CHEM 312 Lecture 14 Plutonium Chemistry Part 1

- Readings
  - Pu chemistry Chapter
    → Chemistry of the Actinides and Transactinides
  - Challenges of Pu chemistry
    → Los Alamos National Laboratory

- Nuclear properties and isotope production
- Pu in nature
- Pu solution chemistry
- Separation and Purification
- Atomic properties
- Metallic state
- Compounds
Plutonium isotopes

- Isotopes from $228 \leq A \leq 247$
- Important isotopes
  - $^{238}\text{Pu}$
    - $^{237}\text{Np}(n,\gamma)^{238}\text{Np}$
      * $^{238}\text{Pu}$ from beta decay of $^{238}\text{Np}$
      * Separated from unreacted Np by ion exchange
    - Decay of $^{242}\text{Cm}$
    - 0.57 W/g
    - Power source for space exploration
      * 83.5 % $^{238}\text{Pu}$, chemical form as dioxide
      * Enriched $^{16}\text{O}$ to limit neutron emission
        - 6000 n s$^{-1}$g$^{-1}$
        - 0.418 W/g PuO$_2$
    - 150 g PuO$_2$ in Ir-0.3 % W container
Pu nuclear properties

• $^{239}\text{Pu}$
  - 2.2E-3 W/g
  - Basis of formation of higher Pu isotopes
  - $^{244-246}\text{Pu}$ first from nuclear test

• Higher isotopes available
  - Longer half lives suitable for experiments

• Most environmental Pu due to anthropogenic sources
• $^{239,244}\text{Pu}$ can be found in nature
  - $^{239}\text{Pu}$ from nuclear processes occurring in U ore
    - n,γ reaction
    - Neutrons from
      - SF of U
      - neutron multiplication in $^{235}\text{U}$
      - α,n on light elements
    - * 24.2 fission/g U/hr, need to include neutrons from $^{235}\text{U}$

• $^{244}\text{Pu}$
  - Based on Xe isotopic ratios
    - SF of $^{244}\text{Pu}$
  - 1E-18 g $^{244}\text{Pu}$/g bastnasite mineral

---

Table 7.2  Minimum critical parameters of common forms of pure $^{239}\text{Pu}$ (Clark, 1981).

<table>
<thead>
<tr>
<th>Material</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>metal</td>
<td>mass plutonium (kg)</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>cylinder diameter (cm)</td>
<td>4.4</td>
</tr>
<tr>
<td></td>
<td>slab thickness (cm)</td>
<td>0.65</td>
</tr>
<tr>
<td>oxide</td>
<td>mass plutonium (kg)</td>
<td>10.2</td>
</tr>
<tr>
<td></td>
<td>mass $\text{PuO}_2$ (kg)</td>
<td>11.5</td>
</tr>
<tr>
<td></td>
<td>cylinder diameter (cm)</td>
<td>7.2</td>
</tr>
<tr>
<td></td>
<td>slab thickness (cm)</td>
<td>1.4</td>
</tr>
<tr>
<td>aqueous plutonium nitrate solution</td>
<td>plutonium mass (kg)</td>
<td>0.480</td>
</tr>
<tr>
<td></td>
<td>H/Pu atomic ratio</td>
<td>7.3</td>
</tr>
<tr>
<td></td>
<td>cylinder diameter (cm)</td>
<td>15.4</td>
</tr>
<tr>
<td></td>
<td>volume (L)</td>
<td>7.3</td>
</tr>
</tbody>
</table>

Table 7.3  Content of plutonium in natural uranium ore deposits.

<table>
<thead>
<tr>
<th>Ore</th>
<th>Uranium content (wt.%)</th>
<th>Ratio $^{239}\text{Pu}/\text{U}$ ($\times 10^{12}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cigar Lake U deposit</td>
<td>31</td>
<td>6.4</td>
<td>Curtis et al. (1999)</td>
</tr>
<tr>
<td>Beaverlodge U deposit</td>
<td>7.09</td>
<td>14.3</td>
<td>Dixon et al. (1997)</td>
</tr>
<tr>
<td>Canadian pitchblende</td>
<td>13.5</td>
<td>7.1</td>
<td>Levine and Seaborg (1951)</td>
</tr>
<tr>
<td>Belgian Congo pitchblende</td>
<td>38</td>
<td>12</td>
<td>Levine and Seaborg (1951)</td>
</tr>
<tr>
<td>Colorado pitchblende</td>
<td>50</td>
<td>7.7</td>
<td>Levine and Seaborg (1951)</td>
</tr>
<tr>
<td>Brazilian monazite</td>
<td>0.24</td>
<td>8.3</td>
<td>Levine and Seaborg (1951)</td>
</tr>
<tr>
<td>N. Carolina monazite</td>
<td>1.64</td>
<td>3.6</td>
<td>Levine and Seaborg (1951)</td>
</tr>
<tr>
<td>Colorado furgusonite</td>
<td>0.25</td>
<td>&lt;4</td>
<td>Levine and Seaborg (1951)</td>
</tr>
<tr>
<td>Colorado carnitite</td>
<td>10</td>
<td>&lt;0.4</td>
<td>Levine and Seaborg (1951)</td>
</tr>
</tbody>
</table>
Pu solution chemistry

- Originally driven by need to separate and purify Pu
- Species data in thermodynamic database
- 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 solution spectroscopy

- A few sharp bands
  - 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

Fig. 7.115  Electronic absorption spectra of major plutonium aqua ions recorded at 25°C. The asterisk marks a spectrophotometer grating change. Plutonium(III) recorded on 1.89 mm solution in 1 M HClO₄ using 1 cm cell. Plutonium(IV) recorded on 2.91 mm solution in 1 M HClO₄ using 1 cm cell. Plutonium(V) recorded on 10.2 mm solution in 1 M (Na₂H)ClO₄ solution at pH 3.14 using 1 cm cell. Plutonium(VI) recorded on 0.89 mm solution in 1 M HClO₄ using 1 cm cell. Plutonium(VII) recorded on 20 mm solution in 2.5 M NaOH using 1 cm cell (spectra courtesy of Phillip D. Palmer of Los Alamos National Laboratory).
Pu solution chemistry

- **Redox chemistry**
  - Potentials close to 1 V for 4 common states
  - Kinetics permit coexistence of oxidation states
  
  \[
  3\text{Pu}^{4+} + 2\text{H}_2\text{O} \leftrightarrow 2\text{Pu}^{3+} + \text{PuO}_2^{2+} + 4\text{H}^+ \\
  \Rightarrow K = 0.0089 \text{ at } 1.0 \text{ M I}
  \]

- **Pu(IV) and Pu(V) tend toward disproportionation**

\[
3\text{Pu}^{4+} + 2\text{H}_2\text{O} \leftrightarrow 2\text{Pu}^{3+} + \text{PuO}_2^{2+} + 4\text{H}^+
\]

- **Pu concentration**
- **Ionic strength**
- **pH**

- Kinetics for disproportionation based on time and Pu concentration
  
  \[\text{Moles seconds (M s)}\]

- **Some redox couples are quasi- or irreversible**
  - Breaking or forming oxo bonds
  
  \[\text{i.e., Pu(V)/Pu(III), Pu(VI)/Pu(III)}\]

- **Equilibrium between redox states**
  - \(K = \text{Pu(III)}\text{Pu(VI)}/\text{Pu(IV)}\text{Pu(V)}\)
  
  \[K = 13.1, \text{ corrected for hydrolysis}\]

---

**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&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Neutral&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Basic&lt;sup&gt;c&lt;/sup&gt;</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(iv)/Pu(iv)</td>
<td>+1.170</td>
<td>+0.70</td>
<td>-0.67; +0.52&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>Pu(iv)/Pu(v)</td>
<td>+0.913</td>
<td>+0.60</td>
<td>+0.12</td>
</tr>
<tr>
<td>Pu(v)/Pu(III)</td>
<td>+1.043</td>
<td>+0.65</td>
<td>+0.34</td>
</tr>
<tr>
<td>Pu(v)/Pu(vi)</td>
<td>+1.076</td>
<td></td>
<td>+0.85</td>
</tr>
<tr>
<td>Pu(v)/Pu(iv)</td>
<td>+1.17</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Formal potential in 1 m HClO<sub>4</sub> solution (Lemire et al., 2001).
<sup>b</sup> pH 8 (Allard et al., 1980).
<sup>c</sup> Determined in 1 m NaOH solution (Peretrukhin et al., 1995).
<sup>d</sup> 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<sub>4</sub> (Lemire et al., 2001), (b) in 1 m HCl (Rabideau and Cowan, 1955; Rabideau et al., 1959), and (c) 1 m HNO<sub>3</sub> (Artyukhin et al., 1958).*

---
Oxidation state distribution diagram showing 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). 

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).

