Lecture 7: Neptunium Chemistry

- From: Chemistry of actinides
  - Nuclear properties and isotope production
  - Separation and Purification
  - Metallic state
  - Compounds
  - Solution chemistry
  - Structure and coordination chemistry
  - Analytical Chemistry
Neptunium nuclear properties

- 22 known Np isotopes
  - $^{237}\text{Np}$ longest lived
    - Neutron irradiation of U
      * Consecutive neutron capture on $^{235}\text{U}$
      * $^{238}\text{U}(n,2n)^{237}\text{U} \rightarrow ^{237}\text{Np} + \beta^-$
      * Alpha decay of $^{241}\text{Am}$
    - Used at target for $^{238}\text{Pu}$ production by neutron irradiation
    - Reaction with 23 MeV and 30 MeV electrons to produce $^{236}\text{Pu}$
    - Critical mass is 73 kg
    - 2500 kg in environment from fallout
  - $^{238,239}\text{Np}$
    - Short half-life, useful radiotracers
      * From neutron irradiation of $^{237}\text{Np}$ and $^{238}\text{U}$
  - $^{235,236}\text{Np}$
    - Cyclotron irradiation of $^{235}\text{U}$
      * $^{235}\text{U}(d,n)^{236}\text{Np}$
      * $^{235}\text{U}(p,n)^{235}\text{Np}$
- Np isotopes formed in Earth’s crust
  - Dynamic equilibrium established
<table>
<thead>
<tr>
<th>Mass number</th>
<th>Half-life</th>
<th>Mode of decay</th>
<th>Main radiations (MeV)</th>
<th>Method of production</th>
</tr>
</thead>
<tbody>
<tr>
<td>226</td>
<td>31 ms</td>
<td>EC, α</td>
<td>α 8.044</td>
<td>209Bi(22Ne,5n)</td>
</tr>
<tr>
<td>227</td>
<td>0.51 s</td>
<td>EC, α</td>
<td>α 7.677</td>
<td>209Bi(22Ne,4n)</td>
</tr>
<tr>
<td>228</td>
<td>61.4 s</td>
<td>EC, α</td>
<td>α 6.890</td>
<td>209Bi(22Ne,3n)</td>
</tr>
<tr>
<td>229</td>
<td>4.0 min</td>
<td>α ≥ 50%</td>
<td>α 6.66</td>
<td>232U(p,5n)</td>
</tr>
<tr>
<td>230</td>
<td>4.6 min</td>
<td>EC ≥ 99%</td>
<td>α 6.66</td>
<td>232U(p,4n)</td>
</tr>
<tr>
<td>231</td>
<td>48.8 min</td>
<td>EC &lt; 99%</td>
<td>α 6.28</td>
<td>233U(d,4n)</td>
</tr>
<tr>
<td>232</td>
<td>14.7 min</td>
<td>EC &gt; 99%</td>
<td>γ 0.371</td>
<td>233U(d,6n)</td>
</tr>
<tr>
<td>233</td>
<td>36.2 min</td>
<td>EC &lt; 99%</td>
<td>γ 0.327</td>
<td>233U(d,3n)</td>
</tr>
<tr>
<td>234</td>
<td>4.4 d</td>
<td>EC 99.95% β+ 0.05%</td>
<td>γ 1.559</td>
<td>233U(d,2n)</td>
</tr>
<tr>
<td>235</td>
<td>396.1 d</td>
<td>EC &gt; 99% α 1.6 × 10−3%</td>
<td>α 5.022 (53%)</td>
<td>235U(p,2n)</td>
</tr>
<tr>
<td>236</td>
<td>22.5 h</td>
<td>β− 50%</td>
<td>β− 0.54</td>
<td>233U(d,n)</td>
</tr>
<tr>
<td></td>
<td>1.54 × 105 yr</td>
<td>EC 87% β− 13%</td>
<td>γ 0.163</td>
<td>235U(d,n)</td>
</tr>
<tr>
<td>237</td>
<td>2.144 × 106 yr</td>
<td>α &gt;1 × 1018 yr SF</td>
<td>γ 0.086 (51%)</td>
<td>237U daughter</td>
</tr>
<tr>
<td>238</td>
<td>2.117 d</td>
<td>β−</td>
<td>β− 1.29</td>
<td>237Np(n,γ)</td>
</tr>
<tr>
<td>239</td>
<td>2.3565 d</td>
<td>β−</td>
<td>β− 0.72</td>
<td>243Am daughter</td>
</tr>
<tr>
<td>240</td>
<td>1.032 h</td>
<td>β−</td>
<td>γ 0.106</td>
<td>238U daughter</td>
</tr>
<tr>
<td></td>
<td>7.22 min</td>
<td>β−</td>
<td>β− 2.09</td>
<td>238U(α,3n)</td>
</tr>
<tr>
<td></td>
<td>13.9 min</td>
<td>β−</td>
<td>γ 0.566</td>
<td>240U daughter</td>
</tr>
<tr>
<td>241</td>
<td>5.5 min</td>
<td>β−</td>
<td>β− 2.05</td>
<td>238U(α,2n)</td>
</tr>
<tr>
<td>242</td>
<td>2.2 min</td>
<td>β−</td>
<td>γ 0.555</td>
<td>240Pu(p,3n)</td>
</tr>
<tr>
<td>242</td>
<td>1.85 min</td>
<td>β−</td>
<td>γ 0.175</td>
<td>240Pu(p,2n)</td>
</tr>
<tr>
<td>244</td>
<td>2.29 min</td>
<td>β−</td>
<td>γ 0.736</td>
<td>240Pu(p,2n)</td>
</tr>
</tbody>
</table>

* Not known whether ground-state nuclide or isomer.
Np separation chemistry

- Most methods exploit redox chemistry of Np
- 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
  - Pyrazolone derivatives
    - Np(IV) extracted from 1 to 4 M HNO₃
    - Prevents Np(IV) hydrolysis
    - No extraction of Np(V) or Np(VI)
  - Pyrazolone derivatives synergistic extraction with tri-n-octylphosphine oxide (TOPO)
    - Separate Np(V) from Am, Cm, U(VI), Pu(IV) and lanthanides
  - 1:2 Np:ligand ratio as extracted species
TABLE 18

