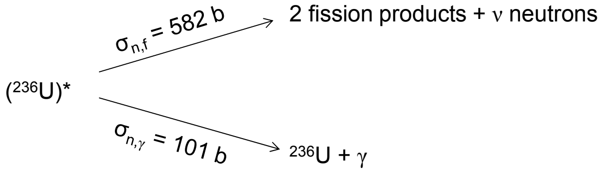
$^{235}U + n \rightarrow$ fission products $+ 2.4\ n + 210$ MeV

Fission of ^{235}U with thermal neutrons

Thermal neutron is captured and forms an excited compound nuclueus

$^{235}U + n \rightarrow (^{236}U)^*$

Excitation energy = captured neutron’s binding energy (6.8 MeV).
Compound nucleus must emit energy. Either as γ or as fission.
Probability for these can be expressed as cross sections $\sigma_{n,\gamma}$ and $\sigma_{n,f}$



$\sigma_{n,f} = 582\ b$ → 2 fission products + ν neutrons

$(^{236}U)^*$

$\sigma_{n,\gamma} = 101\ b$ → $^{236}U + \gamma$

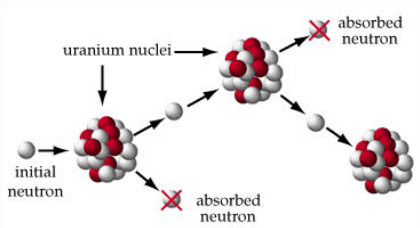
=> 85% of captured neutrons will cause fission

Energy balance

Binding energy/nucleon for heavy nuclei:	7.6 MeV
Binding energy/nucleon for semi-heavy nuclei (A=80-150):	8.5 MeV
Difference:	0.9 MeV
For U-235: 235×0.9 MeV =	**210 MeV**
Kinetic energy of fission products:	175 MeV
Kinetic energy of neutrons:	5 MeV
Kinetic energy of γ:	7 MeV
β from fission products:	7 MeV
γ from fission products	6 MeV
Neutrinos (energy is lost):	10 MeV

Fast and thermal neutrons

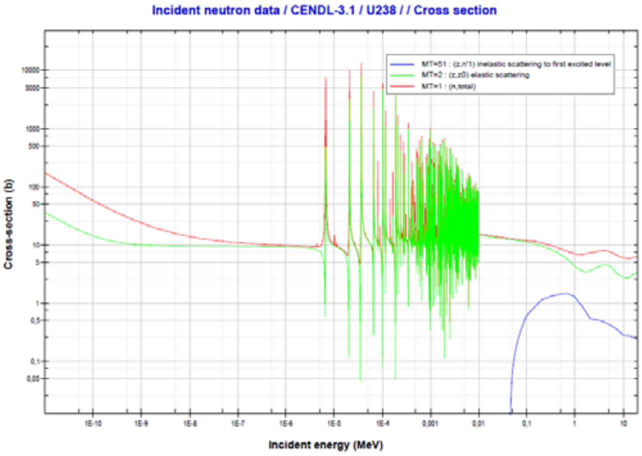
The initial kinetic energy is 5 MeV = **fast** neutron



The kinetic energy will decrease from repeatedly scattering processes

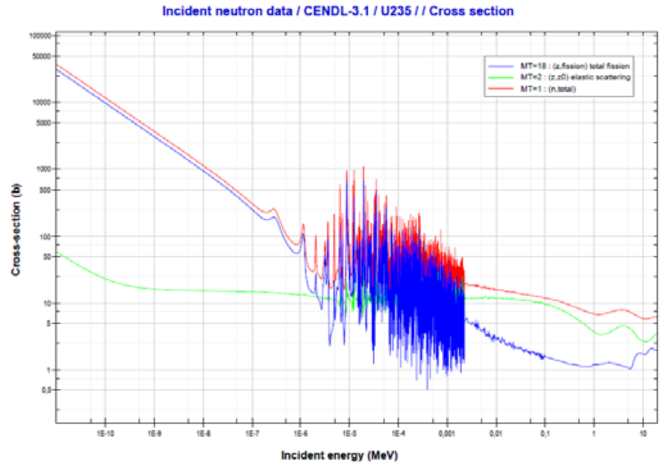
When the energy gain on the average equals the energy loss during a scattering the neutron is called **thermal** (typically 0.0255 eV)

