Nuclear Fuel Cycle 2013

Lecture 2: Basic Nuclear Chemistry, Part 1

Home page of the course: KTH Social

https://www.kth.se/social/course/KD2430/

What is Nuclear Chemistry?

- Chemistry related to nuclear technology
- Chemistry of radionuclides
- Studies of chemical processes by using radionuclides as tracers: Radiochemistry
- Radiation induced chemical reactions: Radiation Chemistry

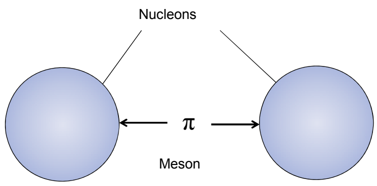
The Nucleus

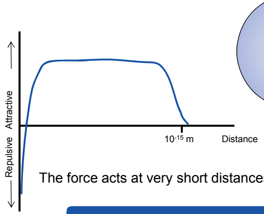
- Building blocks: Protons and neutrons
- Forces: Electromagnetic forces and the Strong Nuclear Force

Property	Proton	Neutron
Mass	1.673×10^{-24} g	1.675×10^{-24} g
Charge	+1	0
Spin	s = ½	s = ½

The (Strong) Nuclear Force

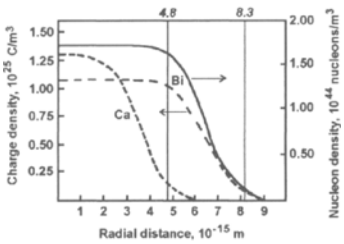
Exchange of mesons keep the nucleons together





The force acts at very short distances

Nuclear density and radius



Measured charge and nuclear density for ^{40}Ca and ^{209}Bi as a function of nuclear radius

Density: 0.2 nucleons/fm^3 => 10^{14} g/cm^3!

The Nucleus

$^{A}_{Z}R$ $\quad Z+N = A$

Z = Number of protons
N = Number of neutrons
A = Mass number (number of nucleons)

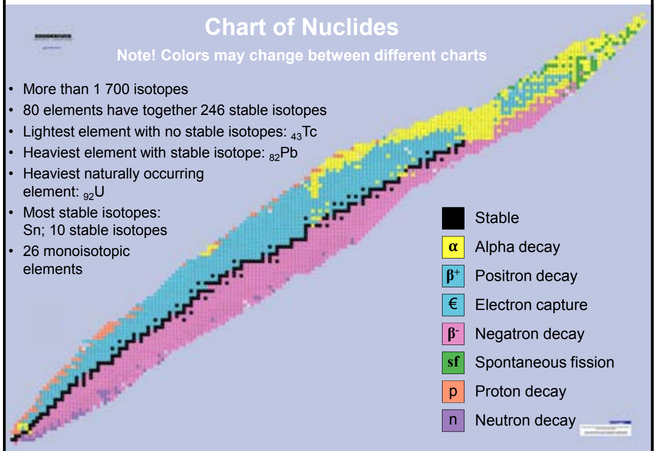
Nuclide	Specific nuclear species	Examples
Isotopes	Identical Z	$^{234}_{92}U$ $\quad ^{235}_{92}U$ $\quad ^{238}_{92}U$
Isotones	Identical N	$^{36}_{16}S$ $\quad ^{37}_{17}Cl$ $\quad ^{38}_{18}Ar$ $\quad ^{39}_{19}K$ $\quad ^{40}_{20}Ca$
Isobars	Identical A	$^{96}_{38}Sr$ $\quad ^{96}_{39}Y$ $\quad ^{96}_{40}Zr$
Isomers	Identical Z and A	$^{99m}_{43}Tc$ $\quad ^{99}_{43}Tc$

$$^{99m}_{43}Tc \xrightarrow{t_{1/2}=6.01h} {}^{99}_{43}Tc + \gamma$$

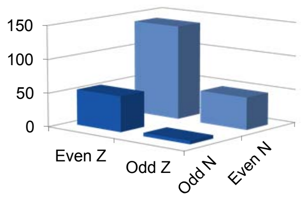
Chart of Nuclides

Note! Colors may change between different charts

- More than 1 700 isotopes
- 80 elements have together 246 stable isotopes
- Lightest element with no stable isotopes: $_{43}Tc$
- Heaviest element with stable isotope: $_{82}Pb$
- Heaviest naturally occurring element: $_{92}U$
- Most stable isotopes: Sn; 10 stable isotopes
- 26 monoisotopic elements