EXTRACTION COEFFICIENTS FOR VARIOUS IONS INTO 0.5M TTA-XYLENE

<table>
<thead>
<tr>
<th>Ion</th>
<th>$\text{HNO}_3$ (M)</th>
<th>Extraction Coefficient at 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Np(III)</td>
<td>1.0</td>
<td>$&lt;3 \times 10^{-8}$</td>
</tr>
<tr>
<td>Np(IV)</td>
<td>1.0</td>
<td>$1 \times 10^4$</td>
</tr>
<tr>
<td>Np(V)</td>
<td>8.0</td>
<td>$&lt;1 \times 10^{-2}$</td>
</tr>
<tr>
<td>Np(VI)</td>
<td>0.8</td>
<td>$&lt;5 \times 10^{-4}$</td>
</tr>
<tr>
<td>Pu(III)</td>
<td>1.0</td>
<td>$1 \times 10^{-6}$</td>
</tr>
<tr>
<td>Pu(IV)</td>
<td>1.0</td>
<td>$1 \times 10^6$</td>
</tr>
<tr>
<td>Pu(V)</td>
<td>8.0</td>
<td>$&lt;1 \times 10^{-2}$</td>
</tr>
<tr>
<td>Pu(VI)</td>
<td>1.0</td>
<td>$&lt;1 \times 10^{-6}$</td>
</tr>
<tr>
<td>U(VI)</td>
<td>1.0</td>
<td>$4 \times 10^{-3}$</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>1.0</td>
<td>$&lt;1 \times 10^{-3}$</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>1.0</td>
<td>375</td>
</tr>
<tr>
<td>Ce(III)</td>
<td>1.0</td>
<td>$1 \times 10^{-5}$</td>
</tr>
<tr>
<td>Ce(IV)</td>
<td>1.0</td>
<td>$1 \times 10^3$</td>
</tr>
<tr>
<td>Zr(IV)</td>
<td>1.0</td>
<td>$1 \times 10^7$</td>
</tr>
<tr>
<td>Am(III)</td>
<td>8.0</td>
<td>250</td>
</tr>
<tr>
<td>Al(III)</td>
<td>1.0</td>
<td>$1 \times 10^{-9}$</td>
</tr>
<tr>
<td>Na</td>
<td>1.0</td>
<td>$1 \times 10^{-20}$</td>
</tr>
<tr>
<td>Nb(V)</td>
<td>1.0</td>
<td>$1 \times 10^{-20}$</td>
</tr>
<tr>
<td>Th(IV)</td>
<td>1.0</td>
<td>$4 \times 10^{-1}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$3.0$</td>
</tr>
</tbody>
</table>

Fig. 6.2 Structure of pyrazole derivatives.
Fig. 6.3  Log $D$ vs $-\log \left[H^+\right]$ plots for the extraction of Np$^{4+}$ in HNO$_3$ solution with $1 \times 10^{-3}$ M $H_2BPn$ and HPMBP in chloroform solution. (From Takeishi et al., 2001, with permission from Elsevier). (1) $H_2BP_3$, (2) $H_2BP_4$, (3) $H_2BP_5$, (4) $H_2BP_6$, (5) $H_2BP_7$, (6) $H_2BP_8$, (7) $H_2BP_{10}$, (8) $H_2BP_{22}$; dotted line, HPMBP.
FIGURE 4. Percentage Extraction of Tracer Quantities of Ac(III), Am(III), Cm(III), Cf(III), Np(IV), and Pa(V) with 0.1M 8-Hydroxyquinoline/CHCl₃, and of Ra(II) with 1.0M 8-Hydroxyquinoline/CHCl₃ [μ = 0.1M (Na, NH₄, H)ClO₄, 25°C]. [C. Keller and M. Mosidzelenski, Radiochim. Acta. 7, 185(1967) Supplemented].
Np solvent extraction

- **Tributylphosphosphate**
  - NpO$_2$(NO$_3$)$_2$(TBP)$_2$ and Np(NO$_3$)$_4$(TBP)$_2$ are extracted species
    - Extraction increases with increase concentration of TBP and nitric acid
      * 1-10 M HNO$_3$
    - Separation from other actinides achieved by controlling Np oxidation state

- **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
<table>
<thead>
<tr>
<th>Ion</th>
<th>Solution</th>
<th>TBP (%)</th>
<th>Extraction Coefficient At 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Am(III)</td>
<td>4.0M HNO₃</td>
<td>30</td>
<td>0.013</td>
</tr>
<tr>
<td>Al</td>
<td>4.7M</td>
<td>15</td>
<td>0.0003</td>
</tr>
<tr>
<td>Ca</td>
<td>4.7M</td>
<td>15</td>
<td>0.0003</td>
</tr>
<tr>
<td>Co(II)</td>
<td>2.14M Co(NO₃)₂</td>
<td>60</td>
<td>0.002</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>3.0M HNO₃</td>
<td>100</td>
<td>0.0001</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>3.0M</td>
<td>100</td>
<td>0.0004</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>4.7M</td>
<td>15</td>
<td>0.0005</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>2.0M</td>
<td>12.5</td>
<td>0.003</td>
</tr>
<tr>
<td>Mg</td>
<td>4.7M</td>
<td>15</td>
<td>0.0003</td>
</tr>
<tr>
<td>Na</td>
<td>2.0M</td>
<td>12.5</td>
<td>0.003</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>3.0M</td>
<td>100</td>
<td>0.00006</td>
</tr>
<tr>
<td>Np(IV)</td>
<td>4.0M</td>
<td>30</td>
<td>3.0</td>
</tr>
<tr>
<td>Np(VI)</td>
<td>4.0M</td>
<td>30</td>
<td>12.0</td>
</tr>
<tr>
<td>Th</td>
<td>4.0M</td>
<td>30</td>
<td>2.8</td>
</tr>
<tr>
<td>Pa</td>
<td>4.0M</td>
<td>50</td>
<td>2.8</td>
</tr>
<tr>
<td>Zn</td>
<td>2.0M Zn(NO₃)₂</td>
<td>12.5</td>
<td>0.0001</td>
</tr>
<tr>
<td>Ru</td>
<td>2.0M HNO₃</td>
<td>30</td>
<td>0.15</td>
</tr>
<tr>
<td>Zr</td>
<td>2.0M</td>
<td>30</td>
<td>0.09</td>
</tr>
<tr>
<td>Nb</td>
<td>2.0M</td>
<td>30</td>
<td>0.03</td>
</tr>
<tr>
<td>Rare earths</td>
<td>2.0M</td>
<td>30</td>
<td>0.02</td>
</tr>
<tr>
<td>Pu(III)</td>
<td>5.0M</td>
<td>20</td>
<td>0.012</td>
</tr>
<tr>
<td>Pu(IV)</td>
<td>5.0M</td>
<td>20</td>
<td>16.6</td>
</tr>
<tr>
<td>Pu(VI)</td>
<td>5.0M</td>
<td>20</td>
<td>2.7</td>
</tr>
<tr>
<td>U(IV)</td>
<td>4.0M</td>
<td>25</td>
<td>10</td>
</tr>
<tr>
<td>U(VI)</td>
<td>4.0M</td>
<td>25</td>
<td>23</td>
</tr>
<tr>
<td>HNO₃</td>
<td>2.0M</td>
<td>30</td>
<td>0.26</td>
</tr>
</tbody>
</table>
Figure 5. Distribution Coefficients for the Extraction of Tetravalent Actinides by 19 vol % TBP-Kerosene from Nitric Acid Solution.\textsuperscript{165}

Figure 6. Distribution Coefficients for the Extraction of Hexavalent Actinides by 19 vol % TBP-Kerosene from Nitric Acid Solution.\textsuperscript{165}
Table 6.2  Distribution ratios of neptunium and plutonium ions between $HNO_3$ solution and 0.1 M CMPO + 1.4 M TBP (dodecane) at (278 ± 1) K (data cited from Mincher, 1989).

