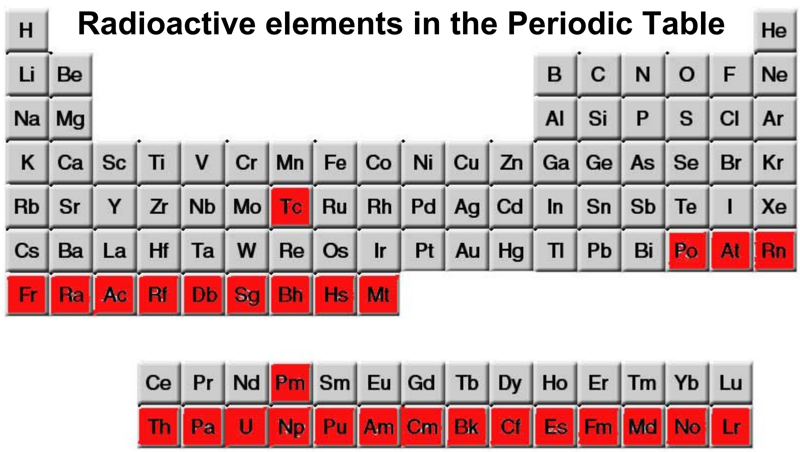
11) The Chemistry of Artificial and Radioelements (1)



11) The Chemistry of Artificial and Radioelements (2)

Technetium (atomic number 43)

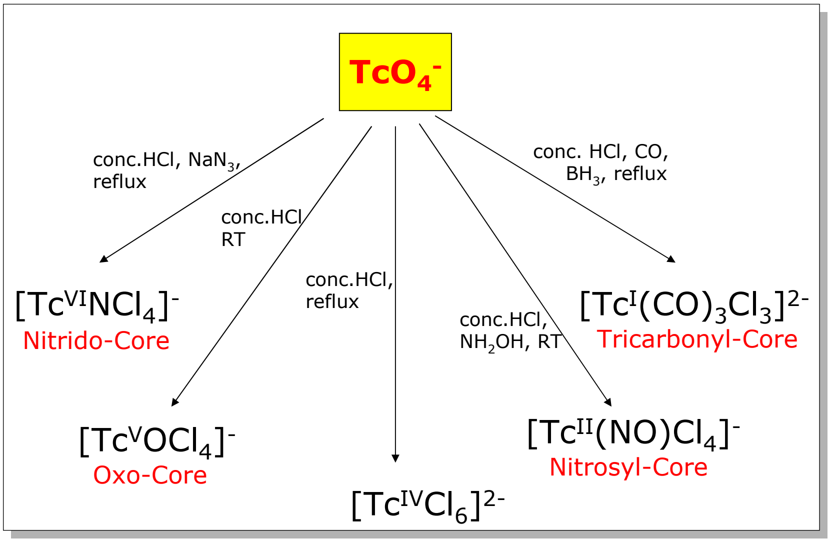
- first artificial element
- discovered in 1939 by deuteron bombardment of a molybdenum plate)
  ^{94}Mo (d,n) ^{95m}Tc, **^{95}Mo (d,n) ^{97m}Tc!!!!!!**
- named in 1947 according "technetos“ (Greek, „The Artificial“)
- nearly no natural resources (only ultra-trace amounts due to spontaneous fission of ^{238}U (1 atom technetium per 10^{12} uranium atoms in uranium minerals)
- but *one of the main products* of nuclear fission
- available in kg-amounts (prize: 1 g ≈ 100 $)

Technetium Chemistry

- typical transition metal
- oxidation states from „0“ to „+7“
- most stable oxidation states +4 and +7,most stable compounds TcO_2, TcO_4^-
- rich coordination chemistry (stabilisation of the different oxidation states depends on the reducing conditions and the ligands supplied)
- rich cluster chemistry

