Actinide Chemistry

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II Letnia Szkoła Energetyki i Chemii Jądrowej

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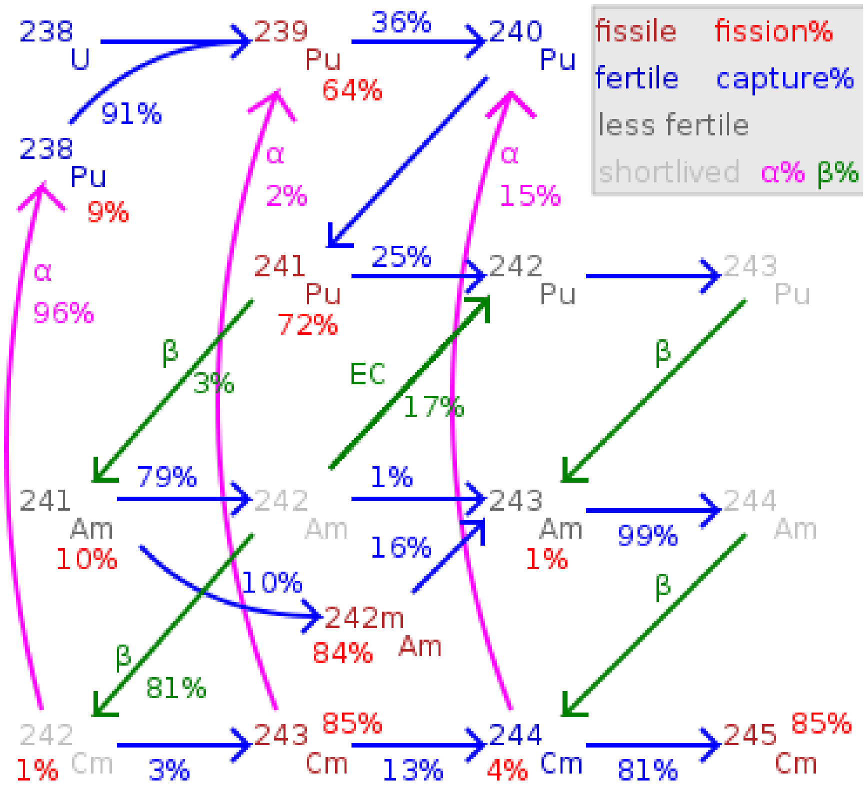
Actinide Chemistry

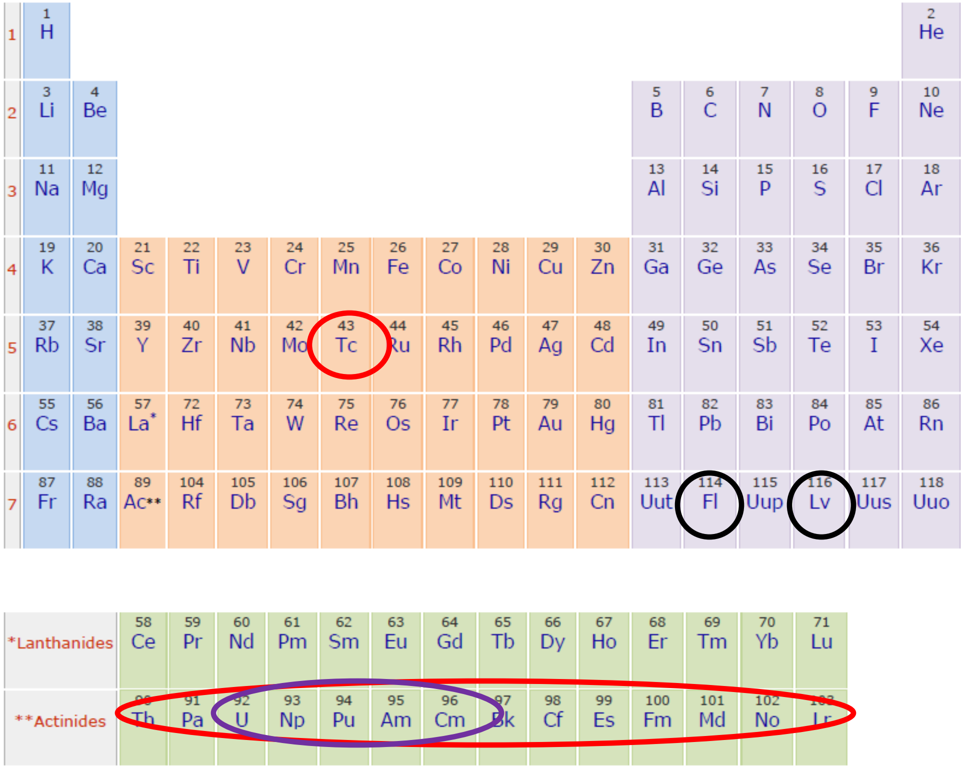
- Discovery of actinides
- Trends in actinide chemistry
    - Oxidation states
    - f-electron role
- Specific elements
    - Uranium
    - Neptunium
    - Plutonium
    - Americium
    - Curium
- Implications on nuclear fuel cycle



- Highlight role of f-electrons in actinide chemistry

Most likely solution stable oxidation state	4	5	6	5	4	3	3
Actinide	Th	Pa	U	Np	Pu	Am	Cm

Actinides in the Periodic Table



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											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	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
7	87 Fr	88 Ra	89 Ac**	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	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	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

- 118 total elements
  - 117 recently discovered
    → UNLV involved
  - 81 stable, 37 radioactive (≈ 30 % of all elements)
- Exploration of radioelements expands understanding of period trends

- Technetium
  - 2nd row transition element (d^7)
  - Macroscopic chemistry with ^{99}Tc
    - half life 2.1E5 a
  - Range of oxidation states
    - 7^+ to 1^-

- Actinides
  - Filling 5f electron shell
    - Different behavior from 4f
  - Range of isotopes available for chemistry
    - Different half lives
  - Varied oxidation states

Np synthesis

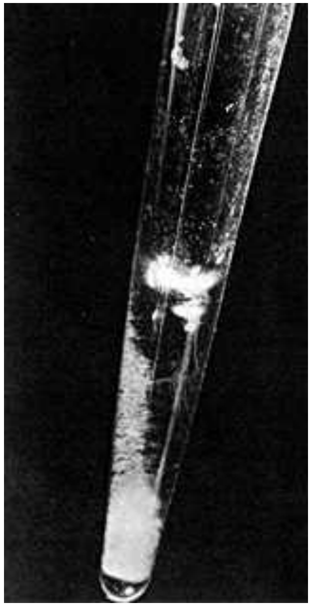
- Neptunium was the first synthetic transuranium element of the actinide series discovered
    - isotope ^{239}Np was produced by McMillan and Abelson in 1940 at Berkeley, California
    - bombarding uranium with cyclotron-produced neutrons
        - → ^{238}U(n,γ)^{239}U, beta decay of ^{239}U to ^{239}Np ($t_{1/2}$=2.36 days)
    - Chemical properties unclear at time of discovery
        - → Actinide elements not in current location
        - → In group with W
- Chemical studies showed similar properties to U
- First evidence of 5f shell
- Macroscopic amounts
    - ^{237}Np
        - → ^{238}U(n,2n)^{237}U
            - * Beta decay of ^{237}U
        - → 10 microgram

Pu synthesis

- **Plutonium was the second transuranium element of the actinide series to be discovered**
  - **The isotope ^{238}Pu was produced in 1940 by Seaborg, McMillan, Kennedy, and Wahl**
  - **deuteron bombardment of U in the 60-inch cyclotron at Berkeley, California**
    - **→ $^{238}U(^{2}H, 2n)^{238}Np$**
      - *** Beta decay of ^{238}Np to ^{238}Pu**
  - **Oxidation of produced Pu showed chemically different**
- **^{239}Pu produced in 1941**
  - **Uranyl nitrate in paraffin block behind Be target bombarded with deuterium**
  - **Separation with fluorides and extraction with diethylether**
  - **Eventually showed isotope undergoes slow neutron fission**

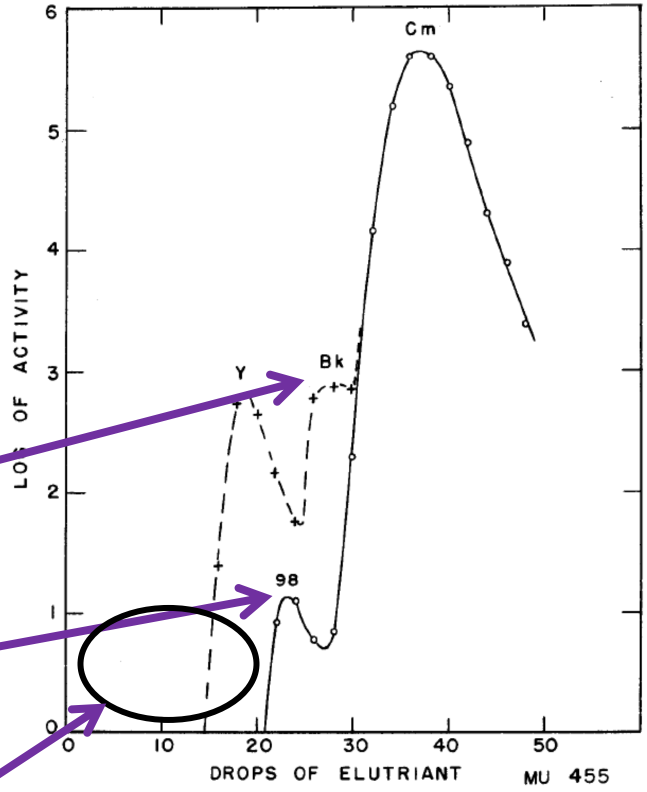
Am and Cm discovery

- First produce in reactor via neutron capture
  - neutron capture on ^{239}Pu
  - ^{239}Pu + n→ ^{240}Pu+n→ ^{241}Pu→ ^{241}Am+β^-
  - Also formed ^{242}Cm from successive neutron capture on ^{241}Am
- Direct production for discovery
  - ^{241}Am from ^{241}Pu produced by ^{238}U +^{4}He
    - → Also directly produced from He on ^{237}Np and ^{2}H on ^{239}Pu
  - ^{239}Pu(^{4}He,n)^{242}Cm
    - → Chemical separation from Pu
    - → Identification of ^{238}Pu daughter from alpha decay
- Difficulties in separating Am from Cm and from lanthanide fission products
  - Trivalent oxidation states
- Am and Cm discovery papers
  - http://www.osti.gov/accomplishments/documents/fullText/ACC0046.pdf
  - http://www.osti.gov/accomplishments/documents/fullText/ACC0049.pdf



Bk and Cf discovery

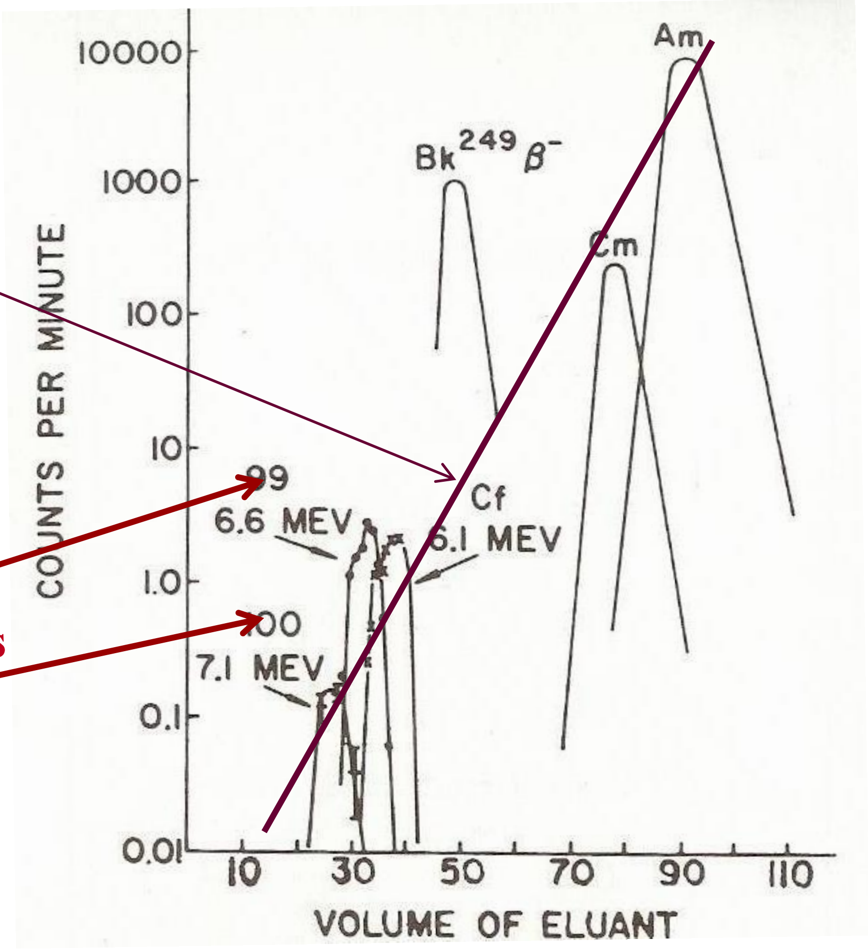
- Required Am and Cm as targets
  - Needed to produce theses isotopes in sufficient quantities
    - → Milligrams
  - Am from neutron reaction with Pu
  - Cm from neutron reaction with Am
- Production of new elements followed by separation
  - ^{241}Am(^{4}He,2n)^{243}Bk
    - → Cation exchange separation
  - ^{242}Cm(^{4}He,n)^{245}Cf
    - → Anion exchange
- Where would the heavier actinides elute?



Dowex 50 resin at 87 °C, elute with ammonium citrate

Einsteinium and Fermium

- Debris from Mike test
  - 1st thermonuclear test
    - → http://www.youtube.com/watch?v=h7vyKDcSTaE
- New isotopes of Pu
  - 244 and 246
    - → Successive neutron capture on ^{238}U
- Correlation of yield versus atomic mass
- Production of transcalifornium isotopes
  - Heavy U isotopes followed by beta decay
    - → Z = 92
      - * Conversion of 7 or 8 neutron
  - Successive neutron capture to form Es and Fm
    - → ^{253}Es and ^{254}Fm
    - → Similar to r-process in nucleosynthesis
- Ion exchange used to separate new elements
  - Elution position based on element Z
    - → Evidence of actinide contraction



Elution of Es (99) and Fm (100) with citrate solution

Mendelevium, Nobelium, and Lawrencium discovery

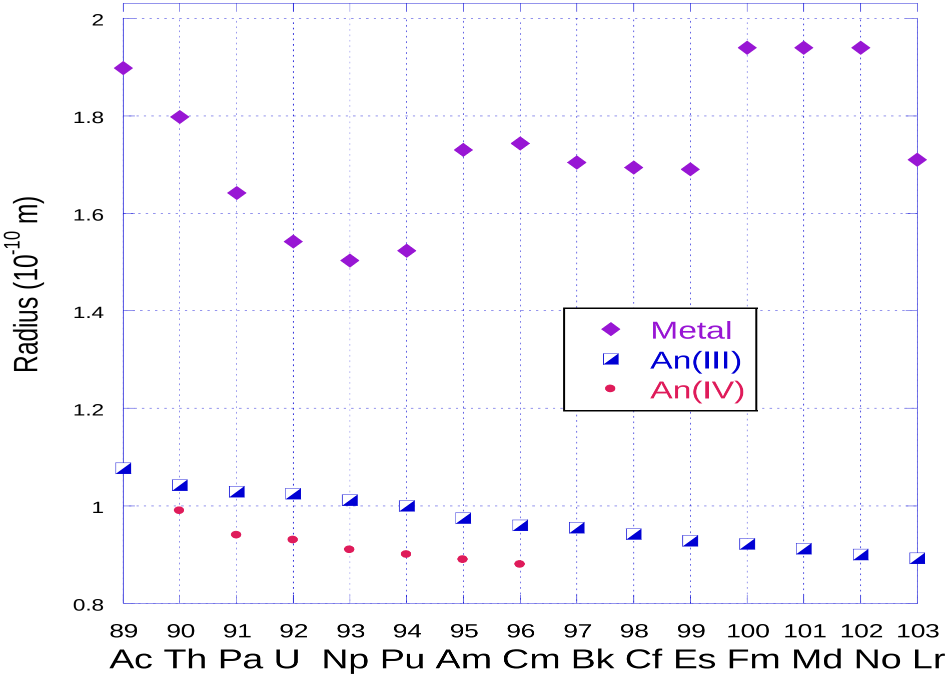
- 1st atom-at-a-time chemistry
  - $^{253}Es(^{4}He,n)^{256}Md$
- Required high degree of chemical separation
- Use catcher foil
  - Recoil of product onto foil
  - Dissolved Au foil, then ion exchange
- Nobelium controversy
  - Expected to have trivalent chemistry
    - → Actually divalent, filled 5f orbital
      - * Divalent from removing 7s electrons
  - 1st attempt could not be reproduced
    - → Showed divalent oxidation state
  - $^{246}Cm(^{12}C,4n)^{254}No$
    - → Alpha decay from ^{254}No
    - → Identification of ^{250}Fm daughter using ion exchange
- For Lr $^{249, 250, 251}Cf$ bombarded with $^{10,11}B$
- New isotope with 8.6 MeV, 6 second half life
  - Identified at ^{258}Lr

Actinide trends

- Properties based on filling 5f orbitals
  - Hybrid bonds involving f electrons
- 5f / 6d / 7s / 7p orbitals are comparable energies from U to Am
  - → Bonding can include any orbitals since energetically similar
  - → Explains tendency towards variable valency
  - → Trend towards covalent
    - * Lanthanide complexes tend to be primarily ionic
    - * Exploit for actinide-lanthanide separations
- Actinide complexes complexation with π-bonding ligands
  - orbital shifts on order of chemical binding energies
  - Electronic structure of element in given oxidation state may vary with ligand
  - Difficult to state which orbitals are involved in bonding

	Ac	Th	Pa	U	Np	Pu	Am	Cm
Z	89	90	91	92	93	94	95	96
M(g)	$6d7s^2$	$6d^27s^2$	$5f^26d7s^2$	$5f^36d7s^2$	$5f^46d7s^2$	$5f^67s^2$	$5f^77s2$	$5f^76d7s^2$
M+(g)	$7s^2$	$6d7s^2$	$5f^27s^2$	$5f^37s^2$	$5f^57s$?	$5f^67s$	$5f^77s$	$5f^77s^2$
M2+(g)	7s	5f6d	$5f^26d$	$5f^36d$?	$5f^5$?	$5f^6$	$5f^7$	$5f^8$
M3+(g)		5f	$5f^2$	$5f^3$	$5f^4$	$5f^5$	$5f^6$	$5f^7$
M4+(g)			5f	$5f^2$	$5f^3$	$5f^4$	$5f^5$	$5f^6$

	Bk	Cf	Es	Fm	Md	No	Lr
Z	97	98	99	100	101	102	103
M(g)	$5f^97s^2$	$5f^{10}7s^2$	$5f^{11}7s^2$	$5f^{12}7s^2$	$(5f^{13}7s^2)$	$(5f^{14}7s^2)$	$(5f^{14}6d7s^2)$
M+(g)	$5f^97s$	$5f^{10}7s$	$5f^{11}7s$	$(5f^{12}7s)$	$(5f^{13}7s)$	$(5f^{14}7s)$	$(5f^{14}7s^2)$
M2+(g)	$5f^9$	$5f^{10}$	$5f^{11}$	$(5f^{12})$	$(5f^{13})$	$(5f^{14})$	$(5f^{14}7s)$
M3+(g)	$5f^8$	$5f^9$	$5f^{10}$	$(5f^{11})$	$(5f^{12})$	$(5f^{13})$	$(5f^{14})$
M4+(g)	$5f^7$	$5f^8$	$(5f^9)$	$(5f^{10})$	$(5f^{11})$	$(5f^{12})$	$(5f^{13})$

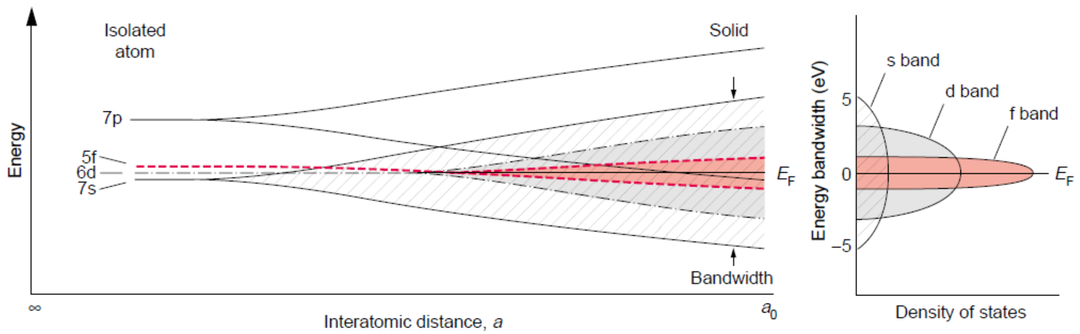


Electronic structure

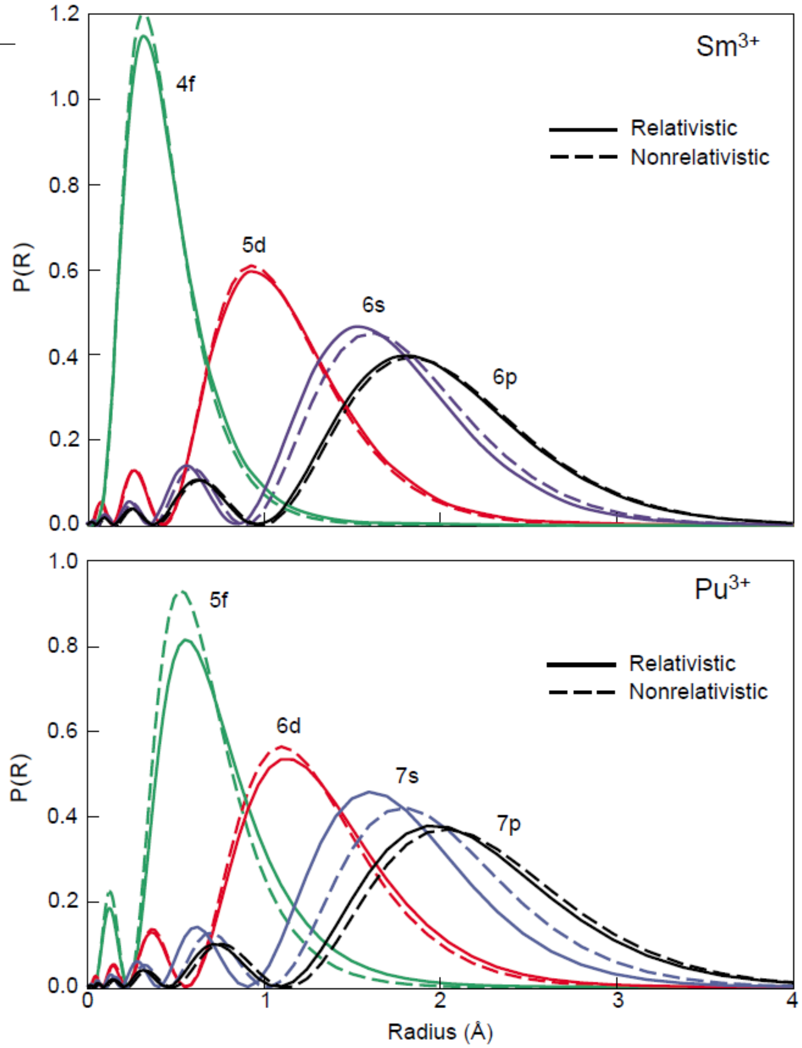
- Electronic Configurations of Actinides are not always easy to confirm
- Competition between $5f^n7s^2$ and $5f^{n-1}6d7s^2$ configurations
    - for early actinides promotion 5f → 6d occurs to provide more bonding electrons
        - → much easier than corresponding 4f → 5d promotion in lanthanides
    - second half of actinide series similar to lanthanides
        - → Similarities for trivalent lanthanides and actinides
- 5f orbitals have greater extension 4f relative s and p orbitals
    - 5 f electrons can become involved in bonding
        - → ESR bonding evidence in UF_3, but not in NdF_3
            - * Lanthanide 4f occupy inner orbits that are not accessible
- Enhanced by relativistic effects
    - Increased velocity of s electrons
        - → Increase mass and shielding
        - → Extension of f orbitals

$$R = \frac{\varepsilon_0 h^2}{\pi \boxed{m_e} e^2}\frac{n^2}{Z}$$

Relativistic effects

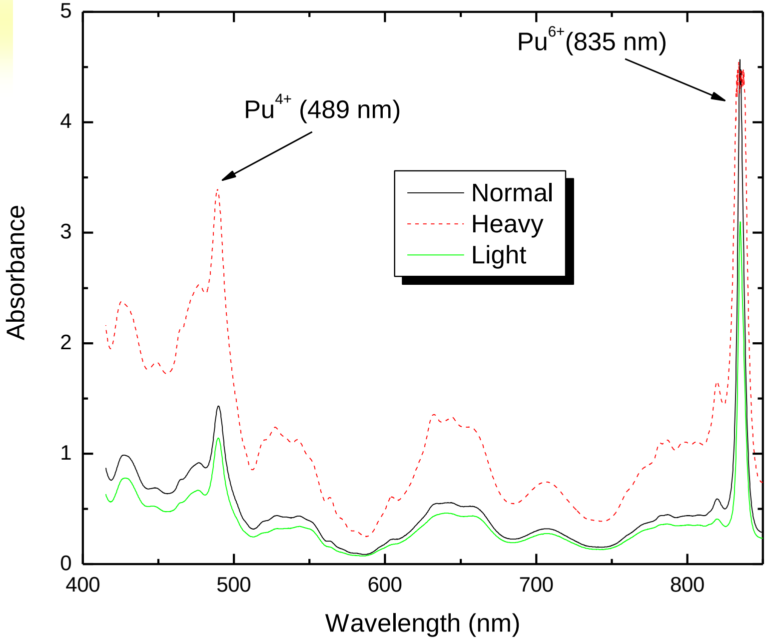


- **Orbitals with probability at nucleus relativistic**
    - **Heavier, shield outer electrons**
- **5f electrons extend relatively far from the nucleus compared to 4f electrons**
    - **5f electrons participate in chemical bonding**
- **much-greater radial extent of probability densities for 7s and 7p valence states compared with 5f valence states**
- **5f and 6d radial distributions extend farther than shown by nonrelativistic calculations**
- **7s and 7p distributions are pulled closer to the ionic cores in relativistic calculations**



Absorption Spectra and Magnetic Properties

- Electronic Spectra
  - $5f^n$ transitions
    - narrow bands (compared to transition metal spectra)
    - relatively uninfluenced by ligand field effects
    - intensities are ca. 10x those of lanthanide bands
    - complex to interpret
      - Laporte forbidden transitions
- Magnetic Properties
  - hard to interpret
  - spin-orbit coupling is large
    - Russell-Saunders (L.S) Coupling scheme doesn't work, lower values than those calculated
      - LS assumes weak spin orbit coupling
        - Sum spin and orbital angular momentum
        - J=S+L
  - Ligand field effects are expected where 5f orbitals are involved in bonding



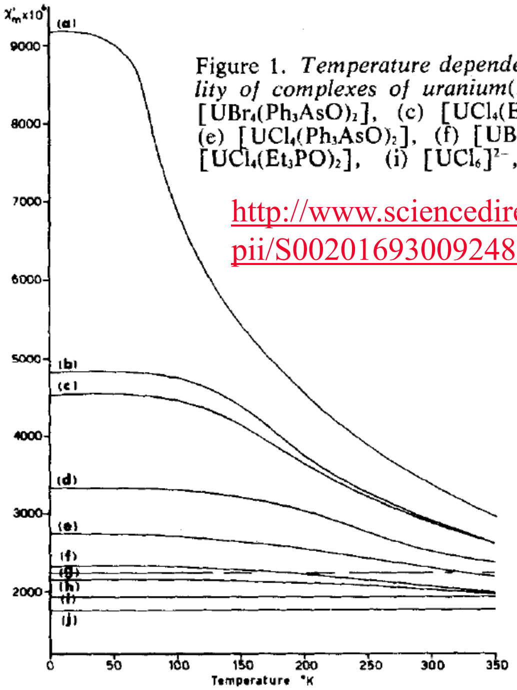


Figure 1. *Temperature dependence of the magnetic susceptibility of complexes of uranium(IV).* (a) $[UBr_4(Et_3AsO)_2]$, (b) $[UBr_4(Ph_3AsO)_2]$, (c) $[UCl_4(Et_3AsO)_2]$, (d) $[UBr_4(Et_3PO)_2]$, (e) $[UCl_4(Ph_3AsO)_2]$, (f) $[UBr_4(Ph_3PO)_2]$, (g) $[UBr_6]^{2-}$, (h) $[UCl_4(Et_3PO)_2]$, (i) $[UCl_6]^{2-}$, (j) $[UCl_4(Ph_3PO)_2]$.

http://www.sciencedirect.com/science/article/pii/S0020169300924873#

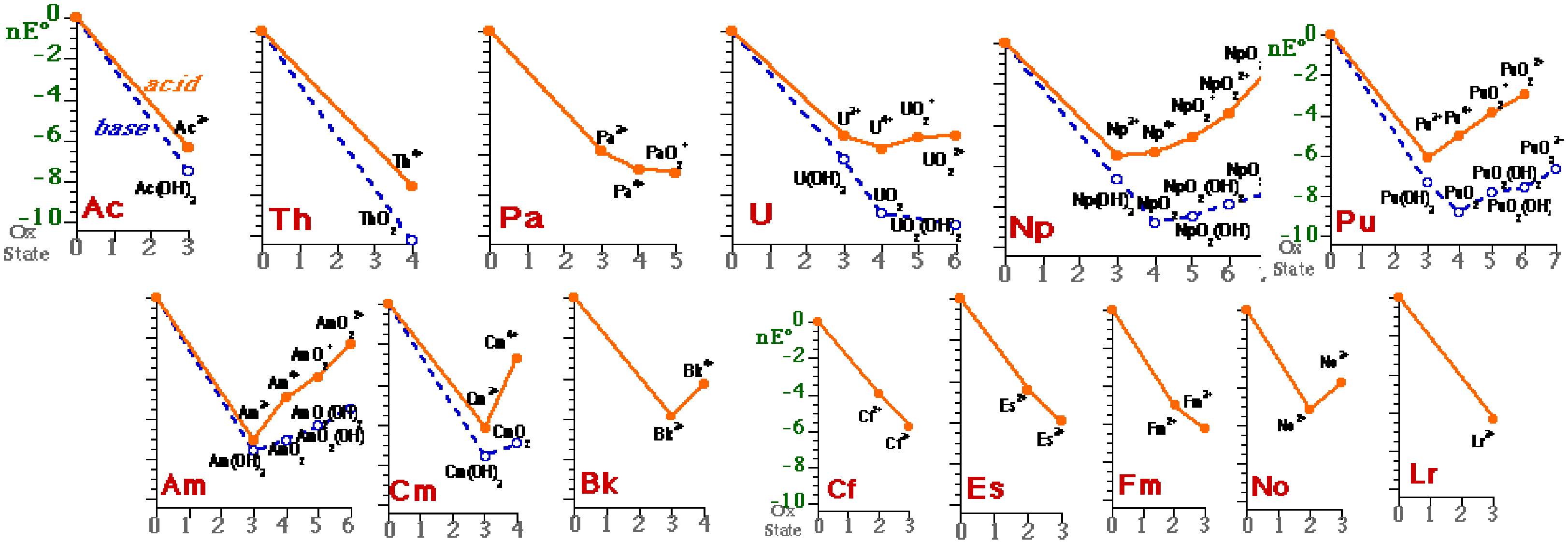
Oxidation states

- General geometries high coordination
  - Trivalent: octahedral
  - Tetravalent: 8 coordination or greater
- +2
  - Unusual oxidation state, common only for heaviest actinides
    - → No^{2+} and Md^{2+} are more stable than Eu^{2+}
      - * 5f→6d promotion
  - Divalent No stabilize by full $5f^{14}$
    - → Element $Rn5f^{14}7s^2$
  - Divalent actinides similar properties to divalent lanthanides and Ba^{2+}
- +3
  - Most common oxidation state across actinides
    - → all trans-Americium elements except No
  - Of marginal stability for early actinides
    - → Pa, U
  - General properties resemble Ln^{3+} and are size-dependent
    - → Binary Halides, MX_3 easily prepared and hydrolyzed to MOX
  - Binary Oxides, M_2O_3 known for Ac, Pu and trans-Am elements
- +4
  - Principal oxidation state for Th
    - → similar to group 4
  - Very important, stable state for Pa, U, Pu
  - Tetravalent Am, Cm, Bk and Cf are easily reduced
    - → Bk^{4+} is more oxidizing than Ce^{4+}
  - MO_2 known from Th to Cf (fluorite structure)
  - MF_4 are isostructural with lanthanide tetrafluorides
    - → MCl_4 only known for Th, Pa, U & Np
  - Hydrolysis / Complexation / Disproportionation are all important in aqueous phase
- +5
  - Principal state for Pa (similar to group 5)
  - For U, Np, Pu and Am the AnO_2^+ ion is known
  - Comparatively few other An(V) species are known
    - → fluorides fluoro-anions, oxochlorides, uranates,
- +6
  - AnO_2^{2+} ions are important for U, Np, Pu, Am UO22+ is the most stable
  - Few other compounds *e.g.* AnF_6 (An = U, Np, Pu), UCl_6, UOF_4, $U(OR)_6$
- +7
  - Only the marginally stable oxo-anions of Np and Pu, (AnO_5^{3-})

Redox chemistry

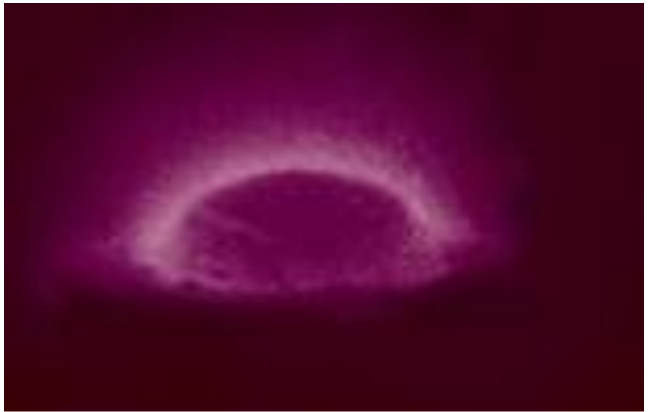
- actinides are electropositive
- Pa - Pu show significant redox chemistry
  - 4 oxidation states of Pu can co-exist in appropriate conditions
- stability of high oxidation states peaks at U (Np)
- redox potentials show strong dependence on pH (data for Ac - Cm)
  - high oxidation states are more stable in basic conditions
  - even at low pH hydrolysis occurs
  - tendency to disproportionation is particularly dependent on pH
  - at high pH $3Pu^{4+} + 2H_2O \rightarrow PuO_2^{2+} + 2Pu^{3+} + 4H^+$
- early actinides have a tendency to form complexes
  - complex formation influences reduction potentials