<table>
<thead>
<tr>
<th>Ions</th>
<th>Concentration of $HNO_3$ (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td>NpO$_2^{2+}$</td>
<td>43</td>
</tr>
<tr>
<td>NpO$_2^+$</td>
<td>$10^{-2}$</td>
</tr>
<tr>
<td>Np$^{4+}$</td>
<td>0.55</td>
</tr>
<tr>
<td>Pu$^{4+}$</td>
<td>16</td>
</tr>
<tr>
<td>Pu$^{3+}$</td>
<td>1.6</td>
</tr>
</tbody>
</table>
Np solvent extraction

• HDEHP
  ▪ In 1 M HNO₃ with addition of NaNO₂
    → U, Pu, Np, Am in most stable oxidation states
    → Np(V) is not extracted
    → Oxidized to Np(VI) then extracted
    → Reduced to Np(V) and back extracted into 0.1 M HNO₃

• Tri-n-octylamine
  ▪ Used for separation of Np from environmental samples
    → Extracted from 10 M HCl
    → Back extracted with 1 M HCl+0.1 M HF
Figure 11. The Extraction of the Quadrivalent Actinide Nitrates by 10 vol % TGA in Xylene.\textsuperscript{198}

Figure 12. The Extraction of the Hexavalent Actinide Nitrates by 10 vol % TGA in Xylene.\textsuperscript{198}
Figure 13. The Extraction of Pentavalent and Trivalent Actinide Nitrates by 10 vol % TOA in Xylene.\textsuperscript{188}
Advanced PUREX separations

- Np(V) not extracted in PUREX
  - Np(V) slowly disproportionates in high acid
    - Formation of extractable Np(IV,VI)
    - Variation of Np behavior based on redox
      * Need to understand redox kinetics
      * Reduction of Np(VI) by a range of compounds
    - Back extraction of Np(V) can be used to separate from Pu and U
      * Controlled Np(VI) reduction in presence of Pu(III)
        - Hydrazine derivatives
        - N-butyraldehyde
        - Hydroxamic acids
        - AHA shows preferential complexation with tetravalent Np and Pu
Separation scheme

UREX → Cs, Sr, Np, Pu, Am, Cm, FP, Ln → CCD-PEG FPEX → Cs, Sr → TRUEX → FP

UREX+1a uses CCD-PEG

Tc, U → Anion exchange → U

Np, Pu, Am, Cm → TALSPEAK → Ln

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Advanced Np separations

- A number of proposed routes
  - Separate Np with U and Pu
    - Reduce Np to separate from U and Pu
- Np behavior in UREX+1a
  - UREX
    - 1 M HNO$_3$, 30 % TBP
    - 30 % TBP, 0.5 M AHA, 0.3 M HNO$_3$
      * Np in raffinate (0.7 M HNO$_3$)
Chemistry in Extraction: Cs and Sr

- **CCD-PEG**
  - Cs and Sr extracted with chlorinated cobalt dicarbollide (CCD)/polyethylene glycol (PEG)
    - \( \rightarrow \) Np to raffinate and wash
    - \( \rightarrow \) Sr and Cs removed with 3 M HNO\(_3\), Guanadine carbonate (100 g/L), and DTPA (20 g/L)
  - Wash with 4 M HNO\(_3\), 250 mg/L PEG

- **FPEX**
  - BOBCalixC6
    - \( \rightarrow \) Calix[4]arene-bis-(tert-octylbenzo-\( ^{-} \))
  - DtBuCH18C6
    - \( \rightarrow \) 4,4,(5)-Di-(t-butyldicyclo-hexano)-18-crowr
  - Cs-7SB modifier
    - \( \rightarrow \) 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol
  - Trioctylamine in Isopar-L
    - \( \rightarrow \) Isopar-L is branched hydrocarbon
  - 0.01 and 1.5 M HNO\(_3\)
  - AHA (from UREX)
Chemistry in Extraction

- **TRUEX**
  - Np goes with Ln and other actinides
  - 0.05 to 7 M HNO₃
  - 1.4 M TBP
  - 0.2 M Diphenyl-N,N-dibutylcarbamoyl oxide (CMPO)

- **TALSPEAK** (lanthanides from actinides)
  - 0.5 M Bis(2-ethyl-hexyl)phosphoric acid (HDEHP)
    - Extracts actinides into aqueous phase
  - 4 M HNO₃
  - DTPA (pH adjustment for Ln removal)
  - Lactic acid
Np extraction

• Diisodecylphosphoric acid (DIDPA)
  ▪ Also extracts trivalent lanthanides
    → Used in TALSPEAK like process

• Chromatography
  ▪ Available for 4-6 oxidation state
    → 4>6>5
  ▪ Np 4+ and 6+ form anionic complexes in high concentration chloride or nitrate
  ▪ Strong sorption onto anion exchange at 7-8 M HNO₃
  ▪ Elute with 0.3 M HNO₃
Figure 18. Sorption of the Elements from Nitric Acid Solutions by Strongly Basic Anion Exchange Resins.
Uranium-Neptunium-Plutonium Separation by Anion Exchange ("Dowex" 1-X10, <400 Mesh, 0.25 cm² x 3 cm Column).
Chromatography with Chelating Resins

- Resin loaded with Aliquat 336
  - TEVA resin
  - $\rightarrow$ Np controlled by redox state
  - *Reduction with Fe(II) sulfamate and ascorbic acid

Ascorbic acid

Horwitz, et al. (HP195)
**Figure 4**

Effect of Matrix Constituents on Neptunium Retention
TEVA Resin 5 M HNO₃

**Figure 5**

Effect of Matrix Constituents on Neptunium Retention
TEVA Resin 2 M HNO₃

Horwitz, et al. (HP195)
Figure 6

Effect of oxalic acid concentration on $k'_{\text{Np(V)}}$ at various HNO$_3$ concentration

TEVA Resin  23-25°C

$[\text{HNO}_3], \text{ M}$

$[\text{H}_2\text{C}_2\text{O}_4], \text{ M}$

Horwitz, et al. (HP195)

Figure 7

Separation of Np and Pu on TEVA Resin

Horwitz, et al. (HP195)
Separation methods

• Co-precipitation
  - Np coprecipitates with
    \[ \text{LaF}_3, \text{BiPO}_4, \text{BaSO}_4, \text{Fe(OH)}_3, \text{MnO}_2 \]
  - Np(V,VI) does not precipitate with LaF$_3$

• Electrodeposition
  - At cathode in LiCl, KCl eutectic
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>
<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.

Table 6.3 Lattice parameters and space groups for allotropes of neptunium. (Lemire et al., 2001)
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 formation of f electron hybridization
- NpAl₃ is ferromagnet,
  → No spin ordering found in NpGe₃ and NpSn₃
- Range of compounds examined
  - RM₂X₂
    → R=Th, Np or Pu, M is transition metal, X = Si, Ge
  - RM₂Al₃
    → R=Np or Pu; M= Ni or Pd
  - NpX₃
    → X=Al, Ga, Ge, In, or Sn
- Alloy research based on waste form development
  - Zr with Np and other actinides
Np hydrides

- Np with H$_2$
  - NpH$_{2+x}$ and NpH$_3$
- NpH$_{2+x}$ is fcc and isostructural with Pu homolog
  - Lattice constant increases with x
- NpH$_3$ is hexagonal and isostructural with Pu
- Np to H ratio examined
  - Pressure composition isotherms show change above 2
    - Other actinides have boundary at 1.9
  - Increasing H with increasing temperature
    - Opposite of the Pu system
- Thermodynamic data shows variation in literature
  - Estimated heat capacity at 298 K 47.279 J K$^{-1}$mol$^{-1}$
Table 6.4 Comparison of lattice parameters for cubic neptunium hydride.