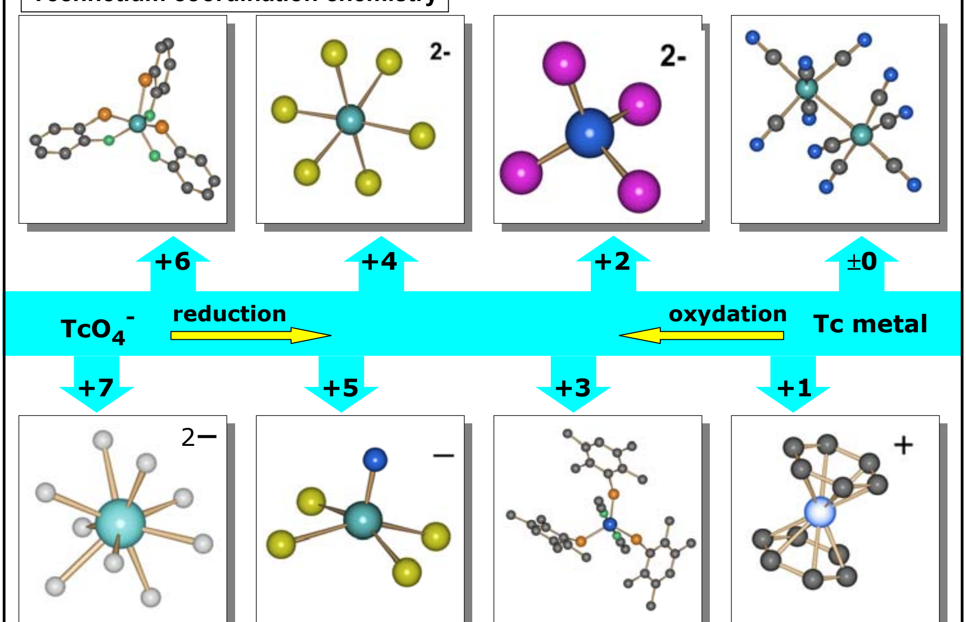
11) The Chemistry of Artificial and Radioelements (3)

Technetium coordination chemistry with halides



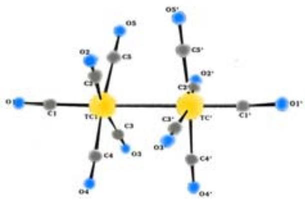
11) The Chemistry of Artificial and Radioelements (4)

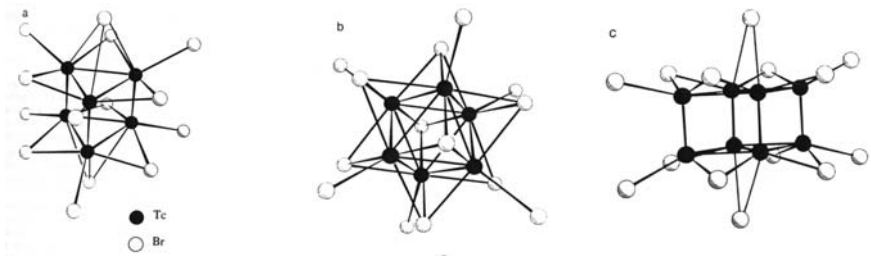
Technetium coordination chemistry



11) The Chemistry of Artificial and Radioelements (5)

Technetium cluster chemistry



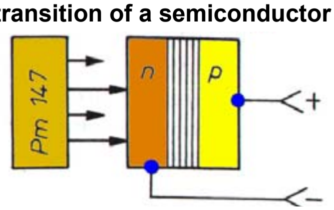


11) The Chemistry of Artificial and Radioelements (6)

Promethium chemistry

- discovery in 1947 (last gap in the Periodic Table was closed)
- Isotopes between ^{136}Pm and ^{154}Pm, longest half-life ^{140}Pm: 17.7 a
- typical lanthanide element
- chemistry is comparable with that of its neighbours Nd and Sm
- commercial use of ^{147}Pm in batteries: direct photovoltaic process !!!
  Energy density of Pm_2O_3: 0,333 W/g

p-n transition of a semiconductor



Radiovoltaic battery

11) The Chemistry of Artificial and Radioelements (7)

Polonium

- heaviest Element of the VI. group
- in nature it is exclusively available as ^{210}Po as a member of the uranium decay family (in pitchblend up to 0.1 mg per ton, 10^{-4} ppm)

$$^{210}_{82}Pb \xrightarrow{\beta^-, 22.3a} {}^{210}_{83}Bi \xrightarrow{\beta^-, 5.01d} {}^{210}_{84}Po \xrightarrow{\alpha, 138.38d} {}^{206}_{82}Pb$$

- discovery in 1898 by Marie Curie by its radioactivity
- use as α-emitter in neutron sources

Chemistry

- marked metal character (similar to bismuth)
- frequent oxidation states +2 and +4
- typical compounds: $PoCl_2$ (rubin-red), $PoCl_4$ (yellow), PoO_2
- more alkaline than the homologes: $Po(NO_3)_4$, $Po(SO_4)_2$ are stable
- no compound with organic ligands (strong radiation would decompose the compound)

