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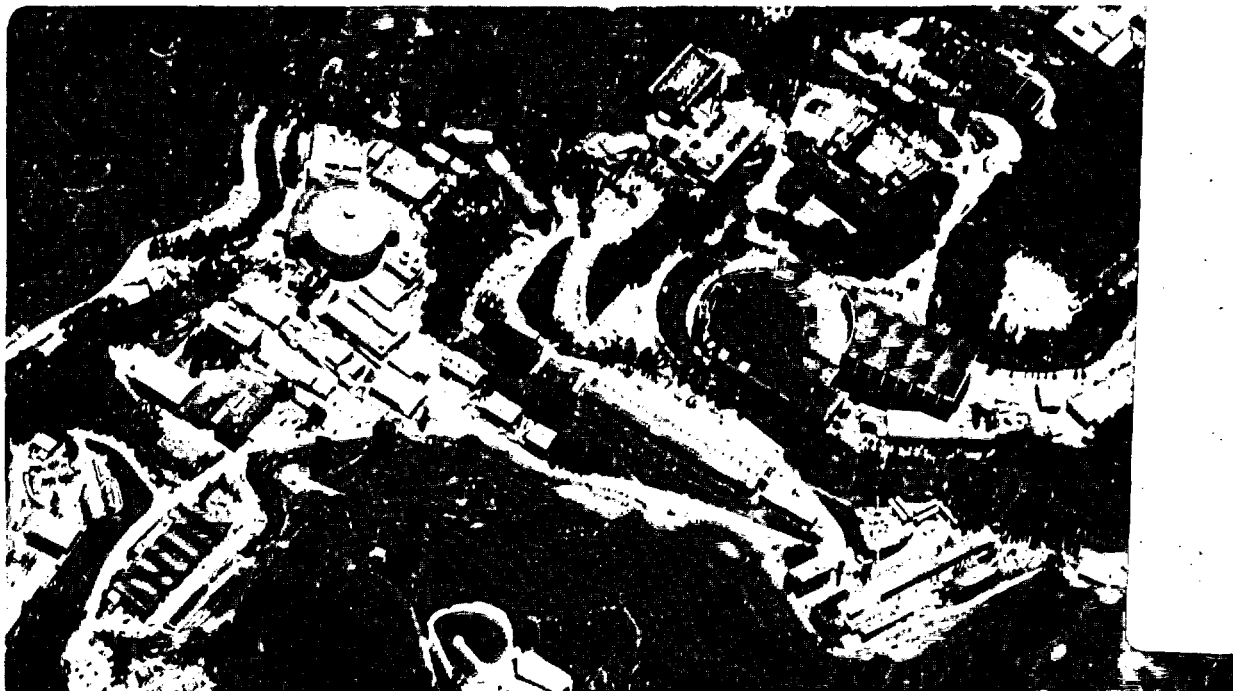
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### Thermodynamic Data Management System for Nuclear Waste Disposal Performance Assessment

S.L. Phillips, F.V. Hale, and M.D. Siegel

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**Thermodynamic Data Management System  
for Nuclear Waste Disposal Performance Assessment**

**Sidney L. Phillips  
and  
Frank V. Hale  
Lawrence Berkeley Laboratory  
University of California  
Berkeley, CA 94720**

**and**

**Malcolm D. Siegel  
Sandia National Laboratories  
Albuquerque, NM 87123**

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## ABSTRACT

Thermodynamic property values for use in assessing the performance of a nuclear waste repository are described. More emphasis is on a computerized data base management system which facilitates use of the thermodynamic data in sensitivity analysis and other studies which critically assess the performance of disposal sites. Examples are given of critical evaluation procedures; comparison of apparent equilibrium constants calculated from the data base, with other work; and of correlations useful in estimating missing values of both free energy and enthalpy of formation for aqueous species.

# THERMODYNAMIC DATA MANAGEMENT SYSTEM FOR NUCLEAR WASTE DISPOSAL PERFORMANCE ASSESSMENT

Sidney L. Phillips and Frank V. Hale  
Lawrence Berkeley Laboratory  
Berkeley, California 94720  
and  
Malcolm D. Siegel  
Sandia National Laboratories  
Albuquerque, New Mexico 87185

## INTRODUCTION

For more than three decades a National program has been in progress to develop the necessary research for disposal of wastes from nuclear energy used in electric power production, defense and energy research and development. The essence of the National effort 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 calculation of geochemical processes such as dissolution of a waste radionuclide is an essential aspect of predicting the performance of a repository such as salt or tuff for 10,000 to 100,000 years (13,36). Computer codes using consistent thermodynamic property values are being developed for this purpose. A critical need in prediction is basic thermodynamic data on radionuclides and other geologic materials, with special emphasis on the quality of the resulting data base. It is understood that this data base must be internally consistent.

A number of data bases of thermodynamic property values are currently available to researchers interested in the behavior of elements present in radioactive waste (9,27,31,35,37). The design and scope of these compilations depend strongly on the intended use of their associated data management systems. The data management system described in this paper is intended for use in sensitivity analysis and studies designed to critically assess the performance of the disposal sites.

This system facilitates management of computerized thermodynamic tables to meet the following eight major specifications: i. All numerical values result from a critical evaluation of relevant experimental measurements, published in refereed research journals. Besides our assessments, critical evaluations include 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 (1,7,8,24,28,29). ii. Emphasis was on the actinides because these elements represented by far the major gap in thermodynamic data. However, data on many other elements such as aluminum and silicon are also needed, and are included in the larger work (9). iii. All values of the Gibbs energy of formation,  $\Delta_f G^\circ$ , have an uncertainty as an indicator of the quality of the value, and for statistical calculations such as propagation of the uncertainty in a calculated equilibrium constant. iv. Important gaps in the tables are filled by interpolation, correlation or theoretically based extrapolation. v. The data base is consistent with: standard reference tables such as CODATA (5) and National Bureau of Standards (2); the fundamental relationship  $\Delta_f G^\circ = \Delta_f H^\circ - 298.15\Delta_f S^\circ$  within defined limits; and, reproducing critically evaluated laboratory results. vi. A literature reference to the source of individual property values is given. vii. The data base is accessible to researchers and other users in the Government, industry and university via computer links on telecommunications networks. viii. Utility programs were developed to facilitate the use of the data in geochemical codes for sensitivity and uncertainty analysis.

## SCOPE AND DESIGN OF THE DATA BASE

### Standard Reference Tables at 25 ° C and Zero Ionic Strength

Values for our auxiliary reference data were obtained from the CODATA Key Values (5), National Bureau of Standards (2), IAEA (3), and other sources such as Brewer (7). Table 1 is a partial listing of the reference values; the more complete tabulation is given in Phillips, et al. (9,31).

The first column in Table 1 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 either of no data, or a defined value; a nine identifies this work.

Citations listed in the reference column (Ref.) in Table 1 are identified in a Comments section immediately following the table. In addition to a list of citations, the Comments section contains additional information relevant to selected substances such as alternative property values, sources of uncertainty and discussions of assumptions implicit in calculation or choice of the intrinsic thermodynamic value.

### Data Evaluation Procedure

The term "critically evaluated data" is defined here as thermodynamic property values resulting from the following procedure:

1. All available data are compiled from other critical evaluations or the best available sources. Data which are consistent with CODATA Key Values are assigned a status index of 2, else the status is 3.
2. Data tables are sent to the researchers who made the initial experimental measurements, or who compiled the original data. This quality check reveals typographical errors in our tabulation, as well as in the sources of the original data. Besides this check, the reviewers often will bring to our attention new data, or other pertinent work.
3. Internal consistency of the data is ensured by calculation of the relationship  $\Delta_r G^\circ = \Delta_r H^\circ - 298.15\Delta_r S^\circ$  for selected reactions. It is not possible to calculate these thermodynamic changes for all reactions, or for all substances. It is recognized that inconsistencies are unavoidable in large, multielement data bases involving thousands of numerical values. Any inconsistencies are corrected quickly with our interactive computerized text editing procedure. Intrinsic equilibrium constants,  $\log K^\circ$  at 25 ° C and zero ionic strength, are often calculated via several different reaction pathways and compared. At this step, consistency with CODATA Key Values is also ensured. When the original data are unreliable or absent, property values are calculated using correlation equations, as described in a later section of this paper. When necessary, property values are recalculated from the original experimental data to ensure consistency of this data base. Changes in thermodynamic values that result in a change of  $\pm 0.2$  units of  $\log K^\circ$  are propagated throughout the data base. As described in a later section, calculated values of equilibrium constants and standard potentials are compared with other work, preferably experimental measurements.
4. After completion of the above process, the data tables are sent to recognized experts for independent review. Reviewers are chosen on the basis of their familiarity with a particular chemical system, or experience with thermodynamic databases.