<table>
<thead>
<tr>
<th>[H]/[Np]</th>
<th>Mulford et al. $a_0$ (Å)</th>
<th>Space group</th>
<th>Ward et al.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>5.343</td>
<td>$Fm3m$</td>
<td>5.3565</td>
</tr>
<tr>
<td>1.5</td>
<td>5.3428</td>
<td>$Fm3m$</td>
<td>5.3475</td>
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<tr>
<td>1.78</td>
<td>5.3431</td>
<td>$Fm3m$</td>
<td>5.3481</td>
</tr>
<tr>
<td>2</td>
<td>5.3431</td>
<td>$Fm3m$</td>
<td>5.349</td>
</tr>
<tr>
<td>2.15</td>
<td>5.3463</td>
<td>$Fm3m$</td>
<td>5.3516</td>
</tr>
<tr>
<td>2.18</td>
<td>5.3478</td>
<td>$Fm3m$</td>
<td>5.3578</td>
</tr>
<tr>
<td>2.3</td>
<td>5.3478</td>
<td>$Fm3m$</td>
<td>5.3578</td>
</tr>
<tr>
<td>2.36</td>
<td>5.36</td>
<td>$Fm3m$</td>
<td>5.3578</td>
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<tr>
<td>2.42</td>
<td>5.36</td>
<td>$Fm3m$</td>
<td>5.3578</td>
</tr>
<tr>
<td>2.5</td>
<td>5.36</td>
<td>$Fm3m$</td>
<td>5.3578</td>
</tr>
<tr>
<td>2.8</td>
<td>5.355</td>
<td>$Fm3m$</td>
<td>5.3578</td>
</tr>
</tbody>
</table>

Fig. 6.6 Partial phase diagram for the neptunium-hydrogen system. Reprinted from Ward et al. (1987) with permission from Elsevier Science.
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
    $\rightarrow$ 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
Fig. 6.7  Phase relation of the neptunium–oxygen system. Reprinted from Richer and Sari (1987), with permission from Elsevier Science.
Np hydroxides

- Np(IV)
  - Hydroxides and oxide hydrates
    - Debate on data and stability of compounds
- Np(V)
  - Precipitation with base
    - Some changes observed with aging of material
    - Absorbance spectroscopy changes
- Np(VI)
  - Base to solutions of Np(VI)
  - Oxidation of Np(V) in molten LiNO₃/KNO₃ with O₃
  - Addition of O₃ to an aqueous solution NpO₂ClO₄ at pH 5 at 363 K
    - NpO₂(OH)₂
    * Different XRD and IR in the literature
- Np(VII)
  - Precipitated with base around pH 10
    - Questions on form of precipitate
      * NpO₂(OH)₃ or NpO₃(OH)
        - Based on titration of hydroxide
    - From reaction of O₃ with Np(V) hydroxide
Table 6.5  Thermodynamic properties of neptunium oxides and hydrated oxides at 298.15 K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta_f H_m^o$ (kJ mol$^{-1}$)</th>
<th>$S_m^o$ (J K$^{-1}$ mol$^{-1}$)</th>
<th>$\Delta_f G_m^o$ (kJ mol$^{-1}$)</th>
<th>$C_{pm}^o$ (J K$^{-1}$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NpO$_2$</td>
<td>$-1074.0\pm 2.5$</td>
<td>$80.3\pm 0.4$</td>
<td>$-1021.731\pm 2.514$</td>
<td>$66.24\pm 0.5$</td>
</tr>
<tr>
<td>Np$_2$O$_5$</td>
<td>$-2162.7\pm 9.5$</td>
<td>$174\pm 20$</td>
<td>$-2031.6\pm 11.2$</td>
<td>$128.6\pm 5$</td>
</tr>
<tr>
<td>NpO$_3$·H$_2$O</td>
<td>$-1377\pm 5$</td>
<td>$129\pm 27$</td>
<td>$-1239.0\pm 6.1$</td>
<td>$120\pm 20$</td>
</tr>
<tr>
<td>NpO$_2$·OH (am, fresh)</td>
<td>$-1222.9\pm 5.5$</td>
<td>$60\pm 27$</td>
<td>$-1114.7\pm 5.7$</td>
<td>$86\pm 20$</td>
</tr>
<tr>
<td>NpO$_2$·OH (am, aged)</td>
<td>$70\pm 28$</td>
<td></td>
<td>$-1118.1\pm 6.3$</td>
<td></td>
</tr>
<tr>
<td>NpO$_2$· (hyd,am)</td>
<td></td>
<td></td>
<td>$-957.3\pm 8.0$</td>
<td></td>
</tr>
</tbody>
</table>
Np ternary oxides

- Prepared from reaction of NpO$_2$ with metal oxides or precipitation from alkaline solutions
- Np(V) ternary oxides
  - Li and Na compounds
  - Heating Np(VI) Li and Na oxides under Ar with NpO$_2$
- Np(VI) ternary oxides
  - Prepared from NpO$_2$ with metal oxides under O$_2$
  - Isostructural with uranium compounds
- Np(VII) ternary oxides
  - Range of compounds
    → XNpO$_6$ based compounds
      * X=Li$_5$, Ba$_2$Li
    → XNpO$_5$
      * X=Rb$_3$, K$_3$, Cs$_3$
    → XNpO$_4$
      * X=Cs, Rb, and K
  - No clear definition of structure, literature includes monclininc
  - Some compounds contain both Np(VI) and Np(VII)
    → Absorption spectra in dilute NaOH
Np halides

- Fluorides
  - NpF$_3$, NpF$_4$, NpF$_5$, and NpF$_6$
  - Prepared from reactions with HF at 773 K
    - NpO$_2$ + 1/2H$_2$ + 3HF $\rightarrow$ NpF$_3$ + 2H$_2$O
    - NpF$_3$ + 1/4O$_2$ + HF $\rightarrow$ NpF$_4$ + 1/2H$_2$O
    - NpO$_2$ + 4HF $\rightarrow$ NpF$_4$ + 2H$_2$O
    - 10NpF$_6$ + I$_2$ $\rightarrow$ 10NpF$_5$ + 2IF$_5$
      * Other route where Np(VI) is reduced
  - NpF$_6$ is volatile
    - Melting point at 327.8 K
      * Higher vapor pressure than U and Pu compound
    - Can form Np(V) species upon reaction with NaF
      * NpF$_6$ + 3NaF $\leftrightarrow$ Na$_3$NpF$_8$ + 1/2F$_2$
        - U will stay as hexavalent compound
        - Range of monovalent species with Np fluorides
    - Synthesis similar to U compound
    - NpO$_2$F$_2$ intermediate species
    - KrF$_2$ used as fluorinating agent for some synthetic routes
# Np halides

## Table 6.7  Crystal structure and lattice constants of selected neptunium halide complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Symmetry</th>
<th>$a_0$ (Å)</th>
<th>$b_0$ (Å)</th>
<th>$c_0$ (Å)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Cs_2$NpCl$_6$</td>
<td>trigonal</td>
<td>7.46</td>
<td></td>
<td></td>
<td>6.03</td>
</tr>
<tr>
<td>Li$_4$NpF$_8$</td>
<td>orthorhombic</td>
<td>9.91 ± 0.01</td>
<td>9.83 ± 0.01</td>
<td>5.98 ± 0.01</td>
<td>Jove and Cousson (1977)</td>
</tr>
<tr>
<td>Cs$_2$NpBr$_6$</td>
<td>cubic</td>
<td>11.082 ± 0.01</td>
<td></td>
<td></td>
<td>Magette and Fuger (1977)</td>
</tr>
<tr>
<td>(NH$_4$)$_2$Np$<em>3$F$</em>{13}$</td>
<td>orthorhombic</td>
<td>7.298 ± 0.005</td>
<td>7.942 ± 0.005</td>
<td>8.392 ± 0.005</td>
<td>Abazli et al. (1979)</td>
</tr>
<tr>
<td>CsNpO$_2$Cl$_5$(H$_2$O)</td>
<td>monoclinic</td>
<td>11.71 ± 0.02</td>
<td>6.99 ± 0.02</td>
<td>8.76 ± 0.02</td>
<td>Tomilin et al. (1986)</td>
</tr>
<tr>
<td>Cs$_2$NaNpCl$_6$</td>
<td>cubic</td>
<td>10.9065</td>
<td></td>
<td></td>
<td>Schoebrechts et al. (1989)</td>
</tr>
</tbody>
</table>

