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Thermodynamic Tables for Nuclear Waste Isolation

Vol. 1. Aqueous Solutions Database

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

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**Thermodynamic Tables for Nuclear Waste Isolation.
Vol 1. Aqueous Solutions Database**

Sidney L. Phillips, Frank V. Hale, and Lenard F. Silvester

Lawrence Berkeley Laboratory
1 Cyclotron Road
Berkeley, California 94720

Malcolm D. Siegel

Sandia National Laboratories
Albuquerque, New Mexico 87185

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ABSTRACT

Tables of consistent thermodynamic property values for nuclear waste isolation are given. The tables include critically assessed values for Gibbs energy of formation, enthalpy of formation, entropy and heat capacity for minerals; solids; aqueous ions; ion pairs and complex ions of selected actinide and fission decay products at 25°C and zero ionic strength. These intrinsic data are used to calculate equilibrium constants and standard potentials which are compared with typical experimental measurements and other work. Recommendations for additional research are given.

Table of Contents

Abstract	ii
List of Figures	vii
List of Tables	viii
Acknowledgment	ix
Symbols and Conversion Factors	x
EXECUTIVE SUMMARY	1
1.0 INTRODUCTION	5
1.1 Introduction	5
1.2 Scope and Quality of the Thermodynamic Tables	6
1.2.1 Scope	6
1.2.2 Internal Consistency and Critical Evaluation of Data	8
1.3 User's Guide for Telecommunication to the Aqueous Solutions Database	10
1.3.1 Introduction	10
1.3.2 Log On and Log Off Procedures	10
1.3.3 Menu for Telecommunication to Current Information	12
1.3.4 Sample Session 1: Obtain Table of Thermodynamic Data for Element	13
1.3.5 Sample Session 2: Obtain List of Reactions for Element	14
1.3.6 Sample Session 3: Obtain Information on Specific Reaction	15
1.3.7 Sample Session 4: Obtain Equilibrium Constant and Uncertainty	16
2.0 ESTIMATION OF THERMODYNAMIC PROPERTY VALUES	17
2.1 Thermodynamics of Aqueous Hydrated Radionuclide Ions	17
2.1.1 Relation Between $\Delta_f G^\circ$ and $\Delta_f H^\circ$	18
2.1.2 Entropy	18
2.1.3 Heat Capacity	18
2.2 Thermodynamics of Complex Ions	24
2.2.1 Effect of Ionic Strength on $\log K^\circ$	24
2.2.2 Calculation of Thermodynamic Property Values	26
2.2.2.1 Free Energy of Formation	26
2.2.2.2 Enthalpy and Entropy of Reaction	27
2.2.2.3 Heat Capacity of Anions and Uncharged Aqueous Species	27
2.3 Thermodynamics of Higher Complexes	35

2.3.1	Correlation Between $\Delta_f G^\circ$ and $\Delta_f H^\circ$	35
2.3.2	Correlation Between $\Delta_f G^\circ$, $\Delta_f H^\circ$ and Number of Ligands	35
2.3.3	Heat Capacity	35
2.3.4	Correlations Between Equilibrium Constants and Ligand Number	39
2.4	Summary	39
3.0	THERMODYNAMIC PROPERTY TABLES	43
3.1	Property Values Tabulated in FORM1	43
3.1.1	Substance	43
3.1.2	Property	43
3.1.3	Standard Deviation	45
3.1.4	References and Comments	45
3.2	Auxiliary Data	46
3.2.1	CODATA Key Values	46
3.2.2	Master Species	46
3.3	Apparent Equilibrium Constants, High Temperatures and Salinities, FORM2	46
4.0	QUALITY CONTROL	49
4.1	Self-Consistency	49
4.2	Consistency with Reaction Processes	49
4.2.1	Program FPLO1	49
4.2.2	Chemical Equilibria	49
4.2.3	Oxidation/Reduction Potentials	50
4.2.4	FPLO2 Program	51
4.3	Reproducibility of Selected Experimental Measurements and Other Work	51
4.3.1	Silica Solubility	51
4.3.2	Silicic Acid Ionization	53
4.3.3	Nickel/Fluoride Electrode System	54
4.3.4	$U^{++++}-OH^-$ System	55
4.3.5	UO_2^{++} Hydrolysis	56
4.3.6	Hydrolysis of Am^{+++}	58
4.3.7	Am - F Complexes	58
4.3.8	Hydrolysis of NpO_2^+	59
4.3.9	NpO_2^+ Carbonate Complexes	60
5.0	UNCERTAINTY IN EQUILIBRIUM CONSTANTS	61

