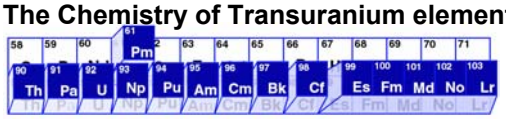
12) The Chemistry of Transuranium elements (1)



Neptunium

- first transuranium element which was discovered in 1940 (McMillan, Abelson)
- bombardment of uranium with thermal neutrons:

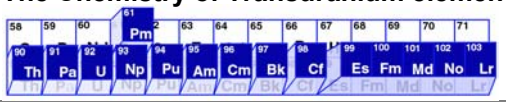
$$^{238}_{92}U\,(n,\gamma)\;^{239}_{92}U \xrightarrow{\beta^-,\,23{,}5\,\mathrm{min}} ^{239}_{93}Np$$

- long-lived isotope: ^{237}Np, $T_{1/2}$ = 2,14 x 10^6 y
- use for the production of ^{238}Pu
- **chemistry**: - similar to uranium with highest oxidation state +7
  - dominating species in aqueous solutions: NpO_2^+ species

Neptunium Chemistry

- similar to uranium, but with highest oxidation state +7
- stable oxidation states „+3“, „+4“ and „+5“
- dominating species in aqueous solutions: NpO_2^+ species
- neptunium halides: NpF_3 (purple), NpF_6 (orange-red), $NpCl_3$ (colorless), $NpCl_4$ (redbrown), $NpBr_3$ (green), $NpBr_4$ (redbrown) NpI_3 (brown)

12) The Chemistry of Transuranium elements (2)



Plutonium

- highly toxic and radiotoxic transuranium element
- discovered in 1940/41 (Seaborg and co-workers) by bombardment of ^{238}U with deuterons

$$^{238}_{92}\mathbf{U}\,\mathbf{(d,2n)}\;^{238}_{93}\mathbf{Np}\xrightarrow{\beta^-,\,2{,}11\,\mathbf{d}}{}^{238}_{94}\mathbf{Pu}$$

- use of ^{238}Pu as energy source (heart pacemaker, spacecrafts)
- use of ^{239}Pu as nuclear fuel
- production from ^{238}U in“ breeding reactors“

$$^{238}_{92}U\,(n,\gamma)\;^{239}_{92}U \xrightarrow{\beta^-,\,23{,}5\,\mathrm{min}} ^{239}_{93}Np \xrightarrow{\beta^-,\,2{,}355\,d} ^{239}_{94}Pu$$

Plutonium Chemistry

- highly toxic
- known oxidation states "+3", "+4", "+5", "+6" und "+7“
- most stable oxidation state: „+4“
- Halides: PuF_3 (purple), $PuCl_3$ (emerald green), $PuBr_3$ (green)

12) The Chemistry of Transuranium elements (3)

Do actinides really exist as distinct group in the Periodic Table?

Contra

- chemistry of Th and Pa is very close to that of the elements of group **4** and **5**
- U forms hexahalides, oxyhalides and oxo complexes as Mo and W
- Np chemistry is (as far as known) similar to the Re chemistry

Pro

- U(VI) compounds (uranates) are yellow (intensity of colour decreases with increasing atom number: MnO_4^- (purple), TcO_4^- (almost colourless), ReO_4^- (colourless))
- course of density (Cr 7.1 g/cm^3, Mo 10.3 g/cm^3, W 19.3 g/cm^3, **U 19 g/cm^3**)
- melting points (Cr 1903 °C, Mo 2620 °C, W 3410 °C, **U 1132 °C**)
- within a transition metal group the stability of low oxidation states decreases (U(III) and U(IV) compounds are stable)
- uranium forms a hydride UH_3 (similar to lanthanum)
- UO_2 crystallizes (as the dioxides of Th, Pa, Np, Pu, Am, Cm, Bk and Cf) in a fluorite lattice (MoO_2 and WO_2 crystallize as rutile lattice)
- uranium occurs in nature together with Th and lanthanides (never with Mo, W)
- no stable hexacarbonyls of uranium are known
- heavier actinides show a very similar behaviour, main oxidation states „+3“, „+4“