- **Oxyfluorides**
  - From the reaction of oxides with HF at elevated temperatures or reaction of Np fluorides with H$_2$O
  - Compounds not extensively studies
    - NpO$_2$F, NpOF$_3$, NpO$_2$F$_2$, NpOF$_4$
Np halides

- **NpCl\(_4\)**
  - From the reaction of NpO\(_2\) with CCl\(_4\)
    - Addition of H\(_2\) yields NpCl\(_3\)
    - Similar to U reactions
  - Several melting point reported
    - Heating for NpOCl\(_2\)
- **NpBr\(_4\)**
  - NpO\(_2\) with AlBr\(_3\)
  - Reaction of elements
    - Same for AlI\(_3\) for NpI\(_3\)
- Complexes for with Group 1 and Group 2
- Synthesis reactions similar to U species
- Measured data on Np compounds limited
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta_f H_m^\circ$ (kJ mol$^{-1}$)</th>
<th>$S_m^\circ$ (J K$^{-1}$ mol$^{-1}$)</th>
<th>$\Delta_f G_m^\circ$ (kJ mol$^{-1}$)</th>
<th>$C_{p,m}^\circ$ (J K$^{-1}$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NpF$_3$</td>
<td>$-1529.0 \pm 8.3$</td>
<td>$130.6 \pm 3.0$</td>
<td>$-1460.5 \pm 8.3$</td>
<td>$94.2 \pm 3.0$</td>
</tr>
<tr>
<td>NpF$_4$</td>
<td>$-1874.0 \pm 16$</td>
<td>$148 \pm 3$</td>
<td>$-1783.8 \pm 16.0$</td>
<td>$116.1 \pm 4.0$</td>
</tr>
<tr>
<td>NpF$_5$</td>
<td>$-1941.0 \pm 25.0$</td>
<td>$200.0 \pm 15.0$</td>
<td>$-1834.4 \pm 25.4$</td>
<td>$132.8 \pm 8.0$</td>
</tr>
<tr>
<td>NpF$_6$</td>
<td>$-1970.0 \pm 20.0$</td>
<td>$229.1 \pm 0.5$</td>
<td>$-1841.9 \pm 20.0$</td>
<td>$167.4 \pm 0.4$</td>
</tr>
<tr>
<td>NpO$_2$F$_2$</td>
<td></td>
<td></td>
<td></td>
<td>$103.2$</td>
</tr>
<tr>
<td>Na$_3$NpF$_8$</td>
<td>$-3514.0 \pm 21.0$</td>
<td>$369.0 \pm 12.0$</td>
<td>$-3521.2 \pm 21.3$</td>
<td>$272.3 \pm 12.0$</td>
</tr>
<tr>
<td>NpCl$_3$</td>
<td>$-896.8 \pm 3.0$</td>
<td>$165.2 \pm 6.0$</td>
<td>$-829.8 \pm 3.0$</td>
<td>$101.9 \pm 4.0$</td>
</tr>
<tr>
<td>NpCl$_4$</td>
<td>$-984.0 \pm 1.8$</td>
<td>$196 \pm 5$</td>
<td>$-895.6 \pm 3.0$</td>
<td>$122.0 \pm 6.0$</td>
</tr>
<tr>
<td>NpOCl$_2$</td>
<td>$-1030.0 \pm 8.0$</td>
<td>$143.5 \pm 5.0$</td>
<td>$-960.6 \pm 8.1$</td>
<td>$95.0 \pm 4.0$</td>
</tr>
<tr>
<td>Cs$_2$NpCl$_6$</td>
<td>$-1976.2 \pm 1.9$</td>
<td>$410.0 \pm 15.0$</td>
<td>$-1833.0 \pm 4.9$</td>
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</tr>
<tr>
<td>Cs$_3$NpO$_2$Cl$_4$</td>
<td>$-2449.1 \pm 4.8$</td>
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<tr>
<td>Cs$_2$NpO$_2$Cl$_4$</td>
<td>$-2056.1 \pm 5.4$</td>
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<tr>
<td>Cs$_2$NaNpCl$_6$</td>
<td>$-2217.2 \pm 3.1$</td>
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</tr>
<tr>
<td>NpBr$_3$</td>
<td>$-730.2 \pm 2.9$</td>
<td>$200 \pm 6$</td>
<td>$-705.5 \pm 3.8$</td>
<td>$103.8 \pm 6.0$</td>
</tr>
<tr>
<td>NpBr$_4$</td>
<td>$-771.2 \pm 1.8$</td>
<td>$233 \pm 5$</td>
<td>$-737.8 \pm 3.5$</td>
<td>$128.0 \pm 4.0$</td>
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<tr>
<td>NpOBr$_2$</td>
<td>$-950.0 \pm 11.0$</td>
<td>$160.8 \pm 4.0$</td>
<td>$-906.9 \pm 11.1$</td>
<td>$98.2 \pm 4.0$</td>
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<tr>
<td>Cs$_2$NpBr$_6$</td>
<td>$-1682.3 \pm 2.0$</td>
<td>$469.0 \pm 10.0$</td>
<td>$-1620.1 \pm 3.6$</td>
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<tr>
<td>NpI$_3$</td>
<td>$-512.4 \pm 2.2$</td>
<td>$218 \pm 5$</td>
<td>$-512.5 \pm 3.7$</td>
<td>$110.0 \pm 8.0$</td>
</tr>
</tbody>
</table>
Other Np compounds

- Range of compounds similar to U, especially for synthesis
- Np sulfides and oxysulfides
  - NpS, NpS₃, Np₂S₅, Np₃S₅, Np₂S₃, Np₃S₄
    - Range of synthetic methods, similar to U
      * NpS
        - from Np₂S₃ and Np at 1873
        - Heating Np and S
        - Isostructural with U and Pu
  - NpOS, Np₄O₄S, Np₂O₅
    - NpO₂ used in synthesis of mixed species
- Np nitrides
  - NpN
    - from NH₃ and NpH₃
    - Np metal with N₂ and H₂ mixture
    - Carbothermic reduction of NpO₂ in N₂
    - Similar to UN and PuN
      * Dissolves in acid, relatively inert toward water
      * Some data (heat capacity)
- Limited data on Np carbides
  - NpC, Np₂C₃ and NpC₂
Np coordination compounds

- Interests driven from different Np oxidation states and systematic studies of actinides
- Np$^{3+}$
  - Very little data
  - Instable in aqueous solutions under air
  - Trivalent state stabilized by sodium formaldehyde sulfoxylate ($\text{NaHSO}_2\cdot\text{CH}_2\text{O}\cdot2\text{H}_2\text{O}$)
  - Formation of oxalate and salicylate species
    * 2 Np, 3 ligands
    * No O$_2$ in synthesis
- Np$^{4+}$
  - $\text{Et}_4\text{NNp(NCS)}_8$
    - Isostructural with U complex
  - Range of nitrate compounds
- Np(V)
  - Exhibit cation-cation interaction
  - $\text{Na}_4(\text{NpO}_4)_2\text{C}_{12}\text{O}_{12}$
    - Dissolve neptunium hydroxide in solution with mellitic acid
    - Adjust to pH 6.5 with base
    - Slowly evaporate
Np coordination compounds