5.1 Uncertainty in Thermodynamic Tables	61
5.2 Contested Substances	61
5.3 Propagation of Standard Deviation	62
5.3.1 ADDREACT Interface to DATATRIEVE	63
5.3.2 COMPLOGK Interface to DATATRIEVE	63
6.0 SUMMARY	65
7.0 RECOMMENDATIONS FOR ADDITIONAL RESEARCH	67
8.0 LITERATURE CITED	71
Appendix I. Tabulation of Thermodynamic Values for Key Values	77
Appendix II. Thermodynamic Tables for Waste Repository Performance Assessment	82
Aluminum	84
Americium	87
Barium	90
Bromine	92
Calcium	93
Carbon	96
Cesium	97
Chlorine	99
Chromium	100
Electron	104
Europium	105
Fluorine	108
Hydrogen	109
Iodine	110
Iron	113
Lanthanum	116
Lead	118
Magnesium	121
Neptunium	124
Nickel	129
Nitrogen	131
Oxygen	132
Palladium	133
Phosphorus	136
Plutonium	137
Potassium	141
Protactinium	143
Radium	144

Ruthenium	148
Selenium	151
Silicon	153
Sodium	155
Strontium	157
Sulfur	159
Technetium	161
Thorium	163
Tin	168
Uranium	171
Distribution	178
Bibliographic Data Sheet	182

LIST OF FIGURES

1-1. Critical evaluation procedure for selection and addition of new data.	9
2-1. Correlation between $\Delta_f G^\circ$ and $\Delta_f H^\circ$ for selected aqueous actinide ions.	19
2-2. C_p° of selected positively charged ions.	22
2-3. Variation in $\log K(I)$ with I , for $2UO_2^{++} + 2H_2O = (UO_2)_2(OH)_2^{++} + 2H^+$	25
2-4. Variation in $\log K(I)$ with I , for reaction $NpO_2^+ + CO_3^{--} = NpO_2CO_3^-$	25
2-5. Correlation between $\Delta_f G^\circ$ and $\Delta_f H^\circ$ for selected actinide ion pairs.	29
2-6. Linear relationship between $\Delta_f G^\circ$ and $\Delta_f H^\circ$ for selected higher complexes.	33
2-7. Plot of $\Delta_f G^\circ$ versus number of ligands for higher complexes.	37
2-8. Plot of $\Delta_f H^\circ$ versus number of ligands for higher complexes.	38
2-9. Plot of cumulative values of $\log K^\circ$ versus ligand number.	41
3-1. First page of :form1, with Am as the example.	44
7-1. Data base for MINEQL pre-processor.	68
7-2. Functions of the thermodynamic data base for sensitivity analysis.	69

Above description of figure contents differs from figure captions.

