Meet the Presenter…

Alena Paulenova

Dr. Alena Paulenova is Associate Professor in the Department of Nuclear Engineering and Director of the Laboratory of Transuranic Elements at the OSU Radiation Center. She is also Adjunct Professor at the Department of Chemistry at Oregon State University , a Joint Research faculty with Idaho National Laboratory, Division of Aqueous Separations and Radiochemistry and a member of the INEST Fuel Cycle Core Committee.

She received her Ph.D. in Physical Chemistry in 1985 from the Moscow/Kharkov State University. Until 1999, she was a faculty member at the Department of Nuclear Chemistry and Radioecology of Comenius University in Bratislava, then a visiting scientist at Clemson University and Washington State University in Pullman. In 2003 she joined the faculty at OSU as a Coordinator of the Radiochemistry Program at OSU Radiation Center to bring her experience to the task of helping to educate a new generation of radiochemists: http://oregonstate.edu/~paulenoa/.

Her research interest has focused on application of radioanalytical and spectroscopic methods to speciation of radionuclides in aqueous and organic solutions and development of separation methods for spent nuclear fuel cycle processing, decontamination and waste minimization. The main efforts of her research group are fundamental studies of the kinetics and thermodynamics of the complexation of metals, primary actinides and fission products, with organic and inorganic ligands and interactions with redox active species, and the effects of radiolysis and hydrolysis in these systems.

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An Overview of Actinide Chemistry

Alena Paulenova

National Analytical Management Program (NAMP)
U.S. Department of Energy Carlsbad Field Office

TRAINING AND EDUCATION SUBCOMMITTEE

What Will You Learn About Actinides Today?

This presentation is a brief introduction to rich and intricate chemistry of actinide.

Today we will speak about:

- Natural and Artificial Actinides
- Actinide Theory
- Thermodynamic Properties
- Oxidation State and Redox Behavior
- Effective Cationic Charge
- Coordination of Actinides
- Hydration and Hydrolysis
- Aqueous Speciation of Actinides

Discovery and Production

- The actinides (An) are all radioactive elements.
- **U, Th, Pa** and **Ac** are the only four actinides that have been found in the environment. Other An are **artificial**, being produced through various nuclear reactions.
- At the creation of the universe, some amount of ^{244}Pu could have been formed; however, with an 80 million year half-life, it would have fully decayed during the past 10 billion years.

- D. Hoffman (1971) reported 1.0×10^{-18} g ^{244}Pu/g in mineral bastnäsite. However, earlier this year, Lachner (2012) reported no detectable event for Pu for the same mineral from the same mine. He set a new lower upper limit for the abundance of ^{244}Pu : 370 atoms per gram ($=1.5 \times 10^{-19}$ g ^{244}Pu/g).

Natural Actinides and their Origin

- U-238, U-235 and Th-232 are initial elements of "decay chains" or "natural radioactivity series" (next slide):
  - named after the longest lived member
  - all members of the chain are in *secular** equilibrium with each other
  - decay mode is either alpha (A=4) or isobaric beta – the atomic mass number of all nuclides within the chain can be expressed as a function A=4n+i
- Uranium: U-238, U-235, U-234
- Thorium: 2 isotopes in each series: Th-234, Th-230 [from U-238]
  Th-231, Th-227 [from U-235]
  Th-232, Th-228
- Actinium: Ac-227 [U-235]; Ac-228 [Th-232]
- Protactinium: Pa-234 [U-238]; Pa-231 [U-235]

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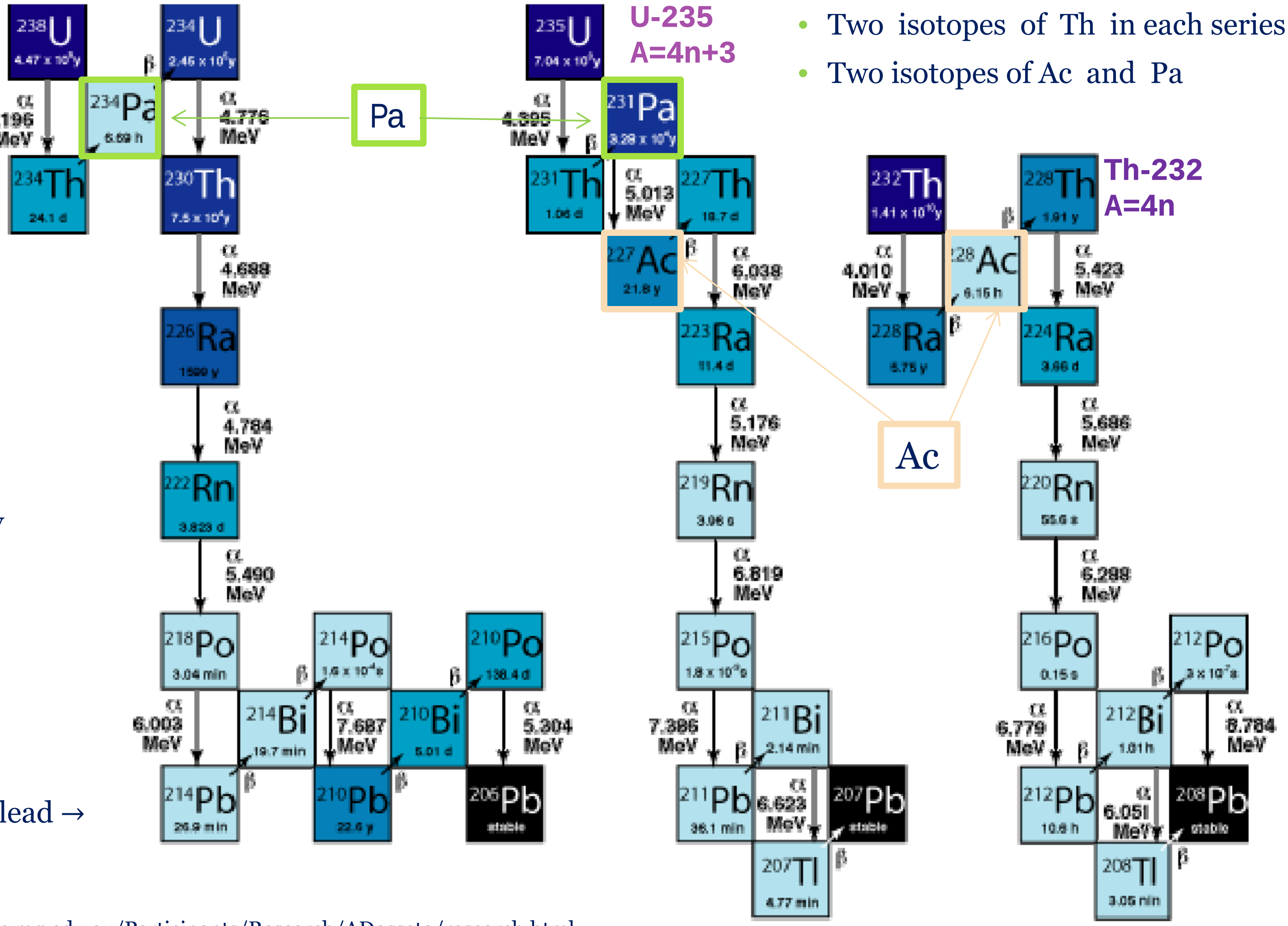
* Secular equilibrium is formed by a so long-lived parent and so short-lived daughter that after a time long about 10 half-lives of daughter their activity are equal to each other.

Natural Decay Series

- Named after the longest lived member
- A= atomic mass number of members
- Two isotopes of Th in each series
- Two isotopes of Ac and Pa

U-238
A= 4n+2



Contribute
to natural
radioactivity

All decay to lead →

http://www.gemoc.mq.edu.au/Participants/Research/ADosseto/research.html

Uranium history

- Uranium was the first actinide element discovered.
- The **use** of uranium in its natural oxide form dates back to at least the year 79 CE (Italy) since when it was used to add a yellow color to ceramic glazes.
- Starting in the late Middle Ages, **pitchblende** (impure, mineralized form of UO2) was extracted from the Habsburg silver mines in Joachimsthal, Bohemia (now Jáchymov in the Czech Republic).
- For centuries, it was used as a coloring agent in the local glassmaking industry.

Uranium glass glowing under UV light

Uranium discovery

1789 - M. H. **Klaproth** identified the presence of a new element in a sample of pitchblende. He named the new element “uranite” after the recently discovered planet Uranus; however, it was only uranium oxide

1841 - Eugene **Peligot**, French chemist, insulated uranium metal. The atomic mass of uranium was then calculated as 120.

1872 -Dmitri **Mendeleev** corrected it to 240 using his periodicity laws.

1882 - K. **Zimmerman** experimentally confirmed the value calculated by Mendeleev.

- Ingmar Grenthe (2006). "Uranium". *The Chemistry of the Actinide and Transactinide Elements*. doi:10.1007/1-4020-3598-5_5.

Radio-active?

Nearly 100 years later, **Becquerel** (1896) made the initial discovery of the ”uranium rays” through experiments with uranium minerals and photographic plates.

Beta Roentgen's hand

- Marie **Sklodowska-Curie,** using electrometer invented by her husband P. Curie, discovered that uranium rays caused the air around a sample to conduct electricity, and she coined the term “radioactivity”.
- 1898 **-** Th is radioactive (not credited)
- 1898 **-** Discovered and separated Po and Ra

Radiochemistry was born

1903 - Nobel Prize in Physics to H. Becquerel, P. Curie and M. Sklodowska-Curie for discovering radioactivity

1911 – Nobel Prize in Chemistry to Madam Curie for discovering radium and polonium.

LE RADIUM

PUBLICATION MENSUELLE

DIRECTEUR
Henri FARJAS

Le Laboratoire de la Rue Lhomond

M. & Mme CURIE

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Thorium

J. J. Berzelius

1827 - **Thorium** oxide was discovered by Fridrich Wöhler in a Norwegian mineral.

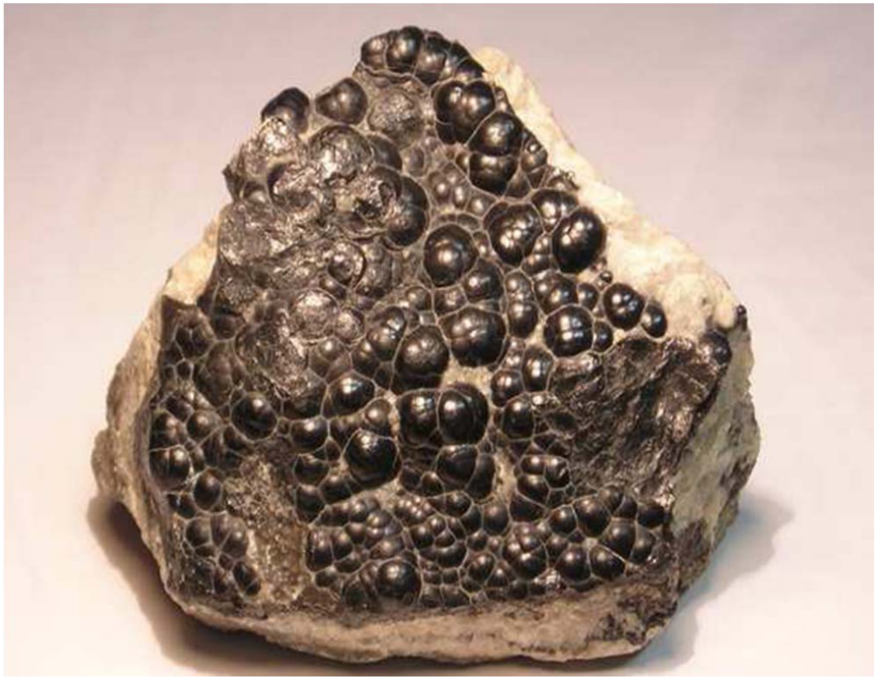
1828 - **Berzellius** characterized this material and discovered and insulated a new element and named it thorium (Th) after Thor, a mythological Norse god of thunder and lightening.

- Berzelius applied reduction of ThCl4 with potassium - later used also for reduction of uranium by Peligot (1841).
- Only 70 years later it was learned that Th is radioactive, in 1898, independently by Marie S. Curie (France) and Gerhard C. Schmidt (England).

Actinium

1899 - The earliest discovery of actinium (Ac) is attributed to A. Debierne, an assistant and collaborator of Pierre and Marie Curie.

He discovered Ac while helping them with isolation of Ra; however, he never insulated actinium.



pitchblende

1902 – Friedrich O. Giesel identified and isolated the element Ac in pitchblende.

The name actinium is derived from ‘aktinos’ (Greek word for ray).

Protactinium

Pa was discovered as the last from the naturally occurring actinides.

Parent of Ac, it is the rarest and most expensive of the naturally occurring actinide elements.

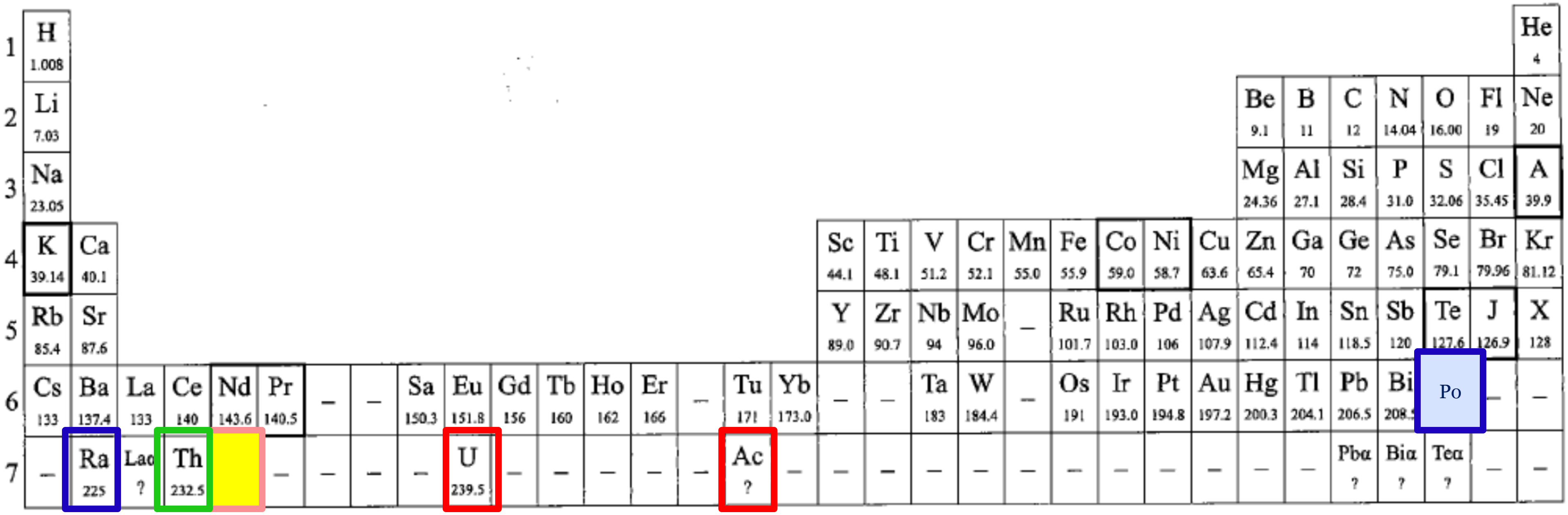
1913 – identified as short-lived isotope ^{234m}Pa (half-life 1.17 minutes) by K. Fajans and O. H. Goehring during their studies of the ^{238}U decay, and named brevium (latin for 'brief ').

1918 - O. Hahn and L. Meitner (Germany) and independently F. Soddy and J. Cranston (United Kingdom); renamed to "*protoactinium*" (Greek word 'protos' =first).

1949 – IUPAC shortened its name to **protactinium**.

