Analysis of Elevated Temperature Data for Thermodynamic Properties of Selected Radionuclides

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Analysis of Elevated Temperature Data  
for Thermodynamic Properties of Selected Radionuclides  

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1. Introduction  

This report is a review of chemical thermodynamic data for Ni, Zr, Tc, U, Np, Pu and Am in aqueous solutions at elevated temperatures. Thermodynamic data for aqueous reactions over the temperature range 20-150°C are needed for geochemical modeling studies of the Yucca Mountain Project [96PAL]. The present review is focused on the aqueous complexes relevant to expected conditions in the Yucca Mountain region: primarily the hydroxide, carbonate, sulfate and fluoride complexes with the metal ions. Existing thermodynamic data are evaluated, and means of extrapolating 25°C data to the temperatures of interest are discussed. There will be a separate review of solubility data for relevant Ni, Zr, Tc, Np, Pu and Am compounds (milestone SPL4C2M4).  

2. Scope and Methods  

The chemical composition of groundwaters in the vicinity of Yucca Mountain has been discussed in [88DOE] and [96PAL]. The water from well J-13 is thought to be representative of interstitial and fracture waters in the Yucca Mountain region and is used as the reference water in this review. The effect of temperature on the composition of J-13 water in contact with Yucca Mountain tuff has been investigated in several studies [84KNA, 85KNA1, 85KNA2, 85OVE, 86KNA, 87KNA]. The studies indicate only minor changes in solution composition as the temperature is increased from 25 to 150°C. The principal changes are an increase in dissolved Si and a slight decrease in dissolved Mg, Ca and carbonate. The J-13 water composition at 25°C and the suggested maximum concentrations in interstitial and fracture waters at high temperatures [86GLA] are summarized in Table 1. Expected water compositions in the Yucca Mountain region are the subject of current research [97GLA, 97VIA].
Table 1a: Cation concentrations (mg/L) of reference waters.

<table>
<thead>
<tr>
<th>Water</th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Mg</th>
<th>Ca</th>
<th>Mn</th>
<th>Fe</th>
<th>Al</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>J-13</td>
<td>0.06</td>
<td>45</td>
<td>5.3</td>
<td>1.76</td>
<td>12</td>
<td>0.001</td>
<td>0.04</td>
<td>0.03</td>
<td>30</td>
</tr>
<tr>
<td>high temp.</td>
<td>&lt;65</td>
<td>&lt;15</td>
<td>&lt;5</td>
<td>&lt;15</td>
<td>-</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;160</td>
<td></td>
</tr>
</tbody>
</table>

Table 1b: Anion concentrations (mg/L) and pH of reference waters.

<table>
<thead>
<tr>
<th>Water</th>
<th>F^-</th>
<th>Cl^-</th>
<th>NO_3^-</th>
<th>HCO_3^-</th>
<th>SO_4^{2-}</th>
<th>O_2</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>J-13</td>
<td>2.1</td>
<td>6.4</td>
<td>10</td>
<td>143</td>
<td>18</td>
<td>5.7</td>
<td>6.9</td>
</tr>
<tr>
<td>high temp.</td>
<td>&lt;5</td>
<td>&lt;10</td>
<td>&lt;15</td>
<td>&lt;140</td>
<td>&lt;25</td>
<td>-</td>
<td>6.9-7.6</td>
</tr>
</tbody>
</table>

To prioritize chemical species, we will focus on species for each element M (M=Ni, Zr, Tc, U, Np, Pu or Am) which account for more than 1% of the total M concentration $C_M$ in J-13 water spiked with M. Significant species have been identified based on equilibrium calculations using HYDRAQL [88PAP] for Ni, Zr and Tc, and EQ3/6 for U, Np, Pu and Am [92PAL]. Anion concentrations in the reference water are approximately independent of temperature, so the temperature dependence of the chemical species distribution for a given element depends on the temperature dependence of the formation constants of the complexes. For inorganic complex formation in aqueous solution, the enthalpy of reaction rarely exceeds 25-30 kJ mol$^{-1}$ [93MAR]. Thus, the formation constant rarely increases by a factor of 10 over the range 25-100°C (see Eq. (1) below). In an equilibrium model, the most likely result of a change in temperature is a redistribution among the species which have significant concentrations at 25°C.

