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HYDROLYSIS AND FORMATION CONSTANTS AT 25° C

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Prologue

For in much wisdom is much vexation;
And he that increaseth knowledge
increases sorrow.

Ecclesiastes 1:18

Rigidity threatens all realization: what lives and glows today may be crusted over tomorrow and, becoming all-powerful, suppress the strivings of the day after.

Martin Buber

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Abstract

A database consisting of hydrolysis and formation constants for about 20 metals associated with the disposal of nuclear waste is given. Complexing ligands for the various ionic species of these metals include OH, F, Cl, SO_4, PO_4 and CO_3. Table 1 consists of tabulated calculated and experimental values of log K_{xy}, mainly at 25°C and various ionic strengths together with references to the origin of the data. Table 2 consists of a column of recommended stability constants at 25°C and zero ionic strength tabulated in the column headed log $K_{xy}(0)$; other columns contain coefficients for an extended Debye-Huckel equation to permit calculations of stability constants up to 3 ionic strength, and up to 0.7 ionic strength using the Davies equation. Selected stability constants calculated with these coefficients for various ionic strengths agree to an average of ±2% when compared with published experimental and calculated values.

INTRODUCTION

Metal speciation and associated equilibrium constants are needed for corrosion research, in sea water chemistry, mineral studies, metal recovery from ores and in nuclear waste disposal. Data needed include solubility, Nernstian potential and stability constants to high temperatures and concentration. However, this report is limited to a database on the stability constants of about 20 metal species mostly at 25°C, and from zero to 3 ionic strength, with emphasis on data for nuclear waste storage.

Critically evaluated data with assigned uncertainties on hydrolysis constants up to 1974 - 1975 are found in the widely referenced book The Hydrolysis of Cations (1). The authors include detailed discussions on experimental procedures, data handling and interpretation, uncertainties and effect of ionic strength together with a substantial number of references to original publications. Summary tables permit use of an extended Debye-Huckel equation to calculate hydrolysis constants from tabulated coefficients at 25° C and mainly at specific ionic strengths, e.g., 0.3, 1.0 and 3.0, and molalities. Critical Stability Constants, Vol. 4, Inorganic Complexes (2) is a widely referenced compilation of formation constants up to about 1974 - 1975. It is a rich source of formation constants mainly at 25° C, and ionic strengths from zero to 3.0. Stability constants tabulated are often the average of an unspecified number of published values, rather than selection of a single value considered the most reliable. Coefficients for calculating stability constants at 25°C and at high ionic strengths are found in the recent publication by Turner, Whitfield and Dickson (3). A detailed discussion is given on use of their database for speciation calculations, and on

a systematic approach to speciation of elements in natural waters. Values of hydrolysis and formation constants were obtained for the most part from Baes and Mesmer (1), and Smith and Martell (2). Stability constants tabulation is limited to 25 ° C and does not include some elements of importance to nuclear waste disposal such as plutonium, neptunium and americium.

Hydrolysis values have also been calculated at zero ionic strength for about 20 species of plutonium and uranium by Lemire and Tremaine (4); these logK values were calculated from Gibbs energies of formation, which were calculated by a modified Criss-Cobble entropy extrapolation. The work is an excellent source of tabulated values for Gibbs energy and entropy of: solids, liquids and gases; ligands; aqueous plutonium and uranium species; and, estimated selected stability constants up to 200° C.

Recent publications containing data on metal species with application to nuclear wastes include Cleveland for plutonium (33), Langmuir for uranium (6); Sylva for lead and copper(8,30), Allard for americium and curium (29), and iron fluoride complexes by Nordstrom and Jenne (34). Chemical Modeling in Aqueous Systems (16) is an excellent summary of stability constants, methods of estimation and correlation, computer codes and other data on speciation in natural waters up to about 1978. Internally consistent critically evaluated data are obtained from the series of publications by the National Bureau of Standards; for example, Gibbs energy values for thorium (13) and uranium halides (35). Key thermodynamic values were obtained from CODATA publications (36). Unfortunately, the common practice of combining log K or other basic data from a number of sources with these values causes a loss in internal consistency, as discussed by Parker (35).

The U. S. Geological Survey Bulletin 1452 is a reliable source of thermodynamic properties for minerals and related substances to over 1000 K (37). Besides minerals and other solids, values of Gibbs energy of formation and entropy are listed for a number of metal

ions and complexing ligands relevant to nuclear waste storage such as U^{4+}, Ni^{2+}, CO_3^{2-}, and SO_4^{2-}.

This database for nuclea waste disposal includes both calculated and estimated logK values for complexes that are believed to form, but for which experimental data are lacking, on the premise that the calculated results are expected to be qualitatively more reliable than those obtained by excluding these species. See Mattigod and Sposito for additional discussion (38).

It is recognized that no literature search can be exhaustive; the reader is urged to forward important publications or references to the author for inclusion in the database.

Uncertainties

Selection of recommended or best values, together with an uncertainty, is based on a number of considerations including:experimental method used; details given of the measurement procedure or calculation; the number of replicate measurements; standard deviation; use of a substitute (surrogate) complex; uncertainty assigned by the investigator; reliability of previous work published by the investigator; and, publications in refereed journals. In many instances a quantitative value ("±") cannot be assigned to a stability constant due to a lack of data; the evaluation has a subjective component. Refer to Latimer (14), Parker (15 ,35) Baes and Mesmer (1), Smith and Martell (2), Ball, Jenne and Nordstrom (32), and papers in the Journal of Physical and Chemical Reference Data as well as the CODATA series (36,39) for critical evaluation of data.

