LBL-23733

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA, BERKELEY

Information and Computing Sciences Division

RECEIVED
LAWRENCE
BERKELEY LABORATORY

OCT 1 9 1987

LIBRARY AND
DOCUMENTS SECTION

Presented at the International Conference
on Thermodynamics of Aqueous Systems with
Industrial Applications, Warrenton, VA,
May 10–14, 1987

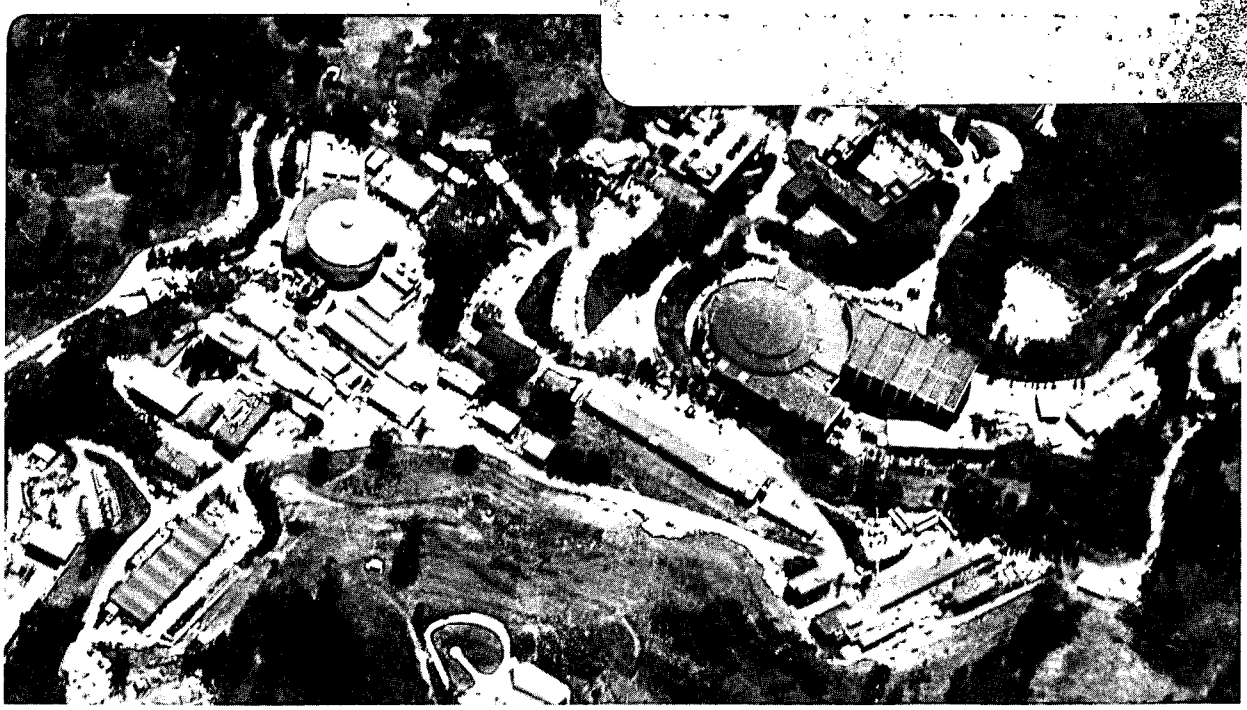
Thermodynamic Tables for Nuclear Waste Isolation: Reference Values and Neptunium

S.L. Phillips and F.V. Hale

July 1987

TWO-WEEK LOAN COPY

This is a Library Circulating Copy
which may be borrowed for two weeks.



LBL-23733

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal 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 its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of 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 any agency thereof or the Regents of the University of California.

LBL-23733

Thermodynamic Tables for Nuclear Waste Isolation Reference Values and Neptunium

Sidney L. Phillips
Computer Science Research Department
Information and Computing Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

and

Frank V. Hale
Earth Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

July, 1987

Presented at the International Conference on Thermodynamics of Aqueous Systems with Industrial Applications, Airlie House, Warrenton, Virginia, May 10-14, 1987.

This research was supported by the Division of Engineering and Geosciences, Office of Energy Research, U.S. Department of Energy under contract DE-AC03-76SF00098.

ABSTRACT

A consistent tabulation of thermodynamic values for neptunium is given. The table consists of values of Gibbs energy of formation, enthalpy of formation, entropy and heat capacity for substances of geochemical interest. The table is consistent with CODATA values and data from other sources; reproduces critically evaluated experimental data; and, is consistent with the relationship $\Delta_r G^o = \Delta_r H^o - 298.15\Delta_r S^o$ within defined limits. Important gaps in the data were filled by calculations based on correlations. Selected equilibrium constants and standard potentials were calculated and compared with other work.

Presented at International Conference on Thermodynamics of Aqueous Systems with Industrial Applications, Airlie House, Warrenton, Virginia May 10-14,1987

THERMODYNAMIC TABLES FOR NUCLEAR WASTE ISOLATION. REFERENCE VALUES AND NEPTUNIUM

Sidney L. Phillips and Frank V.Hale
Lawrence Berkeley Laboratory
One Cyclotron Road
Berkeley, California 94720

For more than three decades a National program has been in progress to develop the necessary research to dispose of wastes from nuclear energy in carefully selected subsurface locations. The essence of this research is to predict with the highest accuracy the performance of a repository to constrain the quantity of waste material which might enter our ambient ground waters. Numerical simulation of geochemical processes such as dissolution of a waste radionuclide is the only viable approach for predicting the long-term performance of repositories (36). Computer codes using self-consistent thermodynamic data are used. One of the critical needs for numerical simulation using computer codes is basic thermodynamic data on radionuclides in a geologic system, with special emphasis on the actinides (36).

This thermodynamic tabulation was developed to meet the following seven major specifications for nuclear waste disposal (i) all numerical values were to result from a critical evaluation of relevant experimental measurements, published in refereed research journals. Besides our assessment, critical evaluations included standard reference data such as CODATA (5), the IAEA series (3), the National Bureau of Standards (2), Chemistry of the Actinides (4), and critical research publications (1,8,24,28,29). (ii) Emphasis was on the actinides because these represent by far the major gap in available thermodynamic data. (iii) All values of the Gibbs energy of formation, $\Delta_f G^o$ were to have an uncertainty as an indicator of the quality of the value, and for statistical calculations such as propagation of errors. (iv) Important gaps in the tables were to be filled, preferably from experimental research, or by calculations. (v) The database had to be consistent with: standard reference tables such as CODATA and National Bureau of Standards; the fundamental relationship $\Delta_r G^o = \Delta_r H^o - T \Delta_r S^o$ within defined limits; critically evaluated experimental laboratory measurements. (vi) A reference to each datum was to be given. (vii) All extrapolations had to have a theoretical basis; else interpolations and correlations were to be employed.

In critically selecting the best experimental data to include in these tables, a number of factors were taken into consideration, including: the number of replicate measurements; experimental methods used by the authors; details given about the laboratory procedure; purity of chemicals used, and any further purification; temperature control; number of replicate measurements for each result; standard deviation from the mean value;

uncertainty assigned by the investigator; and comparison of the experimental results with theoretical expectations.

A substantial effort was made to verify the consistency of this tabulation, e.g., by three or four replicate calculations of $\Delta_r G^o = \Delta_r H^o - 298.15\Delta_r S^o$ for about 50 reactions involving all aqueous species. The reactions included hydrolysis, dissolution of solids, complexation and electrode reactions. Besides this check on consistency, selected electrode potentials and equilibrium constants have been calculated from our data, and then compared with other calculations as well as experimental work. These checks on consistency are described in the appropriate sections of this report. Nevertheless, it is recognized that residual inconsistencies are possible in any work involving numerous numerical values. The reader is urged to communicate any important inconsistencies to the authors for correction in a subsequent report.

This report is limited to tables of values for the Gibbs energy of formation, enthalpy of formation, entropy and heat capacity of standard reference substances, and for the actinide neptunium. More information is given in the larger report, LBL-22860 (9) which covers over 35 elements. Because this tabulation is intended to be both internally consistent and consistent with other thermodynamic tables, high priority was given to the compilation of auxiliary data. These reference data are given in Appendix I for aqueous master species which are used in computer codes. Reference 9 has data for other substances such as Sr^{++}, and simple solids, e.g., oxides and carbonates.

STANDARD REFERENCE VALUES

Values for the reference data were obtained from the CODATA Key Values (5), National Bureau of Standards (2), and other sources such as Brewer (7). Table I is a partial listing of our reference data; the more complete table is in Phillips et al. (9) and the Appendix.

The first column in Table I identifies the substance and state; for example, $O_2(aq)$ is the water soluble form of oxygen. The next four columns have values for each thermodynamic property. Immediately beneath these values is an uncertainty, generally that of the evaluator or researcher publishing the data. The last column consists of four digits, each referring to the source of one of the four property values, reading from left to right. Delimiters are not used to separate the individual references. A zero in the reference column is indicative of no data; a nine identifies this work.

In Table I, Gibbs energy and enthalpy of formation of $O_2(g)$ are zero by definition, S^o is from CODATA and Cp^o from Brewer; $\Delta_f G^o$ of $O_2(aq)$ was calculated from $\Delta_r H^o$ and $\Delta_r S^o$ for the electroreduction reaction shown in Table II, other values are from Brewer; $H_2(g)$: Gibbs energy and enthalpy are zero, by definition, S^o and Cp^o are from Brewer; $H_2(aq)$: $\Delta_f G^o$ calculated from enthalpy of reaction and entropy of reaction for the electrochemical reaction in Table II, Cp^o is from Brewer; $H_2O(l)$ and $H_2O(g)$: Gibbs energy from the NBS tables, enthalpy and entropy from CODATA, heat capacity from Brewer; e^-: $\Delta_f G^o = \Delta_f H^o = 0$ by definition, entropy and heat capacity are from Ryabukhin (6). Note both values are exactly one-half of those for $H_2(g)$; $Si(OH)_4(aq)$: $\Delta_f G^o$ calculated from $\log K^o$ in Baes and Mesmer from quartz solubility (19), $\Delta_f H^o$ calculated from this Gibbs energy, and S^o in the NBS tables, Cp^o is from Naumov et al. (11); H^+: all values are zero, by definition; NH_4^+ : $\Delta_f G^o$ from the

NBS tables, enthalpy and entropy from CODATA, heat capacity calculated from our work. Brewer tabulates Cp^o = 80 J/mol/K which appears high by comparison with other positive ions; Li^+ and Na^+: $\Delta_f G^o$ from NBS tables, $\Delta_f H^o$ and S^o from CODATA, Cp^o from Brewer.

The data in Table I as well as some from Ref. 9 were used to calculate standard electrode potentials for about 20 couples, as well as the magnitude of the difference $\Delta_r G^o - [\Delta_r H^o - 298.15\Delta_r S^o]$. This difference is zero for an ideal internal consistency. See Table II. The second column in Table II shows that this difference, Δ , is less than 500 J/mol, with an average of about ±160 J/mol for the reference data in Table I. The last two columns compare our values of E^o calculated from $\Delta_f G^o$ in Table I with those in Bard et al. (12). Differences are due to use of differing values of $\Delta_f G^o$, for example we selected $\Delta_f G^o [Si(OH)_4(aq)]$ = -1308.0 kJ/mol, compared with -1276 kJ/mol in Bard et al (12). Our selected $\Delta_f G^o$ reproduces the solubility of quartz at 25 °C, as discussed in the next section. The data given in Bard et al. predict $\log K^o$ = -9.56, about 6 units of $\log K$ more negative than our calculated value. However, the data in Bard et al. for $Si(OH)_4(aq)$ are consistent with their Gibbs energy of formation for $SiO_2(quartz)$ which is not the CODATA recommended value. Similarly, our choices differ for both Fe^{++} and Fe^{+++}. These reference data are used to ensure compatibility with other tabulations based on CODATA and NBS tables, and to assure the consistency of our tables.