### 3. Temperature Extrapolations

Most of the available thermodynamic data for aqueous reactions has been derived from experiments at or near 25°C. To model an equilibrium at another temperature, the equilibrium quotient $K^o$ is extrapolated from the reference temperature $T_0$ to the temperature of interest $T$. Discussions of temperature extrapolation methods for aqueous species and reactions are given in [61PIT, 88SHO, 96STU, 97PUI]. Generally only the simpler methods are appropriate here, due to the limited amount of experimental data for the reactions of interest.

If the enthalpy of reaction $\Delta H^o$ is assumed to be constant over the temperature range $T_0$ to $T$ (this is equivalent to neglecting the heat capacity of reaction $\Delta C_p^o$ over the range $T_0$ to $T$), then the equilibrium constant is approximated by the van't Hoff equation

$$\log K^o(T) = \log K^o(T_0) + \frac{\Delta H^o(T_0)}{2.303R} \left( \frac{1}{T_0} - \frac{1}{T} \right)$$

(1)

Here $R$ is the gas constant 8.3145 J mol$^{-1}$ K$^{-1}$. Eq. (1) is often used over small temperature ranges (about 10 K or less), because the error due to neglecting $\Delta C_p^o$ is small compared to the uncertainty in $\log K^o(T_0)$.
Eq. (1) is valid over larger temperature intervals (from about 20 to 200°C) if the reaction is "isoelectric" [38GUR, 88SHO, 97PUI]. An aqueous reaction is defined as isoelectric when the sum of positive charges and the sum of negative charges are the same for reactants and products, for example,

\[ \text{Am}^{3+} + \text{H}_2\text{O} = \text{Am(OH)}^{2+} + \text{H}^+ \]  

(2)

In this case Eq. (1) can be used over larger temperature intervals because part of the enthalpy of reaction arises from electrostatic interactions between the reaction species and the solvent water. The dielectric constant of water depends on the temperature, and the electrostatic terms make the dominant contribution to the heat capacity of reaction. For isoelectric reactions, the electrostatic terms tend to cancel, so the heat capacity of reaction is small.

Complexation reactions can often be converted to isoelectric form by combination with acid dissociation reactions. For example, reaction (5) is the sum of reactions (3) and (4):

\[ \text{Am}^{3+} + \text{CO}_3^{2-} = \text{AmCO}_3^+ \]  

(3)

\[ \text{H}_2\text{CO}_3 = \text{CO}_3^{2-} + 2\text{H}^+ \]  

(4)

\[ \text{Am}^{3+} + 2\text{H}_2\text{CO}_3 = \text{AmCO}_3^+ + 2\text{H}^+ \]  

(5)

If \( K_{(3)}^0 \) and \( \Delta H_{(3)}^0 \) denote the equilibrium constant and enthalpy change for reaction (X), then

\[ \log K_{(3)}^0(T) = \log K_{(3)}^0(T_0) + \log K_{(4)}^0(T) \]  

(6)

\[ \Delta H_{(3)}^0(T) = \Delta H_{(3)}^0(T_0) + \Delta H_{(4)}^0(T) \]  

(7)

Acid dissociation data have been determined for the complexes of interest, and uncertainties in the acid constants are \( \leq 0.03 \) log units over the range 20-100°C. Data for the acid dissociation reactions can be found in the following references: \( \text{H}_2\text{O} [81\text{MAR}], \text{H}_2\text{CO}_3 [82\text{PLU,82PAT,84PAT}], \text{HF} [63\text{ELL}], \text{H}_2\text{SO}_4 \) and \( \text{H}_3\text{PO}_4 [86\text{SMI}] \).

Using the example above, if experimental values of \( \log K_{(3)}^0 \) are available at several temperatures, a two-parameter fit to the data can be made using Eqs. (1) and (6). Alternatively, if experimental values of \( \log K_{(3)}^0(T_0) \) and \( \Delta H_{(3)}^0(T_0) \) are available, Eqs. (6) and (7) at \( T=T_0 \) determine \( \log K_{(3)}^0(T_0) \) and \( \Delta H_{(3)}^0(T_0) \), which can then be substituted in Eq. (1).