O. Hahn and L. Meitner

Atomic Era begins:



1	H 1.008																																He 4
2	Li 7.03																										Be 9.1	B 11	C 12	N 14.04	O 16.00	Fl 19	Ne 20
3	Na 23.05																										Mg 24.36	Al 27.1	Si 28.4	P 31.0	S 32.06	Cl 35.45	A 39.9
4	K 39.14	Ca 40.1																Sc 44.1	Ti 48.1	V 51.2	Cr 52.1	Mn 55.0	Fe 55.9	Co 59.0	Ni 58.7	Cu 63.6	Zn 65.4	Ga 70	Ge 72	As 75.0	Se 79.1	Br 79.96	Kr 81.12
5	Rb 85.4	Sr 87.6																Y 89.0	Zr 90.7	Nb 94	Mo 96.0	–	Ru 101.7	Rh 103.0	Pd 106	Ag 107.9	Cd 112.4	In 114	Sn 118.5	Sb 120	Te 127.6	J 126.9	X 128
6	Cs 133	Ba 137.4	La 133	Ce 140	Nd 143.6	Pr 140.5	–	–	Sa 150.3	Eu 151.8	Gd 156	Tb 160	Ho 162	Er 166	–	Tu 171	Yb 173.0	–	–	Ta 183	W 184.4	–	Os 191	Ir 193.0	Pt 194.8	Au 197.2	Hg 200.3	Tl 204.1	Pb 206.5	Bi 208.	Po	–	–
7	–	Ra 225	Laα ?	Th 232.5	🟨	–	–	–	–	U 239.5	–	–	–	–	–	Ac ?	–	–	–	–	–	–	–	–	–	–	–	–	Pbα ?	Biα ?	Teα ?	–	–

The long form of the Periodic Table published by A. Werner (1905):

- Th is the only correctly localized radionuclide
- Po is not there yet.

Nuclear research became of a really great interest:

1911 – Discrete structure of atom (Rutheford's laboratory)

1913 - Solar model of atom (Niels Bohr)

1928 - Joliot-Curie observed positron and neutron, but failed in interpretation.

First Artificial Radioactivity

- 1932 - Neutron discovery (Chadwick):

$$_{2}\alpha + {}_{4}Be \rightarrow {}^{1}n + {}_{6}C$$

- 1934 – Joliot-Curie observed first artificial radioactivity:

$$^{27}Al + {}^{4}He \longrightarrow {}^{30}P + {}^{1}n$$

- 1940 - **Neptunium** was the **first transuranium** element produced synthetically by bombarding uranium with slow neutrons:

$$_{92}U^{238} + {}_{0}n^{1} \rightarrow {}_{92}U^{239} \rightarrow {}_{93}Np^{239}$$

- ^{239}Np isotope (half-life 2.4 days), discovered by Edwin **McMillan** and Philip H. **Abelson** in Berkeley, CA and named for the planet Neptune (the next planet out from Uranus, after which uranium was named).

Greenwood, N. N.; Earnshaw, A. (1997). *Chemistry of the Elements* (2nd ed.).

Synthesis of Transuranium Elements

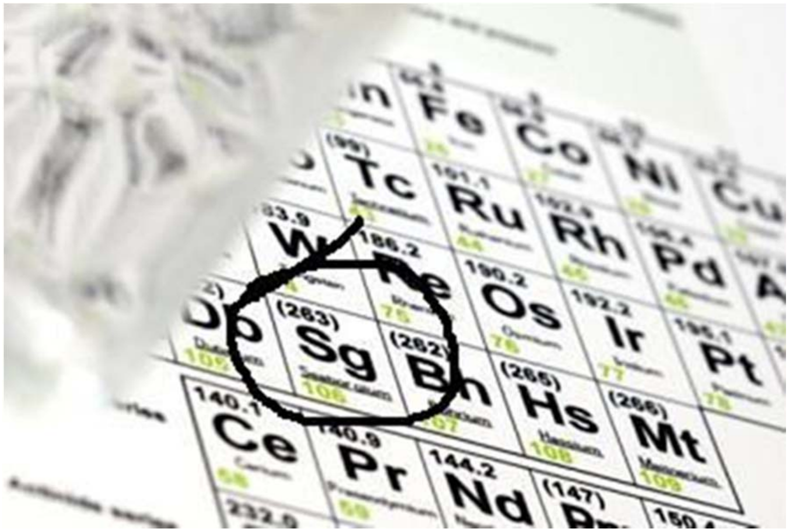
1940- Edwin McMillan was the first ever to produce a transuranium element. He also started bombarding U^{239} with deuterons, but had to leave to MIT to work on the radar project.

1940 - Glenn T. Seaborg joined McMillan's project

1941- February – Seaborg, Kennedy, Wahl and McMillan synthesized element 94, plutonium (Pu, named after Pluto, the next planet to Neptune)

Since then, Seaborg and his group at the UC at Berkeley discovered and synthesized:

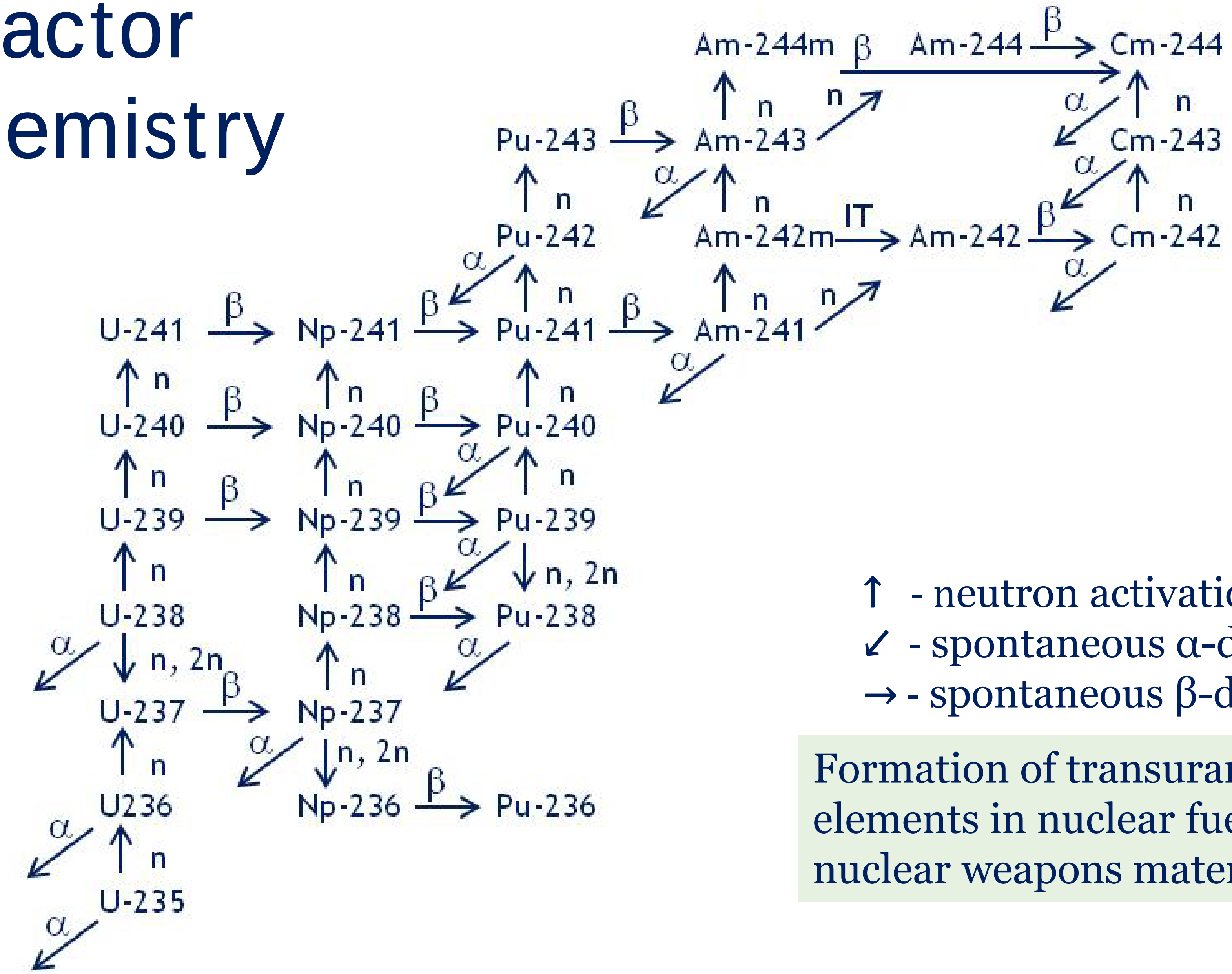
- **10 actinide elements** (Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No) including element 106- Sg (named in his honor while he was still living)
- More than **100 atomic actinide isotopes**



Early Years of Heavy Elements

Element	**Year**	**Method**
Neptunium	1940	Bombarding ^{238}U by neutrons
Plutonium	1941	Bombarding ^{238}U by deuterons
Americium	1944	Bombarding ^{239}Pu by neutrons
Curium	1944	Bombarding ^{239}Pu by α-particles
Berkelium	1949	Bombarding ^{241}Am by α-particles
Californium	1950	Bombarding ^{242}Cm by α-particles
Einsteinium	1952	Product of nuclear explosion
Fermium	1952	Product of nuclear explosion (^{238}U +17n→^{255}U →^{255}Np →…^{255}Fm)
Mendelevium	1955	Bombarding ^{253}Es by α-particles
Nobelium	1965	Bombarding ^{243}Am by ^{15}N or ^{238}U with α-particles
Lawrencium	1961–1971	Bombarding ^{252}Cf by ^{10}B or ^{11}B and Bombarding ^{243}Am with ^{18}O

Reactor Chemistry



↑ - neutron activation
↙ - spontaneous α-decay
→ - spontaneous β-decay

Formation of transuranic elements in nuclear fuel or nuclear weapons material

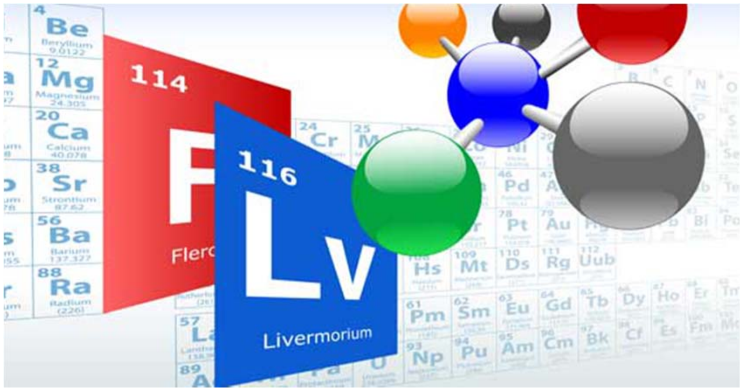
Adopted from : E. Holm, J. Rioseco and H. Peterson; J. Radioanal. Nucl.,Chem. Articles, 1992, **156**, 183

1951- Nobel Prize in Chemistry
Seaborg and McMillan

Awarded for "their discoveries in the chemistry of the first transuranium elements."

[http://cso.lbl.gov/photo/gallery/LBNL_NobelLaureates/index-1.html]

2011 (60 year later):



The Super Heavy Element Research Group, currently led by Seaborg Scientists, Dawn Shaughnessy and Kenton Moody, focuses on investigating the chemical and physical properties of the heaviest elements made by man.

The international team **LLNL**(Lawrence Livermore National Lab)-**JINR** (Joint Institute for Nuclear Research, Dubna, Russia) has discovered up to 6 new elements — 113, 114, 115, 116, 117, and 118. Name “**Flerovium**” (Flerov) was proposed for element 114 and “**Livermorium**” for element 116.

[LLNL; News Releases 12/01/2011]

Element	Major radionuclides	Half-life	Decay mode
Actinium	^{227}Ac	22 y	β^-/α
Thorium	^{232}Th	1.4x10^{10}y	α
	^{230}Th	7.6x10^{4} y	α
	^{228}Th	5.8 y	α
Protactinium	^{231}Pa	3.3 x 10^{4} y	α
Uranium	^{238}U	4.5x10^{9} y	α/SF
	^{235}U	7.0x10^{8} y	α
	^{236}U	2.3x10^{7} y	α
	^{234}U	2.5x10^{5} y	α
Neptunium	^{237}Np	2.1x10^{6} y	α
Plutonium	^{238}Pu	88 y	α
	^{239}Pu	2.4 x10^{4} y	α
	^{240}Pu	6500 y	α
	^{241}Pu	14 y	β^-
Americium	^{241}Am	433 y	α
Curium	^{244}Cm	18 y	α/SF
	^{242}Cm	0.45 y	α/SF
Berkelium	^{247}Bk	1380 y	α
Californium	^{251}Cf	898 y	α
Einsteinium	^{252}Es	1.3 y	α/β^+/EC
Fermium	^{257}Fm	0.27 y	α/SF
Mendelevium	^{258}Md	0.14 y	α/SF/β^+/EC
Nobelium	^{259}No	1 h	α/EC/SF
Lawrencium	^{262}Lr	3.6 h	SF

SF=Spontaneous fission
EC=Electron capture

Applications

- Nuclear fuel
- Nuclear weapons
- Neutron sources (Cf-252 or An-Be)
- Depleted uranium armor and projectiles
- Heart pacemakers (miniature power generators using Pu-238 encased in a tantalum–iridium–platinum alloy)
- Heat sources, space energy sources
- Actinium-225 is used in alpha-particle generators for tumor radiotherapy
- Smoke detectors (200 ug of Am-241)
- Lantern mantles
- Catalysis

Theory of Actinides

Chemistry of Actinides

Since the synthesis of Pu, transuranium chemistry was extensively studied; information was needed to insure that plutonium produced could be successfully extracted from the irradiated uranium:

- Seaborg isolated a weighable sample of plutonium, using lanthanum fluoride as a carrier (1942).
- Isadore Perlman and William J. Knox investigated the peroxide method of separation.
- John E. Willard studied various sorption materials.
- Theodore T. Magel and Daniel K. Koshland, Jr., researched solvent-extraction processes.
- Harrison S. Brown and Orville F. Hill investigated volatility
- Stanley G. Thompson (school friend of Seaborg) found that bismuth phosphate retained over ninety-eight percent plutonium in a precipitate.
- Basic research on plutonium's chemistry continued as did work on radiation and fission products.

Theory of Actinides

With the development of transuranic chemistry, soon it become clear that they do not fit into Mendeleev Periodic Table of Elements:

- What is the relation of An to lanthanides and other chemical elements?
- What is their position in Table of Elements?