After this last review, the data table is assigned a status index of 1.

It is important to note that in the above procedure, the data from other critically evaluated tables are accepted on a provisional basis until consistency checks suggest that unacceptable errors exist. Only if this occurs are the original experimental measurements consulted to resolve the inconsistencies. We feel that this approach is commensurate with the intended use of the data base in sensitivity analyses and performance assessment studies currently being carried out by agencies such as the Nuclear Regulatory Commission and the Department of Energy. This procedure produces tabulations that compare well with experimental data. In addition, in a recent exercise with the National Bureau of Standards Chemical Thermodynamics Division, values in our plutonium data set compared well with those calculated by their rigorous CATCH system (38,39,40).

#### USE OF THERMODYNAMIC DATA BASE MANAGEMENT SYSTEM IN SENSITIVITY AND PERFORMANCE ASSESSMENT

One of the intended uses of the Aqueous Solutions Database (9) is in geochemical sensitivity analyses (40). The purpose of these analyses is the formulation of criteria to establish the validity of simplifying assumptions in models which simulate the transport of radionuclides. In the past, simplified representations of radionuclide chemistry and rock/water reactions have been used in analyses of potential high level waste repositories (41). It has been assumed that a single aqueous species exists for each radionuclide, and that the partitioning of the radionuclides between the water and solid phases could be represented by a retardation factor or a sorption ratio. These sorption ratios and retardation factors are measured in a limited number of solutions with rock and water compositions that are assumed to be typical of the repository sites. It is assumed that minor deviations in water and rock compositions and the ratios of solution to solid outside of these experimental conditions will not significantly affect the intensity of radionuclide uptake. The validity of these simplifying assumptions is a crucial element in the design of performance assessment methods, and must be assessed relative to the appropriate performance measure and experimental frame design. The experimental frames are the ranges of physicochemical parameters expected at the candidate repository sites, such as the tuff site in Nevada.

A series of computer codes have been written to facilitate the use of data in the Aqueous Solutions Database for sensitivity studies. These programs permit the use of well-documented, internally consistent sets of data for use in geochemical speciation codes such as PHREEQE (42) and MINEQL (43). These codes can be used to examine the accuracy of the suppositions used in simplifications for simulating the behavior of radionuclides in a natural rock/groundwater system. For example, MINEQL can be used to estimate retardation factors and distribution coefficients ( $K_d$  values) from calculated concentrations of sorbed and aqueous species as functions of groundwater composition and substrate surface area (40,44).

These calculations, however, do not consider the uncertainty of the thermochemical data used to calculate the values of  $K_d$ , or the activities of aqueous species. These uncertainties may be significant and should be addressed in an application of geochemical sensitivity analysis. Two main types of uncertainty need to be considered. These are questions of the existence of certain key species; and, numerical uncertainties in the values of complexation constants ( $\log K^\circ$ ).

An example of the first type of uncertainty is the controversy concerning the existence of the  $U(OH)_5^-$  species. In their model for the hydrolysis of  $U^{++++}$ , Baes and Mesmer (19) assumed that  $U(OH)_5^-$  was dominant in alkaline media in contact with uraninite,  $UO_2(s)$ . On this assumption and assuming a regular progression of hydrolysis constants, Baes and Mesmer calculated  $\log K^\circ$  values for the postulated intermediate species

$U(OH)_2^{++}$ ,  $U(OH)_3^+$ , and  $U(OH)_4(aq)$ , using the measured value for the first hydrolysis constant,  $UOH^{+++}$ . Recently, however, Ryan and Rai (14) and Bruno, et al. (15,46) have challenged the evidence supporting the existence of  $U(OH)_5^-$  and thus the values of three postulated intermediate species. The controversy over the aqueous model for uranium is a source of uncertainty that should be included in speciation and solubility calculations. This is discussed in the section on Critical Evaluation.

Numerical uncertainties in equilibrium constants can be significant even in systems for which there is general agreement on the aqueous model. For example, estimates of the formation constant of  $PuCO_3^{++}$  have ranged from  $10^{13}$  to  $10^{47}$  (47,48). The calculated solubility and identity of the dominant species depend on the magnitude of the equilibrium constant that is used in speciation calculations.

The Aqueous Solutions Database contains several programs that facilitate examination of the sensitivity of calculated solubility limits and speciation to uncertainties in the thermodynamic data. One kind of analysis, illustrated in Figure 1, involves randomized sampling of  $\log K$  values from user-defined distributions. The extrema and shape of the distributions can be determined from actual experimental uncertainties or can be calculated from the free energies and propagated uncertainties stored in this data base. Values in the distributions are generated by the Latin Hypercube Sample program (49). By sampling repeatedly from  $\log K$  distributions and carrying out the replicate speciation calculations, uncertainties can be calculated for the estimated concentrations of aqueous species. Examination of the resulting response surface by a variety of statistical techniques can identify the particular constants that dominate the uncertainty in the calculated solubility, speciation and sorption.

The auxiliary programs in the Aqueous Solutions Database that are currently used for sensitivity studies are described in Figure 2. The tables of thermodynamic data and several of the utility programs are available to interested users via the Federal Communications Telecommunications System (FTS). A user's guide to the system is available and may be obtained from the authors.

#### EFFECT OF IONIC STRENGTH ON $\log K^\circ$

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 using an extended Debye-Huckel equation limited to the range of ionic strengths,  $0 < I < 3.0$ , in the form

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

$K(I)$  = apparent equilibrium constant, at ionic strength,  $I$ .

$K^\circ$  = the intrinsic equilibrium constant, at 25 °C and  $I = 0$ .

$A_\gamma = 0.511$  at 25 °C.

$\Delta z^2$  = 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.



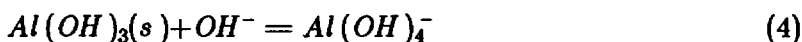
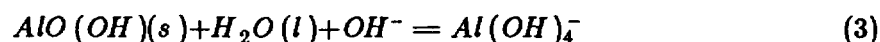
The effect of changing ionic strength on  $\log K(I)$  for three selected reactions involving actinides is shown in Figures 3 to 5, plotted according to eq 1. These plots are discussed in the following section.

## DATA BASE MANAGEMENT FOR CONSISTENCY

The Hewlett-Packard program FPLOT graphs mathematical equations, and prints tables based on these equations. We have modified this program so that the new procedure designated FPLOT1, will calculate the change in thermodynamic quantities for individual chemical reactions. An additional feature is the calculation of the net change in Gibbs energy, enthalpy, entropy and heat capacity, and the value of  $\Delta_r H^\circ - 298.15\Delta_r S^\circ$ ; all at 25 °C. This permits a precise calculation of self-consistency for the various reactions in a geochemical process. The program calculates the variation in  $\log K(T)$  by eq 2 (17,32).

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

Examples of eq 2 are the calculated solubilities for both boehmite,  $AlO(OH)(s)$ , and gibbsite,  $Al(OH)_3(s)$ , over the temperature range  $0 < T < 300$  °C, in alkaline media,



The thermodynamic property values to be used in eq 2 to calculate changes in enthalpy, entropy and heat capacity for these reactions are given in Table 2.

The change in solubility for both reactions is plotted in Figure 6. For comparison, solubility values calculated using the data for  $\Delta_f G^\circ(T)$  for  $0 < T < 300$  °C given in Robinson, et al. (33), Cobble, et al. (29), and Hovey et al. (20) are also shown in this Figure. Prior to use, the  $\Delta_f G^\circ[298.15]$  data in each of these publications was verified for consistency with the Aqueous Solutions Database. For example, free energy of formations were compared for species such as  $H_2O$ ,  $CO_2$ ,  $Al^{+++}$ ,  $Na^+$ ,  $Cl^-$ ,  $OH^-$ ,  $H^+$ , and  $Mg^{++}$ . Our work compares reasonably well with (20) above 150 °C, and are more positive by about 0.2  $\log K$  below 100 °C. The difference may be due to differing free energy values for boehmite.