If \( \Delta C_p^0 \) is treated as a nonzero constant over the temperature range \( T_0 \) to \( T \), the expression for the equilibrium constant is

\[ \log K^0(T) = \log K^0(T_0) + \frac{\Delta H^0(T_0)}{2303R} \left( \frac{T_0}{T} - 1 \right) + \frac{\Delta C_p^0}{2303R} \left( \frac{T_0}{T} - 1 + \ln \frac{T}{T_0} \right) \]  

(8)

There is sufficient experimental data to determine \( \Delta C_p^0 \) for only a few of the reactions of interest. Estimates of \( \Delta C_p^0 \) based on the Criss-Cobble method have been made for some of the U and Pu reactions [80LEM].

4. Ni

Ni is very soluble (to about 0.1 m) as Ni(II) in J-13 water at 25°C. The solubility-controlling solid is Ni(OH)_2, so the Ni solubility is sensitive to pH. Significant aqueous
species are Ni\(^{2+}\) (97% of \(C_{Ni}\)) and NiSO\(_{4}\)\(^{-}\) (3% of \(C_{Ni}\)). These conclusions are based on the equilibrium constants selected in [93MAR].

The complex formation reaction \(Ni^{2+} + SO_{4}^{2-} = NiSO_{4}^{-}\) has been investigated by calorimetry at temperatures near 25°C [59NAI, 69IZA, 73POW] and by electrical conductivity measurements over the range 0 to 45°C [73KAT]. Thermodynamic constants have been calculated from heat of dilution data [70LAR]. A study of the complexation reaction was made by ultraviolet absorption in 5 M perchlorate media and temperatures in the range 25 to 70°C, but the precision was low and extrapolation of the results to low ionic strength is subject to large errors [77ASH]. The experimental results are listed in Table 2. There is a large spread in the values of \(\Delta H^0\). The value of \(\Delta H^0\) selected in [93MAR] is also listed in Table 2. If the smallest experimental values of \(\Delta H^0\) are correct, there is practically no change in the Ni speciation over the range 25-150°C. If the largest experimental value of \(\Delta H^0\) is correct, there is a modest increase in the NiSO\(_{4}\)\(^{-}\) concentration as the temperature increases, and NiSO\(_{4}\)\(^{-}\) accounts for roughly 10% of \(C_{Ni}\) at 100°C.

### Table 2: Thermodynamic data for the reaction \(Ni^{2+} + SO_{4}^{2-} = NiSO_{4}^{-}\).

<table>
<thead>
<tr>
<th>Method</th>
<th>(log K^0)</th>
<th>(\Delta H^0) kJ mol(^{-1})</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>calorimetry</td>
<td>2.32</td>
<td>13.9</td>
<td>[59NAI]</td>
</tr>
<tr>
<td>calorimetry</td>
<td>2.81 ± 0.09</td>
<td>1.72 ± 0.08</td>
<td>[69IZA]</td>
</tr>
<tr>
<td>calorimetry</td>
<td>not stated</td>
<td>1.75 ± 0.15</td>
<td>[73POW]</td>
</tr>
<tr>
<td>conductivity</td>
<td>2.27</td>
<td>5.3</td>
<td>[73KAT]</td>
</tr>
<tr>
<td>heat of dilution</td>
<td>2.30 ± 0.04</td>
<td>6.4 ± 0.8</td>
<td>[70LAR]</td>
</tr>
<tr>
<td>tabulated data</td>
<td>2.34 ± 0.06</td>
<td>5.8</td>
<td>[93MAR]</td>
</tr>
</tbody>
</table>

The hydrolysis of \(Ni^{2+}\) has been investigated by solubility studies of NiO to 300°C [80TRE]. Equilibrium quotients for the formation of \(NiOH^+\), \(Ni(OH)_2^0\), and \(Ni(OH)_3^-\) were determined over the temperature range 20 to 300°C. Although hydrolysis becomes more pronounced at higher temperatures, hydrolyzed Ni(II) species are not significant at temperatures below 150°C and \(pH < 9\).