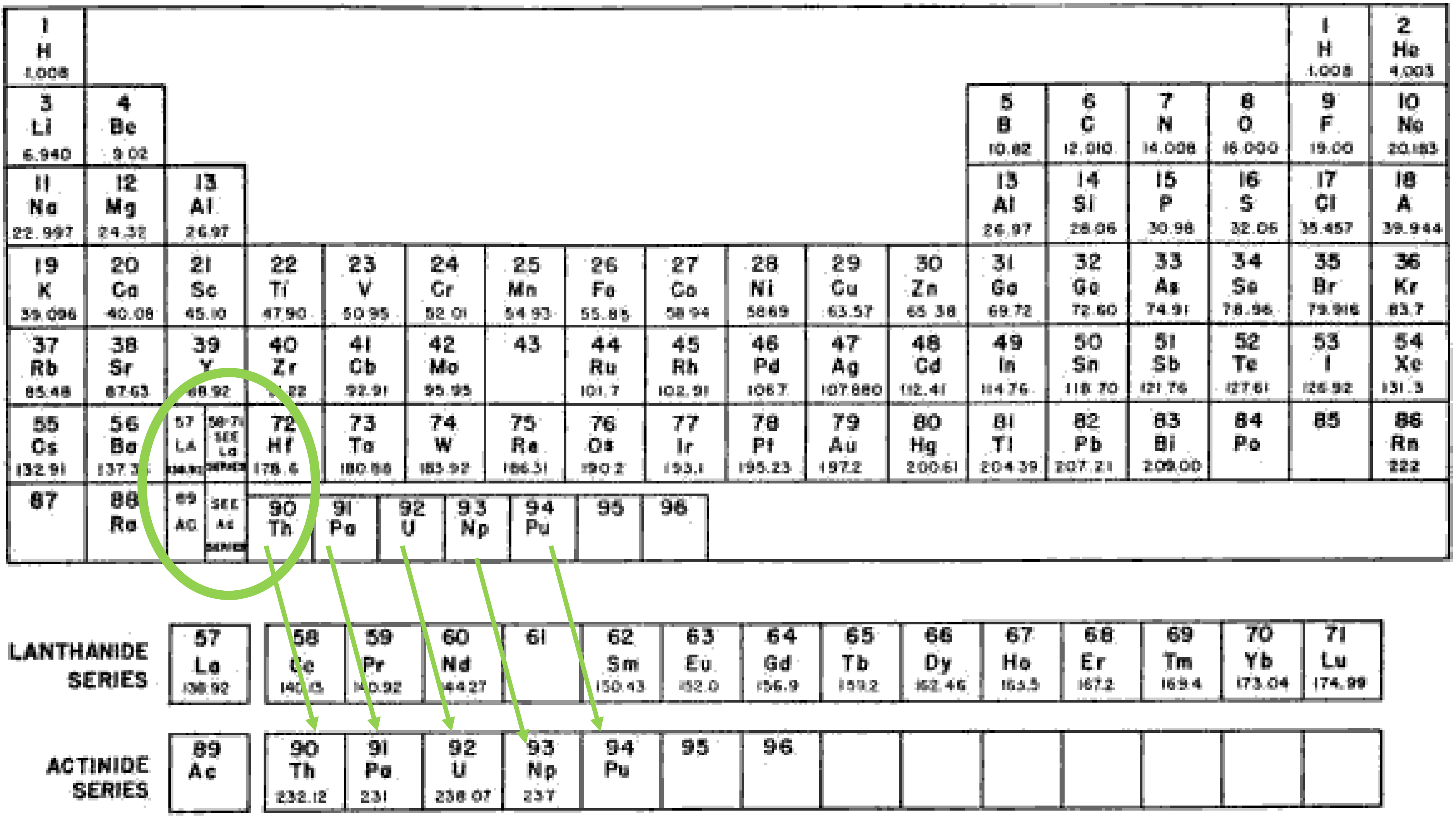
G.T. Seaborg with “Chart of Atoms”, 1956

Studying the similarities and differences in behavior of Transuranic Elements and Lanthanides, Seaborg proposed a historical decision:

F-ELEMENTS SHOULD BE SEPARATED FROM THE OTHER ELEMENTS

PERIODIC TABLE SHOWING HEAVY ELEMENTS AS MEMBERS OF AN ACTINIDE SERIES

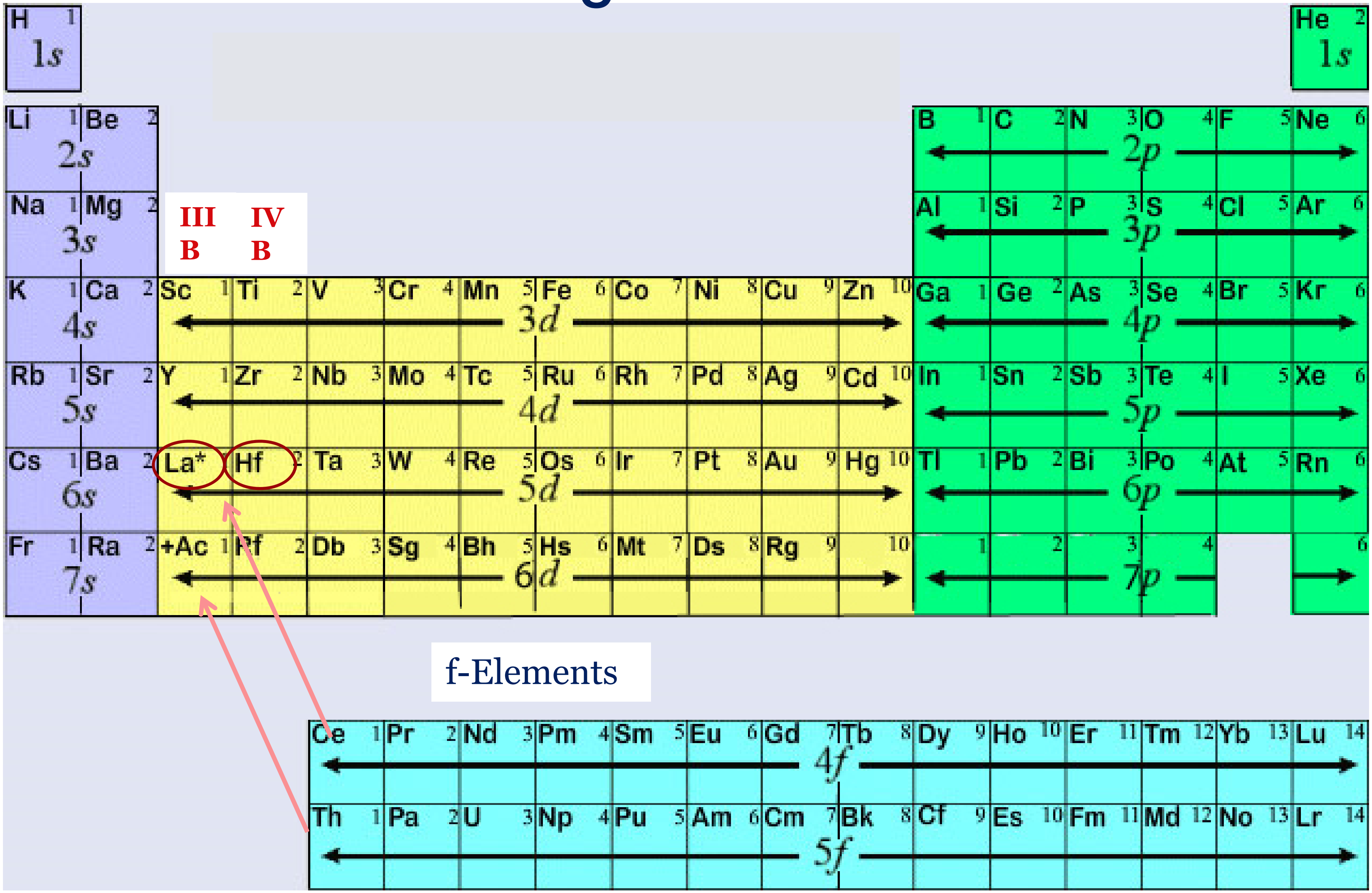
Arrangement by Glenn T. Seaborg, 1945



1 H 1.008																1 H 1.008	2 He 4.003
3 Li 6.940	4 Be 9.02											5 B 10.82	6 C 12.010	7 N 14.008	8 O 16.000	9 F 19.00	10 Ne 20.183
11 Na 22.997	12 Mg 24.32	13 Al 26.97										13 Al 26.97	14 Si 28.06	15 P 30.98	16 S 32.06	17 Cl 35.457	18 A 39.944
19 K 39.096	20 Ca 40.08	21 Sc 45.10	22 Ti 47.90	23 V 50.95	24 Cr 52.01	25 Mn 54.93	26 Fe 55.85	27 Co 58.94	28 Ni 58.69	29 Cu 63.57	30 Zn 65.38	31 Ga 69.72	32 Ge 72.60	33 As 74.91	34 Se 78.96	35 Br 79.916	36 Kr 83.7
37 Rb 85.48	38 Sr 87.63	39 Y 88.92	40 Zr 91.22	41 Cb 92.91	42 Mo 95.95	43	44 Ru 101.7	45 Rh 102.91	46 Pd 106.7	47 Ag 107.880	48 Cd 112.41	49 In 114.76	50 Sn 118.70	51 Sb 121.76	52 Te 127.61	53 I 126.92	54 Xe 131.3
55 Cs 132.91	56 Ba 137.36	57 LA 138.92 58-71 SEE La SERIES	72 Hf 178.6	73 Ta 180.88	74 W 183.92	75 Re 186.31	76 Os 190.2	77 Ir 193.1	78 Pt 195.23	79 Au 197.2	80 Hg 200.61	81 Tl 204.39	82 Pb 207.21	83 Bi 209.00	84 Po	85	86 Rn 222
87	88 Ra	89 AC SEE Ac SERIES	90 Th	91 Pa	92 U	93 Np	94 Pu	95	96								

LANTHANIDE SERIES	57 La 138.92	58 Ce 140.13	59 Pr 140.92	60 Nd 144.27	61	62 Sm 150.43	63 Eu 152.0	64 Gd 156.9	65 Tb 159.2	66 Dy 162.46	67 Ho 163.5	68 Er 167.2	69 Tm 169.4	70 Yb 173.04	71 Lu 174.99
ACTINIDE SERIES	89 Ac	90 Th 232.12	91 Pa 231	92 U 238.07	93 Np 237	94 Pu	95	96							

Electron Configuration Table



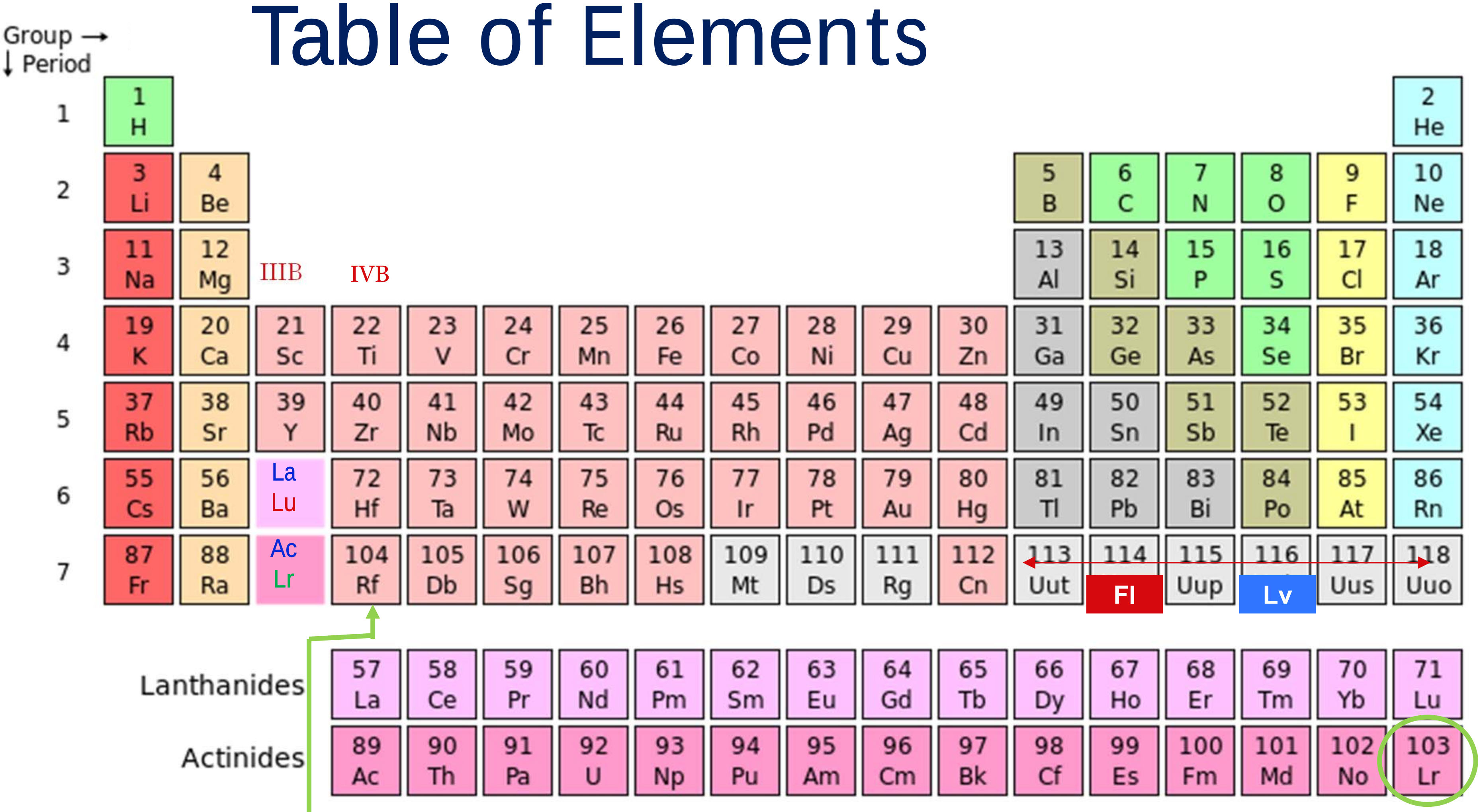
III B **IV B**

H 1																	He 2	1s
Li 1	Be 2											B 1	C 2	N 3	O 4	F 5	Ne 6	2s, 2p
Na 1	Mg 2											Al 1	Si 2	P 3	S 4	Cl 5	Ar 6	3s, 3p
K 1	Ca 2	Sc 1	Ti 2	V 3	Cr 4	Mn 5	Fe 6	Co 7	Ni 8	Cu 9	Zn 10	Ga 1	Ge 2	As 3	Se 4	Br 5	Kr 6	4s, 3d, 4p
Rb 1	Sr 2	Y 1	Zr 2	Nb 3	Mo 4	Tc 5	Ru 6	Rh 7	Pd 8	Ag 9	Cd 10	In 1	Sn 2	Sb 3	Te 4	I 5	Xe 6	5s, 4d, 5p
Cs 1	Ba 2	La* 1	Hf 2	Ta 3	W 4	Re 5	Os 6	Ir 7	Pt 8	Au 9	Hg 10	Tl 1	Pb 2	Bi 3	Po 4	At 5	Rn 6	6s, 5d, 6p
Fr 1	Ra 2	+Ac 1	Rf 2	Db 3	Sg 4	Bh 5	Hs 6	Mt 7	Ds 8	Rg 9	10	1	2	3	4		6	7s, 6d, 7p

f-Elements

Ce 1	Pr 2	Nd 3	Pm 4	Sm 5	Eu 6	Gd 7	Tb 8	Dy 9	Ho 10	Er 11	Tm 12	Yb 13	Lu 14	4f
Th 1	Pa 2	U 3	Np 4	Pu 5	Am 6	Cm 7	Bk 8	Cf 9	Es 10	Fm 11	Md 12	No 13	Lr 14	5f

Table of Elements



Group → ↓ Period																		
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg	IIIB	IVB									13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	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
5	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
6	55 Cs	56 Ba	La Lu	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
7	87 Fr	88 Ra	Ac Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
Lanthanides				57 La	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
Actinides				89 Ac	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

Transactinides (z>103)

Actinide Theory- Fundamental issue

Numerous experiments confirmed the position of actinides, 5f series of elements, in the periodic table as an inner transition series, analogous to the lanthanide transition series as first proposed by G. T. Seaborg.

While other designs of the periodic table could also be considered (for example, 3D with the f-block extending behind the main table), the separation of f-blocks is a fundamental classification issue.