### FPLO2 Program

The FPLOT program was further modified in order to calculate the standard electrode potential for oxidation/reduction equations, over the range  $0 < T < 300$  °C. Equation 2 is used also in this modification (FPLO2) for these calculations. The program was used to calculate standard potentials and consistency at 25 °C (Table 3).

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

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

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 3 shows 13 experimental measurements plotted according to eq 1. Extrapolation to  $I = 0$  gives  $\log K^\circ = -5.66$ , comparing with -5.6 in Ref. 1. Baes and Mesmer calculated -5.62 for this reaction (19).

Only values for perchlorate and nitrate solutions up to  $I = 3$  were used for our plot. Data for sulfate and chloride media were excluded because  $UO_2^{++}$  forms complexes with these anions, so that measured hydrolysis values do not reflect only hydrolytic products. Also, measurements for  $I > 3.0$  were not included because eq 1 is generally valid only up to  $I = 3.0$ . Finally, two data points at  $I = 0.1$  were excluded from the final fit of data to eq 1, because these had the highest residuals when comparing  $\log K(I)$  values calculated using eq 1, with the experimental points.

#### Hydrolysis of $NpO_2^+$

The most reliable information on hydrolysis of  $NpO_2^+$  is obtained from Maya (18) 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 shown in Table 4. Our calculated values for the formation of  $NpO_2OH(aq)$ , and the solubility of  $NpO_2OH(am)$  are given in Table 4. We have assumed the amorphous (am) form of neptunium(V) oxide was used in solubility measurements, and that the reaction on dissolution is  $NpO_2(am) = NpO_2^+ + OH^-$ . The solubility and hydrolysis constants were calculated with eq 1, using the coefficients in Ref. 9.

#### Formation of the Ion Pair $AmSO_4^+$

Figure 5 is a plot of the change in  $\log K(I)$  versus ionic strength for the reaction  $Am^{+++} + SO_4^{--} = AmSO_4^+$ , using data from Refs. 21 and 31. The experimental measurements were obtained at  $I = 0.5, 1$  and  $2$ . We calculate from Figure 5  $\log K^0 = 4.14$ ,  $b = 0.44$  so that  $\log K(I=3)$  is  $1.6$ . The extrapolation is justified because eq 1 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 with  $1.8, 1.57$  and  $1.43$  in Reference 21.

#### $NpO_2^+$ - Carbonate Complexes

Bidoglio, Tanet and Chatt measured  $\log K$  for the complexation of  $NpO_2^+$  with  $CO_3^{--}$  using a solvent extraction technique (22), and Maya used solubility measurements (18). Formation constants for the 1:1, 1:2 and 1:3 complexes are in Table 5. We have plotted the data in Table 5 except for the values at  $I = 0.5$  which are inconsistent (1) in Figure 4 to obtain  $\log K^0$ ; our calculated formation constants are given in Table 5. 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  $\log K^0 = 4.64$  for the 1:1 complex, compared with  $4.78$  using eq 1; and,  $7.06$  for the second complex, compared with  $6.86$  using eq 1. For the 1:3 complex, the plot according to eq 1 extrapolates to  $\log K^0 = 4.91$  at  $I = 0$ . This unexpectedly low value indicates either eq 1 does not apply to such a highly charged species, or that the experimental data are erroneous. We have thus chosen to plot  $\Delta_f G^0 [MX_n]$  versus the number of carbonate ligands, using values for  $n = 1$  and  $2$ , followed by extrapolation to  $n = 3$ . The resulting Gibbs energy of formation of the 1:3 complex is  $-2550$  kJ/mol, comparing well with Lemire's  $-2547$  kJ/mol which we have accepted. From this value, we calculate  $\log K^0 = 8.55$  for the intrinsic formation constant of the 1:3 species.

In summary, the thermodynamic tables in this work (9) are consistent in reproducing evaluated experimental measurements, and with the CODATA and NBS values. However, there are numerous 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.

## THERMODYNAMIC BASIS FOR ESTIMATION OF DATA

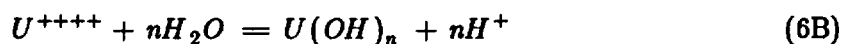
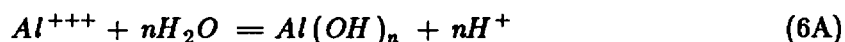
The aqueous actinides covered in this work are hydrated ions with positive charges ranging from +1 to +4. Their oxidation states range from +3 to +6, with the +5 and +6 ions containing two bound oxygens. The values of  $\Delta_f G^\circ$  and  $\Delta_f H^\circ$  are correlated in a linear manner; for example, two parallel lines are obtained for plots of the +3, +4, +5 and +6 oxidation states (9,30). We have found a similar linear correlation for the actinide ion pairs and higher complexes, as shown in Figure 7. 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 will be observed if there is a constancy in the entropy difference  $S^\circ [M^{n+}] - S^\circ [M, s]$  (30). Alternatively, an apparent constancy will be observed if the difference between the two entropies is small (30,34).

A second correlation developed in this work is based on our observation that both  $\Delta_f G^\circ$  and  $\Delta_f H^\circ$  change in a linear manner with the number of ligands added to the metal ion. See for example Figure 8 with the  $Al(OH)_n$  and the  $U(OH)_n$  systems as examples. The decrease in Gibbs energy of formation with increase in the number of ligands follows an equation of the form (9)

$$\Delta_f G^\circ [MX_n] = mn + p \Delta_f G^\circ [M] \quad (5)$$

where  $\Delta_f G^\circ [MX_n]$  is the Gibbs energy of formation for the complexes,  $MX_n$ ,  $m$  is the slope,  $X$  is the ligand,  $M$  the metal cation,  $n$  the number of complexing ligands, and  $\Delta_f G^\circ [M]$  is the standard free energy of formation of the unbound cation, at 25°C and zero ionic strength. The quantity,  $p$ , is equal to one when eq 5 extrapolates to  $\Delta_f G^\circ$ ; however, this is an unusual case (9). Equation 5 was tested for 13  $MX_n$  systems; results are summarized in Table 6 where it is seen the quantity  $p$  is generally greater than one. The slopes,  $m$ , can be grouped according to the kind of ligand in the cation-ligand complex.

These correlations are valuable for calculating missing data. The reader should note, however, the correlation represented by eq 5 applies only to  $\Delta_f G^\circ$ , or to a similar correlation for  $\Delta_f H^\circ$ . Neither the free energy of reaction,  $\Delta_r G^\circ$  nor the enthalpy of reaction,  $\Delta_r H^\circ$  are expected to change linearly with the number of ligands in a complex (34). For example, see Figure 9, where  $\log K^\circ$ ,  $\frac{-\Delta_r G^\circ}{2.303RT}$ , is plotted versus the number of  $OH^-$  ligands for the systems

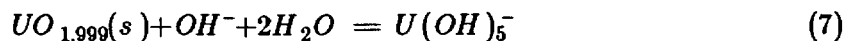


The charges for the hydrolysis products are omitted in eqs 6.

### EXAMPLE OF CRITICAL EVALUATION PROCEDURE

As discussed above, the existence of some aqueous species such as  $U(OH)_5^-$  was questioned because solubility measurements of  $UO_2(s)$  did not apparently support an anionic species of  $U(IV)$  in basic media containing  $Zn$  /dithionite (14) and wet  $H_2$  (15). However, measurements by Tremaine et al. (16) of the  $UO_2(s)$  solubility in alkaline

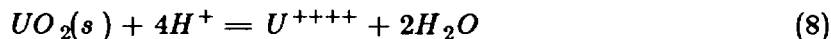
solutions in the presence of wet  $H_2$  were consistent with the reaction



The stoichiometry of the oxide was  $UO_{1.999 \pm 0.012}$ ; the major impurity in the oxide was  $450 \mu \text{ g/g Al}$ ; other impurities were  $< 50 \mu \text{ g/g}$ . They fit their solubility measurements to the equation  $\log K(T) = -5.86 + 32/T$ ; we have plotted this equation in Figure 10, curve B. Note that  $\log K(T)$  decreases slightly with temperature over the range 0 to  $300^\circ \text{C}$ . In this figure, we have also plotted values of  $\log K(T)$  using eq 2 and data for eq 7 from our tables (9), curve A. Our predicted values of  $\log K(T)$  become more negative by about -1 unit of  $\log K$  at  $200^\circ \text{C}$  and -2 units at  $300^\circ \text{C}$ . The higher solubilities measured by Tremaine et al. may reflect the ease of oxidation of crystalline  $UO_2(s)$  (16).

