Actinide Chemistry
Ken Czerwinski

II Letnia Szkoła Energetyki i Chemii Jądrowej
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

<table>
<thead>
<tr>
<th>Most likely solution stable oxidation state</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>5</th>
<th>4</th>
<th>3</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Actinide</td>
<td>Th</td>
<td>Pa</td>
<td>U</td>
<td>Np</td>
<td>Pu</td>
<td>Am</td>
<td>Cm</td>
</tr>
</tbody>
</table>
**Actinides in the Periodic Table**

- **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 (d⁷)
- Macroscopic chemistry with ⁹⁹Tc
  - 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 $^{239}\text{Np}$ was produced by McMillan and Abelson in 1940 at Berkeley, California
  - bombarding uranium with cyclotron-produced neutrons
    $\rightarrow 238\text{U}(n,\gamma)239\text{U}$, beta decay of $^{239}\text{U}$ to $^{239}\text{Np}$ ($t_{1/2}=2.36$ days)
  - Chemical properties unclear at time of discovery
    $\rightarrow$ Actinide elements not in current location
    $\rightarrow$ In group with W

- Chemical studies showed similar properties to U
- First evidence of 5f shell
- Macroscopic amounts
  - $^{237}\text{Np}$
    $\rightarrow 238\text{U}(n,2n)237\text{U}$
    * Beta decay of $^{237}\text{U}$
    $\rightarrow$ 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
    \[ \text{\(238\text{U}(^2\text{H}, 2\text{n})^{238}\text{Np}\)} \]
    * Beta decay of $^{238}\text{Np}$ to $^{238}\text{Pu}$
  - 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 $^{239}\text{Pu}$
  - $^{239}\text{Pu} + n \rightarrow ^{240}\text{Pu} + n \rightarrow ^{241}\text{Pu} \rightarrow ^{241}\text{Am} + \beta^-$
  - Also formed $^{242}\text{Cm}$ from successive neutron capture on $^{241}\text{Am}$

• Direct production for discovery
  - $^{241}\text{Am}$ from $^{241}\text{Pu}$ produced by $^{238}\text{U} + ^4\text{He}$
    → Also directly produced from He on $^{237}\text{Np}$ and $^2\text{H}$ on $^{239}\text{Pu}$
  - $^{239}\text{Pu}(^4\text{He},n)^{242}\text{Cm}$
    → Chemical separation from Pu
    → Identification of $^{238}\text{Pu}$ daughter from alpha decay

• Difficulties in separating Am from Cm and from lanthanide fission products
  - Trivalent oxidation states

• Am and Cm discovery papers
Bk and Cf discovery

• Required Am and Cm as targets
  ▪ Needed to produce these isotopes in sufficient quantities
    → Milligrams
  ▪ Am from neutron reaction with Pu
  ▪ Cm from neutron reaction with Am

• Production of new elements followed by separation
  ▪ $^{241}\text{Am}(^{4}\text{He},2n)^{243}\text{Bk}$
    → Cation exchange separation
  ▪ $^{242}\text{Cm}(^{4}\text{He},n)^{245}\text{Cf}$
    → Anion exchange

• Where would the heavier actinides elute?

Dowex 50 resin at 87 °C, elute with ammonium citrate
Debris from Mike test
- 1st thermonuclear test
  → http://www.youtube.com/watch?v=h7vyKDeSTaE

New isotopes of Pu
- 244 and 246
  → Successive neutron capture on $^{238}\text{U}$

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
  → $^{253}\text{Es}$ and $^{254}\text{Fm}$
  → 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
  - $^{253}\text{Es}(^4\text{He},n)^{256}\text{Md}$
- 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
  - $^{246}\text{Cm}(^{12}\text{C},4n)^{254}\text{No}$
    - Alpha decay from $^{254}\text{No}$
    - Identification of $^{250}\text{Fm}$ daughter using ion exchange
- For Lr $^{249, 250, 251}\text{Cf}$ bombarded with $^{10, 11}\text{B}$
- New isotope with 8.6 MeV, 6 second half life
  - Identified at $^{258}\text{Lr}$
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 $\pi$-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
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 $5f \rightarrow 6d$ occurs to provide more bonding electrons
    - much easier than corresponding $4f \rightarrow 5d$ promotion in lanthanides
  - second half of actinide series similar to lanthanides
    - Similarities for trivalent lanthanides and actinides
- $5f$ orbitals have greater extension than $4f$ relative to $s$ and $p$ orbitals
  - $5f$ 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

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

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
    - No²⁺ and Md²⁺ are more stable than Eu²⁺
      * 5f→6d promotion
  - Divalent No stabilize by full 5f¹⁴
    - Element Rn5f¹⁴7s²
  - Divalent actinides similar properties to divalent lanthanides and Ba²⁺
- +3
  - Most common oxidation state across actinides
    - all trans-Amercium elements except No
  - Of marginal stability for early actinides
    - Pa, U
  - General properties resemble Ln³⁺ and are size-dependent
    - Binary Halides, MX₂ easily prepared and hydrolyzed to MOX
  - Binary Oxides, M₂O₃ 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
    - Bk⁴⁺ is more oxidizing than Ce⁴⁺
  - MO₂ known from Th to Cf (fluorite structure)
  - MF₄ are isostructural with lanthanide tetrafluorides
    - MCl₄ 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 AnO₂⁺ ion is known
  - Comparatively few other An(V) species are known
    - fluorides fluoro-anions, oxochlorides, uranates,
  - AnO₂⁺ ions are important for U, Np, Pu, Am UO₂⁺⁺ is the most stable
  - Few other compounds e.g. AnF₆ (An = U, Np, Pu), UCl₆, UOF₄, U(OR)₆
  - Only the marginally stable oxo-anions of Np and Pu, (AnO₅³⁻)
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, $3\text{Pu}^{4+} + 2\text{H}_2\text{O} \rightarrow \text{PuO}_2^{2+} + 2\text{Pu}^{3+} + 4\text{H}^+$
- Early actinides have a tendency to form complexes
  - Complex formation influences reduction potentials
    - $\rightarrow \text{Am}^{4+}(\text{aq})$ exists when complexed by fluoride (15 M NH$_4$F(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 $\text{AnF}_3$ or $\text{AnF}_4$ with vapors of Li, Mg, Ca or Ba at 1100 – 1400 °C
  - Other redox methods are possible
    → Thermal decomposition of iodine species
    → Am from $\text{Am}_2\text{O}_3$ 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
    - $\rightarrow$ 200 MeV/fission, 2.5 neutrons