- **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
      \[ \rightarrow 0.75 \text{ V vs NHE} \]
    - Hydroxylamine or hydrazine as reductant
  - **Pu(IV)**
    - Electrochemical oxidation of Pu(III) at 1.2 V
      \[ \rightarrow \text{Thermodynamically favors Pu(VI), but slow kinetics due to oxo formation} \]
  - **Pu(V)**
    - Electrochemical reduction of Pu(VI) at pH 3 at 0.54 V (vs SCE)
      \[ \rightarrow \text{Near neutral in 1 micromole/L Pu(V)} \]
  - **Pu(VI)**
    - Treatment of lower oxidation states with hot HClO₄
    - Ozone treatment
  - **Pu(VII)**
    - Oxidation in alkaline solutions
      \[ \rightarrow \text{Hexavalent Pu with ozone, anodic oxidation} \]
Pu reduction

- Pu redox by actinides
  - Similar to disproportionation
  - Rates can be assessed against redox potentials
    → Pu$_{4+}$ reduction by different actinides shows different rates
      * Accompanied by oxidation of An$_{4+}$ with yl bond formation
  - Reduction of Pu(VI) by tetravalent actinides proceeds over pentavalent state
  - Reactions show hydrogen ion dependency
- Rates are generally dependent upon proton and ligand concentration
  - Humic acid, oxalic acid, ascorbic acid
- Poor inorganic complexants can oxidize Pu
  - Bromate, iodate, dichromate
- Reactions with single electron reductants tend to be rapid
  - Reduction by Fe$_{2+}$
- Complexation with ligands in solution impacts redox
  - Different rates in carbonate media compared to perchlorate
  - Mono or dinitrate formation can effect redox
    → Pu(IV) formation or reaction with pentavalent metal ions proceeds faster in nitrate than perchlorate
    → Oxidation of Pu(IV) by Ce(IV) or Np(VI) slower in nitrate
- Pu(VI) reduction can be complicated by disproportionation
- Hydroxylamine (NH$_2$OH), nitrous acid, and hydrazine (N$_2$H$_4$)
  - Used in PUREX for Pu redox control
  - Pu(III) oxidized
    → 2Pu$_{3+}$+3H$^++$NO$_3^-$→2Pu$_{4+}$+HNO$_2$+H$_2$O
    → Re-oxidation adds nitrous acid to system which can initiate an autocatalytic reaction
Pu aqueous chemistry

• Autoradiolysis
  ▪ Formation of radicals and redox agents due to radioactive decay
  ▪ Low reaction if concentrations below 1 M
    → With nitrate can form other reactive species (HNO₂)
    → Formation of Pu(IV)·H₂O₂
  ▪ Rate proportional to Pu concentration and dose rate
  ▪ Pu(VI) reduction proceeds over Pu(V)
    → Formation of HNO₂ and disproportionation
Pu hydrolysis

- Size and charge
  - Smaller ions of same charge higher hydrolysis

\[ \text{For tetravalents} \]

* Pu>Np>U>Pa>Th

### Table 7.55 Hydrolysis constants for plutonium ions.

<table>
<thead>
<tr>
<th>Reaction stoichiometry</th>
<th>( I ) (m)</th>
<th>( \log_{10}{\beta_{m}} )</th>
<th>( \log_{10}{\beta_{n}} )</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Pu}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{Pu(OH)}^{2+} + \text{H}^{+} )</td>
<td>0.1</td>
<td>-6.9</td>
<td>-6.9 ± 0.3</td>
<td>Baes and Mesmer (1976) and Lemire et al. (2001)</td>
</tr>
<tr>
<td>( \text{Pu}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Pu(OH)}^{2+} + 2\text{H}^{+} )</td>
<td>–</td>
<td>-15.0</td>
<td>–</td>
<td>Fuger (1992)</td>
</tr>
<tr>
<td>( \text{Pu}^{4+} + \text{H}_2\text{O} \rightleftharpoons \text{Pu(OH)}^{3+} + \text{H}^{+} )</td>
<td>1.0</td>
<td>-0.45</td>
<td>0.6 ± 0.2</td>
<td>Metivier and Guillaumont (1972) and Guillaumont et al. (2003)</td>
</tr>
<tr>
<td>( \text{Pu}^{4+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Pu(OH)}^{2+} + 2\text{H}^{+} )</td>
<td>1.0</td>
<td>-0.75</td>
<td>0.6 ± 0.3</td>
<td>Metivier and Guillaumont (1972) and Guillaumont et al. (2003)</td>
</tr>
<tr>
<td>( \text{Pu}^{4+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Pu(OH)}^{3+} + 3\text{H}^{+} )</td>
<td>1.0</td>
<td>-0.33</td>
<td>-2.3 ± 0.4</td>
<td>Metivier and Guillaumont (1972) and Guillaumont et al. (2003)</td>
</tr>
<tr>
<td>( \text{Pu}^{4+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Pu(OH)}^{4+} + 4\text{H}^{+} )</td>
<td>1.0</td>
<td>-0.63</td>
<td>-8.5 ± 0.5</td>
<td>Metivier and Guillaumont (1972) and Guillaumont et al. (2003)</td>
</tr>
<tr>
<td>( \text{PuO}_{2}^{+} + \text{H}<em>2\text{O} \rightleftharpoons \text{PuO}</em>{2}\text{(OH)}^{+} + \text{H}^{+} )</td>
<td>0.1</td>
<td>-9.73</td>
<td>( \leq -11.3 \pm 1.5 )</td>
<td>Bennett et al. (1992) and Lemire et al. (2001)</td>
</tr>
<tr>
<td>( \text{PuO}_{2}^{+} + \text{H}<em>2\text{O} \rightleftharpoons \text{PuO}</em>{2}\text{(OH)}^{+} + \text{H}^{+} )</td>
<td>0</td>
<td>-5.5 ± 0.5 ( ^a )</td>
<td></td>
<td>Guillaumont et al. (2003)</td>
</tr>
<tr>
<td>( \text{PuO}_{2}^{+} + 2\text{H}<em>2\text{O} \rightleftharpoons \text{PuO}</em>{2}\text{(OH)}^{+} + 2\text{H}^{+} )</td>
<td>0</td>
<td>-13.2 ± 0.5 ( ^a )</td>
<td></td>
<td>Guillaumont et al. (2003)</td>
</tr>
<tr>
<td>( 2\text{PuO}<em>{2}^{+} + 2\text{H}<em>2\text{O} \rightleftharpoons (\text{PuO}</em>{2})</em>{2}^{+} + 2\text{H}^{+} )</td>
<td>0.1</td>
<td>-7.8</td>
<td>-7.5 ± 0.5 ( ^a )</td>
<td>Okajima and Reed (1993), Guillaumont et al. (2003), Reilly et al. (2000), and Madic et al. (1984)</td>
</tr>
<tr>
<td>( 2\text{PuO}<em>{2}^{+} + 4\text{H}<em>2\text{O} \rightleftharpoons (\text{PuO}</em>{2})</em>{2}^{+} + 4\text{H}^{+} )</td>
<td>0.1</td>
<td>-19.3</td>
<td>–</td>
<td>Okajima and Reed (1993) and Reilly et al. (2000)</td>
</tr>
</tbody>
</table>

\( ^a \) Asymmetric uncertainties (+0.5, -1.5).
Pu(III) 10 mM

Pu(IV) 10 mmol/L

Pu(V) 10 mmol/L

Pu(VI) 10 mmol/L
Pu Hydrolysis/colloid formation

- 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 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.

Fig. 7.119  Electronic absorption spectra of Pu(IV) polymer compared to the Pu(IV) aquo ion. Plutonium(IV) polymer recorded on 9.0 mM solution; plutonium(IV) aquo ion recorded on 2.91 mM solution in 1 M HClO₄ using 1 cm cell. The asterisk indicated a spectrometer grating change (spectra courtesy of P. D. Palmer of Los Alamos).

\[
2\text{Pu(OH)}_2(\text{H}_2\text{O})_6^{2+} + x\text{H}_2\text{O} \rightleftharpoons \text{Pu}_2\text{O}_p(\text{OH})_{8-2p}(\text{OH}_2)_{6+p} + 4\text{H}^+ + (2+x)\text{H}_2\text{O}
\]
Pu aqueous chemistry: colloids

- Characterization
  - SANS
    - Long, thin rods 4.7 nm x 190 nm
  - Light scattering
    - Spherical particles
    - 1 nm to 370 nm
  - Laser induced breakdown
    - 12 nm to 25 nm
- XAFS studies of Pu(IV) colloids
  - demonstrated that average fcc structure is overly simplistic
  - additional chemical forms are present that affect solubility
  - Variations in measured Pu(IV) concentrations may be related to local structure
  - colloids displays many discrete Pu–O distances
    - 2.25 Å Pu–OH to 3.5 Å
  - amplitude of Pu–Pu is reduced, decrease in number of nearest neighbors
    - four H atoms incorporated into Pu(IV) colloid structure could result in one Pu vacancy.
  - EXAFS reveals that many atoms in colloid structure are distributed in a non-Gaussian way when
    - several different oxygen containing groups are present
      * O²⁻, OH⁻, and OH₂
Pu aqueous chemistry