Cross section ^{238}U



Fission only feasible for neutrons with kinetic energy > 0.5 MeV

Cross section ^{235}U



Fission feasible for neutrons thoughout the energy spectra

Cross sections and number of released neutron

Nuclide	Radiative capture	Fission	n	n_fission
^{232}Th	5.13			
^{233}U	46	529	2.49	2.29
^{235}U	99.3	587	2.42	2.07
^{238}U	2.73			
^{239}Pu	271	749	2.87	2.11
^{240}Pu	289.5	0.064		
^{241}Pu	363	1015	2.92	2.15

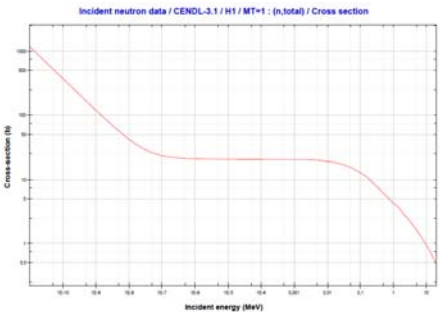
Moderation

Slowing of neutron by various materials

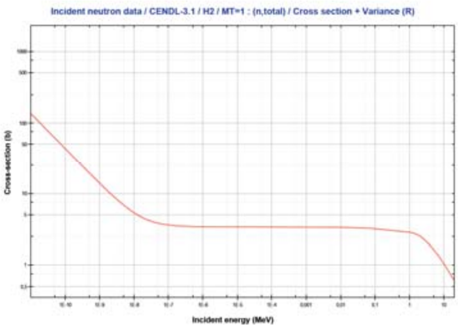
- n denotes the number of elastic scatters to slow down neutron from 2 MeV to 0.025 eV
- L the thermal diffusion length

Material	A	n	L (cm)
H	1	18.2	
H_2O	1 & 16	19.8	2.85
D	2	25.1	
D_2O	2 & 16	35.7	170
He	4	42.8	
Be	9	88.1	21
C	12	115	59
^{238}U	238	2172	

Cross sections for ^1H and ^2H



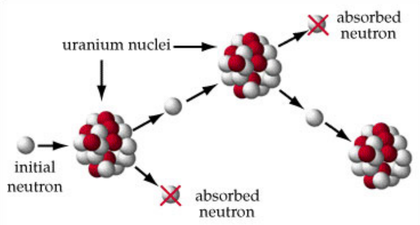
^1H



^2H

Heavy water corresponds to a longer diffusion length

Effective neutron multiplication factor, k



- If the number of produced neutrons, k > 1
  Supercritical => Atomic explosion
- If k< 1 Subcritical=> Chain reaction will die out
- In a nuclear reactor k is controlled to be 1 (critical) with control rods (containing neutron-absorbent)

Void coefficient

A measure how the reactivity of a reactor changes as voids (typically steam bubbles) form in moderator or coolant

A positive void coefficient means that the effect increases as voids are formed. For instance if the coolant acts as neutron absorber all coolant may quickly boil (Chernobyl)

In reactors designed with a negative void coefficient, the reactivity will decrease as voids are formed

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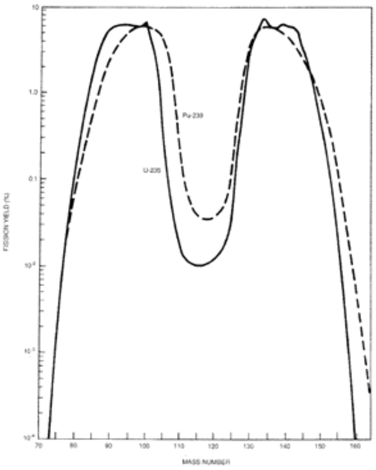
Fission products

Typical distribution between fission fragments for thermal neutron fission of ^{235}U and ^{239}Pu.