Our equilibrium constant for eq 7,  $K = \frac{[U(OH)_5^-]}{[OH^-]}$  is  $1.63 \times 10^{-6}$  at  $25^\circ \text{C}$ , predicting a linear increase in the solubility of  $UO_2(s)$  with increasing concentration of  $OH^-$ . Our prediction is in accord with the data of Ryan and Rai (14) and Gayer and Leider (25) for  $UO_2(am)$  which do show an increase in solubility with an increase in  $OH^-$  concentration in agreement with eq 7. According to eq 1, the solubility of crystalline or amorphous uranium dioxide varies linearly with ionic strength. This is indeed shown to be the case in Figure 11, where  $\log K(I)$  is plotted versus  $I$  for Gayer and Leider's measurement assuming  $OH^-$  is in excess at each  $I$ .

For comparison, we have calculated  $\log K(T)$  for the dissolution of crystalline  $UO_2(s)$  in acidic media according to eq 8



represented by curve C in Figure 10. In this figure, the points are  $\log K(T)$  for eq 8 calculated by Lemire and Tremaine (1).

We conclude that the retrograde solubility of  $UO_2(s)$  in both acidic and basic media coupled with the ease of oxidation is a cause of difficulty in interpreting solubility data. If we use  $\log K^0 = -5.75$  for eq 7 according to Tremaine et al., then  $\Delta_f G^0 [U(OH)_5^-] = -1630.38 \text{ kJ/mol}$  and  $\log K_{15}^0 = -15.09$ . This  $\log K_{15}$  compares with -16.0 calculated incorrectly by Baes and Mesmer (19) from the solubility measurements by Gayer and Leider (25) for a  $UO_2$  solid which may well have been amorphous, since the solid was freshly precipitated. Taking into account the ease of oxidation of  $UO_2$ , the possibility that the solid precipitated by Gayer and Leider which they designated  $U(OH)_4$  was amorphous, the measurements by Tremaine et al., the presence of  $Zn$ /dithionite which may affect the measurements of Ryan and Rai (15), we choose  $\log K_{15}^0 = -15.1$  which we have calculated from Tremaine et al. (16). We calculated the data for the postulated intermediates by interpolation from a plot of  $\Delta_f G^0$  versus number of  $OH^-$  ligands for the 1:1 and 1:5 complexes. Our values for the 1:3 and 1:4 complexes differ from those reported by Bruno et al. (15) in their study of  $UO_2(am)$  solubility as a function of pH for  $U(OH)_3^+$  and  $U(OH)_4(aq)$  which we have calculated to  $I = 0$  using the Davies equation. We recognize that the Davies equation is most accurate for  $I < 0.1$  or  $0.2$ ; but is probably acceptable for our approximation in consideration of all the uncertainties.

#### ACKNOWLEDGMENT

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## **FUNCTIONS OF ASD PREPROCESSOR IN SPECIATION SENSITIVITY ANALYSIS**

1. Reads  $\Delta G$  values and  $\sigma$  from ASD for basis species
2. Calculates log K's and uncertainties for input to LHS
3. Uses LHS to produce nxm array of log K values
- 4.1 Reads vector of log K's input for a single calculation
- 4.2 Performs speciation calculation and writes results to a file
- 4.3 Chooses important species and writes their concentrations or other parameters to a file
- 4.4 Repeats for each vector
5. Prepares input for sensitivity analysis on results by graphical or other methods

Figure 1. Functions of the thermodynamic data base management system in the preprocessor for sensitivity analyses.  $\Delta G = \Delta_f G^\circ$ ;  $\sigma$  = standard deviation; ASD = Aqueous Solutions Database; LHS = Latin Hypercube Sampling procedure.

## **THERMODYNAMIC DATABASE FOR GSA**

- ASD FORMAT 1: GHS and Cp data
- ASD FORMAT 2: log K for specific reaction
- ADDREACT: add new reaction to FORMAT 2
- COMPLOGK: compute log K  $\pm$   $\sigma$  for reaction
- BRIDGE: produce new MINEQL database from ASD data with log K  $\pm$   $\sigma$  and  $\Delta H_r \pm \sigma$
- LHSMIN: prepare file for multiple runs of MINEQL for different log K
- MINQLMLT: carry out multiple MINEQL runs and write specified results to a file for post-processing

Figure 2. Thermodynamic data base management system, for coupling the Aqueous Solutions Database to the MINEQL code (43), and for interactive editing and printing. GSA = Geochemical Sensitivity Analysis; GHS =  $\Delta_f G^\circ$ ,  $\Delta_f H^\circ$ ,  $S^\circ$ ;  $\Delta H_r$  = enthalpy of reaction.



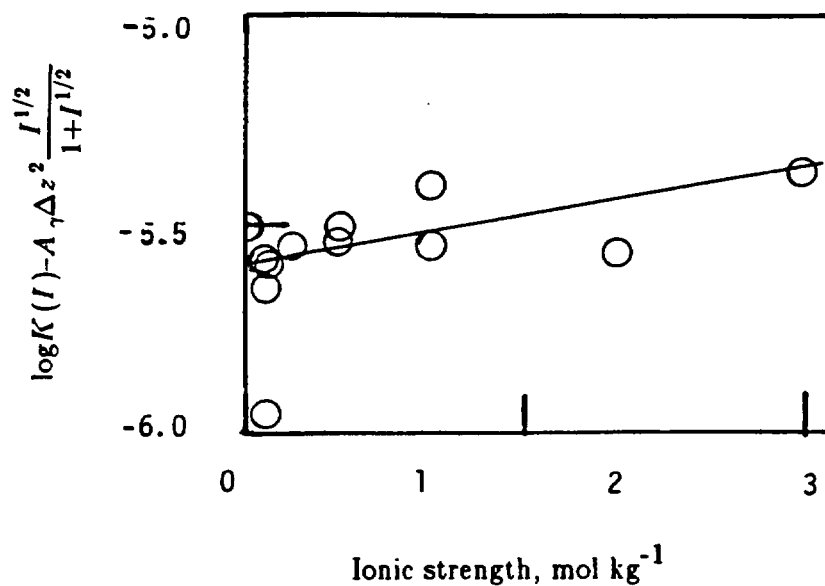


Figure 3. Variation in  $\log K(I)$  as a function of ionic strength,  $I$ , for the reaction  $2\text{UO}_2^{++} + 2\text{H}_2\text{O} = (\text{UO}_2)_2(\text{OH})_2^{++} + 2\text{H}^+$ . Experimental points from Ref. 9. Extrapolation to  $I = 0$  yields  $\log K^{\circ} = -5.66$ ,  $b = 0.101$ .

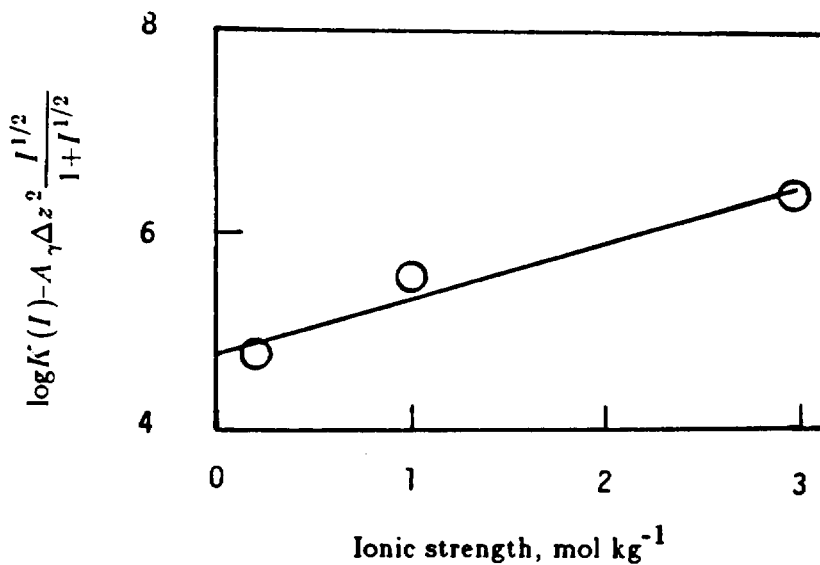


Figure 4. Effect of ionic strength on  $\log K(I)$  for the reaction  $\text{NpO}_2^+ + \text{CO}_3^{--} = \text{NpO}_2\text{CO}_3^-$ . At  $I = 0$ ,  $\log K^{\circ} = 4.64$ ,  $b = 0.55$ ,  $r^2 = 0.980$ .