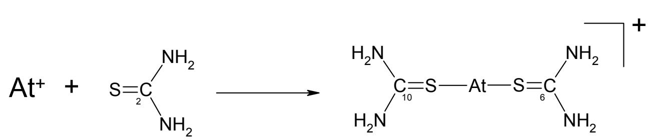
11) The Chemistry of Artificial and Radioelements (8)

Astatine

- heaviest element of main group VII
- practically no occurance in nature (At isotope in natural decay series have half-lifes < 10 sec)
- discovered in1940 by Corson, Mackenzie and Segre
- artificial synthesis by bombardment of ^{209}Bi with α-particles
- longest half-life ^{210}At: 8.1 h

Chemistry

- behaviour similar to iodine, but preference to cationic species
- oxidation states: -1, 0, +1, +3, +5 , +7
- At^+ cations form complexes with thiourea und „interhalogen" compounds

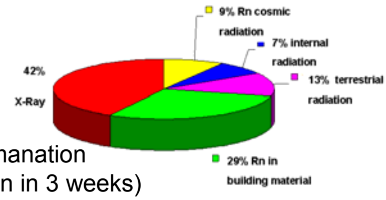


$At^+ + 2\,Cl^- \rightarrow [AtCl_2]^-$

11) The Chemistry of Artificial and Radioelements (9)

Radon

- heaviest noble gas without stable isotopes
- occurs in all natural decay series
- main source of natural radioactivity
- isotopes from ^{200}Rn to ^{226}Rn
- longest half-life ^{222}Rn: 3.8 days
- synonyms: triton, thoron, actinon, radium emanation
- main source: ^{226}Ra (1g Ra yields 0,64cm^3 Rn in 3 weeks)



Radon Chemistry
- heaviest noble gas → easiest polarisation
- should be more reactive than xenon

Francium

- heaviest alkaline metal without stable isotopes
- discovered in 1939 (Margueritte Perey)
- occurrence in natural actinium decay family
- overall amount in earths crust: about 15 g
- isotopes: ^{201}Fr to ^{229}Fr (longest half-life ^{212}Fr: 24 min)

11) The Chemistry of Artificial and Radioelements (10)

Radium

- heaviest alkaline earth element, key element for the development of radiochemistry
- discovered in 1898 by Pierre and Marie Curie (isolation of $RaCl_2$ from several tons of pitch blend (uranium mineral)
- occurs on earth together with uranium (decay product): 1 mg Ra per 3 kg U
- isotopes: ^{206}Ra to ^{230}Ra
- longest half-life ^{226}Ra (1600a)

Actinium

- element of the third transition metal group without stable isotopes
- discovered in 1899 (A. Debierne) in uranium minerals
- natural Ac (^{227}Ac) is a ß$^-$ emitter (half-life: 21.77 a) with highly γ-radioactive decay products (hard to handle)
- pure Ac-metal emits light in the dark

Actinium Chemistry
- typical oxidation state: „+3“
- chemistry is similar to that of lanthanium

11) The Chemistry of Artificial and Radioelements (11)

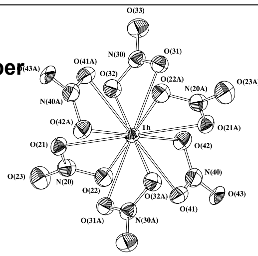
Thorium

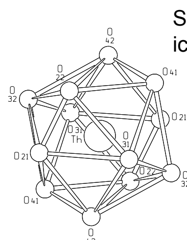
- element of the actinide series without stable isotopes
- chemically related to the lanthanide elements (natural occurance in monazite)
- discovered in 1828 by Berzelius in Thorite (Norwegian mineral)
- thorium isotopes from ^{213}Th to ^{236}Th (longest half-life ^{232}Th: 1.4 x 10^{10} a)
- application in special ceramics

Thorium Chemistry

- typical oxidation state „+4“
- well-established ‚inorganic chemistry‘ (ThO_2, $ThCl_4$, $Th(NO_3)_4$) and coordination chemistry due to the ready availability of the long-living isotope ^{232}Th from natural sources
- large ion with high charge → chemistry of high coordination numbers

e.g. Coordination number 12 in $[Th(NO_3)_6]^{2-}$

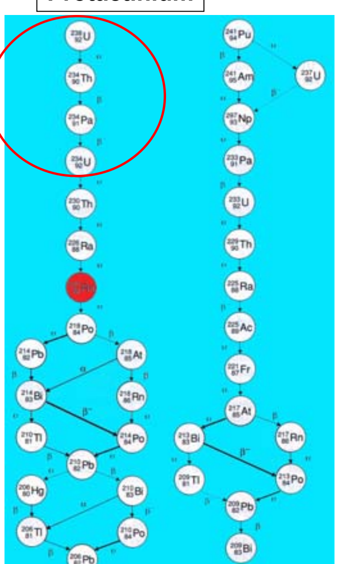




Strongly distorted icosahedron

11) The Chemistry of Artificial and Radioelements (12)

