

Analysis of Elevated Temperature Data for Thermodynamic Properties of Selected Radionuclides

D.A. Wruck
C.E.A. Palmer

August 1997



Lawrence
Livermore
National
Laboratory

This is an informal report intended primarily for internal or limited external distribution. The opinions and conclusions stated are those of the author and may or may not be those of the Laboratory.

Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract W-7405-ENG-48

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

This report has been reproduced
directly from the best available copy.

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information
P.O. Box 62, Oak Ridge, TN 37831
Prices available from (423) 576-8401

Available to the public from the
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Rd.,
Springfield, VA 22161

Analysis of Elevated Temperature Data for Thermodynamic Properties of Selected Radionuclides

David A. Wruck and Cynthia E. A. Palmer
Isotope Sciences Division
Lawrence Livermore National Laboratory
Livermore, CA 94550

Yucca Mountain Project
Milestone SPL4B2M4
August 1997

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.

Water	Li	Na	K	Mg	Ca	Mn	Fe	Al	Si
J-13	0.06	45	5.3	1.76	12	0.001	0.04	0.03	30
high temp.	–	<65	<15	<5	<15	–	–	<5	<160

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

Water	F ⁻	Cl ⁻	NO ₃ ⁻	HCO ₃ ⁻	SO ₄ ²⁻	O ₂	pH
J-13	2.1	6.4	10	143	18	5.7	6.9
high temp.	<5	<10	<15	<140	<25	–	6.9-7.6

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^0 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 ΔH^0 is assumed to be constant over the temperature range T_0 to T (this is equivalent to neglecting the heat capacity of reaction ΔC_p^0 over the range T_0 to T), then the equilibrium constant is approximated by the van't Hoff equation

$$\log K^0(T) = \log K^0(T_0) + \frac{\Delta H^0(T_0)}{2.303R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \quad (1)$$

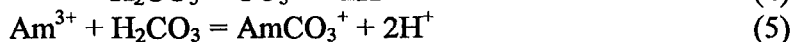
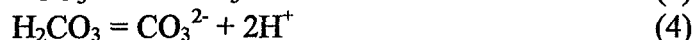
Here R is the gas constant 8.3145 J mol⁻¹ K⁻¹. Eq. (1) is often used over small temperature ranges (about 10 K or less), because the error due to neglecting ΔC_p^0 is small compared to the uncertainty in $\log K^0(T_0)$.

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,



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):



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

$$\log K_{(5)}^0(T) = \log K_{(3)}^0(T) + \log K_{(4)}^0(T) \quad (6)$$

$$\Delta H_{(5)}^0(T) = \Delta H_{(3)}^0(T) + \Delta H_{(4)}^0(T) \quad (7)$$

Acid dissociation data have been determined for the complexes of interest, and uncertainties in the acid constants are ≤ 0.03 log units over the range 20-100°C. Data for the acid dissociation reactions can be found in the following references: H_2O [81MAR], H_2CO_3 [82PLU, 82PAT, 84PAT], HF [63ELL], H_2SO_4 and H_3PO_4 [86SMI].

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 ΔC_p^0 is treated as a nonzero constant over the temperature range T_0 to T , the expression for the equilibrium constant is

$$\log K^0(T) = \log K^0(T_0) + \frac{\Delta H^0(T_0)}{2.303R} \left(\frac{1}{T_0} - \frac{1}{T} \right) + \frac{\Delta C_p^0}{2.303R} \left(\frac{T_0}{T} - 1 + \ln \frac{T}{T_0} \right) \quad (8)$$

There is sufficient experimental data to determine ΔC_p^0 for only a few of the reactions of interest. Estimates of ΔC_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 $\text{Ni}(\text{OH})_2$, so the Ni solubility is sensitive to pH. Significant aqueous

species are Ni^{2+} (97% of C_{Ni}) and NiSO_4^0 (3% of C_{Ni}). These conclusions are based on the equilibrium constants selected in [93MAR].