CONSISTENCY OF THE TABLES

The previous section gave examples of the consistency of these tables in obeying the fundamental thermodynamic relationship $\Delta_r G^o = \Delta_r H^o - 298.15\Delta_r S^o$. In this section, the consistency is considered in two additional ways: self-consistent for geochemical processes, and consistent in reproducing critically selected experimental measurements. An example of self consistency in terms of networks (2) is the series of chemical reactions representing the dissolution of strontianite ($SrCO_3(s)$), using values of $\Delta_f G^o$ from Ref. 9 and the Appendix.

$$Sr(s) + 2H^+ = Sr^{++} + H_2(aq), \Delta_r G^o = -546.05 \pm 1.20 \quad \text{(i)}$$

$$SrCO_3(aq) = Sr^{++} + CO_3^{--}, \Delta_r G^o = 16.26 \pm 1.62 \quad \text{(ii)}$$

$$SrCO_3(s) = SrCO_3(aq), \Delta_r G^o = 36.91 \pm 1.41 \quad \text{(iii)}$$

$$H_2(aq) = H_2(g), \Delta_r G^o = -17.78 \pm 0.90 \quad \text{(iv)}$$

$$H_2(g) = 2H^+ + 2e, \Delta_r G^o = 0 \quad \text{(v)}$$

$$Sr^{++} + 2e = Sr(s), \Delta_r G^o = 563.83 \pm 0.80 \quad \text{(vi)}$$

The net reaction is obtained by summing eqs (i) through (vi) is:

$$SrCO_3(s) = Sr^{++} + CO_3^{--}, \Delta_r G^o = 53.17 \pm \sigma \qquad \text{(vii)}$$

so that $\log K^o$ = -9.313±0.3

Calculated directly according to eq (vii) , $\Delta_r G^o$ = 53.17±1.28 kJ/mol and $\log K^o$ = -9.31. The equilibrium constant compares within 0.18 units of $\log K^o$ with the value -9.13 which was measured experimentally in NaCl media (13); and with $\log K^o$ = -9.66±0.004 measured by Busenberg et al. (14) to within 0.35 units of $\log K^o$. Our propagated uncertainties were calculated as the square root of the sum of the squares of the individual standard deviations for each value of $\Delta_f G^o$, using the computerized procedures, ADDREACT and COMPLOGK (9).

The remainder of this section compares our calculated values of typical equilibrium constants with selected experimental measurements. The comparisons show the consistency with which this tabulation reproduces experimental measurements.

$SiO_2(s)$ Solubility

The solubilites of quartz and amorphous silica have been measured by a number of researchers, at various temperatures. We calculated log K(T) for the solubility of silica using our values for $Si(OH)_4$(aq) and for water from Table I for the reaction,

$$SiO_2(quartz, amorphous) + 2H_2O = Si(OH)_4(aq) \qquad (1)$$

using eq 2, with values for $SiO_2(quartz, amorphous)$ taken from Ref. 9,

$$R \ \ln K(T) = \Delta_r S^o - \frac{\Delta_r H^o}{T} + \Delta_r C_p^o\left[\frac{298.15}{T} - \ln\frac{298.15}{T} - 1\right] \qquad (2)$$

Our results are compared with those calculated by Fournier (15) for quartz and Fournier and Marshall (16) for the amorphous form, both at saturation vapor pressures in Table III. We have assumed that: (a) equation 1 is valid over the temperature range 25 to 350 °C; (b) that the data at 25 °C for reaction 1 can be used to extrapolate to 350 °C using eq 2 (17). Fournier and Fournier and Marshall do not assume a constant value of hydrated waters for reaction 1. The assumption of a constant $\Delta_r Cp^o$ is clearly an oversimplification. As shown in Table III, the calculated results compare within 0.1 unit of $\log K$ up to 300 °C, and 0.2 units at 350 °C, so that the assumption may be more valid for temperatures up to 300 °C.

At 25 °C, log K(quartz) = -3.96, comparing with -4 tabulated by Baes and Mesmer (19); and, log K(amorphous) = -2.98, comparing with -2.74 in Ref. 16 and Ref. 17.

Hydrolysis of UO_2^{++} to form $(UO_2)_2(OH)_2^{++}$

There have been a number of studies of the hydrolysis of UO_2^{++} to form the dimer $(UO_2)_2(OH)_2^{++}$; results are tabulated in Ref. 9 up to the year 1987. Figure 1 is a plot of 13 experimental measurements according to eq 7. Extrapolation to I = 0 gives $\log K^o$ = -5.66, comparing with our calculated value using the thermodynamic tables in Ref. 9 of -5.60. Baes and Mesmer calculated -5.62 for this reaction (19). Only values for perchlorate and nitrate solutions up to I = 3 were used for this plot. Data for sulfate and chloride media were excluded because UO_2^{++} forms complexes with these anions, so that measured hydrolysis quotients do not reflect only hydrolytic products. Also, measurments for I > 3 were not included because eq 7 is generally valid only up to I = 3. Finally, two data points at I = 0.1 were deleted from the final fitting of data to eq 7, because these had the highest residuals when comparing $\log K(I)$ values calculated using eq 7, with the experimental points.

Hydrolysis of NpO_2^+

The most reliable information on the hydrolysis of NpO_2^+ is obtained from Maya (43) and Baes and Mesmer (19). Their results for the reaction $NpO_2^+ + H_2O = NpO_2OH(aq) + H^+$ as well as the solubility of $NpO_2(am?)$ are given in Table IV. Our calculated values for the formation of $NpO_2OH(aq)$, and the solubility of $NpO_2OH(am?)$ are given in Table IV. We have assumed the amorphous (am) form of neptunium oxide was used in solubility measurements, and that the reaction is $NpO_2OH(am) = NpO_2^+ + OH^-$. The solubility and hydrolysis constants were calculated with eq 7, using the coefficients in Table VII.

Am^{+++} - Sulfate Ion Pair

Figure 3 is a plot of the change in log K(I) as a function of ionic strength for $AmSO_4^+$, using data from Refs. 21 and 31. The experimental measurements were obtained at I = 0.5, 1 and 2. We calculate from the plot log K° = 4.14, b = 0.44, and log K(I=3) = 1.6. The extrapolation is justified because eq 7 predicts linear behavior for a plot of the term on the right hand side versus ionic strength. Our calculated values at I = 0.5, 1 and 2 are 1.83, 1.52 and 1.44, respectively. These compare well with 1.8, 1.57 and 1.43 from Reference 21.

NpO_2^+ - Carbonate Complexes

Bidoglio, Tanet and Chatt measured log K for the complexation of NpO_2^+ with carbonate using a solvent extraction technique (22), and Maya used solubility measurements (43). Formation constants for the 1:1, 1:2 and 1:3 complexes are given in Table V. We have plotted the data in Table V except for the data at I = 0.05, which are inconsistent (1) in Figures 2 and 4 to obtain $\log K^o$; our calculated formation constants are given in Table V. We also used the Davies equation and the values at I = 0.2 to calculate both equilibrium constants; the Davies equation is generally most accurate for I≤0.1 (23). We

obtained $\log K^o = 4.64$ for the 1:1 complex, compared with 4.78 using eq 7; and, 7.06 for the second complex, compared with 6.86 using eq 7. For the 1:3 complex, the plot using eq 7 extrapolates to $\log K^o = 4.91$ at I = 0. This unexpectedly low value indicates either eq 7 does not apply to such a highly charged negative species, or that the experimental data are erroneous. We have therefore chosen to plot $\Delta_f G^o [MX_n]$ versus number of carbonate ligands, using values for n = 0,1,2 followed by extrapolation to n = 3. The resulting value for the Gibbs energy of formation of the 1:3 complex is -2550 kJ/mol., comparing well with Lemire's -2547 which we have accepted. From this value, we calculate $\log K^o = 8.55$ for the intrinsic formation constant of the 1:3 species. Figure 4 is a plot of the variation in equilibrium quotient as a function of ionic strength using this value of $\log K^o$, and the two experimental values. In summary, the thermodynamic tables in this work, and in the larger database, are consistent in reproducing evaluated experimental measurements, and with the CODATA and NBS values. However, there are many gaps in the currently available data for the actinides. These gaps are filled by calculations using correlations such as those described in the next section.

THERMODYNAMICS OF AQUEOUS RADIONUCLIDES

The aqueous radionuclides are hydrated ions with positive charges ranging from +1 to +4. Their oxidation states range from +3 to +6, with the +5 and +6 ions containing two bound oxygens. The values of $\Delta_f G^o$ and $\Delta_f H^o$ are correlated in a linear manner; for example two parallel lines are obtained for plots of the +3, +4, +5 and +6 oxidation states (9,30). We have found that there is also a linear relationship for actinide ion pairs and higher complexes. See Figure 5. In our plot, a single line is obtained for all the complexes investigated. This linearity between free energy of formation and enthalpy of formation is not unexpected. Thus, for uncomplexed aqueous actinide ions, Lebedev pointed out that a linearity between $\Delta_f G^o$ and $\Delta_f H^o$ will be observed if there is a constancy in the entropy difference $S^o[M^{n+}]-S^o[M,s]$ (30). Alternatively, an apparent constancy will be observed if the difference between the two entropies is small (30,46). For example, consider the electrode reaction $M^{n+} + ne = M(s)$ for which the free energy of formation and enthalpy of formation are related by the equation $\Delta_f G^o[M^{n+}] = \Delta_f H^o[M^{n+}] + 298.15\Delta_r S^o$. For this kind of reaction, by definition, for a metal in its standard state, $\Delta_f G^o[M] = \Delta_f H^o[M] = 0$, and $\Delta_r S^o = S^o[M] - S^o[M^{n+}] - S^o[e]$, where $S^o[e]$ is the entropy of the electron transferred during the electrode reaction.

For neptunium, Appendix II gives $S^o[Np,s] = 50.3 J(mol\text{-}K)^{-1}$, while values of the entropy of the various complexes range from $-389 J(mol\text{-}K)^{-1}$ to about $+200 J(mol\text{-}K)^{-1}$. The difference in entropy between that of Np metal and the complex ions, multiplied by 298.15, is about -101 to $-56 kJmol^{-1}$. The contribution from the electron term is $19 nkJmol^{-1}$. If n = 1, then the overall entropy term amounts to about -60 $kJmol^{-1}$. This value is substantially less than the values of free energy of formation and enthalpy of formation, which are normally 20 or 30 times higher, and therefore represents only a small perturbation in a plot such as that in Figure 5 (46). Nevertheless, while only approximate, a correlation such as that in Figure 5 is useful as a first estimate of the value for an enthalpy of formation of a complex ion, when the free energy is known. These estimated values will have an uncertainty which includes the entropy term.