• Np(VI)
  ▪ Some simple synthesis
    → Oxalic acid to Np(VI) solutions
      * Reduction of Np over time
    → Ammonium carbonate species
      * Excess (NH₄)₂CO₃ to nitrate solutions of Np(VI)

• Np(VII)
  ▪ Some disagreement on exact species
    → Mixed species with Co, Li, NH₃ and OH
Table 6.9  Lattice parameters of selected neptunium coordination compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Symmetry</th>
<th>Space group</th>
<th>Lattice constants</th>
<th>Angle (deg)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Np(IV)</td>
<td></td>
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</tr>
<tr>
<td>Np₂(C₂O₄)₃·ₙH₂O</td>
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<td></td>
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</tr>
<tr>
<td>Np₂(C₆H₅₃O₃)₃·ₙH₂O</td>
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</tr>
<tr>
<td>Np₂[C₆H₄(OH)COO]₃</td>
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<tr>
<td>Np(VI)</td>
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<tr>
<td>(Net₄)Np(NCS)₈</td>
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<tr>
<td>CoNp₂F₁₀·8H₂O</td>
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<td>CuNp₂F₁₀·6H₂O</td>
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<tr>
<td>NpCl₂·P(i-C₄H₉)₂O</td>
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<tr>
<td>NpCl₂CH₃CON(i-C₃H₇)₂</td>
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<tr>
<td>NpCl₄·2.5HCON(CH₃)</td>
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<tr>
<td>NpCl₄·3.5P(CH₃)(C₆H₅)₂O</td>
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<tr>
<td>Np(NO₃)·C₁₀H₁₀N₂(NO₃)·2H₂O</td>
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<td></td>
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<tr>
<td>(C₁₀H₁₀N₂)[NP(NO₃)]·2H₂O</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Np(V)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₄(NpO₄)₂C₁₂O₁₂·8H₂O</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>(NpO₄)₂CH₅(CO₂)₂·1H₂O</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>(NpO₄)₂CH₂(CO₂)₂·3H₂O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

References:
- Mefod’eva and Gel’mar (1971)
- Mefod’eva and Gel’mar (1971)
- Mefod’eva and Gel’mar (1971)
- Al-Kazzaz et al. (1972)
- Cousson et al. (1985)
- Cousson et al. (1985)
- Bagnall et al. (1985)
- Bagnall et al. (1985)
- Bagnall et al. (1985)
- Bagnall et al. (1985)
- Grigor’ev et al. (1986a)
- Grigor’ev et al. (1987)
- Grigor’ev et al. (1993b)
<table>
<thead>
<tr>
<th>Compound</th>
<th>Crystal System</th>
<th>Space Group</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>α (°)</th>
<th>β (°)</th>
<th>γ (°)</th>
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Mefod'eva et al. (1969)
Marquart et al. (1983)

7-45
Np Organometallic compounds

- Mainly cyclopentadienyl and cyclooctatetraenyl compounds
- Np cyclopentadienyl
  - Reduction of Np$^{4+}$ complex with Na
    \[ \text{Np(C}_5\text{H}_5\text{)}_3\text{Cl} + \text{Na} \rightarrow \text{Np(C}_5\text{H}_5\text{)}_3\cdot3\text{THF} + \text{NaCl} \]
  - Difficult to remove THF
  - Heating and vacuum
- Np$^{4+}$
  - NpCl$_4$+4KC$_5$H$_5$ $\rightarrow$ Np(C$_5$H$_5$)$_4$+4KCl
  - Dissolves in benzene and THF
  - Less sensitive to H$_2$O and O$_2$ than trivalent Pu and Am compound
- Halide salt of Np compound reported
  - NpX$_4$ + 3 KC$_5$H$_5$ $\rightarrow$ Np(C$_5$H$_5$)$_3$X +3KX
  - Can use as starting material and replace X with ligands
    - Inorganic (other halides); NC$_4$H$_4$\textsuperscript{−}, N$_2$C$_3$H$_3$\textsuperscript{−}, CH$^-$
Np Organometallic compounds

- Cyclooctatetraene compounds
  - $\text{NpCl}_4 + 2\text{K}_2(\text{C}_8\text{H}_8) \rightarrow \text{Np}(\text{C}_8\text{H}_8)_2 + 4\text{KCl}$
  - Precipitated by addition of water
  - Isomorphous with U and Pu compounds
    * Air sensitive
  - Trivalent compound also prepared with NpX$_3$ as starting material
    * Isostructural with KPu(\text{C}_8\text{H}_8)_2
      orthorhombic unit cell

- Reactions with other K complexes
  - $\text{K}_2\text{RC}_8\text{H}_7$; R=ethanol, butanol

- Reactions with NpI$_3$
  - Formation of mono- and diMeCP
Np atomic properties

- Ground state configuration $[\text{Rn}]5f^46d^17s^2$
- Term symbol $^6L_{11/2}$

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### Neptunium Np I

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<td>5f(^4) 7s 7p(^2)</td>
<td>8(^{K7/2})</td>
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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
  - Critical evaluation based on specific ion interaction theory
    - Specific ion interaction theory uses an extends Debye-Hückel term for activity
      * long range Debye-Hückel
      * Short range ion interaction term

\[ \log \gamma_i = -Z^2D + \varepsilon_{ij}\mu \]

\[ D = \frac{0.5107\sqrt{\mu}}{1 + 1.5\sqrt{\mu}} \]

\[ \log \beta(\mu) = \log \beta(0) + \Delta Z^2_i D - \Delta \varepsilon_{ij}\mu \]
Np redox

- Basic solutions
  - Difficulty in understanding data
    → Chemical forms of species
- Determine ratios of each redox species from XANES
  - Use Nernst equation to determine potentials

Fig. 6.8 XANES spectra from the pure Np(III), Np(IV), Np(V), and Np(VI) ions in HClO₄; reprinted from Soderholm et al. (1999) with permission from American Chemical Society.
Redox data

\[
\begin{align*}
\text{acidic solution} & : NpO_3^+ \quad 2.04 \quad NpO_2^{2+} \quad 1.24 \quad NpO_2^{2+} \quad 0.66 \quad Np^{4+} \quad 0.18 \quad Np^{3+} \quad -4.7 \quad Np^{2+} \quad -0.3 \quad Np \\
\text{basic solution} & : NpO_5^{3-} \quad 0.58 \quad NpO_2(OH)^2_2 \quad 0.6 \quad NpO_2(OH)^1_2 \quad 0.3 \quad NpO_2^{2-} \quad -2.1 \quad Np(OH)^3_- \quad -2.2 \quad Np
\end{align*}
\]


\[
\begin{align*}
\text{acidic} & : NpO_2^{2+} \quad +1.159 \quad \longrightarrow \quad NpO_2^{1+} \quad +0.604 \quad \longrightarrow \quad Np^{4+} \quad +0.219 \quad \longrightarrow \quad Np^{3+} \quad -1.772 \\
\text{basic} & : NpO_5^{3-} \quad +0.58 \quad \longrightarrow \quad NpO_2(OH)^2_2 \quad +0.6 \quad \longrightarrow \quad NpO_2OH \quad +0.3 \quad \longrightarrow \quad NpO_2 \quad -2.1 \quad \longrightarrow \quad Np(OH)^3_- \quad -2.2 \quad \longrightarrow \quad Np
\end{align*}
\]
Np solution chemistry

