Solvent Extraction

- Based on separating aqueous phase from organic phase
- Used in many separations
  - U, Zr, Hf, Th, Lanthanides, Ta, Nb, Co, Ni
  - Can be a multistage separation
  - Can vary aqueous phase, organic phase, ligands
  - Uncomplexed metal ions are not soluble in organic phase
  - Metals complexed by organics can be extracted into organic phase
- Considered as liquid ion exchangers
Extraction Reaction

- Phases are mixed
- Ligand in organic phase complexes metal ion in aqueous phase
  - Conditions can select specific metal ions
    - oxidation state
    - ionic radius
    - stability with extracting ligands
- Phase are separated
- Metal ion removed from organic phase
  - Evaporation
  - Back Extraction
Solvent extraction

• Influence of chemical conditions
  • Solvent
    ⇒ Overall extraction, phase splitting
  • Metal ion and acid concentration
    ⇒ Phase splitting

• Distribution coefficient
  • \([M]_{\text{org}}/[M]_{\text{aq}} = K_d\)
  • Used to determine separation factors for a given metal ion
    ⇒ Ratio of \(K_d\) for different metal ions
  • Distribution can be used to evaluate stoichiometry
    ⇒ Evaluation distribution against change in solution parameter
      * Plot log \(K_d\) versus log \([X]\), slope is stoichiometry

• Extraction can be explained by complexation
  • Used to determine complexation constants
  • Consider all speciation in aqueous and organic phase
Mechanism

• Solvation
  - Extraction of neutral complex
    $\Rightarrow \text{UO}_2(\text{NO}_3)_2$ forms with TBP
    * Equilibrium shifts with nitrate, back extraction into aqueous at low nitric acid

• Ion exchange
  - Metal ion exchanged into organic phase, ion transfer in aqueous phase
  - Use of organic soluble acid
    $\Rightarrow$ i.e., alkyl phosphinic acid ($R_2\text{PO}_2\text{H}$)

• Ion pair extraction
  - Charged metal complex with extractant of opposite charge
    $\Rightarrow$ i.e., Quaternary ammonium salt with anionic actinide nitrate
Figure 4.6 Effect of nitrates on distribution of $\text{UO}_2(\text{NO}_3)_2$ between diethyl ether and water. ○, saturated solution; temperature 25°C. (From Furman et al. [F2].)

$(\text{CH}_3\text{CH}_2)_2\text{O}$ Diethyl ether
Effect of nitric acid concentration on extraction of uranyl nitrate with TBP
Reactions

• **Tributyl Phosphate (TBP)**

  \[(\text{C}_4\text{H}_9\text{O})_3\text{P}=\text{O}\]

  Resonance of double bond between P and O

  \[\text{UO}_2^{2+\text{(aq)}} + 2\text{NO}_3^-\text{(aq)} + 2\text{TBP\text{(org)}} \rightleftharpoons \text{UO}_2(\text{NO}_3)_2\cdot2\text{TBP\text{(org)}}\]

  Consider \(\text{Pu}^{4+}\)

• **Thenoyltrifluoroacetone (TTA)**

![Chemical structures of TTA in different forms: Keto, Enol, and Hydrate.](image_url)
TTA

• General Reaction

\[ M^{z+}_{(aq)} + zHTTA_{(org)} \iff M(TTA)_z_{(org)} + H^+_{(aq)} \]

What is the equilibrium constant?

Problems with solvent extraction

• Waste
• Degradation of ligands
• Ternary phase formation
• Solubility
Table 8A3. Equilibrium constants, log $K_{11}$, of metal diketonates in benzene at room temperature.