Glenn Seaborg - father of the new table of elements

Thermodynamic Properties of Actinides

Electron Configurations

		[Rn] Atom (g)	M⁺ (g)	M²⁺ (g)	M³⁺ (g)	M³⁺ (aq)	M⁴⁺ (g)
6d	Actinium	$6d7s^{2}$	$7s^{2}$	$7s$			
	Thorium	$6d^{2}7s^{2}$	$6d7s^{2}$	$5f6d$	$5f$		
	Protactinium	$5f^{2}6d7s^{2}$	$5f^{2}7s^{2}$	$5f^{2}6d$	$5f^{2}$		$5f^{1}$
	Uranium	$5f^{3}6d7s^{2}$	$5f^{3}7s^{2}$	$5f^{3}6d$	$5f^{3}$	$5f^{3}$	$5f^{2}$
	Neptunium	$5f^{4}6d7s^{2}$	$5f^{5}7s$	$5f^{5}$	$5f^{4}$	$5f^{4}$	$5f^{3}$
	Plutonium	$5f^{6}7s^{2}$	$5f^{6}7s$	$5f^{6}$	$5f^{5}$	$5f^{5}$	$5f^{4}$
	Americium	$5f^{7}7s^{2}$	$5f^{7}7s$	$5f^{7}$	$5f^{6}$	$5f^{6}$	$5f^{5}$
	Curium	$5f^{7}6d7s^{2}$	$5f^{7}7s^{2}$	$5f^{8}$	$5f^{7}$	$5f^{7}$	$5f^{6}$
	Berkelium	$5f^{9}7s^{2}$	$5f^{9}7s$	$5f^{9}$	$5f^{8}$	$5f^{8}$	$5f^{7}$
	Californium	$5f^{10}7s^{2}$	$5f^{10}7s$	$5f^{10}$	$5f^{9}$	$5f^{9}$	$5f^{8}$
	Einsteinium	$5f^{11}7s^{2}$	$5f^{11}7s$	$5f^{11}$	$5f^{10}$	$5f^{10}$	$5f^{9}$
	Fermium	$5f^{12}7s^{2}$	$5f^{12}7s$	$5f^{12}$	$5f^{11}$	$5f^{11}$	$5f^{10}$
	Mendelevium	$5f^{13}7s^{2}$	$5f^{13}7s$	$5f^{13}$	$5f^{12}$	$5f^{12}$	$5f^{11}$
	Nobelium	$5f^{14}7s^{2}$	$5f^{14}7s$	$5f^{14}$	$5f^{13}$	$5f^{13}$	$5f^{12}$
	Lawrencium	$5f^{14}6d7s^{2}$	$5f^{14}7s^{2}$	$5f^{14}7s$	$5f^{14}$	$5f^{14}$	$5f^{13}$

Electron configuration of actinides consists from the closed radon shell, followed by **two 7s** and **5-f** electrons. **6d-electron** is present only in light An ($Z \le 93$) then appears in Cm and Lr.
No 7s2 and 6d1 electrons are present in trivalent oxidation state.

Lanthanides vs Actinides

- 4f-orbitals of Ln are deeply buried and completely screened by 5s and 5p-electrones; hence, 4f electrons have limited importance in chemical bonding. On the other hand, the 5f orbitals of An have greater spatial extension, and penetrate the core.

- The trivalent oxidation state of Ln is the most stable because it is formed by ionization of two 5s and one 5p electrons

- In solutions, all Ln-elements from La to Lu:
  - have a common oxidation state 3+ and behave chemically in a very similar manner, making their separation very difficult
  - only two lanthanides exhibit a second oxidation state: Ce(IV) is a strong and kinetically stable oxidizer and Eu(II) has an appreciable stability

- Only two uncommon Ln(II) species can be prepared in dilute solution (or solid state) either by electrolysis, gamma irradiation or metallic reduction with alkaline earth metal.

Actinides vs Lanthanides

The principal differences between the two f-series:

- lower binding energies and less effective shielding by outer electrons of 5f of An as compared to 4f electrons of Ln
- oxidation states of An (particularly in the first half of the series) in solutions are far more variable than those of the lanthanides
- energy differences between the 5f, 6d, 7s and 7p orbitals of An are relatively small; hence, multiple oxidation state are possible, and covalent bonding interaction with other atoms is possible
- increase in the stability of the lower oxidation states of the heavier An relative to the Ln may be the result of stronger binding of the 5f electrons in the elements near the heavy end of the An series

Actinide Oxidation States

4^{+}g			5f1	5f2	5f3	5f4	5f5	5f6	5f7	5f8	5f9	5f10	(5f11)	(5f12)	(5f13)
3^{+}aq			5f2	5f3	5f4	5f5	5f6	5f7	5f8	5f9	5f10	5f11	(5f12)	(5f13)	(5f14)
2^{+}g	7s	5f6d	5f26d	5f3d	5f5	5f6	5f7	5f8	5f9	5f10	5f11	5f12	(5f13)	(5f14)	(5f147s2)
0	6d 7s2	6d2 7s2	5f2 6d 7s2	5f3 6d 7s2	5f4 6d 7s2	5f6 7s2	5f7 7s2	5f7 6d 7s2	5f9 7s2	5f10 7s2	5f11 7s2	5f12 7s2	(5f13 7s2)	(5f14 7s2)	(5f14 6d 7s2)
7+					◆	◆									
6+				■	◆	❒	◆								
5+			■	◆	■	❒	❒	◆							
4+		■	■	■	■	■	❒	❒	◆	◆					
3+	■	◆	◆	❒	❒	■	■	■	■	■	■	■	■	❒	■
2+										◆	◆	◆	❒	■	
An	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Importance: ■ > ❒ > ◆

5+ and 6+ Oxidation States:

4+g			5f1	5f2	5f3	5f4	5f5	5f6	5f7	5f8	5f9	5f10	(5f11)	(5f12)	(5f13)
0	6d 7s2	6d2 7s2	5f2 6d 7s2	5f3 6d 7s2	5f4 6d 7s2	5f6 7s2	5f7 7s2	5f7 6d 7s2	5f9 7s2	5f10 7s2	5f11 7s2	5f12 7s2	(5f13 7s2)	(5f14 7s2)	(5f14 6d 7s2)
7+					◆	◆							Importance: ■ > ❐ > ◆		
6+				■	◆	❐	◆								
5+			■	◆	■	❐	❐	◆							
4+		■	■	■	■	■	❐	❐	◆	◆					
3+	■	❐	❐	❐	❐	■	■	■	■	■	■	■	■	❐	■
An	Ac	**Th**	**Pa**	**U**	**Np**	**Pu**	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

A variety of oxidation states (2+ to 7+) in aqueous solution possible, but the light actinides in aqueous acidic solutions are in III, IV, V and VI oxidation states.

The 5+ oxidation state is well established for the elements Pa through Am; and the 6+ state in the elements U through Am.

The close proximity of the energy levels of the 7s, 6d, and 5f electrons almost guarantees multiple oxidation states for the actinide ions in the first half of the actinide series.

The multiplicity of oxidation states, coupled with the hydrolytic behavior of the ions, make the chemical behavior of the elements **from Pa to Am among the most complex of the elements** in the periodic table.

2+ and 3+ Oxidation States

3+aq			5f2	5f3	5f4	5f5	5f6	5f7	5f8	5f9	5f10	5f11	(5f12)	(5f13)	(5f14)
2+g	7s	5f6d	5f26d	5f3d	5f5	5f6	5f7	5f8	5f9	5f10	5f11	5f12	(5f13)	(5f14)	(5f147s2)
3+	■	◆	◆	❐	❐	■	■	■	■	■	■	■	■	❐	■
2+										◆	◆	◆	❐	■	
An	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

While trivalent species are typical for the trans-Pu actinides, the lighter actinides are less stable in trivalent oxidation state.

In acidic solutions:

- U(III) is oxidized by H_2O
- Np(III) is oxidized by O_2 dissolved in H_2O
- Pu(III) is stable, but easily oxidized to Pu(IV) by a variety of mild oxidants.
- Th and Pa do not even exhibit the trivalent state in solutions. Stable Th(III) has been reported only in organometallic compounds.

- Stable No(II) reflects the stability of the full 5f shell (5f14)
- Except for No (II), all actinide divalent species are of only transient stability, having only been observed in pulse radiolysis studies; Am(II), Cm(II), and Cf(II) have half-lives of the order of 5–20 msec.
- The 2+ oxidation state first appears at Am in a few solid compounds and then at Cf in the second half of the series.

Tetravalent An (4+):

4+g			**5f1**	**5f2**	**5f3**	**5f4**	**5f5**	**5f6**	**5f7**	**5f8**	**5f9**	**5f10**	**(5f11)**	**(5f12)**	**(5f13)**
4+		■	■	■	■	■	❒	❒	◆	◆					
3+	■	◆	◆	❒	❒	■	■	■	■	■	■	■	■	❒	■
An	Ac	**Th**	**Pa**	**U**	**Np**	**Pu**	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

The tetravalent species also can be considered transient, since a stable 4+ state is observed only for elements from Th through Pu and then for Bk.

Formation of Bk(IV) is associated with enhanced stability of the half-filled 5f configuration (5f7), while the No(II) state reflects the stability of the full 5f shell (5f14).

- Am(IV) in aqueous media must be stabilized by very strong complexing agents such as carbonate, phosphate or fluoride. With higher (>3) oxidation states of Am, unique options are available for potential Am/Ln group separations.
- The Cm(IV) state is confined to a few solid compounds, particularly CmO_2 and CmF_4, and appears to be present in a stable complex ion that exists in concentrated cesium fluoride solution.
- The Cf(IV) state is limited to the solid compounds CfO_2, CfF_4, complex oxide $BaCfO_3$, and oxidation with tungstophosphate.

Colors of Actinide Ions in Aqueous Solutions

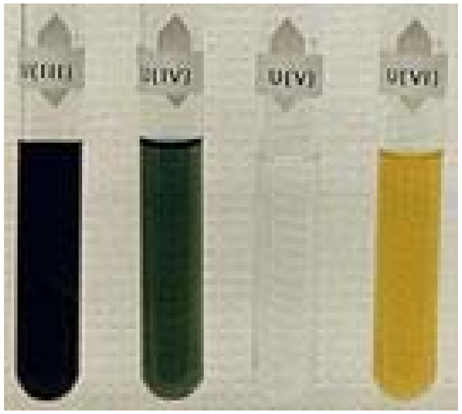
Element	**M^{3+}**	**M^{4+}**	**MO_2^+**	**MO_2^{2+}**	**$MO_4(OH)_2^{3-}$ (alkaline soln.)**
Ac	colorless				
Th		colorless			
Pa		colorless	colorless		
U	red	green	unknown	yellow	
Np	blue to purple	yellow-green	green	pink to red	dark green
Pu	blue to violet	tan to orange	reddish-purple	yellow to pink-orange	dark green
Am	pink or yellow	unknown	yellow	rum-colored	
Cm	pale green	unknown			
Bk	green	yellow			
Cf	green				

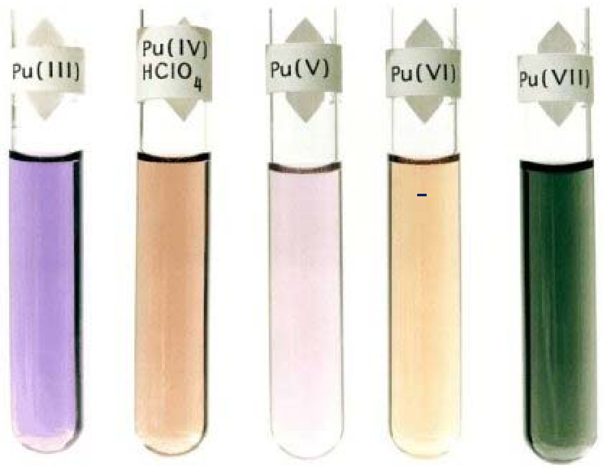
Colors of Actinides

Light actinides (U, Np, Pu) have very rich redox chemistry and also a very colorful solution chemistry, consequently, the spectroscopic methods are quite developed for actinide studies.

Uranium

Aqueous solutions of U (III, IV, V, VI) salts.



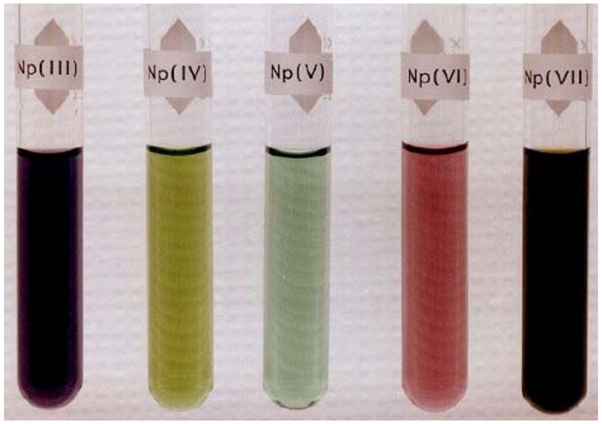


Neptunium:

Colors of the different oxidation states of Np, in 1 M $HClO_4$. (Np(V) is in $NaClO_4$ at pH=7, Np(VII) is in 2.5 M NaOH.)

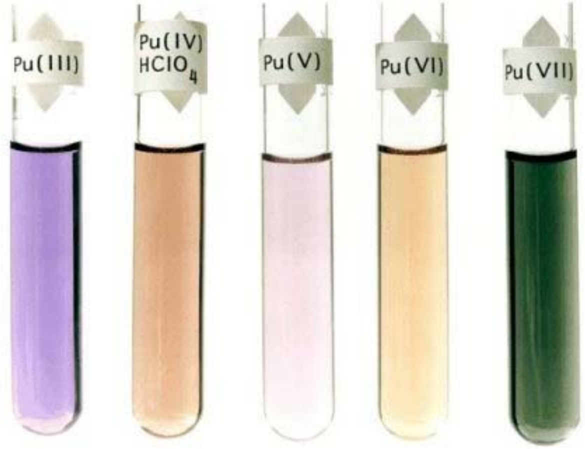
Plutonium:

Colors of the different oxidation states of plutonium, in 1 M $HClO_4$. (Pu(V) is in $NaClO_4$ at pH=7, Pu(VII) is in 2.5 M NaOH.)

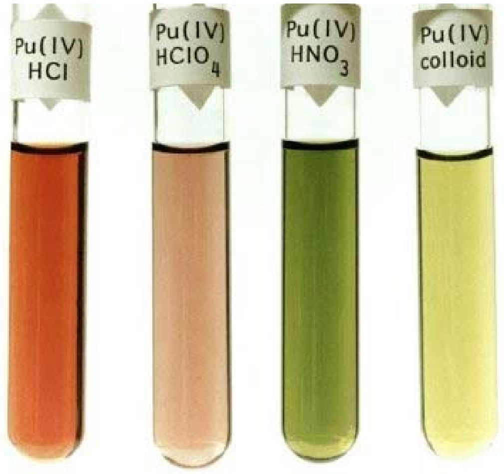


Adopted from: Actinide Research Quarterly ; awq.lanl.gov , available at http://en.wikipedia.org/wiki/Actinide#cite_note-g1263-80.

Beautiful Colors of Plutonium



Each oxidation state has its own characteristic color (upper figure), which is also influenced by interaction with other species in solution (figure below).



Uncomplexed Pu(IV), slightly brownish in HClO4 solution (non-complexing medium) changes its color from red through green to almost yellow when it is dissolved in chloric acid (red), nitric acid (green) or neutral solution (colloid).

Adopted from: Actinide Research Quarterly ; awq.lanl.gov , available at http://en.wikipedia.org/wiki/Actinide#cite_note-g1263-80.

Introduction to Speciation of Actinides

Effective Cationic Charge

Ionic Radius

Actinide Ions in Aqueous Solution:

Actinides in the same oxidation state have essentially the same coordination environments, and in aqueous solutions (at a pH < 3) they appear in four main structural ionic types:

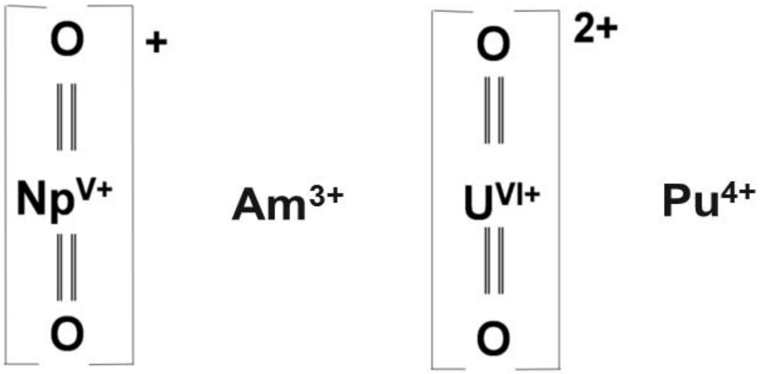
+III and +IV: simple cations **An^{3+}** or **An^{4+}**; with a high charge density, they show a strong inclination to solvation, hydrolysis, and polymerization.