- Natural isotopes
  - Ratios of isotopes established
    - $\rightarrow$ 234: $0.005\pm0.001$, 68.9 a
    - $\rightarrow$ 235: $0.720\pm0.001$, 7.04E8 a
    - $\rightarrow$ 238: $99.275\pm0.002$, 4.5E9 a
Fuel Cycle Chemistry Overview

- **Uranium acid-leach**
  - Crushing & Grinding
  - Acid Leaching
  - Separation
  - Solvent Extraction
  - Recovery, Precipitation
  - Drying ($\text{U}_3\text{O}_8$)

- **Extraction and conversion**
  - U ore concentrates
    - Solvent extraction purification
  - Conversion to $\text{UO}_3$
  - $\text{H}_2$ Reduction
    - $\text{UO}_2$
    - HF
    - $\text{UF}_4$
  - $\text{Mg}$
    - $\text{U}$ metal
    - $\text{MgF}_2$
  - $\text{F}_2$
  - $\text{UF}_6$
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
Aqueous solution complexes

• Strong Lewis acid
• Hard electron acceptor
  ▪ $F^- >> Cl^- > Br^- \approx I^-$
  ▪ 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
  ▪ $\text{HOCH}_2\text{COO}^- \ pK_a = 17, 3.6$ upon complexation of $\text{UO}_2$
    → 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
    \[ \text{UO}_2^{2+} + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{U}^{4+} + 2\text{H}_2\text{O} \]
- 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 $\sigma$ based on 6p orbitals interactions
  - 5f$\delta$ and 5f$\phi$ 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$_2$O)$_5^{2+}$ from a Simplistic “Ionic” Picture and from DFT Calculations

<table>
<thead>
<tr>
<th>Occupied Orbitals in Neutral Atoms</th>
<th>Charge on Each Entity</th>
<th>Occupation of Atomic Orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td>U 6s$^2$6p$^6$5f$^3$6d$^1$7s$^2$7p$^0$</td>
<td>Ionic Model</td>
<td>DFT Results</td>
</tr>
<tr>
<td>O 2s$^2$ 2p$^4$</td>
<td>U +6.0</td>
<td>U +1.66</td>
</tr>
<tr>
<td>H$_2$O 0.0</td>
<td>O -2</td>
<td>O -0.26</td>
</tr>
</tbody>
</table>
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$_2$O)$_5^{2+}$, 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 equatorial 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

<table>
<thead>
<tr>
<th>Uranium(vi) Chemical reaction</th>
<th>$\log^* \beta_{p,q}$</th>
<th>Uranium(iv) Chemical reaction</th>
<th>$\log^* \beta_{p,q}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{UO}_2^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{UO}_2\text{OH}^+ + \text{H}^+$</td>
<td>-5.25</td>
<td>$\text{U}^{4+} + \text{H}_2\text{O} \rightleftharpoons \text{UOH}^{3+} + \text{H}^+$</td>
<td>-0.54</td>
</tr>
<tr>
<td>$\text{UO}_2^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{UO}_2(\text{OH})_2(aq) + 2\text{H}^+$</td>
<td>-12.15</td>
<td>$\text{U}^{4+} + 2\text{H}_2\text{O} \rightleftharpoons \text{U(OH)}_2^{2+} + 2\text{H}^+$</td>
<td>-2.6$^a$</td>
</tr>
<tr>
<td>$\text{UO}_2^{2+} + 3\text{H}_2\text{O} \rightleftharpoons \text{UO}_2(\text{OH})_3^- + 3\text{H}^+$</td>
<td>-20.25</td>
<td>$\text{U}^{4+} + 3\text{H}_2\text{O} \rightleftharpoons \text{U(OH)}_3^+ + 3\text{H}^+$</td>
<td>-5.8$^a$</td>
</tr>
<tr>
<td>$\text{UO}_2^{2+} + 4\text{H}_2\text{O} \rightleftharpoons \text{UO}_2(\text{OH})_4^{4-} + 4\text{H}^+$</td>
<td>-32.40</td>
<td>$\text{U}^{4+} + 4\text{H}_2\text{O} \rightleftharpoons \text{U(OH)}_4(aq) + 4\text{H}^+$</td>
<td>-10.3$^a$</td>
</tr>
<tr>
<td>$2\text{UO}_2^{2+} + \text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_2\text{OH}^{3+} + \text{H}^+$</td>
<td>-2.7</td>
<td>$6\text{U}^{4+} + 15\text{H}_2\text{O} \rightleftharpoons \text{U}<em>6(\text{OH})</em>{15}^9 + 15\text{H}^+$</td>
<td>-16.9</td>
</tr>
<tr>
<td>$2\text{UO}_2^{2+} + 2\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_2(\text{OH})^{2+} + 2\text{H}^+$</td>
<td>-5.62</td>
<td>Uranium(vi): Estimates from Np(v) data</td>
<td></td>
</tr>
<tr>
<td>$3\text{UO}_2^{3+} + 5\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_3(\text{OH})_5^{7+} + 5\text{H}^+$</td>
<td>-15.55</td>
<td>$\text{UO}_2^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{UO}_2\text{OH}(aq) + \text{H}^+$</td>
<td>$\approx -11.3$</td>
</tr>
<tr>
<td>$3\text{UO}_2^{3+} + 7\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_3(\text{OH})_7^{9+} + 7\text{H}^+$</td>
<td>-32.7</td>
<td>$\text{UO}_2^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{UO}_2(\text{OH})_2^+ + 2\text{H}^+$</td>
<td>$\approx -23.6$</td>
</tr>
<tr>
<td>$4\text{UO}_2^{3+} + 7\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_4(\text{OH})_7^{11+} + 7\text{H}$</td>
<td>-21.9</td>
<td>Uranium(III): Estimates from Cm(III) data</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{U}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{UOH}^{2+}$</td>
<td>-7.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{U}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{U(OH)}_2^{2+}$</td>
<td>-15.7</td>
</tr>
</tbody>
</table>