<table>
<thead>
<tr>
<th>Metal diketonate</th>
<th>Acetylacetone</th>
<th>Benzoyleceton</th>
<th>Thenoyltrifluoroacetone</th>
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</thead>
<tbody>
<tr>
<td>AgX</td>
<td>-2.79</td>
<td>-7.8</td>
<td>-4.65</td>
</tr>
<tr>
<td>TiX</td>
<td>-16.65</td>
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<tr>
<td>BeX3</td>
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<tr>
<td>CaX2</td>
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<tr>
<td>SrX2</td>
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<td>-5.34</td>
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<td>BaX2</td>
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<td>-5.32</td>
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<tr>
<td>ZnX2</td>
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<td>-7.6</td>
<td>-5.23</td>
</tr>
<tr>
<td>CdX2</td>
<td>-1.39</td>
<td>-0.5</td>
<td>+3.30</td>
</tr>
<tr>
<td>CuX2</td>
<td>-5.51</td>
<td>-6.30</td>
<td>-4.34</td>
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<tr>
<td>CoX2</td>
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<td>-9.30</td>
<td>-7.39</td>
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<tr>
<td>NiX2</td>
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<td>-10.51</td>
<td>-8.86</td>
</tr>
<tr>
<td>PbX2</td>
<td>-9.43</td>
<td>-8.06</td>
<td>-8.06</td>
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<tr>
<td>MnX2</td>
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<td>-7.68</td>
<td>-7.66</td>
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<tr>
<td>PdX2</td>
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<td>-7.57</td>
<td>-7.57</td>
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<td>-7.6</td>
<td>-5.23</td>
</tr>
<tr>
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<td>-0.5</td>
<td>+3.30</td>
</tr>
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<td>-6.30</td>
<td>-4.34</td>
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<td>InX3</td>
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<td>-7.39</td>
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<td>BiX3</td>
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<tr>
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<td>-7.66</td>
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<td>-7.57</td>
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<td>-18.9</td>
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<td>HoX3</td>
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<td>-7.57</td>
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<td>-7.57</td>
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<td>-6.77</td>
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<tr>
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<td>-7.57</td>
</tr>
<tr>
<td>PuX3</td>
<td>-6.72</td>
<td>-6.77</td>
<td>-6.77</td>
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<tr>
<td>AmX3</td>
<td>-18.9</td>
<td>-7.57</td>
<td>-7.57</td>
</tr>
<tr>
<td>CmX3</td>
<td>-5.51</td>
<td>-6.30</td>
<td>-5.51</td>
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<td>BkX3</td>
<td>-18.9</td>
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<td>CfX3</td>
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<td>-7.57</td>
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<td>EsX3</td>
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<td>-7.57</td>
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<tr>
<td>FmX3</td>
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<td>-7.57</td>
<td>-7.57</td>
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<tr>
<td>ThX4 (**)</td>
<td>-12.16</td>
<td>-7.68</td>
<td>-0.90</td>
</tr>
<tr>
<td>HfX4 (**)</td>
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<td>+0.90</td>
<td>+1.88</td>
</tr>
<tr>
<td>U**+X4</td>
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<td>+0.90</td>
<td>+1.88</td>
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<tr>
<td>Np**+X4</td>
<td>+1.88</td>
<td>+0.90</td>
<td>+1.88</td>
</tr>
<tr>
<td>P**+X4</td>
<td>+1.88</td>
<td>+0.90</td>
<td>+1.88</td>
</tr>
<tr>
<td>PaX4 (**)</td>
<td>-4.68</td>
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<td>-1.37</td>
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<td>UO2X3,HX</td>
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<td>-1.37</td>
</tr>
<tr>
<td>PuO2X2</td>
<td>-4.68</td>
<td>-1.37</td>
<td>-1.37</td>
</tr>
</tbody>
</table>

a) In toluene rather than benzene.
Chart Fe 6  Diisopropyl ketone

Chart Fe 5  Methyl isobutyl ketone (hexone)
Chart Fe 1  Methyl isobutyl ketone (hexone)
Chart Fe 7  0.11 M Triisooctylamine in xylene

Chart Fd 2  Undiluted tributyl phosphate
Chart Fd 3  Undiluted tributyl phosphate
Non-ideal behavior

- Variation in chemical condition during extraction
  - Change in acidity
- Extractant saturation
  - Metal or competing ion
- Phase dissolution
  - Solubility into other phase
- Degradation
- Third phase formation
Third phase formation

- Brief review of third phase formation
- Related prior research
- Laboratory methods
- Np third phase behavior
- Comparison with U and Pu
- Spectroscopic observations
Third Phase Formation

• In liquid-liquid solvent extraction certain conditions cause the organic phase to split
  → PUREX separations using tributyl phosphate (TBP)
  → Possible with future advanced separations

• Limiting Organic Concentration (LOC) – highest metal content in phase prior to split
• Light phase – mostly diluent
• Heavy phase – extractant and metal rich
  → Problematic to safety!
Actinide Third Phases

Light Phase
Heavy Phase
Aqueous Phase

Pu(IV)
Np(IV)
U(VI)
Pu(VI)
Np(VI)
Importance to Safety

• Increased risk of criticality
• Phase inversion
• Difficulty in process fluid separations
• Carry-over of high concentration TBP to heated process units
  → Possible contribution to Red Oil event at Tomsk, Russia
Phase Inverted Plutonium

- Light Organic
- Heavy Organic
- Aqueous
- Inverted Organic
Prior Research

- Majority of work focused on defining LOC boundary (reviewed by Rao and Kolarik)
  - Effects of temp., concs., acid, diluent, etc.