• Complexing ions
  ▪ General oxidation state trends for complexation constants
    $\rightarrow$ Pu(IV)>Pu(VI)≈Pu(III)>Pu(V)
• Oxoanions
  ▪ Pu complexes based on charge and basicity of ligand
    $\rightarrow$ ClO$_4^-$<IO$_3^-$<NO$_3^-$<SO$_4^{2-}$<<CO$_3^{2-}$<PO$_4^{3-}$
    * 7 to 12 ligands (higher value for Pu(IV))
• Carbonate
  ▪ Inner and outer sphere complexation with water
    $\rightarrow$ Outer interaction form chains and layer structures
  ▪ Bidentate with small bite angle
  ▪ Pu(III) carbonate
    $\rightarrow$ Oxidize rapidly to tetravalent state
    $\rightarrow$ Complexation values consistent with Am(III)
  ▪ Pu(IV) carbonate
    $\rightarrow$ Pu(CO$_3$)$_n^{4-2n}$, n from 1 to 5
    * n increases with pH and carbonate concentration
Pu aqueous chemistry

• Pu(V) carbonates
  ▪ Addition of carbonates to Pu(V) solution
  ▪ Reduction of Pu(VI) carbonates
    → Mono and triscarbonato species
• Pu(VI) extension of U(VI) chemistry
Pu solution chemistry

- Pu nitrates
  - First Pu complexes and important species in reprocessing and separations
  - Bidentate and planar geometry
    - Similar to carbonates but much weaker ligand
  - 1 or more nitrates in inner sphere
  - Pu(III) species have been prepared but are unstable
  - Pu(IV) species
    - $\text{Pu(NO}_3\text{)}_{4-n}^n$, n=1-6
      - Tris and pentanitrato complexes not as prevalent
    - Removal of water from coordination sphere with nitrate complexation
      - Pu-O; 2.49 Å for Nitrate, 2.38 Å for H$_2$O
    - Spectrophotometric determination of complexation constants with nitrate and perchlorate
  - $\text{Pu(NO}_3\text{)}_6^{2-}$ complexes with anion exchange resin
  - For Pu(IV) unclear if penta- or hexanitrato species
    - Evidence suggests hexanitrato species in presence of resins
Pu solution chemistry: Nitrates

- Nitrate solids from precipitation from nitric acid solutions
  - Orthorhombic Pu(NO$_3$)$_4$·5H$_2$O
  - M$_2$Pu(NO$_3$)$_6$·2H$_2$O; M=Rb, Cs, NH$_4^+$, pyridinium in 8 to 14 M HNO$_3$
    → Pu-O 2.487 Å

- Mixed species
  - TBP complexes, amide nitrates

- No inner sphere Pu(V) nitrate complexes found
- Only Pu(VI) mononitrate in solution
  - Solid phase PuO$_2$(NO$_3$)$_2$·xH$_2$O; x=3, 6 characterized
Pu solution chemistry: Sulfates

- Pu(III)
  - Mono and disulfate complexes
  - Solid K₅Pu(SO₄)₄·8H₂O
    → Indicates Pu(SO₄)₄⁵⁻ in solution
    → Likely Pu(SO₄)ₙ³⁻₂ⁿ in solution

- Pu(IV)
  - High affinity for sulfate complexes
  - Mono and bisulfate solution species
  - Solid K₄Pu(SO₄)₄·2H₂O
  - Hydrated Pu(SO₄)₂ n=4, 6, 8, 9
  - Mixed Pu₂(OH)₂(SO₄)₃(H₂O)₄
    → Should be in basic solution with high sulfate

- Pu(V) species not well characterized
- Pu(VI) forms mono- and bisulfate from acidic solutions
  - Examined by optical and IR spectroscopy
  - Solids of M₂PuO₂(SO₄)₂
Pu solution chemistry

• Phosphate complexes
  ▪ Low solubility
    → Range of solid species, difficult characterization
      * Range of protonated phosphates
      * \( \text{P}_2\text{O}_7^{4-} \), \((\text{PO}_3)^n^-\)
      * Ternary complexes
        ➢ Halides, organics, uranium
  ▪ Pu(III)
    → Not characterized but proposed
    → \( \text{Pu}(\text{H}_2\text{PO}_4)^n\)\(^{3-n} \) n=1-4
  ▪ Pu(IV)
    → Wide range of complexes
    → Only \( \text{Pu}(\text{HPO}_4)_2\cdot\text{xH}_2\text{O} \) examined in solution phase
  ▪ Pu(V)
    → Ammonium monohydratephosphate Pu(V) tetrahydrate species
    → Evidence of \( \text{PuO}_2\text{HPO}_4^- \)
  ▪ Pu(VI)
    → \( \text{MPuO}_2\text{PO}_4\cdot\text{yH}_2\text{O} \)
      * Solution complexes from Pu(VI) hydroxide and \( \text{H}_3\text{PO}_4 \)
Pu solution chemistry: Peroxide

- Used to form Pu(IV) from higher oxidation states
  - Further reduction of Pu(IV), mixed oxidation states
- Pu(IV) peroxide species determined spectroscopically
  - Two different absorbances with spectral change in increasing peroxide
- No confirmed structure
  - Pu$_2$(µ-O$_2$)$_2$(CO$_3$)$_6$$^{8-}$ contains doubly bridged Pu-O core
- Formation of peroxide precipitate that incorporates surrounding anions
  - High acidity and ionic strength
  - In alkaline media, Pu(VI) reduced to Pu(V) with formation of 1:1 complex
Pu solution chemistry: Carboxylate complexes

- Single or multiple carboxylate ligands for strong complexes with Pu with typical oxidation state stability trend
- Tend to stabilize Pu(IV)
- Pu(III)
  - Oxidation to Pu(IV) at pH > 5
  - Range of mixed species
    - Degree of protonation (H$_x$EDTA)
    - Mixed hydroxide species
- Pu(IV)
  - Stabilized by complexation
  - Solution phase at relatively high pH
  - 1:1 Pu to ligand observed (Pu:EDTA, Pu:DTPA)
    - Range of mixed species can be formed
  - EDTA used in dissolution of Pu(IV) oxide or hydroxide solids
- Pu(V) complexes to be unstable
  - Oxidation or reduction solution dependent
- Pu(VI) species observed
Pu solution chemistry: Carboxylate complexes

- Single or multiple carboxylate ligands for strong complexes with Pu with typical oxidation state stability trend
- Tend to stabilize Pu(IV)
- Pu(III)
  - Oxidation to Pu(IV) at pH > 5
  - Range of mixed species
    - Degree of protonation ($H_x$EDTA)
    - Mixed hydroxide species
- Pu(IV)
  - Stabilized by complexation
  - Solution phase at relatively high pH
  - 1:1 Pu to ligand observed (Pu:EDTA, Pu:DTPA)
    - Range of mixed species can be formed
  - EDTA used in dissolution of Pu(IV) oxide or hydroxide solids
- Pu(V) complexes to be unstable
  - Oxidation or reduction solution dependent
- Pu(VI) species observed
Pu solution chemistry

- **Iodate**
  - Pu(IO$_3$)$_4$ precipitate
    - Not well characterized
    - Prepared by hydrothermal methods
      * Preparation of Pu(VI) diiodate species
  - Mixed Pu(VI) trishydroxide species
    - From Pu(IV) and H$_5$IO$_6$ in hydrothermal reaction, forms (PuO$_2$)$_2$(IO$_3$)(μ-OH)$_3$
  - Pu(V) forms Pu(IV/VI) species

- **Perchlorate**
  - No pure solution or solid phases characterized
  - Most likely does not form inner sphere complexes in aqueous solution

- **Oxalates**
  - Forms microcrystals
  - Mono and bidentate forms
  - Pu(III) form trivalent oxalates with 10 and 6 hydrates
  - Pu(IV) forms with 2, 4, and 5 oxalates with n waters (n=0,1,2,or 6)
    - Tetra and hexa monovalent M salts
    - Mono hydroxide mixed solid species formed
  - Pu(V) disproportionates
  - Pu(VI)O$_2$ oxalates
Pu solution chemistry

- **Halides**
  - Studies related to Pu separation and metal formation
  - Solid phase double salts discussed

- **Cation-cation complexes**
  - Bridging over yl oxygen from plutonyl species
  - Primarily examined for Neptunyl species
  - Observed for UO$_2^{2+}$ and PuO$_2^+$
    - $\rightarrow$ 6 M perchlorate solution
  - Formation of CrOPuO$_4^+$ cation from oxidation of Pu(IV) with Cr(VI) in dilute HClO$_4$
Pu separations