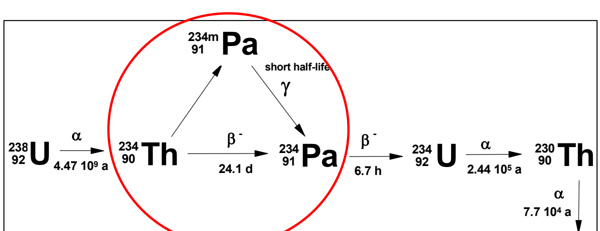
Protactinium



Uranium family   Neptunium family

A part of the Uranium family series is important for the laboratory course:

- ^{238}U (99.27% natural abundance) decays into ^{234}Th (Half-life: 4.4 x 10^9 y, α-decay)
- ^{234}Th is radioactive itself and forms ^{234} Pa (Half-life 24.1 d, ß-decay)
- this disintegration passes a transient state with a certain half-life (the metastable isomer ^{234m}Pa which is a γ -emitter)
- This γ -emitter is the radioactive substance of almost all measuring experiments in the lab course



11) The Chemistry of Artificial and Radioelements (13)

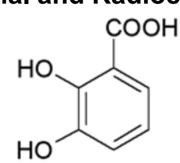
Uranium

- Most important actinide element
- discovered in 1789 by Klaproth from the mineral pitch blend
- element with the highest naturally occuring mass number (with the exception of its disintegration products Np and Pu)
- isotopes ^{225}U to ^{242}U (longest half-life ^{238}U: 4.4 x 10^8 a)
- great importance as „nuclear fuel“ in nuclear power stations

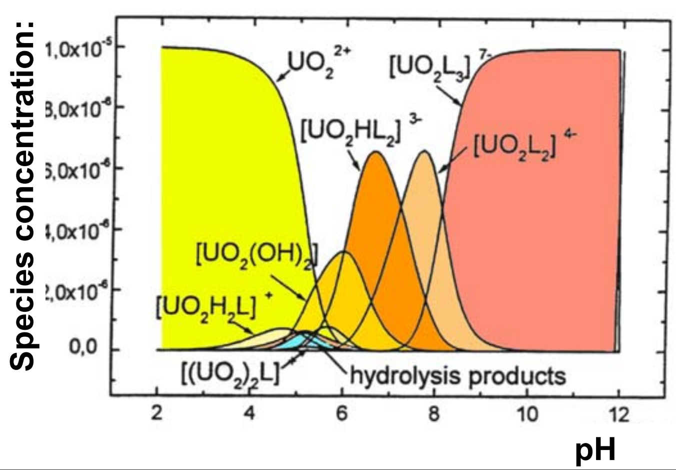
- uranium chemistry
- frequently occuring oxidation states: „+3“, „+4“, „+5“ and „+6“
- complicated coordination chemistry with various species and changes in the oxidation states
- halides: UF_6 (colourless, volatile compound with importance for the isotope separation by means of gas diffussion), UCl_6 (green), UCl_5 (brown), UCl_4 (green), UF_3 (violet)
- uranyl complexes with linear $U(VI)O_2^{2+}$ ions
- remarkable tendency to form multinuclear aggregates by condensation via O-, OH- or OH_2 bridging units

11) The Chemistry of Artificial and Radioelements (14)

Reaction: UO_2^{2+} +

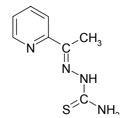


Calculated species contribution:



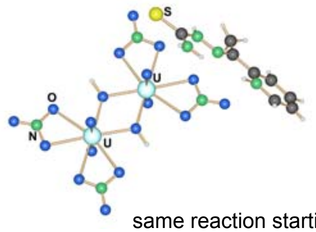
11) The Chemistry of Artificial and Radioelements (15)

Reaction:

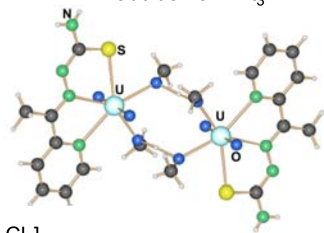
$UO_2(NO_3)_2 \times 6\ H_2O$ + 

in methanol / water

without addition of a supporting base



addition of NEt_3



same reaction starting from $(NBu_4)[UO_2Cl_4]$