- Use of Latimer diagram to construct Frost diagram
- Plot of nE versus oxidation number
  - \( nE = -\Delta G/F \)
  - Most stable oxidation state is lowest nE value
  - Slope related to potential
- Can construct Frost diagrams from Latimer diagram
  - Need to consider electrons transferred in reactions

- Electrochemical behavior of Np
- Voltammetric behavior
  - Glassy carbon electrode in acid or acetate buffer
  - 1 e\(^-\) peaks at NpO\(_2\)\(^{2+}/\)NpO\(_2\)\(^+\) and Np\(^4+/\)Np\(^3+\)
  - Used to determine standard potentials
Np solution chemistry

• Disproportionation
  ▪ NpO$_2^+$ forms Np$^{4+}$ and NpO$_2^{2+}$
    → Favored in high acidity and Np concentration
  ▪ 2NpO$_2^+$ +4 H$^+$ $\leftrightarrow$ Np$^{4+}$ + NpO$_2^{2+}$ + 2H$_2$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$_4$
      * Suggested reaction rate
        ➢ -d[NpO$_2^+$]/dt=k[NpO$_2^+$][H$^+$]$^2$

• Control of redox species
  ▪ Important consideration for experiments
  ▪ LANL write on methods
Np solution chemistry

- Oxidation state control
  - Redox reagents
    - Adjustment from one redox state to another
    - Best for reversible couples
      * No change in oxo group
      * If oxo group change occurs need to know kinetics
    - Effort in PUREX process for controlled separation of Np focused on organics
      * HAN and derivates for Np(VI) reduction
      * Rate 1\textsuperscript{st} order for Np in excess reductant
    - 1,1 dimethylhydrazine and tert-butylhydrazine selective of Np(VI) reduction over Pu(IV)
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Np solution chemistry

• Electrochemical methods (data for Ag/AgCl)
  ▪ Np(V)/Np(VI) at 1.2 V
  ▪ Np(V)/Np(III) at -0.2 V
  ▪ Np(III)/Np(IV) at 0.4 V
    → Glassy carbon or Pt electrodes

• Ultrasonic oxidation
  ▪ Np(V) to Np(VI) in HNO₃ under Ar
    → Driven by formation of HNO₂
Np solution chemistry

- Applied to Np(III) to Np(VII) and coordination complexes
  - Applied to Np(V) spin-orbit coupling for 5f²
- Absorption in HNO₃
  - 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
  - NpO₆⁵⁻
    → 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 Cs₂UO₂Cl₄ lattice
  - Electronic levels identified at following wavenumbers (cm⁻¹)
    → 6880, 13277, 15426, 17478, and 19358
    * 6880 cm⁻¹ belongs to 5f¹ configuration
Np solution chemistry

- Np(IV)
  - Absorbance from 300 nm to 1800 nm permitted assignment at 17 excited state transitions
  - IR identified Np-O vibrational bands
    → 825 cm\(^{-1}\)
  - Absorbance in nitrate
    → Variation seen for nitrate due to coordination sphere
Fig. 6.11  The absorption spectra of neptunium ions in 2 M HClO₄ solution: (a) Np(III); (b) Np(IV); (c) Np(V); (d) Np(VI).
Np solution chemistry
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
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<td>log$^*$K$_{8} = 4.50 \pm 0.06$</td>
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<td>NpO$_2$.OH(s) + H$^+$ ⇌ NpO$_2^{3+}$ + H$_2$O</td>
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<tr>
<td>NpO$_2^{2+}$</td>
<td>pot</td>
<td>25</td>
<td>1.0 M NaClO$_4$</td>
<td>NpO$_2$ + 2H$^+$ ⇌ NpO$_2^{2+}$ + 2H$_2$O</td>
<td>Cassol et al. (1972a)</td>
</tr>
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<td></td>
<td>log$^*$K$_{11} = -5.17 \pm 0.03$</td>
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<td></td>
<td>log$^*$K$_{22} = -6.68 \pm 0.02$</td>
<td>Kato et al. (1996)</td>
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<td>log$^*$K$_{35} = -18.25 \pm 0.02$</td>
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<tr>
<td></td>
<td>sol</td>
<td>25</td>
<td>0.1 M NaClO$_4$</td>
<td>NpO$_3$.H$_2$O + 2H$^+$ ⇌ NpO$_2^{2+}$ + 2H$_2$O</td>
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</tr>
</tbody>
</table>

* K$_{mn}$ is the hydrolysis constant for the equilibrium: $m$M$^{n+} + n$H$_2$O $\rightleftharpoons$ M$_m$(OH)$_n^{m-n}$ $+$ $n$H$^+$. 
Np hydrolysis

![Graph showing Np hydrolysis](image)

- **[mM]**
- **pH**
Np(III) hydrolysis
Np(IV) hydrolysis
Np(V) hydrolysis
Np(V) hydrolysis
Np(VI) hydrolysis
Np solution complexes