- 1855 MT Pu produced
  - Current rate of 70-75 MT/years
  - 225 MT for fuel cycle
  - 260 MT for weapons
- Large scale separations based on manipulation of Pu oxidation state
  - Aqueous (PUREX)
  - Non-aqueous (Pyroprocessing)
- Precipitation methods
  - Basis of bismuth phosphate separation
    → Precipitation of BiPO$_4$ in acid carries tri- and tetravalent actinides
      * Bismuth nitrate and phosphoric acid
      * Separation of solid, then oxidation to Pu(VI)
    → Sulfuric acid forms solution U sulfate, preventing precipitation
  - Used after initial purification methods
  - LaF$_3$ for precipitation of trivalent and tetravalent actinides
Pu separations

- **Solvent extraction**
  - TBP extraction, PUREX process → Some interest in 3rd phase formation

- **Extraction chromatography**
  - Extractant on solid support

- **Ion-exchange**
  - Both cation and anion exchange
    → Anion exchange based on formation of appropriate species in acidic solution
    → Change of solution impact sorption to column

- **Pu separation**
  - Sorb Pu(IV,VI) in 6 M acid, reduce to Pu(III)

- **General cation exchange trends for Pu**
  - HNO₃, H₂SO₄, and HClO₄ show stronger influence than HCl
  - Strong increase in distribution coefficient in HClO₄ at high acidities exhibited for Pu(III) and Pu(VI)

- **Anion exchanges in high acid, formation of charged species**

---

**TABLE IV-20. Absorption and Desorption of Actinides on Strong Base Anion Exchangers in HCl Solutions**

<table>
<thead>
<tr>
<th>Oxidation State of Actinide</th>
<th>Absorption (a)</th>
<th>Desorption (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>III</td>
<td>Not absorbed</td>
<td>-</td>
</tr>
<tr>
<td>IV</td>
<td>8 - 8</td>
<td>2 - 4</td>
</tr>
<tr>
<td>V</td>
<td>8 - 8</td>
<td>2 - 4</td>
</tr>
<tr>
<td>VI</td>
<td>2 - 3</td>
<td>0.1 - 1</td>
</tr>
</tbody>
</table>

(a) Kd = 10 - 100 for absorption.
(b) Kd = 0.1 - 1.0 for desorption.

---

**Fig. 39. Typical distribution coefficients of Pu on Dowex 50 in common acidic solutions.**

**Fig. 32.** Volume distribution coefficients, Dv, for tetravalent U, Np, and Pu between Dowex 1 and hydrochloric acid solutions.
Pu separations

- **Halide volatility (PuF₆, PuCl₆)**
  - PuO₂ in fluidized bed reactor with fluorine at 400° C
    → Can substitute NH₄HF₂ for some fluorination
    → Also use of O₂F₂
  - PuF₆ decomposes to PuF₄ and F₂ in a thermal decomposition column

- **Supercritical fluid extraction**
  - Most research with CO₂
  - Use complexants dissolved in SCF
    → TBP·HNO₃, TTA for extraction from soil
  - Change of pressure to achieve separations
CHEM 312 Lecture 14 Plutonium Chemistry

Part 1

• Readings
  ▪ Pu chemistry Chapter
    → Chemistry of the Actinides and Transactinides
  ▪ Challenges of Pu chemistry
    → Los Alamos National Laboratory

• Nuclear properties and isotope production
• Pu in nature
• Pu solution chemistry
• Separation and Purification
• Atomic properties
• Metallic state
• Compounds
CHEM 312 Lecture 14 Plutonium Chemistry
Part 2

• Readings
  ▪ Pu chemistry Chapter
    → Chemistry of the Actinides and Transactinides
  ▪ Challenges of Pu chemistry
    → Los Alamos National Laboratory

• Nuclear properties and isotope production
• Pu in nature
• Pu solution chemistry
• Separation and Purification
• Atomic properties
  ▪ Metallic state
• Compounds
Metallic Pu

• Interests in processing-structure-properties relationship
  
  **Density** 19.816 g·cm\(^{-3}\)
  
  Liquid density at m.p. 16.63 g·cm\(^{-3}\)
  
  **Melting point** 912.5 K
  
  **Boiling point** 3505 K
  
  **Heat of fusion** 2.82 kJ·mol\(^{-1}\)
  
  **Heat of vaporization** 333.5 kJ·mol\(^{-1}\)
  
  **Heat capacity** (25 °C) 35.5 J·mol\(^{-1}\)·K\(^{-1}\)

• Reactions with water and oxygen

• Impact of self-irradiation

Formation of Pu metal

• Ca reduction
• Pyroprocessing
  
  ▪ **PuF\(_4\)** and Ca metal
    
    → Conversion of oxide to fluoride
    → Start at 600 °C goes to 2000 °C
    → 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
Pu metal

- **Electrorefining**
  - Liquid Pu oxidizes from anode ingot into salt electrode
  - 740 °C 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 °C)**
  - 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

http://arq.lanl.gov/source/orgs/nmt/nmtdo/AQarchive/98fall/magnetic_levitation.html
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 allotropes vary significantly
  - dramatic volume changes with phase transitions
- Crystal structure of 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 melting point
- Pu lattice is very soft vibrationally and very nonlinear

<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 cm$^{-3}$)</th>
<th>Transformation temperature (K)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</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>$\beta$</td>
<td>397.6 – 487.9</td>
<td>body-centered monoclinic I2$_1$/m$^*$</td>
<td>$a = 9.284(3)$</td>
<td>34</td>
<td>17.71 ($\alpha$ – $\beta$)</td>
<td>397.6</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>487.9 – 593.1</td>
<td>face-centered orthorhombic Fdd2</td>
<td>$a = 5.159(1)$</td>
<td>8</td>
<td>17.15 ($\beta$ – $\gamma$)</td>
<td>487.9</td>
</tr>
<tr>
<td>$\delta$</td>
<td>593.1 – 736.0</td>
<td>face-centered cubic Fm$ar{3}$m</td>
<td>$a = 4.637(4)$</td>
<td>4</td>
<td>15.92 ($\gamma$ – $\delta$)</td>
<td>593.1</td>
</tr>
<tr>
<td>$\delta'$</td>
<td>736.0 – 755.7</td>
<td>body-centered tetragonal I$4/mmm$</td>
<td>$a = 3.34(1)$</td>
<td>2</td>
<td>16.03 ($\delta$ – $\delta'$)</td>
<td>736.0</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>755.7 – 913.0</td>
<td>body-centered cubic In$ar{3}$m</td>
<td>$a = 3.636(14)$</td>
<td>2</td>
<td>16.51 ($\delta'$ – $\epsilon$)</td>
<td>913.0</td>
</tr>
</tbody>
</table>

$^*$ Although space group I2$_1$/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 $\beta$ angle of approximately 90° (data from Miner and Schonfeld, 1980).

$^b$ Data from Lemaire 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.
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 actinides
  - Bandwidths are a function of volume.
    $\rightarrow$ narrower for large volumes
Pu metal phase

- atomic-sphere approximation calculations for contributions to orbitals
  - $\delta$ fcc phase
- If Pu had only f band contribution equilibrium lattice constant would be smaller than measured
- Contribution from s-p band stabilizes larger volume
- f band is narrow at larger volume (low symmetry)
- strong competition between repulsive s-p band contribution and attractive f band term induces instability near ground state
- density-of-states functions for different low-symmetry crystal structures
  - total energies for crystal structures are very close to each other
Pu metal phase

- f-f interaction varies dramatically with very small changes in interatomic distances
  - lattice vibrations or heating
- f-f and f-spd interactions with temperature results in localization as Pu transforms from α- to δ-phase
- Low Pu melting temperature due to f-f interaction and phase instability
  - Small temperature changes induce large electronic changes
  - small temperature changes produce relatively large changes in free energy
- Kinetics important in phase transitions
For actinides, f electron bonding increases up to Pu.

Pu has highest phase instability.

At Am, f electrons localize completely and become nonbonding.

At Am, coulomb forces pull f electrons inside valence shell.

2 or 3 electrons in s-p and d bands.