A second correlation developed in this work is based on our observation that both $\Delta_f G^o$ and $\Delta_f H^o$ change in a linear fashion with the number of ligands added to the

cation during formation of ion pairs and higher complexes (9). Figure 6 shows the variation in $\Delta_f G^o$ as a function of the number of ligands, for typical actinides and geologic species. A line is also obtained for the change in $\Delta_f H^o$ with the number of complexing ligands (9). For example, Figure 7 graphs $\Delta_f H^o$ versus number of F^- for the AmF_n complexes, using data from Nash and Cleveland (34) which we corrected to I = 0 using eq 7 or the Davies equation, after redefining terms (40). We have extrapolated from n=2 to n=3, to obtain the enthlapy of formation for the $AmF_3(aq)$ species: $\Delta_f H^o$ = -1570 kJ/mol.

The decrease in Gibbs energy of formation with increase in the number of ligands follows an equation of the form

$$\Delta_f G^o [MX_n] = mX_n + p \Delta_f G^o [M] \tag{3}$$

where $\Delta_f G^o [MX_n]$ is the Gibbs energy of formation for the complexes, MX_n, m= slope, X = ligand, M = metal cation, n = number of complexing ligands, and $\Delta_f G^o [M]$ = standard free energy of formation of the cation, at 25 °C and zero ionic strength. The quantity, p, is equal to one when eq 3 extrapolates to $\Delta_f G^o$ [M]. Equation 3 was tested for 13 MX_n systems; results are summarized in Table VI. Additional research is needed to understand why the quantity p is not always equal to one. This is possibly an indication that experimental data for higher complexes are not accurate. For example, the fit to eq 3 for the Fe(II)-OH series was improved from a correlation coefficient of 0.999 to 1.000 by not including the approximate value of $\Delta_f G^o [Fe(OH)_4^{--}]$ so that $p \Delta_f G^o [Fe^{++}]$ = -93.5 kJ/mol. This value is much closer to the tabulated -91.55 than -98.9 kJ/mol obtained when the Gibbs energy of formation of $Fe(OH)_4^{--}$ was included. Extrapolation to n = 4 gives $\Delta_f G^o$ = -804.3 kJ/mol; a value probably more accurate than that estimated by Cobble et al. (29). However, we note that $p \Delta_f G^o [M]$ is usually more negative than $\Delta_f G^o$, indicating the quantity, p, may not be simply empirical. Also, note that the slopes, m, can be grouped according to the kind of ligand in the cation - ligand complex.

From eq 3 and the data in Table VI, we calculated $\Delta_f G^o$ and $\log K^o$ for the following species: $\Delta_f G^o [Fe(OH)_3(aq)]$ = -647.8 kJ/mol, $\log K^o$ = -14.3; $\Delta_f G^o [AlF_5^{--}]$ = -2040 kJ/mol, $\log K^o$ = 26.3; $\Delta_f G^o [AlF_6^{---}]$ = -2330 kJ/mol, $\log K^o$ = 26.3. Baes and Mesmer (19) assign <-12 to $\log K^o$ for $Fe(OH)_3(aq)$, in agreement with our -14.3. Naumov et al. (11) tabulate $\Delta_f G^o [AlF_5^{--}]$ = -2008.3 kJ/mol and $\Delta_f G^o [AlF_6^{---}]$ = -2291.1 J/mol, agreeing within 40 kJ/mol of our extrapolated values. Smith and Martell (25) tabulate log K(I=0.5) values of 19.4 and 19.8, respectively, for the AlF_5^{--} and AlF_6^{---} species.

These correlations are valuable for calculating enthalpy data and entropy data for complex ions, when experimental values are missing. A caution here is that extrapolation should only be made to the next higher ligand number because the uncertainty increases with the length of the extrapolation. These correlations are applied to calculating values of thermodynamic properties in the table for neptunium. The reader should note that the correlation represented by eq 3, or a similar correlation for $\Delta_f H^o$ versus the number of ligands, is valid only for either the free energy of formation or the enthalpy of formation. Neither the free energy of reaction, $\Delta_r G^o$, nor the enthalpy change in a reaction, $\Delta_r H^o$ are expected to vary linearly with the number of ligands in the complex (46).

Values of the thermodynamic properties of neptunium are consistent with the Key Values in Appendix I. Heat capacity of the aqueous species were calculated from the following three correlations, for positively charges ions [M^+], negative ions [M^-], and neutral uncharged species [M,aq]:

$$C_p^o[M^+] = 209.29 - 135.0/z/ - (2/3)S^o \tag{4}$$

$$C_p^o[M^-] = -4.125 - 133.29/z/ + (2/3)S^o \tag{5}$$

$$C_p^o[M,aq] = -16.564 + 0.958\Sigma C_p^o \tag{6}$$

where $/z/$ is the absolute value of the ionic charge, and the quantity ΣC_p^o is the algebraic sum of the partial molal heat capacities of the metal ion and the ligand, multiplied by the number of ligands in the aqueous species (9).

Reference 1 is the evaluation by Lemire (1), in which values for $\Delta_f G^o$, S° and C_p^o are tabulated. We have used his data to calculate values of $\Delta_f H^o$. Gibbs energy of $NpO_2Cl_2(aq)$ was calculated from an equation similar to eq 3, the enthalpy from a plot of $\Delta_f H^o$ versus the number of ligands (9). Our $\Delta_f G^o [NpO_2Cl_2,aq]$ = -1055 kJ/mol, comparing well with -1054 calculated from Bednarczyk and Fidelis (37) from the log K = -0.57 at I = 2.0, and assuming that log K° = -0.57, also. The entropy, S°, was calculated from the enthalpy and Gibbs energy values. Data for the three NpO_2^+ - carbonates from the tabulation in Bidoglio et al. (22) at I = 0.2, 1.0 and 2.0, and from Maya (43) were plotted according to eq 7. From these plots, intrinsic equilibrium constants were obtained at I = 0; these values were then used to calculate the Gibbs energy of formation for the 1:1, 1:2 and 1:3 complexes which we have tabulated. The same approach was used to calculate $\Delta_f G^o [NpO_2SO_4^-]$ and $\Delta_f H^o [NpO_2SO_4^-]$, using the data in Halperin (41). The variation in $\Delta_r H(I)$ with I using a Debye-Huckel equation was based on analogous plots and the derivation by Vasil'ev (40). Values of $\Delta_f H^o$ for the NpO_2^{++} - carbonates were calculated from Gibbs energy (38) and entropy data (1). The solubility measurements on $NpO_2OH(am?)$ published by Lierse et al. (20) interpreted in terms of two aqueous species, $NpO_2OH(aq)$ and $NpO_2(OH)_2^-$ are not included because NpO_2^+ could be oxidized in basic media to NpO_2^{++} by dissolved oxygen. The electrode potential of the NpO_2^{++}/NpO_2^+ couple was measured as 0.300 v. in 1M $NaOH$ solution, almost 0.9 v. more negative than in 1M $HClO_4$ media (44). Also, the hydrolysis constants for $NpO_2OH(aq)$ are markedly different from other measurements. We therefore do not include the second hydrolysis product in our tables at this time. Table VII summarizes the results of our calculations for these NpO_2^+ and NpO_2^{++} species; the parameters tabulated are based on a fit of experimental measurements to eq 7, and therefore permit calculation of the equilibrium quotients over the range 0<I<3.0. There are no experimental measurements for $NpO_2CO_3(aq)$; we calculated the thermodynamic property values from plots of $\Delta_f G^o$ and $\Delta_f H^o$ versus the number of ligands, and interpolating. The value of S^o was calculated from these data,

and the C_p^o was estimated from eq 6. Gibbs energy of formation for the $NpO_2F(aq)$ and NpO_2F^+ ion pairs were calculated from the recent work by Choppin and Rao (42) and from Smith and Martell (25). Equation 7 was used to correct the formation constants to I = 0.

In summary, missing data in the Np table were filled by correlations, to provide data at 25° and I = 0. In geologic systems, values of equilibrium constants are needed at various ionic strengths, and at elevated temperatures; the change in $\log K^o$ with ionic strength and temperature is treated briefly in the next section.

EFFECT OF IONIC STRENGTH AND TEMPERATURE ON log K°

Experimental data are obtained in media of varying ionic strength, and often differing supporting electrolytes. The formation constants of complex ions are calculated at standard conditions, I = 0, using an extended Debye-Huckel equation for the range 0<I<3.0 in the form

$$\log K(I) - \frac{A_\gamma \Delta z^2 I^{1/2}}{1 + I^{1/2}} = \log K^o + bI \tag{7}$$

where

K(I) = equilibrium quotient or product, at ionic strength I

K° = intrinsic equilibrium constant at 25°C and I = 0

$A_\gamma = 0.511$ at 25°C, $(mol/kg)^{-1/2}$

Δz^2 = sum of squares of charges of products of equilibrium, minus sum of squares of charges of reactants.

I = ionic strength, mol/kg .

b = a constant, $(mol/kg)^{-1}$, usually obtained by fitting experimental values; see however Ref. 19.

The effect of changing ionic strength on log K(I) is shown in Figures 1 to 3, for three reactions, plotted according to eq 7.

The change in equilibrium constant with increasing temperature is calculated using eq 2 when the heat capacity can be assumed constant over the entire temperature interval (17,18,32). Otherwise, the more generally applicable equation derived by Clarke and Glewe (17,35) should be used, eq 8

$$R \ln K(T) = A + \frac{B}{T} + C \ln T + DT + ET^2 + FT^3 \tag{8}$$

In eq 8, the coefficients A to F are:

$$A = \Delta_r S^o - C_o + \frac{\Theta^2}{4} C_2 - 10\frac{\Theta^3}{72} C_3 - C_o \ln\Theta + \Theta C_1 \ln\Theta - \frac{\Theta^2}{2} C_2 \ln\Theta + \frac{\Theta^3}{6} C_3 \ln\Theta$$

$$B = -\Delta_r H^o + \Theta C_o - \frac{\Theta^2}{2} C_1 + \frac{\Theta^3}{6} C_2 - \frac{\Theta^4}{24} C_3$$

$$C = C_o - \Theta C_1 + \frac{\Theta^2}{2} C_2 - \frac{\Theta^3}{6} C_3$$

$$D = \frac{C_1}{2} - \frac{\Theta}{2} C_2 + \frac{\Theta^2}{4} C_3$$

$$E = \frac{C_2}{12} - \frac{\Theta}{12} C_3$$

$$F = \frac{C_3}{72}$$

and, $C_o = \Delta_r C_p^o$; C_1 to C_3 are the first, second and third derivatives of the change in heat capacity, with temperature; $\Theta = 298.15$.

Values of the derivatives of $\Delta_r C_p^o$ are not readily available for most ionic species. One good source of values for the first derivative of $\Delta_r C_p^o$ is the recent publication on $SO_2(g)$ by Goldberg and Parker (33). They have tabulated data for five reactions involving S(IV).

PERFORMANCE ASSESSMENT STUDIES

The thermodynamic database was developed in part to predict the ability of a specific site to contain nuclear waste materials, in view of regulatory and environmental rules and regulations. One important aspect of this performance assessment is to determine the sensitivity of solubility calculations to the aqueous species which form, e.g., assuming a waste such as $NpO_2(s)$ dissolves in a ground water. Natural ground waters contain complexing anions such as Cl^-, F^-, HCO_3^-, and OH^-. These anions are expected to form complexes with actinide cations, for example the hydrolysis product PuO_2OH^+, thereby increasing the total concentration of dissolved radionuclide. The question is how complexation will contribute to the total solubility of a waste nuclide in the ambient waters. However, answering this question is even more complicated because the various complexes react differently, e.g., to form sorption products on rocks. Sorption is expected to be a major factor in retarding the migration of radionuclides from a respository site to our ground waters (39).