+V and +VI: dioxocations **AnO_2^+** and **AnO_2^{2+}**; oxygenated species known as ACTINYL ions, formed by hydrolysis of metal cation of high oxidation state in the hydration shell. The effective charge is decreased by forming covalent bonds between two oxygen atoms **$O{=}An{=}O$**.

The 7+ oxidation state, found in some compounds of neptunium and plutonium in alkaline aqueous solution, contains in some cases **tetraoxo-species $MO_4(OH)_2^{3-}$**.

In acid solution, actinide ions in the 7+ oxidation state oxidize water rapidly. The existence of Am(VII), even in alkaline media, is discussed.

Actinyl Cations in Aqueous Solutions



$\left[\begin{matrix} O \\ \| \\ Np^{V+} \\ \| \\ O \end{matrix}\right]^{+}$ Am^{3+} $\left[\begin{matrix} O \\ \| \\ U^{VI+} \\ \| \\ O \end{matrix}\right]^{2+}$ Pu^{4+}

Formal (gross) charges
of actinide cations

- Actinyl ions $[O=An^{5+}=O]^{+}$ and $[O=An^{6+}=O]^{2+}$ are symmetrical and linear units.
- These dioxocations are very stable ionic species, persisting as a distinct species through many chemical transformations (e.g. , ion-exchange, complexation, extraction, or precipitation to solid phase).
- Crystallographic studies have shown that in solids, their ligands are typically in an equatorial plane perpendicular to the O=An=O axis.
- The An-O bonds in AnO_2^{+} (An(V) = Pa, U, Np, Pu, Am) are weaker than in the actinyl ions AnO_2^{2+} of the An(VI). [reason: 6>5].
- There is a regular decrease in the strength of the An–O bond in the actinyl ions with increasing atomic number from U to Am.
- Actinyl ions are only found for 5 actinides: Pa, U, Np, Pu, and Am. However, the actinyl ions of Am only appear under highly oxidizing conditions.

Strength of Complexes

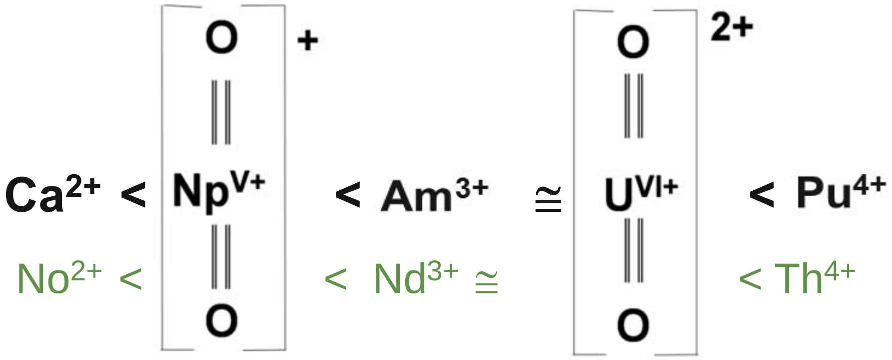
- Ionic radii of An are relatively large, and their charge densities are not as high as for smaller metal cations of corresponding oxidation state; hence, they never bind more than two oxygen atoms, and do not form oxoanions such as $An^{v}O3^{-}$ or $An^{vi}O4^{-}$, respectively.

- The bonds between the actinide cations and the ligands in the equatorial plane are considerably stronger than would be indicated by their formal charge of +1/+2.

- The effective cationic charges of both the actinyl(V) and actinyl(VI) ions, larger than their overall, formal charge, suggest that the oxygen atoms of both $O{=}An^{5}{=}O$ and $O{=}An^{6}{=}O$ cations retain a partial negative charge .

- The values of the effective charge, determined experimentally (Choppin at al, 1984) have been confirmed by theoretical calculations. (Choppin, Jensen, 2006).

Effective Cationic Charge of Actinides



$$Ca^{2+} < \left[O{=}Np^{V+}{=}O\right]^{+} < Am^{3+} \cong \left[O{=}U^{VI+}{=}O\right]^{2+} < Pu^{4+}$$

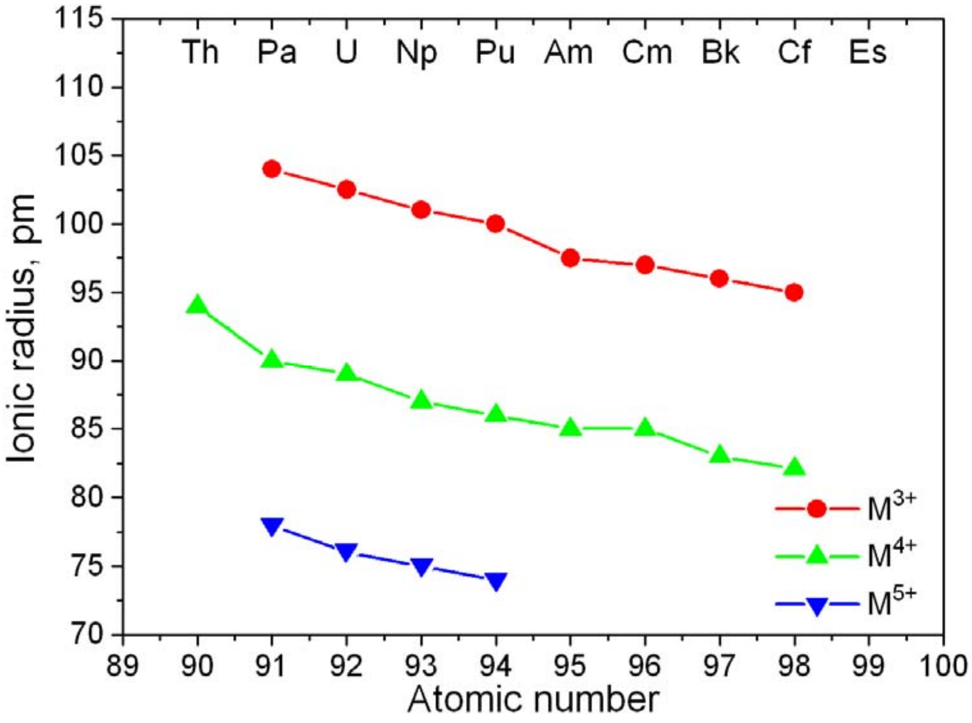
$$No^{2+} < \quad < Nd^{3+} \cong \quad < Th^{4+}$$

Metal cation:	**M^{2+}**	**AnO_2^{+}**	**An^{3+}**	**AnO_2^{2+}**	**An^{4+}**
Effective Cationic Charge*	**2.0**	**2.2**	**3.0**	**3.2**	**4.0**
Overall Formal (“gross”) Charge of Cation	2	1	3	2	4
Metal Cation Valence (oxid state)	2	5	3	6	4

Assuming completely electrostatic bonding (except for the actinyl oxygens) and that the effective charges of Ca^{2+}, Nd^{3+}, Am^{3+}, and Th^{4+} are equal to their formal charges, the effective charge “felt” by ligands bound to pentavalent and hexavalent actinyl cations were estimated empirically by G. Choppin and coworkers*.

*Choppin, Jensen (2006), from: Choppin and Unrein (1976) , Choppin (1983), Choppin and Rao (1984)

Actinide Contraction



The plot of ionic radii of actinides in the oxidation states +Ill, +IV and +V.

Figure adopted from:
http://en.wikipedia.org/wiki/Actinide#cite_note-g1263-80 from Greenwood, N. N.; Earnshaw, A. (1997). *Chemistry of the Elements* (2nd ed.). Butterworth-Heinemann.

Actinide contraction is analogous to the lanthanide contraction.

REASON:

With increase of atomic number, the nuclear charge increases and attracts more effectively the outer electron shell ⇛ ionic radii of the same oxidation states systematically decrease.

EFFECT:

Smaller radius causes larger cationic charge density ⇛ more rapid hydrolysis and complex formation.

USE:

An(III) and Ln (III) are separated from each other mainly on the basis of difference in ionic radius.

Ionic Radius and Oxidation State of An

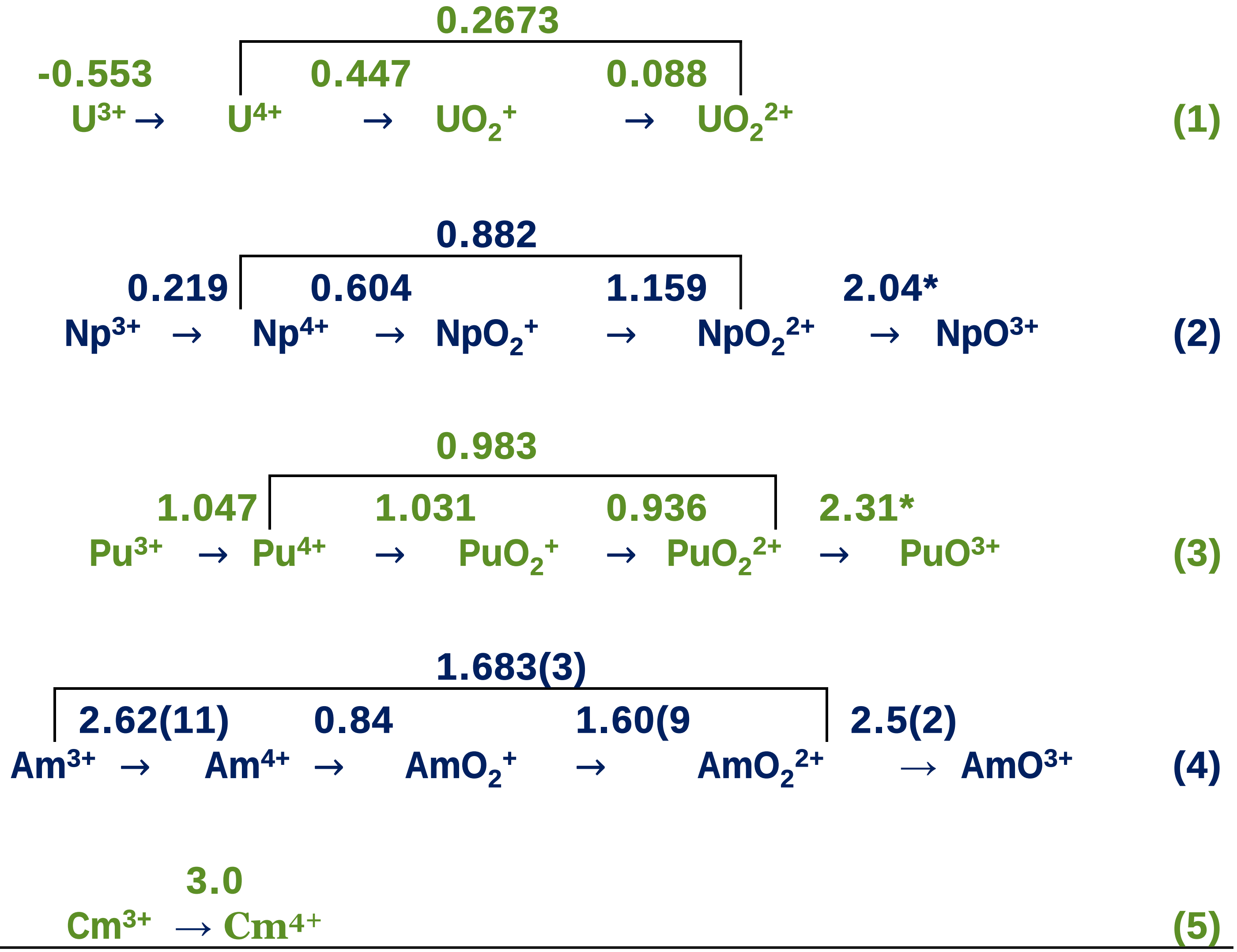
- Besides the oxidation state, ionic radius of metal plays very important role in speciation of actinides.
- The ionic radii of actinides in the same oxidation state systematically decrease with increase of atomic number.   This decrease, known as the actinide contraction, is analogous to the lanthanide contraction.
- With increase of atomic number, the nuclear charge increases and attracts more effectively the 5f electron shell – that ionic radii of the same oxidation states systematically decrease .
- Decrease in the ionic radius affects the hydrolysis and complex formation of the actinides. The smaller the radius, the more readily the ion hydrolyzes and forms complexes.
- Actinide ions in the same oxidation state behave in a closely similar way – they can serve as chemical analog for each other (e.g., UO_2^{2+} for PuO_2^{2+}, NpO_2^{+} for PuO_2^{+}, Am^{3+} for Pu^{3+}, etc.).

Reactivity of Actinides

Reactivity of Actinides

- The solution chemistry of the actinide elements has been investigated in both aqueous and selected organic solutions.
- A variety of oxidation states (2+ to 7+) in aqueous solution possible, but the light actinides in aqueous acidic solutions are in III, IV, V and VI oxidation states.
- The stability of a particular oxidation state is quite variable, and for some actinides (Np, Pu) several oxidation states can coexist in the same solution.
- Pu – the most evident example: there are small differences in the redox potentials of Pu(III), Pu(IV), Pu(V), and Pu(VI) over a range of pH values:

Redox Potentials of An



0.2673

-0.553 0.447 0.088

$U^{3+} \rightarrow U^{4+} \rightarrow UO_2^{+} \rightarrow UO_2^{2+}$ (1)

0.882

0.219 0.604 1.159 2.04*

$Np^{3+} \rightarrow Np^{4+} \rightarrow NpO_2^{+} \rightarrow NpO_2^{2+} \rightarrow NpO^{3+}$ (2)

0.983

1.047 1.031 0.936 2.31*

$Pu^{3+} \rightarrow Pu^{4+} \rightarrow PuO_2^{+} \rightarrow PuO_2^{2+} \rightarrow PuO^{3+}$ (3)

1.683(3)

2.62(11) 0.84 1.60(9 2.5(2)

$Am^{3+} \rightarrow Am^{4+} \rightarrow AmO_2^{+} \rightarrow AmO_2^{2+} \rightarrow AmO^{3+}$ (4)

3.0

$Cm^{3+} \rightarrow Cm^{4+}$ (5)

The scheme of standard redox potentials (V) for U, Pu, Np, Am and Cm in 1M HCl or 1M HClO4(*) [Edelstein, 2006]

Redox Chemistry in Aqueous Solutions: Pu

- The reduction potentials for the four common oxidation states of plutonium (III-VI) under acidic conditions are all near 1 V, and as a result, all four oxidation states can coexist in aqueous solutions.
- The equilibrium concentrations of Pu species existing simultaneously will be determined by these equations:

$$Pu^{4+} + PuO_2^{+} \leftrightarrow Pu^{3+} + PuO_2^{2+} \qquad (1)$$

$$Pu^{4+} + 2H_2O \leftrightarrow Pu^{3+} + PuO_2^{+} + 4H^{+} \qquad (2)$$

- The equilibrium constant for Equation 2 is dependent on $[H^+]^4$; hence, the position of this disproportionation equilibrium changes significantly with acidity.