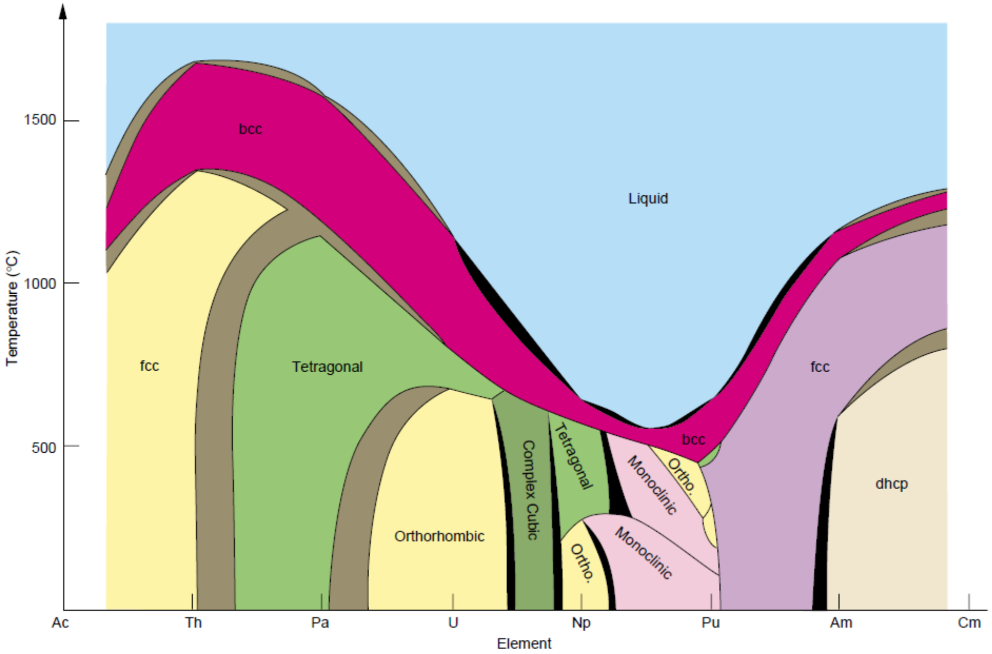
    → Am^{4+}(aq) exists when complexed by fluoride (15 M NH_4F(aq))
- radiation-induced solvent decomposition produces H• and OH• radicals
  - lead to reduction of higher oxidation states e.g. PuV/VI, AmIV/VI



Actinide metals

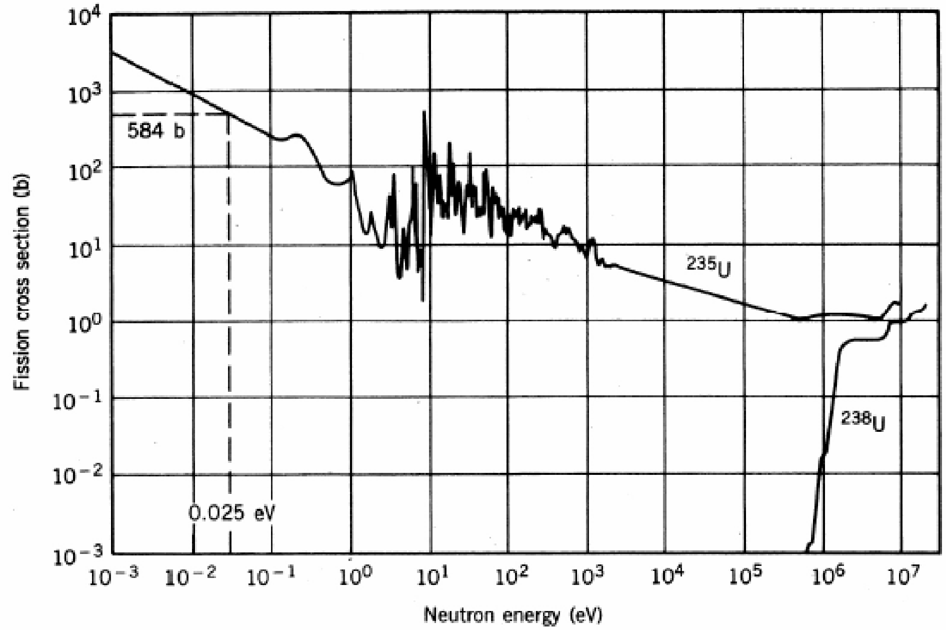
- Preparation of actinide metals
  - Reduction of AnF_3 or AnF_4 with vapors of Li, Mg, Ca or Ba at 1100 – 1400 °C
  - Other redox methods are possible
    - → Thermal decomposition of iodine species
    - → Am from Am_2O_3 with La
      - * Am volatility provides method of separation
- Metals tend to be very dense
  - U 19.07 g/mL
  - Np 20.45 g/mL
  - Am lighter at 13.7 g/mL
- Some metals glow due to activity
  - Ac, Cm, Cf





Uranium Chemistry: Basis for Fuel Cycle

- Chemistry in the fuel cycle
  - Uranium
    - → Solution Chemistry
    - → Separation
    - → Fluorination and enrichment
    - → Metal
- Focus of chemistry in the fuel cycle
  - Speciation (chemical form)
  - Oxidation state
  - Ionic radius and molecular size

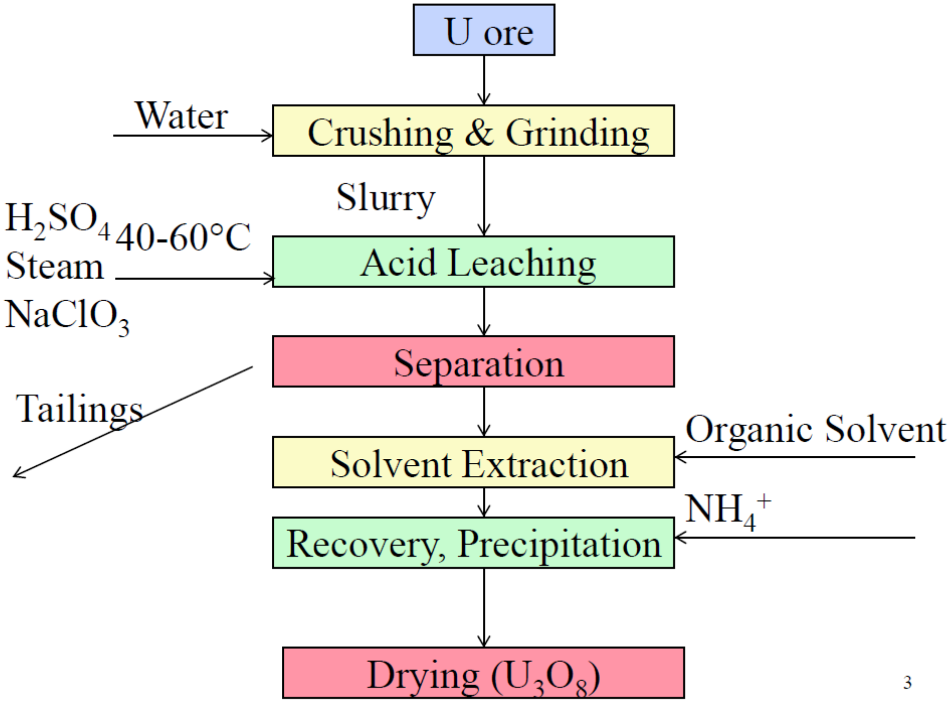


- Utilization of fission process to create heat
  - Heat used to turn turbine and produce electricity
- Requires fissile isotopes
  - ^{233}U, ^{235}U, ^{239}Pu
  - Need in sufficient concentration and geometry
- ^{233}U and ^{239}Pu can be created in neutron flux
- ^{235}U in nature
  - Need isotope enrichment

- Fission properties of uranium
  - Defined importance of element and provided reason of future investigations
  - Identified by Hahn in 1937
    - → 200 MeV/fission, 2.5 neutrons
- Natural isotopes
  - Ratios of isotopes established
    - → 234: 0.005±0.001, 68.9 a
    - → 235: 0.720±0.001, 7.04E8 a
    - → 238: 99.275±0.002, 4.5E9 a

Fuel Cycle Chemistry Overview

- **Uranium acid-leach**



U ore

Water

Crushing & Grinding

Slurry

H_2SO_4 40-60°C

Steam

$NaClO_3$

Acid Leaching

Separation

Tailings

Solvent Extraction

Organic Solvent

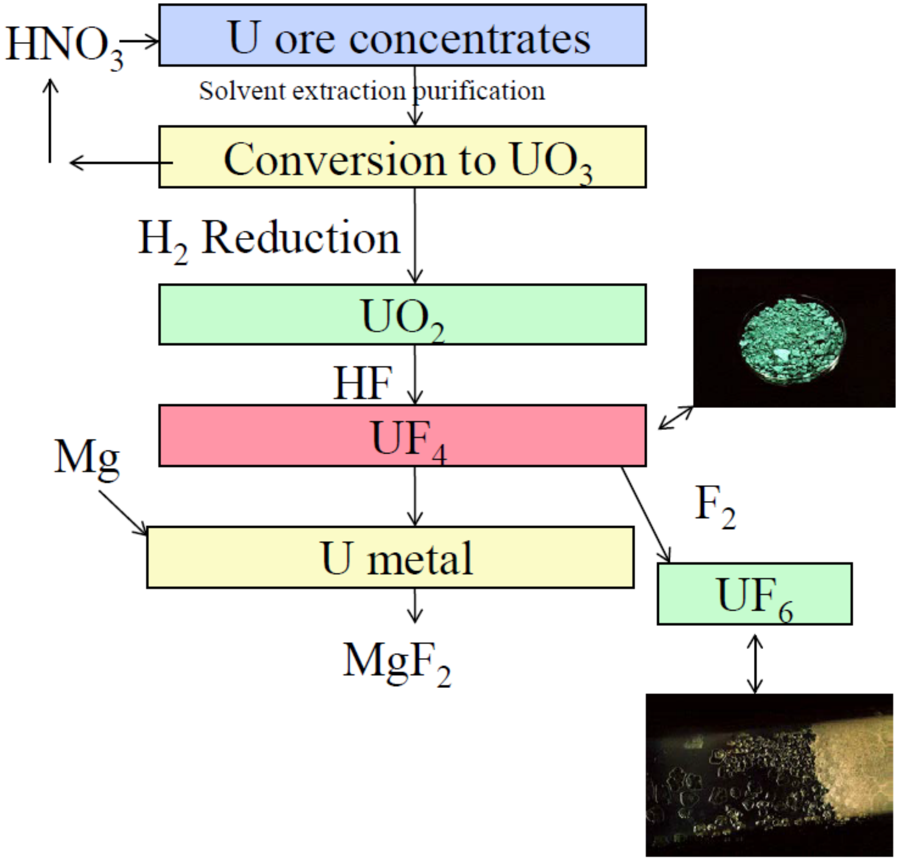
Recovery, Precipitation

NH_4^+

Drying (U_3O_8)

3

- **Extraction and conversion**



HNO_3

U ore concentrates

Solvent extraction purification

Conversion to UO_3

H_2 Reduction

UO_2

HF

UF_4

Mg

U metal

MgF_2

F_2

UF_6

Fuel Fabrication

Enriched UF_6

Calcination, Reduction

UO_2

Pellet Control

40-60°C

Tubes

Fuel Fabrication

Other species for fuel

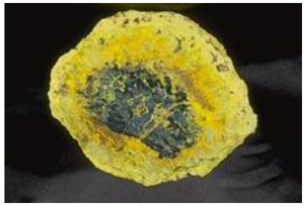
nitrides, carbides

Other actinides: Pu, Th

Uranium chemistry

- Uranium solution chemistry
- Separation and enrichment of U
- Uranium separation from ore
  - Solvent extraction
  - Ion exchange
- Separation of uranium isotopes
  - Gas centrifuge
  - Laser

- 200 minerals contain uranium
  - Bulk are U(VI) minerals
    - → U(IV) as oxides, phosphates, silicates
  - Classification based on polymerization of coordination polyhedra
  - Mineral deposits based on major anion
- Pyrochlore
  - $A_{1-2}B_2O_6X_{0-1}$
    - → A=Na, Ca, Mn, Fe^{2+}, Sr, Sb, Cs, Ba, Ln, Bi, Th, U
    - → B= Ti, Nb, Ta
    - → U(V) may be present when synthesized under reducing conditions
      - * XANES spectroscopy
      - * Goes to B site



Uraninite with oxidation

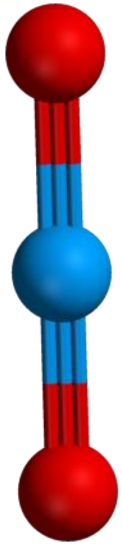
Aqueous solution complexes

- Strong Lewis acid
- Hard electron acceptor
  - $F^- >> Cl^- > Br^- \cong I^-$
  - Same trend for O and N group
    - → based on electrostatic force as dominant factor
- Hydrolysis behavior
  - U(IV)>U(VI)>>>U(III)>U(V)
- Uranium coordination with ligand can change protonation behavior
  - $HOCH_2COO^-$ pKa=17, 3.6 upon complexation of UO_2
    - → Inductive effect
      - * Electron redistribution of coordinated ligand
      - * Exploited in synthetic chemistry
- U(III) and U(V)
  - No data in solution
    - → Base information on lanthanide or pentavalent actinides

Uranium solution chemistry

- Uranyl(VI) most stable oxidation state in solution
    - Uranyl(V) and U(IV) can also be in solution
        - → U(V) prone to disproportionation
    - Stability based on pH and ligands
    - Redox rate is limited by change in species
        - → Making or breaking yl oxygens
            - * $UO_2^{2+}+4H^++2e^- \leftrightarrow U^{4+}+2H_2O$
- yl oxygens have slow exchange
    - Half life 5E4 hr in 1 M $HClO_4$
- 5f electrons have strong influence on actinide chemistry
    - For uranyl, f-orbital overlap provide bonding

Uranyl chemical bonding



- Uranyl (UO_2^{2+}) linear molecule
- Bonding molecular orbitals
  - $\sigma_g^2 \sigma_u^2 \pi_g^4 \pi_u^4$
    - → Order of HOMO is unclear
      - * $\pi_g < \pi_u < \sigma_g << \sigma_u$ proposed
        - ➢ Gap for σ based on 6p orbitals interactions
  - 5fδ and 5fϕ LUMO
  - Bonding orbitals O 2p characteristics
  - Non bonding, antibonding 5f and 6d
  - Isoelectronic with UN_2
- Pentavalent has electron in non-bonding orbital

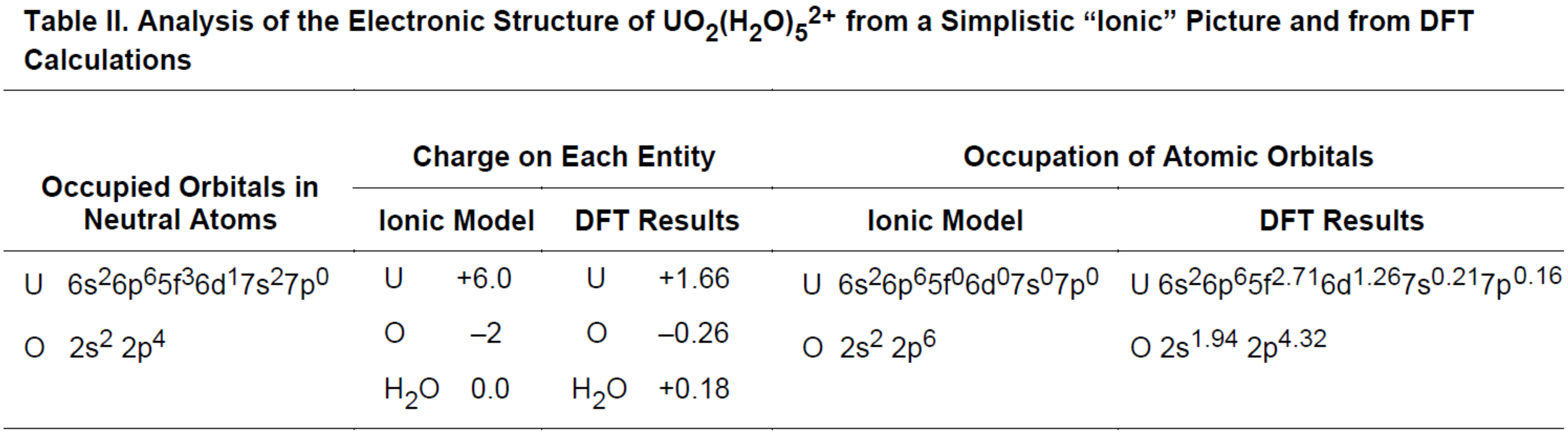


Table II. Analysis of the Electronic Structure of $UO_2(H_2O)_5^{2+}$ from a Simplistic "Ionic" Picture and from DFT Calculations

Occupied Orbitals in Neutral Atoms	Charge on Each Entity		Occupation of Atomic Orbitals	
	Ionic Model	DFT Results	Ionic Model	DFT Results
U $6s^26p^65f^36d^17s^27p^0$	U +6.0	U +1.66	U $6s^26p^65f^06d^07s^07p^0$	U $6s^26p^65f^{2.71}6d^{1.26}7s^{0.21}7p^{0.16}$
O $2s^2 2p^4$	O −2	O −0.26	O $2s^2 2p^6$	O $2s^{1.94} 2p^{4.32}$
	H_2O 0.0	H_2O +0.18		

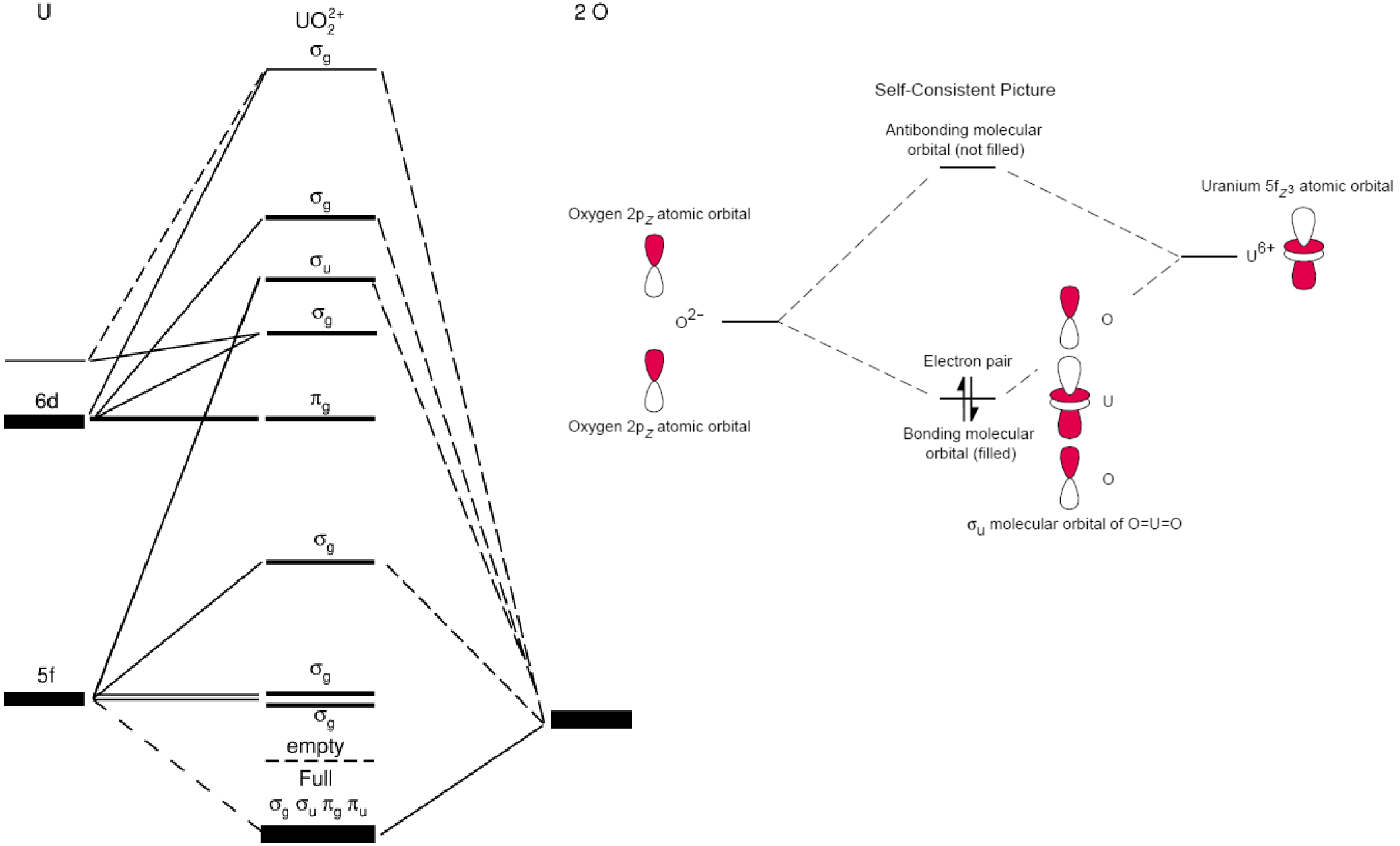


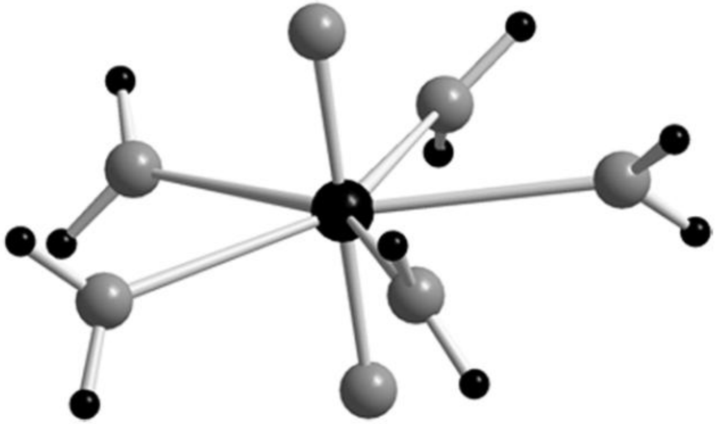
Fig. 5.49 *Schematic molecular orbital diagram for the uranyl(VI) ion.*

Uranyl chemical bonding

- Linear yl oxygens from 5f characteristic
  - 6d promotes cis geometry
- yl oxygens force formal charge on U below 6
  - Net charge 2.43 for $UO_2(H_2O)_5^{2+}$, 3.2 for fluoride systems
    - → Net negative 0.43 on oxygens
    - → Lewis bases
      - * Can vary with ligand in equatorial plane
      - * Responsible for cation-cation interaction
      - * O=U=O- - -M
      - * Pentavalent U yl oxygens more basic
- Small changes in U=O bond distance with variation in equatoral ligand
- Small changes in IR and Raman frequencies
  - Lower frequency for pentavalent U
  - Weaker bond

Hexavalent Uranium

- **Large number of compounds prepared**
    - **Crystallization**
    - **Hydrothermal**
- **Determination of hydrolysis constants from spectroscopic and titration**
    - **Determine if polymeric species form**
    - **Polynuclear species present except at lowest concentration**



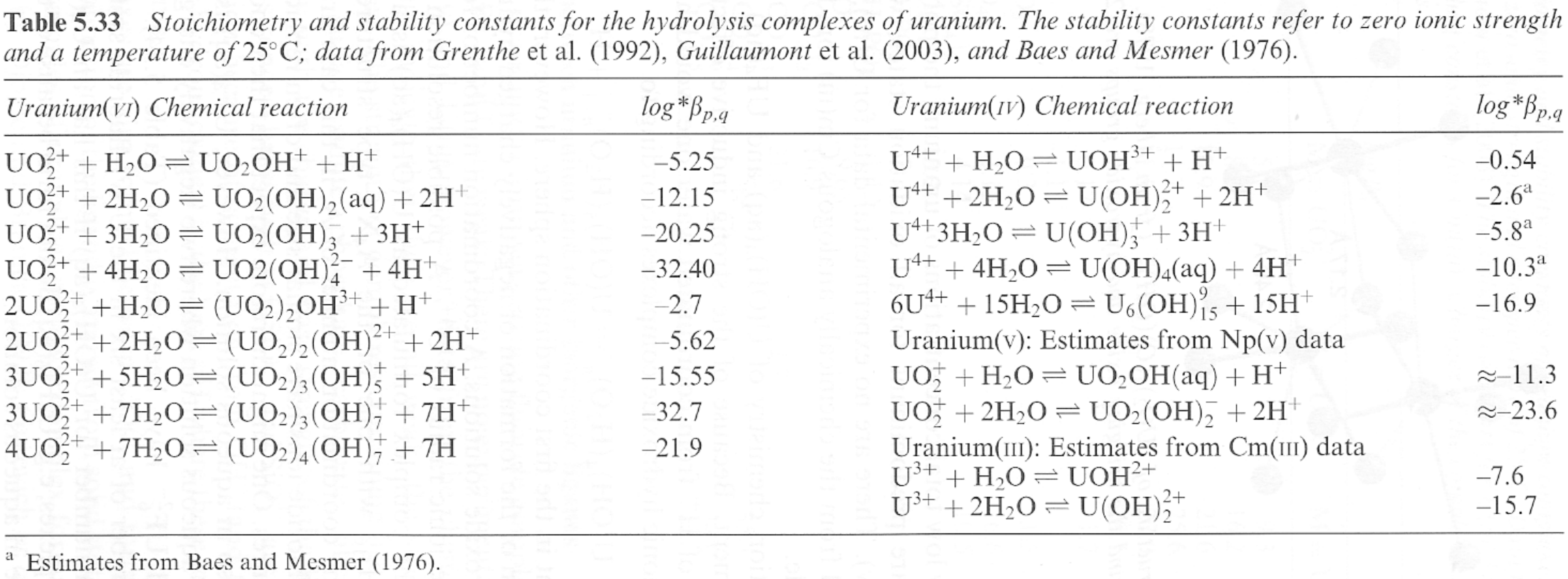


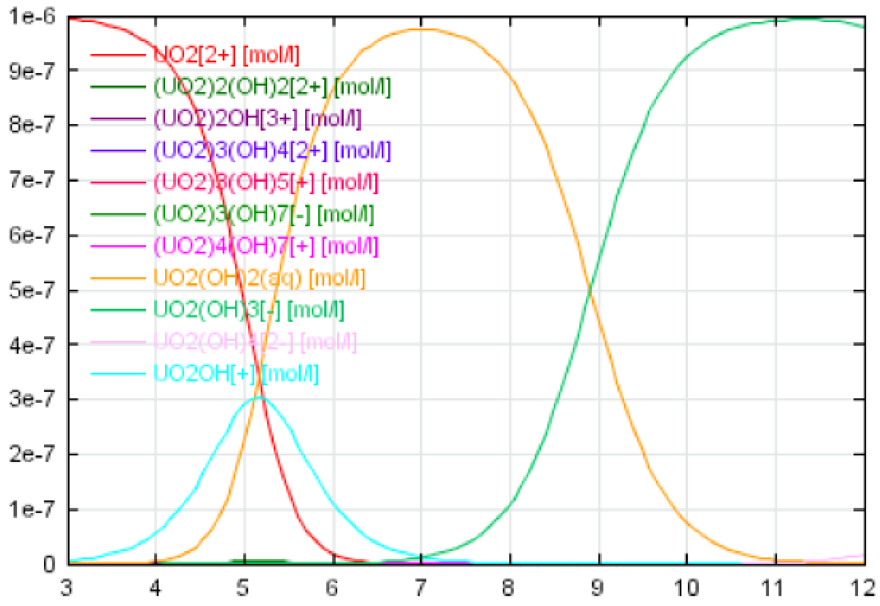
Table 5.33 *Stoichiometry and stability constants for the hydrolysis complexes of uranium. The stability constants refer to zero ionic strength and a temperature of 25°C; data from Grenthe* et al. (1992), *Guillaumont* et al. (2003), *and Baes and Mesmer* (1976).

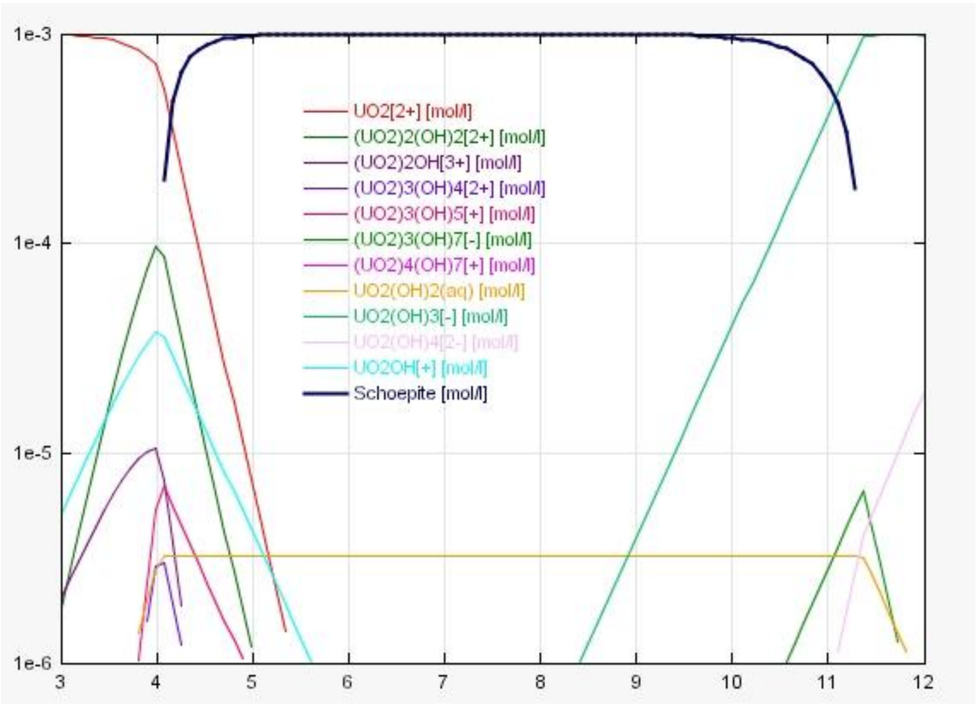
Uranium(VI) *Chemical reaction*	*log*$\beta_{p,q}$*	*Uranium*(IV) *Chemical reaction*	*log*$\beta_{p,q}$*
$UO_2^{2+} + H_2O \rightleftharpoons UO_2OH^+ + H^+$	–5.25	$U^{4+} + H_2O \rightleftharpoons UOH^{3+} + H^+$	–0.54
$UO_2^{2+} + 2H_2O \rightleftharpoons UO_2(OH)_2(aq) + 2H^+$	–12.15	$U^{4+} + 2H_2O \rightleftharpoons U(OH)_2^{2+} + 2H^+$	–2.6[a]
$UO_2^{2+} + 3H_2O \rightleftharpoons UO_2(OH)_3^- + 3H^+$	–20.25	$U^{4+}3H_2O \rightleftharpoons U(OH)_3^+ + 3H^+$	–5.8[a]
$UO_2^{2+} + 4H_2O \rightleftharpoons UO2(OH)_4^{2-} + 4H^+$	–32.40	$U^{4+} + 4H_2O \rightleftharpoons U(OH)_4(aq) + 4H^+$	–10.3[a]
$2UO_2^{2+} + H_2O \rightleftharpoons (UO_2)_2OH^{3+} + H^+$	–2.7	$6U^{4+} + 15H_2O \rightleftharpoons U_6(OH)_{15}^9 + 15H^+$	–16.9
$2UO_2^{2+} + 2H_2O \rightleftharpoons (UO_2)_2(OH)^{2+} + 2H^+$	–5.62	Uranium(V): Estimates from Np(V) data	
$3UO_2^{2+} + 5H_2O \rightleftharpoons (UO_2)_3(OH)_5^+ + 5H^+$	–15.55	$UO_2^+ + H_2O \rightleftharpoons UO_2OH(aq) + H^+$	≈–11.3
$3UO_2^{2+} + 7H_2O \rightleftharpoons (UO_2)_3(OH)_7^+ + 7H^+$	–32.7	$UO_2^+ + 2H_2O \rightleftharpoons UO_2(OH)_2^- + 2H^+$	≈–23.6
$4UO_2^{2+} + 7H_2O \rightleftharpoons (UO_2)_4(OH)_7^+ + 7H$	–21.9	Uranium(III): Estimates from Cm(III) data	
		$U^{3+} + H_2O \rightleftharpoons UOH^{2+}$	–7.6
		$U^{3+} + 2H_2O \rightleftharpoons U(OH)_2^{2+}$	–15.7

[a] Estimates from Baes and Mesmer (1976).

Uranium speciation

- Speciation variation with uranium concentration
  - Hydrolysis as example
  - Precipitation at higher concentration
    - → Change in polymeric uranium species concentration





Uranium chemical bonding: oxidation states

- Tri- and tetravalent U mainly related to organometallic compounds
  - Cp_3UCO and Cp_3UCO^+
    - Cp=cyclopentadiene
      - 5f CO π backbonding
        - Metal electrons to π of ligands
      - Decreases upon oxidation to U(IV)
- Uranyl(V) and (VI) compounds
  - yl ions in aqueous systems unique for actinides
    - VO_2^+, MoO_2^{2+}, WO_2^{2+}
      - Oxygen atoms are cis to maximize $(p_\pi) \rightarrow M(d_\pi)$
    - Linear MO_2^{2+} known for compounds of Tc, Re, Ru, Os
      - Aquo structures unknown
  - Short U=O bond distance of 1.75 Å for hexavalent, longer for pentavalent
    - Smaller effective charge on pentavalent U
  - Multiple bond characteristics, 1 σ and 2 with π characteristics

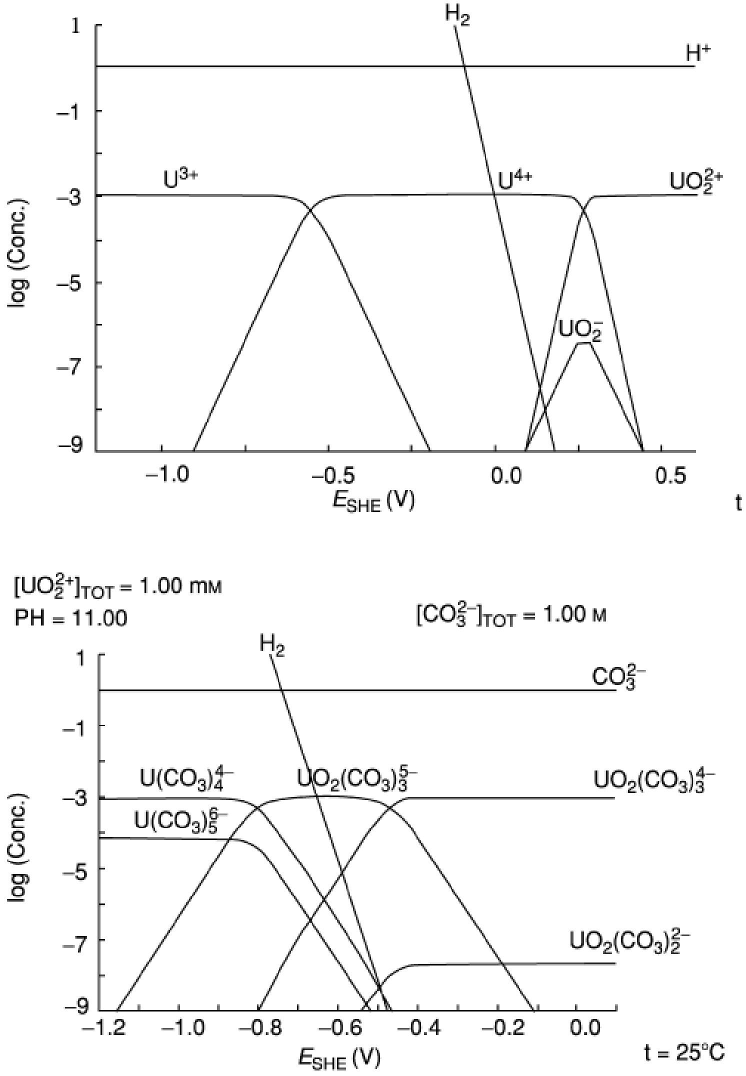


Fig. 5.63 *Logarithmic diagrams showing the distribution of U^{3+}, U^{4+}, UO_2^+ and UO_2^{2+} as a function of the redox potential in 1 M perchloric acid (the first diagram), and in 1 M Na_2CO_3 (the second diagram). U(V) is predominant between –0.7 and –0.4 V in the second diagram.*

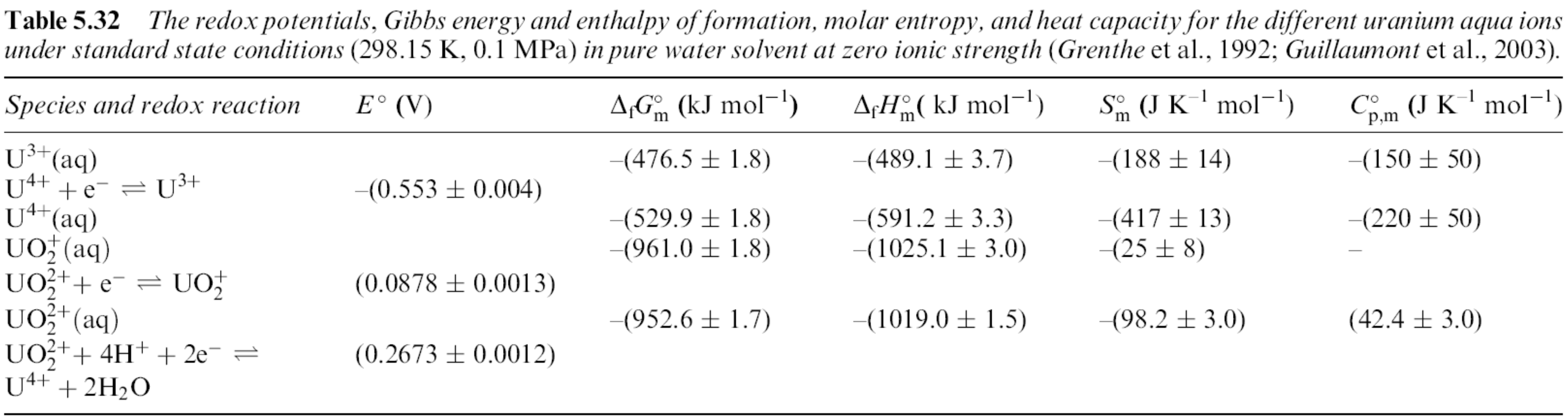


Table 5.32 *The redox potentials, Gibbs energy and enthalpy of formation, molar entropy, and heat capacity for the different uranium aqua ions under standard state conditions* (298.15 K, 0.1 MPa) *in pure water solvent at zero ionic strength* (*Grenthe* et al., 1992; *Guillaumont* et al., 2003).