It is not possible to include detailed discussions of the existence of particular species, or ranges of pH and supporting electrolyte concentrations over which a species may or may not exist. For example, $PbCl_4^{2-}$, $CuCl_4^{2-}$, $Fe_{12}(OH)_{34}^{2+}$ may be important only at 3-4m Cl^- or ClO_4^- concentrations(8,17,19). The reader should consult the original publications for additional information on the existence of particular species. Good discussions are given by Baes and Mesmer (1), Schedin

(18), Bjerrum (19), Langmuir (12), Paulson and Kester (9), Lemire and Tremaine (4), Rabinowitch and Stockmayer (20), May, Helmke and Jackson (40) and Cobble (21) on this subject. Additionally, a selection must be made between species for purposes of calculation; for example, either $Zr_3(OH)_4^{8+}$ or $Zr_3(OH)_5^{7+}$, but not both, should be used in hydrolysis schemes involving Zr^{4+} (1).

Uncertainties listed as "±" following the tabulated stability constant are mainly those from the reference given; for example, Baes and Mesmer, Smith and Martell, Khopkar (22), and Choppin (11). These are classified as follows:

1. The existence of some minor species are inferred by a fit of the experimental data to computer codes, or by other calculations. When the existence of a species has been questioned, a hydrolysis or formation constant is enclosed by parenthesis. Examples are hydrolysis constants of the $(UO_2)_3(OH)_4^{2+}$ species, log K = (-11.75 ± 0.1); $U(OH)_2^{2+}$, $U(OH)_3^{+}$ and $U(OH)_4^{\circ}$ (-2.6±?), (-5.8±?), (-10.3±?), respectively, for logK values.
2. When a judgment as to the reasonableness of an equilibrium constant is not made, the uncertainty is denoted by a question mark; e.g., $Al(OH)_2^{+}$, log K = =-9.3±?; $Al(OH)_3$, log K = -15.0±? See Baes and Mesmer (1).
3. A minor species which may exist only over a specified range of temperature or concentration may be qualified by a "Note": for example, $Al(OH)_4^{-}$ forms in significant amounts only in alkaline media; polymeric species such as $Th_2(OH)_3^{5+}$ and $Th_6(OH)_{14}^{10+}$ form in chloride media; the existence of others may not be supported by experimental data (e.g. $AlCO_3^{+}$).
4. Upper limits for equilibrium constants are denoted by a ≤ or < sign, such as $Th(OH)_3^{+}$ where log K ≤ -11.7 (1).

5. Values calculated on the basis of other elements which match the desired complexes in similarity of cation charge, anion charge, ligand number and by analogy, e.g., with lattice parameters are those given for the "comparison" species. Examples are hydrolysis of Am^{3+} (Nd^{3+}) and Eu^{3+} (In^{3+}). See Turner, Whitfield and Dickson (3), Edelstein, Brown and Silva (10), Baes and Mesmer (1), and Langmuir (5,12).

Calculation of Ionic Strength

The following is largely taken from the lucid discussion of ionic strength in the book Chemical Analysis (31).

Ionic strength is calculated from the molar concentration of the supporting electrolyte and the charge of the electrolyte ions:

$$I = \Sigma\ C_i z_i^2 /2$$

For an electrolyte which is symbolized by $A_m^{p+}B_n^{q-}$, I is calculated as in the following:

$$C_A = mC\ ;\ C_B = nC;\ \text{and}\ I = C(mp^2 + nq^2) / 2$$

for example,

$$A^+B^-,\ I = (C_A Z_A^2 + C_B Z_B^2) /2 = (C_A + C_B)/2 = C$$

$$A^{2+}B_2^-,\ C_A=C,\ C_B=2C,\ I = (4C + 2C)/2 = 3C$$

$$A^{2+}B^{2-},\ C_A=C_B=C,\ I = (4C + 4C)/2 = 4C$$

$$A^{3+}B_3^-,\ C_A=C,\ C_B=3C,\ I = (9C + 3C)/2 = 6C$$

where C_A and C_B are the molar concentrations of the cation and anion of the supporting electrolyte.

Equilibrium Constants

Thermodynamic equilibrium data (e.g., stability constants) are commonly published as hydrolysis and formation constants, and Gibbs energy changes (free energy). Stability constants are defined as apparent overall constants, β_n, for example (33)

$$M + nL = ML_n$$

$$\beta_n = [ML_n]/[M][L]^n \cdot \gamma_{ML_n} / \gamma_M \gamma_L$$

or a stepwise stability constant, K_n (apparent stability constant)

$$ML_{n-1} + L = ML_n$$

$$K_n = [ML_n] / [ML_{n-1}] [L] \cdot \gamma_{ML_n} / \gamma_{ML_{n-1}} \gamma_L$$

$$K_n = \beta_n / \beta_{n-1}$$

where $[ML_n]$ = concentration of the complex
$[M]$ = metal ion concentration
$[L]$ = ligand concentration
n = number of ligands
γ = activity coefficient

Gibbs free energy values, $\Delta G°$, are converted to values of log K° by

$$\log K° = -0.00073295 \Delta G°, \text{ at } 25° \text{ C } (298.15 \text{ K})$$

where log K° = stability constant at I = 0, 25° C, $\Delta G°$ is in cal/mol. In this report, overall formation and hydrolysis constants are tabulated as $\log K_{xy}$ values for the schematic reaction

$$xM + yL = M_xL_y$$

where

$$K_{xy} = [M_xL_y] / [M]^x [L]^y \qquad \text{(for I = 0)}$$

Database

Hydrolysis and formation constants for 18 metals are tabulated in the printout in Table 1, together with an uncertainty, ionic strength and a reference to the origin of the values. The "±" is that assigned by the referenced author when given in the publication. References are listed alphabetically in the Data References printout immediately following Table 1. The following notations are used in Table 1:

1.