Calorimetric studies of the formation of NiF\(^+\) have been made in 0.5 M nitrate medium [74ARU], 3 M perchlorate medium [76KUL] and 0.1 to 3 M perchlorate media [81KUL]. The results indicate the enthalpy of reaction is small at low ionic strengths. We estimate that \(\Delta H^0\) is between 0 and 3 kJ mol\(^{-1}\), and NiF\(^+\) does not become significant under expected conditions.

The value of \(log K^0\) for the formation of NiHPO\(_4\)\(^{-}\) is about 2 [67SIG, 72FRE]. Phosphate concentrations are very low in waters of the Yucca Mountain region, so Ni(II) phosphate complexes are not significant under the conditions of interest.

The Ni species in aqueous solutions under expected repository conditions are relatively well-understood. It is most likely that Ni\(^{2+}\) remains the dominant species over the temperature range of interest. The most significant gap is the lack of data on the formation of NiCO\(_3\)\(^0\) at elevated temperatures.
5. Zr

At 25°C the equilibrium Zr concentration in J-13 water is less than $10^{-8}$ m due to the low solubility of ZrO$_2$. Likely solution species are Zr(OH)$_4^0$, and at higher pH values, Zr(OH)$_5^{-}$. Stability constants for Zr(IV) carbonate and phosphate complexes were not available, so their values were estimated from data for quadrivalent actinides.

In a review of data to 1992, a self-consistent set of thermodynamic constants was listed for Zr, ZrO$_2$ and Zr(OH)$_4$ solids, aqueous Zr$^{4+}$ and the Zr(IV) hydrolysis species [92SLO]. The thermodynamic constants listed for the hydrolysis species were estimates based on limited experimental data. Understanding of Zr(IV) hydrolysis behavior is largely derived from solubility experiments and distribution experiments (extraction or ion exchange). Interpretation of the experimental results is complicated by the tendency of Zr(IV) to form polynuclear species or colloids and errors due to extrapolation of high ionic strength data to standard conditions. One study has been made near 25°C by spectrophotometry of competing complexes in 0.1 M perchlorate and nitrate media [69NAZ].

Thermodynamic functions for Zr(IV) fluoride complex formation in 4 M perchlorate medium have been determined from stability constant and calorimetric measurements [90AHR]. The experiments illustrate a fundamental problem in the study of Zr(IV) complexes (which also applies to Tc(IV) and actinide(IV) complexes). To avoid hydrolysis of Zr$^{4+}$, measurements must be performed in a strongly acid medium of high ionic strength, and extrapolation of the data to low ionic strength is subject to large errors. The alternative is to perform experiments in low ionic strength media and include hydrolysis in the data analysis, but then errors in the hydrolysis constants affect the results.

Stability constants for Zr(IV) sulfate complexes are fairly well-known at high ionic strength and 25°C, but no data was found for the elevated temperature behavior. No experimental data was found for Zr(IV) carbonate or phosphate complex formation.

There is only a small amount of data available for Zr(IV) hydrolysis and complex formation under expected repository conditions. This is partly due to the practical difficulties mentioned above. The Zr solubility is likely to remain low under conditions of interest, so a detailed understanding of the complexation behavior may not be necessary. A more limited set of solubility experiments may establish that maximum Zr concentrations are very small under expected repository conditions.

A review of the chemical thermodynamics of Ni and Zr is currently being conducted by the Yucca Mountain Project and will result in a database for Ni and Zr which is internally consistent with the Nuclear Energy Agency Thermodynamic Data Base (NEA-TDB) data for Tc, U [92GRE, 95GRE], Np, Pu and Am [95SIL].

6. Tc

Tc is highly soluble as pertechnetate ion TcO$_4^-$ in J-13 water at 25°C. TcO$_4^-$ is probably the only significant aqueous Tc species under J-13 conditions. HTcO$_4$ is a strong acid. There is not much data on pertechnetate complexes in aqueous solution, but based
on ion charge to radius ratios, the pertechnetate complexes are expected to be much weaker than the corresponding hydroxide, fluoride, sulfate, or carbonate complexes.

The Tc(VII)/Tc(IV) redox equilibrium has a critical effect on the behavior of Tc under expected repository conditions [96PAL]. At 25°C and reducing conditions such as USW H-3, the Tc concentration is limited to low values (< 10^{-7} m) by the solubility of TcO_2\cdot xH_2O. Under oxic conditions such as J-13, the Tc solubility is high and is controlled by pertechnetate salts [84KER].