Species and redox reaction	E° (V)	$\Delta_f G^\circ_m$ (kJ mol^{-1})	$\Delta_f H^\circ_m$ (kJ mol^{-1})	S°_m (J K^{-1} mol^{-1})	$C^\circ_{p,m}$ (J K^{-1} mol^{-1})
U^{3+}(aq)		–(476.5 ± 1.8)	–(489.1 ± 3.7)	–(188 ± 14)	–(150 ± 50)
$U^{4+} + e^- \rightleftharpoons U^{3+}$	–(0.553 ± 0.004)				
U^{4+}(aq)		–(529.9 ± 1.8)	–(591.2 ± 3.3)	–(417 ± 13)	–(220 ± 50)
UO_2^+(aq)		–(961.0 ± 1.8)	–(1025.1 ± 3.0)	–(25 ± 8)	–
$UO_2^{2+} + e^- \rightleftharpoons UO_2^+$	(0.0878 ± 0.0013)				
UO_2^{2+}(aq)		–(952.6 ± 1.7)	–(1019.0 ± 1.5)	–(98.2 ± 3.0)	(42.4 ± 3.0)
$UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O$	(0.2673 ± 0.0012)				

Uranium solution chemistry: U(III)

- Dissolution of UCl_3 in water
- Reduction of U(IV) or (VI) at Hg cathode
  - Evaluated by color change
    - → U(III) is green
- Very few studies of U(III) in solution
- No structural information
  - Comparisons with trivalent actinides and lanthanides

Uranium solution chemistry

- Tetravalent uranium
  - Forms in very strong acid
    - → Requires >0.5 M acid to prevent hydrolysis
    - → Electrolysis of U(VI) solutions
      - * Complexation can drive oxidation
  - Coordination studied by XAFS
    - → Coordination number 9±1
      - * Not well defined
    - → U-O distance 2.42 Å
  - O exchange examined by NMR
- Pentavalent uranium
  - Extremely narrow range of existence
  - Prepared by reduction of UO_2^{2+} with Zn or H_2 or dissolution of UCl_5 in water
  - UV-irradiation of 0.5 M 2-propanol-0.2 M $LiClO_4$ with U(VI) between pH 1.7 and 2.7
    - → U(V) is not stable but slowly oxidizes under suitable conditions
  - No experimental information on structure
  - Quantum mechanical predictions

Uranium Laser Isotope Separation: Utilization of Electronic Structure

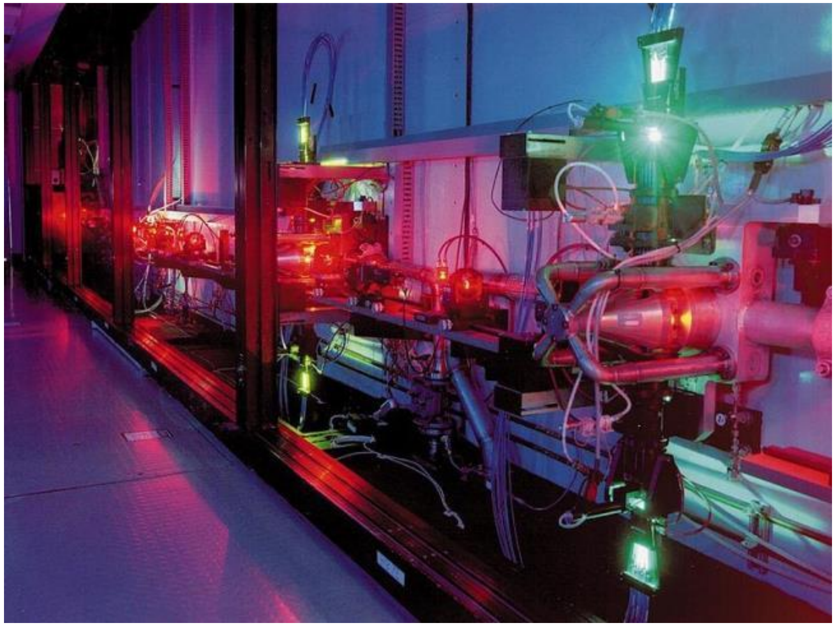
- Isotopic effect in atomic spectroscopy
  - Mass, shape, nuclear spin variation
  - Exploit to separation ^{235}U from ^{238}U
- Observed in visible part of spectra
- Mass difference observed in IR region
- Effect is small compared to transition energies
  - 1 in 1E5 for U species
- Result in difference in absorbance for uranium isotopes
  - ^{238}U absorption peak at 502.74 nm
  - ^{235}U absorption peak at 502.73 nm
- Use laser to tune to exact transition specie
  - Produces molecule in excited state
- Doppler limitations with method
  - Movement of molecules during excitation
- Signature from 234/238 ratio, both depleted

Laser Isotope Separation

- 3 classes of laser isotope separations
    - Photochemical
        - →Reaction of excited state molecule
    - Atomic photoionization
        - →Ionization of excited state molecule
    - Photodissociation
        - →Dissociation of excited state molecule
- AVLIS
    - Atomic vapor laser isotope separation
- MLIS
    - Molecular laser isotope separation

Laser isotope separation

- AVLIS
  - U metal vapor
    - → High reactivity, high temperature
    - → Uses electron beam to produce vapor from metal sample
- Ionization potential 6.2 eV
- Multiple step ionization
  - First step selective ionization
    - → ^{238}U absorption peak 502.74 nm
    - → ^{235}U absorption peak 502.73 nm
- Deflection of ionized U by electromagnetic field



Laser Isotope Separation

- **MLIS (LANL method) SILEX (Separation of Isotopes by Laser Excitation) in Australia**
    - **Absorption by UF_6**
    - **Initial IR excitation at 16 micron**
      → $^{235}UF_6$ in excited state
    - **Selective excitation of $^{235}UF_6$**
    - **Ionization to $^{235}UF_5$**
    - **Formation of solid UF_5 (laser snow)**
    - **Solid enriched and use as feed to another excitation**
- **Process degraded by molecular motion**
    - **Cool gas by dilution with H_2 and nozzle expansion**

Metallic Uranium

- Three different phase
  - α, β, γ phases

    → Dominate at different temperatures
- Uranium is strongly electropositive
  - Cannot be prepared through H_2 reduction
- Metallic uranium preparation
  - UF_4 or UCl_4 with Ca or Mg
  - UO_2 with Ca
  - Electrodeposition from molten salt baths

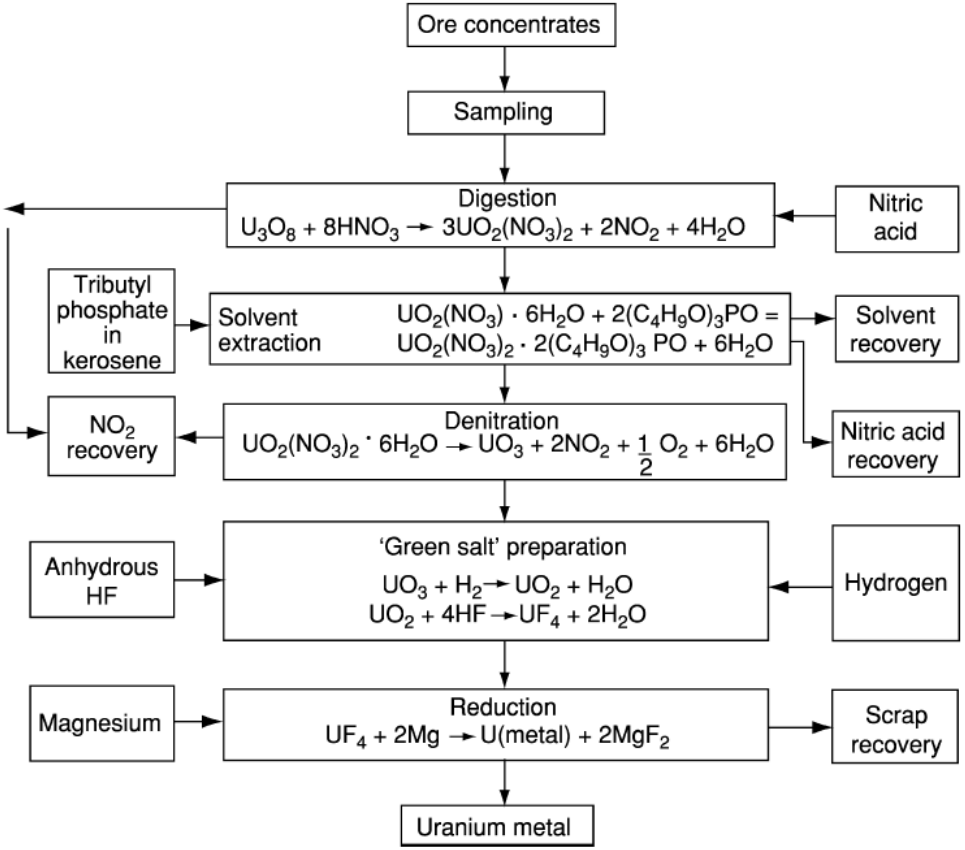
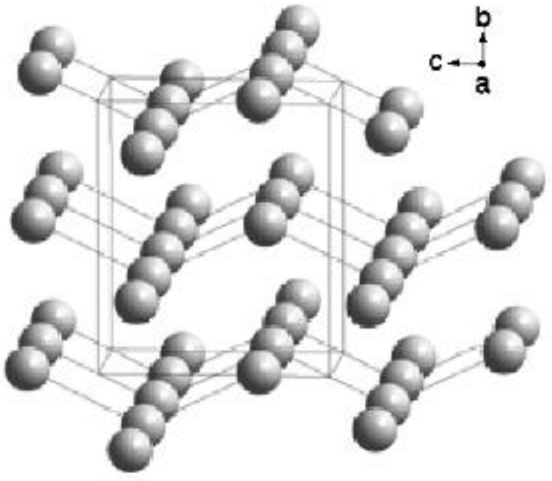


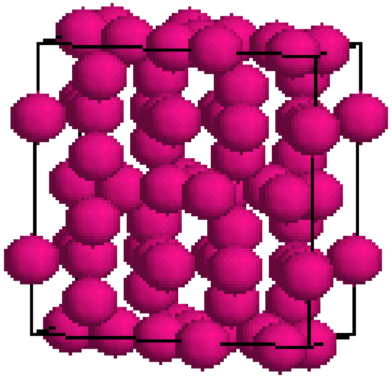
Fig. 5.8 *Flow sheet for the production of uranium metal by reduction of* UF_4 *with magnesium* (*Kelley*, 1955).

Metallic Uranium phases

- α-phase
  - Room temperature to 942 K
  - Orthorhombic
  - U-U distance 2.80 Å
  - Unique structure type
- β-phase
  - Exists between 668 and 775 °C
  - Tetragonal unit cell
- γ-phase
  - Formed above 775 °C
  - bcc structure
- Metal has plastic character
  - Gamma phase soft, difficult fabrication
  - Beta phase brittle and hard
- Paramagnetic
- Temperature dependence of resistivity
- Alloyed with Mo, Nb, Nb-Zr, and Ti



α-phase U-U distances in layer (2.80±0.05) Å and between layers 3.26 Å



β-phase

Intermetallic compounds

- **Wide range of intermetallic compounds and solid solutions in alpha and beta uranium**
    - **Hard and brittle transition metal compounds**
        - **→ U_6X, X=Mn, Fe, Co, Ni**
    - **Noble metal compounds**
        - **→ Ru, Rh, Pd**
            - *** Of interests for reprocessing**
    - **Solid solutions with:**
        - **→ Mo, Ti, Zr, Nb, and Pu**

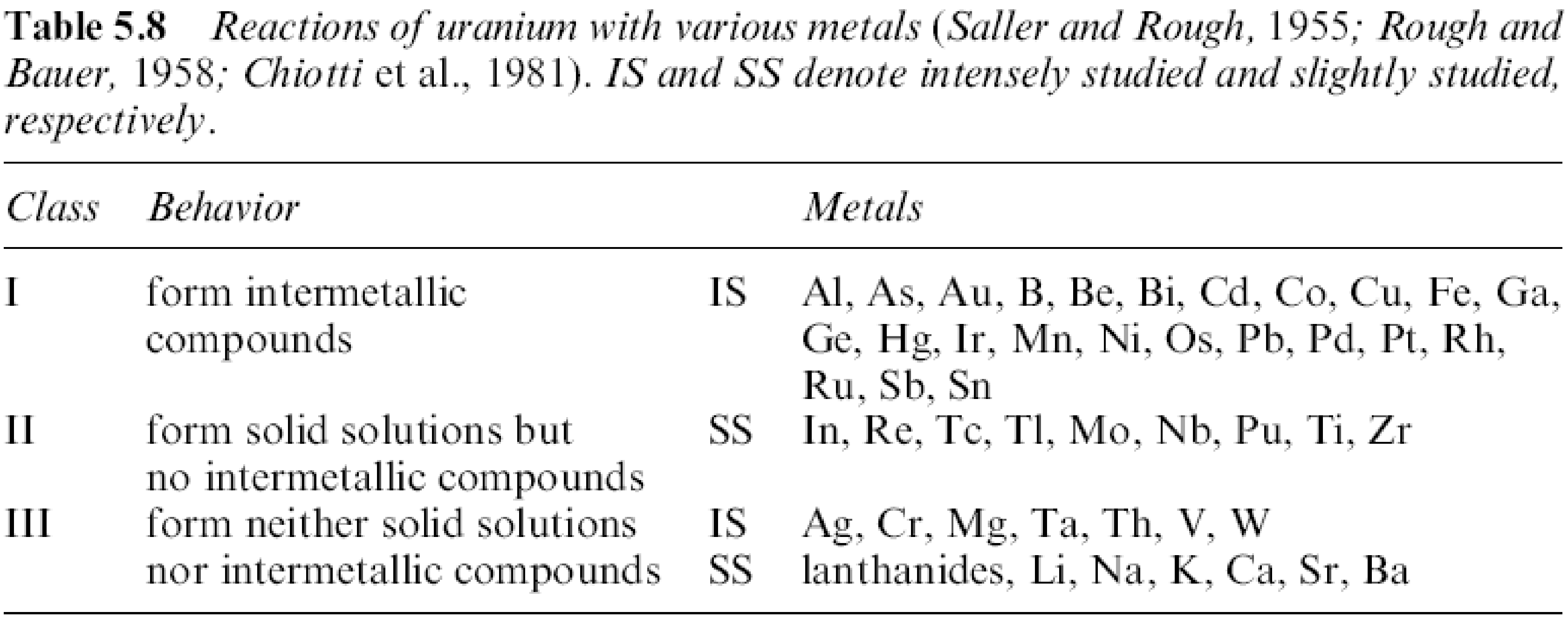
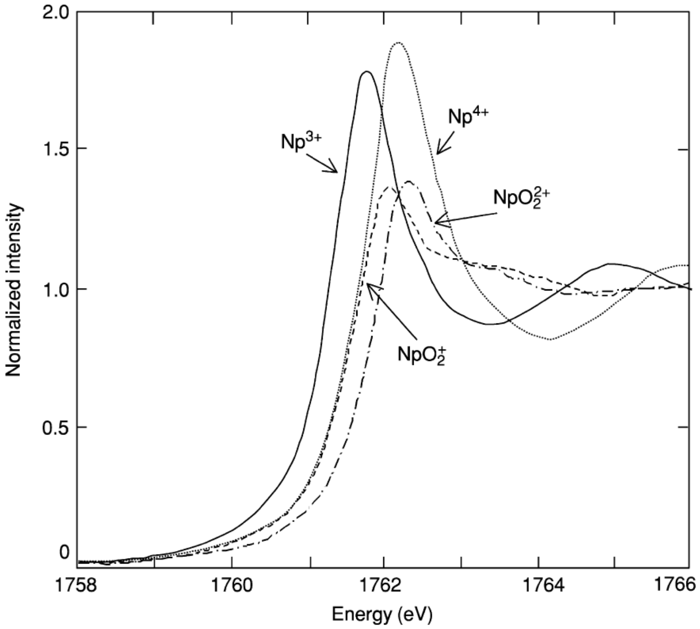


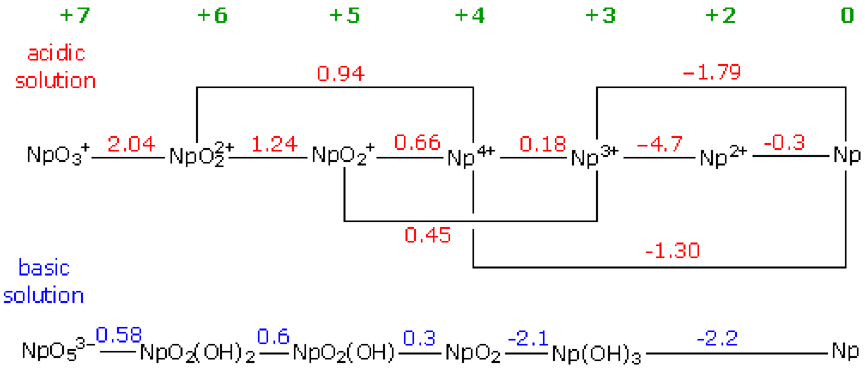
Table 5.8 *Reactions of uranium with various metals (Saller and Rough,* 1955; *Rough and Bauer,* 1958; *Chiotti* et al., 1981). *IS and SS denote intensely studied and slightly studied, respectively*.

Class	*Behavior*		*Metals*
I	form intermetallic compounds	IS	Al, As, Au, B, Be, Bi, Cd, Co, Cu, Fe, Ga, Ge, Hg, Ir, Mn, Ni, Os, Pb, Pd, Pt, Rh, Ru, Sb, Sn
II	form solid solutions but no intermetallic compounds	SS	In, Re, Tc, Tl, Mo, Nb, Pu, Ti, Zr
III	form neither solid solutions nor intermetallic compounds	IS	Ag, Cr, Mg, Ta, Th, V, W
		SS	lanthanides, Li, Na, K, Ca, Sr, Ba

Np solution chemistry

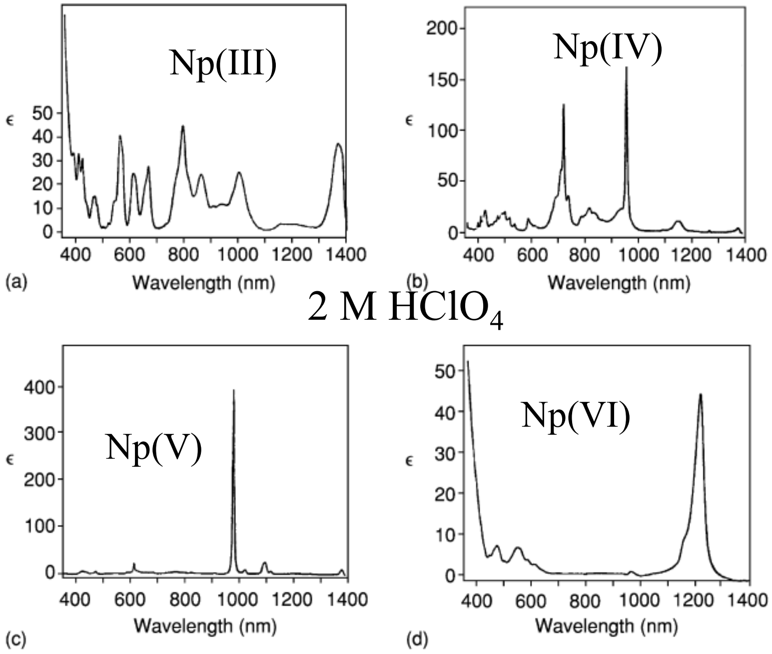
- Np exists from 3+ to 7+
  - Stable oxidation state favored by acidity, ligands, Np concentration
- 5+ and 6+ forms dioxocations
- Redox potentials
  - Some variations in values
    - → Due to slow kinetics from Np-O bond making and breaking
- Determine ratios of each redox species from XANES
  - Use Nernst equation to determine potentials
- Disproportionation
  - NpO_2^+ forms Np^{4+} and NpO_2^{2+}
    - → Favored in high acidity and Np concentration
  - $2NpO_2^+ + 4\,H^+ \leftrightarrow Np^{4+} + NpO_2^{2+} + 2H_2O$
  - K for reaction increased by addition of complexing reagents
    - → K=4E-7 in 1 M $HClO_4$ and 2.4E-2 in H_2SO_4
- Control of redox species important consideration for experiments



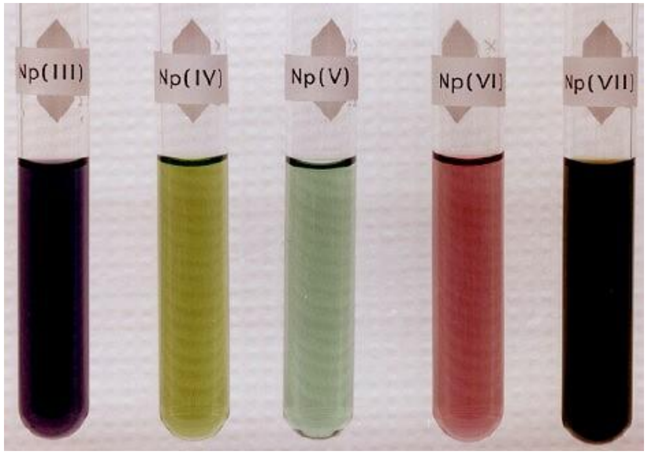


Np solution chemistry

- Applied to Np(III) to Np(VII) and coordination complexes
  - Applied to Np(V) spin-orbit coupling for $5f^2$
- Absorption in HNO_3
  - Np(IV): 715 nm
  - Np(V): weak band at 617 nm
  - Np(VI): below 400 nm
    - → No effect from 1 to 6 M nitric
- Np(VII) only in basic media
  - NpO_6^{5-}
    - → 2 long (2.2 Å) and 4 short (1.85 Å)
    - → Absorbance at 412 nm and 620 nm
      - * O pi→ 5f
      - * Number of vibrational states
        - ➢ Between 681 cm^{-1} and 2338 cm^{-1}
- Np(VI)
  - Studies in $Cs_2UO_2Cl_4$ lattice
  - Electronic levels identified at following wavenumbers (cm^{-1})
    - → 6880, 13277, 15426, 17478, and 19358
      - * 6880 cm^{-1} belongs to $5f^1$ configuration

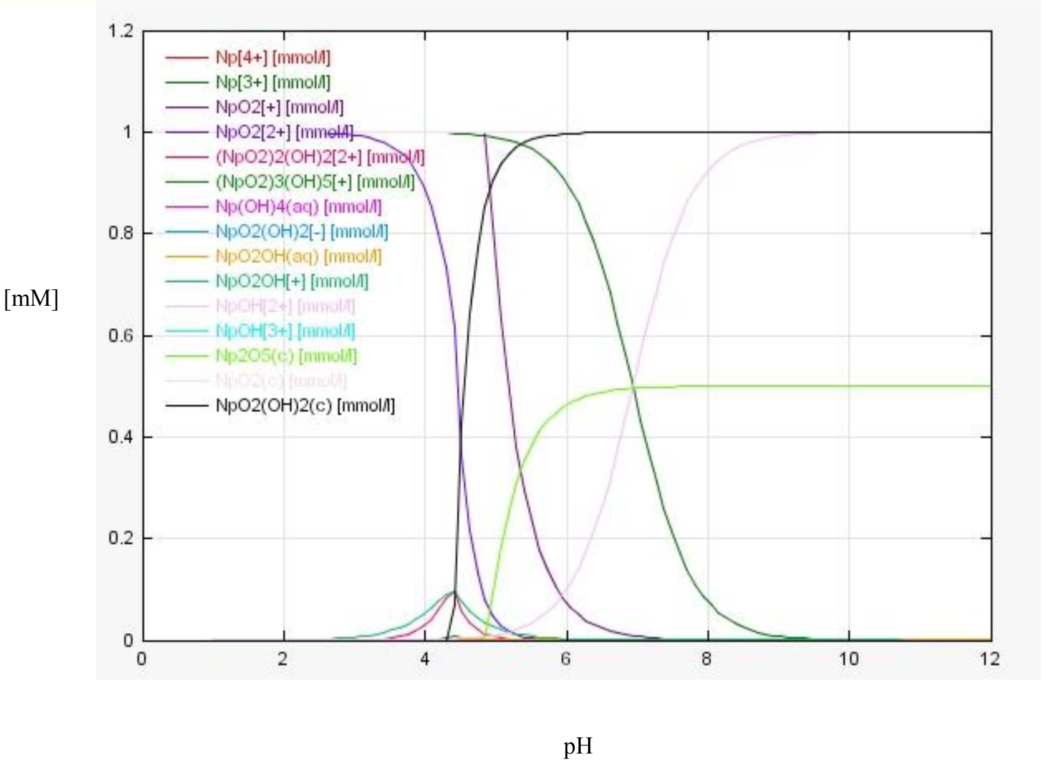


2 M $HClO_4$



Np solution chemistry

- **Np hydrolysis**
  - Np(IV)>Np(VI)>Np(III)>Np(V)
  - For actinides trends with ionic radius
- **Np(III)**
  - below pH 4
  - Stable in acidic solution, oxidizes in air
  - Potentiometric analysis for determining K
  - No K_{sp} data
- **Np(IV)**
  - hydrolyzes above pH 1
    - → Tetrahydroxide main solution species in equilibrium with solid based on pH independence of solution species concentration
- **Np(V)**
  - not hydrolyzed below pH 7
- **Np(VI)**
  - below pH 3-4
- **Np(VII)**
  - No data available
- **Oxidation state trends same as hydrolysis**
- **Stability trends for inorganic**
  - $F^- > H_2PO_4^- > SCN^- > NO_3^- > Cl^- > ClO_4^-$
  - $CO_3^{2-} > HPO_4^{2-} > SO_4^{2-}$
- **NpO_2^+ forms cation-cation complexes**
  - Fe>In>Sc>Ga>Al



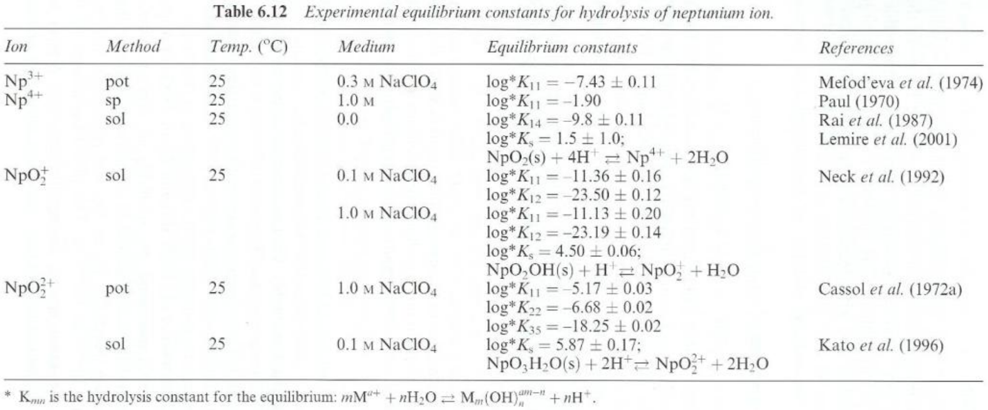


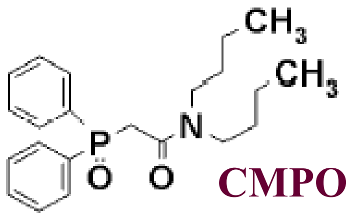
Table 6.12 *Experimental equilibrium constants for hydrolysis of neptunium ion.*

Ion	*Method*	*Temp. (°C)*	*Medium*	*Equilibrium constants*	*References*
Np^{3+}	pot	25	0.3 M $NaClO_4$	$\log{}^*K_{11} = -7.43 \pm 0.11$	Mefod'eva *et al.* (1974)
Np^{4+}	sp	25	1.0 M	$\log{}^*K_{11} = -1.90$	Paul (1970)
	sol	25	0.0	$\log{}^*K_{14} = -9.8 \pm 0.11$	Rai *et al.* (1987)
				$\log{}^*K_s = 1.5 \pm 1.0$; $NpO_2(s) + 4H^+ \rightleftarrows Np^{4+} + 2H_2O$	Lemire *et al.* (2001)
NpO_2^+	sol	25	0.1 M $NaClO_4$	$\log{}^*K_{11} = -11.36 \pm 0.16$ $\log{}^*K_{12} = -23.50 \pm 0.12$	Neck *et al.* (1992)
			1.0 M $NaClO_4$	$\log{}^*K_{11} = -11.13 \pm 0.20$ $\log{}^*K_{12} = -23.19 \pm 0.14$ $\log{}^*K_s = 4.50 \pm 0.06$; $NpO_2OH(s) + H^+ \rightleftarrows NpO_2^+ + H_2O$	
NpO_2^{2+}	pot	25	1.0 M $NaClO_4$	$\log{}^*K_{11} = -5.17 \pm 0.03$ $\log{}^*K_{22} = -6.68 \pm 0.02$ $\log{}^*K_{35} = -18.25 \pm 0.02$	Cassol *et al.* (1972a)
	sol	25	0.1 M $NaClO_4$	$\log{}^*K_s = 5.87 \pm 0.17$; $NpO_3H_2O(s) + 2H^+ \rightleftarrows NpO_2^{2+} + 2H_2O$	Kato *et al.* (1996)

* K_{mn} is the hydrolysis constant for the equilibrium: $mM^{a+} + nH_2O \rightleftarrows M_m(OH)_n^{am-n} + nH^+$.