FOR	READ
numeric subscript	number following metal or ligand
numeric superscript	number following "^" symbol

Examples:

FOR	READ
$AlOH^{2+}$	AlOH^2+
$Al_3(OH)_4^{5+}$	Al3(OH)4^5+
$(PuO_2)_4(OH)_7^{+}$	(PuO2)4(OH)7^+
$NiCl_2^{o}$	NiCl2
$Pb(CO_3)_2^{2-}$	Pb(CO3)2^2-

2. K_{xy} is the hydrolysis or formation constant of the species formed:

$PuO_2^{2+} + H_2O = PuO_2OH^{+} + H^{+}$

$4Zr^{4+} + 8H_2O = Zr_4(OH)_8^{8+} + 8H^{+}$

$Sr^{2+} + 2F^{-} = SrF_2$

$Cu^{2+} + SO_4^{2-} = CuSO_4$

$Am^{3+} + H_2PO_4^{-} = AmH_2PO_4^{2+}$

$Fe^{3+} + HSO_4^{-} = FeHSO_4^{2+}$

3. Numbers in parenthesis following a LogKxy value denote temperature and ionic strength, when either or both differ from 25° C and zero:

2.20(20C,.25) is LogKxy at 20°C, I = 0.25

3.27(.1) is LogKxy at I=0.1 with 25°C implied

Ionic Strength

A Debye-Huckel equation is used to correct for ionic strength. Hydrolysis and formations constants are calculated as a function of ionic strength using eq(1) up to I = 3.

$$\log K(I) = \log K^\circ + \frac{A \, \Delta Z^2 \, I^{1/2}}{1 + B \, I^{1/2}} + C \, I \qquad (1)$$

where

$K(I)$	=	equilibrium constant at ionic strength I, $0<I<3$
K°	=	equilibrium constant at I = 0
A	=	0.511 at 25° C; 0.596 at 100°C
ΔZ^2	=	sum of square of charges of products of equilibrium minus sum of squares of charges of reactants
B	=	1.6 , or other value taken from Table 2
C	=	constant

See the series of publications by Vasil'ev (23,24,25) and by Paulson and Kester (9). Figures 1 and 2 show the variation in log K with I for UO_2OH^+ and $FeCl^{2+}$, as examples of eq(1).

When the parameter C is known, the variation follows eq (1); variation in log K° with ionic strength is calculated using the Davies equation when C is not known (27)

$$\log K(I) = \log K^\circ + 0.5 \Delta Z^2 \left[\frac{I^{1/2}}{1 + I^{1/2}} - 0.3I \right] \qquad (2)$$

Davies equation is widely used to calculate single ion activity coefficients for $0<I<0.72$ (26); however, the error increases at ionic strengths exceeding about 0.1 from a few tenths of a percent to about 2 - 5% (27). The value of A (0.5115) is frequently used instead of 0.5 in eq(2).

The best values for log K° and coefficients $A\Delta Z^2$, B, C for eq(1) and eq(2) are listed in Table 2.

We have included selected coefficients published by Turner, Whitfield and Dickson (3), Baes and Mesmer (1), Rabinowitch and Stockmayer (20), and Freeman (28), as well as those calculated here, in Table 2. However, all coefficients are to be used in eq (1) except those indicated for eq (2). The references in Table 2 refer to the source of the log K°, $A\Delta z^2$, B and C values.

In some instances data from Baes and Mesmer or Smith and Martell were used to calculate discrete values of log K,e.g., from the Debye-Huckel equation given in Baes and Mesmer. These values were used to calculate the parameter C for all values of I up to I = 3 using the following form of eq (1):

$$\log K(I) - \frac{A\Delta Z^2 \quad I^{1/2}}{1+1.6 \quad I^{1/2}} = \log K^\circ + CI \qquad (3)$$

See the publications by Vasil'ev (23,24,25) for more information on eq (3), and Figs. 3 and 4.

Table 3 consists of a comparison of selected hydrolysis and formation constants at 25°C and I up to 3 using eq (1), eq (2) and the coefficients in Table 2, with published values. The average error between calculated and these published values is ± 2%. Tables 4-13,20 are printouts of the variation in logK values with ionic strength for selected waste nuclides using these two equations and the coefficients in Table 2. Tables 14 - 18 are tabulations of the variation in ionization constants of ligand sources (e.g., HSO_4^-) as a function of ionic strength. Data were obtained from Smith and Martell (2).

In summary, a computer-stored table of formation and hydrolysis constants covering about 20 metals at 25°C is given. A second tabulation consists of coefficients for an extended Debye-Huckel equation and Davies equation to permit estimation of log K values up to 3 ionic strength. These values will change as results of additional measurements are published.

Selection of Recommended Stability Constants

References are not given in parenthesis in the following discussion. See instead the alphabetical listing in the Data References section for references to the publications cited here.

Aluminum

The instrinsic hydrolysis constant for $AlOH^{2+}$ is given as -4.97 by Baes and Mesmer; -4.99 by Ball et al; -4.99 by Smith and Martell; and -5.00 in the tabulation by Sokolova and Khodakovskiy. The value selected is -4.98 which agrees with -4.98 obtained by Schofield and Taylor, and is within the uncertainties assigned by the first three referenced authors. For $Al(OH)_2^+$, -10.1 calculated by Ball et al from the careful measurements of May et al is selected. This compares with the log K_{12} = -10.5 estimated by Baes and Mesmer, and -10.7 tabulated by Sokolova and Khodakovskiy; a value more negative than -9.3 calculated from Kubota's experimental data by Baes and Mesmer. Similarly, $\log K_{13}$ = -16.0 is adopted for $Al(OH)_3^\circ$, although this may be somewhat too positive when compared with -16.9 from Sokolova; and, -16.5 estimated by Baes and Mesmer, but which they did not tabulate. For $Al(OH)_4^-$ log K_{14} = -23.0 given by Baes and Mesmer also splits the difference between the value listed by Sokolova (-23.8) and that which we calculate from May et al (-22.2). See Table 20 and Figure 8 for Al^{3+} data.