Number of Nucleons on the Stability of the Nuclei

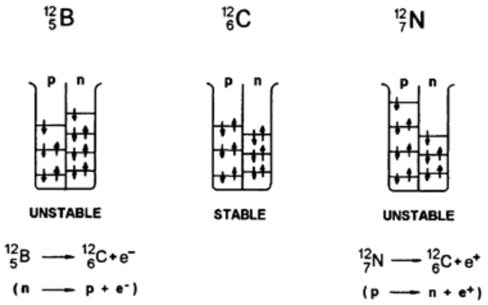


Magic numbers of protons or neutrons: 2, 8, 20, 50, 82 and 126

$^{135}_{54}Xe \quad (\sigma_n = 2.6\times10^6 \text{ barns}) \quad N=81$

$^{136}_{54}Xe \quad (\sigma_n = 0.28 \text{ barns}) \quad N=82$

Nuclear Stability: Nucleon Orbitals



Mass Defect (ΔM) and Mass Excess (δ_A)

$\Delta M_A = M_A - Z\,M_p - N\,M_n$
M_A = Mass of atom
M_H = Mass of Proton (hydrogen)
M_n = Mass of Neutron

Deuterium,
$M_p + M_n$ = 1.007 825 + 1.008 665
$^{2}_{1}H$ = 2.016 490 u
M_A = 2.014 102 u
=> ΔM_A = -0.002 388 u

All stable isotopes have negative mass defect, ΔM_A

Mass excess: $\delta_A = M_A - A$
(sometimes used in tables, no practical use)

M = atomic mass unit, measured in u.

Binding energy

$\Delta E = \Delta mc^2$ ”Nuclear Heat of formation”

$\Delta m = M_A - (Z\,m_p + N\,m_n)$
$c = 3 \times 10^8$ m/s

Nucleus: 5-10 MeV / nucleon (5-10 × 10^{11} J/mol)

Covalent bond: 4.4 × 10^5 J/mol

Isotope effects

Due to the difference in nucleons there are very small differences between two isotope's

- Freezing point
- Boiling point
- Density
- Heat of vaporization
- Viscosity
- Surface tension
- Optical emission spectra

Isotope effects

Replacing ^{1}H with D (deuterium, ^{2}H) increases the mass 100%

Replacing ^{12}C with ^{13}C increases the mass 8%

- A reaction involving C-H bond is typically 6-10 times faster than that for a C-D bond
- A reaction involving ^{12}C-H bond is 1.04 times faster than that for a ^{13}C-H bond

Isotope separation

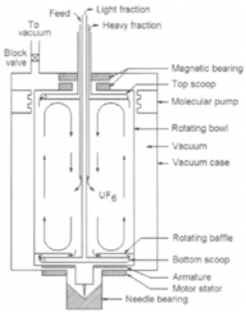
i. Equilibrium processes (light elements)
ii. Rate processes

Multi-stage processes (for instance distillation)
Chemical exchange
Electrolysis
Gaseous diffusion
Electromagnetic separation
Gas centrifugation

Gaseous diffusion

Lighter isotopes diffuse faster than heavy isotopes

$^{235}UF_6/^{238}UF_6$



Other methods of isotope separation

Distillation

Extraction

Ion-exchange

Photoionization

Photoexcitation

Radioactive decay

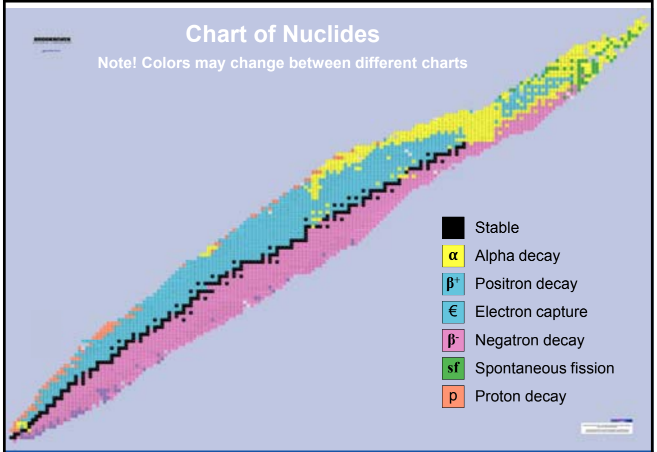
α-decay (He-nucleus)