- For Pu, degree of f electron localization varies with phase.
Pu phase transitions demonstrates change in f-electron behavior at Pu
Metallic Pu

• Pu liquid is denser than 3 highest temperature solid phases
  ▪ Liquid density at 16.65 g/mL
  ▪ Pu contracts 2.5 % upon melting
• Pu alloys and δ phase
  ▪ Ga stabilizes phase
  ▪ Complicated phase diagram
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 Pu₃Ga 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.
Metallic Pu

- Other elements that stabilize $\delta$ phase
  - Al, Ga, Ce, Am, Sc, In, and Tl stabilize phase at room temperature
  - Si, Zn, Zr, and Hf retain phase under rapid cooling
- Microstructure of $\delta$ phase due to Ga diffusion in cooling
- Np expands $\alpha$ and $\beta$ phase region
  - $\beta$ phase stabilized at room temperature with Hf, Ti, and Zr
- Pu eutectics
  - Pu melting point dramatically reduced by Mn, Fe, Co, or Ni
    - With Fe, mp=410 °C, 10 % Fe
    - Used in metallic fuel
  - Limit Pu usage (melting through cladding)
- Interstitial compounds
  - Large difference in ionic radii (59 %)
  - O, C, N, and H form interstitial compounds
Modeling Pu metal electronic configuration

- Pu metal configuration $7s^26d^15f^5$
  - From calculations, all eight valence electrons are in conduction band,
  - $5f$ electrons in $\alpha$-plutonium behave like $5d$ electrons of transition metals than $4f$ of lanthanides
- Bonding and antibonding orbitals from sum and differences of overlapping wavefunctions
  - Complicated for actinides
    - Small energy difference between orbital can overlap in solids
    - Accounts for different configurations
Metallic Pu

- Modeling to determine electronic structure and bonding properties
  - Density functional theory
    → Describes an interacting system of fermions via its density not via many-body wave function
    → 3 variables \((x, y, z)\) rather than 3 for each electron
      * For actinides need to incorporate
        - Low symmetry structures
        - Relativistic effects
        - Electron-electron correlations
  - Local-density approximation (LDA)
    → Include external potential and Coulomb interactions
    → approximation based upon exact exchange energy for uniform electron gas and from fits to correlation energy for a uniform electron gas
  - Generalized gradient approximation (GGA)
    → Localized electron density and density gradient
- Total energy calculations at ground state
Relativistic effects

- Enough f electrons in Pu to be significant
  - Relativistic effects are important
- 5f electrons extend relatively far from 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 ionic cores in relativistic calculations
Pu metal mechanical properties

- Stress/strain properties
  - High strength properties bend or deform rather than break
    → Beyond a limit material abruptly breaks
      * Fails to absorb more energy
  - $\alpha$-plutonium is strong and brittle, similar to cast iron
    - elastic response with very little plastic flow
    - Stresses increase to point of fracture
    - strength of unalloyed $\alpha$-phase decreases dramatically with increasing temperature
      → Similar to bcc and hcp metals.
  - Pu-Ga $\delta$-phase alloys show limited elastic response followed by extensive plastic deformation
    - low yield strength
    - ductile fracture
  - For $\alpha$-Pu elastic limit is basically fracture strength
  - Pu-Ga alloy behaves more like Al
    - Fails by ductile fracture after elongation
Pu mechanical properties

- Tensile-test results for unalloyed Pu
  - Related to temperature and resulting change in phases
- Strengths of $\alpha$- and $\beta$-phase are very sensitive to temperature
  - Less pronounced for $\gamma$-phase and $\delta$-phase
- Data represent work of several investigators
  - Different purity materials, and different testing rates
    → Accounts for variations in values, especially for $\alpha$-Pu phase
Pu metal mechanical properties

- Metal elastic response due to electronic structure and resulting cohesive forces
  - Metallic bonding tends to result in high cohesive forces and high elastic constants
    - Metallic bonding is not very directional since valence electrons are shared throughout crystal lattice
    - Results in metal atoms surrounding themselves with as many neighbors as possible
      * close-packed, relatively simple crystal structures
- Pu 5f electrons have narrow conduction bands and high density-of-states
  - energetically favorable for ground-state crystal structure to distort to low-symmetry structures at room temperature
  - Pu has typical metal properties at elevated temperatures or in alloys
Pu metal corrosion and oxidation

- Formation of oxide layer
  - Can include oxides other than dioxide
  - Slow oxidation in dry air
    - Greatly enhanced oxidation rate in presence of water or hydrogen
- Metal has pyrophoric properties
- Corrosion depends on chemical condition of Pu surface
  - Pu$_2$O$_3$ surface layer forms in absence or low amounts of O$_2$
    - Promotes corrosion by hydrogen
- Pu hydride (PuH$_x$, where 1.9 < x < 3) increases oxidation rate in O$_2$ by $10^{13}$
- PuO$_{2+x}$ surface layer forms on PuO$_2$ in presence of water
  - Enhances bulk corrosion of Pu metal in moist air
Pu oxidation in dry air

- O₂ sorbs on Pu surface to form oxide layer
- Oxidation continues but O₂ must diffuse through oxide layer
  - Oxidation occurs at oxide/metal interface
- Oxide layer thickness initially increases with time based on diffusion limitation
- At oxide thickness around 4–5 μm in room temperature surface stresses cause oxide particles to spall
  - oxide layer reaches a steady-state thickness
    → further oxidation and layer removal by spallation
- Eventually thickness of oxide layer remains constant
Oxidation kinetics in dry air at room temperature

- steady-state layer of $\text{Pu}_2\text{O}_3$ at oxide-metal interface
  - $\text{Pu}_2\text{O}_3$ thickness is small compared with oxide thickness at steady state
  - Autoreduction of dioxide by metal at oxide-metal interface produces $\text{Pu}_2\text{O}_3$
    $\rightarrow$ $\text{Pu}_2\text{O}_3$ reacts with diffusing $\text{O}_2$ to form dioxide
Arrhenius Curves for Oxidation of Unalloyed and Alloyed Plutonium in Dry Air and Water Vapor

- \( \ln \) of reaction rate \( R \) versus \( 1/T \)
  - slope is proportional to activation energy for corrosion reaction
- Curve 1 oxidation rate of unalloyed plutonium in dry air or dry \( \text{O}_2 \) at a pressure of 0.21 bar.
- Curve 2a to water vapor up to 0.21 bar
  - Curves 2b and 2c temperature ranges of 61°C–110°C and 110°C–200°C, respectively
- Curves \( 1' \) and \( 2' \) oxidation rates for \( \delta \)-phase gallium-stabilized alloy in dry air and moist air
- Curve 3 transition region between convergence of rates at 400°C and onset of autothermic reaction at 500°C
- Curve 4 temperature-independent reaction rate of ignited metal or alloy under static conditions
  - rate is fixed by diffusion through an \( \text{O}_2 \)-depleted boundary layer of \( \text{N}_2 \) at gas-solid interface
- Curve 5 temperature-dependent oxidation rate of ignited droplets of metal or alloy during free fall in air
Oxide Layer on Plutonium Metal under Varying Conditions

- corrosion rate is strongly dependent on metal temperature
  - varies significantly with isotopic composition, quantity, geometry, and storage configuration
- steady-state oxide layer on plutonium in dry air at room temperature (25°C)
  - Over time, isolating PuO₂-coated metal from oxygen in a vacuum or an inert environment turns surface oxide into Pu₂O₃ by autoreduction reaction
  - At 25°C, transformation is slow
    - time required for complete reduction of PuO₂ depends on initial thickness of PuO₂ layer
    - highly uncertain because reaction kinetics are not quantified
- above 150°C, rapid autoreduction transforms a several micrometer-thick PuO₂ layer to Pu₂O₃ within minutes
  - Exposure of steady-state oxide layer to air results in continued oxidation of metal
- Kinetic data indicate a one-year exposure to dry air at room temperature increases oxide thickness by about 0.1 μm
- At a metal temperature of 50°C in moist air (50% relative humidity), corrosion rate increases by a factor of approximately 10⁴
  - corrosion front advances into unalloyed metal at a rate of 2 mm per year
- 150°C–200°C in dry air, rate of autoreduction reaction increases relative oxidation reaction
  - steady-state condition in oxide shifts toward Pu₂O₃,
Rates for Catalyzed Reactions of Pu with $H_2$, $O_2$, and Air

- **Plutonium hydride** (PuH$_x$)
  - fcc phase
  - forms a continuous solid solution for $1.9 < x < 3.0$
    \[ \text{Pu}(s) + \frac{x}{2}H_2(g) \rightarrow \text{PuH}_x(s) \]
  - $x$ depends on hydrogen pressure and temperature
- Pu hydride is readily oxidized by air
- Hydriding occurs only after dioxide layer is penetrated
  - Hydrogen initiates at a limited
- hydriding rates values are constant
  - indicate surface compounds act as catalysts
- hydride sites are most reactive location
  - Hydriding rate is proportional to active area covered by hydride
- Temperatures between –55°C and 350°C and a $H_2$ pressure of 1 bar
  - reaction at fully active surface consumes Pu at a constant rate of 6–7 g/cm$^2$ min
  - Advances into metal or alloy at about 20 cm/h
Hydride-Catalyzed Oxidation of Pu

- hydride-coated Pu exposed to O₂
  - oxidation of PuHₓ forms surface layer of oxide with heat evolution
- Produced H₂ reforms PuHₓ at hydride-metal interface
  - Exothermic, helps drive reaction
- sequential processes in reaction
  - oxygen adsorbs at gas-solid interface as O₂
  - O₂ dissociates and enters oxide lattice as anionic species
  - thin steady-state layer of PuO₂ may exist at surface
  - oxide ions are transported across oxide layer to oxide-hydride interface
    - oxide may be Pu₂O₃ or PuO₂₋ₓ (0 < x < 0.5)
  - Oxygen reacts with PuHₓ to form heat (~160 kcal/mol of Pu) and H₂
• Readings
  ▪ Pu chemistry Chapter
    → Chemistry of the Actinides and Transactinides
  ▪ Challenges of Pu chemistry
    → Los Alamos National Laboratory
• Nuclear properties and isotope production
• Pu in nature
• Pu solution chemistry
• Separation and Purification
• Atomic properties
  ▪ Metallic state
• Compounds
CHEM 312 Lecture 14 Plutonium Chemistry
Part 3