LIST OF TABLES

1-1. Current content of Aqueous Solutions Database.	7
2-1. Gibbs energy of formation and enthalpy of formation for selected actinides.	20
2-2. S° and C_p° for some positively charged ions.	23
2-3. Thermodynamic data for selected actinide ion pairs.	28
2-4. Values of C_p° from eq 7 compared with other data.	31
2-5. C_p° values for uncharged aqueous species.	31
2-6. Values of S° and C_p° used to develop correlation for negatively charged ions.	32
2-7. Comparison of values of C_p° calculated by eq 7B.	32
2-8. C_p° values for selected negatively charged ions.	34
2-9. Change in enthalpy of formation with number of ligands.	36
2-10. Correlation between $\Delta_f G^\circ$ and number of ligands.	39
4-1. Standard electrode potentials.	52
4-2. Solubility of $\text{SiO}_2(\text{s})$	53
4-3. Ionization constants of $\text{Si}(\text{OH})_4(\text{aq})$ to high temperatures.	53
4-4. Ionization constants of $\text{Si}(\text{OH})_4(\text{aq})$ to high ionic strengths.	54
4-5. Electrode potentials of $\text{Ni}/\text{NiF}_2(\text{s})$ couple to 350°C	55
4-6. Standard hydrolysis constants of U^{++++}	57
4-7. Apparent hydrolysis constants of UO_2^{++}	57
4-8. Apparent hydrolysis constants of Am^{+++}	58
4-9. Thermodynamic data for AmF_n	59
4-10. Apparent formation constants of $\text{NpO}_2\text{OH}(\text{aq})$	59
4-11. Apparent formation constants of NpO_2^+ carbonates.	60
5-1. Propagated uncertainties calculated by COMPLOGK.	64

Above description of tables may differ from table headings, in the text.

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SYMBOLS, UNITS AND CONVERSION FACTORS

log = common logarithm, base 10

ln = natural logarithm, base e

° = superscript, indicating standard conditions: 25°C, I = 0

I = ionic strength, mol/kg

K = degrees Kelvin (273.15 + ° C)

J = joules

kJ = kilojoules

mol = gram molecular weight (mole)

z = ionic charge: z_a = anion; z_c = cation

$\Delta z^2 = \sum z_p^2 - \sum z_r^2$; p and r refer to reactants and products

$\Delta_f G^\circ$ = Gibbs free energy of formation, kJ/mol

$\Delta_f H^\circ$ = Enthalpy of formation, kJ/mol

S° = entropy, J/mol/K

C_p° = heat capacity at constant pressure, J/mol/K

$\Delta_r G^\circ$ = Gibbs energy of reaction, kJ/mol

$\Delta_r H^\circ$ = Enthalpy of reaction, kJ/mol

$\Delta_r S^\circ$ = Entropy of reaction, J/mol/K

$\Delta_r C_p^\circ$ = Heat capacity change for a reaction, J/mol/K

$\Delta_f G_p^\circ$ = Gibbs energy of product of reaction

$\Delta_f G_q^\circ$ = Gibbs energy of reactant of a reaction

K° = Intrinsic equilibrium constant

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

g = gaseous form

s = solid form (crystalline)

am = amorphous form

aq = aqueous form

l = liquid form

σ = standard deviation from mean

R = gas constant, 8.314510 J/mol/K (8.3143 J/mol/K used here)

F = faraday, 96,485.309 coulombs/mole (96,487 used here)

cal (calorie) = 4.184 J

molal = gram moles per 1000 g water

molar = gram moles per 1000 mL water

pH = $-\log a_{\text{H}}$, a = activity of hydrogen ion (H)

pe = $-\log a_{\text{e}}$, activity of electron (e)

r^2 = coefficient of determination, measure of predictive accuracy of regression equation and strength of linear association between the dependent and the independent variables. (degree of dependence between the two variables)

EXECUTIVE SUMMARY

Sensitivity studies of the performance of high level waste repository systems suggest that geochemical interactions between radionuclides, groundwater and rocks could provide an important barrier to radionuclide migration. For this reason, an accurate prediction of the solubility and speciation of aqueous radionuclides is an important component of overall repository performance assessments. The use of consistent thermodynamic data in geochemical speciation and reaction codes is an essential part of these determinations.

This report describes the tabulation of a well-documented set of critically evaluated thermodynamic property values and associated uncertainties for use in geochemical speciation codes. These tables contain values of the following four thermodynamic properties: Gibbs energy of formation, enthalpy of formation, entropy and heat capacity for solids, simple ions, ion pairs and higher complexes of elements occurring in nuclear wastes, natural waters and geologic materials. A computerized data base management system, the Aqueous Solutions Database, contains all of the data described in this report. The data base is accessible via telecommunications to interested researchers.