ACKNOWLEDGEMENT

Thanks are given to Malcolm D.Siegel,Sandia National Laboratories (Albuquerque), and John A.Apps and Heino Nitsche, Lawrence Berkeley Laboratory, for their critical review. Harold C.Helgeson, University of California, is thanked for his discussion of eq 3 and on the need for higher quality laboratory measurements on values of Gibbs free energy. Gregory R.Choppin, Florida State University, provided important insight into the reasons for the linearity between free energy of formation and enthalpy of formation, and the observed linearity between these two properties and the number of ligands.

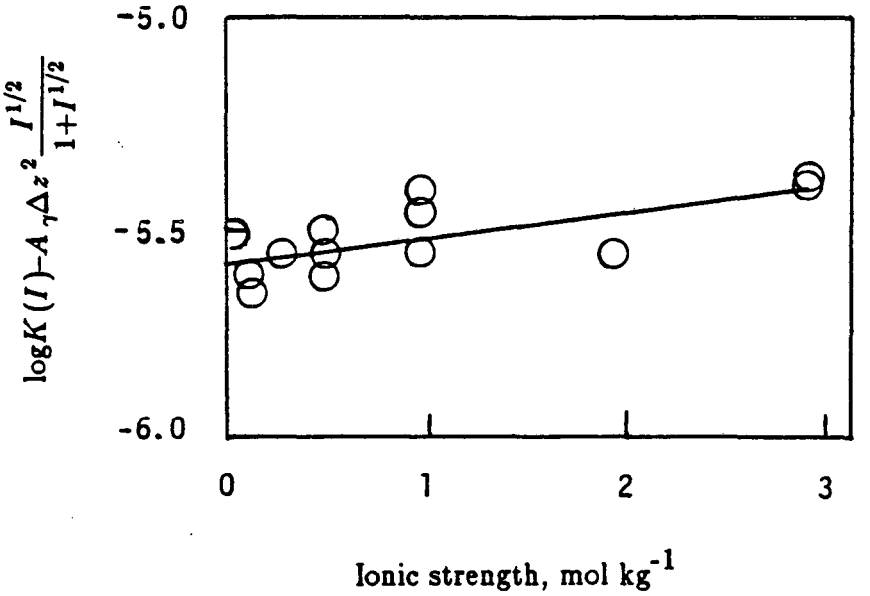


Figure 1. Variation in log K(I) as a function of ionic strength, I, for the reaction $2UO_2^{++} + 2H_2O = (UO_2)_2(OH)_2^{++} + 2H^+$. Experimental points from Ref. 9. log K° = -5.66.

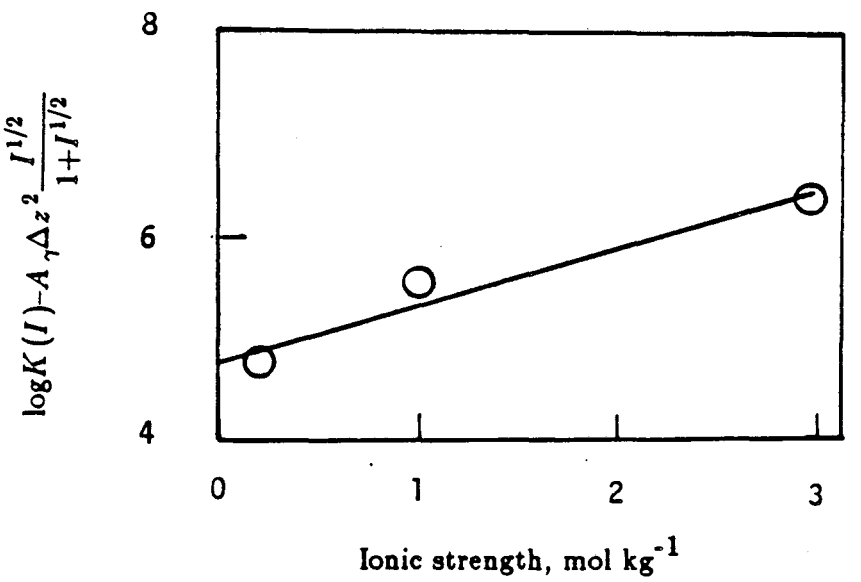


Figure 2. Effect of ionic strength on log K(I) for reaction $NpO_2^+ + CO_3^{--} = NpO_2CO_3^-$. log K° = 4.64.

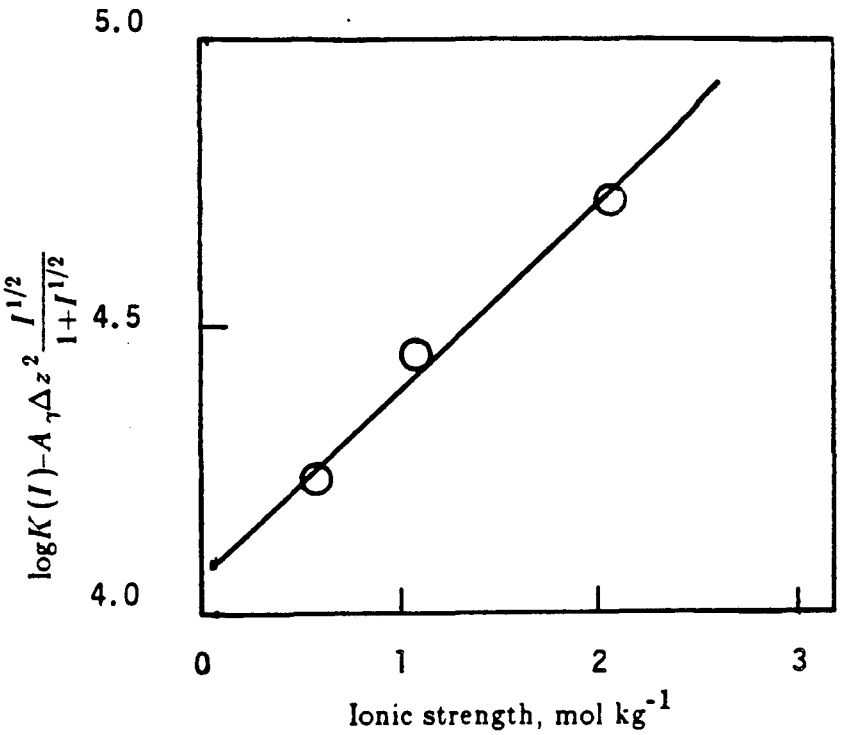


Figure 3. Formation of americium sulfate, $Am^{+++} + SO_4^{--} = AmSO_4^+$ using data from Ref. 21. $\log K^\circ$ = 4.14.

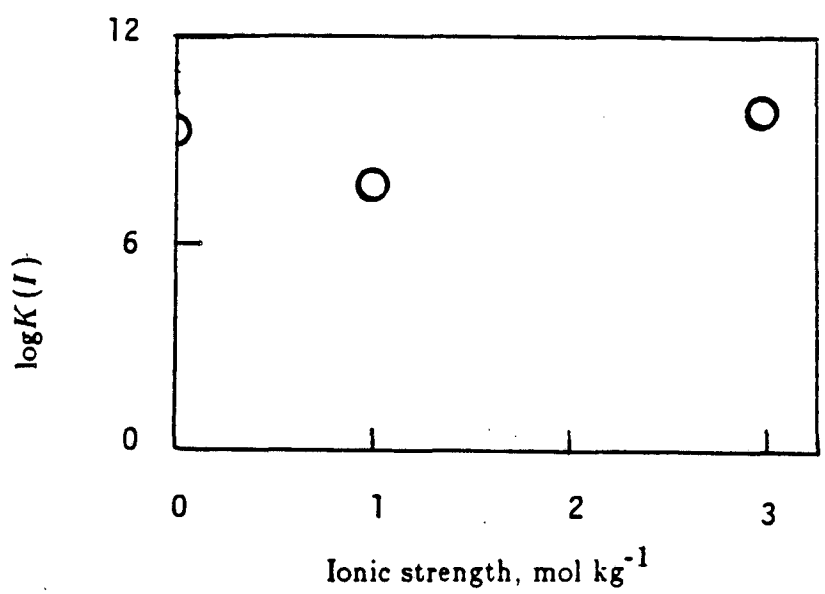


Figure 4. $\log K(I)$ versus I for reaction $NpO_2^+ + 3CO_3^{--} = NpO_2(CO_3)_3^{-----}$. log K° = 8.55.

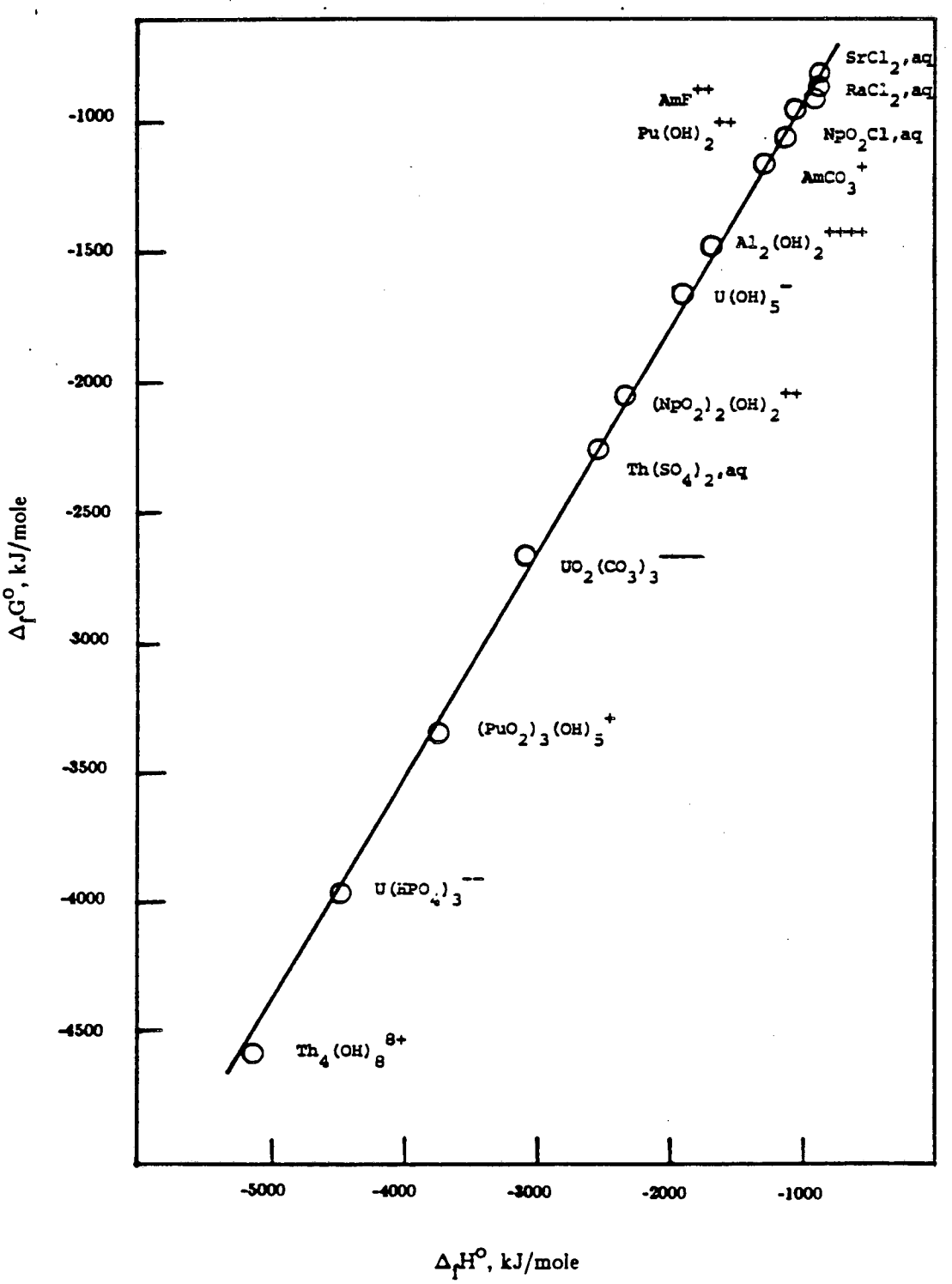


Figure 5. Linear relationship between Gibbs energy of formation, and enthalpy of formation for selected aqueous complexes. Data are from Ref. 9.