• Readings
  ▪ Pu chemistry Chapter
    → Chemistry of the Actinides and Transactinides
  ▪ Challenges of Pu chemistry
    → Los Alamos National Laboratory
• Nuclear properties and isotope production
• Pu in nature
• Pu solution chemistry
• Separation and Purification
• Atomic properties
• Metallic state
• Compounds
Radiation damage

- Decay rate for $^{239}$Pu is sufficient to produce radiation damage
  - Buildup of He and radiation damage within metal
- Radiation damage is caused mainly by uranium nuclei
  - Recoil energy from decay to knock plutonium atoms from their sites in crystal lattice of metal
    → Vacancies are produced
- Effect can produce void swelling
- On microscopic level, vacancies tend to diffuse through metal and cluster to form voids
- Macroscopic metal swelling observed
Pu Decay and Generation of Defects

- α particle has a range of about 10 μm through Pu
  - U recoil nucleus range is only about 12 nm
- Both particles produce displacement damage
  - Frenkel pairs
    - namely vacancies and interstitial atoms
    - Occurs predominantly at end of their ranges
- Most of damage results from U nucleus
- Distortions due to void swelling are likely to be larger than those from helium-bubble formation
Pu Compounds

- Original difficulties in producing compounds
  - Amount of Pu
  - Purity
- Aided by advances in microsynthesis and increase in amount of available starting material
- Much early effort in characterization by XRD

Pu Hydrides
- $\text{PuH}_x$
  - $x$ varies from $1.9 < x < 3.0$
  - $\text{Pu} + \frac{x}{2} \text{H}_2 \leftrightarrow \text{PuH}_x$
    - $\text{H}_2$ partial pressure used to control exact stoichiometry
    - Variations and difficulties rooted in desorption of $\text{H}_2$
- Pu hydride crystallizes in a fluorite structure
- Pu hydride oxidation state
  - $\text{PuH}_2$ implies divalent Pu,
  - measurements show Pu as trivalent and $\text{PuH}_2$ is metallic
    - $\text{Pu(III)}$, 2 $\text{H}^-$ and 1 $\text{e}^-$ in conduction band
  - Consistent with electrical conductivity measurements
- Hydride used to prepare metal (basis of Aries process)
  - Formation of hydride from metal
  - Heated to 400 °C under vacuum to release hydrogen
  - Can convert to oxide (with $\text{O}_2$) or nitride ($\text{N}_2$) gas addition during heating
Pu carbides

- Four known compounds
  - \( \text{Pu}_3\text{C}_2 \), \( \text{PuC}_{1-x} \), \( \text{Pu}_2\text{C}_3 \), and \( \text{PuC}_2 \)
  - \( \text{PuC} \) exists only as substoichiometric compound
    \( \rightarrow \) \( \text{PuC}_{0.6} \) to \( \text{PuC}_{0.92} \)
  - Compound considered candidate for fuels
- Synthesis
  - At high temperatures elemental C with:
    \( \rightarrow \) Pu metal, Pu hydrides, Pu oxides
    * Oxygen impurities present with oxide starting material
    * High Pu carbides can be used to produce other carbides
      \( \rightarrow \) \( \text{PuC}_{1-x} \) from \( \text{PuH}_2 \) and \( \text{Pu}_2\text{C}_3 \) at 700 °C
  - Final product composition dependent upon synthesis temperature, atmosphere (vacuum or Ar) and time
- Chemical properties
  - \( \text{PuC}_{1-x} \) oxidizes in air starting at 200 °C
  - Slower reaction with \( \text{N}_2 \)
    \( \rightarrow \) Formation of \( \text{PuN} \) at 1400 °C
  - All Pu carbides dissolve in HNO\textsubscript{3}-HF mixtures
- Ternary phases prepared
  - Pu-U-C and Pu-Th-C
  - Mixed carbide-nitrides, carbide-oxides, and carbide hydrides

---

**Table 7.29**  
X-ray crystallographic data for plutonium carbides.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Symmetry</th>
<th>Space group</th>
<th>( a_0 ) (Å)</th>
<th>( b_0 ) (Å)</th>
<th>( c_0 ) (Å)</th>
<th>Formula units per cell</th>
<th>Calculated density (g cm(^{-3}))</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{PuC}_{1-x} )</td>
<td>fcc</td>
<td>( \text{Fm}3\text{m} )</td>
<td>4.9582(3) (C-poor)</td>
<td>4.9737(3) (C-rich)</td>
<td>4</td>
<td>13.6</td>
<td>Mulford et al. (1960)</td>
<td></td>
</tr>
<tr>
<td>( \text{Pu}_2\text{C}_3 )</td>
<td>bcc</td>
<td>( \text{I}4\text{3}d )</td>
<td>8.1258(3) (C-poor)</td>
<td>8</td>
<td>12.70</td>
<td></td>
<td>Mulford et al. (1960)</td>
<td></td>
</tr>
<tr>
<td>( \text{PuC}_2 )</td>
<td>tetragonal</td>
<td>( \text{I}4/\text{mmm} )</td>
<td>3.63</td>
<td>3.63</td>
<td>6.094</td>
<td>2</td>
<td>10.88</td>
<td>Chackrabortty and Jayadevan (1965)</td>
</tr>
</tbody>
</table>
Pu nitride

- Only PuN known with certainty
  - Narrow composition range
  - Liquid Pu forms at 1500 °C, PuN melting point not observed
- Preparation
  - Pu hydride with N₂ between 500 °C and 1000 °C
  - Can react metal, but conversion not complete
  - Formation in liquid ammonia
    \[ \text{PuI}_3 + \text{NH}_3 + 3 \text{M}^+ \leftrightarrow \text{PuN} + 3 \text{MI}^+ + 1.5 \text{H}_2 \]
    * Intermediate metal amide MNH₂ formation, PuN precipitates
- Structure
  - fcc cubic NaCl structure
  - Lattice 4.905 Å
    \[ \text{Pu-N} 2.45 \text{ Å} \]
    \[ \text{Pu-Pu} 3.47 \text{ Å} \]
    \[ \text{Data variation due to impurities, self-irradiation} \]
- Properties
  - High melting point (estimated at 2830 °C)
  - Compatible with steel (up to 600 °C) and Na (890 °C, boiling point)
  - Reacts with O₂ at 200 °C
  - Dissolves in mineral acids
  - Moderately delocalized 5f electrons
    \[ \text{Behavior consistent with f}^5 (\text{Pu}^{3+}) \]
    \[ \text{Supported by correlated spin density calculations} \]
• Pu storage, fuel, and power generators
• PuO (minor species)
• Pu$_2$O$_3$
  ▪ Forms on PuO$_2$ of δ-stabilized metal when heated to 150-200 °C under vacuum
  ▪ Metal and dioxide fcc, favors formation of fcc Pu$_2$O$_3$
  ▪ Requires heating to 450 °C to produce hexagonal form
  ▪ PuO$_2$ with Pu metal, dry H$_2$, or C
    \[ \text{→ } 2\text{PuO}_2 + \text{C} \rightarrow \text{Pu}_2\text{O}_3 + \text{CO} \]
• PuO$_2$
  ▪ fcc, wide composition range (1.6 <x<2)
  ▪ Pu metal ignited in air
  ▪ Calcination of a number of Pu compounds
    \[ \text{→ No phosphates} \]
    \[ \text{→ Rate of heating can effect composition due to decomposition and gas evolution} \]
• PuO$_2$ is olive green
  ▪ Can vary due to particle size, impurities
• Pressed and sintered for heat sources or fuel
• Sol-gel method
  ▪ Nitrate in acid injected into dehydrating organic (2-ethylcyclohexanol)
  ▪ Formation of microspheres
    \[ \text{→ Sphere size effects color} \]
Pu oxide preparation

- Hyperstoichiometric sesquioxide (PuO$_{1.6+x}$)
  - Requires fast quenching to produce PuO$_2$ in melt
    → Slow cooling resulting in C-Pu$_2$O$_3$ and PuO$_{2-x}$
    → $x$ at 0.02 and 0.03

- Substoichiometric PuO$_{2-x}$
  - From PuO$_{1.61}$ to PuO$_{1.98}$
    → Exact composition depends upon $O_2$ partial pressure
  - Single phase materials
    → Lattice expands with decreasing $O$
Pu oxide preparation

- $\text{PuO}_{{2+x}}$, $\text{PuO}_3$, $\text{PuO}_4$
  - Tetravalent Pu oxides are favored
    - Unable to oxidize $\text{PuO}_2$
      * High pressure $\text{O}_2$ at 400 °C
      * Ozone
  - $\text{PuO}_{{2+x}}$ reported in solid phase
    - Related to water reaction
      * $\text{PuO}_{{2+x}} \cdot x\text{H}_2\text{O} \rightarrow \text{PuO}_{{2+x}} + x\text{H}_2$
      * Final product $\text{PuO}_{{2.3}}$, fcc
  - $\text{PuO}_3$ and $\text{PuO}_4$ reported in gas phase
    - From surface reaction with $\text{O}_2$
      * $\text{PuO}_4$ yield decreases with decreasing $\text{O}_2$ partial pressure

---

Table 7.36  X-ray crystallographic data for plutonium oxides.