Recommended values for the following polynuclear species of Al^{3+} are taken from Baes and Mesmer and given in Table 2: log K_{22} = -7.7; log K_{34} = -13.94; log $K_{13\ 24}$ = -98.73.

Formation constants at zero ionic strength for six Al^{3+} fluoro complexes were estimated here using the data given in Smith and Martell and eq (3) as: 7.02 for AlF^{2+}; 12.7 for AlF_2^+; 16.7 for AlF_3°; 19.7 for AlF_4^-; and, 20.7 for AlF_5^{2-} and 20.6 for AlF_6^{3-}, the last two were estimated using the Davies equation. These compare within 1% of the constants given in Smith and Martell, and the tabulation by Turner et al. We have taken the values from Turner et al as recommended formation constants in our Table 2 for the six fluoro complexes.

Formation constants for sulfate complexes were taken from Ball et al. We cannot recommend log K's for the phosphate complexes which are based on one published value as calculated by Langmuir using a correlation with the corresponding iron complexes. Similarly, only one value is available for $AlCO_3^+$, a species which may not exist.

Americium

Published experimental data on the hydrolysis of Am^{3+} are considered unreliable by Baes and Mesmer, possibly due to the scatter in the data, or to an incorrect assumption of the mechanism of solvent extraction . Baes and Mesmer suggest that the hydrolysis behavior of the trivalent actinides are expected to be similar to those of the lanthanides. This suggestion was utilized by Edelstein, Brown and Silva and Allard who used the hydrolysis constants of Nd^{3+} as more reasonable estimates for Am^{3+}. The solubility limits for $Am(OH)_3$ in 0.1 M $NaClO_4$ were calculated as function of pH using Nd^{3+} hydrolysis values, and agreed better for the solubility limit line for Am as compared to the published experimental values. Accordingly, we have tabulated hydrolysis constants for Nd^{3+} as estimates of those for Am^{3+} in Table 2.

We have found $\log K_{11} = 3.8$ and $\log K_{12} = 4.8$ for the sulfate complexes of Am^{3+} by calculation with eq (1) and eq (2); these compare within about 10% of the estimates by Allard of 3.5 and 5.2. The values 3.6 and 5.0 split the difference. The K_{11}, K_{12} and K_{13} constants for the fluoride complexes were obtained from eq (1) and eq (2). Similarly, log K's were calculated for the chloro complex using the Davies equation.

The values for the phosphate complexes were taken from Lebedev, $\log K_{11} = 2.73$, $\log K_{12} = 3.72$, assuming temperature variations ($23 \pm 2°C$) were negligible.

Cesium

The correlation given by Turner et al is selected for CsCl; log K measured by Fisher is taken for $CsSO_4^-$.

Copper

New data for the hydrolysis constants of Cu^{2+} have been published by Sylva and Davidson and by Paulson and Kester. Measurements were made by Sylva and Davidson at 25.0°C using potentiometric titration in 0.1 M (0.1 mol/dm^3) KNO_3 solutions for 0.212 - 2.125 x 10^{-3} M solutions of Cu^{2+}. A precision of $\pm$ 0.001 pH units or better was obtained; addition of 0.01 M NaOH was done with a 5 cm^3 buret calibrated to $\pm$ 0.0001 cm^3. Titrations were done in an argon atmosphere. A computer program, MINIQUAD 75, was used to fit the data to 27 hydrolysis models to assist in selection of the best speciation scheme. Base model selected was the species $Cu_2(OH)_2^{2+}$; rejection criteria for a new species was either rejection by MINIQUAD 75 (the value of K becomes negative), or if the error square sum was not decreased. The major hydrolytic species was $Cu_2(OH)_2^{2+}$, with $CuOH^+$ and $Cu_3(OH)_4^{2+}$ present in lesser quantities. From the author's data, we calculate hydrolysis constants at I = 0 for three species as log K_{11} = -7.93; log K_{22} = -11.2; log K_{34} = -22.0, using the Davies equation, eq (2). These agree within 2 to 7% of the values selected.

Paulson and Kester measured the first and second hydrolysis constants over the range pH 6.8 - 8.4 at 25°C using a Cu^{2+} ion selective electrode. Measurements were made in 0.7m and 0.05m $NaClO_4$ solutions under a nitrogen atmosphere. Correction to zero ionic strength was done using the following estimated single ion activity coefficients: Cu^{2+} (0.25); $CuOH^+$ (0.4); $Cu(OH)_2$ (0.8); H^+ (0.95). The Kielland modification of the Debye-Huckel equation was used for I = 0.05 values of logK. Their corrected values for I = 0 were: log K_{11} = -7.99, -7.93; and log K_{12} = -16.26, -16.21.

We have selected log K_{11} = -7.93, log K_{12} = -16.24 from these data; the remaining hydrolysis constants listed in Table 2 are adopted from Baes and Mesmer critical evaluation.

From ΔG_f° values in Gedansky et al, we calculate the following hydrolysis constants using the CODATA values for ΔG_f° OH^- and ΔG_f° Cu^{2+}: log K_{11} = -7.33; log K_{13} = -26.7; log K_{14} = -39.7; log K_{22} = -11.0. These compare to a 0 - 7% difference with the values selected here. Gedansky et al calculate for CuF^+ log K_{11} = 0.70 versus 1.52, and for $CuSO_4^\circ$, log K = 2.29 compared with our selected value of 2.36.