$^a$ 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
  - $\text{Cp}_3\text{UCO}$ and $\text{Cp}_3\text{UCO}^+$
    - $\text{Cp}=\text{cyclopentadiene}$
    - * 5f CO $\pi$ backbonding
      - Metal electrons to $\pi$ of ligands
    - * Decreases upon oxidation to U(IV)
- Uranyl(V) and (VI) compounds
  - $\text{yl}$ ions in aqueous systems unique for actinides
    - $\text{VO}_2^+,$ $\text{MoO}_2^{2+},$ $\text{WO}_2^{2+}$
    - * Oxygen atoms are cis to maximize $(p_\pi) \rightarrow M(d_\pi)$
    - Linear $\text{MO}_2^{2+}$ 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 $\sigma$ and 2 with $\pi$ characteristics

Fig. 5.63 Logarithmic diagrams showing the distribution of $\text{U}^{3+}, \text{U}^{4+}, \text{UO}_2^{2+}$ and $\text{UO}_2^{4+}$ as a function of the redox potential in 1 M perchloric acid (the first diagram), and in 1 M $\text{Na}_2\text{CO}_3$ (the second diagram). $\text{U}(v)$ is predominant between −0.7 and −0.4 V in the second diagram.
Uranium solution chemistry: U(III)

- Dissolution of UCl₃ 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

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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).

<table>
<thead>
<tr>
<th>Species and redox reaction</th>
<th>( E^\circ ) (V)</th>
<th>( \Delta_f G_m^\circ ) (kJ mol(^{-1}))</th>
<th>( \Delta_f H_m^\circ ) (kJ mol(^{-1}))</th>
<th>( S_m^\circ ) (J K(^{-1}) mol(^{-1}))</th>
<th>( C_{p,m}^\circ ) (J K(^{-1}) mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>U³⁺(aq)</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>U⁴⁺ + e⁻ ⇌ U³⁺</td>
<td></td>
<td>-(0.553 ± 0.004)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U⁴⁺(aq)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UO₂⁺(aq)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UO₂⁺ + e⁻ ⇌ UO₂⁺</td>
<td>(0.0878 ± 0.0013)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UO₂⁺(aq)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UO₂⁺ + 4H⁺ + 2e⁻ ⇌ U⁴⁺ + 2H₂O</td>
<td>(0.2673 ± 0.0012)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---
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 $^{235}\text{U}$ from $^{238}\text{U}$
- 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
  - $^{238}\text{U}$ absorption peak at 502.74 nm
  - $^{235}\text{U}$ 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**
    - $^{238}\text{U}$ absorption peak 502.74 nm
    - $^{235}\text{U}$ 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
    $\rightarrow$ $^{235}$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
  - $\alpha, \beta, \gamma$ 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 ºC
  - Tetragonal unit cell

- **γ-phase**
  - Formed above 775 ºC
  - 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
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.

<table>
<thead>
<tr>
<th>Class</th>
<th>Behavior</th>
<th>Metals</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>form intermetallic compounds</td>
<td>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</td>
</tr>
<tr>
<td>II</td>
<td>form solid solutions but no intermetallic compounds</td>
<td>SS In, Re, Tc, Tl, Mo, Nb, Pu, Ti, Zr</td>
</tr>
<tr>
<td>III</td>
<td>form neither solid solutions nor intermetallic compounds</td>
<td>IS Ag, Cr, Mg, Ta, Th, V, W lanthanides, Li, Na, K, Ca, Sr, Ba</td>
</tr>
</tbody>
</table>
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$$^{2+}$
    → Favored in high acidity and Np concentration
  - 2NpO$_2^+$ +4 H$^+$ ⇌ Np$^{4+}$ + NpO$_2$$^{2+}$ + 2H$_2$O
  - K for reaction increased by addition of complexing reagents
    → K=4E-7 in 1 M HClO$_4$ and 2.4E-2 in H$_2$SO$_4$
- 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 π→ 5f
      * Number of vibrational states
        → Between 681 cm$^{-1}$ and 2338 cm$^{-1}$
- Np(VI)
  - Studies in Cs$_2$UO$_2$Cl$_4$ lattice
  - Electronic levels identified at following wavenumbers (cm$^{-1}$)
    → 6880, 13277, 15426, 17478, and 19358
      * 6880 cm$^{-1}$ belongs to 5f$^1$ configuration
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_{2}PO_{4}->SCN->NO_{3}->Cl->\text{ClO}_{4}^{-}
  - CO_{3}^{2-}->HPO_{4}^{2-}->SO_{4}^{2-}
- NpO_{2}^{+} forms cation-cation complexes
  - Fe>In>Sc>Ga>Al