The Tc(VII)/Tc(IV) redox equilibrium has been investigated by emf measurements of TcO_2\cdot xH_2O electrodes in contact with TcO_4^- solutions at 24-25°C [53COB, 55CAR, 91MEY]. The reaction can be written as

\[
\text{TcO}_4^- + 4 \text{H}^+ + 3e^- = \text{TcO}_2\cdot x\text{H}_2\text{O}(s) + (2-x)\text{H}_2\text{O}
\]  

The Nernst equation for reaction (9) is

\[
E = E^0 + \frac{2303RT}{3F} \left( \log a(TcO_4^-) - 4pH \right)
\]

where

- \( E \) is the potential,
- \( R \) is the ideal gas constant,
- \( F \) is the Faraday constant,
- \( a(TcO_4^-) \) is the TcO_4^- activity.

The standard potential \( E^0 \) is 0.75 ± 0.02 V [91MEY]. The Nernstian behavior has been verified as a function of pH and TcO_4^- activity, but not temperature.

There is little or no data available on the temperature dependence of Tc complexation reactions in aqueous solutions. However, the Tc(VII)/Tc(IV) redox equilibrium has a strong effect on the Tc solubility and is likely to be the critical issue for repository modeling. The Tc(VII)/Tc(IV) redox behavior is relatively well-understood at 25°C. The validity of temperature extrapolations using the Nernst equation could be verified by emf measurements on TcO_2\cdot xH_2O electrodes at a number of temperatures. High carbonate or Si concentrations may alter the TcO_2\cdot xH_2O surface and this could be checked by measurements in various solutions. A small number of Tc solubility experiments in reference waters may also help verify the expected behavior.

The NEA-TDB review of the chemical thermodynamics of Tc is in preparation.

7. U

U is sparingly soluble (to about 10^{-6} m) as U(VI) in J-13 water at 25°C. Significant aqueous species are UO_2(CO_3)_2^{2-} (about 90% of Cu), UO_2(CO_3)_3^{4-} and UO_2CO_3^{0} (each about 5% of Cu).

The temperature dependence of the formation reactions for the U(VI) carbonate complexes has been determined based on calorimetric studies and measurements of the solubility of UO_2CO_3 to 200°C. Discussions of the original references and interpretation of the experimental data are available in the U NEA-TDB review [92GRE, 95GRE]. The UO_2CO_3^{0} data is also analyzed in [97PUI]. Enthalpy data or elevated temperature formation constant data are also available for U(VI) hydrolysis species, sulfate complexes and fluoride complexes [92GRE]. At low U concentrations, the U(VI) hydrolysis species, sulfate complexes and fluoride complexes are not expected to be significant compared to the U(VI) carbonate complexes under the conditions of interest.

A recent study of the interaction of U(VI) and silicic acid in aqueous solutions by time-resolved laser-induced fluorescence spectroscopy has suggested that the complexes
may be significant under expected repository conditions [97MOL]. The interaction was described by the reaction

\[
\text{UO}_2^{2+} + \text{Si(OH)}_4^0 = \text{UO}_2\text{O}\text{Si(OH)}_3^+ + \text{H}^+ 
\]

(11)

The stability constant for reaction (11) was determined to be \( \log K^o = -1.60 \pm 0.36 \), which indicates that the reaction would be competitive with carbonate complex formation under the conditions of interest. Smaller values of the stability constant have been determined in earlier studies: \( \log K^o = -2.25 \pm 0.13 \) [71POR] and \( \log K^o = -2.70 \pm 0.34 \) [92SAT]. There is no elevated temperature data for the interaction of U(VI) and silicic acid.

The aqueous U species under expected repository conditions are relatively well-understood, with the exception of the U(VI)-silicic acid interaction. Si concentrations are relatively high in the reference waters and are expected to increase with temperature, so a better understanding of the interaction of U(VI) and silicic acid at elevated temperatures is needed.

8. Np

The maximum Np concentration in J-13 water at 25°C is on the order of \( 10^{-4} \) m and is limited by the solubility of NaNpO₃·xH₂O, at least over time scales of a few months or less. Significant aqueous species are NpO₂⁺ (about 90% of CN₆) and NpO₂CO₃⁻ (about 10% of CN₆).