The complex formation reaction $\text{Ni}^{2+} + \text{SO}_4^{2-} = \text{NiSO}_4^0$ 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 ΔH^0 . The value of ΔH^0 selected in [93MAR] is also listed in Table 2. If the smallest experimental values of ΔH^0 are correct, there is practically no change in the Ni speciation over the range 25-150°C. If the largest experimental value of ΔH^0 is correct, there is a modest increase in the NiSO_4^0 concentration as the temperature increases, and NiSO_4^0 accounts for roughly 10% of C_{Ni} at 100°C.

Table 2: Thermodynamic data for the reaction $\text{Ni}^{2+} + \text{SO}_4^{2-} = \text{NiSO}_4^0$.

Method	$\log K^0$	ΔH^0 , kJ mol^{-1}	Reference
calorimetry	2.32	13.9	[59NAI]
calorimetry	2.81 ± 0.09	1.72 ± 0.08	[69IZA]
calorimetry	not stated	1.75 ± 0.15	[73POW]
conductivity	2.27	5.3	[73KAT]
heat of dilution	2.30 ± 0.04	6.4 ± 0.8	[70LAR]
tabulated data	2.34 ± 0.06	5.8	[93MAR]

The hydrolysis of Ni^{2+} has been investigated by solubility studies of NiO to 300°C [80TRE]. Equilibrium quotients for the formation of NiOH^+ , $\text{Ni}(\text{OH})_2^0$, and $\text{Ni}(\text{OH})_3^-$ 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 $\text{pH} < 9$.

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 ΔH^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_4^0 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].

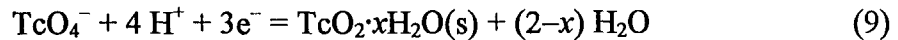
6. Tc

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 $\text{TcO}_2 \cdot x\text{H}_2\text{O}$. 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 $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ electrodes in contact with TcO_4^- solutions at 24-25°C [53COB, 55CAR, 91MEY]. The reaction can be written as



The Nernst equation for reaction (9) is

$$E = E^0 + \frac{2.303RT}{3F} (\log a(\text{TcO}_4^-) - 4\text{pH}) \quad (10)$$

E is the potential, R is the ideal gas constant, F is the Faraday constant, and $a(\text{TcO}_4^-)$ 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 $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ electrodes at a number of temperatures. High carbonate or Si concentrations may alter the $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ 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.

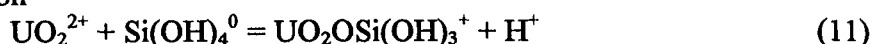
7. U

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

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



The stability constant for reaction (11) was determined to be $\log K^0 = -1.60 \pm 0.36$, 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: $\log K^0 = -2.25 \pm 0.13$ [71POR] and $\log K^0 = -2.70 \pm 0.34$ [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 $\text{NaNpO}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$, at least over time scales of a few months or less. Significant aqueous species are NpO_2^+ (about 90% of C_{Np}) and $\text{NpO}_2\text{CO}_3^-$ (about 10% of C_{Np}).

The $\text{NpO}_2\text{CO}_3^-$ 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 ΔH is positive, but the nir work indicates ΔH 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 3: Experimental $\log K$ values for the reaction $\text{NpO}_2^+ + \text{CO}_3^{2-} = \text{NpO}_2\text{CO}_3^-$.

T, °C	[93LEM] model A (I = 1 M)	[93LEM] model B (I = 1 M)	[96CLA] (I = 0.1 M)
25	4.6 ± 0.1	–	4.1 ± 0.2
50	5.6 ± 0.1	5.6 ± 0.2	3.9 ± 0.2
75	5.2 ± 0.3	6.0 ± 0.7	3.7 ± 0.3

Calorimetric measurements of the enthalpy of reaction for formation of the hydrolysis product NpO_2OH^0 have been reported [91SUL]. The formation of NpO_2OH^0

has been investigated by near absorption spectroscopy to 70°C, but very few experimental details were given [95TAI].