<table>
<thead>
<tr>
<th>Ion</th>
<th>Method</th>
<th>Temp. (°C)</th>
<th>Medium</th>
<th>Equilibrium constants</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Np^{3+}</td>
<td>pot</td>
<td>25</td>
<td>0.3 m NaClO_{4}</td>
<td>log_{2}K_{11} = 0.14</td>
<td>Mejido et al. (1974)</td>
</tr>
<tr>
<td>Np^{3+}</td>
<td>sp</td>
<td>25</td>
<td>1.0 m</td>
<td>log_{2}K_{12} = 0.10</td>
<td>Paul (1970)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>0.0</td>
<td>log_{2}K_{13} = 0.15</td>
<td>Rai et al. (1987)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>0.1 m NaClO_{4}</td>
<td>log_{2}K_{11} = 0.16</td>
<td>Lemire et al. (2001)</td>
</tr>
<tr>
<td>NpO_{2}</td>
<td>sol</td>
<td>25</td>
<td>0.1 m NaClO_{4}</td>
<td>log_{2}K_{11} = 0.13</td>
<td>Neck et al. (1992)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>1.0 m NaClO_{4}</td>
<td>log_{2}K_{11} = 0.12</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>0.0</td>
<td>log_{2}K_{11} = 0.14</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>0.1 m NaClO_{4}</td>
<td>log_{2}K_{11} = 0.06</td>
<td></td>
</tr>
<tr>
<td>NpO_{2}</td>
<td>pot</td>
<td>25</td>
<td>1.0 m NaClO_{4}</td>
<td>log_{2}K_{11} = 0.14</td>
<td>Cassol et al. (1972a)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>0.0</td>
<td>log_{2}K_{11} = 0.06</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>0.1 m NaClO_{4}</td>
<td>log_{2}K_{11} = 0.14</td>
<td>Kato et al. (1996)</td>
</tr>
</tbody>
</table>

* K_{eq} is the hydrolysis constant for the equilibrium: mM^{x+} + nH_{2}O = M_{n}OH_{x}^{x-} + nH^{+}.
Np Separations

- Varied oxidation states
  - In solution oxidation states 4+, 5+, and 6+ readily accessible
  - NpO₂⁺ 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 HNO₃
      * Back extract in 8 M HNO₃
        - Oxidation to Np(V), extraction into 1 M HNO₃
- Tributylphosphate (TBP)
  - NpO₂(NO₃)₂(TBP)₂ and Np(NO₃)₄(TBP)₂ are extracted species
    - Extraction increases with increase concentration of TBP and nitric acid
      - 1-10 M HNO₃
    - 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
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$_2$NpO$_2$Cl$_4$ and Cs$_3$NpO$_2$Cl$_4$
    → LiCl/KCl as electrolyte at 723 K
  - NpC reduction with Ta followed by volatilization of Np
  - Electrodeposition from aqueous solution
    → Amalgamation with Hg from 1 M CH$_3$COOH and 0.3 M CH$_3$COONa 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
    - \( \Delta S = 10.1 \text{ JK}^{-1}\text{mol}^{-1} \)
    - \( \Delta H = 5.607 \text{ kJmol}^{-1} \)
    \[ \beta \rightarrow \gamma \]
    - Transition T 856 K
    - \( \Delta S = 6.23 \text{ JK}^{-1}\text{mol}^{-1} \)
    - \( \Delta H = 5.272 \text{ kJmol}^{-1} \)

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

<table>
<thead>
<tr>
<th>Allotrope</th>
<th>Symmetry</th>
<th>Space group</th>
<th>( a_0 ) (Å)</th>
<th>( b_0 ) (Å)</th>
<th>( c_0 ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )-Np</td>
<td>orthorhombic</td>
<td>( Pnma )</td>
<td>6.663</td>
<td>4.723</td>
<td>4.887</td>
</tr>
<tr>
<td>( \beta )-Np(^a)</td>
<td>tetragonal</td>
<td>( P42 )</td>
<td>4.897</td>
<td>–</td>
<td>3.388</td>
</tr>
<tr>
<td>( \gamma )-Np(^b)</td>
<td>Body-centered cubic</td>
<td>( Im3m )</td>
<td>3.518</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

\(^a\) 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$_2$X$_2$
    → R=Th, Np or Pu, M is transition metal, X = Si, Ge
  - RM$_2$Al$_3$
    → 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
  - $\text{Np}_2\text{O}_5$ and $\text{NpO}_2$
- $\text{NpO}_2$
  - 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
- $\text{Np}_2\text{O}_5$
  - From thermal decomposition of $\text{NpO}_3 \cdot \text{H}_2\text{O}$ or $\text{NpO}_2\text{OH}_{(am)}$
  - $\text{Np}_2\text{O}_5$ decomposes to $\text{NpO}_2$ 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 coexistence of oxidation states
    → Pu(IV) and Pu(V) tend toward disproportionation
      * 3Pu^{4+} + 2H_2O ⇌ 2Pu^{3+} + PuO_2^{2+} + 4H^+
      → K=0.0089 at 1.0 M I
    → 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).