- Recent work on possible mechanisms
  - Reverse micelle evidence from neutron scattering (Osseo-Asare; Chiarizia)
  - Spectroscopic studies - UV, IR, EXAFS (Jensen)
Reverse Micelle Theory

Possible Reverse Micelle

\[ \text{Classical Stoichiometry} \]

\[ \text{UO}_2^{2+} + 2\text{NO}_3^- + 2\text{TBP} \rightarrow \text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP} \]
Role of the Metal

- LOC behavior well known for U(VI), U(IV), Pu(IV), and Th(IV)
- Little data available on Pu(VI)
- No data on any Np systems
- Mixed valence systems not understood
Mixed Systems

• Observed effect of Pu(VI) in HPT vs. C_{12}
• Large impact of presence of Pu(VI) in HPT
  - Indications heavy phase enriched in Pu(VI)
• Opposite found with U(VI) inhibiting phase separation in U(IV) system (Zilberman 2001)

→ Suggests possible role of trinitrato species
  \[ \text{AnO}_2(\text{NO}_3)_3^- \]
Neptunium Study

- Unique opportunity to examine trends in the actinides [LOC curve for U(IV) vs Pu(IV)]
  - Effective ionic charge
  - Ionic radii
  - Stability constants for trinitrato species
- Never been investigated
- Ease of preparing both tetravalent and hexavalent nitrate solutions
Neptunium Methods

• Worked performed at Argonne National Laboratory, Argonne, IL
• Stock prepared from nitric acid dissolution of $^{237}$Np oxide stock
• Anion exchange purification
  - Reillex HPQ resin, hydroquinone (Pu reductant), hydrazine (nitrous scavenger)
• Np(IV) reduction with hydrogen peroxide reduction
• Np(VI) oxidation with concentrated HNO$_3$ under reflux
LOC Behavior

- Np(VI) near linear
- Np(IV) slight parabolic
  - Appears between linear U(IV) and parabolic Pu(IV)
- Both curves similar resemblance to distribution values Purex systems
  - Suggests possible link with metal-nitrate speciation
Np Third Phase Boundaries

![Graph showing Np Third Phase Boundaries](image-url)
## Comparison with Other Actinides

**LOC in 7M HNO<sub>3</sub> / 1.1M TBP/dodecane 20-25 °C, M**

<table>
<thead>
<tr>
<th></th>
<th>U</th>
<th>Np</th>
<th>Pu</th>
</tr>
</thead>
<tbody>
<tr>
<td>An (IV)</td>
<td>0.08</td>
<td>0.15</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>(Wilson 1987)</td>
<td></td>
<td>(Kolarik 1979)</td>
</tr>
<tr>
<td>An (VI)</td>
<td>No 3Φ</td>
<td>0.17</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>(Chiarizia 2003)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Organic Nitric Acid

- Balance available TBP and organic H⁺
- Np(IV) = mixture of the monosolvate (TBP · HNO₃) and hemisolvate (TBP · 2HNO₃) species
- Np(VI) = hemisolvate

→ Agrees with literature data on U(VI) and Th(IV) acid speciations
Valence Trends – An (IV)

• General trend = decreasing LOC as ionic radii increases
  → Lowest charge density = lowest LOC
• Np intermediate between U and Pu
• Literature Th(IV) data consistent with trend
Valence Trends – An(VI)

• An(VI) = LOC increases as ionic radii decreases
  ➔ Opposite trend for An(IV), including Th(IV)

• Charge density using effective cationic charge and 6-coordinate radii

  ➔ No evidence of correlation with charge density within error of effective charge data

• Oxo group interactions not fully considered

  ➔ Future work required
Spectral Study Methods

- Look for spectral trends in Np(VI) system
- Examined trends for:
  - LOC
  - Metal loading
  - Nitrate loading (using NaNO₃)
- 5 mm quartz cuvette with Cary 5 Spectrometer
LOC Spectra