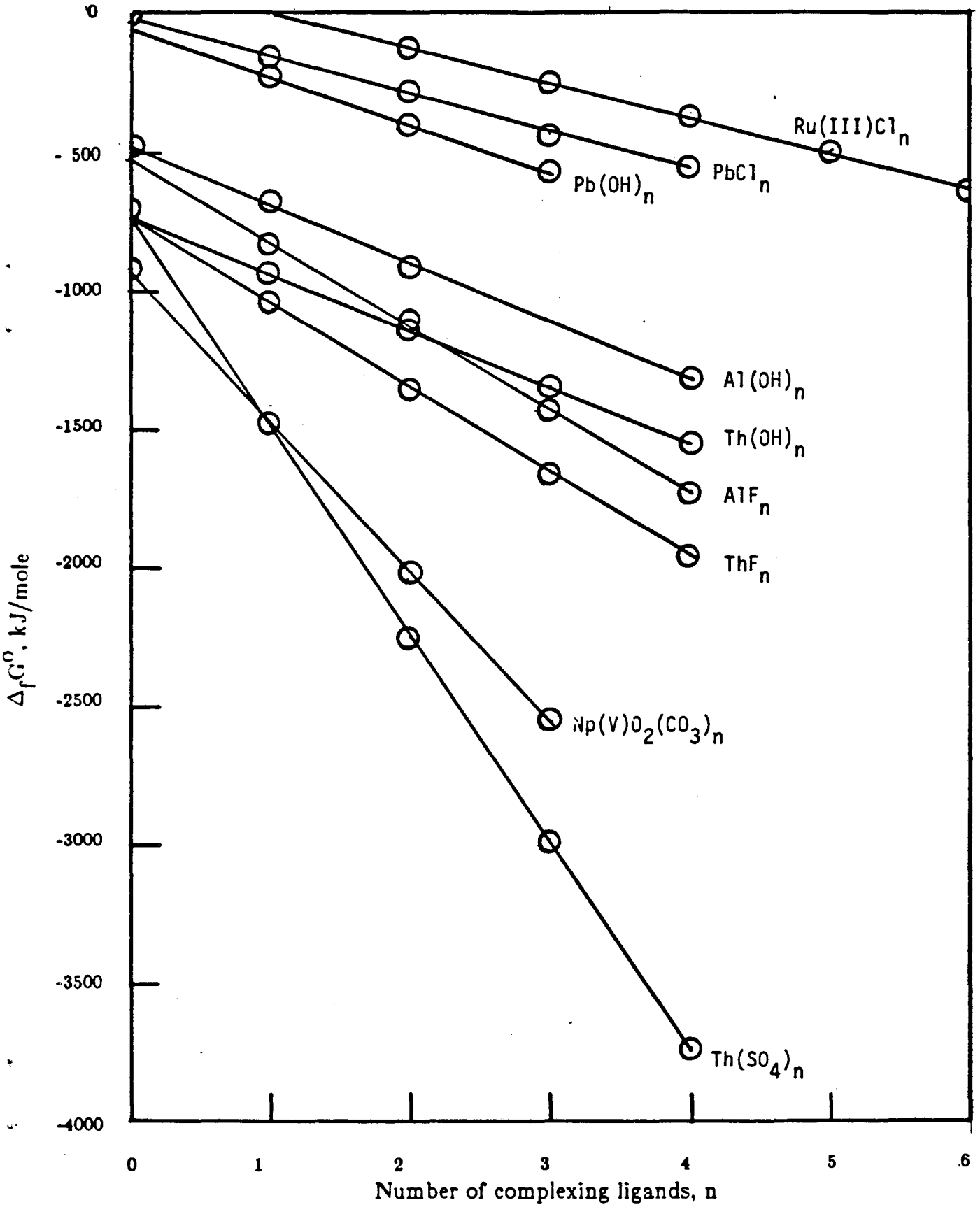


Figure 6. Plot of $\Delta_f G^o$ for complex ions versus number of ligands
Data from Ref. 9.

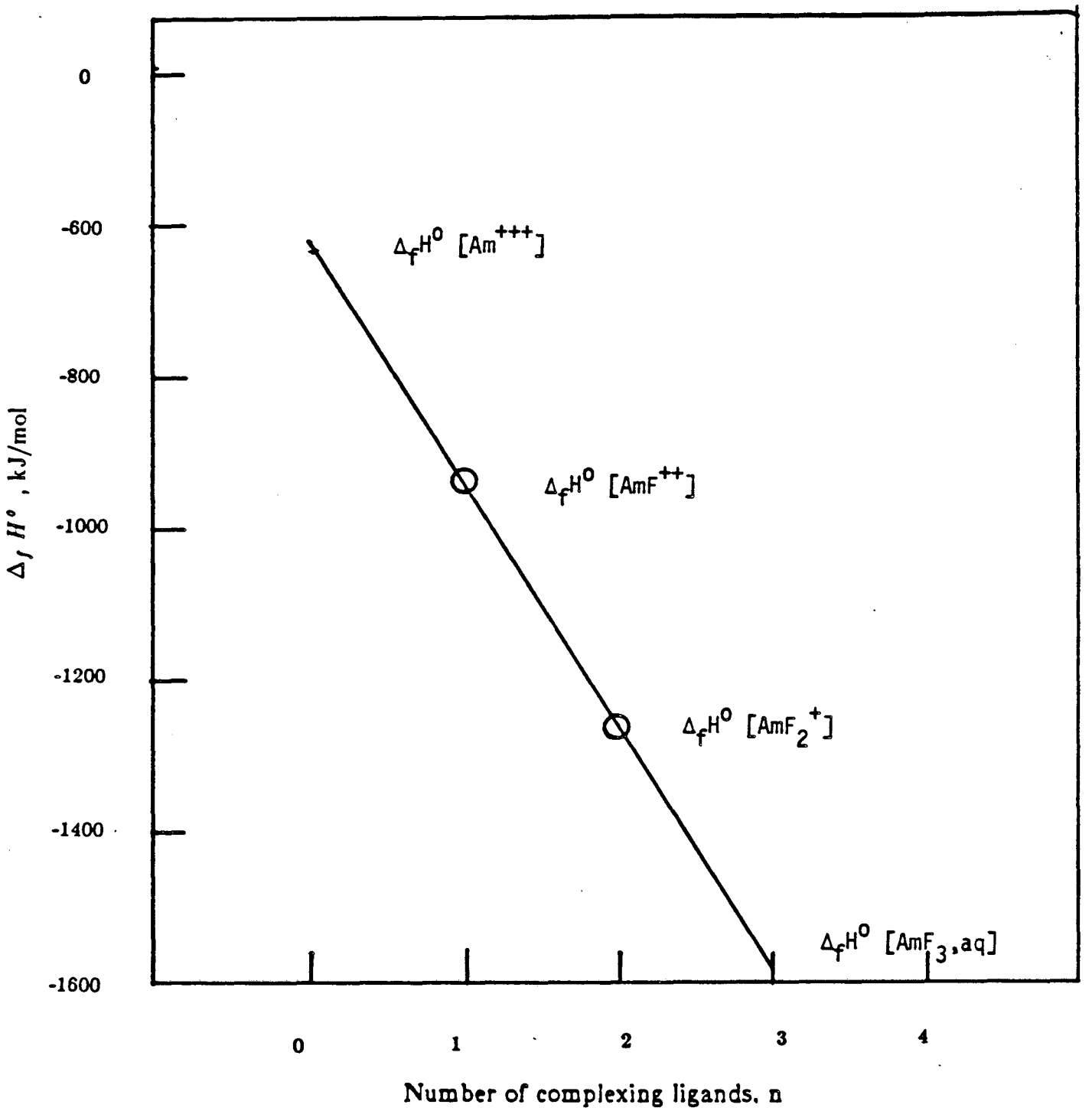


Figure 7. Change in $\Delta_f H^o$ as a function of number of F^- ligands for $Am^{+++} + nF^- = AmF_n$ (charges omitted). Circles are values from Nash and Cleveland (34), calculated to I = 0, using the Davies equation (23), or eq 7.

Table I. Portion of reference thermodynamic data used for this database. Complete table is in Ref. 9 and the Appendix.

Key Values for Thermodynamic Properties at 298.15 K and Zero Ionic Strength, for Crystalline (s), Gaseous (g) and Aqueous (aq) Forms. Data obtained from CODATA, National Bureau of Standards, or as Noted. All Ions are in the Aqueous (aq) Form.

Substance	$\Delta_f G^\circ$	$\Delta_f H^\circ$	S°	Cp°	Ref.
	kJ mol^{-1}		J mol^{-1} K^{-1}		
$O_2(g)$	0.000	0.000	205.04	29.36	2557
			0.03	0.0	
$O_2(aq)$	16.530	-12.138	108.90	224.00	9777
	0.2	0.2	0.80	25.0	
$H_2(g)$	0.000	0.000	130.57	28.82	2557
			0.03		
$H_2(aq)$	17.780	-4.040	57.37	175.00	9777
	0.9	0.8	2.50	25.0	
$H_2O(g)$	-228.572	-241.814	188.72	33.61	2557
	0.1	0.0	0.04		
$H_2O(l)$	-237.129	-285.830	69.95	75.29	2557
	0.1	0.0	0.08		
e^-,electron	0.000	0.000	65.28	14.42	0066
			0.01	0.1	
$Si(OH)_4(aq)$	-1308.000	-1460.100	180.00	215.00	9923
	1.7	1.7	4.20		
H^+	0.000	0.000	0.00	0.00	2222
	0.0	0.0	0.00	0.0	
NH_4^+	-79.310	-133.260	111.17	25.00	2559
	0.1	0.3	0.75	4.1	
Li^+	-292.620	-278.455	11.30	60.70	2557
	0.2	0.1	0.35		
Na^+	-261.905	-240.300	58.41	42.40	2557
	0.1	0.1	0.20		

Table II. Standard electrode potentials for selected redox couples, 25 °C and zero ionic strength. Values of E° calculated from $\Delta_f G^o$ values in Table I, Ref. 9 and the Appendix. $\Delta = \Delta_r G^o - [\Delta_r H^o - 298.15 \Delta_r S^o]$