Redox Chemistry in Aqueous Solutions: Np

The redox couples in which only an electron is transferred, e.g., Pu^{3+}/Pu^{4+} or NpO_2^{+}/NpO_2^{2+}:

- are electrochemically reversible
- redox reactions are rapid

Redox reactions that involve forming or rupturing of the An-O bond, e.g., Np^{4+}/NpO_2^{+} and Pu^{4+}/PuO_2^{2+}:

- are not electrochemically reversible
- have a slower reaction rate because of the barrier introduced by the subsequent reorganization of the solvent shell and also because some of these are two-electron reductions

Proton and Redox Chemistry in Aqueous Solutions:

The role of proton in redox processes is principal; for example:

- Disproportionation of Np is appreciable only for the Np(V) oxidation state, and the reaction is favored by high concentration of acid:

$$2NpO_2^{+} + 4H^{+} \leftrightarrow Np^{4+} + NpO_2^{2+} + 2H_2O \tag{3}$$

- Both the tetravalent and hexavalent cations, having higher effective cationic charge, are more strongly complexed by ligands, thus the disproportionation reaction will be accelerated toward completion by an addition of complexing agents.

- Obviously, the synproportionation reaction will be promoted by lower acidity of solution:

$$Np^{4+} + NpO_2^{2+} + 2H_2O \leftrightarrow \ 2NpO^{2+} + 4H^{+} \tag{4}$$

Redox Chemistry in HNO_3 Solutions

- The oxidation of Np(V) by nitrate ion is favored by high HNO_3 and low concentrations of nitrous acid (HNO_2), and vice versa, Np(VI) is rapidly reduced to Np(V) at high concentrations of nitrous acid:

$$2NpO_2^+ + NO_3^- + 3H^+ \leftrightarrow 2NpO_2^{2+} + HNO_2 + H_2O$$

- It was found that oxidation of Np(V) to Np(VI) by nitric acid is very slow, but it can be accelerated by small concentrations of nitrous acid (Siddall, Dukes, 1959).
- However, under these conditions, the $\cdot NO_2$ radical is generated by synproportionation of HNO_2 and HNO_3:

$$H^+ + NO_3^- + HNO_2 \leftrightarrow 2NO_2 + H_2O$$

- Then, the accelerated oxidation of pentavalent neptunium may be due to reaction with the $\cdot NO_2$ radical, which actually acts as an oxidizing agent with Np(V), rather than the nitrous acid itself (Mincher, 2012):

$$2NpO_2^+ + 2H^+ + 2\ \cdot NO_2 \leftrightarrow 2NpO_2^{2+} + 2HNO_2$$

Self-Radiolysis in Aqueous Solutions

Self-radiolysis may greatly affect the chemical equilibrium, redox and speciation of actinides in their solutions. For example, ^{239}Pu:

$$Pu^{4+} \sim\longrightarrow Pu^{3+}$$

$$PuO_2^{2+} \sim\longrightarrow PuO_2^{+}$$

$$Pu^{4+} + PuO_2^{+} \leftrightarrow Pu^{3+} + PuO_2^{2+}$$

$$2PuO_2^{+} + 4H^{+} \leftrightarrow Pu^{4+} + PuO_2^{2+} + 2H_2O$$

- In acidic solution of ^{239}Pu, the self-radiolysis results in changes of the oxidation state of PuO_2^{2+} which "degrades" by being reduced to Pu^{4+} at a rate of approximately 1.5% per day.
- Intermediate Pu(V) is unstable in acidic solutions; it disproportionates to produce Pu^{4+} and Pu(VI); may reproportionate as well.
- Hydrogen peroxide, produced by higher concentrations of ^{239}Pu in a sufficient amount, may decrease the concentration of Pu(IV) by forming a precipitate of plutonium peroxide.

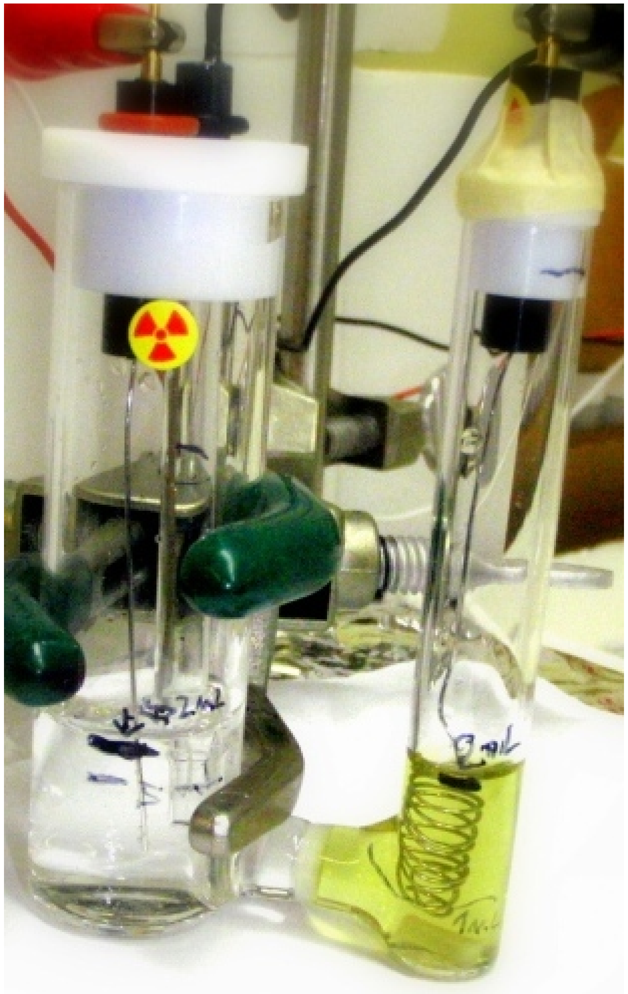
Unusual Oxidation States

Generating an unusual oxidation states opens new separation opportunities:

- For example, typically trivalent Am, if oxidized to hexavalent Am(VI), behaves as a chemical analog of UO_2^{2+}, and can be separated from lanthanides by extraction with PUREX solvent (AmO_2^{2+} +NO_3^- + TBP).

Heptavalent An:

- Increase from 1 M acid to 10 M base causes a change in redox potential of 2 V and makes possible the oxidation of Np(VI) to Np(VII).
- Also Pu(VII) can be prepared only in strongly basic solution.



Hexavalent neptunium (15 mM) prepared electrolytically in 4M HNO3 in H-cell with a Pt electrode (OSU, Nov 2009).

Speciation of Actinides:

Coordination
Complexation
Hydrolysis

Coordination of Actinide Ions in Solutions

- The rich chemistry of lighter actinides, from Pa to Am, is based on their:
  - multiple oxidation states,
  - hydrolytic behavior of their cations and,
  - strong coordination of organic ligands

- Coordination can be split into two groups: **lower oxidation** state (di-, tri- and tetravalent) and **higher oxidation** state (penta-, hexa- and heptavalent) ions.

- The **coordination number** (CN) and **geometry** of their aqueous complexes is determined by the electronic configuration and steric size and shape of the ligands.

- While **ionicity** is the predominant characteristic of both lanthanide and actinide bonding, an appreciable **covalency**, stronger in the actinide bonds, has been confirmed by many spectroscopic studies.

- **Covalency** is attributed to the **6d orbital interactions** with the ligands, which are significantly stronger than the 5f interactions.

Aqueous An Coordination Chemistry

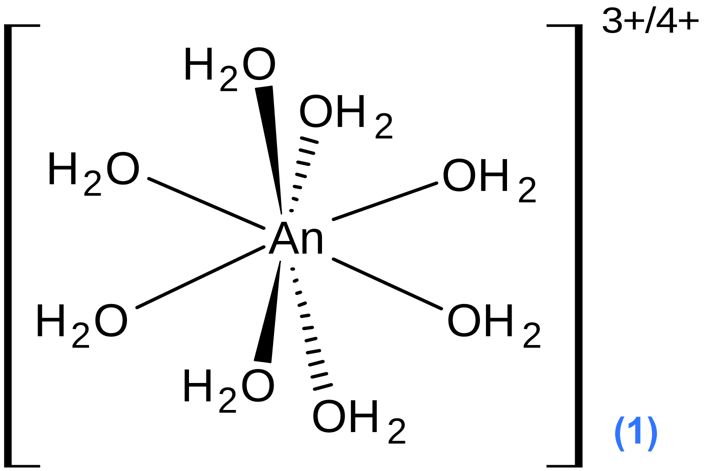
- The actinide ions are relatively large cations with high coordination numbers. Coordination numbers range from **6** to **14**.
- Because of cation contraction, their ionic radii range. With increasing atomic number, they decrease from 0.112 to 0.095 nm for An(III) and from 0.094 to 0.082 nm for An(IV).
- For a majority of the actinides, the exact numbers of water molecules that are bound to the metal centers in the hydrated metal ions are still controversial.
- The uncertainty in the structures can be explained by the limited number of crystal structures that exist for their aquo complexes, related to the difficulty in crystallizing materials from aqueous solutions.

Hydration of Actinides$^{III/IV}$

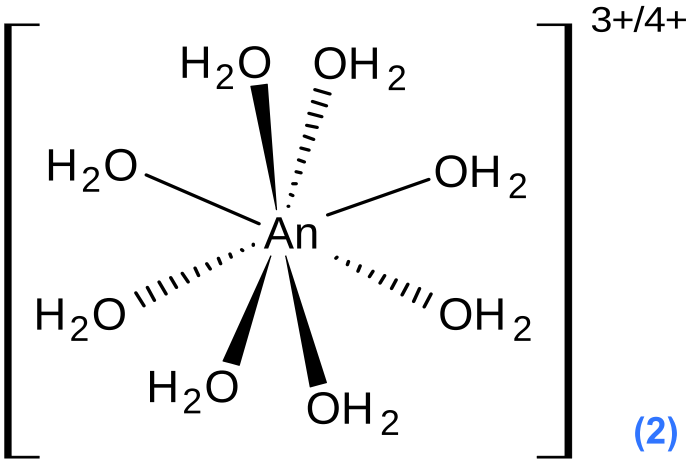
- Structures with 9–12 molecules of water have been proposed for **tetravalent** actinides in aqueous solutions.
- In general, the most accepted values for the number of H_2O molecules bound to the metal center are 10 for Th and 9 for U to Pu.
- The An-OH_2 distances in these ions range from 0.25 to 0.24 nm.

Typical coordination structures of $An^{3/4+}$

Structures (1-3) are octa-coordinate with a cubic, square antiprism, and a bicapped trigonal prism arrangement of the ligands (water molecules), respectively.



(1)



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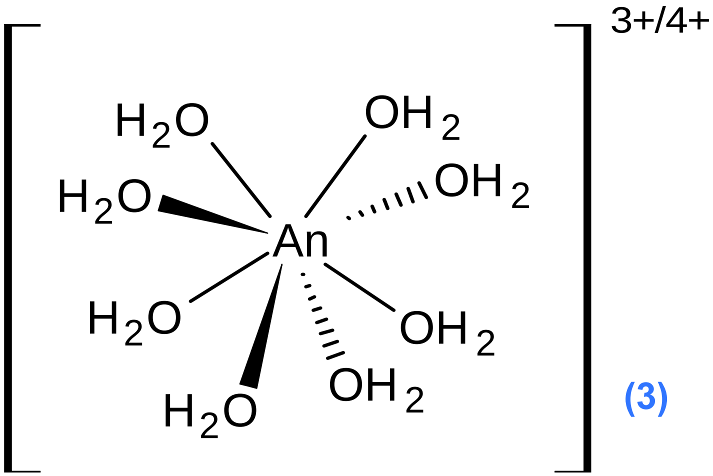
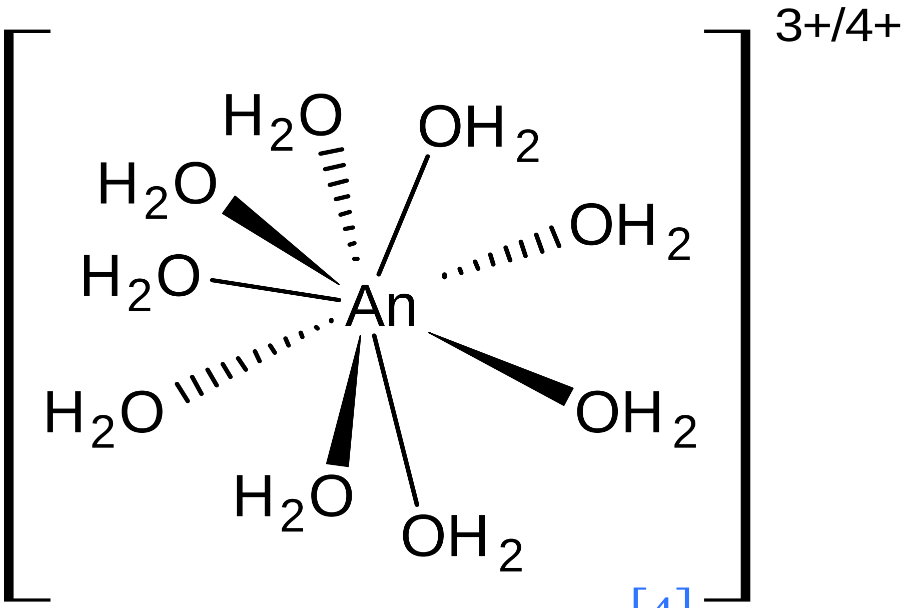
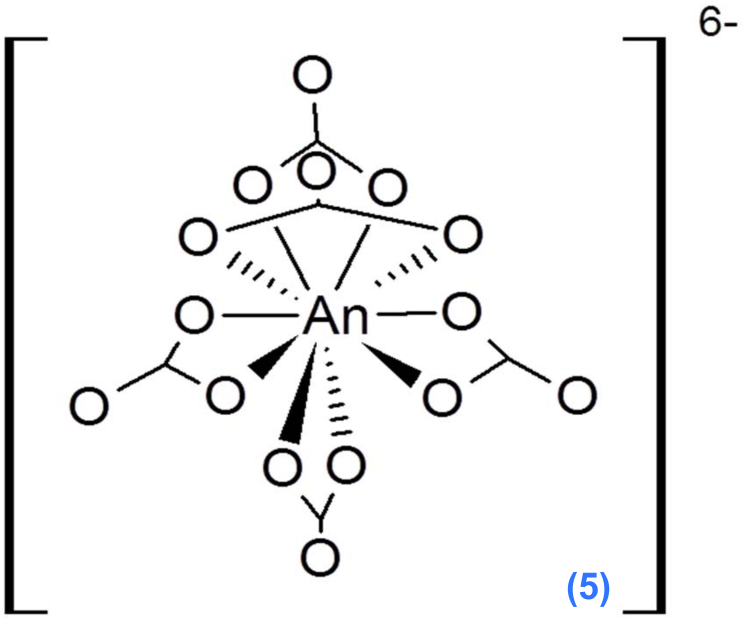


(3)

Typical coordination structures of An$^{3/4+}$



[4]



(5)

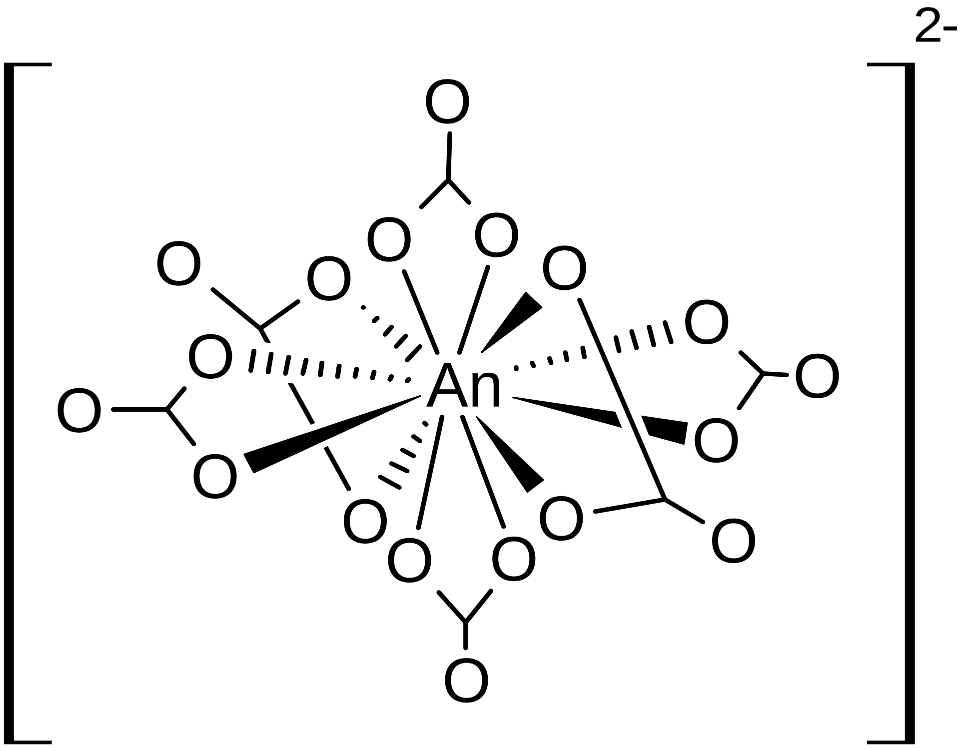
The nine-coordinate structure (4) is a tricapped trigonal prism.