<table>
<thead>
<tr>
<th>Couple</th>
<th>Acidic^a</th>
<th>Neutral^b</th>
<th>Basic^c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pu(iv)/Pu(III)</td>
<td>+0.982</td>
<td>−0.39</td>
<td>−0.96</td>
</tr>
<tr>
<td>Pu(v)/Pu(iv)</td>
<td>+1.70</td>
<td>+0.70</td>
<td>−0.67, +0.52^d</td>
</tr>
<tr>
<td>Pu(vi)/Pu(v)</td>
<td>+0.913</td>
<td>+0.60</td>
<td>+0.12</td>
</tr>
<tr>
<td>Pu(vi)/Pu(iv)</td>
<td>+1.043</td>
<td>+0.65</td>
<td>+0.34</td>
</tr>
<tr>
<td>Pu(v)/Pu(HI)</td>
<td>+1.076</td>
<td></td>
<td>+0.85</td>
</tr>
<tr>
<td>Pu(v)/Pu(v)</td>
<td>+1.17</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

^a Formal potential in 1 m HClO₄ solution (Lemire et al., 2001).
^b pH 8 (Allard et al., 1980).
^c Determined in 1 m NaOH solution (Peretrakhin 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 HClO₄ (Lemire et al., 2001), (b) in 1 m HCl (Rabideau and Cowan, 1955; Rabideau et al., 1959), and (c) 1 m HNO₃ (Artyukhin et al., 1958).
Oxidation state distribution diagram showing the predominant oxidation state of plutonium in 1 M (H,Na)ClO₄ 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)ClO₄ 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 HClO₄
    - 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 PuO₂
  - Basis for theory that colloids are tiny crystallites PuO₂,
    → 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 $OH_2^-$
Plutonium Chemistry: Metal Pu

- Ca reduction
- Pyroprocessing
  - PuF₄ 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
    - PuO₂, Ca, and CaCl₂
  - Molten salt extraction
    - Separation of Pu from Am and lanthanides
    - Oxidize Am to Am³⁺, remains in salt phase
    - MgCl₂ 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 MgCl₂ 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

**Table 7.9 Crystal structure data for plutonium.**

<table>
<thead>
<tr>
<th>Phase</th>
<th>Stability range (K)</th>
<th>Crystal lattice and space group</th>
<th>Unit cell dimensions (Å)</th>
<th>Atoms per unit cell</th>
<th>X-ray density (g/cm³)</th>
<th>Transformation temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>below 397.6</td>
<td>simple monoclinic P2_1/m</td>
<td>a = 6.183(1)</td>
<td>16</td>
<td>19.85</td>
<td></td>
</tr>
<tr>
<td>β</td>
<td>397.6 – 487.9</td>
<td>body-centered monoclinic 12/m</td>
<td>a = 9.28(3)</td>
<td>34</td>
<td>17.71 (α→β)</td>
<td>397.6</td>
</tr>
<tr>
<td>γ</td>
<td>487.9 – 593.1</td>
<td>face-centered orthorhombic Fddd</td>
<td>a = 3.159(1)</td>
<td>8</td>
<td>17.15 (β→γ)</td>
<td>487.9</td>
</tr>
<tr>
<td>δ</td>
<td>593.1 – 736.0</td>
<td>face-centered cubic Fm3/m</td>
<td>a = 4.637(4)</td>
<td>4</td>
<td>15.92 (γ→δ)</td>
<td>593.1</td>
</tr>
<tr>
<td>δ'</td>
<td>736.0 – 755.7</td>
<td>body-centered tetragonal I4/m</td>
<td>a = 4.337(1)</td>
<td>2</td>
<td>16.03 (δ→δ')</td>
<td>736.0</td>
</tr>
<tr>
<td>ε</td>
<td>755.7 – 913.0</td>
<td>body-centered cubic Im3/m</td>
<td>a = 3.636(4)</td>
<td>2</td>
<td>16.51 (δ'→ε)</td>
<td>913.0</td>
</tr>
</tbody>
</table>

Pu 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 $\alpha$ 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
  - \(^{239}\text{Pu}\) to \(^{240}\text{Pu}\) to \(^{241}\text{Pu}\), then beta decay of \(^{241}\text{Pu}\)

- \(^{241,243}\text{Am}\) main isotopes of interest
  - Long half-lives
  - Produced in kilogram quantity
  - Chemical studies
  - Both isotopes produced in reactor

- \(^{241}\text{Am}\)
  - Source for low energy gamma and alpha
    → Alpha energy 5.44 MeV and 5.49 MeV
  - Smoke detectors
  - Neutron sources
    → \((\alpha,\text{n})\) on Be
  - Thickness gauging and density
  - \(^{242}\text{Cm}\) production from thermal neutron capture

- \(^{243}\text{Am}\)
  - Irradiation of \(^{242}\text{Pu}\), beta decay of \(^{243}\text{Pu}\)

- Critical mass
  - \(^{242}\text{Am}\) 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$_4$F
    → Phosphoric or pyrophosphate (P$_2$O$_7^{4-}$) solution with anodic oxidation
    → Ag$_3$PO$_4$ and (NH$_4$)$_4$S$_2$O$_8$
    → 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$_2$O$_8^{2-}$ 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$_2$O or S$_2$O$_8^{2-}$ 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

\[ n_{\text{H}_2\text{O}} = \frac{x}{\tau} - y \]
- \( x = 2.56 \times 10^{-7} \text{ s}, y = 1.43 \)
- Measurement of fluorescence lifetime in H\(_2\)O and D\(_2\)O