Np(VI) 30% TBP / dodecane at LOC

Absorbance

Wavelength, nm

[HNO₃], M
4
6
7
8
10
Metal Loading

Absorbance

[Wp(VI)]_org, M
LOC = 0.27
0.18
0.09
0.03

900 1000 1100 1200 1300
Wavelength, nm
Nitrate Effects

\[ [\text{NO}_3^-], \text{M} \]
- 4
- 5
- 6
- saturated

\[ [\text{H}^+], \text{M} = 4 \]

\[ [\text{Np(VI)}], \text{M} = 0.03 \]

Aqueous

Organic

\[ [\text{H}^+] = 4 \text{M}, [\text{Np(VI)}] = 0.03 \text{M} \]
Valence Scoping Experiments

- Examined various mixes of Pu(IV)/Pu(VI)
- Solutions prepared by method of slow addition of concentrated HNO₃ to heated syrupy Pu nitrate solution
- Use UV-Vis peak analysis for determination of initial aqueous composition
- Perform mole balance on aqueous phase before and after contact for organic content of each valence species (some samples)
Spectrum – Mixed Valence Phases

Absorbance

Pu^{4+} (489 nm)

Pu^{6+} (835 nm)

Wavelength (nm)

Normal
Heavy
Light
Third phase conclusions

• Third phase behavior measured in Np
• LOC trends consistent with U and Pu
• Np(IV) LOC trends with charge density
• No clear correlation for Np(VI)
• Spectroscopic evidence suggests possible role of trinitrato species in third phase
Basic decay equations

- The radioactive process is a subatomic change within the atom.
- The probability of disintegration of a particular atom of a radioactive element in a specific time interval is independent of its past history and present circumstances.
- The probability of disintegration depends only on the length of the time interval.

Probability of decay: \( p = \lambda \Delta t \)

Probability of not decaying: \( 1 - p = 1 - \lambda \Delta t \)
Statistics of Radioactive Decay

1 - p = 1 - \lambda \Delta t = \text{probability that atom will survive } \Delta t

(1 - \lambda \Delta t)^n = \text{probability that atom will survive } n \text{ intervals of } \Delta t

n\Delta t = t, \text{ therefore } (1 - \lambda \Delta t)^n = (1 - \lambda t/n)^n

Since \lim_{n \to \infty} (1 + x/n)^n = e^x, (1 - \lambda t/n)^n = e^{-\lambda t}, \text{ the limiting value.}

Considering \( N_0 \) atoms, the fraction remaining unchanged after time \( t \) is \( N/N_0 = e^{-\lambda t} \)

\[
N = N_0 e^{-\lambda t}
\]

where \( \lambda \) is the decay constant
Radioactivity as Statistical Phenomenon

- Binomial Distribution for Radioactive Disintegrations
  - The probability $W(m)$ of obtaining $m$ disintegrations in time $t$ from $N_0$ original radioactive atoms is given by:
  $$W(m) = \frac{N_0^m}{(N_0-m)!m!} p^m (1-p)^{N_0-m}$$

- The probability of an atom not decaying in time $t$, i.e., $1-p$, is $(N/N_0) = e^{-\lambda t}$, where $N$ is the number of atoms that survive in time interval $t$ and $N_0$ is the initial number of atoms.

- Time Intervals between Disintegrations
  - The probability of a time interval having value between $t$ and $t+d$ is given by:
  $$P(t)dt = N_0 \lambda e^{-N_0 \lambda t} dt$$
• **Average Disintegration Rate**

\[ W(r) = \frac{n!}{(n-r)!r!} p^r q^{n-r} \]

where \( 1-p=q \)

\[ np = \sum_{r=0}^{n} rW(r) = \bar{r} \]

★ for radioactive disintegration--if \( n=N_0 \) and \( p=1-e^{-\lambda t} \)--average number \( M \) of atoms disintegrating in time \( t \) is \( M=N_0(1-e^{-\lambda t}) \); for small \( \lambda t \), \( M=N_0\lambda t \) and disintegration \( R=M/t=N_0\lambda \), which corresponds to \(-dN/dt=\lambda N\)

• **Expected Standard Deviation**

\[ \sigma = \sqrt{N_0(1-e^{-\lambda t})e^{-\lambda t}} = \sqrt{Me^{-\lambda t}} \]

*Since in counting practice \( \lambda t \) is generally small, \( \sigma = \sqrt{M} \)*

• **M** is number of counts

• **Relative error** = \( \sigma^{-1} \)