β-decay (electron/positron)

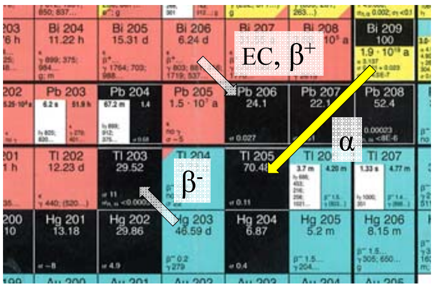
γ-decay

Unusual modes of decay (proton, neutron, heavy particles)

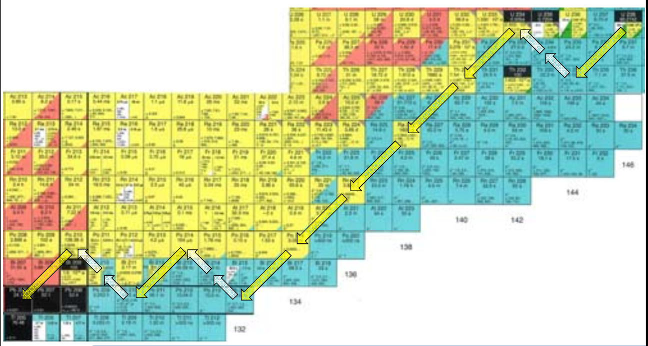
Spontaneous fission



Nuclide chart



Decay chain of ^{238}U



Decay chain of ^{238}U

$^{238}U \rightarrow {}^{234}Th + \alpha$

$^{234}Th \rightarrow {}^{234}Pa + \beta^-$

$^{234}Pa \rightarrow {}^{234}U + \beta^-$

$^{234}U \rightarrow {}^{230}Th + \alpha$

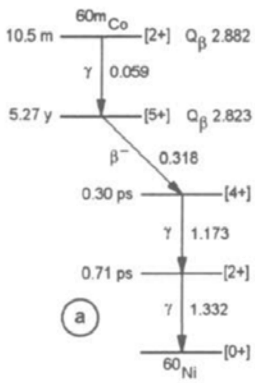
$^{230}Th \rightarrow {}^{226}Ra + \alpha$

…

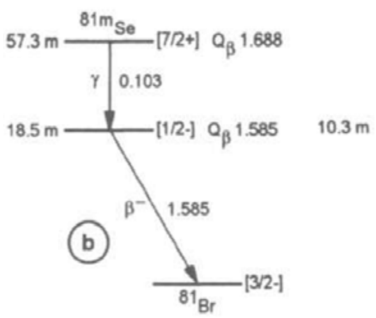
Or simplified

$^{238}U(\alpha)\,{}^{234}Th(\beta^-)\,{}^{234}Pa(\beta^-)\,{}^{234}U(\alpha)\,{}^{230}Th(\alpha)\,{}^{226}Ra$…