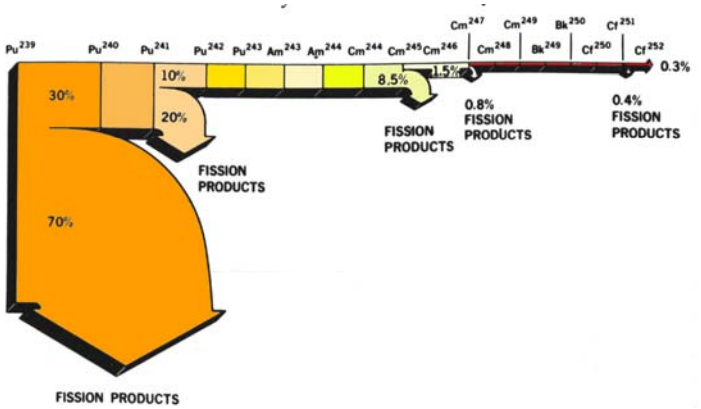
- **Conclusion: Actinides represent a separate f-block element group !!!**

12) The Chemistry of Transuranium elements (4)

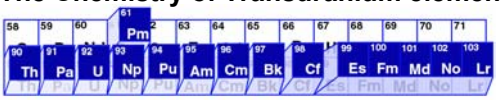
Heavy actinides

Americium, Curium, Berkelium, Californium, Einsteinium, Fermium, Mendelevium, Lawrencium

- synthesis by subsequent electron captures and ß$^-$ -decays (lighter elements) or heavy atom bombardment reactions (heavier elements)
- synthesis of only a few atoms



12) The Chemistry of Transuranium elements (5)



Americium

- produced by subsequent neutron capturing from ^{239}Pu (nuclear reactor)
- typical sequence:

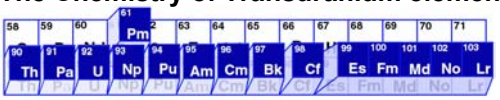
$$^{239}_{94}\mathrm{Pu}\,(n,\gamma)\ ^{240}_{94}\mathrm{Pu}\,(n,\gamma)\ ^{241}_{94}\mathrm{Pu}\xrightarrow{\beta^-,14.4a}\ ^{241}_{95}\mathrm{Am}\,(n,\gamma)\ ^{242}_{95}\mathrm{Am}\xrightarrow{\beta^-,16,01h}\ ^{242}_{96}\mathrm{Cm}$$

-discovered in 1944 (Seaborg and co-workers)
- available in weightable amounts
- long-lived isotope ^{243}Am (half-life: 7370 a)
- α-decay and spontaneous fission
- chemistry: typical oxidation states „+3“ and „+4“

Curium

- production similar to that of Am (nuclear reactor), see above
- discovered in 1944 (Seaborg and co-workers)
- available in weightable amounts
- long-lived isotope ^{247}Cm (half-life: 1.56 x 10^7 a)
- α-decay and spontaneous fission
- chemistry: typical oxidation states „+3“ and „+4“

12) The Chemistry of Transuranium elements (6)



Berkelium and Californium

- production by bombardment of Am or Cm isotopes with α-particles in a cyclotron

$$^{241}_{95}\mathrm{Am}\,(\alpha,2n)\ ^{243}_{97}\mathrm{Bk}\qquad\qquad ^{242}_{96}\mathrm{Cm}\,(\alpha,n)\ ^{245}_{98}\mathrm{Cf}$$

- strong α-emitters, available in weightable amounts
- long-lived isotopes ^{247}Bk (half-life: 1389 a) and ^{251}Cf (898 a)
- chemistry: typical oxidation states „+3“ and „+4“

Einsteinium and Fermium

- first detection in the products of the first thermonuclear bomb (multiple neutron capturing starting from ^{238}U)

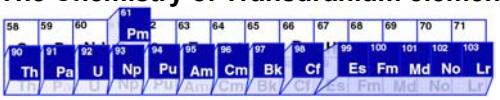
$$^{238}_{92}\mathrm{U}\xrightarrow{+15n,-7\beta}\ ^{253}_{99}\mathrm{Es}$$