Fig. 8.4  Coordination environment of Am\(^{3+}\) and crystal packing in [Am(H\(_2\)O)\(_9\)][CF\(_3\)SO\(_3\)] (Matonic et al., 2001).
Am solution chemistry

- Autoreduction
  - Formation of $\text{H}_2\text{O}_2$ and HO$_2$ radicals from radiation reduces Am to trivalent states
    - Difference between $^{241}\text{Am}$ and $^{243}\text{Am}$
  - 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) $\rightarrow$ Am(III) + Am(V)
      * Am(IV) + Am(V) $\rightarrow$ 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$_2$O
    - 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
    \[ \rightarrow \text{SO}_4^{2-}, \text{HS}_2\text{O}_8^{-} \]
  - Oxidation to Am(VI)
    \[ \rightarrow \text{0.1 M to 10 nM Am(III)} \]
  - Acid above 0.3 M limits oxidation
    \[ \rightarrow \text{Decomposition of S}_2\text{O}_8^{2-} \]
  - Induction period followed by reduction
  - Rates dependent upon temperature, [HNO_3], [S_2O_8^{2-}], and [Ag^{+2}]
  - \[ \frac{3}{2} \text{S}_2\text{O}_8^{2-} + \text{Am}^{3+} + 2 \text{H}_2\text{O} \rightarrow 3 \text{SO}_4^{2-} + \text{AmO}_2^{2+}+4\text{H}^+ \]
    \[ \rightarrow \text{Evaluation of rate constants can yield 4 due to peroxydisulfate decomposition} \]
  - In carbonate proceeds through Am(V)
    \[ \rightarrow \text{Rate to Am(V) is proportional to oxidant} \]
    \[ \rightarrow \text{Am(V) to Am(VI)} \]
    * 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**
  - $\text{H}_2\text{O}_2$ in perchlorate is 1$^{st}$ order for peroxide and Am
    \[ 2 \text{AmO}_2^{2+} + \text{H}_2\text{O}_2 \rightarrow 2 \text{AmO}_2^+ + 2 \text{H}^+ + \text{O}_2 \]
  - $\text{NpO}_2^+$
    \[ \rightarrow 1^{st} \text{order with Am(VI) and Np(V)} \]
    
    * $k=2.45\text{E}4 \text{ L / mol s}$

- Oxalic acid reduces to equal molar Am(III) and Am(V)

- **Am(V) reduction**
  - Reduced to Am(III) in NaOH solutions
    \[ \rightarrow \text{Slow reduction with dithionite (Na}_2\text{S}_2\text{O}_4), \text{sulfite (SO}_3^{2-}), \text{or thiourea dioxide ((NH}_2\text{)}_2\text{CSO}_2) \]
  - $\text{Np(IV)}$ and $\text{Np(V)}$
    \[ \rightarrow \text{In both acidic and carbonate conditions} \]
    
    * For $\text{Np(IV)}$ reaction products either $\text{Np(V)}$ or $\text{Np(VI)}$
      
      > Depends upon initial relative concentration of Am and Np

  \[ \rightarrow \text{U(IV) examined in carbonate} \]
Solution absorption spectroscopy

- **Am(III)**
  - $^7\text{F}_0 \rightarrow ^5\text{L}_6$ at 503.2 nm ($\varepsilon$=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$_3$PO$_4$
  - Resembles solid AmF$_4$ spectrum

Fig. 8.13  Electronic absorption spectra of Am$^{3+}$ in 1 M HClO$_4$ and of the predominant Am($m$) species in carbonate-containing solutions (inset) (Meinrath and Kim, 1991a).

Fig. 8.14  Absorption spectrum of Am($iv$) in 13 M NH$_4$F (Asprey and Penneman, 1962).
Solution absorption spectroscopy

- **Am(V)**
  - $^5\text{I}_4 \rightarrow ^3\text{G}_5$; 513.7 nm; 45 L mol cm$^{-1}$
  - $^5\text{I}_4 \rightarrow ^3\text{I}_7$; 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

![Absorption spectrum of Am(VI) in 1 M HClO$_4$ and in carbonate solution (inset) (Penneman and Asprey, 1955).](image)

![Electronic absorption spectra of AmO$_2^{2+}$ in 1 M HClO$_4$ and in carbonate-containing solutions (inset) (Studler and Knm, 1988).](image)
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$_5$Am
    → 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$_2$O$_3$, AmO$_2$
      - Non-stoichiometric phases between Am$_2$O$_3$ and AmO$_2$
    - AmO lattice parameters varied in experiments
      - 4.95 Å and 5.045 Å
      - Difficulty in stabilizing divalent Am
  - Am$_2$O$_3$
    - 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.)