This consistent tabulation includes material from other critical evaluations such as the widely referenced CODATA tables, the National Bureau of Standards tables, the series of reports on actinides published by the International Atomic Energy Agency, research papers from scientific journals, as well as our critical evaluation of experimental work. The data are presented in the form of individual tables for each element, and a tabulation of auxiliary data. The table of auxiliary values consists of standard reference data from CODATA and other sources; this table also contains values of thermodynamic properties for master species used in geochemical codes. The uncertainty in each property value is given; a literature reference for each datum is listed. A rationale for the selection of data is given in the Comments section found in Appendix II for property values that have been obtained by critical evaluation of experimental results or estimated by correlation procedures.

Reliable experimental data are not available for many potentially important radionuclide species. For this reason, correlation methods were developed to estimate missing values. For all substances in the data base, thermodynamic properties are related by the fundamental equation

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ \quad (i)$$

The value of the intrinsic equilibrium constant for any reaction is related to the thermodynamic properties of the reactants and products by eq ii:

$$\Delta_r G^\circ = -RT \ln K^\circ \quad (\text{ii})$$

where

$$\Delta_r G^\circ = \sum \Delta_f G_p^\circ - \sum \Delta_f G_q^\circ \quad (\text{iii})$$

In the case of uncomplexed aqueous ions such as Am^{+++} , the values of $\Delta_f G^\circ$ and $\Delta_f H^\circ$ are linearly correlated; this relationship has been used to fill gaps in the thermodynamic tables. Similarly, we have developed a correlation between heat capacity, entropy and ionic charge for positively charged ions and negatively charged ions. The heat capacity of neutral aqueous species was estimated from a third correlation developed as a result of this research. Other correlations developed from this research include a linear relationship between Gibbs energy of formation and enthalpy of formation for ion pairs and higher complexes; Gibbs energy of formation and enthalpy for crystalline solids; Gibbs energy of formation and number of ligands; and, enthalpy of formation and the number of ligands. The last two correlations are valuable because they permit linear extrapolation and interpolation to any ligand number.

These correlations are important in that all gaps in a tabulation of thermodynamic values such as this data base can be filled with estimated values of the four properties. Correlation methods were used extensively to obtain data for the higher complexes. The Gibbs energy of formation and enthalpy of formation are strongly correlated over a range of oxidation states, electronic configurations and ligand numbers.

The scope and quality of the data as well as the structure of the computerized data management system facilitate application of the data base to analyses of the sensitivity of calculated radionuclide speciation and release, to uncertainties in available thermodynamic data. The sensitivity studies are related to uncertainties in the values of thermodynamic quantities used to compute equilibrium constants for chemical processes, or to the lack of experimental measurements which unequivocally verify the existence of an aqueous species.

One type of sensitivity analysis might examine the importance of including or excluding contested species in calculations of the total aqueous concentration of a particular radionuclide available for convective transport. A second kind of analysis may involve the propagation of experimental errors and uncertainties in thermodynamic property values in the interpretation of laboratory measurements. In the past, this type of sensitivity analysis has led to recommendations for improved analytical techniques.

A final type of sensitivity analysis involves randomized sampling of values of $\log K$ from user-defined distributions. By sampling repeatedly from assumed distributions of $\log K$'s and carrying out replicate speciation calculations, uncertainties could be calculated for the estimated concentrations of aqueous species. Examination of the resulting response surface by a variety

of statistical techniques could identify the particular constants that dominate the uncertainty in the calculated solubilities and speciation.

Constraints on the level of accuracy and internal consistency of the data base are commensurate with the intended use in sensitivity analyses. This data base is internally self-consistent in the following ways: 1. the relationship described by eq (i) above is valid for each substance to better than ± 1000 J/mol, and 2. an intrinsic equilibrium constant calculated from the Gibbs energy of reaction will have a single value irrespective of the number of chemical equations added to obtain a given final reaction. If the criteria are not met, then the necessary changes are made in the data base, and these changes propagated throughout the data base. The accuracy of the data is verified by comparing our calculated values of equilibrium constants with the original experimental data, for typical reactions.