- alternative synthesis by bombardment of uranium with heavier nuclei

$$^{238}_{92}\mathrm{U}\xrightarrow{+^{14}_{7}\mathrm{N},-6n}\ ^{246}_{99}\mathrm{Es}$$

- long-lived isotopes ^{252}Es (half-life: 471 d) and ^{257}Fm (100 d)
- not available in macroscopic amounts

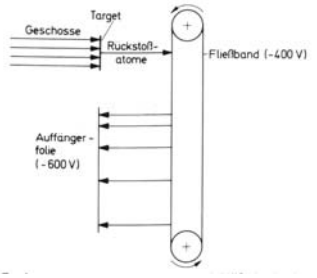
12) The Chemistry of Transuranium elements (7)



Mendeleyevium, Nobelium, Lawrencium

- not available by neutron capturing in a nuclear reactor
- production by bombardment of heavy targets with ^{14}N, ^{16}O or $^{10,11}B$
- only a few atoms are formes (single-atom synthesis)
- half-lifes in range of minutes
- problem of separation from matrix
- use of coupled synthesis and detection apparatuses

Apparatus for the online-detection of short-living products, which are produced in an accelerator

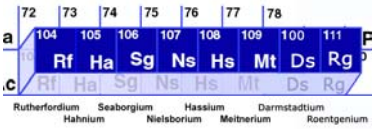


12) The Chemistry of Transuranium elements (8)

Availability of heavy actinides

Nuclide	$t_{½}$	Decay Mode	Specific Amounts * Available	Specific Activity (Bq/g)
^{237}Np	$2.14 \cdot 10^{6}$ y	α, SF (10^{-10} %)	kg	$2.61 \cdot 10^{7}$
^{238}Pu	87.7 y	α, SF (10^{-7} %)	kg	$6.33 \cdot 10^{11}$
^{239}Pu	$2.41 \cdot 10^{4}$ y	α, SF (10^{-4} %)	kg	$2.30 \cdot 10^{9}$
^{240}Pu	$6.56 \cdot 10^{3}$ y	α, SF (10^{-6} %)	kg	$8.40 \cdot 10^{10}$
^{241}Pu	14.4 y	β,α (10^{-3} %)	1-10 g	$3.82 \cdot 10^{12}$
^{242}Pu	$3.76 \cdot 10^{5}$ y	α, SF (10^{-3} %)	100 g	$1.46 \cdot 10^{8}$
^{244}Pu	$8.00 \cdot 10^{7}$ y	α, SF (10^{-1} %)	10 –100 mg	$6.52 \cdot 10^{5}$
^{241}Am	433 y	α, SF (10^{-10} %)	kg	$1.27 \cdot 10^{11}$
^{243}Am	$7.38 \cdot 10^{3}$ y	α, SF (10^{-8} %)	10 –100 g	$7.33 \cdot 10^{9}$
^{242}Cm	162.9 d	α, SF (10^{-5} %)	100 g	$1.23 \cdot 10^{14}$
^{243}Cm	28.5 y	α, ε (0.2 %)	10 – 100 mg	$1.92 \cdot 10^{12}$
^{244}Cm	18.1 y	α, SF (10^{-4} %)	10 – 100 g	$3.00 \cdot 10^{12}$
^{248}Cm	$3.40 \cdot 10^{5}$ y	α, SF (8.3 %)	10 – 100 g	$1.57 \cdot 10^{8}$
^{249}Bk	320 d	β,α (10^{-3} %), SF (10^{-8} %)	10 – 100 mg	$6.00 \cdot 10^{10}$
^{249}Cf	350.6 y	α, SF (10^{-7} %)	10 – 50 mg	$1.52 \cdot 10^{11}$
^{250}Cf	13.1 y	α, SF (0.08 %)	1 – 10 mg	$4.00 \cdot 10^{12}$
^{252}Cf	2.6 y	α, SF (3.1 %)	10 mg	$2.00 \cdot 10^{13}$
^{254}Cf	60.5 d	α, SF (0.3 %)	10 – 1000 mg	$3.17 \cdot 10^{14}$
^{253}Es	20.4 d	α, SF (10^{-5} %)	µg	$9.33 \cdot 10^{14}$
^{254}Es	276 d	α	1 – 10 mg	$6.83 \cdot 10^{13}$
^{257}Fm	100.5 d	α, SF (0.2 %)	1 – 5 µg	$1.83 \cdot 10^{14}$
			1 pg	