A better understanding of the $\text{NpO}_2\text{CO}_3^-$ 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^+ , $\text{PuO}_2\text{CO}_3^0$ and $\text{PuO}_2(\text{CO}_3)_2^{2-}$. 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 $\text{PuO}_2\text{CO}_3^-$ at elevated temperatures due to rapid disproportionation of Pu(V) to low-solubility Pu(IV) and Pu(VI) forms, so an improved understanding of $\text{NpO}_2\text{CO}_3^-$ would also be valuable as an analog for $\text{PuO}_2\text{CO}_3^-$. No data was found for the temperature behavior of Pu(IV) carbonate complexation, but there is enthalpy data for the formation of $\text{U}(\text{CO}_3)_5^{6-}$ [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^+ 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 AmOHCO₃. Significant aqueous species are AmCO₃⁺ (about 75% of C_{Am}), AmOH²⁺ (about 20% of C_{Am}) and Am³⁺ (about 5% of C_{Am}).

The AmCO₃⁺ 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 $\Delta H_{(5)}^0 = 66 \pm 10$ kJ/mol.

Table 4: Formation constants for reactions (3), (4) and (5).

$T, ^\circ\text{C}$	$\log K_{(3)}^0(T)$	$\log K_{(4)}^0(T)$	$\log K_{(5)}^0(T)$
25	7.54 ± 0.12	-16.686	-9.14 ± 0.12
50	8.02 ± 0.12	-16.459	-8.44 ± 0.12
75	8.95 ± 0.43	-16.422	-7.47 ± 0.43

No experimental data was found for the temperature dependence of the AmOH²⁺ formation reaction. There is enthalpy data for the rare-earth analog SmOH²⁺ [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 AmCO₃⁺ 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 CO₂ 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+}). Several areas of need have been identified, including an improved understanding of Tc redox behavior and the formation of $\text{NpO}_2\text{CO}_3^-$ 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

- [38GUR] Gurney, R.W., Exchange forces and electrostatic forces between ions in solution, *J. Chem. Phys.* **6**, 499 (1938).
- [53COB] Cobble, J.W., Smith, W.T., Boyd, G.E., Thermodynamic properties of technetium and rhenium compounds: II. Heats of formation of technetium heptoxide and pertechnetic acid, potential of the technetium(IV)-technetium(VII) couple and a potential diagram for technetium, *J. Am. Chem. Soc.* **75**, 5777 (1953).
- [55CAR] Cartledge, G.H., Smith, W.T., Revision of the electrode potential diagram for technetium, *J. Phys. Chem.* **59**, 1111 (1955).
- [59NAI] Nair, V.S.K., and Nancollas, G.H., *J. Chem. Soc.* **1959**, 3934 (1959).
- [61PIT] Pitzer, K.S., and Brewer, L., *Thermodynamics*, 2nd edition, McGraw-Hill, New York, 1961.
- [63ELL] Ellis, A.J., The effect of temperature on the ionization of hydrofluoric acid, *J. Chem. Soc.* **1963**, 4300 (1963).
- [67SIG] Sigel, H., Becker, K., McCormick, D., *Biochim. Biophys. Acta* **148**, 655 (1967).
- [69IZA] Izatt, R.M., *J. Chem. Soc. A* **1969**, 47 (1969).
- [69NAZ] Nazarenko, V.A., Mandzhgaladze, O.V., *Zh. Neorg. Khim.* **14**, 1219 (1969).
- [70LAR] Larson, J.W., Thermodynamics of divalent metal sulfate dissociation and the structure of the solvated metal sulfate ion pair, *J. Phys. Chem.* **74**, 3392 (1970).
- [71POR] Porter, R.A., Weber, W.J., The interaction of silicic acid with iron(III) and uranyl ions in dilute aqueous solution, *J. Inorg. Nucl. Chem.* **33**, 2443 (1971).
- [72FRE] Frey, C.M., Stuehr, J.E., *J. Amer. Chem. Soc.* **94**, 8898 (1972).
- [72SER] Sergeyeva, E.I., Nikitin, A.A., Khodakovskiy, I.L., Naumov, G.B., Vernadskiy, V.I., Experimental investigation of equilibria in the system $\text{UO}_3\text{-CO}_2\text{-H}_2\text{O}$ in 25-200°C temperature interval, *Geochim. Int.* **11**, 900 (1972).
- [73KAT] Katayama, S., Conductometric determination of ion-association constants for magnesium and nickel sulfates in aqueous solutions at various

temperatures between 0°C and 45°C, *Bull. Chem. Soc. Japan* **46**, 106 (1973).