Higher coordination numbers are observed with multidentate ligands, such as carbonate and nitrate.

The 0-coordinate species (5) include, e.g., anionic penta-carbonate species of An(IV) which has irregular geometry with two trans carbonate ligands at the axial sites and three nearly planar carbonate ligands in a pseudo-equatorial plane - remains the structure of dioxocation complexes of hexavalent actinides

An^{4+} coordination chemistry

- The hexanitrate anion $An(NO_3)_6^{2-}$ is extremely important in separation of actinides, for example plutonium, under conditions when other metals are in cationic form.
- Cation exchange resins have a strong affinity for the **hexanitrato species** $Pu(NO_3)_6^{2-}$.

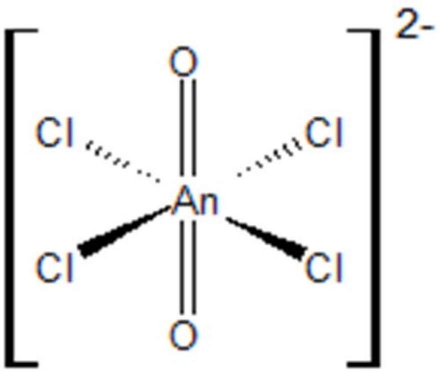


(6)

- Structure 6 represents the coordination geometry for this anion, which has six bidentate nitrate ligands, giving the central Pu^{4+} ion a **coordination number of 12**.

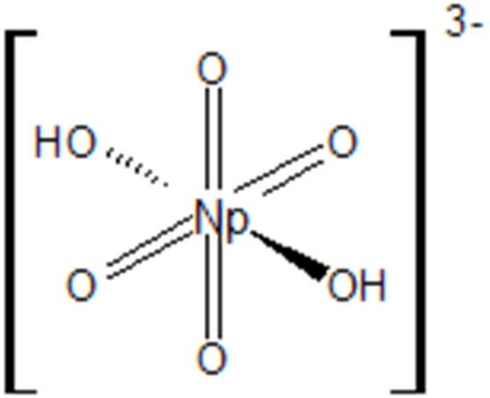
Actinyl Coordination Complexes

- Typical aqueous species of penta- and hexavalent actinides include the linear dioxo-unit **O=An=O** with two oxygen atoms positioned at 180º.
- An average An=O distance in dioxocations is larger for hexavalent actinides:
  - An(VI): 0.175-0.180 nm
  - An(V): 0.181-0.193 nm
- The structures of a variety of aqueous-based coordination complexes have been observed. Examples of tetragonal symmetry:



(9)

$[AnO_2Cl_4]^{2-}$



(10)

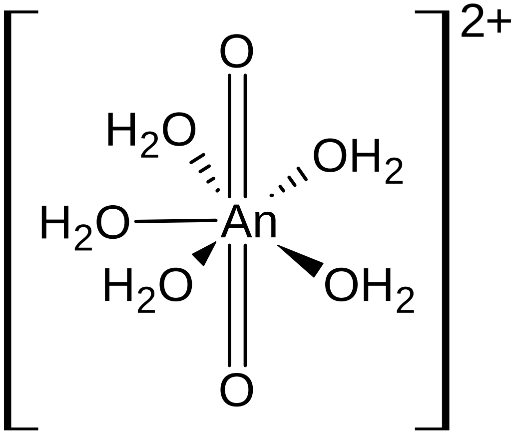
$[NpO_4(OH)_2]^{3-}$

Penta- and Hexavalent Actinides (cont.)

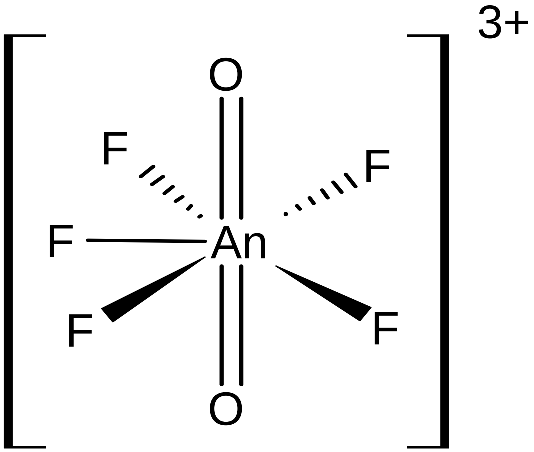
- The bonding for these ions has **significant covalency with the axial** An-O ligands, while the bonding for the majority of the ligands residing in the equatorial plane is primarily **ionic**.
- As a result of this **dual behavior** (covalency and ionicity) of the trans dioxo ions, the linear dioxo unit is unperturbed (with the exception of bond distance changes) in all of the aqueous-based complexes.
- The **coordination numbers** of the central actinide cation are defined by the equatorial size of ligands and their electronic properties.

Aqueous Coordination Complexes (cont.)

- The **penta-aqua** ion (A) and **pentafluoro-**complex (B) for the hexavalent actinides are 7-coordinate structures, prevalent in An chemistry.
- They are the highest coordination numbers achievable with all monodentate ligands; however, coordination complexes with eight atoms bound to the actinide are achievable.
- **$UO_2(H_2O)_5^{2+}$** (A) is the best studied aquo-ion:



penta-aquo- **(A)**



pentafluoro- **(B)**

Actinides - Lewis Acids

- Actinides in aqueous solution form aqua ions, of the general formula $An(H_2O)_n^{m+}$.
- The aqua ions undergo hydrolysis, to a greater or lesser extent. The first hydrolysis step is given generically as:

$$An(H_2O)_n^{m+} + H_2O \leftrightarrow An(H_2O)_{n-1}(OH)^{(m-1)+} + H_3O^+$$

- Thus, the aqua ion is behaving as an acid in terms of Brønsted-Lowry acid-base theory (Lewis acids).
- This is easily explained by considering the inductive effect of the positively charged metal ion, which weakens the O-H bond of an attached water molecule, making the liberation of a proton relatively easy.

Hydrolysis of Actinides

- +III: $Ac^{3+} < Pu^{3+} < Am^{3+} < Cm^{3+} < Bk^{3+}$ etc.
- +IV: $Th^{4+} < U^{4+} < Np^{4+} \sim Pu^{4+}$
- +V: $PaO_2^{+} > NpO_2^{+} < PuO_2^{+}$
- +VI: $UO_2^{2+} < PuO_2^{2+}$

For the same An, hydrolysis and complex formation increase in the order of the effective charge of the metal:

$AnO_2^{+} < An^{3+} < AnO_2^{2+} < An^{4+}$

Hydrolysis and Polymerization of $An^{3/4+}$

- **Trivalent** actinides form the hydrolysis products $AnOH^{2+}$, $An(OH)_2{}^{+}$, and An(OH)3, the last of which precipitates if the concentration of the actinide in solution is high enough.

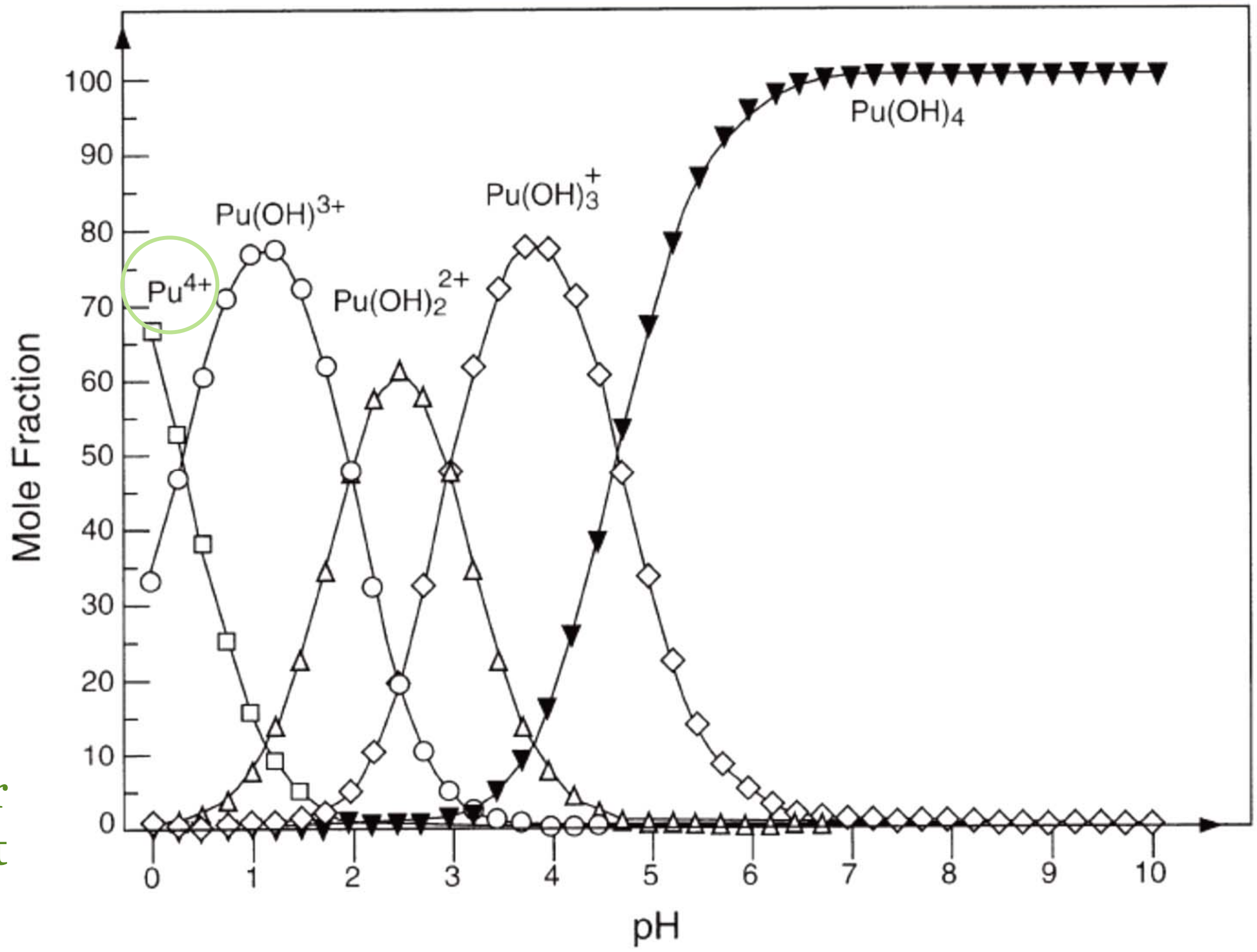
- **Tetravalent** actinides form the following products: $AnOH^{3+}$, $An(OH)_2{}^{2+}$, $An(OH)_3{}^{+}$, and $An(OH)_4$. Again, the last species will precipitate if the concentration of the actinide is, sufficiently high.

- Since actinides are least soluble at oxidation state +IV the precipitation of hydroxides takes place at very low concentrations.

- Hydrolysis of the tetravalent actinides commences even at pH 2- 3.

- Before precipitation occurs, the actinides form simple, monomeric An(OH)4 complexes and, as the concentration increases, also dimeric and polymeric complexes, such as $Th_2(OH)_2{}^{6+}$ and $Th_6(OH)_{15}{}^{9+}$.

Hydrolysis of Actinides



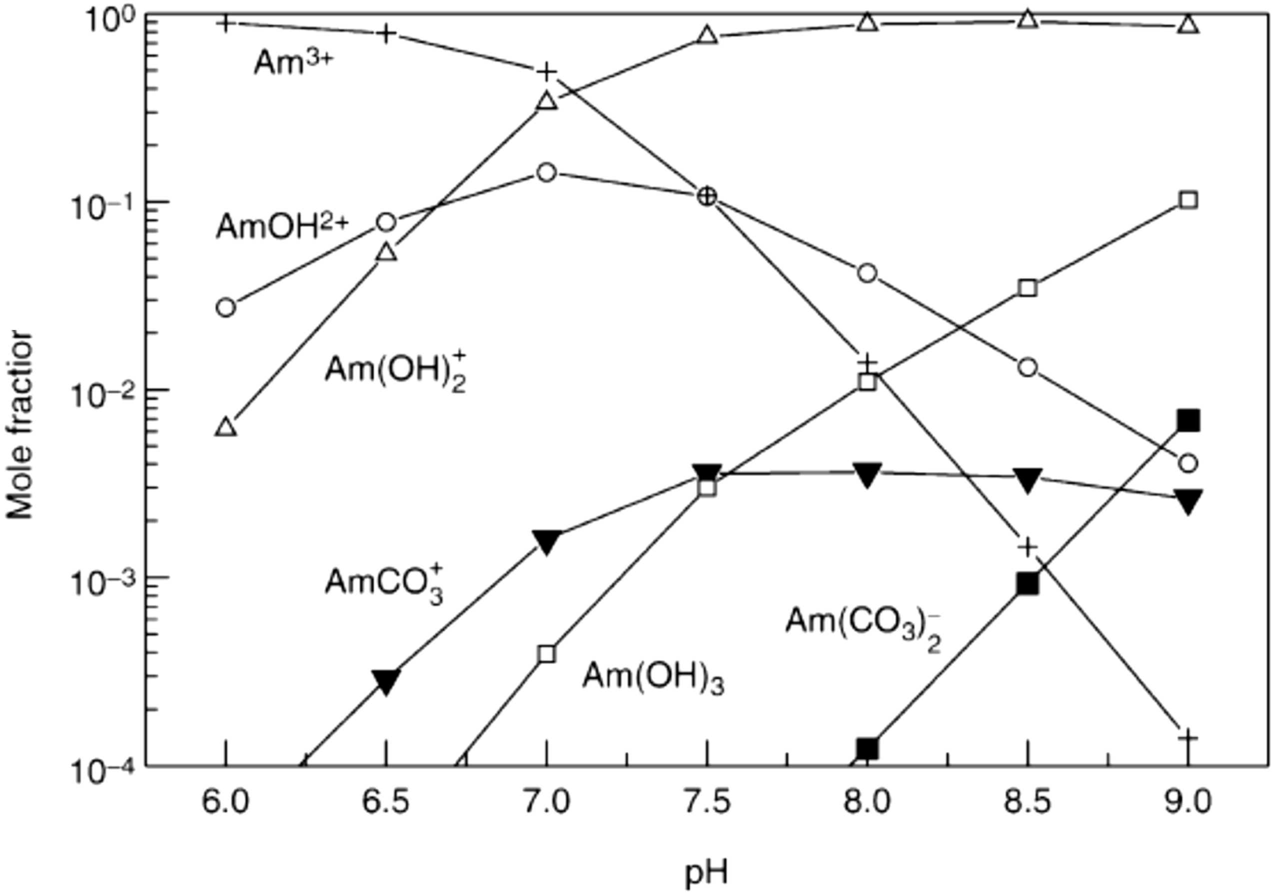
Fraction of mononuclear Pu(IV) hydrolysis product as a function of pH:

Already at pH 0.5, the concentrations of Pu_4^+ and $Pu(OH)^{3+}$ are almost equal.
With increasing pH, the fraction of hydrolyzed species increases rapidly, and at pH 4.5, Pu(IV) is evenly distributed between $Pu(OH)_3^+$ and $Pu(OH)_4$. At pH>7, all Pu is presented by $Pu(OH)_4$.