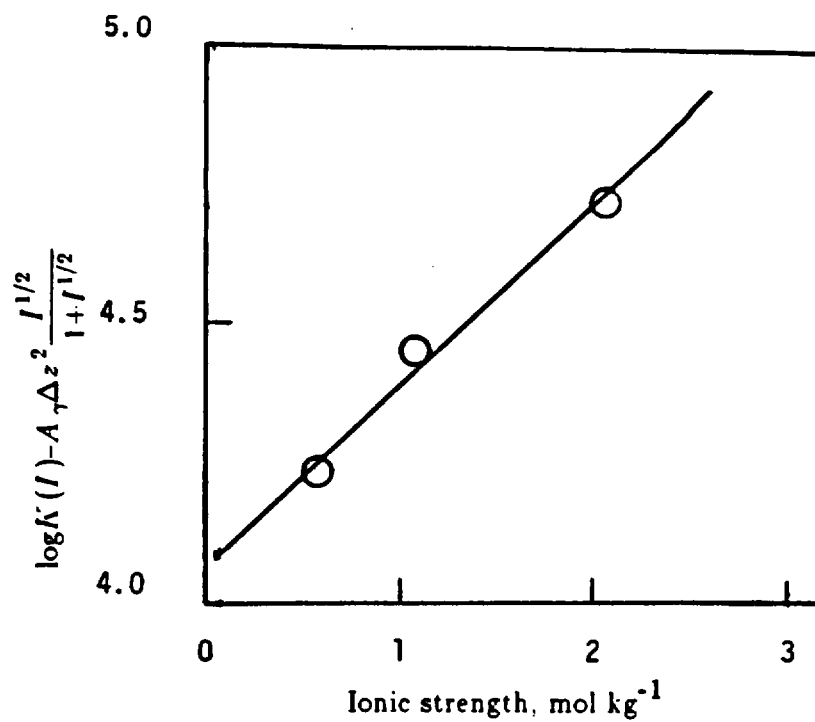


Figure 5. Formation of americium sulfate,  $Am^{+++} + SO_4^{--} = AmSO_4^+$  using data from Ref. 9.  $\log K^o = 4.14$ , at  $I = 0$ ,  $b = 0.44$ ,  $r^2 = 0.993$ .

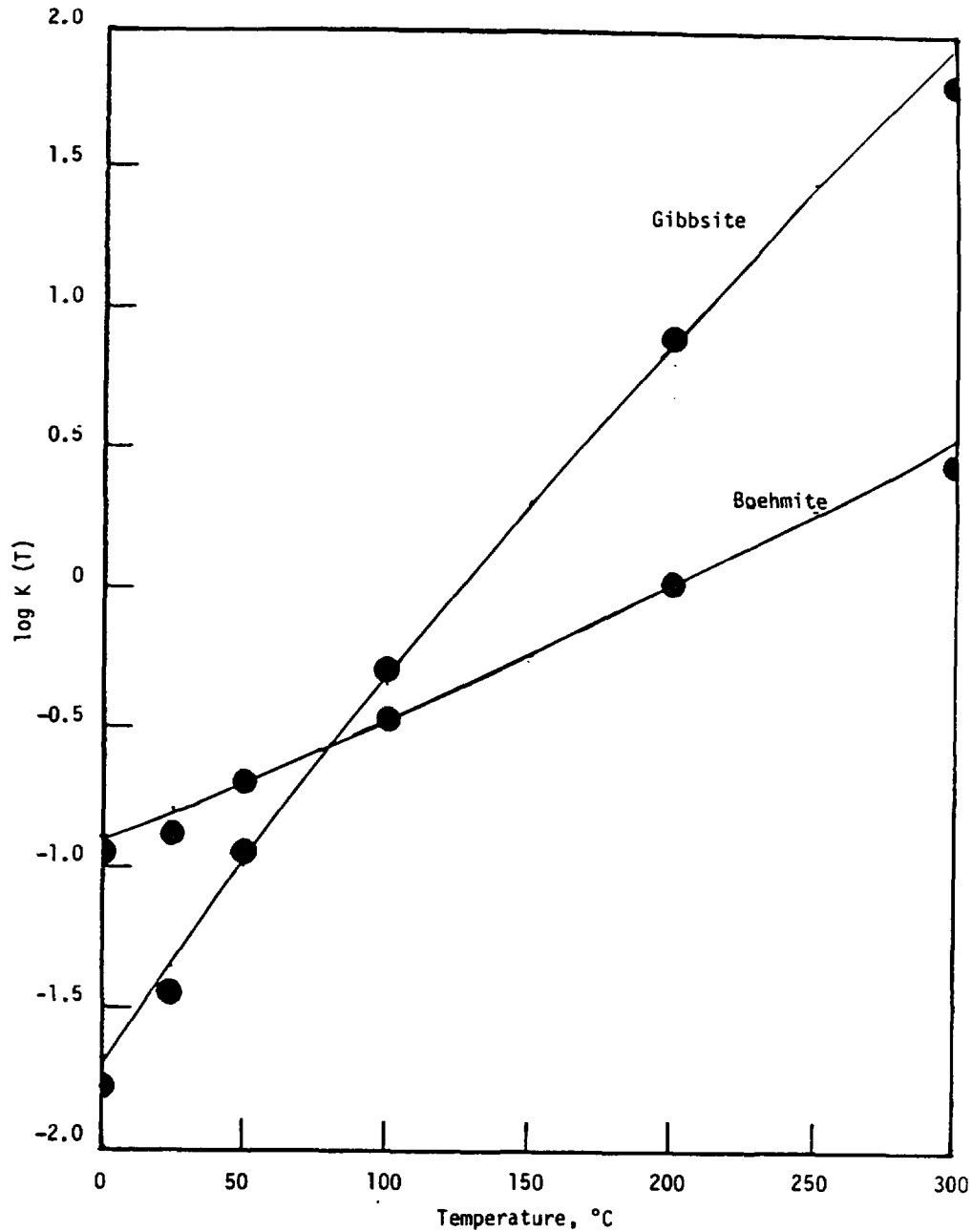


Figure 6. Plot of  $\log K(T)$  versus temperature for solubility reactions, eq 3 and eq 4, calculated with eq 2 (solid lines). Circles are values calculated from  $\Delta_f G^\circ(T)$  for gibbsite and boehmite (33),  $Al(OH)_4^-$  (20), and  $OH^-$  (29). Each thermodynamic tabulation (20,29,33) was checked for consistency with the Aqueous Solutions Database. Gibbsite dehydrates to boehmite:  $Al(OH)_3(s) = AlO(OH)(s) + H_2O$  in acidic solution. We calculate  $\Delta_r G = 0$  at  $225.5^\circ C$  for dehydration in acid solution.