Electrode Reaction	Δ	E^o(volt) This Work	E^o(volt) Ref.12
$O_2(aq) + 4H^+ + 4e = 2H_2O$	122	1.272	–
$2H^+ + 2e = H_2(aq)$	5	-0.092	–
$Na^+ + e = Na(s)$	12	-2.714	-2.714
$K^+ + e = K(s)$	251	-2.925	-2.925
$Cs^+ + e = Cs(s)$	321	-3.027	-2.923
$Ag^+ + e = Ag(s)$	14	0.7991	0.7991
$NpO_2^+ + 4H^+ + 5e = Np(s) + 2H_2O$	182	-0.913	–
$PuO_2^{++} + 4H^+ + 6e = Pu(s) + 2H_2O$	500	-0.488	–
$Ca^{++} + 2e = Ca(s)$	59	-2.865	-2.84
$Sr^{++} + 2e = Sr(s)$	1	-2.922	-2.89
$Cu^{++} + 2e = Cu(s)$	75	0.339	0.340
$Pb^{++} + 2e = Pb(s)$	3	-0.124	-0.125
$UO_2^{++} + 4H^+ + 6e = U(s) + 2H_2O$	100	-0.826	–
$Zn^{++} + 2e = Zn(s)$	0	-0.763	-0.7626
$Fe^{++} + 2e = Fe(s)$	62	-0.474	-0.44
$Fe^{+++} + 3e = Fe(s)$	110	-0.059	-0.037
$Th^{++++} + 4e = Th(s)$	447	-1.826	-1.83
$F_2(g) + 2e = 2F^-$	19	2.920	2.87
$Cl_2(g) + 2e = Cl^-$	126	1.360	1.358
$I_2(s) + 2e = 2I^-$	531	0.5355	0.5355
$O_2(g) + 2H_2O + 4e = 4OH^-$	247	0.401	0.401
$Si(OH)_4(aq) + 4H^+ + 4e = Si(s) + 4H_2O$	209	-0.931	-0.848
$Np^{++++} + 4e = Np(s)$	52	-1.303	-1.30
$Np^{+++} + 3e = Np(s)$	99	-1.786	-1.79
$Np^{++++} + e = Np^{+++}$	753	0.15	0.15
$NpO_2^+ + 4H^+ + e = Np^{++++} + 2H_2O$	130	0.644	0.66
$NpO_2^{++} + e = NpO_2^+$	730	1.235	1.24
$Np(OH)_3(s) + 3e = Np(s) + 3OH^-$	--	-2.146	-2.2
$NpO_2(OH)_2(s) + 2H_2O + 6e = Np(s) + 6OH^-$	432	-1.325	–
$NpO_2OH(am) + 2H_2O + 5e = Np(s) + 5OH^-$	194	-1.691	–
$Np(OH)_4(s) + 4e = Np(s) + 4OH^-$	323	-2.119	–

Table III. Comparison of calculated solubility of both quartz and amorphous silica with experimentally related values, from 75 °C to 350 °C.

T, °C	75	100	150	200	250	300	350	Reference
logK(quartz)	-3.35	-3.10	-2.68	-2.36	-2.11	-1.94	-1.90	15
	-3.39	-3.16	-2.76	-2.43	-2.16	-1.91	-1.71	This work
logK(amorphous)	-2.37	-2.23	-1.99	-1.81	-1.67	-1.59	-1.54	16
	-2.59	-2.43	-2.15	-1.91	-1.71	-1.54	-1.39	This work

Table IV. Experimental measurements on the solubility of $NpO_2OH(am)$ and hydrolysis of NpO_2^+ compared with this work.

Medium	**$\log K_{sp}$	logK(I)	Method	Ref.
0	-9.41	-8.82	Calculated	This work
0.1	<-9.2	-8.85	Solubility	19
0.1	-9.2	-	Titration	in 20
0.2,20 °C	-9.02	-10.1	Solubility	in 20
0.2	-9.07	-8.88	Calculated	This work
0.02,23 °C	-9.73	-8.91	Potentiometry	44
1.0M $NaClO_4$	-	-9.12	Solubility	43
1.0M $NaClO_4$	-8.81	-11.43	Titration	20
0.2M $NaClO_4$	-	-9.59	Extraction	22
0.1M $NaClO_4$	-9.15	-8.85	Calculated	This work
1.0M $NaClO_4$	-8.81	-9.12	Calculated	This work
2.0	-8.62	-9.42	Calculated	This work
3.0	-8.48	-9.72	Calculated	This work

* Reaction: $NpO_2^+ + H_2O = NpO_2OH(aq) + H^+$

** Calculated from eq 7, with $\log K^* = -9.41$, $b = 0.094$.

Table V. Formation quotients of NpO_2^+ - carbonates.

Medium	$\log K_{11}(I)$	$\log K_{12}(I)$	$\log K_{13}(I)$	Method	Ref.
0.05	5.9±0.5	-	16.3±0.5	Electrochemical	in 22
0.2	4.13±0.03	7.06±0.05	-	Extraction	in 22
0.2	4.26	6.94	-	Calculation	This work
1.0	4.49±0.06	7.11±0.07	8.53	Solubility	in 22
1.0	4.31	7.27	-	Calculation	This work
3.0	5.09	8.15±0.25	10.46	Solubility	in 22
3.0	5.14	8.09	-	Calculation	This work

Table VI . Variation in Gibbs energy of formation of selected cation-ligand complexes, with the number of ligands, n. Average correlation coefficient is 0.999.

$M\text{-}X_n$	n_{max}	$\Delta_f G[MX_n]$	$p\Delta_f G[MX_n]$,eq3	m	Ref.
Pb-OH	3	-23.97	-28.63	-183.70	19
Fe(II)-OH	3	-91.55	-93.49	-177.7	19,29
Fe(III)-OH	4	-17.87	-30.47	-205.56	19
Al-OH	4	-489.4	-491.83	-205.49	19
Eu-OH	2	-576.2	-574.63	-194.8	28
Am-OH	2	-599.1	-599.95	-188.9	This work
Ru-Cl	6	173.4	164.34	-134.15	24
Th-OH	4	-704.6	-707.5	-214.2	19
Al-F	4	-489.4	-497.96	-309.1	25
Th-F	4	-704.6	-714.64	-314.73	25
Pb-Cl	4	-23.97	-27.77	-133.04	26
$La\text{-}SO_4$	2	-683.7	-687.4	-758.7	2
$Th\text{-}SO_4$	4	-704.6	-718.76	-757.05	27

Table VII. Debye-Huckel parameters for use in calculating the effect of ionic strength on the equilibrium constants for the reactions shown, over the range $0<I<3.0$.

Formation Reaction	logK*	$A_\gamma \Delta z^2$	b
$NpO_2^+ + H_2O = NpO_2OH(aq) + H^+$	-8.82	0	-0.30
$NpO_2^+ + SO_4^- = NpO_2SO_4^-$	-0.60	-2.04	0.41
$NpO_2^+ + CO_3^- = NpO_2CO_3^-$	4.78	-2.04	0.55
$NpO_2^+ + 2CO_3^- = NpO_2(CO_3)_2^-$	6.86	0	0.41
$NpO_2^+ + 3CO_3^- = NpO_2(CO_3)_3^{--}$	8.55	6.12	-
$NpO_2^+ + F^- = NpO_2F(aq)$	1.95	-1.02	-0.18
$NpO_2^{++} + F^- = NpO_2F^+$	4.59	-2.04	0.76
$^*Am^{+++} + F^- = AmF^{++}$	3.24	-3.06	0.78

*$\Delta_r H^o = 23.02$ kJ/mol, b = 6.11, calculated from eq 7 in the form:

$$\Delta_r H(I) - A_\gamma \Delta z^2 I^{1/2}(1+I^{1/2})^{-1} = \Delta_r H^o + bI.$$

LITERATURE CITED

(1) Lemire, R.J., Tremaine,P.R., J.Chem.Eng.Data, 25, 361 (1980). Lemire,R.J., "An Assessment of the Thermodynamic Behaviour of Neptunium in Water and Model Groundwaters from 25 to 150 °C",AECL-7817 (March 1984).

(2) Wagman,D.D.,Evans,W.H.,Parker,V.B.,Schumm,R.H.,Halow,I.,Bailey,S.M.,Churney,K.L., Nuttall,R.L., J.Phys.Chem.Ref.Data, 11, Suppl.2 (1982).

(3) "The Chemical Thermodynamics of Actinide Elements and Compounds. Parts 1 - 14", International Atomic Energy Agency, Vienna, Austria (various dates).

(4) Morss,L.R., "Thermodynamic Properties",in,"The Chemistry of the Actinide Elements", 2nd ed., Katz,J.J.,Seaborg,G.T.,Morss,L.R.,eds., Chapman and Hall (1986).

(5) CODATA Task Group on Key Values for Thermodynamics: CODATA Recommended Key Values for Thermodynamics 1977, CODATA Bull. 28, CODATA Secretariat, Paris, France (1978).

(6) Ryabukhin,A.G., Russ.J.Phys.Chem., 51, 573 (1977). Ibid., 54, 1197 (1980).

(7) Brewer,L., "Thermodynamic Data for Flue-Gas Desulfurization Processes",in, "Flue Gas Desulfurization", LBL-12342, Lawrence Berkeley Laboratory (1981), p.303.

(8) Rard,J.A., "Thermodynamic Data Bases for Multivalent Elements: An Example for Ruthenium", Intl.Conf. on Thermodynamics of Aqueous Systems with Industrial Applications, May (1987).

(9) Phillips,S.L.,Siegel,M.D.,Hale,F.V., LBL-22860. To be published, 1987.

(10) Busey,R.H.,Mesmer,R.E., Inorg.Chem., 16, 2444 (1977).

(11) Naumov,G.B.,Ryzhenko,B.N.,Khodakovsky,I.L., "Handbook of Thermodyamic Data",Translated by Soleimani,G.J., PB-226 722, National Technical Information Service (1974).

(12) Bard,A.J.,Parsons,R.,Jordan,J., eds.,"Standard Potentials in Aqueous Solution", Marcel Dekker, Inc., New York (1985).

(13) Millero,F.J.,Milne,P.J.,Thurmond,V.L., Geochim.Cosmochim.Acta, 48, 1141 (1984).

(14) Busenberg,E.,Plummer,L.N.,Parker,V.B., Geochim.Cosmochim.Acta, 48, 2021 (1984).

(15) Fournier,R.O., Geochim.Cosmochim.Acta, 47, 579 (1983).

(16) Fournier,R.O.,Marshall,W.L., Geochim.Cosmochim.Acta, 47, 587 (1983).

(17) Phillips,S.L.,Silvester,L.F., High Temperatures-High Pressures, 16, 81 (1984).

(18) Phillips,S.L.,Silvester,L.F., Inorg.Chem., 22, 3848 (1983)

(19) Baes,C.F.,Mesmer,R.E., "The Hydrolysis of Cations", John Wiley & Sons, Inc., New York (1976).

(20) Lierse,C.,Treiber,W.,Kim,J.I., Radiochim.Acta, 38, 27 (1985).

(21) Phillips,S.L., "Hydrolysis and Formation Constants at 25 °C", LBL-14313, Berkeley, CA (1982).

(22) Bidoglio,G.,Tanet,G.,Chatt,A., Radiochim.Acta, 38, 21 (1985).

(23) Davies,C.W., "Ion Association", Butterworths, Washington,D.C. (1962).

(24) Rard,J.A., Chem.Rev., 85, 1 (1985).