<table>
<thead>
<tr>
<th>Property</th>
<th>Values$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallographic data symmetry</td>
<td>$&lt;658^\circ$ C, dhcp (α) 793-1004$^\circ$ C, fcc (β) 1050-1173$^\circ$ C, bcc (γ)</td>
</tr>
<tr>
<td>space group</td>
<td>$P6_3/mmc$ and $Fm3m$</td>
</tr>
<tr>
<td>lattice parameters</td>
<td>dhcp: $a = 3.4681$ Å, $c = 11.241$ Å</td>
</tr>
<tr>
<td></td>
<td>fcc: $a = 4.894$ Å</td>
</tr>
<tr>
<td>density</td>
<td>13.671 g cm$^{-3}$ (calc.); 13.671 g cm$^{-3}$ (obs.)$^b$</td>
</tr>
</tbody>
</table>
| 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  
|                                | $x$-Pu; >15-23 GPa Am(iv): orthorhombic  
|                                | $x$-U or monoclinic ($x$-U alloys)                                      |
| metallic radius (CN 12)         | 1.73 Å                                                                  |
| melting point                   | (1149 ± 5) K                                                             |
| boiling point                   | 2067$^\circ$ C (calc.)                                                   |
| coefficient of thermal expansion| $x_a = 7.5 ± 0.2 \times 10^{-6}$ K$^{-1}$ and $x_c = 6.2 ± 0.2 \times 10^{-6}$ K$^{-1}$ |
| compressibility at 1 atm vapor  | 0.00277 kbar$^{-1}$ at 23$^\circ$C                                        |
| pressure$^d$                    | log ($p$/atm) = $(6.578 \pm 0.046) - (14315 ± 55)/T$ at 990-1358 K        |
| magnetic susceptibility         | $Z_{20^\circ}C = (881 \pm 46) \times 10^{-6}$ cm$^2$ mol$^{-1}$           |
| magnetic moment                  | ~0                                                                      |
| microhardness (Vickers) at 25$^\circ$ | 800 MN m$^{-2}$                                                        |
| electrical resistivity          | 68 $\mu$Ω cm (300 K), 71 $\mu$Ω cm (298 K)                              |
| crystal entropy, $S_0^{298}$    | 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($p$/atm) = 5.185-13191/T.
Cm Chemistry

- 5f⁷ 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 CmF₄
    → CmF₃ under strong fluorination conditions

- Isotopes from mass 237 to 251
- Three isotopes available in quantity for chemical studies
  - ²⁴²Cm, t₁/₂=163 d
    → 122 W/g
    → Grams of the oxide glows
    → Low flux of ²⁴¹Am target decrease fission of ²⁴²Am, increase yield of ²⁴²Cm
  - ²⁴⁴Cm, t₁/₂=18.1 a
    → 2.8 W/g
  - ²⁴⁸Cm, t₁/₂= 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
  - $^{242}\text{Pu} + n \rightarrow ^{243}\text{Pu} (\beta^-, 4.95 \text{ h}) \rightarrow ^{243}\text{Am} + n \rightarrow ^{244}\text{Am} (\beta^-, 10.1 \text{ h}) \rightarrow ^{244}\text{Cm}$
  - Favors production of $^{244,246,248}\text{Cm}$
    - Isotopes above $^{244}\text{Cm}$ to $^{247}\text{Cm}$ are not isotopically pure
    - Pure $^{248}\text{Cm}$ available from alpha decay of $^{252}\text{Cf}$
- Large campaign to product Cm from kilos of Pu
- $^{244}\text{Cm}$ 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
- $^{242}\text{Cm}$ at 1g/L will boil
- 9 coordinating H$_2$O 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 ($\text{Cm}^{3+}+\text{H}_2\text{O} \rightarrow \text{CmOH}^{2+}+\text{H}^+$)
  - $K_{11}=1.2\text{E}-6$
  - Evaluated under different ionic strength

![Graphs showing species distribution](image)

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 Fanghânel et al. (1994).
Cm atomic and spectroscopic data

- $5f^7$ has enhanced stability
  - Half filled orbital
    - Large oxidation potential for III$\rightarrow$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
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
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 ($\text{AlCl}_4^-$)
  - 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,N-trimethylmethanaminium
- 1-butyl-1-methylpyrrolidinium
- Tri-n-ocylmethyliammonium
- 1-butyl-3-methylpiperidinium
- 1-butyl-3-methylimidazolium
- Chloride
- Trifluoromethylsulfonate
- Nitrate
- Bis(trifluoromethanesulfonyl)imide
- Tetrafluoroborate
- 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
- Possible recovery of metals through electrodeposition
  - direct from the organic phase following solvent extraction

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$_3$NBu][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

- 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 [Me₃NBu][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 AgNO₃ dissolved and a Vycor™ frit
  • Reference electrode standardized with 4mM Ferrocene in [Me₃NBu][TFSI]

1) Working electrode: chemistry occurs
2) Counter electrode: current path
3) Reference electrode: controls potential
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 $[\text{Me}_3\text{NBu}][\text{TFSI}]$

Determined by Karl-Fisher Titration

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

Addition of acid (HTFSI) increases water

<table>
<thead>
<tr>
<th>Water contact standards</th>
<th>% water</th>
<th>Mean (%)</th>
<th>ST DEV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0986</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.1033</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.1008</td>
<td>0.1009</td>
<td>0.0016</td>
</tr>
</tbody>
</table>

"old" $\text{Me}_3\text{NBuTFSI}$ sample

| 1 | 0.0737 |
| 2 | 0.0782 |
| 3 | 0.0775 | 0.0765 | 0.0024 |

"new" $\text{Me}_3\text{NBuTFSI}$ sample

| 1 | 0.0303 |
| 2 | 0.0293 |
| 3 | 0.0299 | 0.0298 | 0.0005 |

8.83 M HTFSI in $\text{Me}_3\text{NBuTFSI}$ sample

| 1 | 0.1801 |
| 2 | 0.1805 |
| 3 | 0.1775 | 0.1794 | 0.0016 |
Synthesis and dissolution of TFSI species

\[
\text{Sm}_2\text{O}_3 + 6\text{H(TFSI)} \xrightarrow{\text{H}_2\text{O}} 2\text{Sm(TFSI)}^2_2
\]