- [73POW] Powell, H.K.J., *J. Chem. Soc. Dalton Trans.* **1973**, 1947 (1973).
- [74ARU] Aruga, R., Calorimetric study of the association of fluoride ion with several bivalent metal ions, *Ann. Chim. (Rome)* **64**, 439 (1974).
- [76BAE] Baes, C.F, Mesmer, R.E., *The hydrolysis of cations*, Wiley-Interscience, New York, 1976.
- [76KUL] Kul'vinova, L.A., Blokhin, V.V., Mironov, V.E., Thermodynamic properties of certain transition fluoride complexes in aqueous salt solutions, *Zh. Fiz. Khim.* **50**, 1287 (1976).
- [77ASH] Ashurst, K.G., Hancock, R.D., Characterization of inner- and outer-sphere complexes by thermodynamics and absorption spectra. Part 1. Sulphato-complexes of the first-row transition elements, *J. Chem. Soc. Dalton* **1977**, 1701 (1977).
- [80LEM] Lemire, R.J., and Tremaine, P.R., Uranium and plutonium equilibria in aqueous solutions to 200°C, *J. Chem. Eng. Data* **25**, 361 (1980).
- [80TRE] Tremaine, P.R., Leblanc, J.C., The solubility of nickel oxide and hydrolysis of Ni²⁺ in water to 573 K, *J. Chem. Thermodynamics* **12**, 521 (1980).
- [81KUL] Kul'vinova, L.A., Blokhin, V.V., Makashev, Y.A., Mironov, V.E., Thermodynamics of the formation of fluoride complexes of transition metals in water-salt solutions, *Soviet J. Coord. Chem.* **7**, 104 (1981).
- [81MAR] Marshall, W.L., Franck, E.U., Ion product of water substance, 0-1000°C, 1-10,000 bars, new international formulation and its background, *J. Phys. Chem. Ref. Data* **10**, 295 (1981).
- [82PAT] Patterson, C.S., Slocum, G.H., Busey, R.H., Mesmer, R.E., Carbonate equilibria in hydrothermal systems: first ionization of carbonic acid in NaCl media to 300°C, *Geochim. Cosmochim. Acta* **46**, 1653 (1982).
- [82PLU] Plummer, L.N., Busenberg, E., The solubilities of calcite, aragonite, and vaterite in CO₂-H₂O solutions between 0 and 90°C, and an evaluation of the aqueous model for the system CaCO₃-CO₂-H₂O, *Geochim. Cosmochim. Acta* **46**, 1011 (1982).
- [82SUL] Sullivan, J.C., Woods, M., Bertrand, P.A., and Choppin, G.R., *Radiochim. Acta* **31**, 45 (1982).

- [84KER] Kerrisk, J.F., Solubility limits on radionuclide dissolution at a Yucca Mountain repository, LA-9995-MS, Los Alamos National Laboratory, Los Alamos, NM, May 1984.
- [84KNA] Knauss, K.G., Beiriger, W.J., Report on static hydrothermal alteration studies of topopah spring tuff wafers in J-13 water at 150°C, UCRL-53576, Lawrence Livermore National Laboratory, Livermore, CA, 1984.
- [84PAT] Patterson, C.S., Busey, R.H., Mesmer, R.E., Second ionization of carbonic acid in NaCl media to 250°C, *J. Solution Chem.* **13**, 647 (1984).
- [85KNA1] Knauss, K.G., Beiriger, W.J., Peifer, D.W., Hydrothermal interaction of crushed topopah spring tuff and J-13 water at 90, 150, and 250°C using dickson-type, gold-bag rocking autoclaves, UCRL-53630, Lawrence Livermore National Laboratory, Livermore, CA, 1985.
- [85KNA2] Knauss, K.G., Beiriger, W.J., Peifer, D.W., Piwinski, A.J., Hydrothermal interaction of solid wafers of topopah spring tuff with J-13 water and distilled water at 90, 150, and 250°C using dickson-type, gold-bag rocking autoclaves, UCRL-53645, Lawrence Livermore National Laboratory, Livermore, CA, 1985.
- [85OVE] Oversby, V.M., The reaction of topopah spring tuff with J-13 water at 150°C - samples from drill cores USW G-1, USW GU-3, USW G-4, and UE-25h#1, UCRL-53629, Lawrence Livermore National Laboratory, Livermore, CA, 1985.
- [86GLA] Glassley, W.E., Reference waste package environment report, UCRL-53726, Lawrence Livermore National Laboratory, Livermore, CA, 1986.
- [86KNA] Knauss, K.G., Peifer, D.W., Reaction of vitric topopah spring tuff and J-13 ground water under hydrothermal conditions using dickson-type, gold-bag rocking autoclaves, UCRL-53795, Lawrence Livermore National Laboratory, Livermore, CA, 1986.
- [86SMI] Smith, R.W., Popp, C.J., Norman, D.I., The dissociation of oxy-acids at elevated temperatures, *Geochim. Cosmochim. Acta* **50**, 137 (1986).
- [87KNA] Knauss, K.G., Beiriger, W.J., Peifer, D.W., Hydrothermal interaction of solid wafers of topopah spring tuff with J-13 water at 90 and 150°C using dickson-type, gold-bag rocking autoclaves: long-term experiments, UCRL-53722, Lawrence Livermore National Laboratory, Livermore, CA, 1987.
- [88DOE] U.S. Department of Energy, Site characterization plan, Yucca Mountain site, Nevada research and development area, Nevada, DOE/RW-0199,