(25) Smith,R.M.,Martell,A.E., "Critical Stability Constants. Vol.4.: Inorganic Complexes", Plenum Press, New York (1976).

(26) Seward,T.M., Geochim.Cosmochim.Acta, 48, 121 (1984).

(27) Nuclear Energy Agency Database, Paris, France (1986).

(28) Rard,J.A., Chem.Rev., 85, 555 (1985).

(29) Cobble,J.W.,Murray,R.C.,Turner,P.J.,Chen,K., "High-Temperature Thermodynamic Data for Species in Aqueous Solution", NP-2400, San Diego, CA (1982).

(30) Lebedev,I.A., Radiokhimiya, 21, 686 (1980). Ibid., 23, 6 (1981).

(31) Phillips,S.L.,Phillips,C.A.Skeen,J., "Hydrolysis, Formation and Ionization Constants at 25 °C and at High Temperature - High Ionic Strength", LBL-14996 (1985).

(32) Phillips,S.L., "Thermochemical Data for Nuclear Waste Disposal",in,"The Role of Data in Scientific Progress",Glaeser,P.S.,ed., Elsevier (1985), p.315.

(33) Goldberg,R.N.,Parker,V.B., J.Res.Natl.Bur.Stand., 90, 341 (1985).

(34) Nash,K.L.,Cleveland,J.M., Radiochim.Acta, 37, 19 (1984). Choppin,G.R.,Unrein,P.J., in, "Transplutonium Elements", North Holland (1976), p.97.

(35) Clarke,E.C.W.,Glewe,D.N., Trans.Faraday Soc., 62, 539 (1966).

(36) "Conference on the Application of Geochemical Models to High-Level Nuclear Waste Repository Assessment", NUREG/CP-0062, Proceedings, Oct.2-5,1984 (May 1985).

(37) Bednarczyk,L.,Fidelis,I., J.Radioanal.Chem., 45, 325 (1978).

(38) Ullman,W.J.,Schreiner,F., Radiochim.Acta, 40, 179 (1986). Ibid., in press.

(39) Siegel,M.D.,Phillips,S.L.,Leckie,J.O.,Kelly,W., Submitted to 87 DOE/AECL International Conference on Geostatistical Sensitivity and Uncertainty Methods for Ground-Water Flow and Radionuclide Modeling, San Francisco, September 15-17,1987.

(40) Vasil'ev,V.P.,Kokurin,N.I.,Vasil'eva,V.N., Russ.J.Inorg.Chem., 21, 218 (1976).

(41) Halperin,J.,Oliver,J.H., Radiochim.Acta, 33, 29 (1983).

(42) Choppin,G.R.,Rao,L.F., Radiochim.Acta, 37, 143 (1984).

(43) Maya,L., Inorg.Chem., 22, 2093 (1983).

(44) Sevost'yanova,E.P.,Khalturin,G.V., Radiokhimiya, 18, 870 (1976). English translation.

(45) Simakin,G.A.,Matyashchuk,I.V.,Vladimirova,N.A., Radiokhimiya, 15, 98 (1973). In English.

(46) Choppin,G.R., Private Communication, July 22,1987.

Appendix I. Table of Auxiliary Values

Key Values for Thermodynamic Properties at 298.15 K and Zero Ionic Strength, for Crystalline (s), Gaseous (g) and Aqueous (aq) Forms. Data obtained from CODATA, National Bureau of Standards, or as Noted. All Ions are in the Aqueous (aq) Form.

Substance	$\Delta_f G^\circ$	$\Delta_f H^\circ$	S°	Cp°	Ref.
	kJ mol^{-1}		J mol^{-1} K^{-1}		
$O_2(g)$	0.000	0.000	205.04	29.36	2557
			0.03	0.0	
$O_2(aq)$	16.530	-12.138	108.90	224.00	9777
	0.2	0.2	0.80	25.0	
$H_2(g)$	0.000	0.000	130.57	28.82	2557
			0.03		
$H_2(aq)$	17.780	-4.040	57.37	175.00	9777
	0.9	0.8	2.50	25.0	
$H_2O(g)$	-228.572	-241.814	188.72	33.61	2557
	0.1	0.0	0.04		
$H_2O(l)$	-237.129	-285.830	69.95	75.29	2557
	0.1	0.0	0.08		
e^-,electron	0.000	0.000	65.28	14.42	0066
			0.01	0.1	
$Si(OH)_4(aq)$	-1308.000	-1460.100	180.00	215.00	9923
	1.7	1.7	4.20		
H^+	0.000	0.000	0.00	0.00	2222
	0.0	0.0	0.00	0.0	
NH_4^+	-79.310	-133.260	111.17	25.00	2559
	0.1	0.3	0.75	4.1	
Li^+	-292.620	-278.455	11.30	60.70	2557
	0.2	0.1	0.35		
Na^+	-261.905	-240.300	58.41	42.40	2557
	0.1	0.1	0.20		

Substance	$\Delta_f G^\circ$	$\Delta_f H^\circ$	S°	Cp°	Ref.
	kJ mol^{-1}		J mol^{-1}K^{-1}		
K^+	-282.224	-252.170	101.04	13.00	9557
	0.1	0.1	0.25		
Rb^+	-283.980	-251.120	120.46	-6.00	2559
	0.2	0.1	0.40		
Cs^+	-292.020	-258.040	132.84	-14.00	2559
	0.2	0.1	0.40		
Tl^+	-32.430	5.360	125.50	-9.00	2229
	0.2	1.2	4.00		
Cu^+	49.980	71.670	40.60	47.00	2229
	0.1	0.1	0.40		
Ag^+	77.107	105.750	73.38	25.00	2559
	0.1	0.1	0.40		
NpO_2^+	-915.000	-978.200	-21.00	92.00	4448
	5.4	4.6	8.00		
Hg_2^{++}	153.607	166.820	65.52		9550
	0.1	0.2	0.80		
Hg^{++}	164.700	170.160	-36.32		9550
	0.1	0.2	0.80		
Fe^{++}	-91.550	-92.730	-107.00	-4.00	1197
	1.0	0.8	2.50	33.0	
Mg^{++}	-454.800	-466.850	-138.10	-16.00	2227
	1.7	1.3	1.70	8.0	
Ca^{++}	-552.870	-543.100	-56.40	-30.00	9557
	0.8	0.8	0.40		
Sr^{++}	-563.830	-550.900	-31.50	-34.80	****
	0.8	0.5	2.00		
Ba^{++}	-555.360	-532.500	8.40	-45.60	****
	0.1	0.1	0.85		
Ra^{++}	-561.500	-527.600	54.00	-97.00	2229
	10.0				
Cu^{++}	65.520	65.690	-97.10	-17.00	955*
	0.1	0.8	1.20		
Sn^{++}	-27.200	-8.900	-15.80	-50.00	9559
	0.8	0.8	4.00		
Pb^{++}	-23.970	0.920	17.70	-73.00	9559
	0.1	0.3	0.80		
Ni^{++}	-45.600	-54.000	-128.90	-42.00	222*
	0.9	0.9	0.90		

Substance	$\Delta_f G°$	$\Delta_f H°$	$S°$	$Cp°$	Ref.
	kJ mol^{-1}		J mol^{-1}K^{-1}		
Mn^{++}	-230.300	-221.160	-67.76	-11.00	9777
	0.9	0.1	0.85	3.0	
UO_2^{++}	-952.700	-1019.200	-98.30	5.00	9558
	2.1	2.5	4.00		
PuO_2^{++}	-756.900	-822.200	-88.00	11.00	4448
	7.1	6.7	8.00		
Zn^{++}	-147.230	-153.390	-109.60	-21.00	955*
	0.2	0.2	0.70		
Al^{+++}	-489.530	-525.090	-286.80	-119.00	999*
	1.4	1.4	15.00	10.0	
Fe^{+++}	-17.280	-50.110	-279.00	-10.00	*999
	1.0	0.8	4.10	0.1	
Th^{++++}	-704.600	-769.000	-423.00	-49.00	4449
	5.4	2.5	17.00		
Pa^{++++}	-565.000	-619.700	-397.00	-66.00	4449
	17.0	13.0	42.00		
F^-	-281.750	-335.350	-13.18	-117.00	9557
	0.7	0.7	0.54	4.0	
Cl^-	-131.228	-167.080	56.73	-125.50	2557
	0.1	0.1	0.16		
Br^-	-103.960	-121.500	82.84	-132.20	2557
	0.2	0.2	0.20	4.2	
I^-	-51.669	-56.900	106.70	-120.50	9557
	0.8	0.8	0.20	4.2	
OH^-	-157.244	-230.025	-10.71	-140.50	2557
	0.1	0.1	0.20	4.0	
NO_3^-	-110.780	-206.860	146.94	-72.00	9777
	0.0	0.0	0.85	0.0	
SO_4^{--}	-744.530	-909.600	18.83	-278.00	2557
	0.4	0.4	0.50	6.7	
CO_3^{--}	-527.730	-675.150	-49.96	-273.50	9777
	0.3	0.3	0.80	4.0	

Comments:

Reference 0 = no data; 1 = Cobble et al.,1982; 2 = Wagman et al.,1982;
3 = Naumov et al.,1974; 4 = Fuger and Oetting,1976; 5 = CODATA, 1978;
6 = Ryabukhin, 1977,1980; 7 = L.Brewer,1981; 8 = Lemire and Tremaine,1980, and Lemire 1984
9 = This work.

For O_2(aq),H_2(aq),we calculated $\Delta_f G$ using $\Delta_f H$ and S from
L.Brewer:"Thermodynamic Data for Flue-Gas Desulfurization",in"Flue

Comments:

Gas Desulfurization",LBL-12342, Lawrence Berkeley Laboratory (Sept.1981). Heat capacity of O_2(aq) and H_2(aq) are from L.Brewer,1981. Entropy and Cp of electron(gas) are from A.G.Ryabukhin:Russ.J.Phys.Chem. 1977, v.51, 573; and Ibid., 1980, v.54, 1197. Gibbs energy of formation for Hg^{++},Hg_2^{++} compare well with Hepler;Olofsson:Chem.Rev.1975, v.75,585. * Gibbs energy and enthalpy of Fe^{++} from J.W.Cobble;R.C.Murray; P.J.Turner;K.Chen: "High-Temperature Thermodynamic Data for Species in Aqueous Solution",NP-2400, San Diego State Univ.,San Diego, CA(May 1982). GHS values for Sr^{++} from E.Busenberg;L.N.Plummer; V.B.Parker:Geochim.Cosmochim.Acta 1984,v.48,2021.$\Delta_f G[UO_2^{++}]$ was calculated here using CODATA values of $\Delta_f H$ and S;$Cp[UO_2^{++}]$ from R.J.Lemire;P.R.Tremaine: J.Chem.Eng.Data 1980, v.25, 361. $\Delta_f H[Fe^{+++}]$ calculated from free energy and entropy. $\Delta_f G[Fe^{+++}]$ from Flynn:Chem.Rev.1984,v.84,31. $Cp[OH^-]$ is from J.A.Barbero;L.G.Hepler;K.G.McCurdy;P.R.Tremaine: Can.J.Chem. 1983,v.61,2509. $Cp[SO_4^-]$ from Larson;Zeeb; Hepler: Can.J.Chem. 1982,v.60,2141. $Cp[Cl^-]$,$Cp[Br^-]$ are both from L.Brewer,1981. For Cl-, S.N.L'vov;Ya.D.Rakhmilevich; I.A.Dibrov: Russ.J.Phys.Chem. 1984, v.58, 1364 find from emf measurements, S = 75.6 J/mol/K, and Cp = -61 J/mol/K. The enthalpy of formation, entropy and heat capacity for CO_3^- are from Brewer,1981. Heat capacity of Al^{+++} from Hovey;Tremaine: Geochim.Cosmochim. Acta 1986,v.50,453. Gibbs energy and enthalpy calculated from data in Y.Couturier;G.Michard;G.Sarazin:Geochim.Cosmochim.Acta 1984,v.48,649. Heat capacity of Sr^{++},Ba^{++} from J.K.Hovey;L.G.Hepler;P.R..Tremaine: J.Solution Chem.1986,v.15,969. Cp of Zn^{++},Cu^{++},Ni^{++} are from J.J.Spitzer;I.V.Olofsson;P.P.Singh;L.G.Hepler: J.Chem.Thermodynamics 1979,v.11,233. Gibbs energy,enthalpy,entropy of Ba^{++} from E.Busenberg;L.N.Plummer: Geochim.Cosmochim.Acta 1986,v.50,2225. NBS Tables list $S[F^-]$ = -13.8 J/mol/K which may be adopted by CODATA. $\Delta_f G[Al^{+++}]$ from May et al.,$\Delta_f H[Al^{+++}]$ from Couturier et al.; $S[Al^{+++}]$ calculated from values of Gibbs energy and entropy. For Fe^{+++}, Brewer tabulates $\Delta_f H$=-48.5kJ/mol, S=-316 J/mol/K.