Formation constants for the Cu^{2+} complexes were selected as follows: fluoro from Turner et al; chloro from Ball et al; sulfate from Freeman; bicarbonate from Mattigod and Sposito; carbonate from Sunda et al; $CuHPO_4$ from the careful calculation by Wolery, and our calculation.

Curium

The log K_{11} values for $CmOH^{2+}$ differ by a factor of over two when calculated at I = 0 using the Davies equation. Due to the large uncertainty, we cannot recommend a value, but suggest that the mean -4.4±1.0 might be used as a first approximation for $CmOH^{2+}$, and -9.1 for $Cm(OH)_2^+$.

Fluoro formation constants at zero ionic strength were calculated via the Davies equation from data in Smith and Martell; log K_{11} for the chloro complex was taken from Ward.

Europium

The log K_{11} hydrolysis constant was taken from Baes and Mesmer; the remaining hydrolysis constants are adopted from the tabulation by Turner et al which were based on Y^{3+} data.

Turner, Whitfield and Dickson calculated values for the $EuOH^{2+}$, $Eu(OH)_2^+$, $Eu(OH)_3$ and $Eu(OH)_4^-$ species by fitting log K values for Y^{3+} from Baes and Mesmer to an extended Debye-Huckel equation of the form

$$\log K(I) = \log K^\circ + AI^{1/2} / (1 + BI^{1/2}) + CI + DI^2$$

The selection of Y^{3+} as a model ion for Eu^{3+} was based on such criteria as cation charge, anion charge, number of OH ligands, ionic strength range, and the nature of the model species. This approach provides estimates of logK° values for four of the species of Eu^{3+} that agree within 1 - 3% with published values. Refer to Table 3.

Log K_{11} for EuF^{2+} was taken from Bilal, and is also the value listed by Turner et al. The remaining formation constants were obtained from Turner et al, except that we calculated $\log K_{11}=3.61$ for $EuSO_4^-$ using eq (1). This value compares well with 3.59 given by Turner et al, and agrees with 3.67 measured by Hale and Spedding within 2%, and with 3.54 by Izzat et al. Also log K_{12} = 5.41 agrees well with 5.32 from Izzat et al.

Iron

Hydrolysis constants were taken from Baes and Mesmer for both Fe^{3+} and Fe^{2+} species. Coefficients for estimating apparent stability constants were either calculated here or selected from Turner et al. We calculated log K_{11} for $FeOH^{2+}$ using the Davies equation to be -2.19 from log K_{11} value at ionic strength I = 0.5; and, -2.13 calculated from log K_{11} at I=0.25. These agree to better than 1% with -2.19 given by Baes and Mesmer, the value recommended. The constant for log K_{22} was estimated using eq (1) and the data in Smith and Martell for log K values over the range 0.1<I<3.0. We obtained 25.1 which compares exactly with 25.1 given in Smith and Martell. This calculates out as -2.90 for the hydrolysis constants, comparing well with -2.95 given by Baes and Mesmer: a difference of about 2%. Similar calculations for $FeOH^{2+}$ using eq (1) and the data in Smith and Martell give 11.9, compared with their 11.8. The log K_{11} hydrolysis constant is thus -2.10, differing by 4% from the value given by Baes and Mesmer. The $\log K_{13}=-13.6$ given by Ball et al is accepted here; we cannot recommend a log $K_{12\ 34}$, as the value estimated by Ciavatta was obtained at I=3.0 so that the Davies equation is inappropriate.

For the Fe^{3+} fluoro complexes, we calculate log K_{11}=6.00 from the Davies equation; log K_{12}=10.6 from eq (1); and, log K_{13}=13.4 from eq (1). These compare with 6.2, 10.8 and 14.0 given by Ball et al; log K_{11}=6.0 selected by Smith and Martell; and 6.00, 10.76 and 13.79 given by Turner et al. We recommend log K_{12} = 10.8, log K_{13} =13.8. However, log K_{11} = 6.2 gives 5.38 at I=0.5 and I=1.0, compared with 5.18 given in Smith and Martell for I=0.5 and I.0. Accordingly, the best value is 6.0.

We have selected for $FeCl^{2+}$:log K_{11} = 1.48 from Rabinowitch and Stockmayer, this compares with 0.95 $\pm$0.02 measured by Nikolaeva and Tsvelodub and represents a difference of about 35%; log K_{12} = 2.44 from Turner et al; log K_{13} = 1.06 splits the difference between Ball et al, and Turner et al.

From Smith and Martell, log K_{11} = 8.30(.5) for $FeHPO_4^+$ and log K_{11} = 3.47(.5) for $FeH_2PO_4^{2+}$; we calculate from these values using the Davies equation log K_{11} = 9.92 for $FeHPO_4^+$ and log K_{11} = 4.26 for $FeH_2PO_4^{2+}$. Ball et al list log K_{11} = 5.43 for both species; the value for $FeHPO_4^{+}$ is clearly in error; that for $FeH_2PO_4^{2+}$ appears too large. We have selected 10.1 as the best value for $FeHPO_4^+$ and 4.2 as best for the formation constant of $FeH_2PO_4^{2+}$. Wolery has calculated 10.27 for the first species, and 4.44 for $FeH_2PO_4^{2+}$; Langmuir (1979) gives 9.92 and 4.17, respectively, for $FeHPO_4^+$ and $FeH_2PO_4^{2+}$.

Other stability constants and coefficients for an extended Debye-Huckel equation were taken from Turner et al.

Hydrolysis constants for Fe^{2+} were adopted from Baes and Mesmer; fluoro,monochloro, sulfate and carbonate constants were taken from Turner et al. The values for phosphate are those of Nriagu; bicarbonate from Mattigod and Sposito; and, $FeCl_2^{\circ}$ was estimated from Lu by assuming negligible temperature effect between 12°C and 25°C. Izatt et al calculated log K_{11}° = 2.20 for $FeSO_4^{\circ}$, comparing very well with the value 2.12 selected in Table 2.