Nuclear waste policy act (section 113), Office of civilian radioactive waste management, Washington, D.C., 1988.

- [88PAP] Papelis, C., Hayes, K.F., Leckie, J.O., HYDRAQL: a program for the computation of chemical equilibrium composition of aqueous batch systems including surface-complexation modeling of ion adsorption at the oxide/solution interface, Technical report no. 306, Dept. of Civil Engineering, Stanford University, September 1988.
- [88SHO] Shock, E.L., Helgeson, H.C., Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: correlation algorithms for ionic species and equations of state predictions to 5kb and 1000°C, *Geochim. Cosmochim. Acta* **52**, 2009 (1988).
- [88ULL] Ullman, W.J., and Schreiner, F., *Radiochim. Acta* **40**, 179 (1986).
- [90AHR] Ahrland, S., Hefter, G., Noren, B., A calorimetric study of the mononuclear fluoride complexes of zirconium(IV), hafnium(IV), thorium(IV) and uranium(IV), *Acta Chem. Scand.* **44**, 1 (1990).
- [91MEY] Meyer, R.E., Arnold, W.D., The electrode potential of the Tc(IV)-Tc(VII) couple, *Radiochim. Acta* **55**, 19 (1991).
- [91SUL] Sullivan, J.C., Choppin, G.R., and Rao, L.F., Calorimetric Studies of NpO_2^+ hydrolysis, *Radiochim. Acta* **54**, 17 (1991).
- [92GRE] Grenthe, I., Fuger, J., Konings, R.J.M., Lemire, R.J., Muller, A.B., Nguyen-Trung, C., and Wanner, H., *Chemical Thermodynamics of Uranium*, North-Holland, Amsterdam, 1992.
- [92PAL] Palmer, C.E.A., Silva, R.J., and Miller, C.W., Speciation calculations of Pu, Np, Am, and U in J-13 well water. Effects of anion concentration and pH. Lawrence Livermore National Laboratory, Livermore, CA, draft dated September 1992.
- [92SAT] Satoh, I., Choppin, G.R., Interaction of uranyl(VI) with silicic acid, *Radiochim. Acta* **56**, 85 (1992).
- [92SLO] Slobodov, A.A., Kritskii, A.V., Zarembo, V.I., Puchkov, L.V., Thermodynamic analysis of the chemical reactions of zirconium with aqueous solutions, *Zh. Prikl. Khim.* **65**, 1031 (1992).
- [93LEM] Lemire, R.J., Boyer, G.D., Campbell, A.B., The solubilities of sodium and potassium dioxoneptunium(V) carbonate hydrates at 30, 50, and 75°C, *Radiochim. Acta* **61**, 57 (1993).