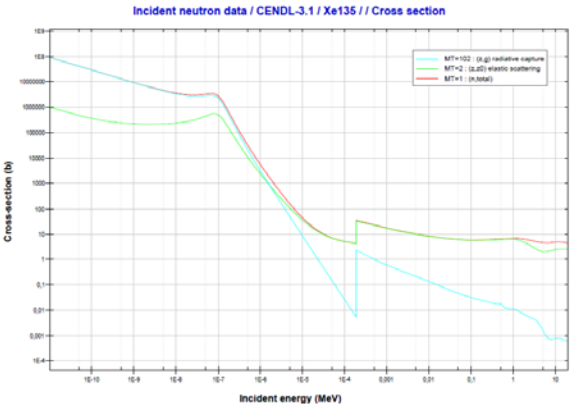
More likely to get fission fragments with mass numbers 90 and 140. The asymmetry becomes less pronounced for increasing bombarding energy

Most fission products are relatively short lived, while some are extremely long lived, i.e. ^{99}Tc ($t_{½}$=211 000y) and ^{129}I ($t_{½}$=15 700 000y)

Even fission products are subjected to neutron irradiation. Some have extreme σ_n, such as ^{135}Xe and ^{149}Sm.



Cross section (can´t get enough)



Note: cross sections in the order of 1E7 b !!! (^{235}U < 1000 b)
When the amount of reactor poison are too high, the chain reaction cannot continue and the fuel must be replaced

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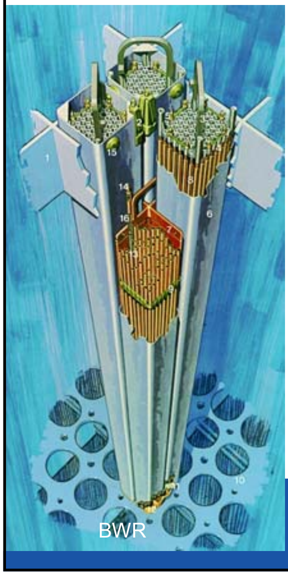
Main components in Nuclear Reactors

- **The fuel**: Natural U
  Enriched U (>3% ^{235}U)
  Breeder fuel (^{232}Th or ^{238}U)
- **Moderator**: H_2O
  D_2O
  graphite
- **Coolant**: H_2O
  D_2O
  He
  CO_2
  Na or Pb
  Molten salt

Fuel assemblies



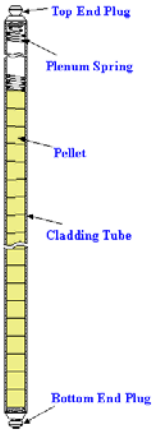
Data	Boiling Water Reactor BWR	Pressurized Water Reactor PWR
Length	4.4 m	4.2 m
Width	0.14 m	0.21 m
Weight	c:a 300 kg	c:a 660 kg
Weight UO_2	c:a 200 kg	c:a 520 kg
Fuel rods	63	204/264
No. fuel assemblies	700	157
Total amount of U in core	120 000 kg	82 000 kg

Fuel rod in LWR

Cladding material: Zircalloy (Zirkonium):
- Hard
- Ductile
- Corrosion resistance
- Low neutron absorption cross section

But above 1000 °C:
$Zr + 2H_2O \rightarrow ZrO_2 + 2 H_2$
(ΔH = 586.6 KJ/mole Zr)
which severily accelerates the melting of the core.

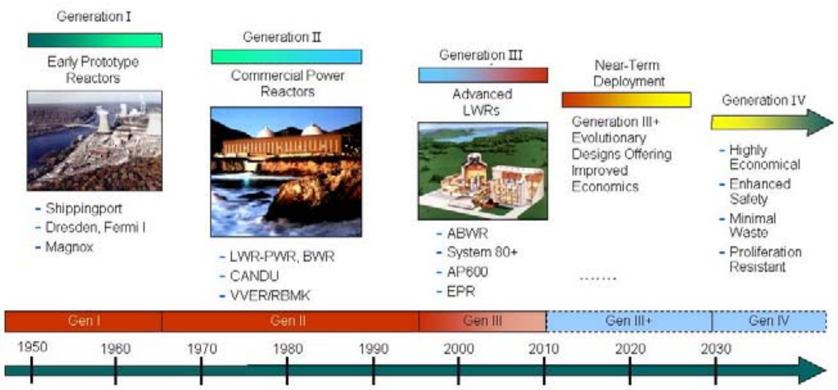
Keep in mind:
- a melted core is (in general) not critical (no moderator)
- but has residual heat and will generate even more heat due to oxiditation of Zr, B_4C, SS, etc..