[Figure adopted from: Choppin, G. R., Czech J, Phys, **56**, Supplement D (2006), D13-D21].

Hydrolysis of Actinides(III)

Fraction of Am(III) species in water in equilibrium with atmospheric CO_2 as a function of pH.

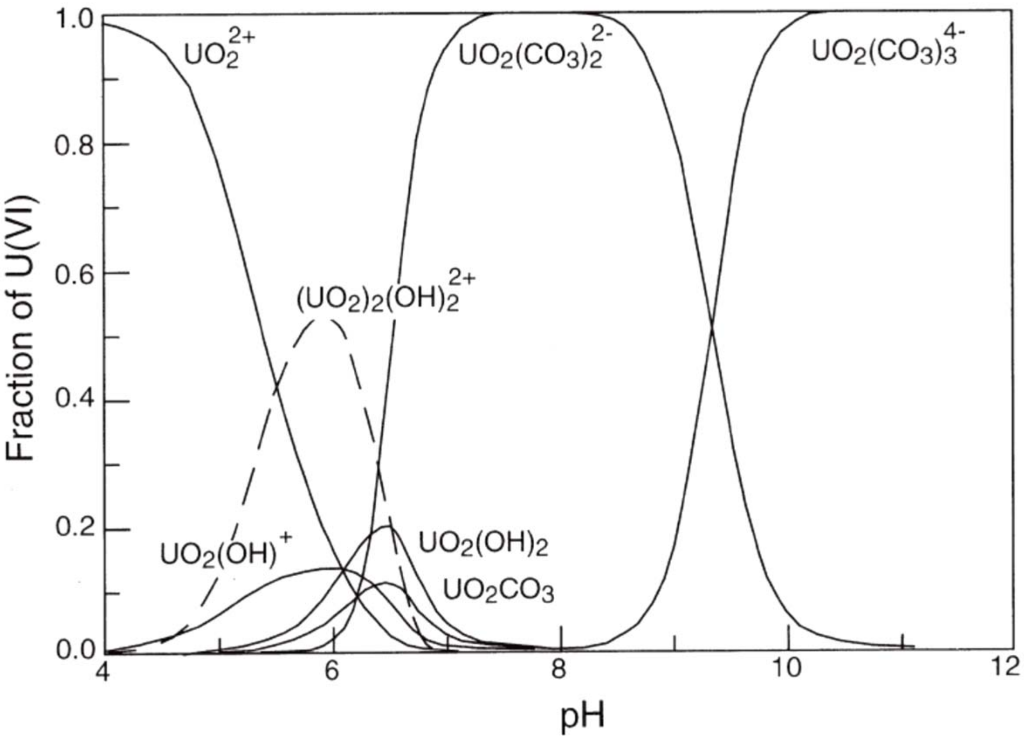


Carbonate is one of the most important ligands for actinides. In carbonate-free environments, $Am(OH)^{2+}$ and $Am(OH)2^{+}$ are the major species at pH 8.2, while, in carbonate-rich waters, $Am(CO_3)^+$ and $Am(CO_3)_2^-$ may also be significant components (Choppin, Jensen, 2006).

Hydrolysis of Actinides

Example:

Speciation of U(VI)O_2^{2+} in natural waters as a function of pH



- Hexavalent actinyl ions form the mono, di, and trimeric hydrolysis products AnO2OH+, (AnO2)2(OH)$_c$, and $(AnO_2)_3(OH)_5^+$.
- In carbonate-free environments, $UO_2(OH)^+$ and $(UO_2)_2(OH)_2^{2+}$ are the major species, while, in carbonate-rich waters (pH>7), $(UO_2)_2(CO_3)_2^{2-}$ and $(UO_2)(CO_3)_2^{2+}$ are the significant components.
- In oxic waters, U(VI) is present and is capable of forming more soluble species, e.g., UO2$(CO_3)_3^{4-}$, allowing greater migration rates.
- In anoxic waters, U(IV) forms insoluble, polymeric, mixed hydroxides and carbonates which sorb in the soil.

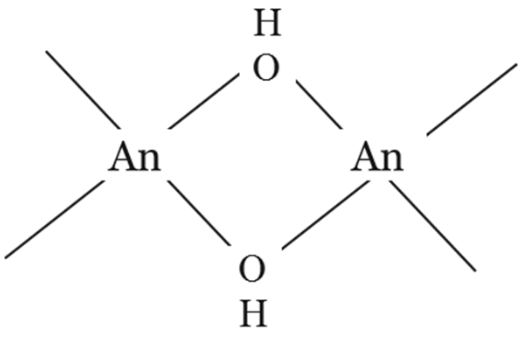
Hydrolysis and Polymerization of An

- The hydrolysis of polyvalent actinides is complex. Monomeric hydrolysis products are formed in dilute solutions.
- In the polymeric hydrolysis products, bonds are formed between metal atoms, hydrogen bonds through the OH group (An-OH-An) or covalent bonds through oxygen (An-O-An).
- Trend toward polymer formation is a function of the charge density of the actinide cation and drops in the order:

$$An^{4+} > AnO_2^{2+} > An^{3+} > AnO_2^{+}$$

$An^{VI}(OH)_4 + An^{VI}(OH)_4 + \ldots + An^{VI}(OH)_4 \rightarrow$

→ Hydroxide-bridged polynuclear complexes



Hydrolysis and Polymerization of An

- As the concentration increases, so does the proportion of polymers, and when the concentration is high enough, precipitation as hydroxide occurs.
- Besides monomers and polymers, hydrolysis products appear in solution as colloids, small 1-100 nm particles of nonstoichiometric composition, which are kept in suspension by Brownian motion.
- The slower rate of depolymerization compared with the rate of polymer formation is due to an equilibrium between hydroxo and oxo bridge formation with **aging**.
- The kinetics of polymerization–depolymerization becomes more complicated for Pu^{4+}.

Actinide Complexes in Aqueous Solutions

Actinide ions in their common solution oxidation states (3+ to 6+) are all hard Lewis acids, and their bonds with aqueous ligand are predominantly ionic. They have a great complex ability.

For a given cation, the strength of actinide complexes decreases in orders:

Monovalent inorganic ligands: $F^- > NO_3^- > Cl^- > ClO_4^-$

Divalent inorganic ligands: $CO_3^{2-} > C_2O_4^{2-} > SO_4^{2-}$

Trivalent inorganic ligands: PO_4^{3-} (organic phosphates for analytical separations by solvent extraction)

For a given ligand, the strength of actinide complexes increases with the "effective" cationic electrostatic charge of the actinide ions:

$$AnO_2^{+} < An^{3+} < AnO_2^{2+} < An^{4+}$$

Important Aqueous Actinides Species

Important Aqueous Actinide Species

- U (III, IV, V, VI): environmentally mobile, extractable, ubiquitous
- Np (III, IV, V, VI): environmentally mobile as NpO_2^+
- Pu (III, IV, V, VI): environmentally mobile as 4+-colloid polymer, extractable, co-exist in several oxidation states
- Am (III, IV, V, VI)
- Cm (III)

Most significant aqueous complex species ⇛ review ⇛

Wymer, R. G., Complexation Reaction, In: CRESP Introduction to Nuclear Chemistry and Fuel Cycle Separations, Vanderbilt U, Nashville, 2008

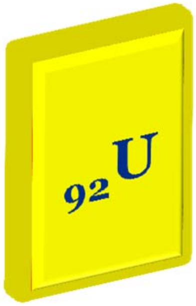
Aqueous Species of Uranyl:

U^{3+}, **U^{4+}, UO_2^{+}, UO_2^{2+} :**

UO_2^{+} is unstable and rapidly disproportionates into U^{3+} and UO_2^{2+}

UO_2^{2+} forms complexes:

- with many anions Cl^-, SO_4^{2-}, NO_3^-, PO_4^{3-}…
- very strong anion carbonate $[UO_2(CO_3)_3]^{4-}$
- anion acetate complexes $NaZn[UO_2(C_2H_3O_2)_3]^{4-}$
- nitrate complex that extracts with tributylphosphate as $UO_2(NO_3)_2.2TBP$
- diuranates ($Na_2U_2O_7$) when fused with ammonium and sodium hydroxides
- UO_2^{2+} precipitates as the peroxide $UO_4.2H_2O$
- UO_2^{2+} salts in acidic solutions are stable up 300°C



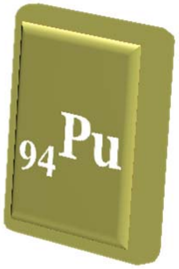
Plutonium Aqueous Species

Pu^{3+}, Pu^{4+}, PuO_2^{+}, PuO_2^{2+}:

- **Pu^{3+}** more stable than Np^{3+}:
  - fluoride and peroxide are insoluble
  - precipitated by carbonate and oxalate
- **Pu^{4+}** is the predominate species:
  - relatively easily oxidizes (to PuO_2^{2+}) or reduces (to Pu^{3+})
  - forms complexes with nitrate, peroxide, fluoride and chloride; nitrate and chloride form anionic complexes,
  - with oxalate and peroxide precipitate Pu^{4+}:

$$2\ H_2C_2O_4 + Pu(NO_3)_4 \leftrightarrow Pu(C_2O_4)_2 + 4\ HNO_3$$

  - nitrate complex that extracts with tributylphosphate as $Pu(NO_3)_4.2TBP$ or can be retained by extraction resin (TRU)



Plutonium Stable Aqueous Species

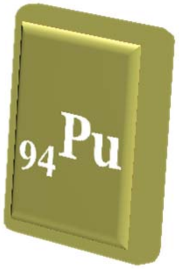
Pu^{3+}, Pu^{4+}, PuO_2^{+}, PuO_2^{2+}:

PuO_2^{+} more stable than Np^{3+}

- fluoride and peroxide are insoluble, precipitated by carbonate and oxalate

PuO_2^{2+}:

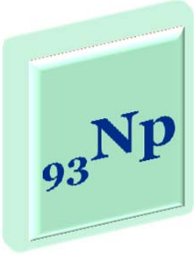
- forms complexes with carbonate, fluoride chloride, sulfates, etc.;
- similarly to UO_2^{2+}, its nitrate complex extracts with tributylphosphate as $PuO_2(NO_3)_2.2TBP$



Neptunium Stable Aqueous Species

Np^{3+}, Np^{4+}, NpO_2^{+}, NpO_2^{2+}:

- Np^{3+} behaves analogically to REE: precipitates with OH^-, PO_4^{3-}, and F^-
- Np^{4+} behaves like Pu^{4+}: hydrolyzes and forms stable SO_4^{2-}, F^-, $C_2O_4^{2-}$ complexes
- **NpO_2^{+}** is not easily complexed, precipitated or extracted
- NpO_2^{2+} behaves like UO_2^{2+} and PuO_2^{2+}, forms similar complexes and is extracted by organic solvents



Americium Aqueous Species

Am^{3+}, Am^{4+}, Am^{5+}, Am^{6+}

- Am^{3+} behaves analogically to REE: hydrolyzes, precipitates with OH^-, PO_4^{3-}, and F^-
- Am^{3+} forms stable complexes with Cl^-, NO_3^- CNS^-, and SiF_6^{2-}
- Am^{3+} forms a soluble carbonate complex, while Cm^{3+} doesn't, is not easily complexed, precipitated or extracted
- AmO_2^+ (Am=5+) forms insoluble $KAmO_2CO_3$ (Am^{3+} or Ln^{3+} don't)
- AmO_2^{2+} (Am=6+) is a strong oxidizer and very unstable in solutions

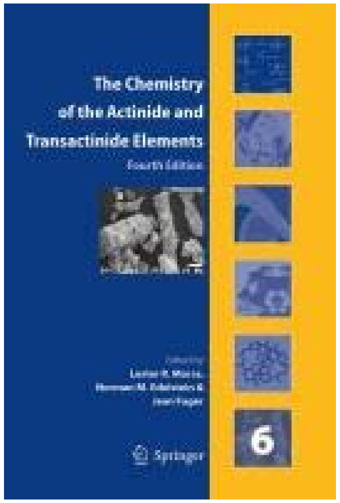
Curium Aqueous Species

- Cm(III) is the only oxidation state found normally in solution
- Cm(III) fluoride, oxalate, phosphate, iodate, and hydroxide are insoluble
- Cm(III) is very stable toward oxidation
- Cm(III) chemistry studies are hampered by radiolytic and heating effects
- CmF_3 can be precipitated from solution
- Cm(III) forms complexes with α-hydroxyisobutyrate and CNS that can be separated from Am, other TRU-elements, and rare earths using ion exchange

Conclusion

- It has been more than 65 years since the first reactors and huge chemical separation plants at Hanford were constructed.
- Since the first industrial-scale separations of Pu began in December 1944, fundamental studies of the chemistry, physics, and nuclear properties of Pu and other actinides have advanced understanding of their properties.
- Actinide studies also have had a significant influence on the development of all other aspects of chemistry, physics, and engineering.
- From the very beginning (M. Curie!), the separations methods (precipitation/ coprecipitation, ion-exchange, solvent extraction) have played a crucial role in the development of nuclear chemistry and discovery of transuranic elements.
- Rapid and reliable separation methods are key to solving problems related to use of radionuclides: spent nuclear fuel reprocessing, environmental monitoring, decontamination and radioecological problems.
- More element-specific chemistry you will learn in future web presentations and **recommended reading** (next slide).

Recommended Reading



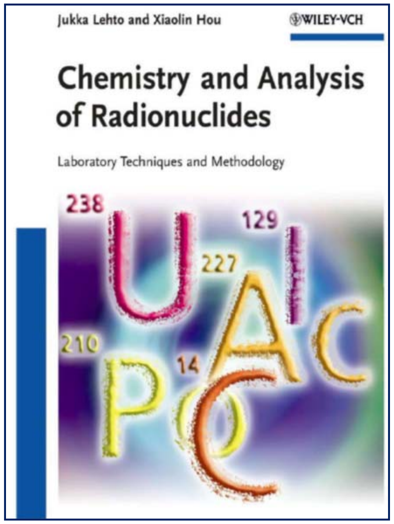
The Chemistry of the Actinide and Transactinide Elements
Fourth Edition

Edited by
Lester R. Morss,
Norman M. Edelstein &
Jean Fuger

Springer

Fundamental chemistry of actinides has been reviewed a few times during the past decade. The benchmark book in recent years is "***The Chemistry of the Actinide and Transactinide Elements***", a five volume series edited by Norman M. Edelstein, Jean Fuger and Lester R. Morss, and published by Springer, 2006, with the last, sixth volume added in 2010.

"Chemistry and Analysis of Radionuclides" (Wiley-CH, 2011) by Lehto, J. , Hou, X. is a great reference book written by chemists for chemists. It is a comprehensive guide to the important radionuclides as well as technique for their separation and analysis. It provides both the theoretical background and practical instructions on how to handle nuclear waste and radioactivity in the environment.



Jukka Lehto and Xiaolin Hou
WILEY-VCH

Chemistry and Analysis of Radionuclides

Laboratory Techniques and Methodology

What we have learned today

A brief review of aqueous chemistry of actinides, including:

- History, discovery
- Thermodynamic properties of actinides
- Oxidation state and redox behavior
- Effective cationic charge
- Hydration and coordination in aqueous solutions
- Hydrolysis

We wished to give you more, but our time is limited.
Other aspects, significant for this area of environmental and process chemistry, for example, complexation of actinide metals with important aqueous and organic ligands, effect of their structure and functional groups, will be discussed in future webinars, devoted to specific actinides and their chemistry, including applications for waste processing and environmental monitoring .

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