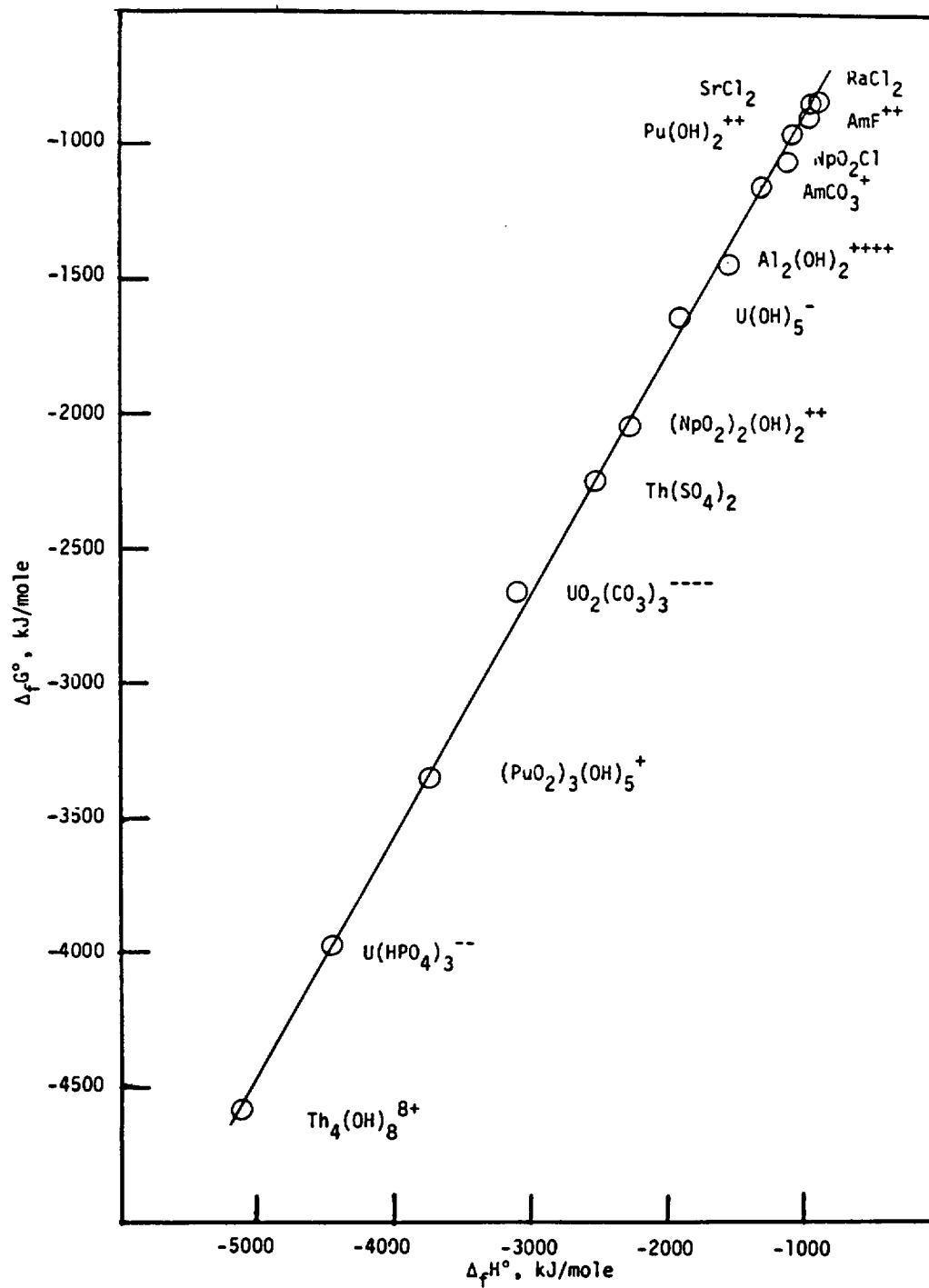


Figure 7. Linear relationship between  $\Delta_f G^\circ$  and  $\Delta_f H^\circ$ , for selected aqueous complexes. Data from Ref. 9.

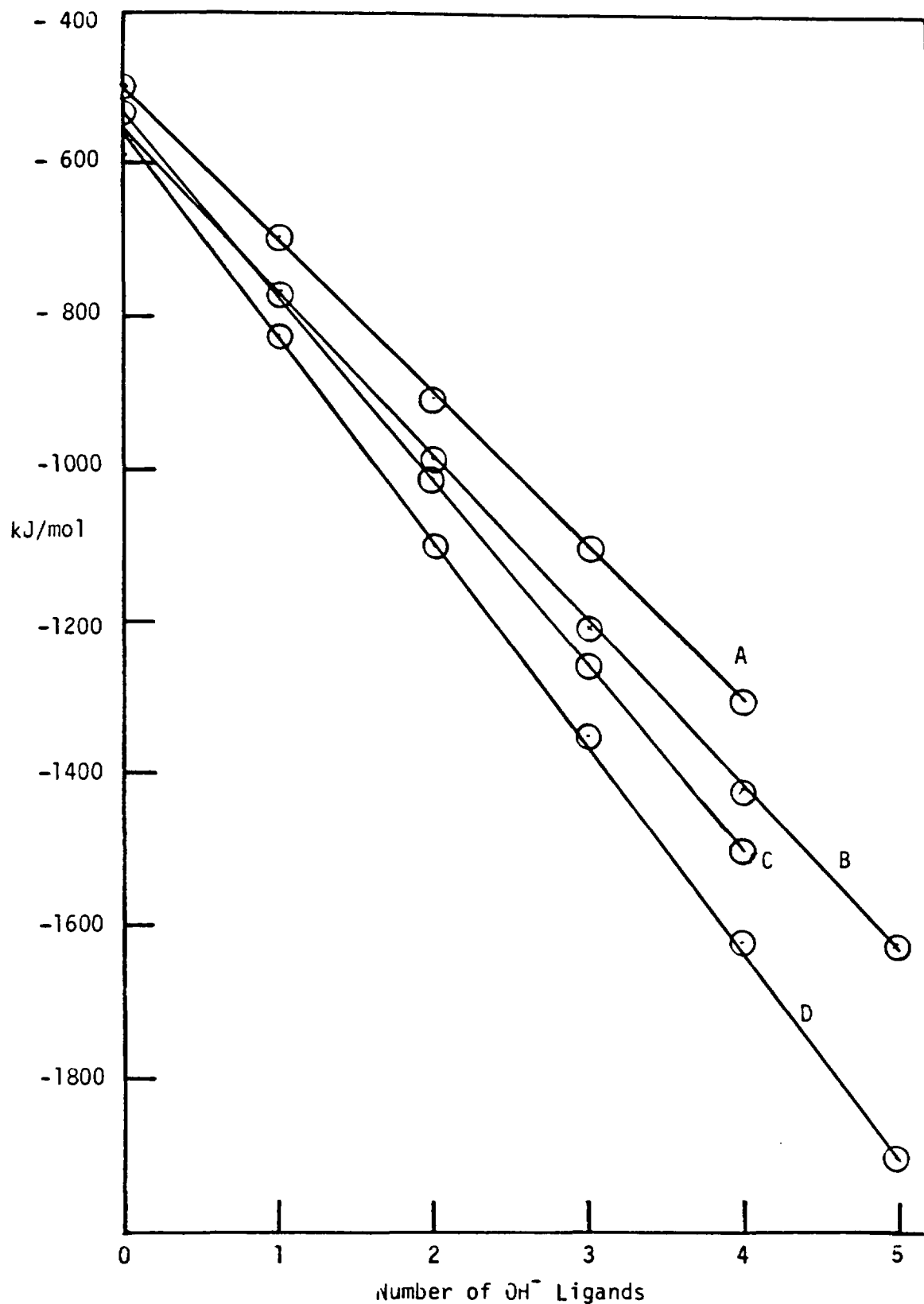


Figure 8. Variation in  $\Delta_f G^\circ$  and  $\Delta_f H^\circ$  versus the number of  $OH^-$  ligands for the  $Al(OH)_n$  and  $U(OH)_n$  systems. Data from Ref. 9. A.  $\Delta_f G^\circ [Al(OH)_n]$ . B.  $\Delta_f G^\circ [U(OH)_n]$  C.  $\Delta_f H^\circ [Al(OH)_n]$ . D.  $\Delta_f H^\circ [U(OH)_n]$ .