Lead

Log K_{xy} values are from Baes and Mesmer, except that log K_{35} is adopted from Sylva and Brown. We calculate log K_{11} = 2.31 for PbF^+, using eq (1), which compares better with 2.06 calculated by Turner et al, and 2.09 calculated by Wolery. For PbF_2^o, Wolery estimates 3.48, in very good agreement with 3.42 estimated by Turner et al. The comparable values listed by Ball et al are 1.25 and 2.56 which seem low and compare better with 1.26 and 2.55 listed by Smith and Martell at I=2.0. The best values are 2.07 and 3.42 for log K_{11} and log K_{12}, respectively. We cannot recommend constants for log K_{13} or log K_{14} based on existing data.

For $PbCl^+$ we have taken log K_{11} = 1.59 from Smith and Martell, the remaining three are adopted from Turner et al. We calculate log K_{12} = 2.1 and log K_{13} = 2.1 using eq (1) and the data in Smith and Martell. These compare with 1.82 and 1.71 calculated by Turner et al. The work of Byrne et al indicates that $PbCl_4^{2-}$ is a minor species at low ionic strength, e.g., < 1.0.

For $PbSO_4$, we tabulate the value from Smith and Martell; while for $Pb(SO_4)_2^{2-}$ our best value is 4.0, the average of 3.47 reported by Hem, and 4.51 calculated by Turner et al. Phosphate data were taken from Nriagu.

Neptunium

Hydrolysis constants for NpO_2^{2+}, NpO_2^+, Np^{4+} and Np^{3+} are mainly from Baes and Mesmer, and calculations by Allard. Using eq (1) and data calculated from Baes and Mesmer at I=0.3, 1.0 and 3.0, we estimate log K_{35} = -17.26 for $(NpO_2)_3(OH)_5^+$. This compares quite well with -17.49 given by Baes and Mesmer. Similarly, we estimate log K_{11} = -1.39 for $NpOH^{3+}$ versus -1.49 in Baes and Mesmer; log K_{11} = -5.09 for NpO_2OH^+ compared with - 5.15 in Baes and Mesmer; log K_{22} = -6.28

for $(NpO_2)_2(OH)_2^{2+}$ versus -6.39. Log K_{11} = -8.85 for NpO_2OH is in agreement with -8.88 obtained at 20°C (I=0.02) by Sevast'yanova. We adopt the hydrolysis constants estimated by Allard et al, but caution the reader that high uncertainties are given by the authors.

We estimate log K_{11} = 4.5 for NpO_2F^+ and log K_{12} = 7.6 for $NpO_2F_2^\circ$ using eq (1) and data from Smith and Martell. The 4.5 agrees well with 4.6 in Smith and Martell. We calculate log K = 0.34 using the Davies equation and log K_{11} = -0.3 at I=0.5 from Smith and Martell for NpO_2Cl^+. The data of Moskvin were used with the Davies equation to estimate formation constants for bicarbonate, phosphate and oxalate complexes of NpO_2^+. Temperature corrections between 20°C and 25°C were assumed negligible. Carbonate values are from Nitsche et al.

We cannot make recommendations for other Np^{4+} and Np^{3+} formation constants based on currently available data.

Nickel

Hydrolysis constants are from Baes and Mesmer, except that log K_{12} and log K_{13} were selected from Tremaine and LeBlanc as -20.63 and -29.03, respectively; these compare with -19 and -30 values estimated by Baes and Mesmer. We calculate log K_{21} = -10.8 for Ni_2OH^{3+} using eq (1) and data calculated from Baes and Mesmer's Debye-Huckel equation at I=0.3, 1.0 and 3.0. This compares very well with -10.7 given by Baes and Mesmer, the value adopted.

For NiF^+, log K_{11} = 1.2 splits the difference between Ball et al (1.3) and Turner et al (1.12). Other formation constants were adopted from Ball et al, Turner et al, and Mattigod and Sposito. The log K_{11} = 2.29 is in fair agreement with 2.81 calculated from enthalpy measurements by Izzat et al for $NiSO_4^\circ$.

Plutonium

Hydrolysis constants were taken largely from Baes and Mesmer, Lemire and Tremaine, and Allard et al. Using data from Smith and Martell we estimate via eq (1) log K_{11} = 8.45 vs. 8.4 in Smith and Martell for PuO_2OH^+. This gives -5.55 versus -5.6 given in Baes and Mesmer. From the Davies equation we calculate log K_{11} = -0.81 for $PuOH^{3+}$, using log K_{11} = -1.60 at I=0.5. This is in about 35% agreement with -0.5±0.1 given by Baes and Mesmer. We adopt the other values for Pu^{4+} hydrolysis from Baes and Mesmer, but note that these have been criticized by Cleveland(1979). For $(PuO_2)_2(OH)_2^{2+}$, we have calculated log K_{22} = -8.29 from data given in Baes and Mesmer at I=0.3, 1.0, and 3.0; this compares with -8.36±0.15 in the reference.

Using Moskvin's data, the Davies equation, and assuming no significant temperature effect between 20°C and 25°C, we estimate log K_{11} = 2.8 for $PuO_2HPO_4^-$. Estimates for the oxalate complexes were made in a similar manner. Other formation constants were obtained mainly from Cleveland, Lemire and Tremaine. For PuO_2HPO_4, the exponent should be 10^8 in Cleveland's paper, rather than 10(1979).