Np Separations

- Varied oxidation states
  - In solution oxidation states 4+, 5+, and 6 + readily accessible
  - NpO_2^+ is primary solution species
- Most methods exploit redox chemistry of Np
  - Variation in oxidation state can result in separation issues
- Solvent extraction
  - 2-thenoyltrifluoroacetone
    - Reduction to Np(IV)
      - Extraction in 0.5 M HNO_3
      - Back extract in 8 M HNO_3
        - Oxidation to Np(V), extraction into 1 M HNO_3
- Tributylphosphate (TBP)
  - $NpO_2(NO_3)_2(TBP)_2$ and $Np(NO_3)_4(TBP)_2$ are extracted species
    - Extraction increases with increase concentration of TBP and nitric acid
      - 1-10 M HNO_3
    - Separation from other actinides achieved by controlling Np oxidation state
- Carbamoylphosphine oxide (CMPO)
  - Usually used with TBP
  - Nitric acid solutions
  - Separation achieved with oxidation state adjustment
    - Reduction of Pu and Np by Fe(II) sulfamate
    - Np(IV) extracted into organic, then removed with carbonate, oxalate, or EDTA



CMPO

Metallic Np

- First synthesis from NpF_3 with Ba at 1473 K
- Current methods
  - NpF_4 with excess Ca
  - NpO_2 in a molten salt process
    - → Can also use $Cs_2NpO_2Cl_4$ and $Cs_3NpO_2Cl_4$
    - → LiCl/KCl as electrolyte at 723 K
  - NpC reduction with Ta followed by volatilization of Np
  - Electrodepostion from aqueous solution
    - → Amalgamation with Hg from 1 M CH_3COOH and 0.3 M CH_3COONa at pH 3.5
    - → Distillation to remove Hg

Metallic Np data

- Melting point 912 K
    - Boiling point estimated at 4447 K
- Density 19.38 g/mL
- Three metallic forms
    - Enthalpies and entropies of transitions
        - $\alpha \rightarrow \beta$
            - Transition T 553 K
            - $\Delta S=10.1\ JK^{-1}mol^{-1}$
            - $\Delta H=5.607\ kJmol^{-1}$
        - $\beta \rightarrow \gamma$
            - Transition T 856 K
            - $\Delta S=6.23\ JK^{-1}mol^{-1}$
            - $\Delta H=5.272\ kJmol^{-1}$

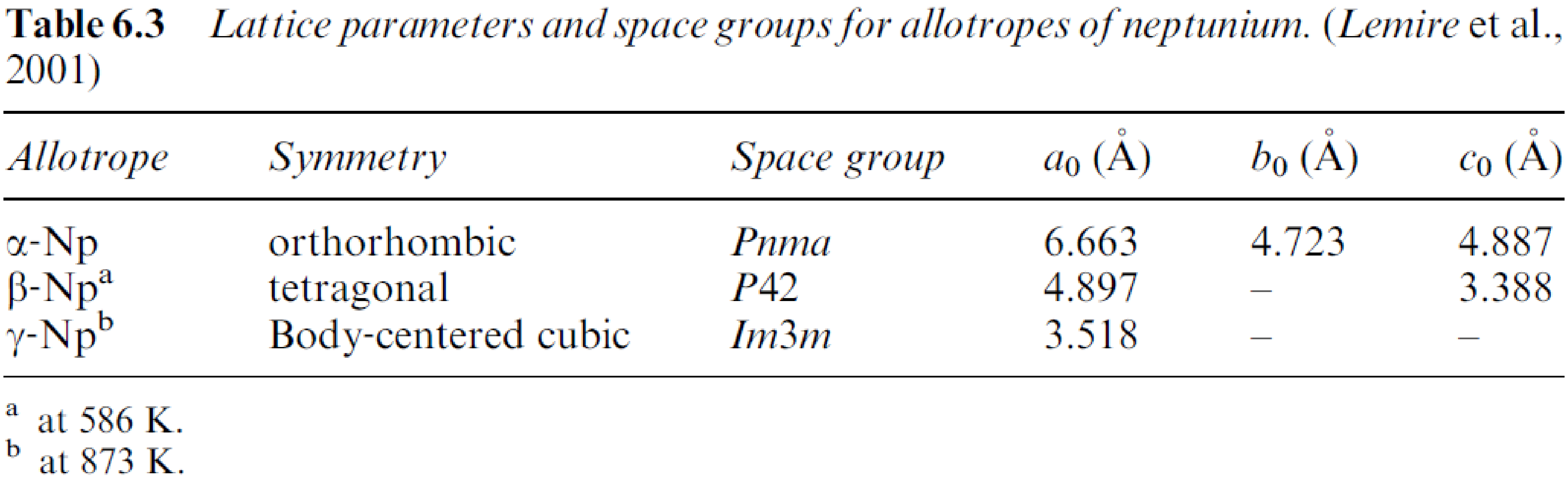


Table 6.3 *Lattice parameters and space groups for allotropes of neptunium.* (*Lemire* et al., 2001)

Allotrope	*Symmetry*	*Space group*	a_0 (Å)	b_0 (Å)	c_0 (Å)
α-Np	orthorhombic	*Pnma*	6.663	4.723	4.887
β-Np[a]	tetragonal	*P*42	4.897	–	3.388
γ-Np[b]	Body-centered cubic	*Im*3*m*	3.518	–	–

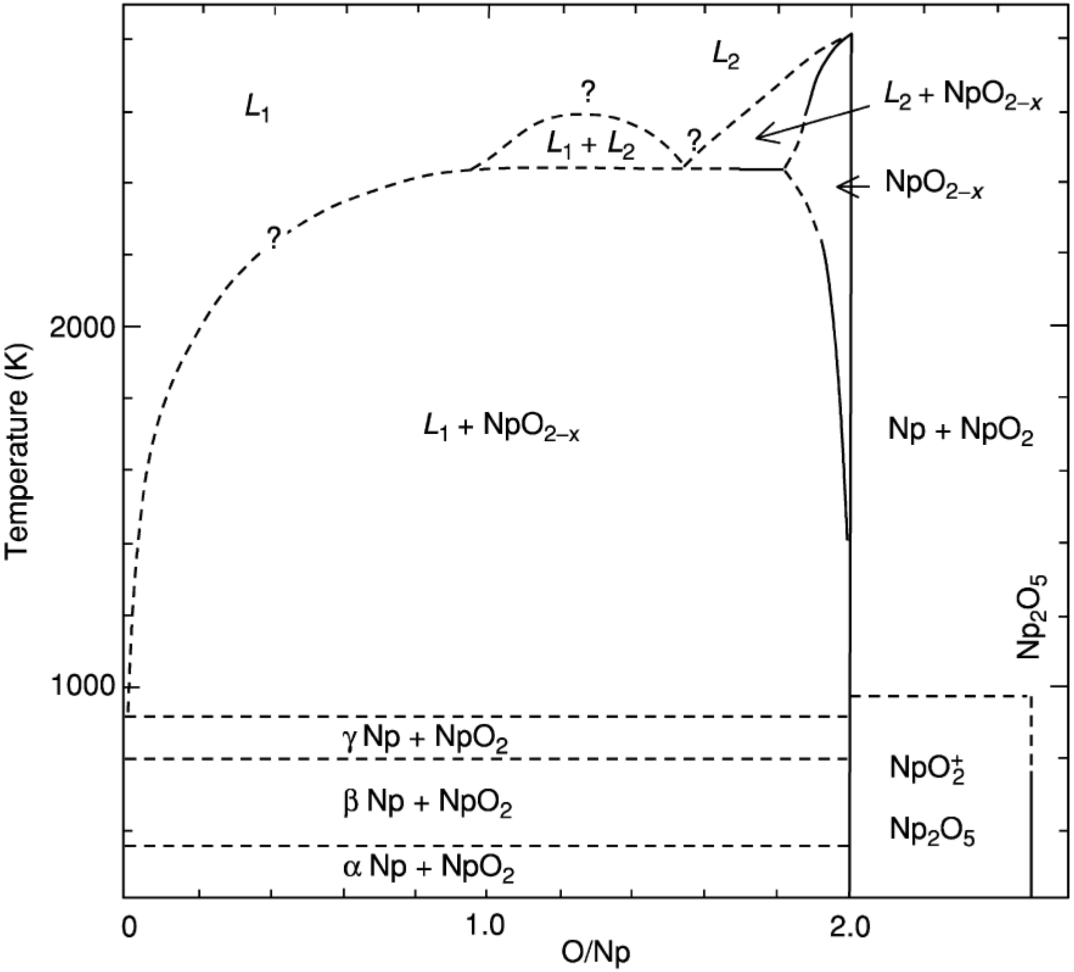
[a] at 586 K.
[b] at 873 K.

Np alloys and intermetallic compounds

- Complexes show presence of f-shell electrons
  - 5f electrons can be unshielded from crystalline electric field interactions
- Range of magnetic behavior
  - Itinerant band like behavior (transition metals)
  - Localized moment behavior (lanthanides)
    - → Variation in behavior based on overlap of 5f wavefunctions or hybridization of f electron
- $NpAl_3$ is ferromagnet,
  - No spin ordering found in $NpGe_3$ and $NpSn_3$
- Range of compounds examined
  - RM_2X_2
    - → R=Th, Np or Pu, M is transition metal, X = Si, Ge
  - RM_2Al_3
    - → R=Np or Pu; M= Ni or Pd
  - NpX_3
    - → X=Al, Ga, Ge, In, or Sn
- Alloy research based on waste form development
  - Zr with Np and other actinides

Neptunium oxides

- Two known anhydrous oxides
  - Np_2O_5 and NpO_2
- NpO_2
  - From thermal decomposition of a range of Np compounds
  - Isostructural with other actinides
  - Fluorite lattice parameter
  - Stable over a range of temperatures
  - Phase change from fcc to orthorhombic at 33 GPa
    - → Stable to 2.84 MPa and 673 K
- Np_2O_5
  - From thermal decomposition of $NpO_3 \cdot H_2O$ or $NpO_2OH_{(am)}$
  - Np_2O_5 decomposes to NpO_2 from 693 K to 970 K

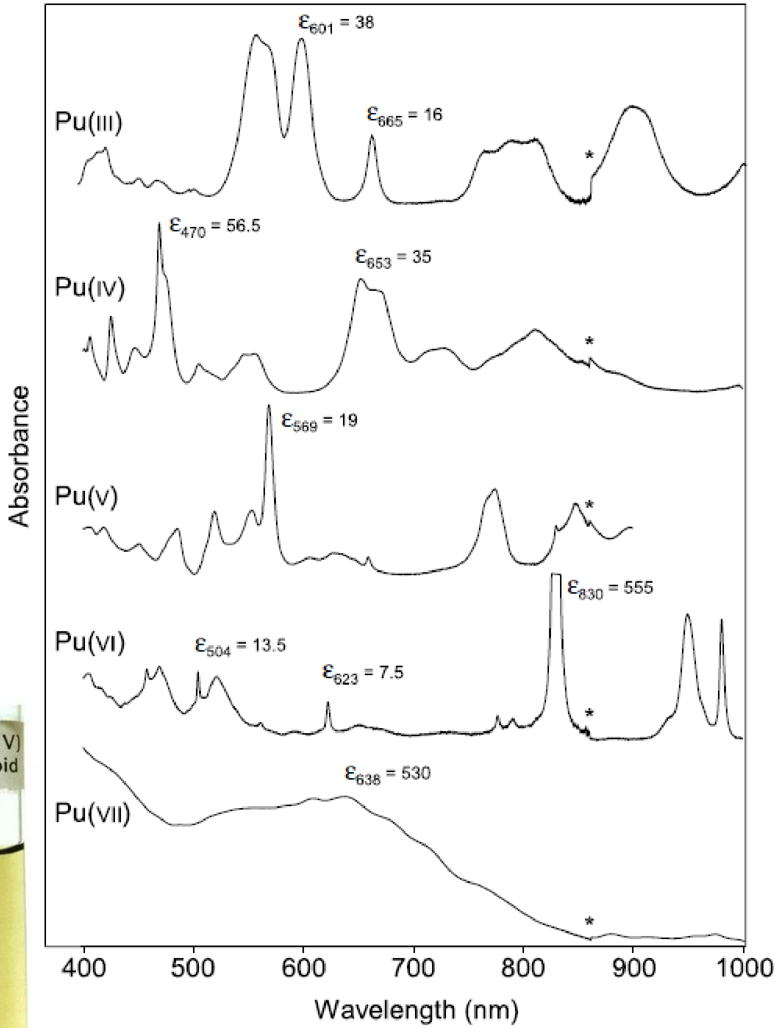


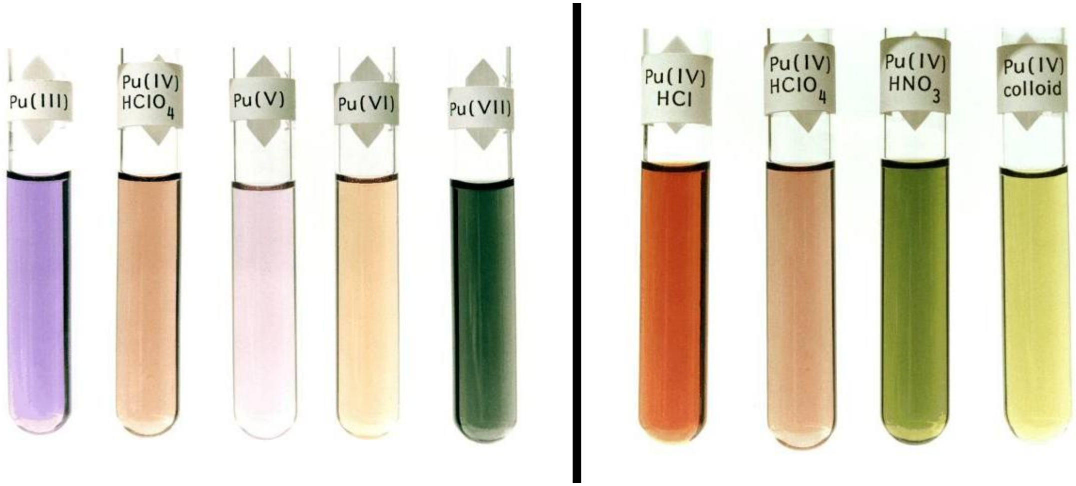
Pu solution chemistry

- Originally driven by the need to separate and purify Pu
- Complicated solution chemistry
  - Five oxidation states (III to VII)
    - → Small energy separations between oxidation states
    - → All states can be prepared
      - * Pu(III) and (IV) more stable in acidic solutions
      - * Pu(V) in near neutral solutions
        - ➢ Dilute Pu solutions favored
      - * Pu(VI) and (VII) favored in basic solutions
        - ➢ Pu(VII) stable only in highly basic solutions and strong oxidizing conditions
  - Some evidence of Pu(VIII)
- Pu^{3+} and Pu^{4+} simple hydrates free species
- Plutonyl oxo species for Pu(V) and Pu(VI)
  - Pu(V) effective charge 2.2
  - Pu(VI) effective charge 3.2
- PuO_4^-
- Redox chemistry instrumental in identifying species

Pu solution chemistry

- Coordination number varies
  - Large values, 8 to 10 for water coordination
- Spectroscopic properties
  - 5f-5f transitions
    - → More intense than 4f of lanthanides
    - → Relativistic effects accentuate spin-orbit coupling
    - → Transitions observed spectroscopically
      - * Forbidden transitions
      - * Sharp but not very intense
- Pu absorption bands in visible and near IR region
  - Characteristic for each oxidation state





Pu solution chemistry

- Redox chemistry
  - Potentials close to 1 V for 4 common states
  - Kinetics permit coexistance of oxidation states
    - → Pu(IV) and Pu(V) tend toward disproportionation
      - * $3Pu^{4+}+2H_2O \leftrightarrows 2Pu^{3+}+PuO_2^{2+}+4H^+$
        - ➢ K=0.0089 at 1.0 M I
      - * $3PuO_2^{+}+4H^+ \leftrightarrows Pu^{3+}+2PuO_2^{2+}+2H_2O$
    - → Pu concentration
    - → Ionic strength
    - → pH
  - Kinetics for disproportionation based on time and Pu concentration
    - → Moles seconds (M s)
- Some redox couples are quasi- or irreversible
  - Breaking or forming oxo bonds
    - → i.e., Pu(V)/Pu(III), Pu(VI)/Pu(III)
- Equilibrium between redox states
  - K=Pu(III)Pu(VI)/Pu(IV)Pu(V)
    - → K=13.1, corrected for hydrolysis

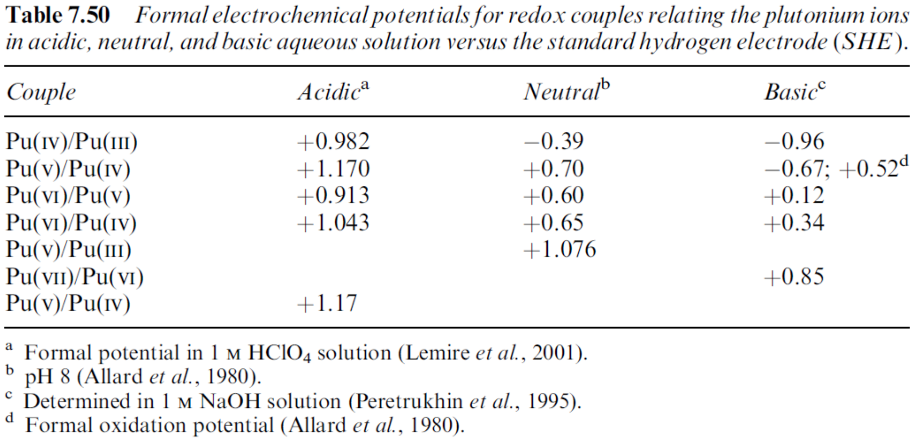


Table 7.50 *Formal electrochemical potentials for redox couples relating the plutonium ions in acidic, neutral, and basic aqueous solution versus the standard hydrogen electrode (SHE).*

Couple	*Acidic*[a]	*Neutral*[b]	*Basic*[c]
Pu(IV)/Pu(III)	+0.982	−0.39	−0.96
Pu(V)/Pu(IV)	+1.170	+0.70	−0.67; +0.52[d]
Pu(VI)/Pu(V)	+0.913	+0.60	+0.12
Pu(VI)/Pu(IV)	+1.043	+0.65	+0.34
Pu(V)/Pu(III)		+1.076	
Pu(VII)/Pu(VI)			+0.85
Pu(V)/Pu(IV)	+1.17		

[a] Formal potential in 1 M $HClO_4$ solution (Lemire *et al.*, 2001).
[b] pH 8 (Allard *et al.*, 1980).
[c] Determined in 1 M NaOH solution (Peretrukhin *et al.*, 1995).
[d] Formal oxidation potential (Allard *et al.*, 1980).

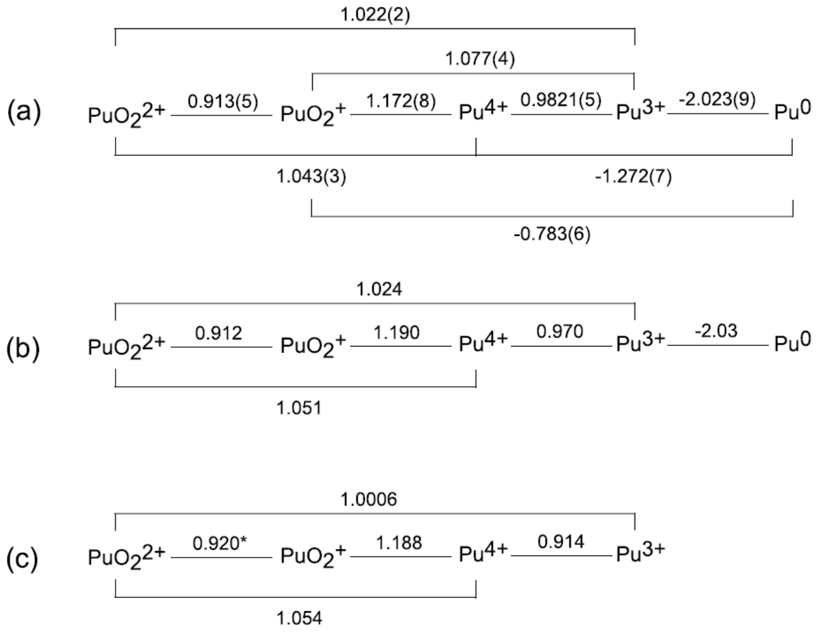
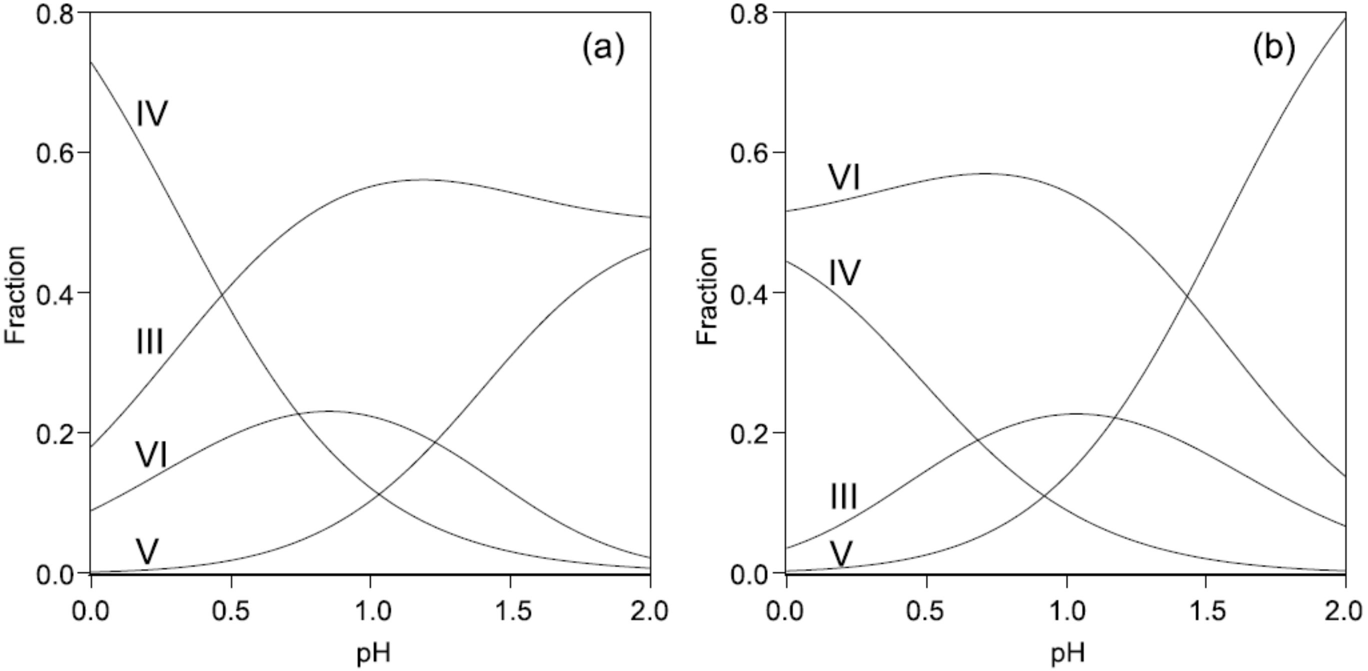
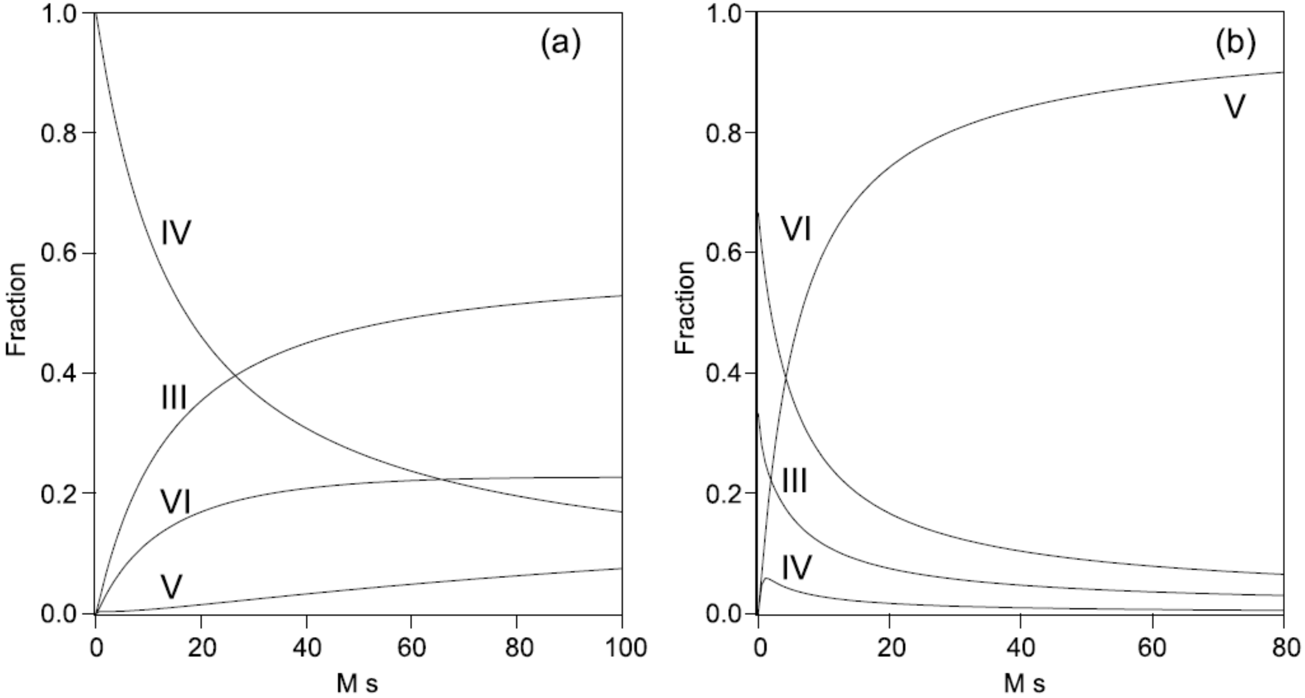


Fig. 7.116 *Formal redox potentials for selected plutonium couples at 25°C in V vs SHE (a) in 1 M $HClO_4$ (Lemire* et al., 2001), *(b) in 1 M HCl (Rabideau and Cowan,* 1955; *Rabideau* et al., 1959), *and (c) 1 M HNO_3 (Artyukhin* et al., 1958).

Oxidation state distribution diagram showing the predominant oxidation state of plutonium in 1 M (H,Na)ClO_4 solution as a function of pH and (a) average oxidation state Pu(IV), and (b) average oxidation state Pu(V) (calculations courtesy of T. W. Newton).



Kinetics for disproportionation of plutonium in 1 M (H,Na)ClO_4 solution at (a) pH 1 and average oxidation state Pu(IV), and (b) pH 3 and average oxidation state Pu(V) (calculations courtesy of T. W. Newton of Los Alamos).

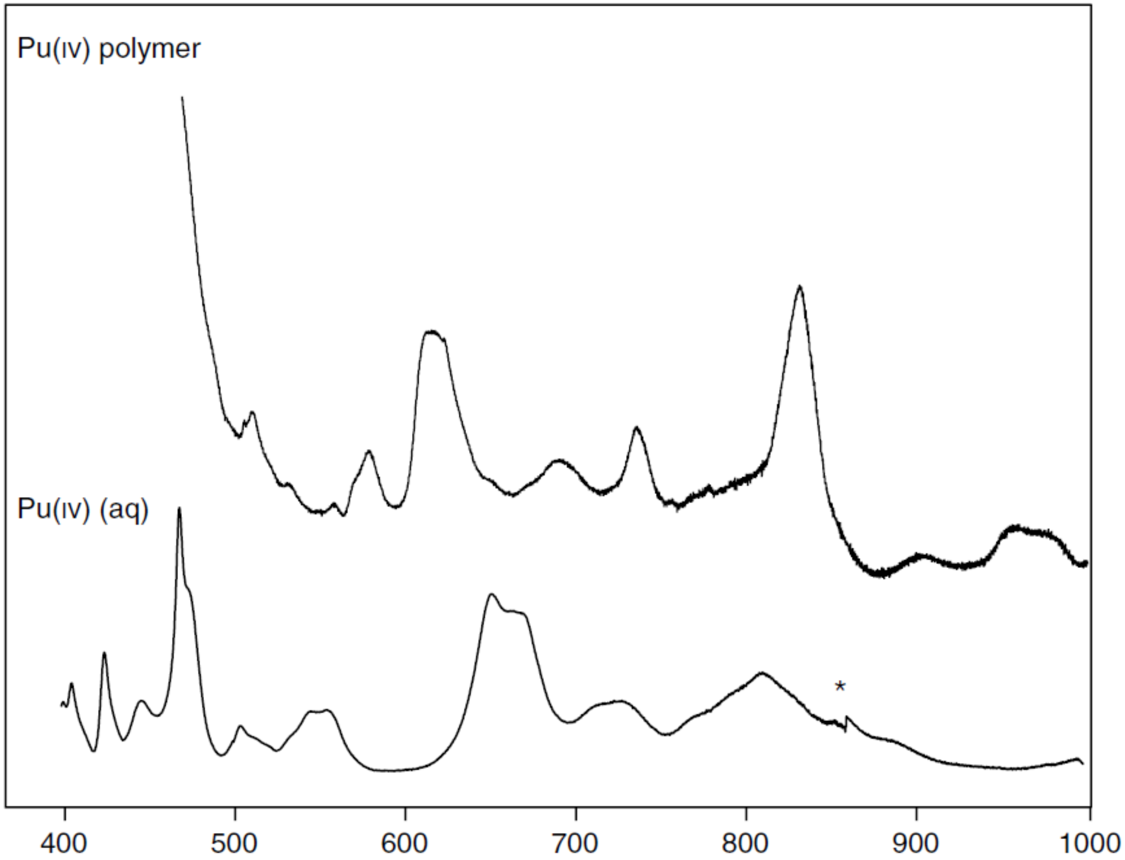


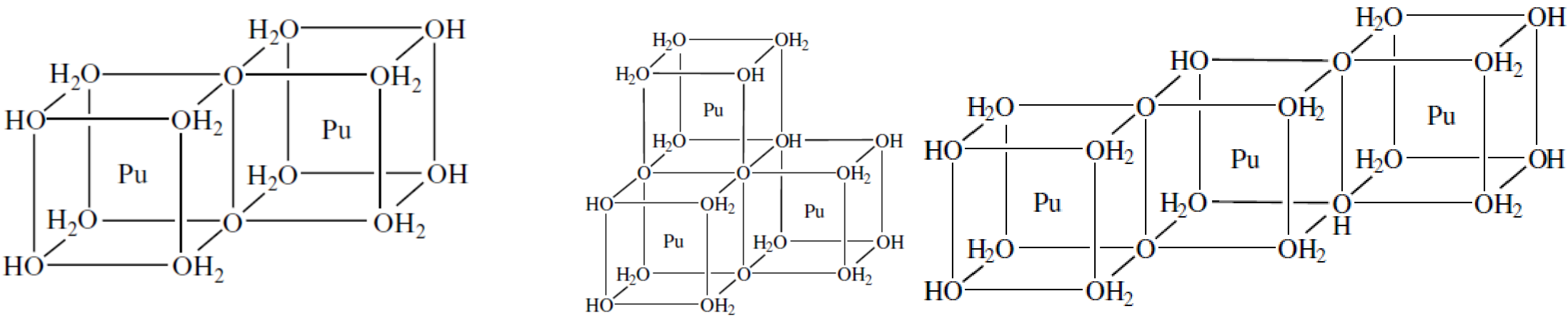
Pu solution chemistry

- Preparation of pure oxidation states
    - Pu(III)
        - → Generally below pH 4
        - → Dissolve α-Pu metal in 6 M HCl
        - → Reduction of higher oxidation state with Hg or Pt cathode
            - * 0.75 V vs NHE
        - → Hydroxylamine or hydrazine as reductant
    - Pu(IV)
        - → Electrochemical oxidation of Pu(III) at 1.2 V
            - * Thermodynamically favors Pu(VI), but slow kinetics due to oxo formation
    - Pu(V)
        - → Electrochemical reduction of Pu(VI) at pH 3 at 0.54 V (vs SCE)
            - * Near neutral in 1 micromole/L Pu(V)
    - Pu(VI)
        - → Treatment of lower oxidation states with hot $HClO_4$
        - → Ozone treatment
    - Pu(VII)
        - → Oxidation in alkaline solutions
            - * Hexavalent Pu with ozone, anodic oxidation

Pu aqueous chemistry: Hydrolysis/colloids

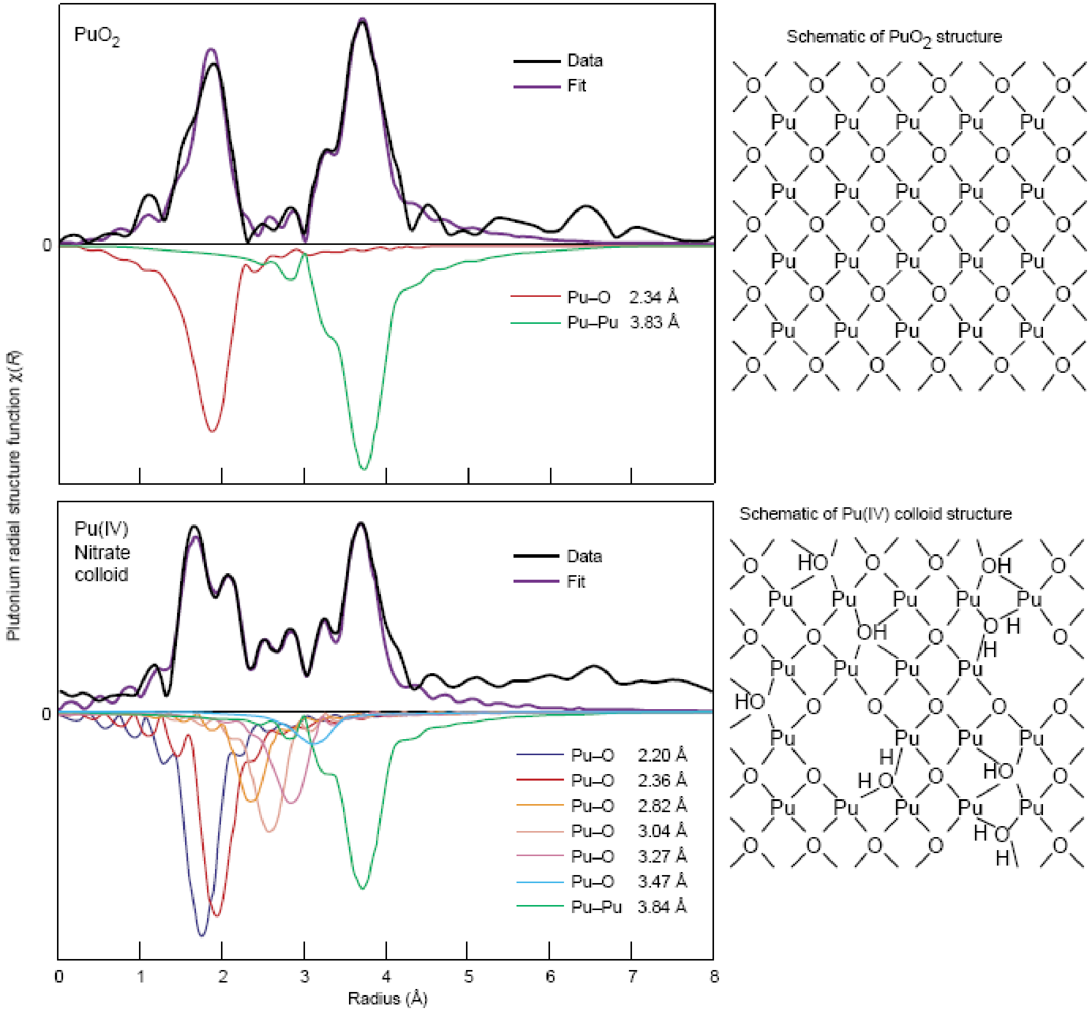
- In many systems solubility derived Pu(IV) concentrations vary due to colloid formation
- Colloids are 1- to 1000-nm size particles that remain suspended in solution
- x-ray diffraction patterns show Pu(IV) colloids are similar to the fcc structure of PuO_2
  - Basis for theory that colloids are tiny crystallites PuO_2,
    - → May include some water saturated of hydrated surface
- Prepared by addition of base or water to acidic solutions





Pu aqueous chemistry: colloids

- XAFS studies of Pu(IV) colloids
  - demonstrated that average fcc structure is simplistic
  - additional chemical forms are present
  - Variations in measured Pu(IV) concentrations may be related to the local structure
  - colloids displays many discrete Pu–O distances
    - → 2.25 Å to 3.5 Å
  - amplitude of Pu–Pu is reduced, decrease in number of nearest neighbors
    - → four H atoms incorporated into the Pu(IV) colloid structure could result in one Pu vacancy.
  - EXAFS reveals that many atoms in the colloid structure are distributed in a non-Gaussian way
    - → several different oxygen containing groups are present
      - * O^{2-}, OH^-, and OH_2

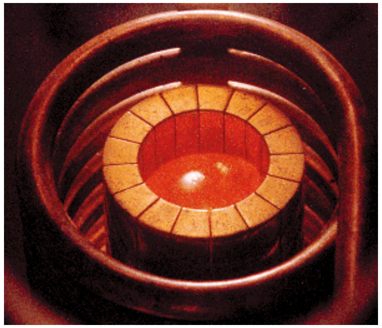


Schematic of PuO$_2$ structure

Schematic of Pu(IV) colloid structure

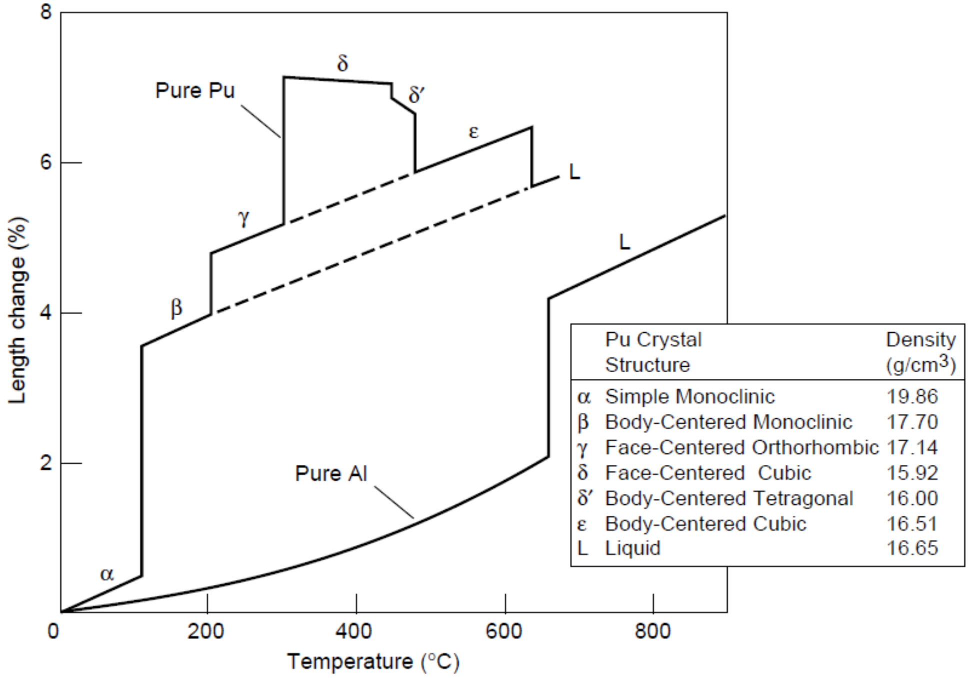
Plutonium Chemistry: Metal Pu

- Ca reduction
- Pyroprocessing
  - PuF_4 and Ca metal
    - → Start at 600 ºC goes to 2000 ºC
    - → Pu solidifies at bottom of crucible
  - Direct oxide reduction
    - → Direct reduction of oxide with Ca metal
    - → PuO_2, Ca, and $CaCl_2$
  - Molten salt extraction
    - → Separation of Pu from Am and lanthanides
    - → Oxidize Am to Am^{3+}, remains in salt phase
    - → $MgCl_2$ as oxidizing agent
      - * Oxidation of Pu and Am, formation of Mg
      - * Reduction of Pu by oxidation of Am metal
  - Electrorefining
    - → Liquid Pu oxidizes from anode ingot into
    - → molten salt electrode
    - → 740 ºC in NaCl/KCl with $MgCl_2$ as oxidizing agent
      - * Oxidation to Pu(III)
      - * Addition of current causes reduction of Pu(III) at cathode
      - * Pu drips off cathode
- Zone refining (700-1000 ºC)
  - Purification from trace impurities
    - → Fe, U, Mg, Ca, Ni, Al, K, Si, oxides and hydrides
  - Melt zone passes through Pu metal at a slow rate
    - → Impurities travel in same or opposite direction of melt direction
  - Vacuum distillation removes Am
  - Application of magnetic field levitates Pu



Pu phase stability

- 6 different Pu solid phases
  - 7th phase at elevated pressure
  - fcc phase least dense
- Energy levels of allotropic phases are very close to each other
  - Pu extremely sensitive to changes in temperature, pressure, or chemistry
- Densities of the allotropes vary significantly
  - dramatic volume changes with phase transitions
- Crystal structure of the allotropes closest to room temperature are of low symmetry
  - more typical of minerals than metals.
- Pu expands when it solidifies from a melt
- Low melting point
- Liquid Pu has very large surface tension with highest viscosity known near the melting point.
- Pu lattice is very soft vibrationally and very nonlinear



	Pu Crystal Structure	Density (g/cm^3)
α	Simple Monoclinic	19.86
β	Body-Centered Monoclinic	17.70
γ	Face-Centered Orthorhombic	17.14
δ	Face-Centered Cubic	15.92
δ′	Body-Centered Tetragonal	16.00
ε	Body-Centered Cubic	16.51
L	Liquid	16.65

Table 7.9 *Crystal structure data for plutonium.*

Phase	*Stability range* (K)	*Crystal lattice and space group*	*Unit cell dimensions* (Å)	*Atoms per unit cell*	*X-ray density* (g cm^{-3})	*Transformation temperature* (K)[b]
α	below 397.6	simple monoclinic $P2_1/m$	at 294 K $a = 6.183(1)$ $b = 4.822(1)$ $c = 10.963(1)$ $\beta = 101.79°(1)$	16	19.85	
β	397.6 – 487.9	body-centered monoclinic $I2/m$[a]	at 463 K $a = 9.284(3)$ $b = 10.463(4)$ $c = 7.859(3)$ $\beta = 93.13°(3)$	34	17.71 (α→β)	397.6
γ	487.9 – 593.1	face-centered orthorhombic $Fddd$	at 508 K $a = 3.159(1)$ $b = 5.768(1)$ $c = 10.162(2)$	8	17.15 (β→γ)	487.9
δ	593.1 – 736.0	face-centered cubic $Fm3m$	at 593 K $a = 4.6371(4)$	4	15.92 (γ→δ)	593.1
δ′	736.0 – 755.7	body-centered tetragonal $I4/mmm$	at 738 K $a = 3.34(1)$ $c = 4.44(4)$	2	16.03 (δ→δ′)	736.0
ϵ	755.7 – 913.0	body-centered cubic $Im3m$	at 763 K $a = 3.6361(4)$	2	16.51 (δ′→ϵ) m.p.	755.7 913.0

[a] Although space group $I2/m$ is not one of the 'standard' space groups tabulated in the International Union of Crystallography, *International Tables for X-ray Crystallography*, vol. 1, Kynoch Press, Birmingham, its notation is retained to obtain a β angle of approximately 90° (data from Miner and Schonfeld, 1980).