Classification of Nuclear Reactors

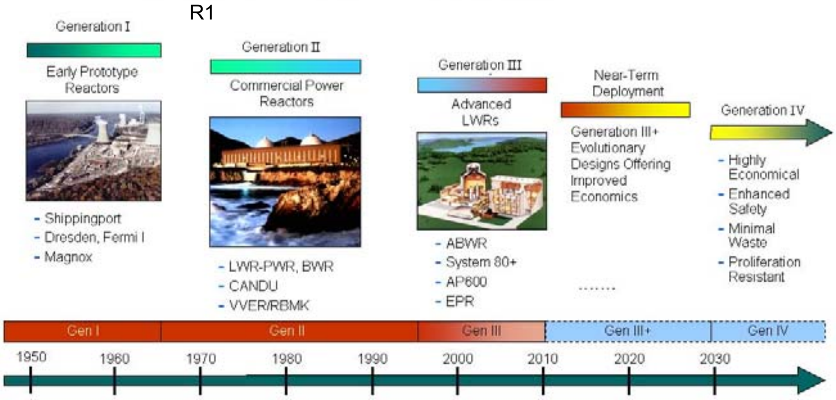
Classification by neutron energy:	Fast reactors Thermal reactors Epithermal reactors
Classification by configuration:	Homogeneous reactors Heterogeneous reactors
Classification by generation:	Gen I Gen II (current reactors) Gen III (improvements of Gen II) Gen IV
Classification by use:	Research Electricity production Heat production Propulsion Transmutation Neutron source Safety functions …

Reactor generations



Reactor generations

O1, O2, O3
F1-2, F3
R1



Homo- & Heterogeneous Reactors

Homogeneous reactors:
Main parts are one unit, i.e. 235U-salt dissolved in water or molten Li-Be.
Mostly used in research reactors

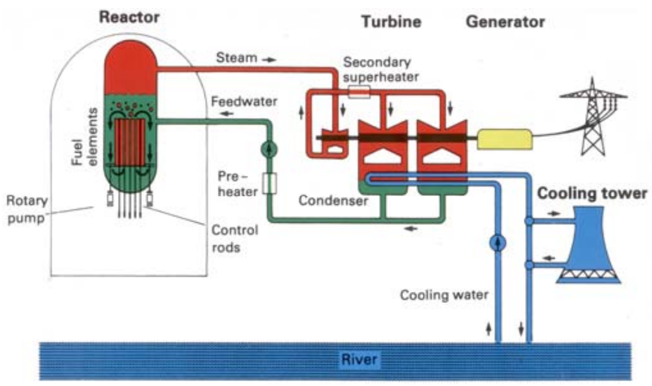
Heterogeneous reactors:
The main parts are divided. Moderator and coolant can be the same.
The fuel is encapsulated and distributed in a certain pattern in the moderator

Principle for a electricity production

- The nuclear chain reaction releases heat
- The heat boils water to steam
- The steam is directed to turbines and electricity is produced

90% of all reactors are BWR or PWR

Boiling Water Reactor (BWR)



Ringhals I
Oskarshamn I, II, III
Forsmark I, II III

BWR design

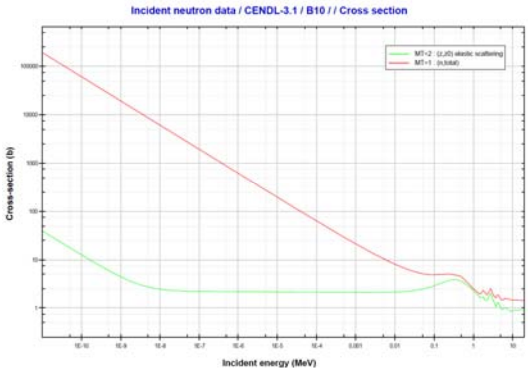
A BWR is designed to have a negative void coefficient

Sudden changes in pressure may cause less voids, leading to increased power.

Reactivity control: Short term – changing the flow of coolant through the core
Intermediate – Control rods (B_4C)
Long term – Compensate fuel burnup by GdO_2 mixed in fuel pellets

Boron injection used as a safety function

Why Boron?