Using Fuger and Oetting's values for ΔG_f° of PuO_2^{2+}, PuO_2^+, Pu^{4+} and Pu^{3+}, we calculate from the ΔG_f° data in Lemire and Tremaine for $PuO_2SO_4^\circ$ log K_{11} = 3.3; this compares with 2.95 for $UO_2SO_4^\circ$ in Smith and Martell: Cleveland suggests UO_2^{2+} approximates PuO_2^{2+} for some complexes (1979). Similarly, log K_{11} = -5.64, is in exact agreement with Baes and Mesmer for PuO_2OH^+. From Lemire and Tremaine, log K_{11} = 5.8 for $PuSO_4^{2+}$, whereas we calculate 7.3 using eq (1) and data from Table 1; also, for $Pu(SO_4)_2^\circ$, log K_{12} = 10.2, in poor agreement with our calculated 6.6 using the Davies equation, and 7.4 from eq (1). We select 5.8 and 7.4 as best values, these being within the lower uncertainties given by Lemire and Tremaine.

We have included a number of hydrolysis and formation constants calculated by Allard et al, and Lemire and Tremaine for completeness. However, the reader must consider the high uncertainties associated with these values, e.g., -7±6 for $Pu_2(OH)_5^{3+}$.

Samarium

We have adopted the hydrolysis and formation constants given by Turner et al.

Strontium

The recommended values were taken from Baes and Mesmer, Rai et al, Smith and Martell, and Wolery. We calculate log K_{11} = 5.6 using the Davies equation and the value listed in Smith and Martell; this compares very well with 5.5 calculated by Wolery for $SrPO_4^{\circ}$.

Technetium

We estimate log K_{11} = -1.0 and log K_{12} = -3.2 using the Davies equation, data from Jensen and assuming negligible temperature effects from 20°C to 25°C for $TcOOH^+$ and $Tc(OH)_2$.

Thorium

The stability constants were largely taken from Baes and Mesmer, Langmuir and Herman, Moskvin and Wagman et al. We calculate log K_{11} = 12.9, for $ThHPO_4^{2+}$; log K_{12} = 28.0 for $Th(HPO_4)_2^{\circ}$; and log K_{13} = 34.5 for $Th(HPO_4)_3^{2-}$ using the Davies equation and Moskvin's data.

Using the ΔG_f° values in Wagman et al and the CODATA values for F^- and OH^-, we calculate the following formation constants: for ThF^{3+}, log K_{11} = 7.55 compared with 8.03 from Langmuir and Herman; for ThF_3^+, log K_{13} = 17.4 versus 18.9 estimated by Langmuir; for ThF_2^{2+}, log K_{12} = 13.2 vs. 14.3 given by Langmuir et al. Smith and Martell select: log K_{11} = 8.44, log K_{12} = 15.08, log K_{13} = 19.8, log K_{14} = 23.2 - in better agreement with Langmuir and Herman than Wagman et al. Accordingly, we adopt the values from Langmuir and Herman in Table 2.

We calculate from Wagman et al: log K_{11} = -3.81 for $ThOH^{3+}$ compared with -3.20 in Baes and Mesmer; log K_{12} = -6.74 compared with -6.93; and log K_{22} = -4.00, compared with -6.14. Langmuir and Herman select the hydrolysis values from Baes and Mesmer; we have tabulated these in Table 2. The values have been used by Turner et al.

Tin

Hydrolysis and chloride values were obtained from Baes and Mesmer, and Smith and Martell. We are unable to recommend values for other stability constants due to a lack of data; however, the measurements by Pettine et al. appear useful at I = 1.0.

Uranium

Baes and Mesmer cite -5.8 for log K_{11}; Dongarra and Langmuir calculate -5.1. We calculate -5.3 using the Davies equation from log K_{11} = -5.5 at I=0.1 for Sylva and Davidson measurements. Langmuir found -5.1 gave better values in calculating log K for UO_2^{2+} phosphate complex than -5.8; also, our estimated constant is closer to -5.1. Accordingly, the best value is -5.1. For UOH^{3+}, we calculate log

K_{11} = 13.32 using eq (1) and the data in Smith and Martell; this compares with 13.3 given in Smith and Martell; and, -0.68 vs. -0.65 hydrolysis constant listed by Baes and Mesmer. Similarly, we obtain log K_{22} = -5.68 compared with -5.62 in Baes and Mesmer for $(UO_2)_2(OH)_2^{2+}$; log K_{35} = -15.43 for $(UO_2)_3(OH)_5^{+}$ using the Davies equation compared with -15.63 in Baes and Mesmer; log K_{34} = -12.1 for $(UO_2)_3(OH)_4^{2+}$ versus -11.75 given by Baes and Mesmer using eq (1) and data from Smtih and Martell. Other hydrolysis constants are from Lemire and Tremaine and Allard et al.

Values for formation constants were taken mostly from Langmuir, Lemire and Tremaine, and Turner et al.

From ΔG_f° values listed in Langmuir, and from CODATA, we calculate log K_{11} = 8.63 for UF^{3+}; log K_{12} = 14.5 for UF_2^{2+}; log K_{13} = 19.1 for UF_3^{+}; these compared with the following estimates by Turner et al from data at I=4.0 in Smith and Martell: 10.23, 16.30, 23.20. Parker has reported 7.15, 12.4, 17.7; and log K_{14} = 23.1, apparently at I=0. We have adopted the values by Langmuir.

We select for $UO_2CO_3^{\circ}$, log K_{11} = 9.9 calculated from Langmuir and in better agreement with 10.1 from Lemire and Tremaine, and 9.16 from Ciavatta et al, than 7.51 from Turner et al. The log K_{12} and log K_{13} values selected here (16.7, 21.4) agree well with published data shown in Table 1, such as O'Cinneide, Maya and Sergeyeva.

For USO_4^{2+} we calculate from Langmuir's data log K_{11} = 5.48, compared with the selected 5.47 given by Langmuir, and 5±1 estimated by Lemire and Tremaine.