[b] Data from Lemire *et al.* (2001). The reader is cautioned that the transformation temperatures vary between sources, and are sensitive to heating and cooling rates and metal purity.

Plutonium exhibits six different crystallographic phases at ambient pressure (it has a seventh phase under pressure) and contracts on melting. Transformations to different crystal structures occur readily and are accompanied by very large volume changes. The dashed lines show that thermal contraction on cooling the liquid (L) phase of plutonium extrapolates to that of the β-phase; the thermal contraction on cooling the ε-phase extrapolates to that of the γ-phase.

Pu metal phases

- Low symmetry ground state for α phase due to 5f bonding
  - Higher symmetry found in transition metals
- f orbitals have odd symmetry
  - Basis for low symmetry (same as p orbitals Sn, In, Sb, Te)
  - odd-symmetry p orbitals produce directional covalent-like bonds and low-symmetry noncubic structures
- Recent local density approximation (LDA) electronic-structure calculations show narrow width of f bands leads to low-symmetry ground states of the actinides
  - Bandwidths are a function of volume.
    - → narrower for large volumes

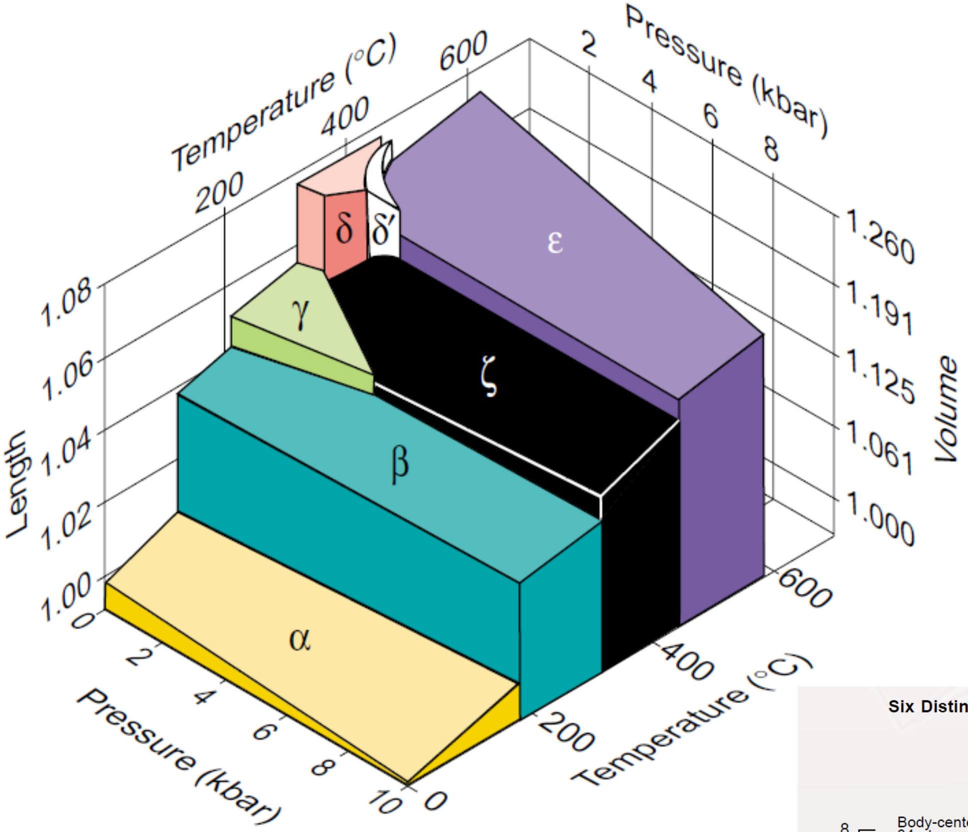
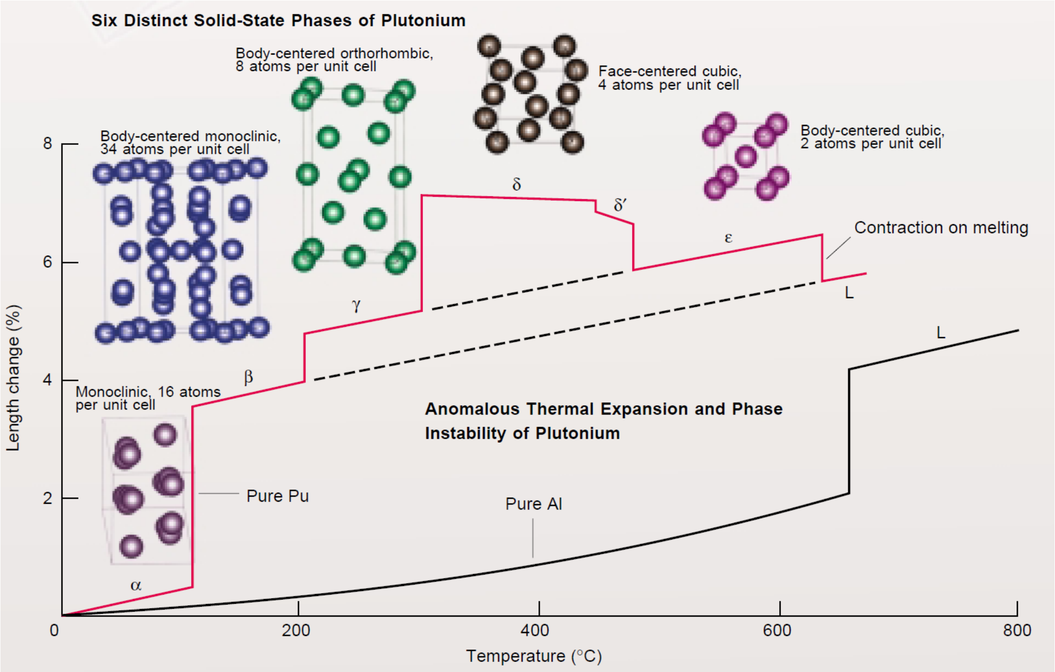
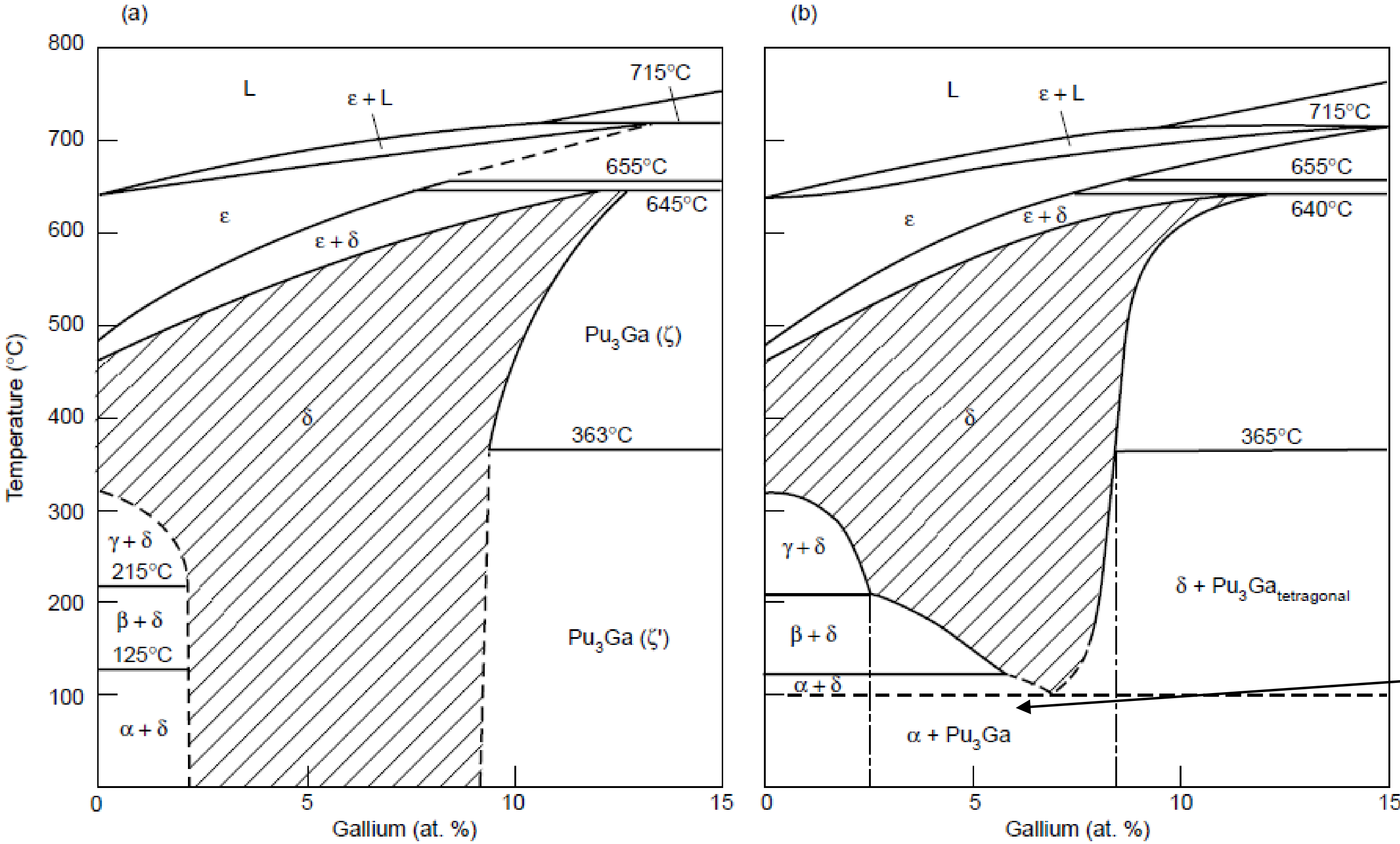


Figure 16. Plutonium Instability with Temperature and Pressure

Over a span of 600°, Pu exhibits six different allotropic phases with large accompanying volume changes before it melts. Pressures on the order of kilobar (100 megapascals) are sufficient to squeeze out the high-volume allotropes (Morgan 1970). Small chemical additions can stabilize these high-volume phases.





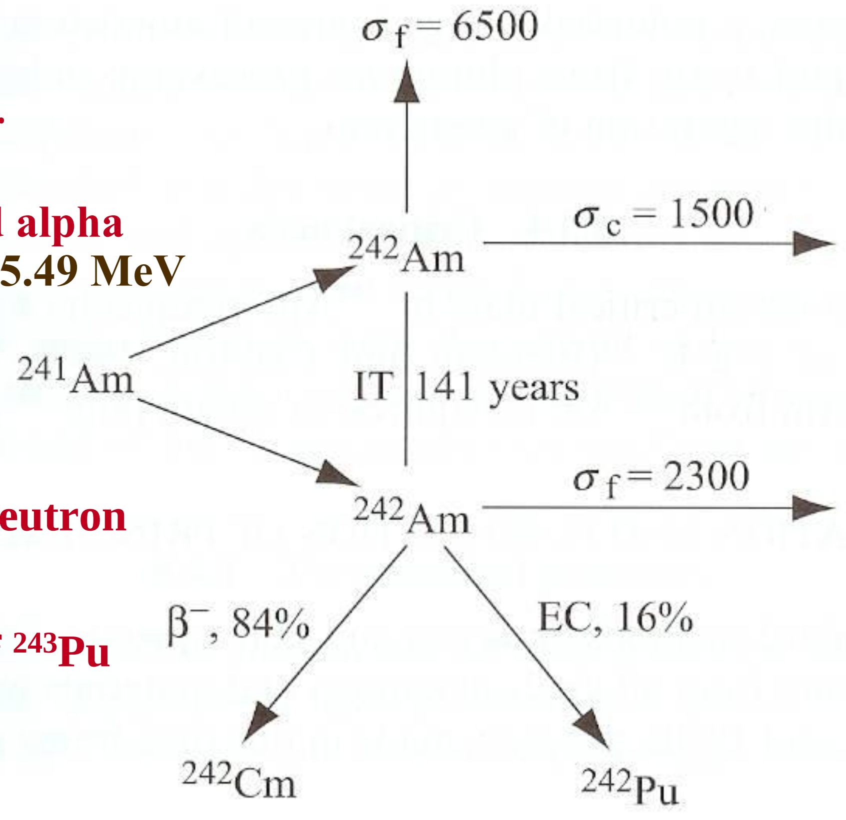
Phase never observed, slow kinetics

Figure 1. U.S. and Russian Equilibrium Pu-Ga Phase Diagrams

The U.S. equilibrium Pu-Ga phase diagram in (a) was reported by Peterson and Kassner (1988) and is based on the work of Ellinger et al. (1964). The Russian phase diagram in (b) was reported by Chebotarev et al. (1975). The principal difference is that Ellinger et al. found the fcc δ-phase to be retained at room temperature by gallium concentrations greater than approximately 2 at. % and less than approximately 9 at. %, whereas Chebotarev et al. reported a eutectoid decomposition of the δ- to the α-phase plus Pu$_3$Ga below 100°C. Both diagrams have dashed lines at the lower end of the temperature spectrum because diffusion processes become so slow that it is very difficult to determine what the real "equilibrium" structure is. So, both diagrams represent extrapolations to equilibrium—but with very different conclusions. The dash-dotted lines in (b) represent the metastable phase boundaries.

Production of Am isotopes

- Am first produced from neutron irradiation of Pu
  - ^{239}Pu to ^{240}Pu to ^{241}Pu, then beta decay of ^{241}Pu
- ^{241,243}Am main isotopes of interest
  - Long half-lives
  - Produced in kilogram quantity
  - Chemical studies
  - Both isotopes produced in reactor
- ^{241}Am
  - source for low energy gamma and alpha
    - → Alpha energy 5.44 MeV and 5.49 MeV
  - Smoke detectors
  - Neutron sources
    - → (α,n) on Be
  - Thickness gauging and density
  - ^{242}Cm production from thermal neutron capture
- ^{243}Am
  - Irradiation of ^{242}Pu, beta decay of ^{243}Pu
- Critical mass
  - ^{242}Am in solution
    - → 23 g at 5 g/L
    - → Requires isotopic separation



Am solution chemistry

- Oxidation states III-VI in solution
  - Am(III,V) stable in dilute acid
  - Am(V, VI) form dioxo cations
- Am(III)
  - Easy to prepare (metal dissolved in acid, AmO_2 dissolution)
    - → Pink in mineral acids, yellow in $HClO_4$ when Am is 0.1 M
- Am(IV)
  - Requires complexation to stabilize
    - → dissolving $Am(OH)_4$ in NH_4F
    - → Phosphoric or pyrophosphate ($P_2O_7^{4-}$) solution with anodic oxidation
    - → Ag_3PO_4 and $(NH_4)_4S_2O_8$
    - → Carbonate solution with electrolytic oxidation
- Am(V)
  - Oxidation of Am(III) in near neutral solution
    - → Ozone, hypochlorate (ClO^-), peroxydisulfate
    - → Reduction of Am(VI) with bromide
- Am(VI)
  - Oxidation of Am(III) with $S_2O_8^{2-}$ or Ag^{2+} in dilute non-reducing acid (i.e., sulfuric)
  - Ce(IV) oxidizes IV to VI, but not III to VI completely
  - 2 M carbonate and ozone or oxidation at 1.3 V
- Am(VII)
  - 3-4 M NaOH, mM Am(VI) near 0 °C
  - Gamma irradiation 3 M NaOH with N_2O or $S_2O_8^{2-}$ saturated solution

Am solution chemistry

- **Am(III) has 9 inner sphere waters**
    - **Others have calculated 11 and 10 (XAFS)**
    - **Based on fluorescence spectroscopy**
        - → **Lifetime related to coordination**
            - * **$n_{H2O}=(x/\tau)-y$**
                - ➢ **x=2.56E-7 s, y=1.43**
                - ➢ **Measurement of fluorescence lifetime in H_2O and D_2O**

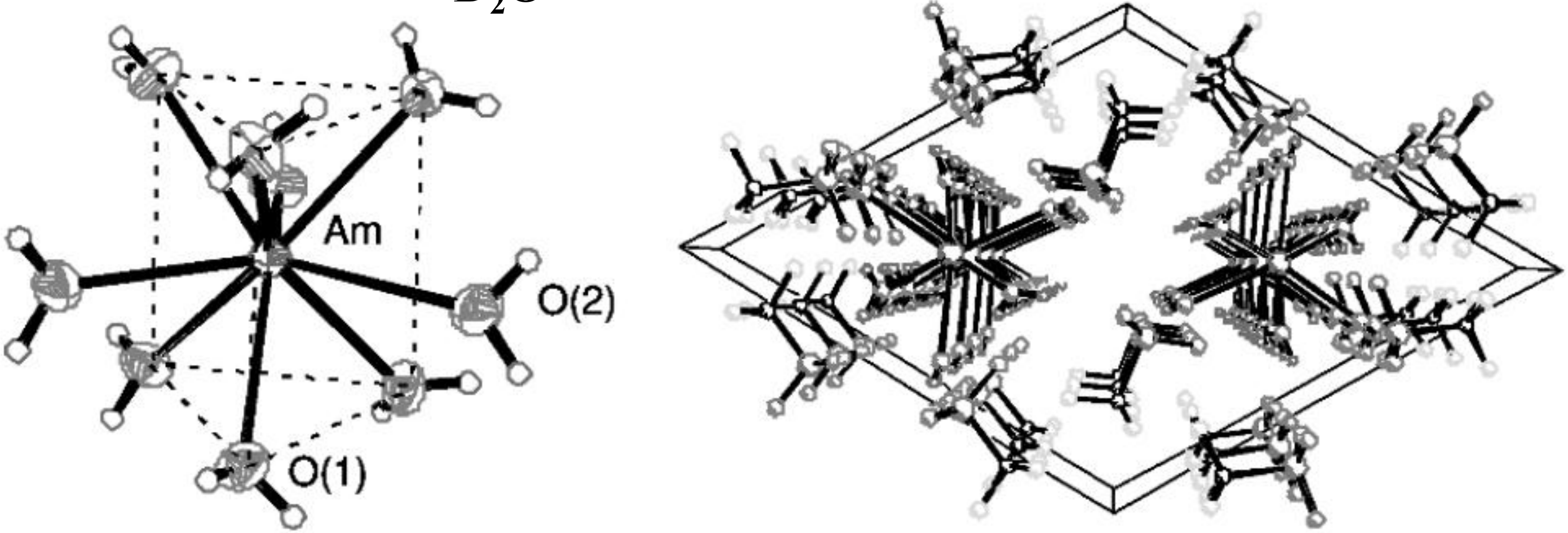


Fig. 8.4 *Coordination environment of Am^{3+} and crystal packing in* $[Am(H_2O)_9][CF_3SO_3]$ (*Matonic* et al., 2001).

Am solution chemistry

- **Autoreduction**
  - **Formation of H_2O_2 and HO_2 radicals from radiation reduces Am to trivalent states**
    - → **Difference between ^{241}Am and ^{243}Am**
  - **Rate decreases with increase acid for perchloric and sulfuric**
  - **Some disagreement role of Am concentration**
    - → **Concentration of Am total or oxidation state**
  - **Rates of reduction dependent upon**
    - → **Acid, acid concentration,**
    - → **mechanism**
      - * **Am(VI) to Am(III) can go stepwise**
    - → **starting ion**
      - * **Am(V) slower than Am(VI)**

Am solution chemistry

- **Disproportionation**
  - Am(IV)
    - → In nitric and perchloric acid
    - → Second order with Am(IV)
      - * 2 Am(IV)→Am(III) + Am(V)
      - * Am(IV) + Am(V)→Am(III) + Am(VI)
        - ➢ Am(VI) increases with sulfate
  - Am(V)
    - → 3-8 M $HClO_4$ and HCl
      - * $3\ Am(V) + 4\ H^+ \rightarrow Am(III) + 2Am(VI) + 2\ H_2O$
    - → Solution can impact oxidation state stability

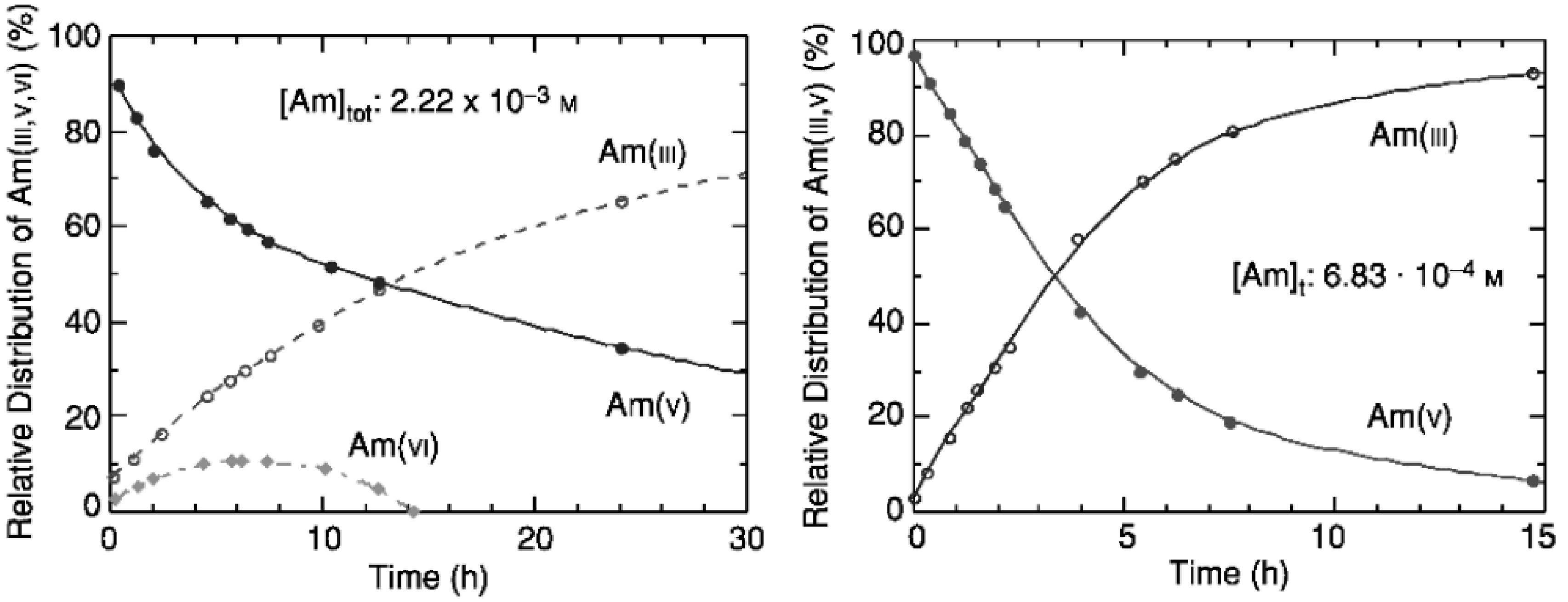


Fig. 8.5 *Disproportionation of Am(V) in 5 M $HClO_4$ (left) and 5 M HCl (right) (Runde and Kim, 1994).*

Am solution chemistry: Redox Kinetics

- Am(III) oxidation by peroxydisulfate
  - Oxidation due to thermal decomposition products
    - → $SO_4^{\cdot -}$, $HS_2O_8^-$
  - Oxidation to Am(VI)
    - → 0.1 M to 10 nM Am(III)
  - Acid above 0.3 M limits oxidation
    - → Decomposition of $S_2O_8^{2-}$
  - Induction period followed by reduction
  - Rates dependent upon temperature, $[HNO_3]$, $[S_2O_8^{2-}]$, and $[Ag^{+2}]$
  - $3/2\ S_2O_8^{2-} + Am^{3+} + 2\ H_2O \leftrightarrow 3\ SO_4^{2-} + AmO_2^{2+} + 4H^+$
    - → Evaluation of rate constants can yield 4 due to peroxydisulfate decomposition
  - In carbonate proceeds through Am(V)
    - → Rate to Am(V) is proportional to oxidant
    - → Am(V) to Am(VI)
      - * Proportional to total Am and oxidant
      - * Inversely proportional to K_2CO_3

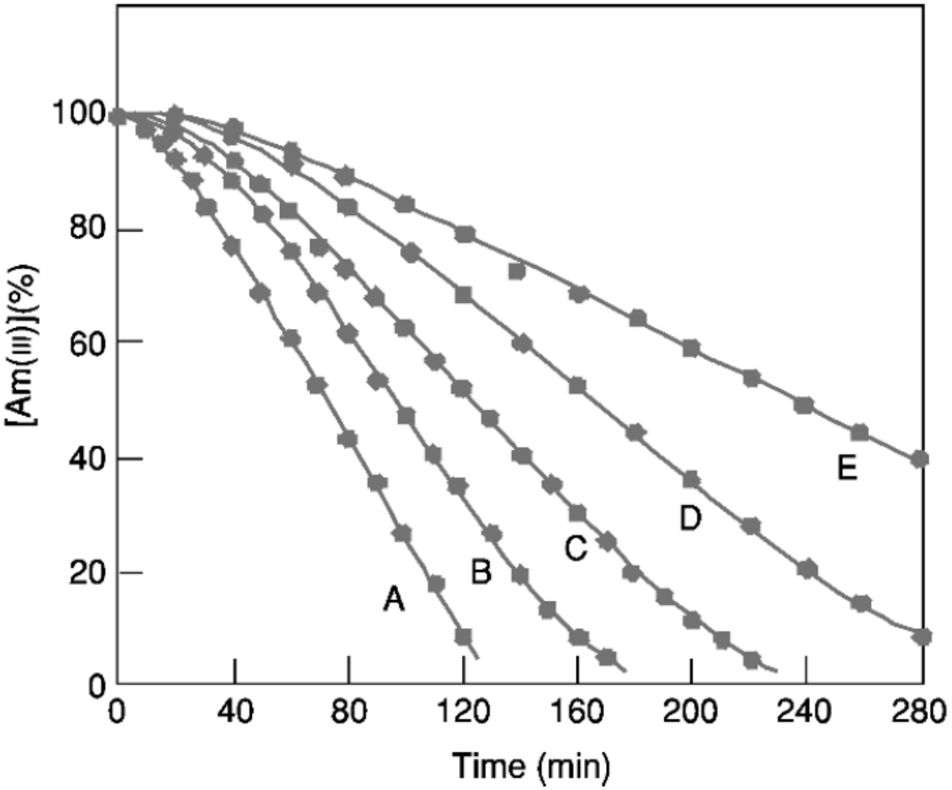


Fig. 8.6 *Kinetics of Am(III) oxidation by peroxydisulfate in nitric acid at* 50.6°C ($[S_2O_8^{2+}]_0$ = 0.40 M (*Ermakov* et al., 1971a, 1973, 1974)). HNO_3 *concentrations: A*, 0.09 M; *B*, 0.14 M; *C*, 0.19 M; *D*, 0.24 M; *E*, 0.28 M.

Am solution chemistry: Redox kinetics

- Am(VI) reduction
  - H_2O_2 in perchlorate is 1st order for peroxide and Am
    - → $2\ AmO_2^{2+} + H_2O_2 \rightarrow 2\ AmO_2^{+} + 2\ H^{+} + O_2$
  - NpO_2^{+}
    - → 1st order with Am(VI) and Np(V)
      - * k=2.45E4 L / mol s
  - Oxalic acid reduces to equal molar Am(III) and Am(V)
- Am(V) reduction
  - Reduced to Am(III) in NaOH solutions
    - → Slow reduction with dithionite ($Na_2S_2O_4$), sulfite (SO_3^{2-}), or thiourea dioxide ($(NH_2)_2CSO_2$)
  - Np(IV) and Np(V)
    - → In both acidic and carbonate conditions
      - * For Np(IV) reaction products either Np(V) or Np(VI)
        - ➢ Depends upon initial relative concentration of Am and Np
    - → U(IV) examined in carbonate

Solution absorption spectroscopy

- Am(III)
  - $^7F_0 \rightarrow {}^5L_6$ at 503.2 nm (ε=410 L mol cm^{-1})
  - Shifts in band position and molar absorbance indicates changes in water or ligand coordination
  - Solution spectroscopy compared to Am doped in crystals
  - Absorbance measured in acids and carbonate
- Am(IV)
  - In acidic media, broad absorption bands
    - → 13 M HF, 12 M KF, 12 M H_3PO_4
  - Resembles solid AmF_4 spectrum

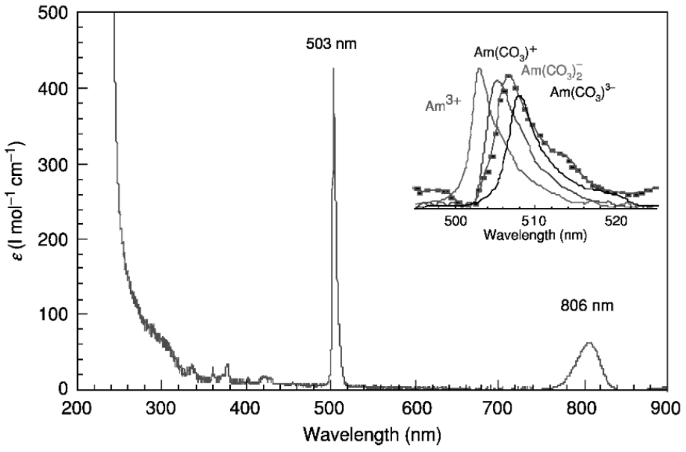


Fig. 8.13 *Electronic absorption spectra of Am^{3+} in 1 M $HClO_4$ and of the predominant Am(III) species in carbonate-containing solutions (inset)* (*Meinrath and Kim*, 1991a).

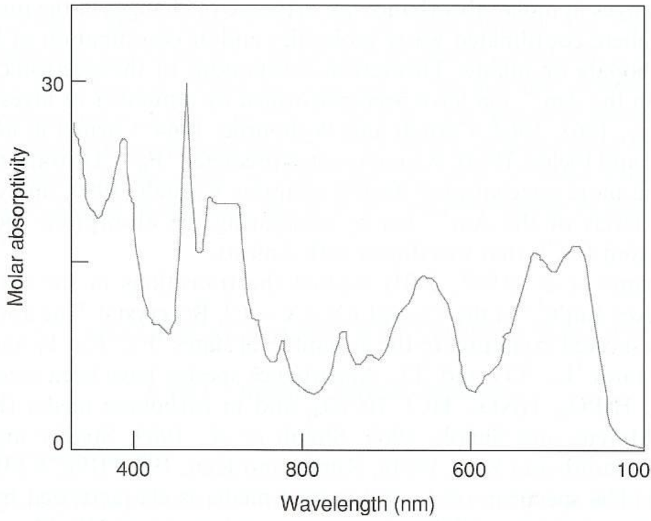


Fig. 8.14 *Absorption spectrum of Am(IV) in 13 M NH_4F* (*Asprey and Penneman*, 1962).