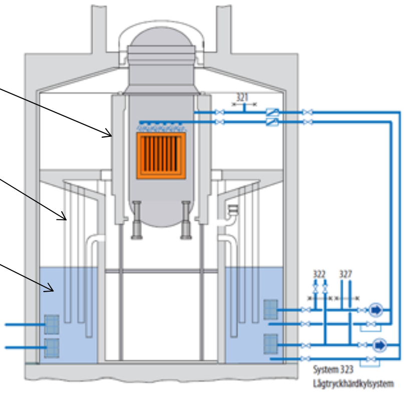
As always, large cross-section, but also highly solvable

BWR containment

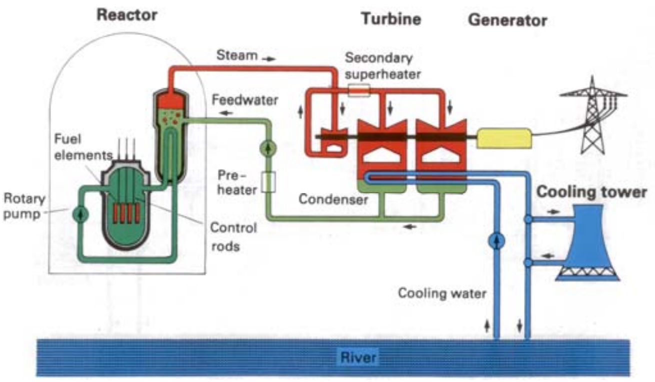
Biological shield

Blow down pipes

Condensation pool



Pressurized Water Reactor (PWR)



Ringhals II, III, IV

PWR design

PWRs operate with no voids. All water is moderator and coolant

Reactivity control: Short term – Control rods (B_4C or Ag-I-Cd)
Intermediate – Varying concentration of boric acid
Long term – Burnable poison in fuel fuel assemblies

A large negative void coefficient ensures that when voids are formed the power output will decrease

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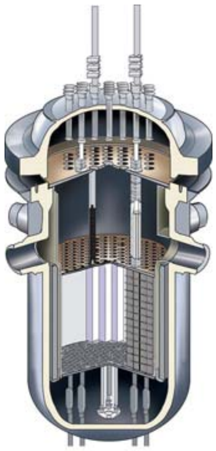
RPW (Reactor Pressure Vessel)

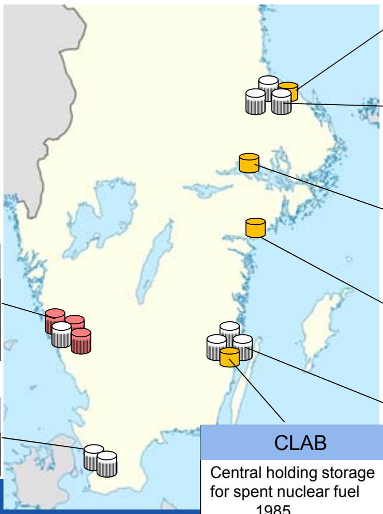
BWR

PWR



Swedish Nuclear Power System

- BWR (ASEA Atom)
- PWR (Westinghouse)
- Other



SFR

Low- and intermediate level waste repository
1988

Forsmark

FI	1006 MW	1980
FII	1006 MW	1981
FIII	1200 MW	1985

Västerås

Nuclear Fuel Factory
1971

Studsvik

Research reactor
1960 - 2005

Oskarshamn

OI	500 MW	1972
OII	630 MW	1975
OIII	1450 MW	1985

CLAB

Central holding storage for spent nuclear fuel
1985

Ringhals

RI	860 MW	1976
RII	917 MW	1975
RIII	1045 MW	1981
RIV	960 MW	1983

Barsebäck

BI	615 MW	1976-1999
BII	615 MW	1977-2005

Gen IV: Pros & cons

+ Nuclear waste that lasts for decades instead of millennia

+ 100-300 times more energy yield from same amount of fuel

+ Possibility to consume existing waste for energy production

+ Improved safety

- Operators have little experience

- Advanced technology more difficult to handle

Reactor safety

Absolutely safe: Does not exist

Inherent safe: Melt down not possible due to nature laws

Structurally safe: Dense containment, filters hinder any release at melt down

Structurally unsafe: Lack dense containment, and any release limiting arrangements

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RBMK: (Chernobyl type)

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Inherent unsafe: Reactivity increase when coolant disappears