- [93MAR] Martell, A.E, Smith, R.M., Critical stability constants of metal complexes, NIST, October 1993.
- [93NEU] Neu, M.P., Coordination chemistry of two heavy metals: I. Ligand preferences in lead(II) complexation, toward the development of therapeutic agents for lead poisoning. II. Plutonium solubility and speciation relevant to the environment, Ph.D. dissertation, University of California, Berkeley, available as LBL-34872, Lawrence Berkeley Laboratory, Berkeley, CA, November 1993.
- [93NIT] Nitsche, H., Gatti, R.C., Standifer, E.M., Lee, S.C., Mullaer, A., Prussin, T., Deinhammer, R.S., Maurer, H., Becraft, K., Leung, S., and Carpenter, S.A., Measured solubilities and speciations of neptunium, plutonium, and americium in a typical groundwater (J-13) from the Yucca Mountain region, Milestone Report 3010-WBS 1.2.3.4.1.3.1, LA-12562-MS, Los Alamos National Laboratory, Los Alamos, NM, July 1993.
- [95GRE] Grenthe, I., Puigdomenech, I., Sandino, M.C.A., and Rand, M.H., Corrections to the uranium NEA-TDB review, appendix D of Silva, R.J., Bidoglio, G., Rand, M.H., Robouch, P.B., Wanner, H., and Puigdomenech, I., Chemical Thermodynamics of Americium, North-Holland, Amsterdam, 1995.
- [95SIL] Silva, R.J., Bidoglio, G., Rand, M.H., Robouch, P.B., Wanner, H., and Puigdomenech, I., Chemical Thermodynamics of Americium, North-Holland, Amsterdam, 1995.
- [95TAI] Tait, C.D., Clark, D.L., Neu, M.P., Ekberg, S.A., and Palmer, P.D., Temperature dependence of the hydrolysis and carbonate complexation reactions of NpO_2^+ , Abstract PA2-02, Migration '95, Saint-Malo, France, September 10-15, 1995.
- [96CLA] Clark, D.L., Conradson, S.D., Ekberg, S.A., Hess, N.J., Janecky, D.R., Neu, M.P., Palmer, P.D., and Tait, C.D., A multi-method approach to actinide speciation applied to pentavalent neptunium carbonate complexation, *New J. Chem.* **20**, 211 (1996).
- [96PAL] Palmer, C.E.A., Silva, R.J., Bucher, J.J., Thermodynamic data base needs for modeling studies of the Yucca Mountain Project, UCRL-ID-125343, Lawrence Livermore National Laboratory, Livermore, CA, 1996.
- [96STU] Stumm, W., and Morgan, J.J., *Aquatic Chemistry*, 3rd. edition, Wiley-Interscience, New York, 1996.
- [96WRU] Wruck, D.A., Palmer, C.E.A., Silva, R.J., A study of americium(III) carbonate complexation at elevated temperatures by pulsed laser photoacoustic spectroscopy, UCRL-JC-125198, Lawrence Livermore

National Laboratory, Livermore, CA, 1996; manuscript submitted to *Radiochimica Acta*.

- [97GLA] Glassley, W., Lawrence Livermore National Laboratory, Livermore, CA, ongoing work, Yucca Mountain Project reference water compositions.
- [97MOL] Moll, H., Geipel, G., Brendler, V., Bernhard, G., Nitsche, H., Interaction of uranium(VI) with silicon species in aqueous solutions, in Institute of Radiochemistry Annual Report 1996, H. Nitsche, editor, FZR-180, Forschungszentrum Rossendorf e.V., Dresden, Germany, May 1997, p. 10.
- [97PUI] Puigdomenech, I., Rard, J.A., Plyasunov, A.V., Grenthe, I., Temperature corrections to thermodynamic data and enthalpy calculations, UCRL-JC-126374, Lawrence Livermore National Laboratory, Livermore, CA, January 1997, preprint of chapter 10 of *Thermodynamic Modelling of Aqueous Systems*, edited by I. Grenthe and I. Puigdomenech, to be published under the sponsorship of the NEA-TDB project.
- [97VIA] Viani, B., Lawrence Livermore National Laboratory, Livermore, CA, ongoing work, water passage through EBS materials.

Technical Information Department • Lawrence Livermore National Laboratory
University of California • Livermore, California 94551