Appendix II. Tabulation of Values for Selected Substances of Neptunium.

PROPERTIES OF ELEMENTAL NEPTUNIUM:

Atomic Number: 93
Formula Mass: 237.05
Electronic Configuration: $5f^5\ 7s^2$
Electronegativity: 1.1
Hydration Number:
Ionic Radius: 1.01 angstrom (Np^{+++});0.91 angstrom (Np^{++++})
Selected Average for Soils:
Concentration in Natural Waters:

THERMODYNAMIC PROPERTIES OF SUBSTANCES: 25 °C; I=0

Substance	$\Delta_f G°$	$\Delta_f H°$	S°	Cp°	Ref.
	kJ mol^{-1}		J mol^{-1} K^{-1}		
Np(s)	0.000	0.000	50.30	29.62	4444
			1.00	0.6	
Np_2O_5(s)	-2013.000	-2147.250	163.00	129.00	1911
	14.0	15.0	23.00		
NpO_2(s)	-1021.800	-1074.000	80.30	66.21	1911
	2.5	2.5	0.40		
$NpO_3.H_2O$(s)	-1247.000	-1379.000	146.00	112.00	3339
	8.0	4.6	33.00		
$NpO_2(OH)_2$(s)	-1236.000	-1377.010	118.00	112.00	1911
	12.0	12.0	20.00		
NpO_2(OH)(am)	-1128.000	-1224.100	101.00	86.00	1911
	5.5	6.0	8.00		
$Np(OH)_4$(s)	-1447.000	-1621.365	139.00	131.00	1911
	20.0	20.0	25.00		
NpF_4(s)	-1783.630	-1874.000	152.72	116.06	2222
		13.0	4.10		
NpF_3(s)	-1460.310	-1528.830	124.68	98.32	2222
		5.0	4.00		
$NpCl_4$(s)	-896.208	-984.100	201.67	120.46	2222
		1.7	4.10		
$NpCl_3$(s)	-831.699	-898.500	161.50	104.39	2222
		2.5	8.40		

Substance	$\Delta_f G^\circ$	$\Delta_f H^\circ$	S°	Cp°	Ref.
	kJ mol^{-1}		J mol^{-1}K^{-1}		
$NpBr_4(s)$	-737.644	-771.100	242.67	128.62	2222
		1.7	12.50		
$NpBr_3(s)$	-706.031	-730.500	196.65	109.24	2222
		2.1	17.00		
$NpO_2(NO_3)_2(s)$		-1190.000			0400
$NpO_2(NO_3)_2.H_2O(s)$		-1505.000			0400
$NpO_2(NO_3)_2.6H_2O(s)$	-2429.200	-3009.100	516.30		3330
	5.4	5.0	4.60		
$NpOCl_2(s)$	-967.760	-1037.600	141.00		2220
		13.0	8.40		
$NaNpO_2CO_3.3.5H_2O(s)$	-2601.000		314.00	269.00	1011
	10.0		50.00		
$Np(C_2O_4)_2(s)$	-1975.000				3000
	21.0				
$Np(HPO_4)_2(s)$	-2858.000	-3121.300	200.00	224.00	1911
	14.0		20.00		
$Na_2Np_2O_7(s)$		-2893.500			0400
		9.9			
NpO_2^{++}	-795.800	-860.600	-94.00	2.00	4449
	5.4	4.6	8.00		
NpO_2^{+}	-915.000	-978.200	-20.90	88.00	4449
	5.4	4.6	8.00		
Np^{++++}	-502.900	-556.100	-389.10	-71.00	4449
	7.5	4.2	21.00		
Np^{+++}	-517.100	-527.200	-179.10	-76.00	4449
	3.3	2.1	6.40		
NpO_2OH^{+}	-1004.000	-1102.990	24.00	58.00	1919
	5.0	6.0	50.00		
$(NpO_2)_2(OH)_2^{++}$	-2029.380	-2246.210	-14.00	-51.00	1919
	10.0	10.0	50.00		
$(NpO_2)_3(OH)_5^{+}$	-3474.000	-3897.550	116.00	-3.00	1919
	17.0	17.0	50.00		
$NpO_2(OH)(aq)$	-1101.000	-1220.100	25.00	57.00	1919
	5.0		60.00		
$NpOH^{+++}$	-734.000	-790.540	-167.00	-84.00	1919
	9.0	40.0	40.00		
$Np(OH)_2^{++}$	-961.000	-1050.400	-44.00	-31.00	1919
	15.0	15.0	80.00		

Substance	$\Delta_f G^\circ$	$\Delta_f H^\circ$	S°	Cp°	Ref.
	kJ mol^{-1}		J mol^{-1}K^{-1}		
$Np(OH)_3^+$	-1181.000	-1313.705	44.00	45.00	1919
	20.0	20.0	110.00		
$Np(OH)_4(aq)$	-1397.000	-1699.900	75.00	-126.00	1919
	20.0		130.00		
$Np(OH)_5^-$	-1607.000	-1863.350	96.00	-73.00	1919
	40.0		170.00		
$NpOH^{++}$	-714.300	-762.900	-75.00	-11.00	1919
	4.0	4.0	30.00		
NpO_2F^+	-1103.800	-1194.400	-14.00	84.00	1919
	5.7	7.0	80.00		
$NpO_2F_2(aq)$	-1403.800	-1527.735	40.00	-239.00	1919
	6.0	6.0	80.00		
$NpO_2F(aq)$	-1207.900	-1284.700	100.00	-44.00	6919
	6.0	9.0	100.00		
NpF^{+++}	-834.300	-894.800	-247.00	-31.00	1919
	8.0	8.0	50.00		
NpO_2Cl^+	-926.000	-1015.540	0.00	74.00	1919
	6.0	5.0	150.00		
$NpO_2Cl_2(aq)$	-1055.000	-1175.300	73.80	-249.00	9999
	5.0	5.0			
$NpO_2Cl(aq)$	-1044.000	-1129.892	80.00	-52.00	1919
	8.0	10.0	200.00		
$NpCl^{+++}$	-636.000	-703.475	-260.00	-22.00	1919
	9.0	9.0	150.00		
$NpCl_2^{++}$	-765.000	-795.795	40.00	-87.00	1919
	9.0	10.0	200.00		
$NpO_2SO_4(aq)$	-1558.900	-1753.500	42.80	-281.00	7779
	1.0	0.5	2.00		
$NpO_2(SO_4)_2^{--}$	-2311.400	-2653.800	119.70	-191.00	7779
	1.0	1.0	6.00		
$NpO_2SO_4^-$	-1656.100	-1856.400	91.90	-91.00	8889
	1.0	8.0	50.00	3.0	
$NpSO_4^{++}$	-1279.000	-1444.790	-195.00	69.00	1919
	10.0	10.0	50.00		
$Np(SO_4)_2(aq)$	-2048.000	-2334.600	-27.00	-617.00	1919
	10.0		70.00		
$NpO_2(CO_3)(aq)$	-1360.000	-1540.000	-36.00	-271.00	9999
	5.0	5.0			

Substance	$\Delta_f G^\circ$	$\Delta_f H^\circ$	S°	Cp°	Ref.
	kJ mol^{-1}		J mol^{-1}K^{-1}		
$NpO_2(CO_3)_2^{--}$	-1953.800	-2221.700	116.10	-157.00	7779
	2.0	2.0	30.00	30.0	
$NpO_2(CO_3)_3^{----}$	-2505.200	-2927.900	38.10	-529.00	7779
	2.0	2.0	9.00		
$NpO_2CO_3^{-}$	-1470.020	-1599.900	200.00	-4.00	5919
	1.0	1.0	200.00		
$NpO_2(CO_3)_2^{--}$	-2009.600	-2298.800	110.00	331.00	5919
	1.0	1.0	200.00		
$NpO_2(CO_3)_3^{----}$	-2547.000	-2977.700	80.00	617.00	1919
	1.0	1.0	50.00		
$Np(CO_3)_5^{----}$	-3361.000	-3912.310	160.00	-697.00	1919
	14.0	15.0	200.00		
$NpO_2HPO_4(aq)$	-1932.000	-2159.000	10.00	-252.00	1919
	8.0		200.00		
$NpO_2H_2PO_4^{+}$	-1940.000	-2184.900	-50.00	108.00	1919
	8.0		200.00		
$NpO_2HPO_4^{-}$	-2025.000	-2221.200	180.00	-17.00	1919
	6.0		200.00		
$NpO_2H_2PO_4(aq)$	-2049.000	-2292.700	20.00	-258.00	1919
	6.0		200.00		
$NpH_2PO_4^{++}$	-1661.000	-1854.200	-146.00	37.00	1919
	10.0		200.00		
$Np(H_2PO_4)_2^{+}$	-2799.000	-3195.300	-180.00	194.00	1919
	10.0		200.00		
$Np(H_2PO_4)_3(aq)$	-3941.000	-4549.600	-245.00	-311.00	1919
	20.0		200.00		
$NpHPO_4^{++}$	-1666.000	-1840.900	-150.00	39.00	1919
	20.0		200.00		
$Np(HPO_4)_2(aq)$	-2817.000	-3175.900	-120.00	-571.00	1919
	20.0		200.00		
$Np(HPO_4)_3^{--}$	-3962.000	-4478.200	0.00	-271.00	1919
	20.0		200.00		
$Np(HPO_4)_4^{----}$	-5107.000	-5792.400	80.00	-484.00	1919
	20.0		200.00		
$Np(HPO_4)_5^{----}$	-6246.000	-7100.500	160.00	-697.00	1919
	20.0		200.00		

Comments:

Ref.1=Lemire (1,this work); 2=IAEA,Part8,1983; 3=IAEA,Part 3,1978;
4=Morss (4,this work); 5=Bidoglio (22,this work); 6=Choppin (42,this work).
7=Ullman (38,this work); 8=Halperin (41,this work).
9=this work

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720