12) The Chemistry of Transuranium elements (9)

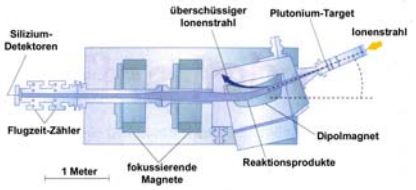


Transactinide elements

- production by bombardment of heavy, neutron-rich nuclei with heavy ions
- typical reactions:

$$^{207,\ 208}Pb + {}^{54}Cr \rightarrow {}^{259,260}Sg + 2n$$
$$^{209}Bi + {}^{54}Cr \rightarrow {}^{262}Ns + n$$
$$^{208}Pb + {}^{58}Fe \rightarrow {}^{265}Hs + n$$
$$^{209}Bi + {}^{58}Fe \rightarrow {}^{266}Mt + n$$

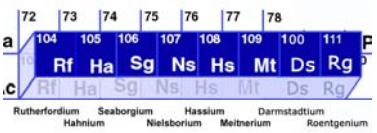
- typical device: Heavy atom accelerator
- typical „yield“:
  Ns (38 atoms),
  Hs (3 atoms),
  Mt (3 atoms)

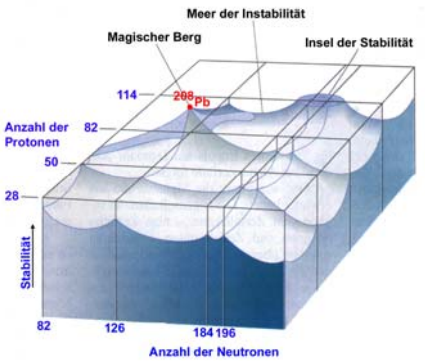


12) The Chemistry of Transuranium elements (10)

Transactinide elements – „The Island of Stability“

- atom nucei with „magical numbers“ protons and neutrons (z.B. $^{298}114$)
- main problem: **How to provide the large number of neutrons?**





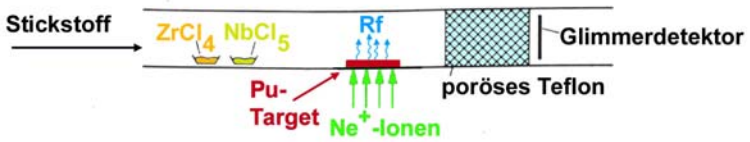
- nuclides of elements up to element 118 are detected
- relatively „stable“ isotopes of element 114: 173 neutrons → $T_{1/2}$ = 5 s
  175 neutrons → $T_{1/2}$ = 30 s

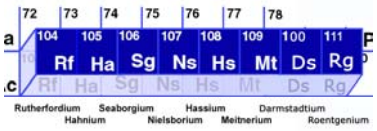
12) The Chemistry of Transuranium elements (11)

Transactinide elements – „Chemistry“

- frequently gas-phase reactions
- long-lived or stable nuclides are used as „carrier“
- thermochromatography:
  - chromatography of volatile compounds (oxides, halides) in a gas jet
  - comparison with the behaviour of known compounds

  - e.g. properties of element 104 (Rf. homologue of Nb and Ta)





12) The Chemistry of Transuranium elements (12)

Transactinide elements – The extended Periodic Table

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112	(113)	(114)	(115)	(116)	(117)	(118)
(119)	(120)	(121)	(154)	(155)	(156)	(157)	(158)	(159)	(160)	(161)	(162)	(163)	(164)	(165)	(166)	(167)	(168)

Lanthanide	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinide	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Superactinide	(122)	(123)	(124)	(125)	(126)	(127)	(128)	(129)			(150)	(151)	(152)	(153)