<table>
<thead>
<tr>
<th>Compound or phase</th>
<th>Structure type</th>
<th>Symmetry</th>
<th>Space group</th>
<th>Unit cell dimensions (Å)</th>
<th>Formula units per cell</th>
<th>X-ray density (g cm$^{-3}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{PuO}$</td>
<td>NaCl</td>
<td>fcc</td>
<td>$\text{Fm}$</td>
<td>$a = 4.96(1)$</td>
<td>4</td>
<td>13.88</td>
<td>Ellinger (1961)</td>
</tr>
<tr>
<td>$\text{PuO}_{0.5}$</td>
<td>$\text{La}_2\text{O}_3$</td>
<td>hexagonal</td>
<td>$\text{P}$</td>
<td>$a = 3.644(6)$</td>
<td>1</td>
<td>11.47</td>
<td>Ellinger (1961)</td>
</tr>
<tr>
<td>$\text{PuO}_{0.5}$</td>
<td>$\text{Mn}_2\text{O}_3$</td>
<td>bcc</td>
<td>$\text{I}6$</td>
<td>$a = 1.02(2)$</td>
<td>16</td>
<td>10.44</td>
<td>Ellinger (1961)</td>
</tr>
<tr>
<td>$\text{PuO}_{0.5}$</td>
<td>$\text{Mn}_3\text{O}_4$</td>
<td>bcc</td>
<td>$\text{I}6$</td>
<td>$a = 10.95 - 11.01$</td>
<td></td>
<td>11.46</td>
<td>Gardner et al. (1965)</td>
</tr>
<tr>
<td>$\text{PuO}_2$</td>
<td>$\text{CaF}_2$</td>
<td>fcc</td>
<td>$\text{Fm}$</td>
<td>$a = 5.386(3)$</td>
<td>4</td>
<td>11.46</td>
<td>Ellinger (1961)</td>
</tr>
<tr>
<td>$^{239}\text{PuO}_2$</td>
<td>$\text{CaF}_2$</td>
<td>fcc</td>
<td>$\text{Fm}$</td>
<td>$a = 5.384(1)$</td>
<td>4</td>
<td>11.46</td>
<td>Roof (1973)</td>
</tr>
<tr>
<td>$\text{PuO}_{2.26}$</td>
<td>$\text{CaF}_2$</td>
<td>fcc</td>
<td>$\text{Fm}$</td>
<td>$a = 5.404$</td>
<td>4</td>
<td>11.46</td>
<td>Haschke et al. (2000b)</td>
</tr>
<tr>
<td>$\text{PuO}_{2.9}$</td>
<td>$\text{CaF}_2$</td>
<td>fcc</td>
<td>$\text{Fm}$</td>
<td>$a = 5.396(3)$</td>
<td>4</td>
<td>11.46</td>
<td>Ellinger (1961)</td>
</tr>
<tr>
<td>$\text{PuO}_{3.0}$</td>
<td>$\text{CaF}_2$</td>
<td>fcc</td>
<td>$\text{Fm}$</td>
<td>$a = 5.384(1)$</td>
<td>4</td>
<td>11.46</td>
<td>Roof (1973)</td>
</tr>
</tbody>
</table>

---

Table 7.37  Qualitative characteristics of $\text{PuO}_{{2+x}}$ from decomposition of selected materials at 870 °C (Drummond and Welch, 1957).

<table>
<thead>
<tr>
<th>Material</th>
<th>Color</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>metal</td>
<td>dull yellow</td>
<td>powder</td>
</tr>
<tr>
<td>sulfate</td>
<td>yellow-green to green</td>
<td>bulky powder</td>
</tr>
<tr>
<td>nitrate</td>
<td>dull yellow</td>
<td>bulky solid</td>
</tr>
<tr>
<td>chloride</td>
<td>dull yellow</td>
<td>powder</td>
</tr>
<tr>
<td>fluoride</td>
<td>khaki with black traces</td>
<td>granular solid</td>
</tr>
<tr>
<td>oxalate</td>
<td>yellow-buff</td>
<td>bulky powder</td>
</tr>
<tr>
<td>iodate</td>
<td>buff</td>
<td>very bulky</td>
</tr>
<tr>
<td>hydroxide</td>
<td>black with yellow traces</td>
<td>dense, shiny particles</td>
</tr>
</tbody>
</table>
Mixed Pu oxides

- **Perovskites**
  - CaTiO$_3$ structure (ABO$_3$)
  - Pu(IV, VI, or VII) in octahedral PuO$_6^{n-}$
  - Cubic lattice
  - BO$_6$ octahedra with A cations at center unit cell

- **Double perovskites**
  - (Ba,Sr)$_3$PuO$_6$ and Ba(Mg,Ca,Sr,Mn,Zn)PuO$_6$
  - M and Pu(VI) occupy alternating octahedral sites in cubic unit cell

- **Pu-Ln oxides**
  - PuO$_2$ mixed with LnO$_{1.5}$
  - Form solid solutions
  - Oxidation of Pu at higher levels of Ln oxides to compensate for anion defects
  - Solid solutions with CeO$_2$ over entire range

**Fig. 7.99** Polyhedral representation of the idealized double perovskite structure of Ba$_2$MPuO$_6$, compounds. This polyhedral representation emphasizes the alternating octahedral PuO$_6$ (gray) and MO$_6$ (black) sites in the structure. The central barium ion is light gray.
Pu oxide chemical properties

- Thermodynamic parameter available for Pu oxides
- Dissolution
  - High fired PuO$_2$ difficult to dissolve
  - Rate of dissolution dependent upon temperature and sample history
    - Irradiated PuO$_2$ has higher dissolution rate with higher burnup
  - Dissolution often performed in 16 M HNO$_3$ and 1 M HF
    - Can use H$_2$SiF$_6$ or Na$_2$SiF$_6$
  - KrF$_2$ and O$_2$F$_2$ also examined
  - Electrochemical oxidation
    - HNO$_3$ and Ag(II)
  - Ce(IV) oxidative dissolution
Pu fluoride preparation

- Used in preparation of Pu metal
- \[ 2\text{PuO}_2 + \text{H}_2 + 6 \text{HF} \rightarrow 2 \text{PuF}_3 + 4 \text{H}_2\text{O} \text{ at } 600 \, ^\circ\text{C} \]
- \[ \text{Pu}_2(\text{C}_2\text{O}_4)_3 + 6 \text{HF} \rightarrow 2 \text{PuF}_3 + 3 \text{CO} + 3 \text{CO}_2 + 3 \text{H}_2\text{O} \text{ at } 600 \, ^\circ\text{C} \]
  - At lower temperature (RT to 150 °C) Pu(OH)$_2$F$_2$ or Pu(OH)F$_3$ forms
    \[ \rightarrow \text{PuF}_3 \text{ from HF and H}_2 \]
    \[ \rightarrow \text{PuF}_4 \text{ from HF and O}_2 \]
  - Other compounds can replace oxalates (nitrates, peroxides)
- Stronger oxidizing conditions can generate PuF$_6$
  - \[ \text{PuO}_2 + 3 \text{F}_2 \rightarrow \text{PuF}_6 + \text{O}_2 \text{ at } 300 \, ^\circ\text{C} \]
  - \[ \text{PuF}_4 + \text{F}_2 \rightarrow \text{PuF}_6 \text{ at } 300 \, ^\circ\text{C} \]
- **PuF$_3$**
- Insoluble in water
- Prepared from addition of HF to Pu(III) solution
  - Reduce Pu(IV) with hydroxylamine (NH$_2$OH) or SO$_2$
- Purple crystals
  - \[ \text{PuF}_3 \cdot 0.40\text{H}_2\text{O} \]
Pu fluoride preparation

- PuF₄
  - Insoluble in H₂O
    → From addition of HF to Pu(IV) solution
      * Pale pink PuF₄·2.5H₂O
      * Soluble in nitric acid solutions that form fluoride species
        ➢ Zr, Fe, Al, BO₃³⁻
  - Heating under vacuum yields trifluoride
    → Formation of PuO₂ from reaction with water
      * PuF₄+2H₂O→PuO₂+4HF
    → Reaction of oxide with fluoride
      * 3PuF₄+2PuO₂→4PuF₃+O₂
    → Net: 4PuF₄+2H₂O→4PuF₃+4HF+O₂
      * High vacuum and temperature favors PuF₃ formation
  - Anhydrous forms in stream of HF gas
PuF$_6$ preparation