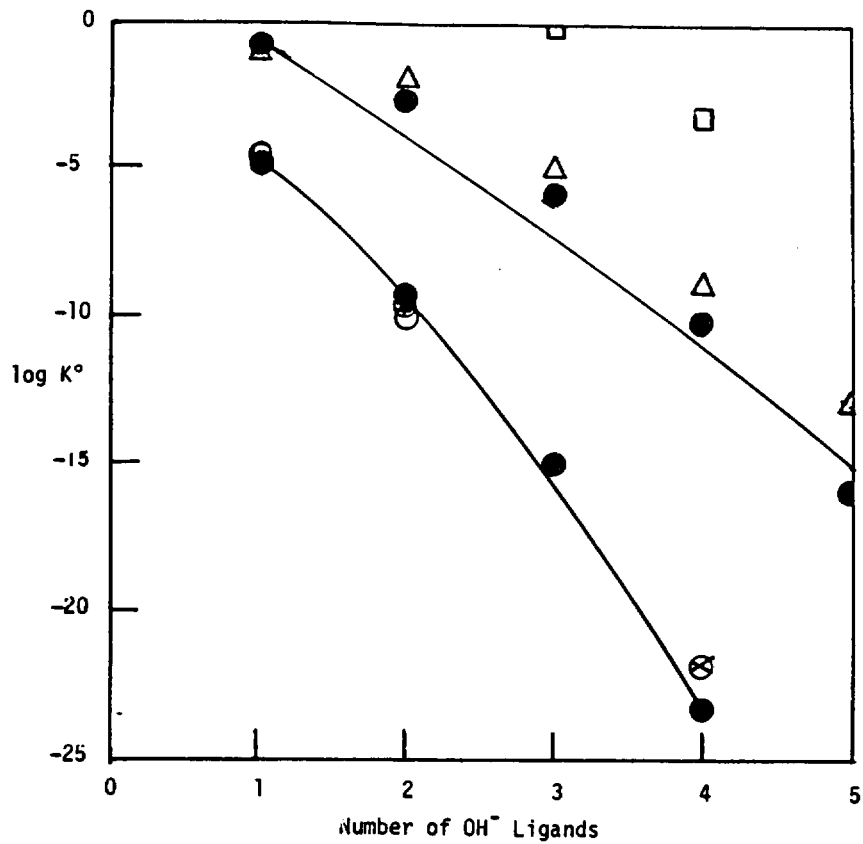


Figure 9. Typical nonlinear relation between  $\log K^\circ$  and number of ligands,  $n$ , using the  $Al(OH)_n$  and  $U(OH)_n$  systems as examples. This work:  $\square$ ; Brown et al. (26):  $\circ$ ; Baes; Mesmer (19):  $\bullet$ ; May et al. (10):  $\otimes$ ; Lemire; Tremaine (1)  $\triangle$  Bruno et al. (15), calculated to  $I=0$ :  $\square$ . The two points from Bruno et al. (15) are for  $UO_2(am)$ .

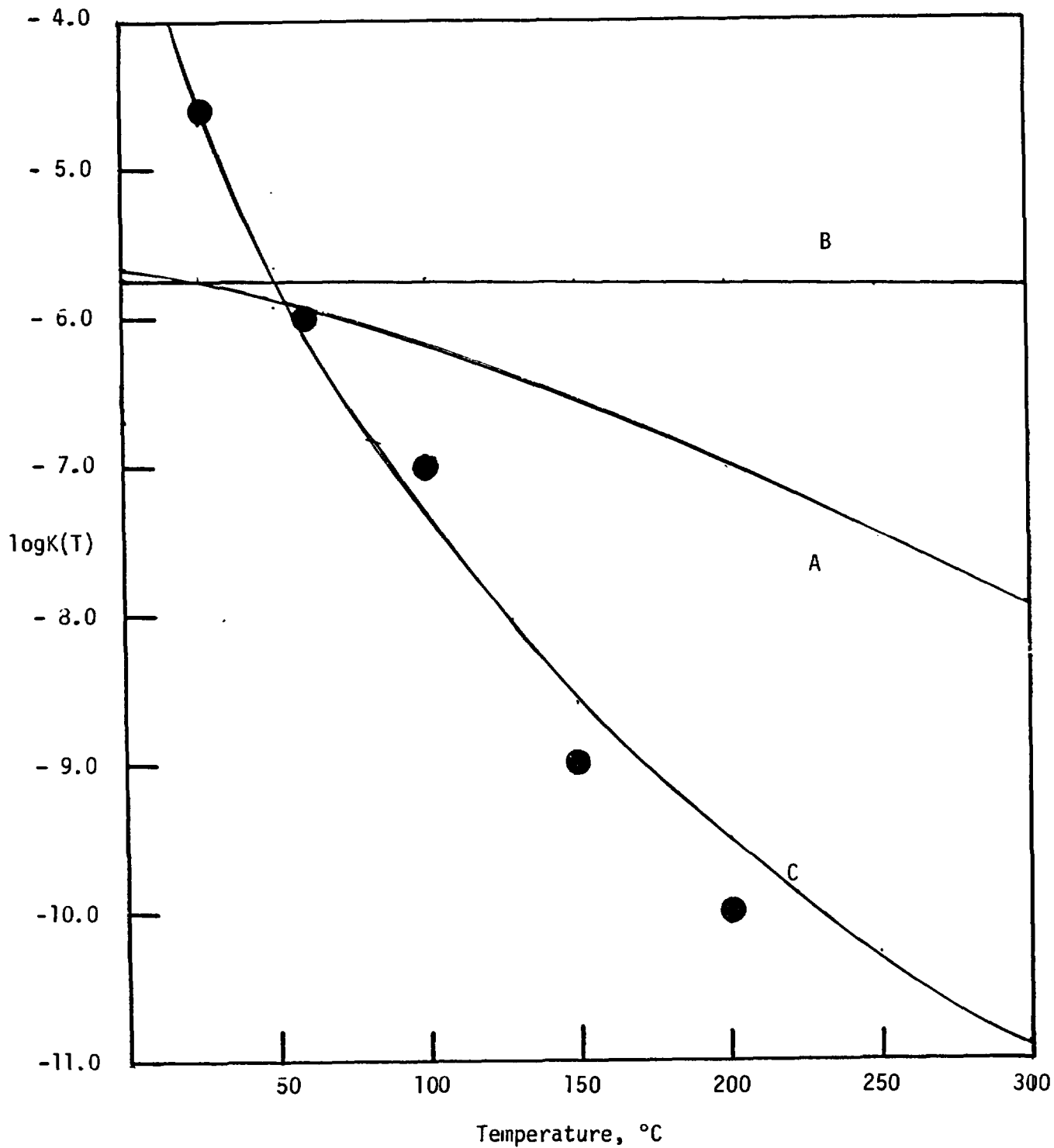


Figure 10. Solubility of  $UO_2(s)$  (crystalline) in basic and acidic media.

A.  $UO_2(s) + OH^- + 2H_2O = U(OH)_5^-$ , This work.

B. Same reaction as A, Tremaine et al. (16).

C.  $UO_2(s) + 4H^+ = U^{++++} + 2H_2O$ , This work.

●●●, Same reaction as C, data from Lemire; Tremaine (1).

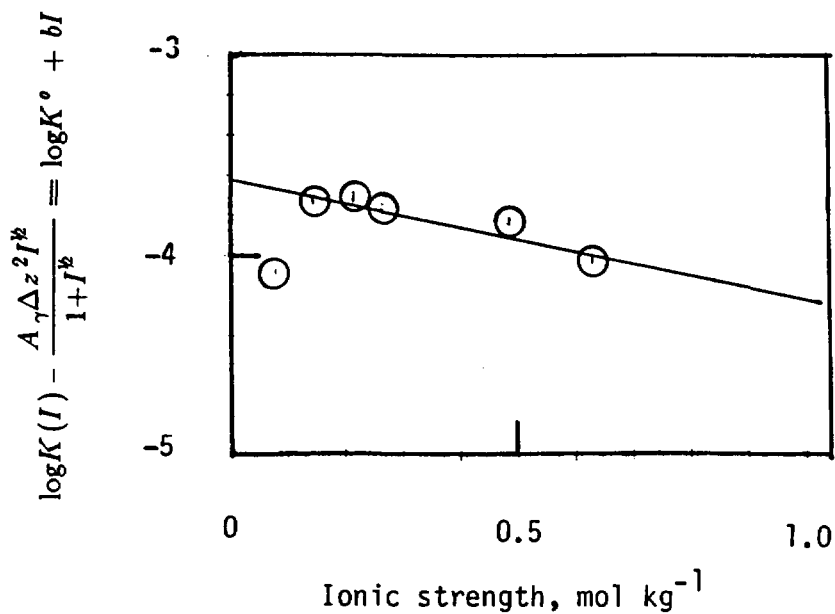


Figure 11. Plot of  $\log K(I)$  versus  $I$  using measurements from Gayer and Leider (25). Measurement at  $OH^- = 0.080$  M is an outlier, and is rejected. At  $I = 0$ ,  $\log K^o = -3.82$ .



Table 1. Selected portion of reference thermodynamic property values for the Aqueous Solutions Database. Ref. 3 is (11) in this work.