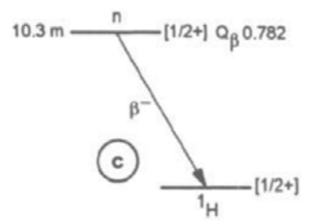
Decay of ^{60m}Co



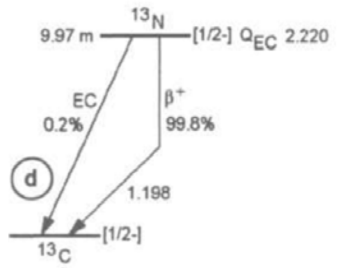
Decay of ^{81m}Se



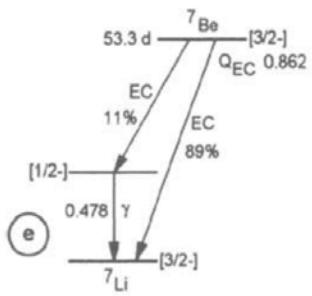
Devay of a neutron



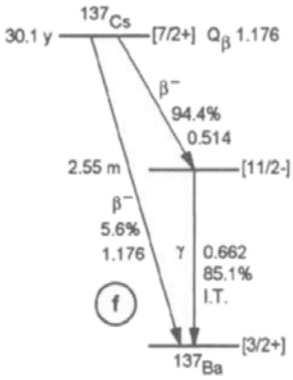
Decay of ^{13}N



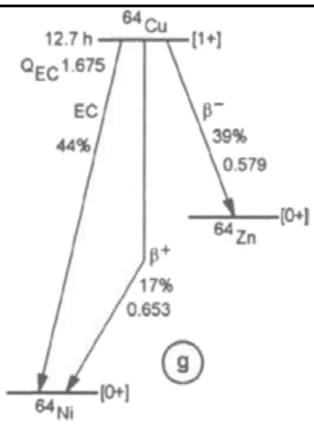
Decay of ^7Be



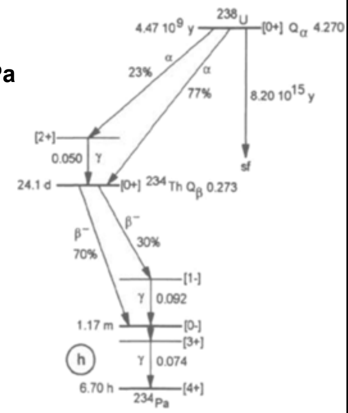
Decay of ^{137}Cs



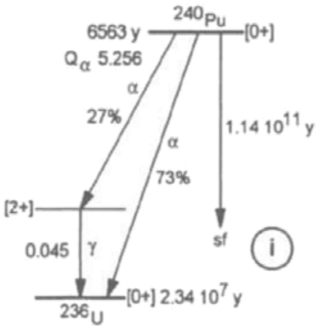
Decay of ^{64}Cu



$^{238}U \rightarrow {}^{234}Th \rightarrow {}^{234}Pa$



$^{240}Pu \rightarrow {}^{236}U$



Conservation laws

Nuclear Reaction: $X_1 + X_2 \rightarrow X_3 + X_4$

Energy (mass): $E_1 + E_2 = E_3 + E_4$

Linear momentum: p=mv
$p_1 + p_2 = p_3 + p_4$

Charge: $Z_1 + Z_2 = Z_3 + Z_4$

Mass number: $A_1 + A_2 = A_3 + A_4$

α-decay

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

$$^{238}U \rightarrow {}^{234}Th + {}^{4}He$$
$$^{238}U \rightarrow {}^{234}Th + \alpha$$

Decay energy (Q-value)

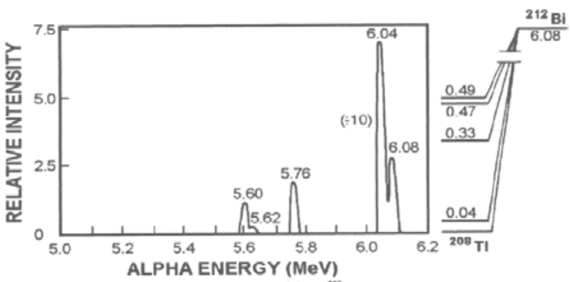
$E=mc^2$
1 u = 1/6.022×10^{23} = 1.66×10^{-24} g
c^2 = 8.99×10^{16} m^2/s^2
1 J = 6.24×10^{12} MeV
E = 1.66×10^{-24} * 8.99×10^{16} * 6.24×10^{12} = 931.5 MeV/u

Q(MeV) = -931.5 ΔM (u)

$Q_\alpha = -931.5\,(M_{Z-2} + M_{He} - M_Z)$
$Q_\alpha > 0$ if $(M_{Z-2} + M_{He} - M_Z) < 0$
$Q_\alpha > 0$ => Spontaneous decay

For α-particles the Q-value is 2–10 MeV

Alpha spectrum



β-decay: Two types of β-decay

$^{A}_{Z}X \rightarrow {}^{A}_{Z+1}Y + \beta^-$

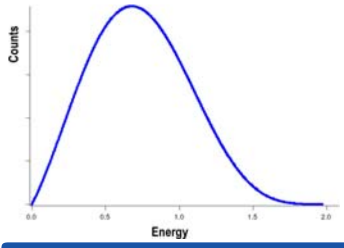
A negatron (electron) is emitted
A neutron in the nucleus is 'coverted' to a proton

$^{A}_{Z}X \rightarrow {}^{A}_{Z-1}Y + \beta^+$

A positron (anti-particle to the electron) is emitted.
A protron in the nucleus is 'converted' to a neutron

β-decay

$^{137}Cs \rightarrow {}^{137m}Ba + \beta^-$



Why not one peak?