- **Preparation of Sm and U TFSI species**
  - Direct dissolution in ionic liquid
  - 1.5 g \( \text{Sm}_2\text{O}_3 \) and 7.3 g of \( \text{H(TFSI)} \) 15 mL of \( \text{H}_2\text{O} \)
  - 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\(_{1}3\)**
  - Consistent with the literature on La-TFSI complex
  - Sm coordinated through sulfonyle 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

\[ \text{UI}_3(\text{THF})_4 + 3\text{K(TFSI)} \xrightarrow{\text{THF}} \text{U(TFSI)}_3 + 3\text{KI}_s \]

- 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$_3$NBu][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 $\text{U}_3\text{O}_8$ into ionic liquid

- Original dissolution conditions:
- 45 mg $\text{U}_3\text{O}_8$ with 3.27 M HTFSI in Me$_3$NBuTFSI Stirred for weeks with no change

- RESULT: dissolution of material
  - oxidizing gas used
    - $\text{O}_3$, NO$_2$
  - Addition of HTFSI
    - Promote formation of uranium-TFSI complex
Direct dissolution of U$_3$O$_8$ into IL

Proposed dissolution mechanism:

$$\text{U}_3\text{O}_8 + 6 \text{HTFSI} + \text{O}_3 \rightleftharpoons 3 \text{UO}_2^{2+} + 6 \text{TFSI}^- + 3 \text{H}_2\text{O} + \text{O}_2$$

- 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

- - - 0.1 M HTFSI in RTIL
Sample prior
1 hour
12 hours
24 hours
36 hours
48 hours
60 hours
72 hours
24 hours

Absorbance (a.u.)

Wavelength (nm)

Absorbance (a.u.)
UV-Vis of U₃O₈ dissolution into IL

- noticeable band in the U₃O₈ 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 U₃O₈ dissolution into Ionic Liquid

Up to 300 mg U₃O₈ (~50 mM U) directly dissolved into Me₃NBuTFSI with 0.1 M HTFSI
- not saturation limited
- Will impact electroplating
Electrodeposition of targets

- **Stainless steel**
  - Deposit density up to 0.6 mg/cm²

- **Au foil**
  - Appears to be UOx by SEM

- **Designed electrochemistry cell**
  - 9.23 cm² deposition area

- **Electrodeposition procedure**
  - Cyclic voltammetry (negative potential region) 400-800 segments
  - Constant potential held
    - \(E = -2.8 \text{ up to } -3.2 \text{ V}\) for 24 hours periods
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 temperature

• 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% 235U)
(By courtesy of Siemens/KWU)

<table>
<thead>
<tr>
<th>Element</th>
<th>Fuel burnup (MWd/kg HM)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>13.0</td>
</tr>
<tr>
<td>Bromine</td>
<td>0.0093</td>
</tr>
<tr>
<td>Krypton</td>
<td>0.16</td>
</tr>
<tr>
<td>Rubidium</td>
<td>0.19</td>
</tr>
<tr>
<td>Strontium</td>
<td>0.47</td>
</tr>
<tr>
<td>Yttrium</td>
<td>0.24</td>
</tr>
<tr>
<td>Zirconium</td>
<td>1.56</td>
</tr>
<tr>
<td>Niobium</td>
<td>0.045</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>1.33</td>
</tr>
<tr>
<td>Technetium</td>
<td>0.33</td>
</tr>
<tr>
<td>Ruthenium</td>
<td>0.84</td>
</tr>
<tr>
<td>Rhodium</td>
<td>0.17</td>
</tr>
<tr>
<td>Palladium</td>
<td>0.23</td>
</tr>
<tr>
<td>Silver</td>
<td>0.015</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.011</td>
</tr>
<tr>
<td>Indium</td>
<td>0.0007</td>
</tr>
<tr>
<td>Tin</td>
<td>0.014</td>
</tr>
<tr>
<td>Antimony</td>
<td>0.0058</td>
</tr>
<tr>
<td>Tellurium</td>
<td>0.16</td>
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<tr>
<td>Iodine</td>
<td>0.080</td>
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<tr>
<td>Xenon</td>
<td>2.02</td>
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<tr>
<td>Cesium</td>
<td>1.14</td>
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<tr>
<td>Barium</td>
<td>0.56</td>
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<tr>
<td>Lanthanum</td>
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<td>Cerium</td>
<td>1.30</td>
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<tr>
<td>Praseodymium</td>
<td>0.43</td>
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<tr>
<td>Neodymium</td>
<td>1.38</td>
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<tr>
<td>Promethium</td>
<td>0.13</td>
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<tr>
<td>Samarium</td>
<td>0.23</td>
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<tr>
<td>Europium</td>
<td>0.036</td>
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<tr>
<td>Gadolinium</td>
<td>0.0094</td>
</tr>
<tr>
<td>Totals</td>
<td>13.5</td>
</tr>
</tbody>
</table>
Distribution in Fuel

- Radial distribution of fission products mainly governed by thermal neutron flux profile.
- Higher Pu concentration in outer zone of fuel
  - Epithermal neutron capture on $^{238}\text{U}$
  - 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

- 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

Figure 3.9. Fission product distribution as a function of the relative fuel pellet radius in a LWR high-burnup oxide fuel (Kleykamp, 1990a)
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
- **Catalytic property in used fuel**
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 UO₂ lattice

Relative partial molar Gibbs free energy of oxygen of the fission product oxides and UO₂
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