- Range of complexation constants available
- Oxidation state trends same as hydrolysis
- Stability trends for inorganic
  - \( F^- \rightarrow H_2PO_4^- \rightarrow SCN^- \rightarrow NO_3^- \rightarrow Cl^- \rightarrow ClO_4^- \)
  - \( CO_3^{2-} \rightarrow HPO_4^{2-} \rightarrow SO_4^{2-} \)
- \( \text{NpO}_2^+ \) forms cation-cation-cation complexes
  - Fe>In>Sc>Ga>Al
<table>
<thead>
<tr>
<th>Anion</th>
<th>Ion</th>
<th>Method</th>
<th>Temp. (°C)</th>
<th>Medium</th>
<th>Equilibrium constants</th>
<th>References</th>
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<tbody>
<tr>
<td>Fluoride, F^-</td>
<td>Np^{4+}</td>
<td>dis</td>
<td>25</td>
<td>1.0 M HClO₄</td>
<td>$\log^{*} \beta_1 = 4.60 \pm 0.20$</td>
<td>Choppin and Unrein (1976)</td>
</tr>
<tr>
<td></td>
<td>Np^{4+}</td>
<td>dis</td>
<td>25</td>
<td>2.0 M HClO₄</td>
<td>$\log^{*} \beta_1 = 4.70 \pm 0.15$</td>
<td>Bagawde et al. (1976)</td>
</tr>
<tr>
<td></td>
<td>clix, red</td>
<td>20</td>
<td>4.0 M HClO₄</td>
<td>$\log^{*} \beta_2 = 4.82 \pm 0.02$</td>
<td>Ahlander and Brandt (1966)</td>
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<td>$\log^{*} \beta_3 = 7.57 \pm 0.15$</td>
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<td></td>
<td>$\log^{*} \beta_4 = 9.85$</td>
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<td>$\log^{*} \beta_5 = 11.15$</td>
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<td>$\log^{*} \beta_6$; Np^{4+} + nHL $\rightleftharpoons$ NpL_{n-}^{4+} + nH^+</td>
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<tr>
<td></td>
<td>O₂⁻</td>
<td>dis</td>
<td>23</td>
<td>1.0 M NaClO₄</td>
<td>$\log K_1 = 1.26 \pm 0.30$</td>
<td>Choppin and Rao (1984)</td>
</tr>
<tr>
<td></td>
<td>O₂⁻</td>
<td>dis</td>
<td>25</td>
<td>2.0 M NaClO₄</td>
<td>$\log K_1 = 0.99 \pm 0.10$</td>
<td>Rao et al. (1979)</td>
</tr>
<tr>
<td></td>
<td>O₂⁻⁺</td>
<td>ise</td>
<td>20</td>
<td>0.1 M NaClO₄</td>
<td>$\log K_1 = 4.18 \pm 0.15$</td>
<td>Sawant et al. (1985)</td>
</tr>
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<td></td>
<td>$\log K_2 = 6.96 \pm 0.15$</td>
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<td></td>
<td>$\log K_3 = 9.64$</td>
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<td>$\log K_4 = 1.11 \pm 0.20$</td>
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<td>$\log K_5 = 1.14 \pm 0.40$</td>
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<td>$\log K_6 = 1.11 \pm 0.10$</td>
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<td>$\log K_{1-}$; NpO₂^{4+} + nHL $\rightleftharpoons$ NpO₂L_{n-}^{4+} + nH^+</td>
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<td>Chloride, Cl⁻</td>
<td>Np^{4+}</td>
<td>dis</td>
<td>20</td>
<td>0.5 M HClO₄</td>
<td>$\log K_1 = 0.15 \pm 0.20$</td>
<td>Shilin and Nazarov (1966)</td>
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<td>1.0 M HClO₄</td>
<td>$\log K_1 = -0.04 \pm 0.20$</td>
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<td>2.0 M HClO₄</td>
<td>$\log K_1 = -0.04 \pm 0.20$</td>
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<td>2.0 M HClO₄</td>
<td>$\log K_1 = -0.05 \pm 0.05$</td>
<td>Patil and Ramakrishna (1975)</td>
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<td></td>
<td>NpO₂^{4+}</td>
<td>dis</td>
<td>25</td>
<td>2.0 M HClO₄</td>
<td>$\log K_1 = -0.42 \pm 0.04$</td>
<td>Rao et al. (1979)</td>
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<tr>
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<td>NpO₂^{2+}</td>
<td>dis</td>
<td>25</td>
<td>2.0 M NaClO₄</td>
<td>$\log K_1 = -0.35 \pm 0.40$</td>
<td>Al-Niaimi et al. (1970b)</td>
</tr>
<tr>
<td>Bromide, Br⁻</td>
<td>Np^{4+}</td>
<td>dis</td>
<td>25</td>
<td>2.0 M HClO₄</td>
<td>$\log K_1 = -0.21 \pm 0.01$</td>
<td>Raghavan et al. (1975)</td>
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<tr>
<td>Iodide, I⁻</td>
<td>Np^{4+}</td>
<td>dis</td>
<td>25</td>
<td>2.0 M HClO₄</td>
<td>$\log K_1 = 0.04 \pm 0.30$</td>
<td>Patil et al. (1981)</td>
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<tr>
<td>Iodate, IO₃⁻</td>
<td>NpO₂^{3+}</td>
<td>dis</td>
<td>25</td>
<td>2.0 M HClO₄</td>
<td>$\log K_1 = 0.32 \pm 0.30$</td>
<td>Rao et al. (1979)</td>
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<td></td>
<td>NpO₂^{2+}</td>
<td>sp</td>
<td>25</td>
<td>0.3 M HClO₄</td>
<td>$\log K_1 = 0.61 \pm 0.02$</td>
<td>Blokhin et al. (1972)</td>
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<tr>
<td>Azide, N₃⁻</td>
<td>NpO₂^{3+}</td>
<td>sp</td>
<td>25</td>
<td>5.0 M NaClO₄</td>
<td>$\log K_1 = 1.08$</td>
<td>Musikas and Marteau (1978)</td>
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<td>$\log K_2 = 0.77$</td>
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<td>$\log K_3 = 0.38$</td>
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<tr>
<td>Nitrite, NO₂⁻</td>
<td>NpO₂⁻</td>
<td>dis</td>
<td>25</td>
<td>2.0 M NaClO₄</td>
<td>$\log K_1 = -0.05 \pm 0.05$</td>
<td>Rao et al. (1979)</td>
</tr>
<tr>
<td>Nitrate, NO₃⁻</td>
<td>NpO₃⁻</td>
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</tbody>
</table>
Np organic solution complexes

• Most data with Np(V)
• Evaluated with spectroscopy
  ▪ Monocarboxylic ligands
    → 1:3 Np:L ratio
    → Complexation constants increase with increasing pKa of ligand
  ▪ Aromatic polycarboxylates
    → Strength based on number of carboxylic acids
Analytical methods

• Environmental levels
  ▪ General levels 1E-15 g/L
  ▪ Elevated levels up to 1E-11 g/L

• Radiometric methods
  ▪ Alpha
    → 2.6E7 Bq/g
    → Isolation from seawater
    * Hydroxide co-precipitation, ion-exchange, LaF₃, solvent extraction with HTTA
  ▪ Liquid scintillation
  ▪ Activation analysis
    → Formation of $^{238}$Np
    * 170 barns, 2.117 day half life for $^{238}$Np
    * 500 more sensitive than alpha spectroscopy
Soil sample (10 - 40 g)

Leaching (aqua regia, \(^{239}\)Np spike)

Isopropylether extraction (remove Fe)

Np reduction (to Np(IV) with HI)

TOA extraction of Np (IV)

Back-extraction of Np (IV)
with 1 M HCl + 0.1 M HF

Np reduction (Np(IV) with \(\text{NH}_2\text{OH} + \text{HCl}\))

Co-precipitation of Np(IV) with \(\text{LaF}_3\)

Anion-exchange chromatography
8 M HNO\(_3\), Dowex 1 × 8

→ Sample in 8 M HNO\(_3\), wash

→ 8 M HNO\(_3\), wash (U off)

→ 10 M HCl, wash (Th off)

→ 10 M HCl + 0.1 M Hl (Pu off)

4 M HCl (Np elution)

Dissolution in 1 M HNO\(_3\) (20 ml)

\(^{239}\)Np measurement (γ spectrometry)

\(^{237}\)Np measurement (ICP-MS)

Fig. 6.12 Chemical separation scheme for the determination of \(^{237}\)Np by high-resolution ICP-MS. (Yamamoto et al., 1994, with permission from Elsevier Science).
Analytical methods

• Spectrophotometric methods
  ▪ Direct absorbance
    → Detection limit in M (1 cm cell, 0.02 absorbance)
      * Np(III) 5E-4, Np(IV) 1E-4, Np(V) 5E-5, Np(VI) 5E-4
    → Laser induced photoacoustic spectroscopy (LIPAS)
    → Increase factor by over an order of magnitude
  ▪ Indicator dyes
  ▪ Fluorescence
    → New work in tetrachlorides and solids
    → Luminescence at 651 nm and 663 nm from Np in CaF$_2$ at 77 K
• X-ray fluorescence
• Mass spectroscopy
Analytical methods

• Moessbauer spectroscopy
  - $^{237}\text{Np}$
    $\rightarrow$ 68 ns excited state lifetime
    $\rightarrow$ Isomer shift suitable for analysis of chemical bonds
    $\rightarrow$ Can record radiation spectrum from absorber
      * 60 keV from $^{241}\text{Am}$
    $\rightarrow$ Shift correlated with oxidation state and number of 5f electrons present
Fig. 6.14  Isomer shifts of Np(IV), (V), (VI), and (VII) compounds.
Fig. 3. $^{237}$Np Mössbauer spectra of NpFeGa$_6$ at 10 K.