The NpO₂CO₃ formation reaction has been investigated by solubility studies of sodium and potassium neptunyl carbonates to 75°C [93LEM] and by near-infrared (nir) absorption spectroscopy to 70°C [95TAI, 96CLA]. The results are listed in Table 3 with estimated uncertainties. In [93LEM] the solubility data were analyzed using two models labeled A and B. We have extrapolated the nir data to 75°C for easier comparison. The solubility studies indicate \( \Delta H \) is positive, but the nir work indicates \( \Delta H \) is negative. The difference may be an ionic strength effect, or possibly the use of tetrabutylammonium salts affected the nir results. It is difficult to assess the nir data because few experimental details were provided in [95TAI, 96CLA]. Direct measurements on Np-spiked J-13 water at temperatures up to 90°C have indicated that the Np(V) carbonate complex is significant at elevated temperatures [93NIT].

<table>
<thead>
<tr>
<th>T, °C</th>
<th>[93LEM] model A (1 - 1 M)</th>
<th>[93LEM] model B (1 - 1 M)</th>
<th>[96CLA] (1 - 0.1 M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>4.6 ± 0.1</td>
<td>–</td>
<td>4.1 ± 0.2</td>
</tr>
<tr>
<td>50</td>
<td>5.6 ± 0.1</td>
<td>5.6 ± 0.2</td>
<td>3.9 ± 0.2</td>
</tr>
<tr>
<td>75</td>
<td>5.2 ± 0.3</td>
<td>6.0 ± 0.7</td>
<td>3.7 ± 0.3</td>
</tr>
</tbody>
</table>

Calorimetric measurements of the enthalpy of reaction for formation of the hydrolysis product NpO₂OH⁰ have been reported [91SUL]. The formation of NpO₂OH⁰
has been investigated by NIR absorption spectroscopy to 70°C, but very few experimental
details were given [95TAI].

A better understanding of the NpO$_2$CO$_3$ formation reaction at elevated
temperatures is needed. There is also a need for improved understanding of the
Np(V)/Np(IV) solid state transformation kinetics, but this is outside the scope of the
present report and is discussed in the solubility report.

9. Pu

Pu is sparingly soluble (to about 10$^{-7}$ m) in J-13 water at 25°C. Significant
aqueous species include PuO$_2^+$, PuO$_2$CO$_3$ and PuO$_2$(CO$_3$)$_2$$. Identification of Pu species
in reference waters is complicated by the redox chemistry of Pu, the limited amount of
data for aqueous Pu(IV) species and the tendency of Pu(IV) to form colloidal hydrous
oxides.

Measurements on J-13 water spiked with Pu$^{4+}$ indicate that the Pu concentration
decreases from about 10$^{-7}$ m at 25°C to about 10$^{-8}$ m at 90°C [93NIT]. The observed
decrease in Pu concentrations with temperature may have been a kinetics effect rather than
a true temperature-dependent solubility effect, because the precipitates were low-
crystallinity mixtures of Pu(IV) hydrous oxide and Pu carbonates. Experiments in which
Pu was introduced as Pu$^{4+}$, PuO$_2^+$ or PuO$_2^{2+}$ to dilute bicarbonate solutions at pH 6 have
been reported [93NEU]. The dominant aqueous Pu species was PuO$_2^+$ in the PuO$_2^+$ and
PuO$_2^{2+}$ experiments. In the Pu$^{4+}$ experiments the Pu concentration was very low and the
solution species were not determined.

Enthalpy data for Pu(VI) carbonate complexation is available [82SUL, 88ULL]. The U(VI) carbonate complexes should be good analogs for Pu(VI) carbonate complexes, because the entropy difference due to electron configuration is small. It is difficult to
perform direct studies of PuO$_2$CO$_3$ at elevated temperatures due to rapid
disproportionation of Pu(V) to low-solubility Pu(IV) and Pu(VI) forms, so an improved
understanding of NpO$_2$CO$_3$ would also be valuable as an analog for PuO$_2$CO$_3$$. No data
was found for the temperature behavior of Pu(IV) carbonate complexation, but there is
enthalpy data for the formation of U(CO$_3$)$_3$$^{6-}$ [92GRE].