We calculate from the ΔG_f° data in Langmuir, and CODATA values for U^{4+} and OH^- the following hydrolysis constants: log K_{11} = -0.3; log K_{12} = -2.3; log K_{13} = -4.9; log K_{14} = -8.6; log K_{15} = -13.2; and log $K_{6\ 15}$ = -17.4. Lemire and Tremaine have adopted the ΔG_f° values given by Langmuir for the U^{4+} hydrolysis products. We adopt log K_{11} and log K_{15} from Baes and Mesmer.

Zirconium

Hydrolysis constants were taken from Baes and Mesmer; formation constants from Turner et al. A log K_{11} = 0.3 compares with 0.3 in Smith and Martell; log K_{48} = 6.0 is in exact agreement with Smith and Martell; as are log K_{15}, and log K_{34}.

From Turner et al. we calculate log K_{11} = 3.68 for $ZrSO_4^{2+}$ at I=2; this compares with 3.67 given in Smith and Martell. Similarly, log K_{12} = 6.40, log K_{13} = 7.41; these compare well with 6.40 and 7.4, respectively, in Smith and Martell.

For Zr^{4+} fluoride, we calculate from Turner et al., the following at I=2.0: log K_{11} = 8.97; log K_{12} = 16.4; log K_{13} = 22.4. These compare within better than 1% of the log K's given in Smith and Martell at I=2.

Ionization Constants

Ionization constants as a function of ionic strength were taken from Smith and Martell for water, and the following acids: H_2SO_4, HF, H_2CO_3 and H_3PO_4. Correlation equations were developed using an extended Debye-Huckel equation. The effect of ionic strength on the log K values is given in Tables 14-18 as calculated from the coefficients listed in Table 19, taken from our correlations.

For HF, we calculate log K = -2.98 at I=0.1; -2.93 for I=0.5; -2.98 at I=1.0; and, -3.30 at I=3.0. These compare with -2.92, -2.93, -2.96, and -3.30 in Smith and Martell. The calculated log K values for HCO_3^- are compared with Smith and Martell: -9.97 (-10.00), I=0.1; -9.66 (-9.57), I=1.0; -9.54 (-9.56), I=3.0.

Similar agreement is obtained for the remaining ionization constants. Figures 5 and 6 show the effect of ionic strength on log K values for H_2O and HCO_3^-.

Summary and Recommendations

In summary, a database consisting of hydrolysis and formation constants for 18 metals associated with the disposal of nuclear wastes is presented. Complexing ligands for the various species include OH, F, Cl, SO_4, PO_4 and CO_3. The data are mainly at 25° C and ionic strengths

from zero to 3. Tabulated values were obtained from original publications, as well as critical compilations such as those by Langmuir for uranium and thorium; Wagman, Schumm and Parker for thorium; Baes and Mesmer for hydrolysis constants; Smith and Martell for formation constants; and Allard for actinides. A table is included of coefficients for an extended Debye-Huckel equation to permit calculations of stability constants up to 3 ionic strength, and up to 0.7 ionic strength using the Davies equation. Selected stability constants calculated with these coefficients agree to an average of $\pm 2\%$ when compared with other experimental and calculated values.

Table 1 contains logK values published up to 1982 for F, Cl, SO_4, CO_3 and PO_4 ligands, mostly at 25°C and various ionic strengths. Selected values for C_2O_4 are included, e.g., Th^{4+} and AmO_2^+, because they are useful to nuclear waste chemistry and because logK values for CO_3 complexes are correlated with C_2O_4 values; thereby providing means of estimating logK values for CO_3 complexes, e.g., $ThCO_3^{2+}$, $EuCO_3^+$, $PaCO_3$, $FeCO_3^+$ (12).

The estimation of leaching and migration of waste elements from nuclear storage repositories requires a large quantity of reliable data at high temperatures and concentrations. A substantial amount of data are calculated: some from correlation, others from extrapolation procedures. For example, over five different equations are used to correct for the effects of ionic strength up to I=3.0, and these are empirical, or semi-empirical. Similar considerations apply for calculating data at high temperatures, where the Criss-Cobble approach is extensively used (4).

Future research on stability constants for nuclear waste disposal might include the following recommended research:

1. Development of methods for extrapolation of data from low temperatures such as 25°C up to 200°C to 300°C. Stability constants at elevated temperatures are useful for estimating leaching of waste nuclides from storage canisters; in corrosion research for power plants; and, in solution mining

of ores. Current approaches include use of the Criss-Cobble approach, and the integrated van't Hoff equation (4,6).

2. Derivation of a theoretically based equation for calculating stability constants as a function of supporting electrolyte concentrations which is applicable to 3 molal or greater concentrations. This would permit calculation of stability constants in a variety of natural media such as sea water and brines. At present, empirical approaches such as the Davies equation and addition of polynomial terms to the Debye-Huckel equation are widely used.
3. Gibbs energy values for the formation of multiligand complex ions such as $CuCl_4^{2-}$ and $PbCl_4^{2-}$. These can be used to calculate stability constants for comparison with experimental values, and also may show trends which could be used to estimate other Gibbs energy values, e.g., for higher complexes. Current CODATA and NBS tabulations generally include the first or second complexation values.
4. Experimental measurements of stability constants at high temperatures; especially above 100°C. Much of the data above 100°C are calculated; leading to the dual question of how accurate is the calculation, and whether particular species even exist at 100-200°C. The publication by Tremaine and LeBlanc provides needed data on Fe^{2+} at high temperatures (7).
5. Instrumental methods for both identifying specific species, and measuring at ambient concentrations. The existence of some species, e.g., $U(OH)_4$, are inferred, some are a result of computer fits such as $Zr_3(OH)_4^{8+}$; while the existence of others is a scientific guess e.g., $Al(OH)_3^{\circ}$.