Aqueous Solutions Database	Lawrence Berkeley Laboratory	KEY VALUES Evaluated Status 1 October 1987
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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	$\Delta_f G^\circ$ kJ mol <sup>-1</sup>	$\Delta_f H^\circ$ kJ mol <sup>-1</sup>	$S^\circ$ J mol <sup>-1</sup> K <sup>-1</sup>	$C_p^\circ$ J mol <sup>-1</sup> K <sup>-1</sup>	Ref.
O <sub>2</sub> (g)	0.000	0.000	205.04	29.36	2557
			0.03	0.0	
O <sub>2</sub> (aq)	16.530	-12.138	108.90	224.00	9777
	0.2	0.2	0.80	25.0	
H <sub>2</sub> (g)	0.000	0.000	130.57	28.82	2557
			0.03		
H <sub>2</sub> (aq)	17.780	-4.040	57.37	175.00	9777
	0.9	0.8	2.50	25.0	
H <sub>2</sub> O(g)	-228.572	-241.814	188.72	33.61	2557
	0.1	0.0	0.04		
H <sub>2</sub> O(l)	-237.129	-285.830	69.95	75.29	2557
	0.1	0.0	0.08		
e <sup>-</sup> ,electron	0.000	0.000	65.28	14.42	0066
			0.01	0.1	
Si(OH) <sub>4</sub> (aq)	-1308.000	-1460.100	180.00	215.00	9923
	1.7	1.7	4.20		
H <sup>+</sup>	0.000	0.000	0.00	0.00	2222
	0.0	0.0	0.00	0.0	
NH <sub>4</sub> <sup>+</sup>	-79.310	-133.260	111.17	25.00	2559
	0.1	0.3	0.75	4.1	
Li <sup>+</sup>	-292.620	-278.455	11.30	60.70	2557
	0.2	0.1	0.35		
Na <sup>+</sup>	-261.905	-240.300	58.41	42.40	2557
	0.1	0.1	0.20		

Table 2. Thermodynamic property values for use in predicting the solubility of boehmite,  $AlO(OH)(s)$ , and gibbsite,  $Al(OH)_3(s)$ , using eq 2, according to the dissolution reactions, eq 3 and eq 4.

Substance	$\Delta_f G^\circ$ kJ/mol	$\Delta_f H^\circ$ kJ/mol	$S^\circ$ J/mol/K	$C_p^\circ$ J/mol/K	Ref.
$Al(OH)_3(s)$	-1156.50	-1294.63	68.44	91.76	33,33,33,33
$AlO(OH)(s)$	-916.072	-990.675	48.45	65.43	33,33,33,33
$H_2O(l)$	-237.129	-285.830	69.95	75.29	9,5,5,9
$OH^-$	-157.244	-230.025	-10.71	-140.5	9,5,5,9
$Al(OH)_4^-$	-1305.60	-1500.94	111.30	96.50	20,9,20,20

Table 3. Standard electrode potentials for selected redox couples at 25 °C and zero ionic strength.  $E^\circ$  calculated from  $\Delta_f G^\circ$  values in Ref. 9. In these calculations,  $S^\circ [e^-, aq] = 65.28 \text{ J/mol/K}$ , and the faraday is 96,485.309 coulombs/mol (CODATA Bull. No. 63, November 1986).  $\Delta = \Delta_f G^\circ - [\Delta_f H^\circ - 298.15\Delta_f S^\circ]$ .

Electrode Reaction	$\Delta$	$E^\circ(\text{volt})$ This Work	$E^\circ(\text{volt})$ Ref.12
$\text{O}_2(\text{aq}) + 4\text{H}^+ + 4\text{e} = 2\text{H}_2\text{O}$	124	1.272	--
$2\text{H}^+ + 2\text{e} = \text{H}_2(\text{aq})$	5	-0.092	--
$\text{Na}^+ + \text{e} = \text{Na}(\text{s})$	22	-2.714	-2.714
$\text{K}^+ + \text{e} = \text{K}(\text{s})$	230	-2.925	-2.925
$\text{Cs}^+ + \text{e} = \text{Cs}(\text{s})$	322	-3.027	-2.923
$\text{Ag}^+ + \text{e} = \text{Ag}(\text{s})$	12	0.7991	0.7991
$\text{NpO}_2^+ + 4\text{H}^+ + 5\text{e} = \text{Np}(\text{s}) + 2\text{H}_2\text{O}$	175	-0.913	--
$\text{PuO}_2^{++} + 4\text{H}^+ + 6\text{e} = \text{Pu}(\text{s}) + 2\text{H}_2\text{O}$	700	-0.488	--
$\text{Ca}^{++} + 2\text{e} = \text{Ca}(\text{s})$	62	-2.865	-2.84
$\text{Sr}^{++} + 2\text{e} = \text{Sr}(\text{s})$	2	-2.922	-2.89
$\text{Cu}^{++} + 2\text{e} = \text{Cu}(\text{s})$	78	0.339	0.340
$\text{Pb}^{++} + 2\text{e} = \text{Pb}(\text{s})$	6	-0.124	-0.125
$\text{UO}_2^{++} + 4\text{H}^+ + 6\text{e} = \text{U}(\text{s}) + 2\text{H}_2\text{O}$	109	-0.826	--
$\text{Zn}^{++} + 2\text{e} = \text{Zn}(\text{s})$	0	-0.763	-0.7626
$\text{Fe}^{++} + 2\text{e} = \text{Fe}(\text{s})$	62	-0.474	-0.44
$\text{Fe}^{+++} + 3\text{e} = \text{Fe}(\text{s})$	98	-0.059	-0.037
$\text{Th}^{++++} + 4\text{e} = \text{Th}(\text{s})$	441	-1.826	-1.83
$\text{F}_2(\text{g}) + 2\text{e} = 2\text{F}^-$	19	2.920	2.87
$\text{Cl}_2(\text{g}) + 2\text{e} = 2\text{Cl}^-$	129	1.360	1.358
$\text{I}_2(\text{s}) + 2\text{e} = 2\text{I}^-$	0	0.5355	0.5355
$\text{O}_2(\text{g}) + 2\text{H}_2\text{O} + 4\text{e} = 4\text{OH}^-$	252	0.401	0.401
$\text{Si}(\text{OH})_4(\text{aq}) + 4\text{H}^+ + 4\text{e} = \text{Si}(\text{s}) + 4\text{H}_2\text{O}$	175	-0.931	-0.848

Table 4. Experimental measurements on the solubility of  $\text{NpO}_2\text{OH(am)}$  and hydrolysis of  $\text{NpO}_2^+$  compared with this work.

Medium	**logK <sub>sp</sub>	logK(I)	Method	Ref.
0	-9.41	-8.82	Calculated	This work
0.1M Cl <sup>-</sup>	<-9.2	-8.85	Solubility	19
0.1	-9.2	-	Titration	in 45
0.2, 20 °C	-9.0	-10.1	Solubility	in 45
0.2	-9.07	-8.88	Calculated	This work
0.02, 23 °C	-9.73	-8.91	Potentiometry	45
1.0M NaClO <sub>4</sub>	-	-9.12	Solubility	18
1.0M NaClO <sub>4</sub>	-8.81	-11.43	Titration	45
0.2M NaClO <sub>4</sub>	-	-9.59	Extraction	22
0.1M NaClO <sub>4</sub>	-9.15	-8.85	Calculated	This work
1.0M NaClO <sub>4</sub>	-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:  $\text{NpO}_2^+ + \text{H}_2\text{O} = \text{NpO}_2\text{OH(aq)} + \text{H}^+$

\*\* Calculated from eq 1, with  $\log K^\circ = -9.41$ ,  $b = 0.094$ .

Table 5. Formation quotients of  $\text{NpO}_2^+$  - carbonates.

Medium	logK <sub>11</sub> (I)	logK <sub>12</sub> (I)	logK <sub>13</sub> (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±0.09	Solubility	in 22
1.0	4.31	7.27	-	Calculation	This work
3.0	5.09	8.15±0.25	10.46±0.08	Solubility	in 22
3.0	5.14	8.09	-	Calculation	This work

Table 6. Variation in Gibbs energy of formation for selected cation-ligand complexes, with the number of ligands, n. Average correlation coefficient is 0.99.

$M-X_n$	$n_{max}$	$\Delta_f G[M]$	intercept, b	m
Pb-OH	4	-23.97	-28.77	-183.84
Fe(II)-OH	5	-91.55	-99.29	-177.23
Fe(III)-OH	5	-17.28	-30.39	-206.03
Al-OH	4	-489.53	-494.04	-203.98
Eu-OH	3	-576.2	-574.63	-194.8
Am-OH	4	-599.1	-601.43	-186.6
Ru-Cl	7	173.4	164.34	-134.16
Th-OH	5	-704.6	-706.6	-214.5
Al-F	7	-489.53	-510.92	-297.79
Th-F	5	-704.6	-713.98	-310.48
Pb-Cl	5	-23.97	-27.82	-133.0
La-SO <sub>4</sub>	3	-686.2	-685.62	-741.7
Th-SO <sub>4</sub>	5	-704.6	-718.62	-757.13

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