Solution absorption spectroscopy

- Am(V)
  - $^5I_4 \rightarrow {}^3G_5$; 513.7 nm; 45 L mol cm^{-1}
  - $^5I_4 \rightarrow {}^3I_7$; 716.7 nm; 60 L mol cm^{-1}
    - → Collected in acid, NaCl, and carbonate
- Am(VI)
  - 996 nm; 100 L mol cm^{-1}
  - Smaller absorbance at 666 nm
    - → Comparable to position in Am(V)
    - → Based on comparison with uranyl, permits analysis based on uranyl core with addition of electrons

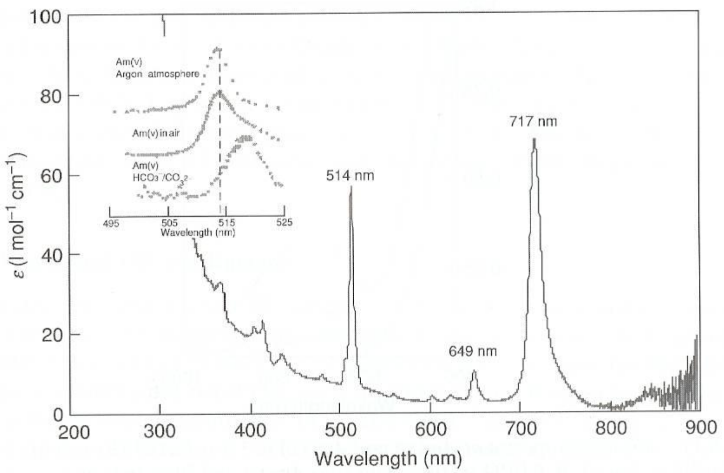


Fig. 8.15 *Electronic absorption spectra of* AmO_2^+ *in* 1 M $HClO_4$ *and in carbonate-containing solutions (inset) (Stadler and Kim,* 1988).

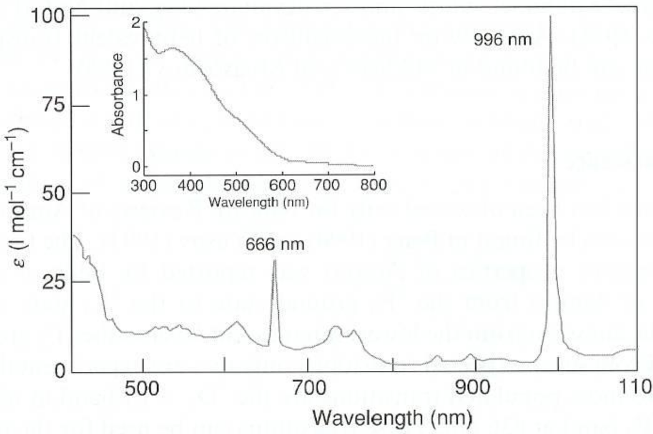


Fig. 8.16 *Absorption spectrum of Am*(VI) *in* 1 M $HClO_4$ *and in carbonate solution (inset) (Penneman and Asprey,* 1955).

Solution absorption spectroscopy

- Am(VII)
  - Broad absorbance at 740 nm
- Am(III) luminescence
  - $^7F_0 \rightarrow {}^5L_6$ at 503 nm
    - → Then conversion to other excited state
  - Emission to ^7F_J
  - $^5D_1 \rightarrow {}^7F_1$ at 685 nm
  - $^5D_1 \rightarrow {}^7F_2$ at 836 nm
  - Lifetime for aquo ion is 20 ns
    - → 155 ns in D_2O
  - Emission and lifetime changes with speciation
    - → Am triscarbonate lifetime = 34.5 ns, emission at 693 nm

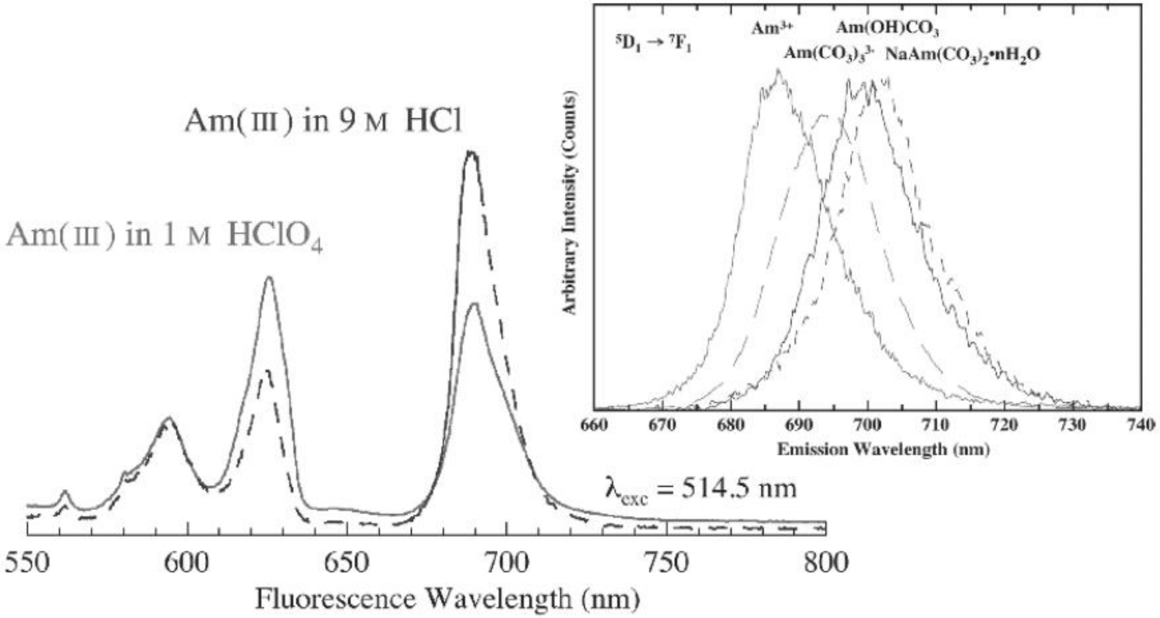


Fig. 8.18 *Luminescence spectrum of Am^{3+} in acidic media and of Am(III) carbonate complexes*. (*Runde* et al., 2000, 2002).

Am metal and alloys

- Preparation of Am metal
  - Reduction of AmF_3 with Ba or Li
  - Reduction of AmO_2 with La
  - Bomb reduction of AmF_3 with Ca
  - Decomposition of Pt_5Am
    - 1550 °C at 10^{-6} torr
  - La or Th reduction of AmO_2 with distillation of Am
- Metal properties
  - Ductile, non-magnetic
  - Double hexagonal closed packed (dhcp) and fcc
  - Evidence of three phase between room temperature and melting point at 1170 °C
    - Alpha phase up to 658 °C
    - Beta phase from 793 °C to 1004 °C
    - Gamma above 1050 °C
  - Some debate in literature
    - Evidence of dhcp to fcc at 771 °C
  - Interests in metal properties due to 5f electron behavior
    - Delocalization under pressure
    - Different crystal structures
      - Conversion of dhcp to fcc
    - Discrepancies between different experiments and theory

Am metal, alloys, and compounds

- **Alloys investigated with 23 different elements**
- **Phase diagrams available for Np, Pu, and U alloys**
- **Am compounds**
  - **Oxides and hydroxides**
    - → **AmO, Am_2O_3, AmO_2**
      - * **Non-stoichiometric phases between Am_2O_3 and AmO_2**
    - → **AmO lattice parameters varied in experiments**
      - * **4.95 Å and 5.045 Å**
      - * **Difficulty in stabilizing divalent Am**
    - → **Am_2O_3**
      - * **Prepared in H_2 at 600 °C**
      - * **Oxidizes in air**
      - * **Phase transitions with temperature**
        - ➢ **bcc to monoclinic between 460 °C and 650 °C**
        - ➢ **Monoclinic to hexagonal between 800 °C and 900 °C**

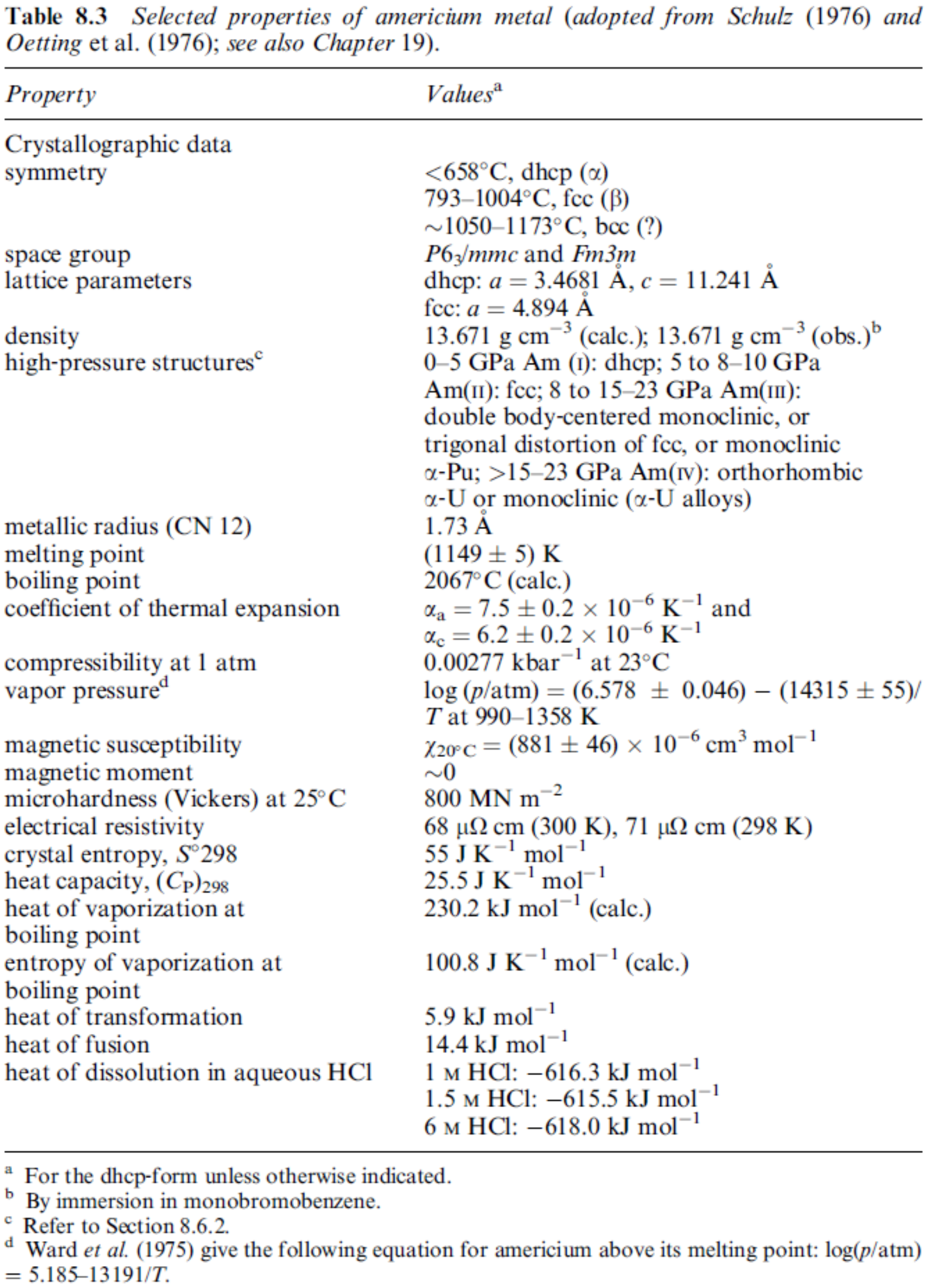


Table 8.3 *Selected properties of americium metal (adopted from Schulz (1976) and Oetting* et al. *(1976); see also Chapter* 19).

Property	*Values*[a]
Crystallographic data	
symmetry	<658°C, dhcp (α) 793–1004°C, fcc (β) ~1050–1173°C, bcc (?)
space group	$P6_3/mmc$ and $Fm3m$
lattice parameters	dhcp: $a = 3.4681$ Å, $c = 11.241$ Å fcc: $a = 4.894$ Å
density	13.671 g cm^{-3} (calc.); 13.671 g cm^{-3} (obs.)[b]
high-pressure structures[c]	0–5 GPa Am (I): dhcp; 5 to 8–10 GPa Am(II): fcc; 8 to 15–23 GPa Am(III): double body-centered monoclinic, or trigonal distortion of fcc, or monoclinic α-Pu; >15–23 GPa Am(IV): orthorhombic α-U or monoclinic (α-U alloys)
metallic radius (CN 12)	1.73 Å
melting point	(1149 ± 5) K
boiling point	2067°C (calc.)
coefficient of thermal expansion	$\alpha_a = 7.5 \pm 0.2 \times 10^{-6}$ K^{-1} and $\alpha_c = 6.2 \pm 0.2 \times 10^{-6}$ K^{-1}
compressibility at 1 atm	0.00277 $kbar^{-1}$ at 23°C
vapor pressure[d]	$\log (p/\mathrm{atm}) = (6.578 \pm 0.046) - (14315 \pm 55)/T$ at 990–1358 K
magnetic susceptibility	$\chi_{20°C} = (881 \pm 46) \times 10^{-6}$ cm^3 mol^{-1}
magnetic moment	~0
microhardness (Vickers) at 25°C	800 MN m^{-2}
electrical resistivity	68 μΩ cm (300 K), 71 μΩ cm (298 K)
crystal entropy, $S°298$	55 J K^{-1} mol^{-1}
heat capacity, $(C_P)_{298}$	25.5 J K^{-1} mol^{-1}
heat of vaporization at boiling point	230.2 kJ mol^{-1} (calc.)
entropy of vaporization at boiling point	100.8 J K^{-1} mol^{-1} (calc.)
heat of transformation	5.9 kJ mol^{-1}
heat of fusion	14.4 kJ mol^{-1}
heat of dissolution in aqueous HCl	1 M HCl: −616.3 kJ mol^{-1} 1.5 M HCl: −615.5 kJ mol^{-1} 6 M HCl: −618.0 kJ mol^{-1}

---

[a] For the dhcp-form unless otherwise indicated.

[b] By immersion in monobromobenzene.

[c] Refer to Section 8.6.2.

[d] Ward *et al.* (1975) give the following equation for americium above its melting point: $\log(p/\mathrm{atm}) = 5.185–13191/T$.

Cm Chemistry

- $5f^7$ has enhanced stability
  - Half filled orbital
    - → Large oxidation potential for III→IV
    - → Cm(IV) is metastable
- Cm(III) absorbance
  - Weak absorption in near-violet region
  - Solution absorbance shifted 20-30 Å compared to solid
    - → Reduction of intensity in solid due to high symmetry
      - * f-f transitions are symmetry forbidden
  - Spin-orbit coupling acts to reduce transition energies when compared to lanthanides
- Cm(IV) absorbance
  - Prepared from dissolution of CmF_4
    - → CmF_3 under strong fluorination conditions
- Isotopes from mass 237 to 251
- Three isotopes available in quantity for chemical studies
  - ^{242}Cm, $t_{1/2}$=163 d
    - → 122 W/g
    - → Grams of the oxide glows
    - → Low flux of ^{241}Am target decrease fission of ^{242}Am, increase yield of ^{242}Cm
  - ^{244}Cm, $t_{1/2}$=18.1 a
    - → 2.8 W/g
  - ^{248}Cm, $t_{1/2}$= 3.48E5 a
    - → 8.39% SF yield
    - → Limits quantities to 10-20 mg
    - → Target for production of transactinide elements

Cm Production

- From successive neutron capture of higher Pu isotopes
  - ^{242}Pu+n→^{243}Pu (β^{-}, 4.95 h)→^{243}Am+n→^{244}Am (β^{-}, 10.1 h)→^{244}Cm
  - Favors production of ^{244,246,248}Cm
    - → Isotopes above ^{244}Cm to ^{247}Cm are not isotopically pure
    - → Pure ^{248}Cm available from alpha decay of ^{252}Cf
- Large campaign to product Cm from kilos of Pu
- ^{244}Cm separation
  - Dissolve target in HNO_3 and remove Pu by solvent extraction
  - Am/Cm chlorides extracted with tertiary amines from 11 M LiCl in weak acid
    - → Back extracted into 7 M HCl
  - Am oxidation and precipitation of Am(V) carbonate
- Other methods for Cm purification included NaOH, HDEHP, and EDTA
  - Similar to Am

Cm aqueous chemistry

- Trivalent Cm
- ^{242}Cm at 1g/L will boil
- 9 coordinating H_2O from fluorescence
  - Decreases above 5 M HCl
  - 7 waters at 11 M HCl
  - In HNO_3 steady decrease from 0 to 13 M
    - → 5 waters at 13 M
    - → Stronger complexation with NO_3^-
- Inorganic complexes similar to data for Am
  - Many constants determined by TRLFS
- Hydrolysis constants ($Cm^{3+} + H_2O \rightarrow CmOH^{2+} + H^+$)
  - K_{11}=1.2E-6
  - Evaluated under different ionic strength

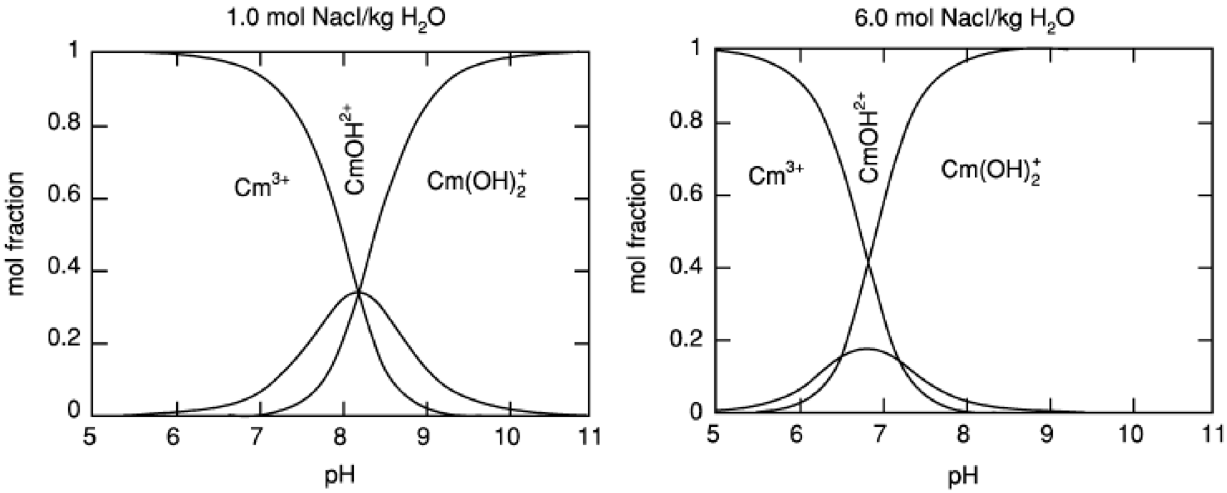


Fig. 9.4 *Comparison of Cm(III) species distribution as function of pH at two NaCl molalities. The speciation determination is based on Cm(III) fluorescence spectra. Used with permission from Fanghänel* et al. (1994).

Cm atomic and spectroscopic data

- $5f^7$ has enhanced stability
  - Half filled orbital
    - → Large oxidation potential for III→IV
    - → Cm(IV) is metastable
- Cm(III) absorbance
  - Weak absorption in near-violet region
  - Solution absorbance shifted 20-30 Å compared to solid
    - → Reduction of intensity in solid due to high symmetry
      - * f-f transitions are symmetry forbidden
  - Spin-orbit coupling acts to reduce transition energies when compared to lanthanides
- Cm(IV) absorbance
  - Prepared from dissolution of CmF_4
    - → CmF_3 under strong fluorination conditions

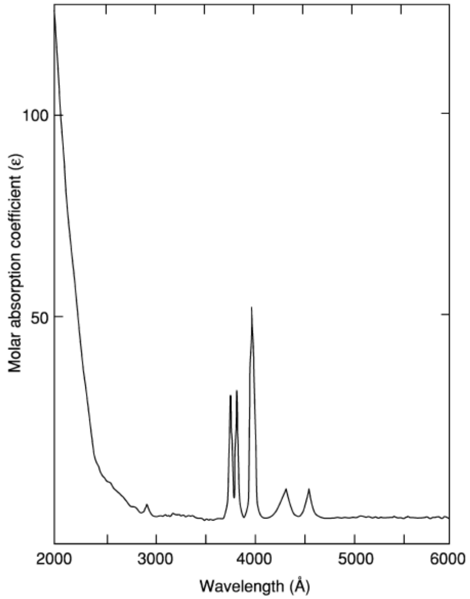


Fig. 9.1 *The absorption spectrum of Cm(III) in* 0.04 N *$HclO_4$ (aq). (Adapted from Carnall* et al., 1958.)

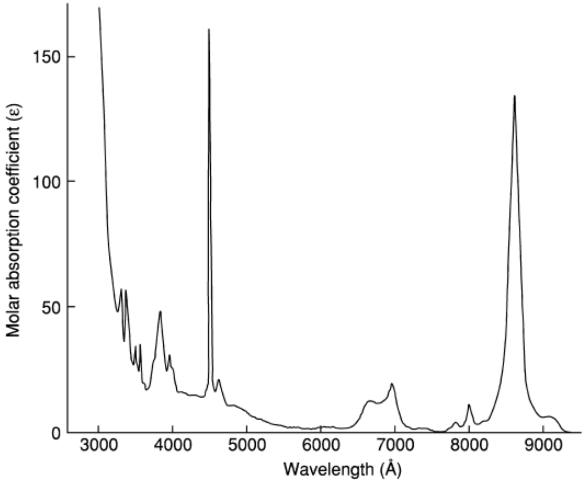


Fig. 9.2 *The absorption spectrum of Cm(IV) in* 15 M *CsF (aq). (Adapted from Keenan,* 1961.)

Cm fluorescence

- **Fluoresce from 595-613 nm**
  - **Attributed to $^6D_{7/2} \rightarrow {}^8S_{7/2}$ transition**
  - **Energy dependent upon coordination environment**
    - **→Speciation**
    - **→Hydration**
    - **→complexation constants**

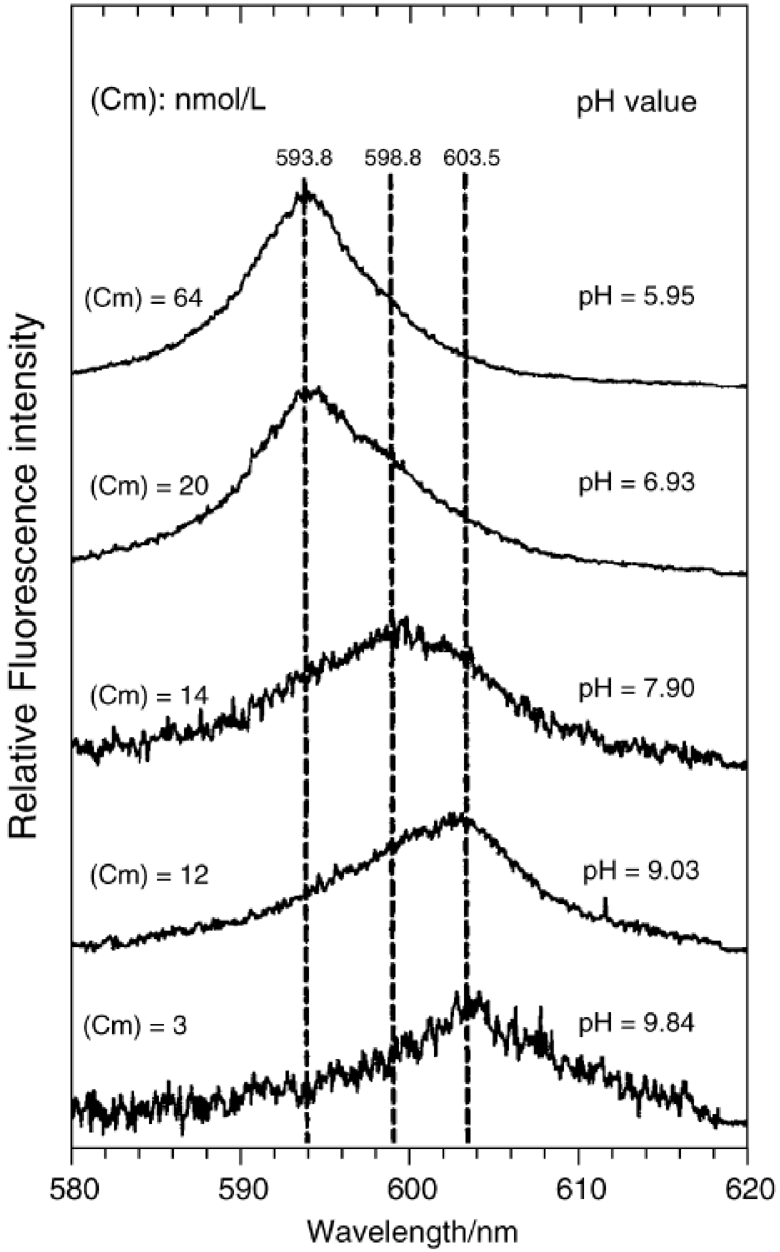
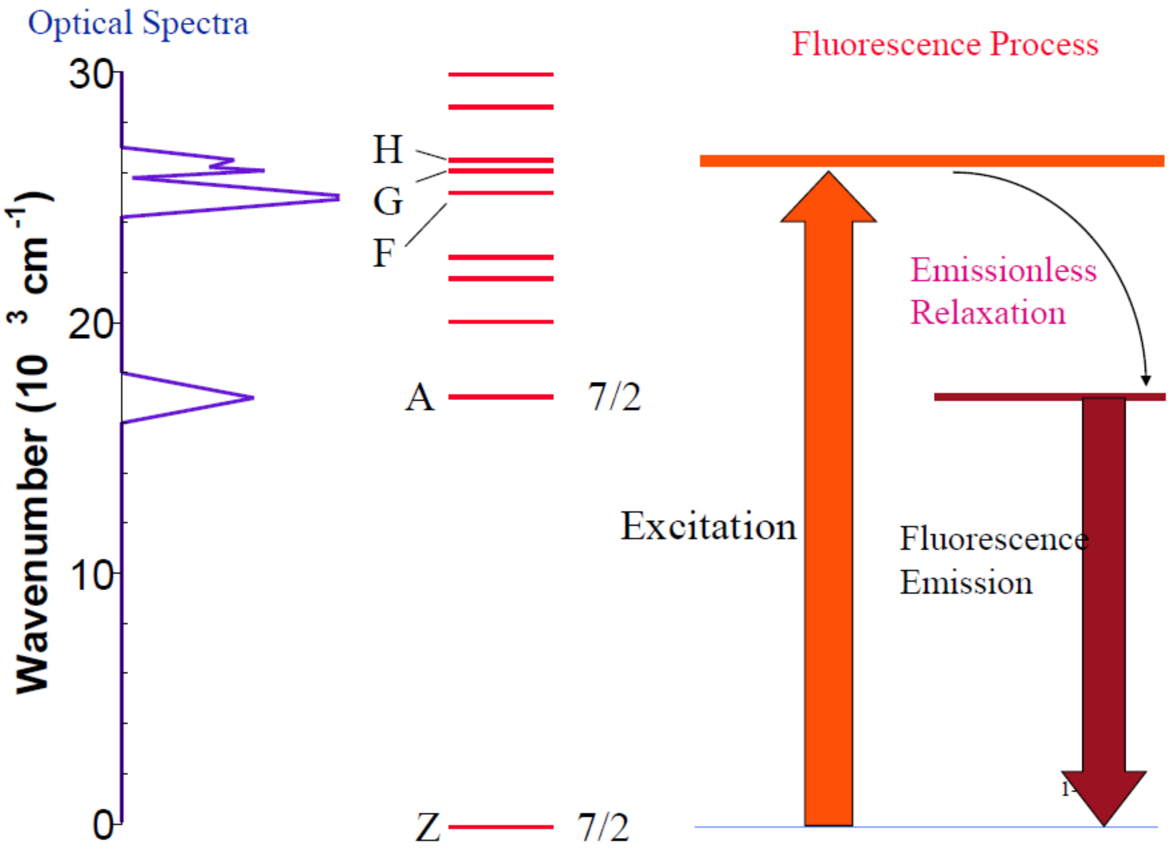


Fig. 9.3 *Curium(III) fluorescence emission spectra taken in the course of hydrolysis reaction in the pH range of 5.05–9.84. Used with permission from Wimmer* et al. (1992).

Atomic and spectroscopic data

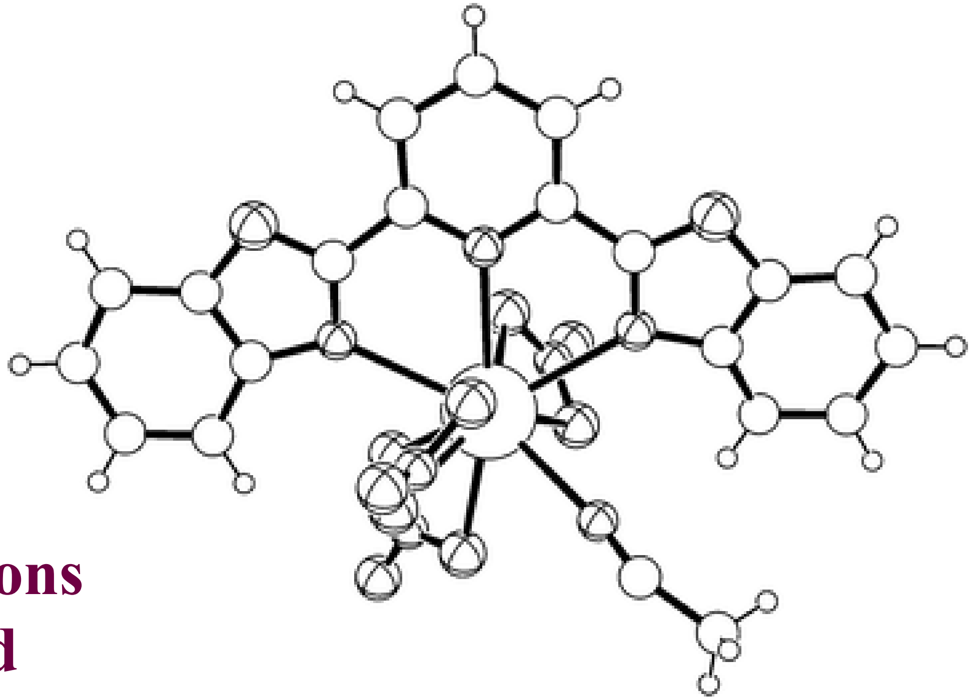
- **Fluoresce from 595-613 nm**
  - **Attributed to $^6D_{7/2} \rightarrow {}^8S_{7/2}$ transition**
  - **Emission lifetime and wavelength dependent upon coordination environment**

Absorption and fluorescence process of Cm^{3+}



Actinide Separations

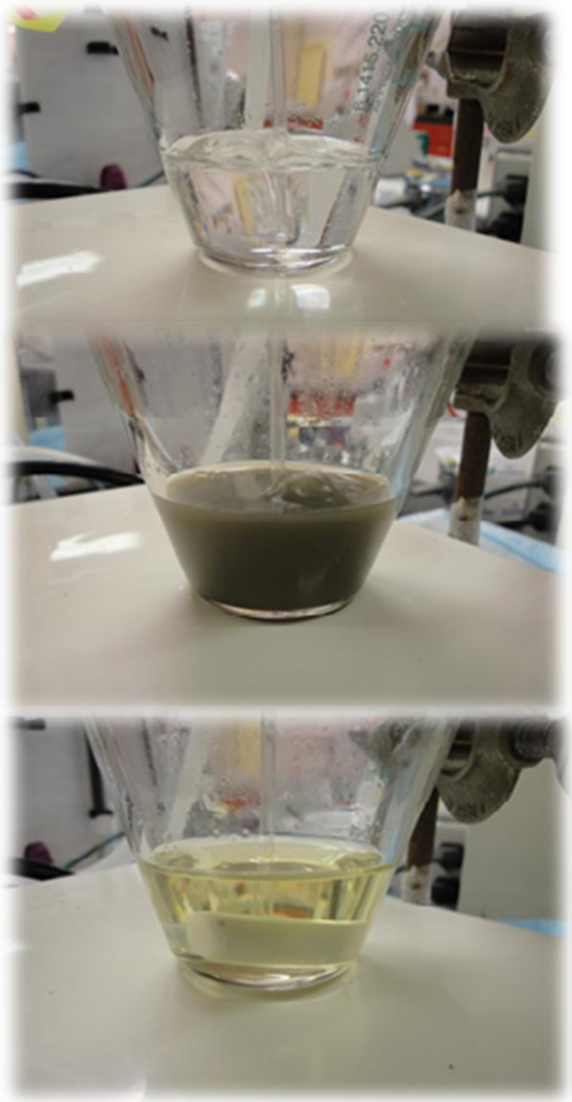
- Separation methods
  - Solvent extraction
  - Ion exchange
  - Electrochemistry
  - Volatility
- Specific actinide separations



- Basic concept of separations
- Development of advanced separations
- Necessary for fuel cycle due to formation of mixtures
  - Actinides
  - Fission products

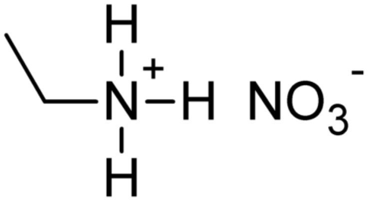
Separations: ionic liquids

- Room temperature ionic liquid (ILs) composed of ions that are liquid below 373 K
- Composed of a bulky, unsymmetrical organic cation and an organic or inorganic anion
    - Range of possible pairs, can be task specific
        - Low vapor pressure
        - Ability to dissolve organic and inorganic compounds
        - Conductive
        - Wide electrochemical window
- Ionic liquids are tunable to obtain properties needed for particular application
    - Solubility
    - Reaction Rate
    - Electrochemical window
    - Specific metal ion interaction



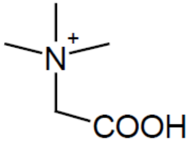
Introduction: Ionic liquids

- Ethylammonium nitrate electrochemistry in 1914

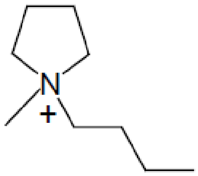


- Initial efforts focused on chloroaluminate anion ($AlCl_4^-$)
  - Electroplate aluminum
    - J. Electrochem. Soc. 98, 203 (1951)
  - Detailed studies, identification of limitations with chloroaluminate
    - Moisture sensitivity
    - Requires non-ambient conditions
      - Inorg. Chem. 17, 2728 (1978)
- Newer ionic liquids have non-hydrolyzing or stable anions
  - Moisture stable ionic liquids developed
    - JACS, 965 (1992)