- Formation from reaction of F$_2$ and PuF$_4$
- Fast rate of formation above 300 °C
  - Reaction rate
    \[ \text{Log(rate/mg PuF}_4 \text{ cm}^{-2}\text{hr}^{-1}=5.917-2719/T} \]
  - Faster reaction at 0.8 F$_2$ partial pressure
- Condensation of product near formation
  - Liquid nitrogen in copper condenser near PuF$_4$
- Can be handled in glass

Fluorination of PuF$_4$ by fluorine diluted with He/O$_2$ mixtures to produce PuF$_6$ (Steindler, 1963).
• **PuF₄**
  - Isostructural with An and Ln tetrafluorides
  - Pu surrounded by 8 F  → Distorted square antiprism

• **PuF₆**
  - Gas phase O₉ symmetry

absorption spectrum of gaseous PuF₆ from Steindler and Gunther (1964a)
Pu fluoride properties

- **PuF₃**
  - Melting point: 1425 °C
  - Boiling point: decomposes at 2000 °C

- **PuF₄**
  - Melting point: 1037°C

- **PuF₆**
  - Melting point: 52°C
  - Boiling point: 62°C
  - $\Delta_{\text{subl}}H^\circ=48.65 \text{ kJ/mol}$, $\Delta_fH^\circ=-1861.35 \text{ kJ/mol}$
  - IR active in gas phase, bending and stretching modes
  
  $\rightarrow$ Isotopic shifts reported for 239 and 242
  
  - Equilibrium constant measured for $\text{PuF}_6 \rightarrow \text{PuF}_4 + F_2$
  
  $\rightarrow \Delta G=2.55E4+5.27T$
  
  $\rightarrow$ At 275 °C, $\Delta G=28.36 \text{ kJ/mol}$
  
  $\rightarrow \Delta S=-5.44 \text{ J/K mol}$
  
  $\rightarrow \Delta H=25.48 \text{ kJ/mol}$
Pu halides

- **PuF$_6$ decomposition**
  - Alpha decay and temperature
    - Exact mechanism unknown
  - Stored in gas under reduced pressure
- **Higher halide preparation**
  - PuCl$_3$ from hydrochlorination
    - Pu$_2$(C$_2$O$_4$)$_3$·10H$_2$O+6HCl→2PuCl$_3$+3CO$_2$+3CO+13H$_2$O
    - Reaction of oxide with phosgene (COCl$_2$) at 500 °C
    - Evaporation of Pu(III) in HCl solution
  - PuCl$_4$
    - PuCl$_3$+0.5Cl$_2$→PuCl$_4$
      * Gas phase
      * Identified by peaks in gas phase IR
Ternary halogenoplatonates

- Pu(III-VI) halides with ammonia, group 1, group 2, and some transition metals
- Preparation
  - Metal halides and Pu halide dried in solution
  - Metal halides and PuF₄ or dioxide heat 300-600 °C in HF stream
  - PuF₄ or dioxide with NH₄F heated in closed vessel at 70-100 °C with repeated treatment
  - PuF₆ or PuF₄ with group 1 or 2 fluorides

Phase diagram of KCl–PuCl₃ system
Pu non-aqueous chemistry

- Very little Pu non-aqueous and organometallic chemistry
  - Limited resources
- Halides useful starting material
  - Pu halides insoluble in polar organic solvents
  - Formation of solvated complexes
    - \( \text{PuI}_3(\text{THF})_x \) from Pu metal with 1,2-diiodoethane in THF
      - *Tetrahydrofuran*
        - Also forms with pyridine, dimethylsulfoxide
  - Also from reaction of Pu and I\(_2\)
  - Solvent molecules displaced to form anhydrous compounds
  - Single THF NMR environment at room temperature
    - Two structures observed at -90 °C
Pu non-aqueous chemistry

- **Borohydrides**
  - \( \text{PuF}_4 + 2\text{Al(BH}_4\text{)}_3 \rightarrow \text{Pu(BH}_4\text{)}_4 + 2\text{Al(BH}_4\text{)}\text{F}_2 \)
  - Separate by condensation of Pu complex in dry ice
  - IR spectroscopy gives pseudo \( T_d \)
    \( \rightarrow \) 12 coordinate structure

- **Cyclooctatraene (C}_8\text{H}_8 \) complexes**
  - \([\text{NEt}_4\text{]}_2\text{PuCl}_6 + 2\text{K}_2\text{C}_8\text{H}_8 \rightarrow \text{Pu(C}_8\text{H}_8\text{)}_2 + 4\text{KCl} + 2[\text{NEt}_4\text{]}\text{Cl in THF} \)
    \( \rightarrow \) Slightly soluble in aromatic and chlorinated hydrocarbons
    \( \rightarrow \) \( D_{8h} \) symmetry
    \( \rightarrow \) 5f-5f and 5f-6d mixing
    * Covalent bonding, molar absorptivity approaching 1000 L mol\(^{-1}\)cm\(^{-1}\)
Pu non-aqueous chemistry

- Cyclopentadienyl \((C_5H_5), \text{Cp}\)
  - \(\text{PuCl}_3\) with molten \((C_5H_5)_2\text{Be}\)
    \(\rightarrow\) trisCp Pu
    
    * Reactions also possible with Na, Mg, and Li Cp
  - \(\text{Cs}_2\text{PuCl}_6 + 3\text{Tl}(C_5H_5)\) in acetonitrile
  - Formation of Lewis base species
    \(\rightarrow\) \(\text{CpPuCl}_3L_2\)
    
    * From \(\text{PuCl}_4L_2\) complex
  - Characterized by IR and Vis spectroscopy
Pu electronic structure

- Ionic and covalent bonding models
  - Ionic non-directional electrostatic bonds
    → Weak and labile in solution
      * Core 5f
  - Covalent bonds are stronger and exhibit stereochemical orientation
  - All electron orbitals need to be considered
    → Evidence of a range of orbital mixing
- PuF_{6}
  - Expect ionic bonding
    → Modeling shows this to be inadequate
  - O_{h} symmetry
  - Sigma and pi bonds
    → t_{2g} interacts with 6d
    → t_{2u} interacts with 5f or 6p and 7p for sigma bonding
    → t_{1g} non-bonding
  - Range of mixing found
    → 3t_{1u} 71% Pu f, 3% Pu p, 26% F p characteristics
  - Spin-orbital coupling splits 5f state
    → Necessary to understand full MO, simple electron filling does not describe orbital
      * 2 electrons in 5f orbital
        Different arrangements, 7 f states
**PuO$_2^{n+}$ electronic structure**

- **Linear dioxo**
  - Pu oxygen covalency
  - Linear regardless of number of valence 5f electrons
  - D$_{\infty h}$

- Pu oxygen sigma and pi bonds
  - Sigma from 6p$_z$ and hybrid 5f$_z$ with 6p$_z$
  - Pi 6d and 5f pi orbitals

- Valence electrons include non-bonding orbital
  - δ and φ higher than pi and sigma in energetics
  - 5f add to non bonding orbitals

- Weak ionic bonds in equatorial plane
- Spin-orbital calculations shown to lower bond energy

---

Fig. 7.124 A qualitative molecular orbital interaction diagram for a linear trisatomic PuO$_2^{n+}$ ion interacting with four equatorial ligands, L, to form PuO$_2$L$_4^{n+}$. 
Review

- Nuclear properties and isotope production
  - Production from $^{238}$U
  - Fissile and fertile isotopes
- Pu in nature
  - Location, levels and how produced
- Separation and Purification
  - Role of redox in aqueous and non-aqueous separations
- Metallic state
  - Phases, alloys, and reactions with gases
- Compounds
  - Preparation and properties
- Solution chemistry
  - Oxidation state
  - Spectroscopic properties
  - Structure and coordination chemistry
Questions

• Which isotopes of Pu are fissile, why?
• How can one produce $^{238}\text{Pu}$ and $^{239}\text{Pu}$?
• How is Pu naturally produced?
• How does redox influence Pu chemistry?

Odd A Pu isotopes are fissile
Unpaired neutron

$^{237}\text{Np}(n,\gamma)^{238}\text{Np}$

$^{238}\text{Np} \rightarrow ^{238}\text{Pu} + \beta^- + \nu$

$^{238}\text{U}$ neutron capture,
Beta decay to $^{239}\text{Pu}$

• Five oxidation states in solution (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
Questions

• How can you identify Pu oxidation states in solution?
• How many phase can Pu metal form at standard pressure?
Questions

• How do electron relativistic effects impact Pu chemistry?

• How does Pu metal oxidize?

• What is a useful starting compound for Pu non-aqueous chemistry?

5f electrons extend relatively far from nucleus compared to 4f electrons
5f electrons participate in chemical bonding

Formation of oxide layer on metal surface
Can include oxides other than dioxide
Slow oxidation in dry air
Greatly enhanced oxidation rate in presence of water or hydrogen

PuI$_3$(THF)$_x$ from Pu metal
PDF quiz

• Comment on blog
• Respond to PDF Quiz 14