The chemistry of Pu in natural waters can be quite complex, involving slow
Pu(V)/Pu(IV) and Pu(VI)/Pu(IV) solid-state transformation reactions, polymeric or
colloidal Pu(IV) forms and strong sorption to mineral or humic material. There is some
experimental evidence that indicates PuO$_2^{2+}$ is the dominant dissolved species under near-
neutral pH conditions in the absence of strong complexing agents. Due to practical
difficulties in the direct study of Pu(V) complexes at elevated temperatures, it will
probably be necessary to estimate Pu(V) complexation behavior based on Np(V) analogs.

The NEA-TDB review of the chemical thermodynamics of Np and Pu is in
preparation.
10. Am

The Am concentration in J-13 water at 25°C is limited to about $10^{-7}$ m by the solubility of AmOHCO$_3$. Significant aqueous species are AmCO$_3$\(^{+}\) (about 75% of C$_{Am}$), AmOH$^{2+}$ (about 20% of C$_{Am}$) and Am$^{3+}$ (about 5% of C$_{Am}$).

The AmCO$_3$\(^{+}\) formation reaction has been investigated by laser-induced photoacoustic spectroscopy to 75°C [96WRU]. In Table 4, the experimental data have been extrapolated to zero ionic strength and analyzed by the isoelectric method discussed in section 3 of this report. Data for reaction (4) is from [82PLU, 82PAT, 84PAT]. The result of the analysis is $\Delta H_{(\beta)} = 66 \pm 10$ kJ/mol.

<table>
<thead>
<tr>
<th>$T$, °C</th>
<th>log $K_{(\beta)}(T)$</th>
<th>log $K_{(\gamma)}(T)$</th>
<th>log $K_{(\delta)}(T)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>7.54 ± 0.12</td>
<td>-16.686</td>
<td>-9.14 ± 0.12</td>
</tr>
<tr>
<td>50</td>
<td>8.02 ± 0.12</td>
<td>-16.459</td>
<td>-8.44 ± 0.12</td>
</tr>
<tr>
<td>75</td>
<td>8.95 ± 0.43</td>
<td>-16.422</td>
<td>-7.47 ± 0.43</td>
</tr>
</tbody>
</table>

No experimental data was found for the temperature dependence of the AmOH$^{2+}$ formation reaction. There is enthalpy data for the rare-earth analog SmOH$^{2+}$ [93MAR]. The Am(III) hydrolysis behavior could be investigated by solubility studies of Am(OH)$_3$ at elevated temperatures.

11. FY97 Experiments

In the mid-year report (milestone SPL4B1M4) we identified the limited number of direct measurements at higher temperatures as an area of need and proposed to extend our investigation of AmCO$_3$\(^{+}\) complexation by laser-induced photoacoustic spectroscopy to temperatures above 75°C. Analysis of the earlier experiments suggested that much of the uncertainty at 75°C could be traced to loss of CO$_2$ from the samples, therefore we have developed a photoacoustic cell that can be sealed and maintained at temperatures from 25 to 150°C. The cell body was constructed from commercially available high pressure chromatography fittings. The quartz windows, piezoelectric transducer and cell heater assemblies were fabricated in-house. The wetted parts are fused silica, Ti and a graphite-filled polyimide which has been treated at high temperatures. The sample volume is 0.2 mL. The cell has been tested with deionized water and dilute Nd(III) solutions to 155°C. The Am(III) carbonate experiments have not been completed, however, work is in progress and we expect to have results by the end of FY97.
11. Summary

Reasonably accurate temperature extrapolations can be made for a number of species of interest (NiSO$_4^0$, the U(VI) carbonate complexes, AmCO$_3^-$), i.e., the estimated uncertainty in log $K^0$ over the range 20-150°C is about 0.5. Analog data is available for some species which lack direct measurements (Pu carbonates and AmOH$_2^3$). Several areas of need have been identified, including an improved understanding of Tc redox behavior and the formation of NpO$_2$CO$_3^-$ at elevated temperatures. There are very few direct measurements at temperatures above 75°C. Of the significant species identified, such data are only available for the U(VI) carbonate complexes.
12. References


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