Examples of IL cations and anions



carboxy-N,N,N-trimethylmethanaminium



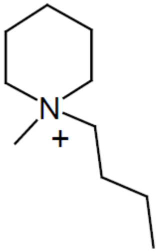
1-butyl-1-methylpyrrolidinium

Cl^-

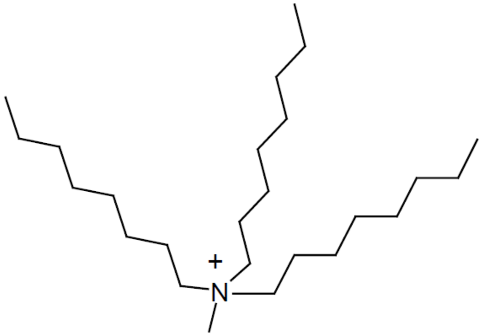
chloride

$-SO_2CF_3$

trifluoromethylsulfonate



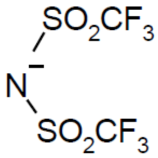
1-butyl-3-methylpiperidinium



tri-n-ocylmethylammonium

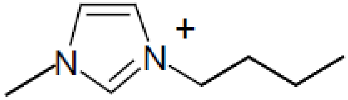
NO_3^-

nitrate



$N^-(SO_2CF_3)_2$

bis(trifluoromethanesulfonyl)imide



1-butyl-3-methylimidazolium

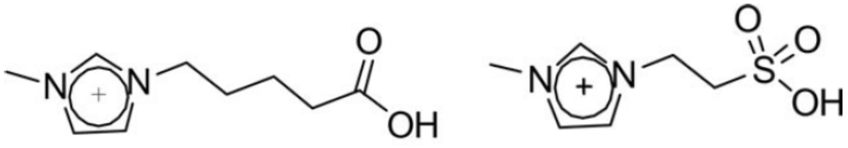
BF_4^-

tetrafluroborate

PF_6^-

hexafluorophosphate

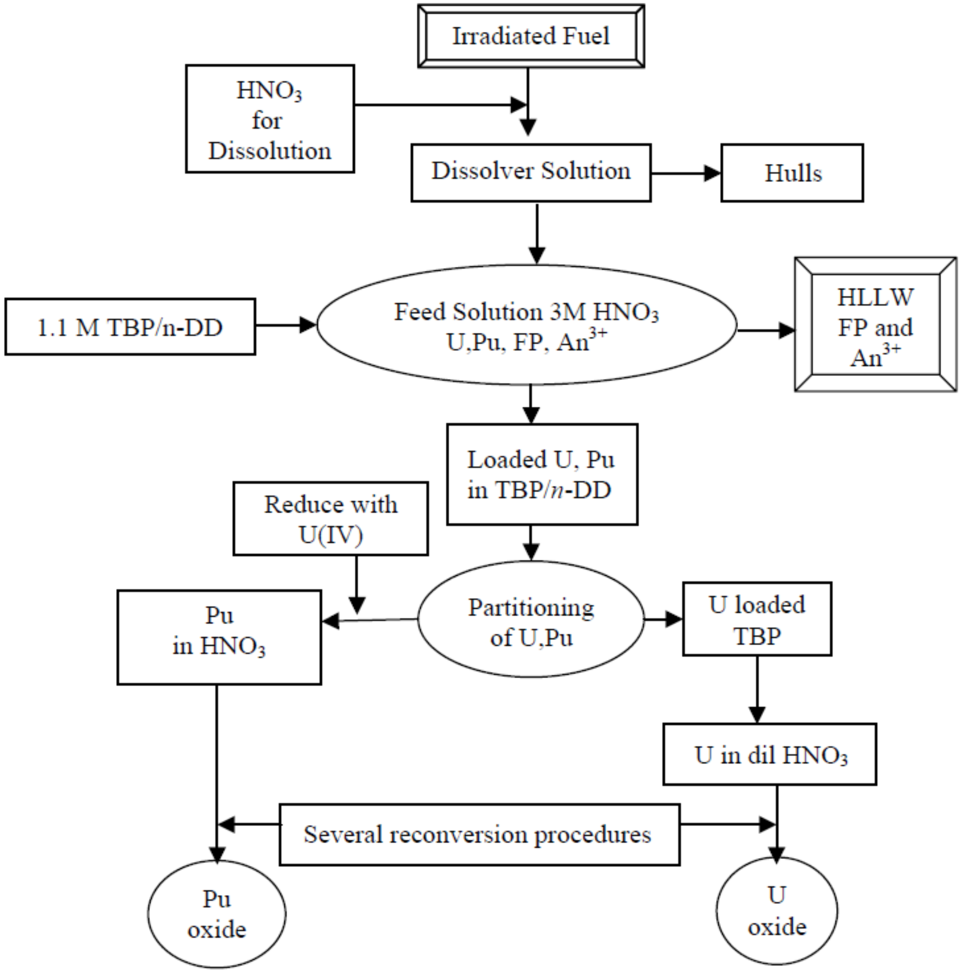
Can functionalize ILs



- 10^{18} possible combinations
- Route for task specific properties
  - Group actinide separation

Ionic liquids in separations

- Ionic liquids can replace traditional solvents in the PUREX
  - Studies showed favorable extraction when ILs used in conjunction with extractants
  - Chem. Commun. 1765 (1998)
- Possible recovery of metals through electrodeposition
  - direct from the organic phase following solvent extraction



From J. Nucl. Radiochem. Sci., 10(1), 1-6 (2009)

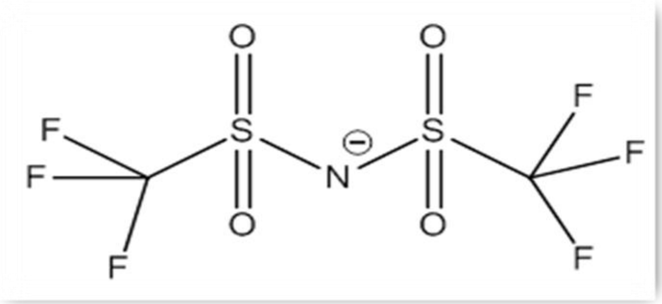
f-element reduction in ionic liquids

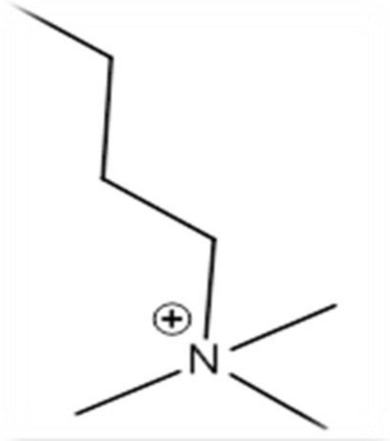
- Haloaluminates not stable to reduction of An(III) or Ln(III) to metal state
- Development of moisture-stable ILs
  - good cathodic stability
  - large ~6V electrochemical windows
- Application based upon the molten salt system (450 - 800°C)
  - Ionic liquids eliminate
    - Specialized corrosion resistant cell
    - Operation at elevated temperatures
    - Production of caustic side reactions
- Electrochemistry of Sm^{3+}, La^{3+}, Eu^{3+} and Th^{4+} in $[Me_3NBu][TFSI]$
  - Reported reduction of Sm, La, and Eu to the metallic state
  - Th was reported to reduce to Th^0 but subsequently was converted to ThO_2 by moisture in ionic liquid
    - Dalton Trans, 24, 4532-4534 (2002)

- Role of water central, useful in dissolution by problematic in full reduction

Choice of Ionic Liquid

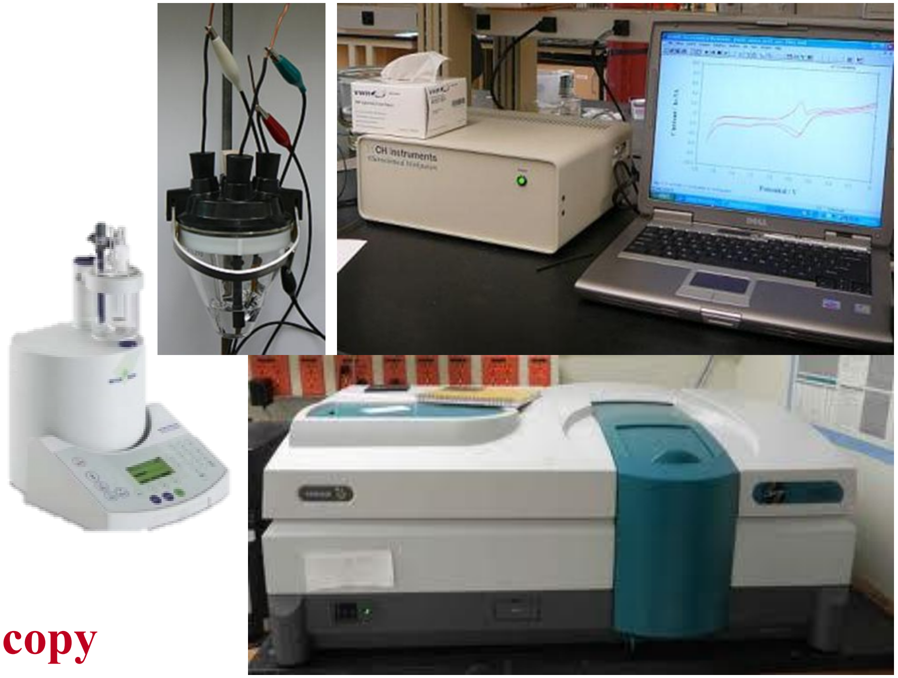
- A number of ionic liquids initially investigated
  - Functionalized TFSI evaluated
    - propyl and imidazolium
  - bis(trifluoromethanesulfonyl)imide (TFSI) anion selected
  - large potential window with Au, Pt, and Glassy carbon electrodes
    - Suitable for reduction of lanthanides and actinides
- Ionic liquid
  - N-trimethyl-N-butylammonium bis(trifluoromethanesulfonyl)imide
    - Based on interaction with Dave Costa, LANL
    - Used with actinides
  - Written as [Me_3NBu][TFSI]





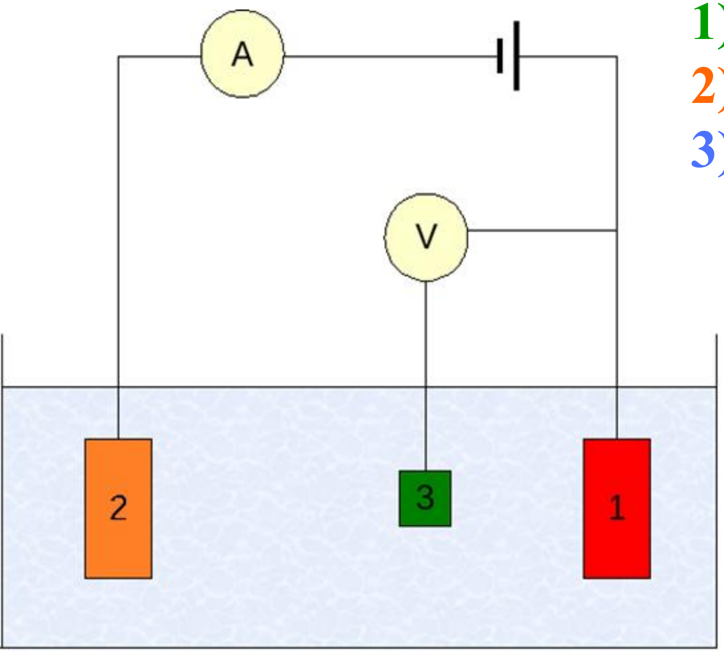
Experimental Methods

- **Electrochemistry**
  - **CH Instruments Potentiostats**
  - **(models 440a, 660c, 740b)**
- **Karl-Fischer Titrations**
  - **Mettler–Toledo Model DL32**
- **UV-Visible Spectroscopy**
  - **Cary 6000i UV-Vis-Near IR spectrophotometer**
- **SEM/EDX**
  - **JEOL scanning electron microscopy model JSM-5610**
  - **Equipped with Oxford ISIS EDX**
- **XAFS spectroscopy**
  - **Advanced photon source, ANL**
    - **BM-12**
    - **XANES and EXAFS**



Ionic Liquid Electrochemical Cell

- **Three electrode cell**
  - **Reference electrode is Ag wire in IL with 0.1M $AgNO_3$ dissolved and a Vycor^{TM} frit**
  - **reference electrode standardized with 4mM Ferrocene in [Me_3NBu][TFSI]**



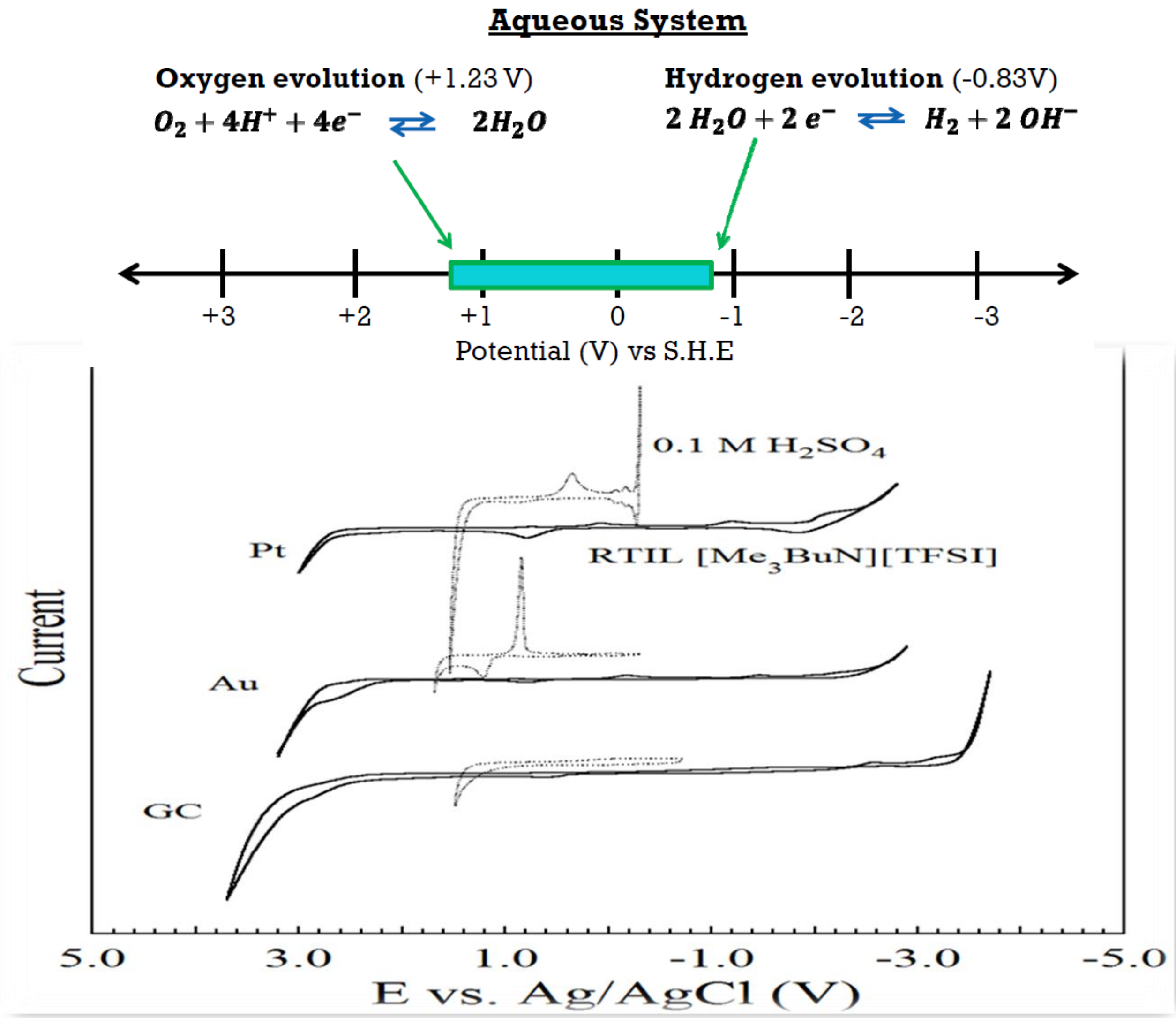
1) Working electrode: chemistry occurs
2) Counter electrode: current path
3) Reference electrode: controls potential

1)

2)

3)

Electrochemistry in ionic liquids



- ILs have wider potential window
  - Actinide electrochemistry possible
  - Must limit water in the system
- TFSI is a poor ligand
  - Moves deposition to favorable potential
- Electrode can influence window
  - Glassy Carbon (GC) widest potential window

Water in [Me_3NBu][TFSI]

Determined by Karl-Fisher Titration

low presence of water (0.0298-0.0765 %): May still influence chemistry

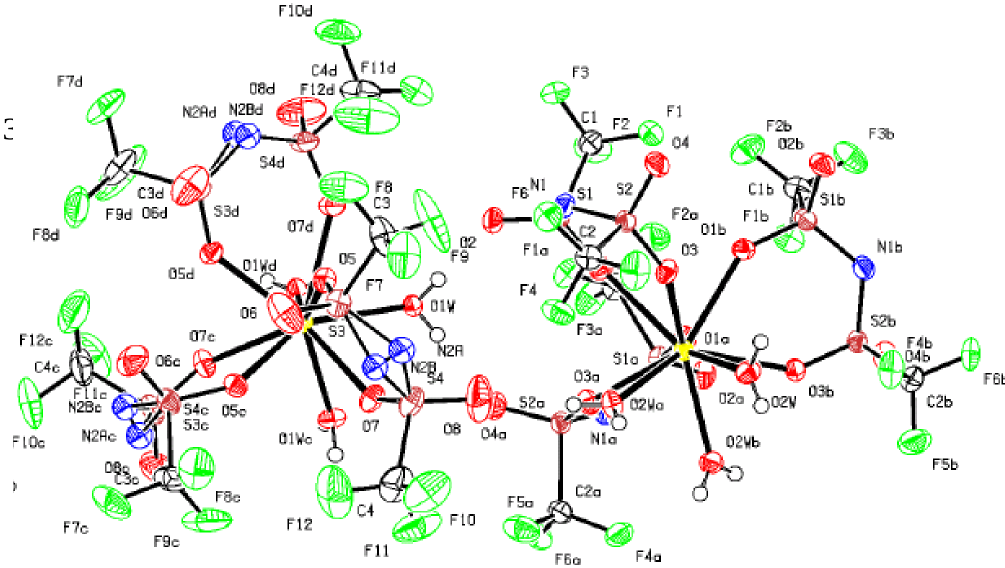
Addition of acid (HTFSI) increases water

Water contact standards	% water	Mean (%)	ST DEV
1	0.0986		
2	0.1033		
3	0.1008	0.1009	0.0016
"old" $Me_3NBuTFSI$ sample			
1	0.0737		
2	0.0782		
3	0.0775	0.0765	0.0024
"new" $Me_3NBuTFSI$ sample			
1	0.0303		
2	0.0293		
3	0.0299	0.0298	0.0005
8.83 M HTFSI in $Me_3NBuTFSI$ sample			
1	0.1801		
2	0.1805		
3	0.1775	0.1794	0.0016

Synthesis and dissolution of TFSI species

$$Sm_2O_3 + 6HTFSI \xrightarrow{H_2O} 2Sm(TFSI)_3$$

- **Preparation of Sm and U TFSI species**
    - **Direct dissolution in ionic liquid**
- **1.5 g Sm_2O_3 and 7.3 g of H(TFSI) 15 mL of H_2O**
- **Reacted for 20 minutes, treated on rotary evaporator at 60 °C**
- **Formation of crystal product, 85 % yield**
- **Characterize by single crystal XRD and IR spectroscopy**

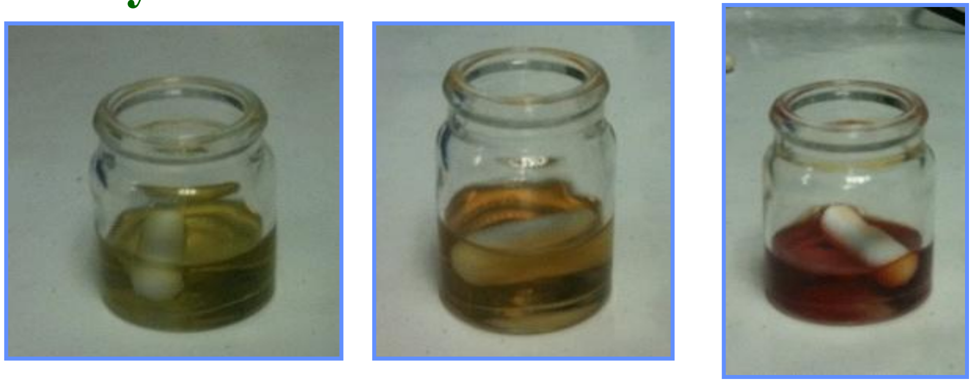


- **Chiral spacegroup $P2_13$**
    - **Consistent with the literature on La-TFSI complex**
- **Sm coordinated through sulfonyl oxygens**
    - **Six atom ring structure**
    - **Sm-O (TFSI) bond lengths of 2.4639(18) to 2.4888(19) Å**
- **Weak coordination**

U TFSI compound synthesis

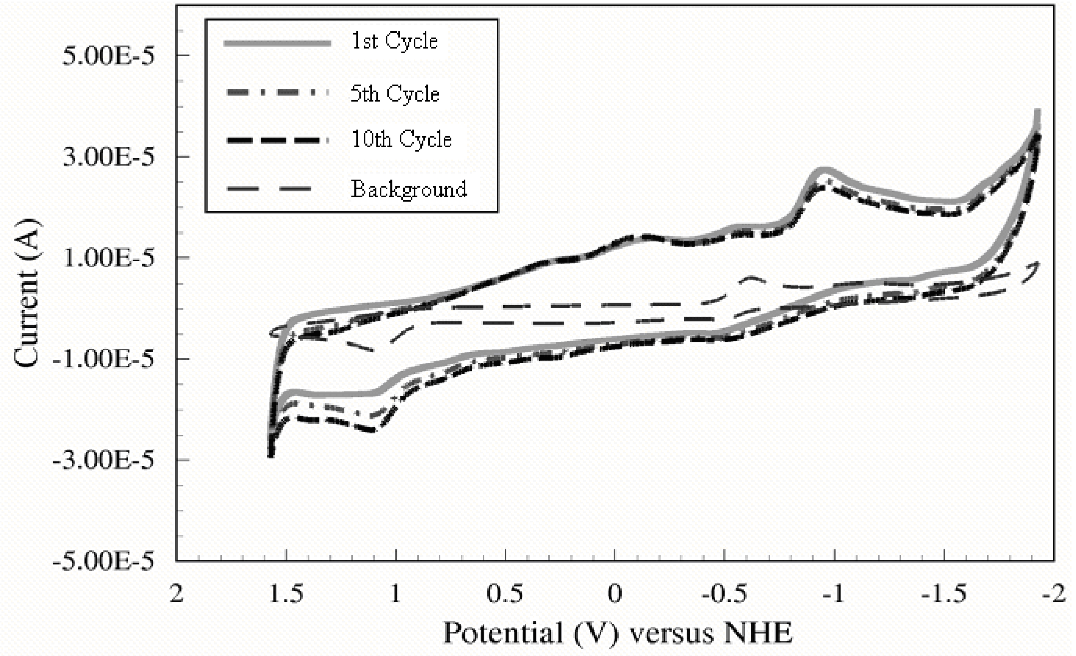
$$UI_3(THF)_4 + 3KTFSI \xrightarrow{THF} U(TFSI)_3 + 3KI_s$$

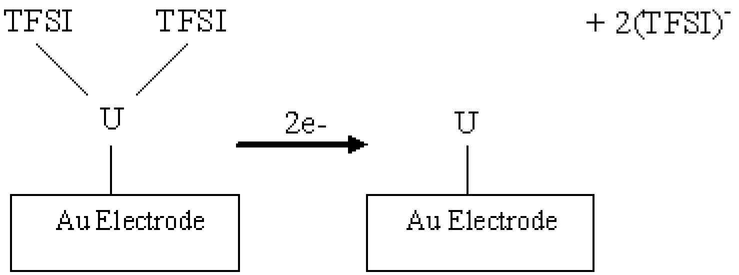
- **All reactions were performed in an argon filled glove box**
- **K(TFSI)(s) synthesized by adding H(TFSI) and KH THF solution**
  - **K(TFSI) separated by decanting excess THF**
    - **→ 90% yield**
- **K(TFSI) and $UI_3(THF)_4$ dissolved in THF**
  - **Excess of K(TFSI) added to ensure reaction completion**
  - **Clear pale yellow solution was stirred for 24 hours**
  - **Final orange red solution**
    - **→ Contained off white KI solid precipitate**
    - **→ THF solution contained product $U(TFSI)_3$**
    - **→ Solid was isolated by evaporating excess THF**
      - *** 74% yield**



Electrochemistry of U TFSI

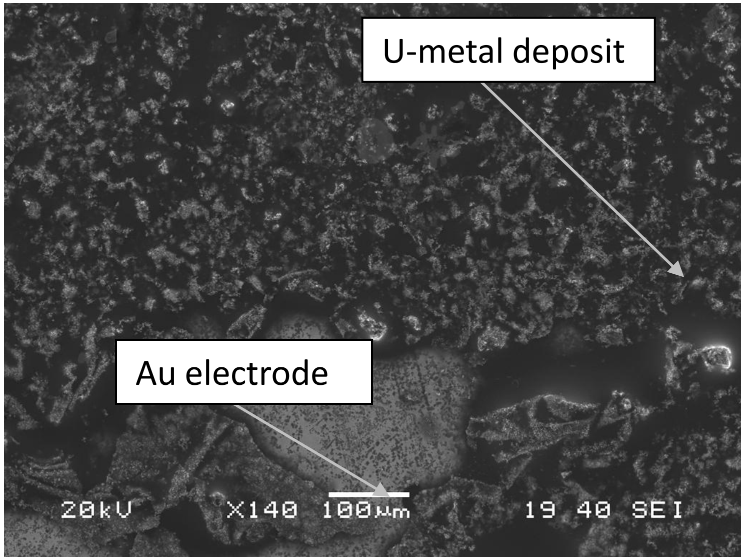
- 5 mM $U(TFSI)_3$ in $[Me_3NBu][TFSI]$
- Evaluated by cyclic voltammetry to determine oxidation/reduction
    - Reduction at -0.61 and -0.93 V decreasing with each successive cycle
    - Reduction of metal identified at -0.93 V vs NHE
    - $U(TFSI)_3$ deposited onto the surface of the electrode by first removing TFSI ligands in a stepwise manner
        - → Response at -0.9 V represents deposition of uranium metal on the electrode surface

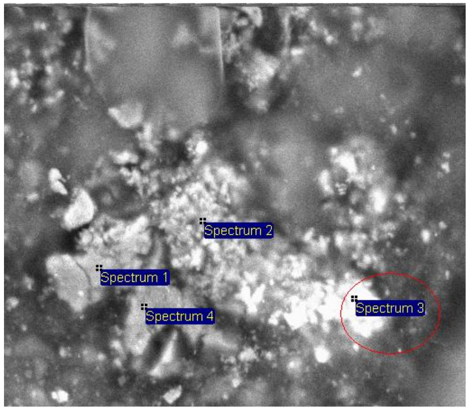


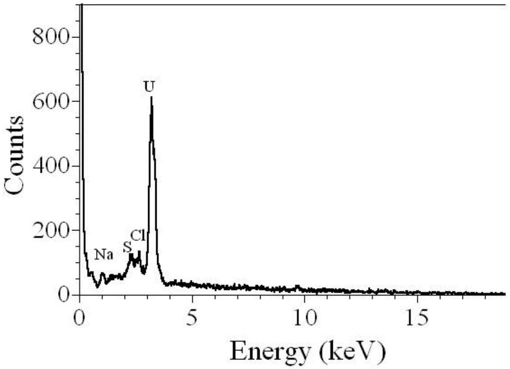


Formation of Uranium Deposits

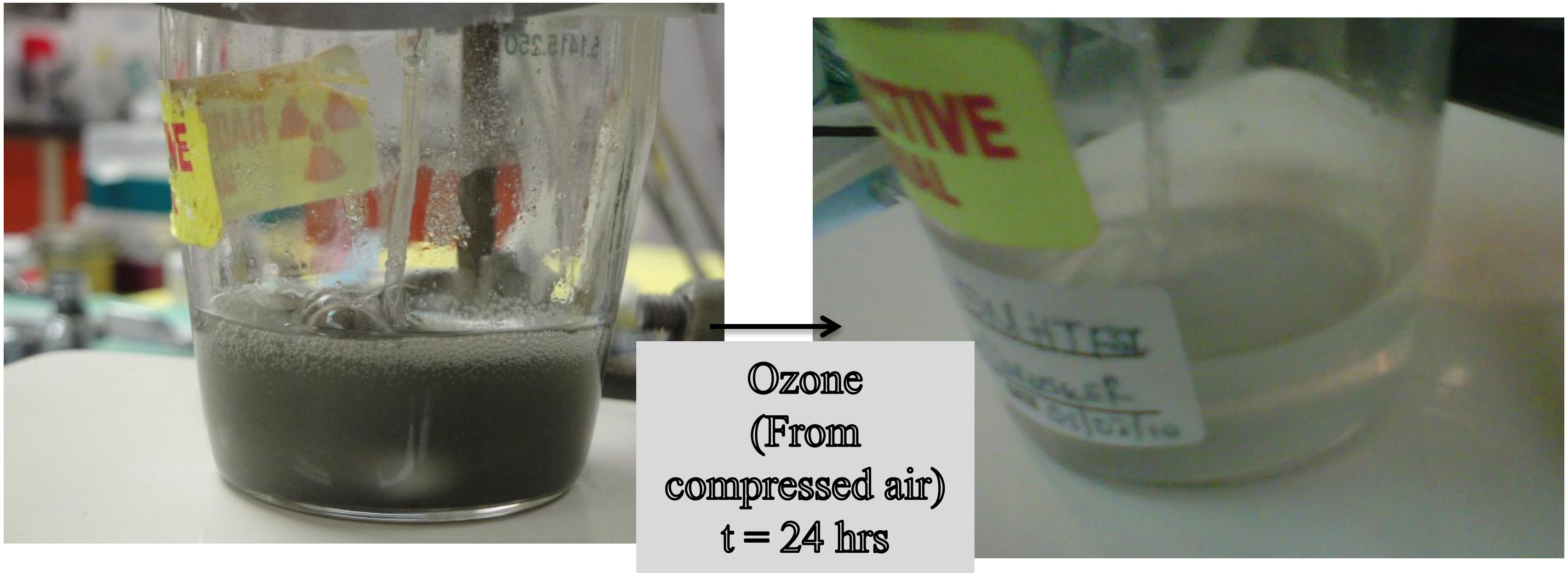
- Constant potential of -1.5 V versus NHE
- SEM, EDS, and XRD analysis performed
- SEM of U deposited on Au foil
- XRD evaluation of sample
    - Alpha U metal
- SEM EDS
    - No oxygen at 5.5 keV







Direct dissolution of U_3O_8 into ionic liquid



Ozone
(From
compressed air)
t = 24 hrs

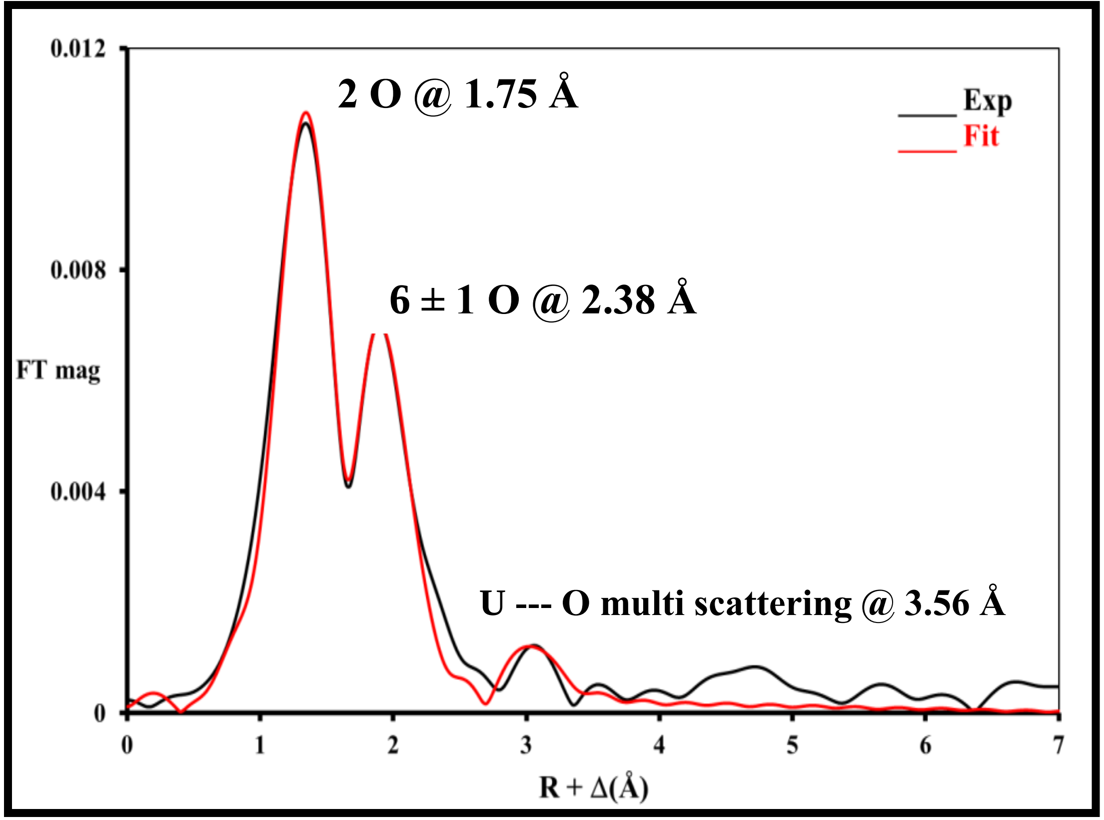
- **Original dissolution conditions:**
- **45 mg U_3O_8 with 3.27 M HTFSI in $Me_3NBuTFSI$ Stirred for weeks with no change**

- **RESULT: dissolution of material**
- **oxidizing gas used**
  - **O_3, NO_2**
- **Addition of HTFSI**
  - **Promote formation of uranium-TFSI complex**