(also the *nuclear spin quantum number* of the reaction is not an integer, which is a forbidden transition)

β-decay continued

⇒ Another particle is emitted: a neutrino (ν)

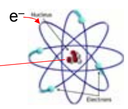
The neutrino has no charge and very small or no mass and does not interact readily with matter

$^{137}Cs \rightarrow {}^{137m}Ba + \beta^- + \bar{\nu}$

ν is an anti-neutrino, emitted in a β^--decay

$\bar{\nu}$ is a neutrino, emitted in a β^+-decay

Energy of β^- decay



$${}^{A}_{Z}X \rightarrow {}^{A}_{Z+1}Y + \beta^- + \bar{\nu}$$

The formed Y has Z orbit electrons and must capture one electron from the surroundings.

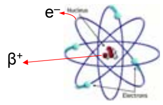
=> The mass of the β^--particle shall thus **not** to be included when calculating the energy of the decay.

$Q_{\beta^-} = -931.513\ (M_{Z+1} - M_Z)$

Example: n → H + β^-

$Q_{\beta^-} = -931.513(1.007825 - 1.008665) = 0{,}782$ MeV

Energy of β⁺ decay



$$ {}^{A}_{Z}X \rightarrow {}^{A}_{Z-1}Y^{-} + \beta^{+} + \nu \rightarrow {}^{A}_{Z-1}Y + e^{-} + \beta^{+} + \nu $$

The formed Y has now one extra orbit electron which it must loose.

=> Both emitting a β^{+}-particle and loosing an electron must be included when calculating the energy of the decay.

Q_{β^-} = -931.513 (M_{Z-1} + 2 M_e – M_Z)

Example: ${}^{13}_{7}N \rightarrow {}^{13}_{6}C + \beta^{+}$

Q_{β^-} = -931.513(13.003355– 13.005739) + 2* 0.511) = 1,2 MeV

Electron capture

$$ {}^{A}_{Z}X \xrightarrow{EC} {}^{A}_{Z-1}Y + \nu $$

An inner shell electron is captured by the nucleus.
Energy similar to β^{-} decay.

Q_{β^-} = -931.513 (M_{Z-1}– M_Z)

γ-emisson

Most α and β-decays do not go all the way to the daughter's ground state.
The remaining energy is released as γ-rays.

Isomeric transition

When the meta-stable state is more long-lived

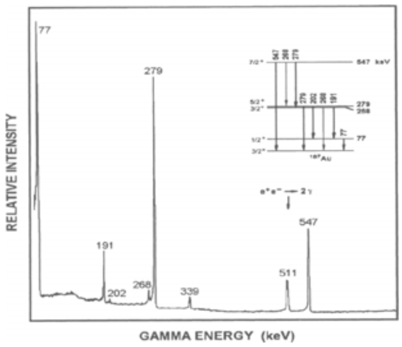
Spontaneous fission

Some heavy radionuclides are so unstable that they undergo spontaneous fission

Rare modes of decay

Proton emission
Neutron emission
Emission of heavy particles

Gamma spectrum



Rate of a radioactive decay

$$N \rightarrow \text{Daughter} + \text{particle}$$

First order rate reaction: $-\frac{dc}{dt} = kc$

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

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

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

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

Half-life

$$-\int_{N_0}^{N}\frac{1}{N}dN=\int_{0}^{t_{½}}\lambda dt \Rightarrow \ln N-\ln N_0=-\lambda t_{½}$$

$$N=\frac{N_0}{2}$$

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

Units

SI unit:
1 Becquerel (Bq) = 1 decay / s

Older unit:
1 Curie (Ci) = 3.7×10^{10} Bq

(1 Ci is approximately the actvity of 1 gram ^{226}Ra)