Direct dissolution of U_3O_8 into IL

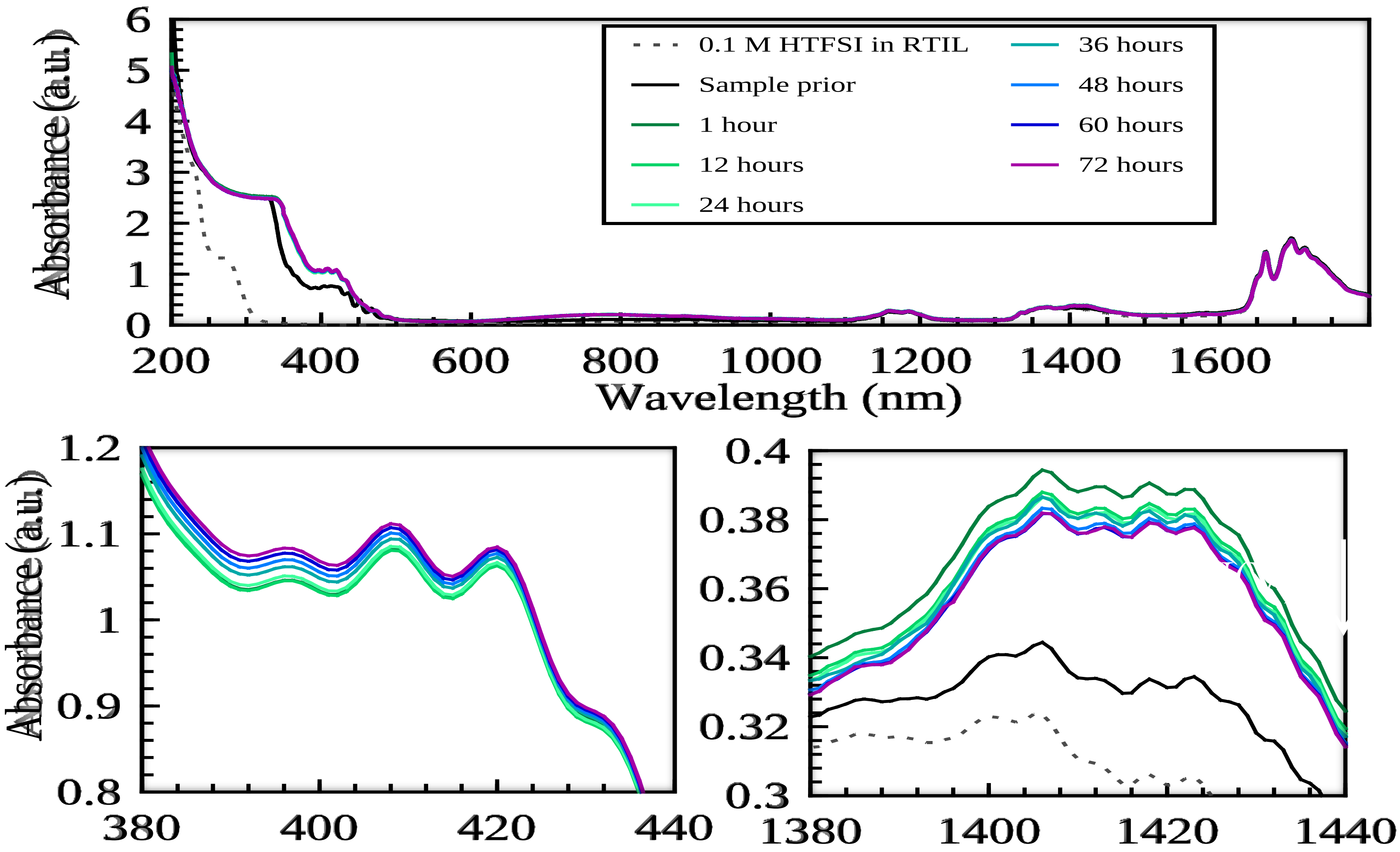
Proposed dissolution mechanism:

$$U_3O_8 + 6\ \mathrm{HTFSI} + O_3 \rightleftharpoons 3\ UO_2^{2+} + 6\ \mathrm{TFSI}^- + 3\ H_2O + O_2$$

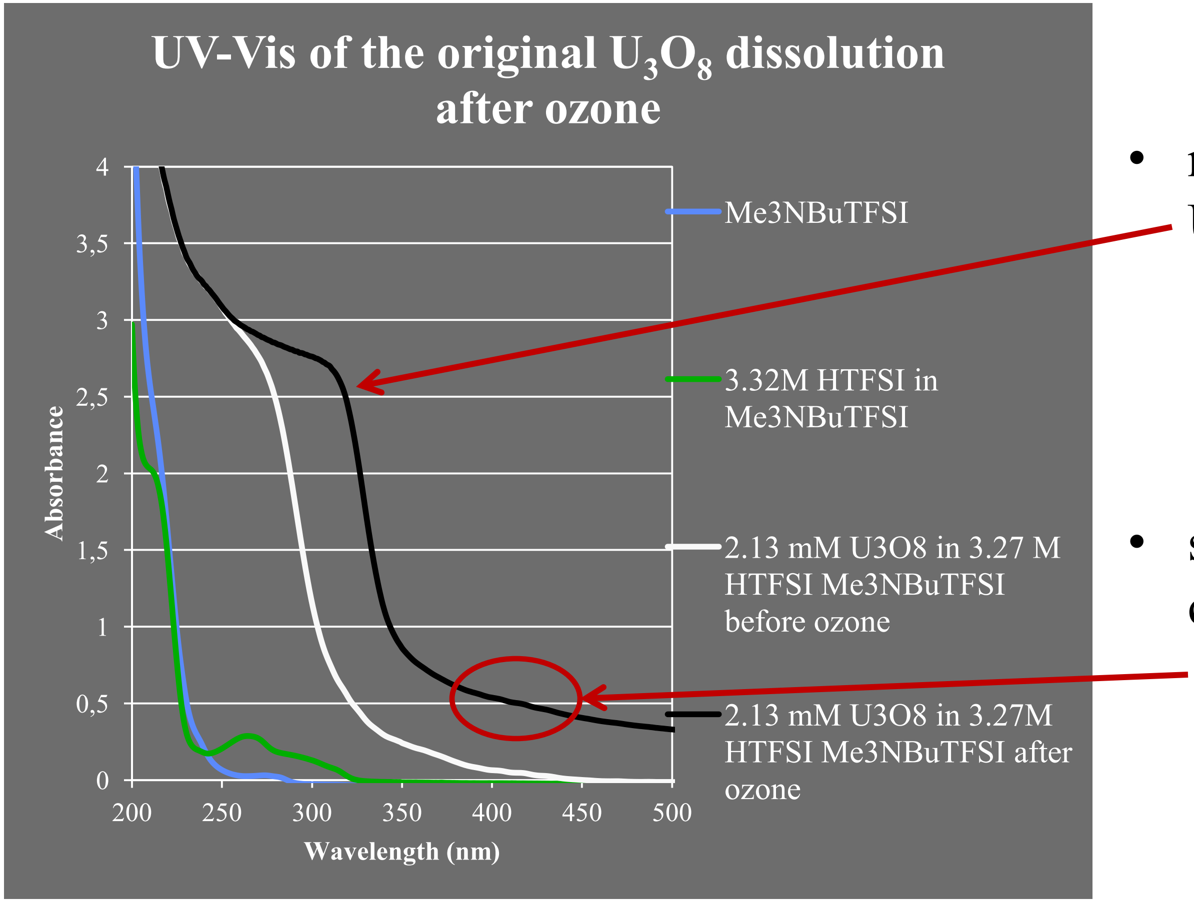


- Supporting EXAFS data of the original dissolution solution
- confirmed presence of UO_2^{2+}
- coordinated with five to six equatorial oxygens.

U(VI) and U(V) absorbance

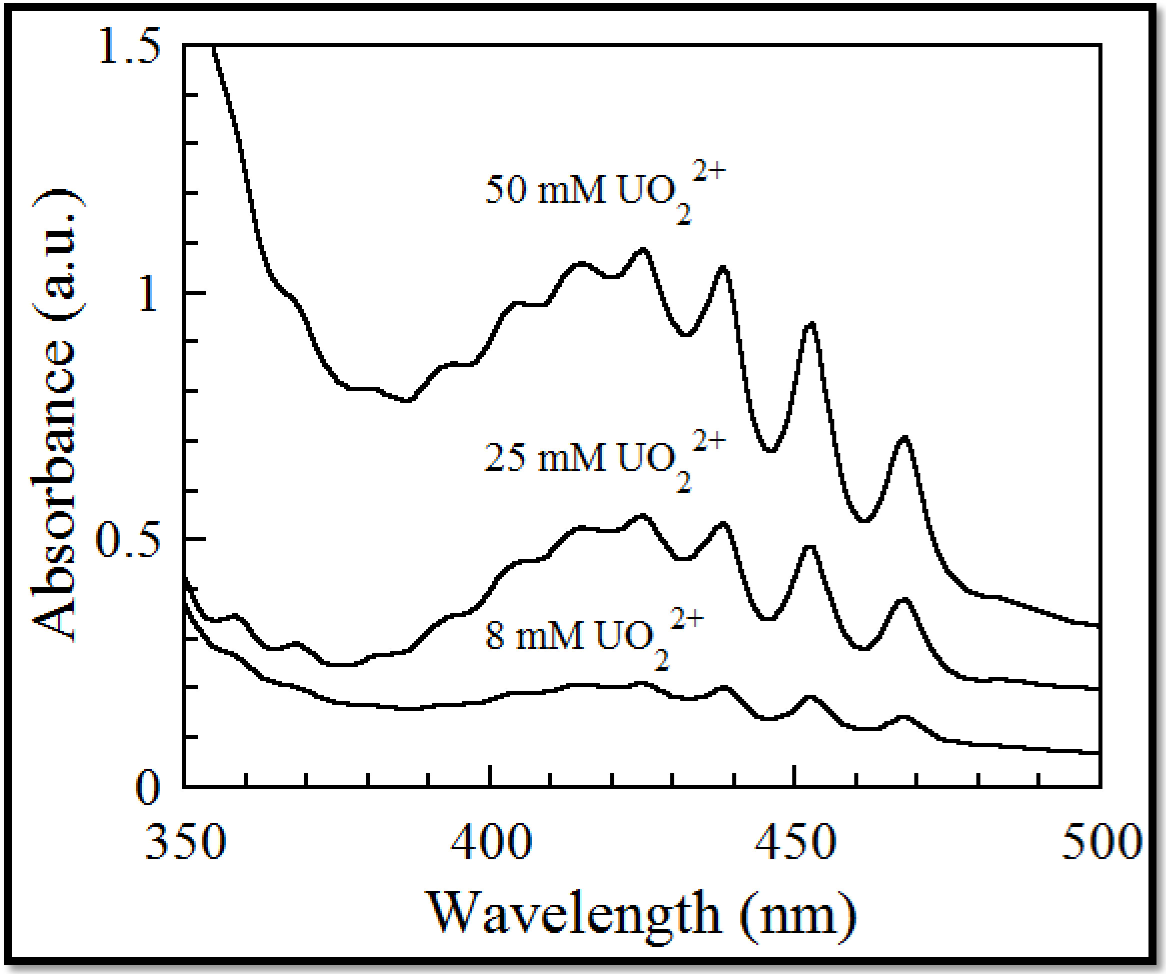


UV-Vis of U_3O_8 dissolution into IL



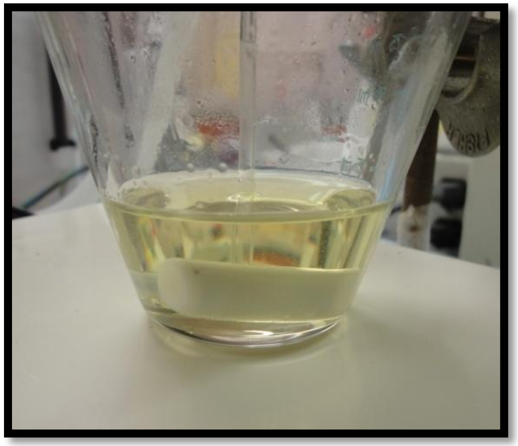
- noticeable band in the U_3O_8 samples with HTFSI
    - evidence of Ligand-metal transfer band
    - Coordination of U with TFSI
- some uranyl fine structure centered around 425 nm
    - Water coordination

UV-Vis of U_3O_8 dissolution into Ionic Liquid



Up to 300 mg U_3O_8 (~50 mM U) directly dissolved into $Me_3NBuTFSI$ with 0.1 M HTFSI

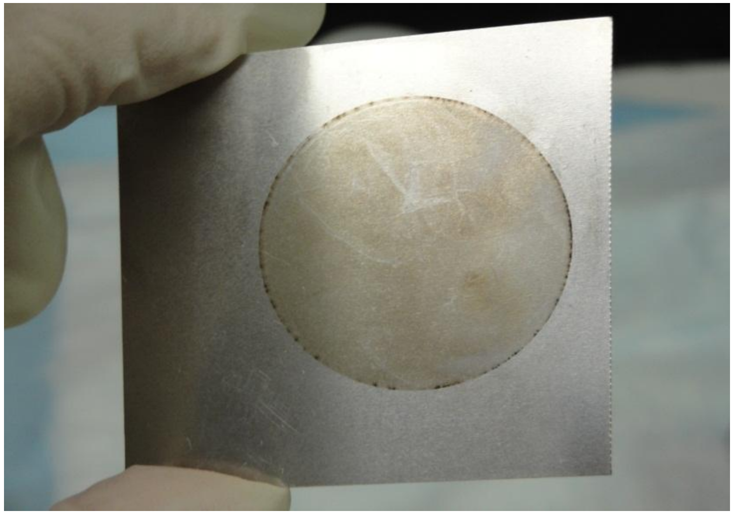
- not saturation limited
- Will impact electroplating



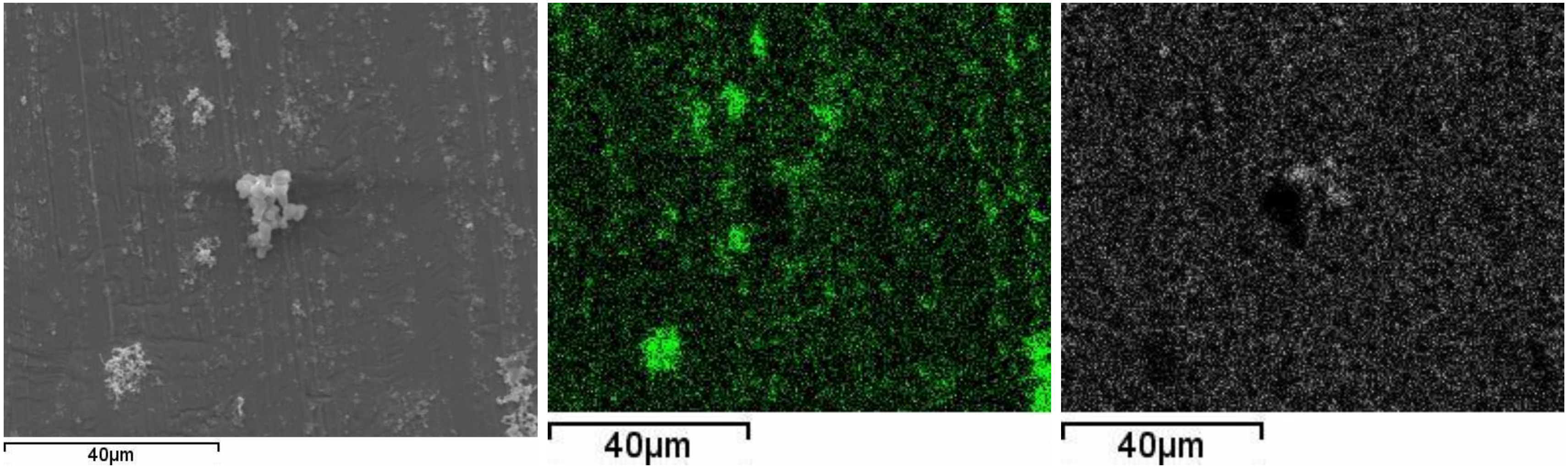
Electrodeposition of targets

- Designed electrochemistry cell
  - 9.23 cm^2 deposition area
- Electrodeposition procedure
  - Cyclic voltammetry (negative potential region) 400-800 segments
  - Constant potential held
    - (E = -2.8 up to -3.2 V) for 24 hours periods

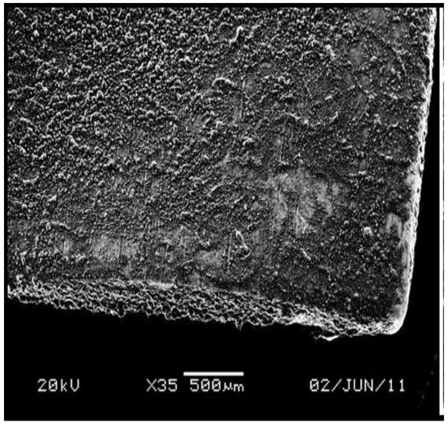
- Stainless steel
  - Deposit density up to 0.6 mg/cm^2
- Au foil
  - Appears to be UOx by SEM



SEM and EDS mapping of Deposits



- SEM at x1000 magnification of deposits on the S.S.
- SEM of the deposit on Au foil x35 magnification
  - EDS confirms a uranium oxide
- EDS mapping of Uranium (in green)
  - Thin layers of uranium oxide deposit developing into clusters
- EDS mapping of oxygen on the deposit (in white)
  - Oxide formation driven by presence of water



Actinide metals

- Range of melting points
  - Low around 600 °C for Np and Pu
- Number of phases
  - Change in density with temperture
- Formation of alloy species
  - Some low melting alloys
    - →Pu with Fe
- Implications for advanced reactor metal fuel
  - High burnup of U will form Pu

Radiochemistry in reactors

- Fuel confined in reactor to fuel region
  - Potential for interaction with cladding material
    - → Initiate stress corrosion cracking
  - Chemical knowledge useful in events where fuel is outside of cladding
- Some radionuclides generated in structural material
- Recoil length about 10 microns, diameter of 6 nm
  - About size of UO_2 crystal
  - 95 % of energy into stopping power
    - → Remainder into lattice defects
      - * Radiation induced creep
  - High local temperature from fission
    - → 3300 K in 10 nm diameter
- Delayed neutron fission products
  - 0.75 % of total neutrons
    - → $^{137-139}$I and $^{87-90}$Br as examples
- Some neutron capture of fission products

Fuel variation during irradiation

- Chemical composition
- Radionuclide inventory
- Pellet structure
- Higher concentrations of Ru, Rh, and Pd in Pu fuel
- Total activity of fuel effected by saturation
  - Tends to reach maximum
- Radionuclide fuel distribution studied
  - Fission gas release
  - Axial distribution by gamma scanning
- Radial distribution to evaluate flux
- Pu fuel has higher concentrations of:
  - Ru, Rh, Pd

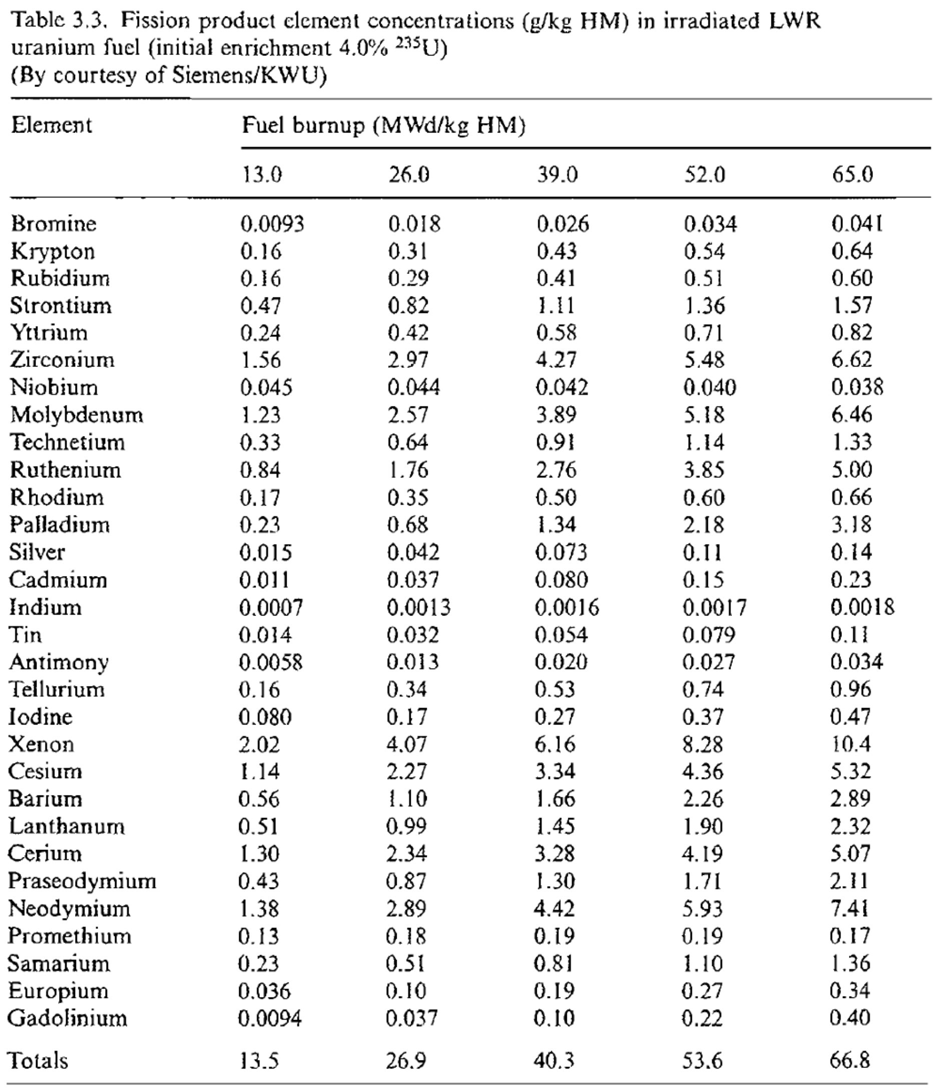
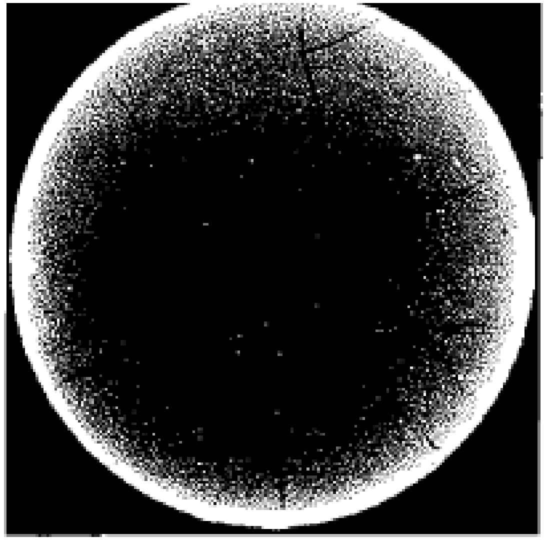


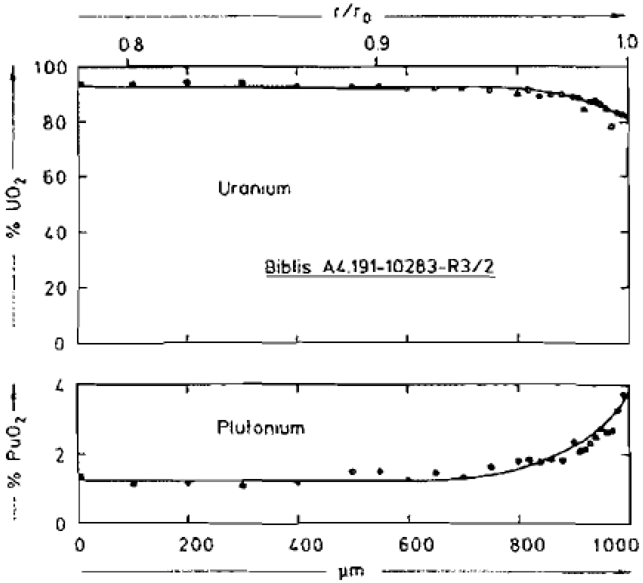
Table 3.3. Fission product element concentrations (g/kg HM) in irradiated LWR uranium fuel (initial enrichment 4.0% ^{235}U)
(By courtesy of Siemens/KWU)

Element	Fuel burnup (MWd/kg HM)				
	13.0	26.0	39.0	52.0	65.0
Bromine	0.0093	0.018	0.026	0.034	0.041
Krypton	0.16	0.31	0.43	0.54	0.64
Rubidium	0.16	0.29	0.41	0.51	0.60
Strontium	0.47	0.82	1.11	1.36	1.57
Yttrium	0.24	0.42	0.58	0.71	0.82
Zirconium	1.56	2.97	4.27	5.48	6.62
Niobium	0.045	0.044	0.042	0.040	0.038
Molybdenum	1.23	2.57	3.89	5.18	6.46
Technetium	0.33	0.64	0.91	1.14	1.33
Ruthenium	0.84	1.76	2.76	3.85	5.00
Rhodium	0.17	0.35	0.50	0.60	0.66
Palladium	0.23	0.68	1.34	2.18	3.18
Silver	0.015	0.042	0.073	0.11	0.14
Cadmium	0.011	0.037	0.080	0.15	0.23
Indium	0.0007	0.0013	0.0016	0.0017	0.0018
Tin	0.014	0.032	0.054	0.079	0.11
Antimony	0.0058	0.013	0.020	0.027	0.034
Tellurium	0.16	0.34	0.53	0.74	0.96
Iodine	0.080	0.17	0.27	0.37	0.47
Xenon	2.02	4.07	6.16	8.28	10.4
Cesium	1.14	2.27	3.34	4.36	5.32
Barium	0.56	1.10	1.66	2.26	2.89
Lanthanum	0.51	0.99	1.45	1.90	2.32
Cerium	1.30	2.34	3.28	4.19	5.07
Praseodymium	0.43	0.87	1.30	1.71	2.11
Neodymium	1.38	2.89	4.42	5.93	7.41
Promethium	0.13	0.18	0.19	0.19	0.17
Samarium	0.23	0.51	0.81	1.10	1.36
Europium	0.036	0.10	0.19	0.27	0.34
Gadolinium	0.0094	0.037	0.10	0.22	0.40
Totals	13.5	26.9	40.3	53.6	66.8

Distribution in Fuel



Transuranics on fuel rim



- **Radial distribution of fission products mainly governed by thermal neutron flux profile .**
- **Higher Pu concentration in outer zone of fuel**
  - **Epithermal neutron capture on ^{238}U**
  - **Small influence of thermal migration on Cs**
    - → **Gaseous and volatile fission products**
    - → **Influence by fuel initial composition (O to M ratio)**
  - **Xe trapped in region with high gas bubble density**

Distribution in Fuel

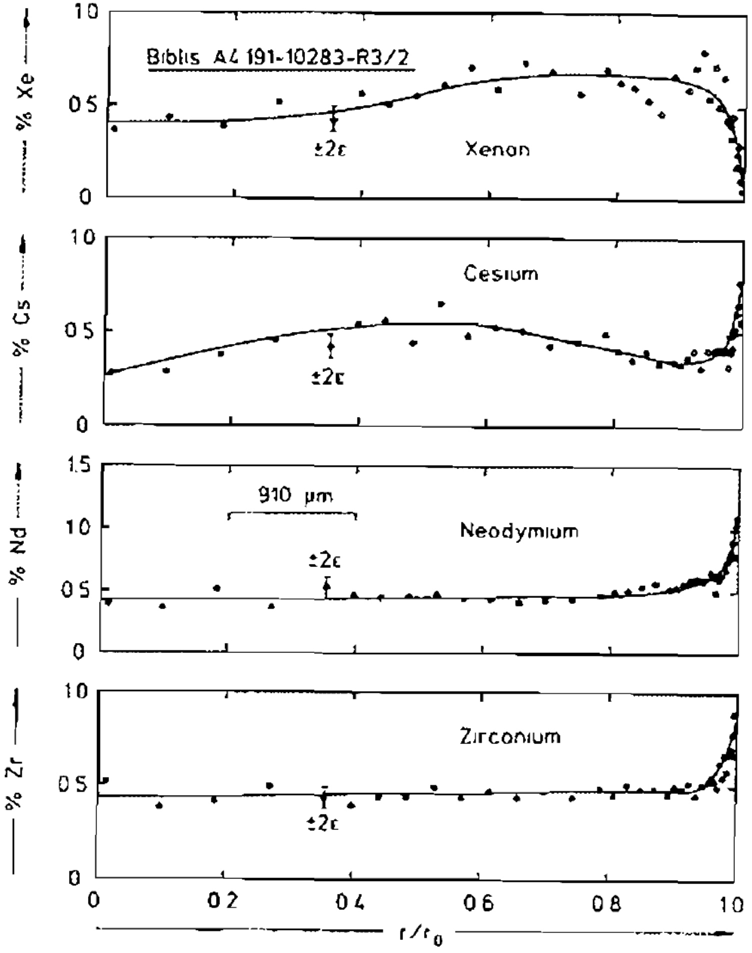


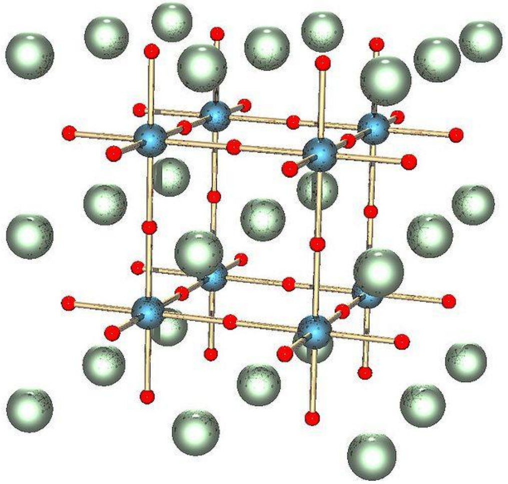
Figure 3.9. Fission product distribution as a function of the relative fuel pellet radius in a LWR high-burnup oxide fuel
(Kleykamp, 1990a)

- **Increased Pu concentration on rim leads to increased fission product density**
  - **Xe behavior influenced by bubble gas location**
- **Consumption of burnable poison**
  - **Gd isotopes 157 and 155 depleted in outer zone**

Distribution in fuel: Thermal behavior

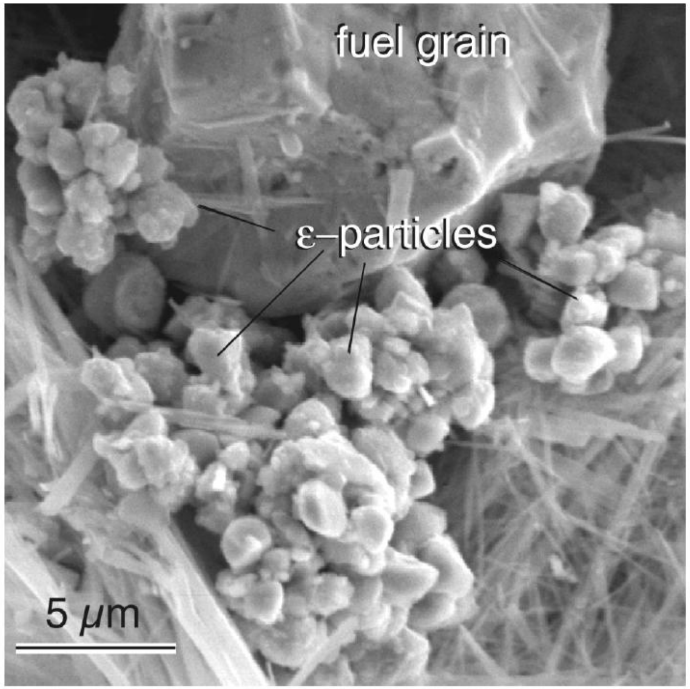
- Mainly affects the gaseous and the volatile fission products
  - linear heat rating
  - pellet temperatures during reactor operation
  - stoichiometry of the fuel
- Halogens and alkali elements
  - Cs and I volatility
    - → High fission yields
    - → Enhanced mobility
  - Can be treated similarly, different chemical behavior

Separate phases in fuel



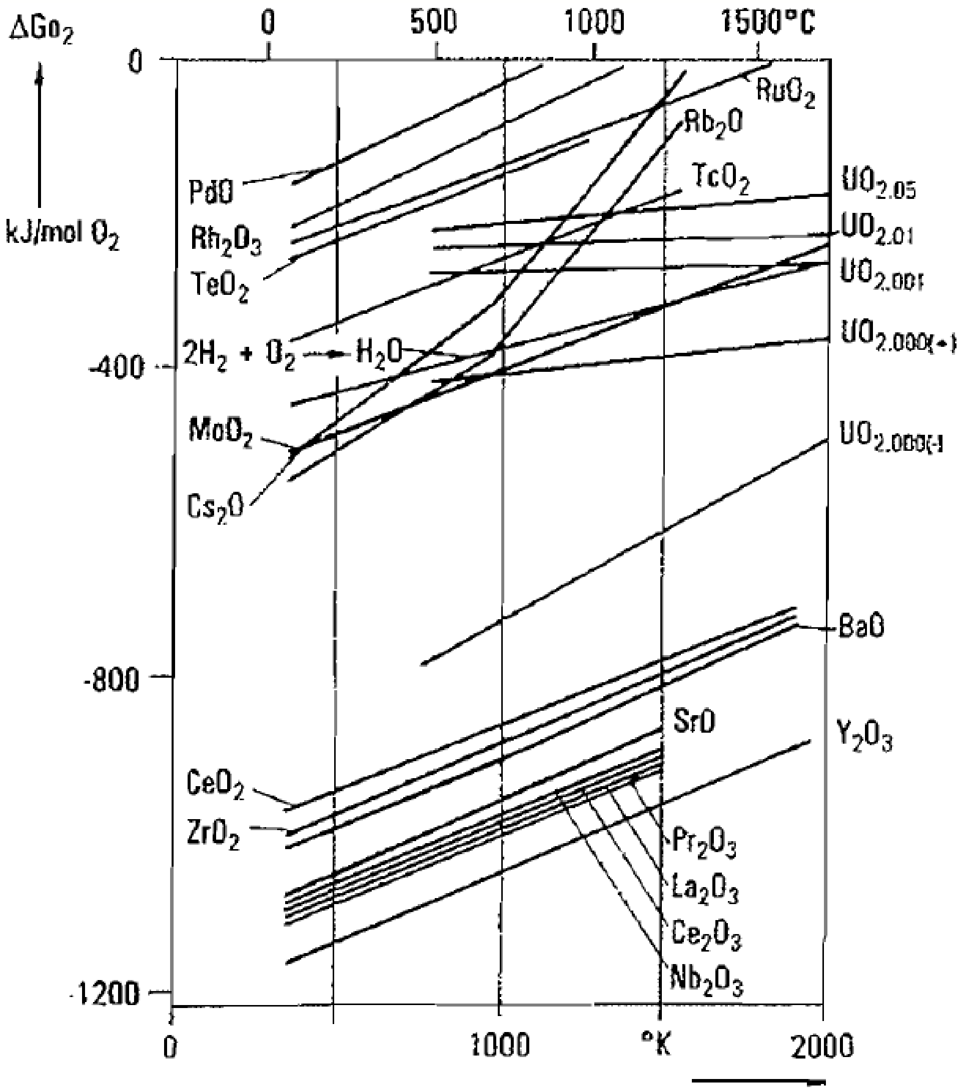
- Perovskite ($A^{2+}B^{4+}O_3$) identified oxide phase
  - U, Pu, Ba, Sr, Cs, Zr, Mo, and Lanthanides
  - Mono- and divalent elements at A
- Mechanism of formation
  - Sr and Zr form phases
  - Lanthanides added at high burnup

- Metallic phase of fission products in fuel
  - Mo (24-43 wt %)
  - Tc (8-16 wt %)
  - Ru (27-52 wt %)
  - Rh (4-10 wt %)
  - Pd (4-10 wt %)
- Grain sizes around 1 micron
- Concentration nearly linear with fuel burnup
  - 5 g/kg at 10MWd/kg U
  - 15 g/kg at 40 MWd/kg U
- <u>Catalytic property in used fuel</u>



Epsilon Phase

- **Formation of metallic phase promoted by higher linear heat**
  - **high Pd concentrations (20 wt %) indicate a relatively low fuel temperature**
  - **Mo behavior controlled by oxygen potential**
    - **→ High metallic Mo indicates O:M of 2**
    - **→ O:M above 2, more Mo in UO_2 lattice**



Relative partial molar Gibbs free energy of oxygen of the fission product oxides and UO_2

Overview

- **Radius trends for ions and metals of the actinides**
- **General trends in actinide electronic structure**
- **Electronic and magnetic spectroscopy**
    - **Variations in the actinides**
- **Range of oxidation states for the actinides**
- **Metallic state**
    - **Phases, alloys, and reactions with gases**
- **Solution chemistry**
    - **Oxidation state**
    - **Spectroscopic properties**
    - **Structure and coordination chemistry**