1.0 INTRODUCTION

1.1 Introduction

The Nuclear Waste Policy Act, as amended (NWPA), established disposal of high level waste (HLW) in deep geologic repositories as the preferred method of HLW management. The subsurface formations will be carefully evaluated to ensure that the wastes are isolated and contained within defined limits for 10,000 years (1). The Environmental Protection Agency has set maximum allowable cumulative release limits for all of the radionuclides included in and generated by the wastes (2). In addition, the U.S. Nuclear Regulatory Commission has established additional performance objectives for different parts of the repository system (3,79). Two important questions that must be addressed in support of the NWPA are: how can the repository performance with respect to the containment objectives be predicted; and, what is the uncertainty in these predictions? Computer codes have been used to simulate the release of radionuclides from hypothetical repositories (1). Sensitivity studies of the performance of repository systems suggest that geochemical interactions between radionuclides, groundwater and rocks could provide an important barrier to radionuclide migration (96). Accurate prediction of the speciation and solubility of aqueous radionuclides is an important component of overall repository performance assessment. The use of thermodynamic data in geochemical speciation and reaction codes is an essential part of these determinations (4,11).

The objective of this research is tabulation of thermodynamic data for waste nuclides for use in sensitivity analysis of HLW repository performance. The sensitivity studies take different forms; but all are related to uncertainties in values of the thermodynamic properties used to calculate equilibrium constants for chemical processes. In one type of analysis, the potential importance of one or more aqueous species in calculating the solubility, and therefore integrated discharge, of a radionuclide can be examined. A calculation would be made using expected repository conditions, including and then excluding a specific species. For example, the importance of the aqueous species $U(OH)_5^-$ in calculating the solubility of uranium in tuff, basalt and saline waters could be assessed. Both the existence of $U(OH)_5^-$ in alkaline solution (5), and the solubility data of $UO_2(s)$ (6,59) in alkaline solution have been questioned (7,98).

Other analyses involve the selection of an equilibrium constant for a particular chemical reaction. It is common practice to use the mean value of an equilibrium constant in speciation calculations; the standard deviation is not taken into account in the final results. Users of codes appear to rely on intuitive reasoning based on their own experience, in order to assign uncertainties to the final calculations, and therefore results of the predicted behavior of a waste nuclide. Sensitivity analysis can be performed on equilibrium constants and their propagated uncertainties to quantify both the mean value and standard deviation. A result could be recommendations for additional measurements to obtain an improved mean value; and also to suggest a better laboratory method. An excellent example of this approach is the recent work by Fish and Morel in which three analytical methods were compared for propagation of error in fulvic acid titration data (8). Their objective was to measure the precision of each method, and then quantify the propagation of error for each transformation of data. This approach is an

alternative to numerous replicate titrations.

A final type of sensitivity analysis involves randomized sampling of $\log K$ values from user-defined distributions. The extrema and shape of the distributions can be determined from actual ranges of experimental data or from mean values and associated standard deviations of equilibrium constants. For example, the $\log K$ could describe dissolution, hydrolysis and complexation of an actinide. The total aqueous concentration of the radionuclide will place an upper bound on the amount of solute available for convective transport and will be related to each $\log K$. By sampling repeatedly from assumed distributions of $\log K$ and carrying out replicate speciation calculations, uncertainties could be calculated for the estimated concentrations of aqueous species. Examination of the relationships between the distributions of input and output variables by a variety of statistical techniques could identify the particular constants that dominate the uncertainty in the calculated solubilities, speciation and releases (11,97).

1.2 Scope and Quality of the Thermodynamic Tables

1.2.1 Scope

These tables provide a well documented set of critically evaluated thermodynamic property values and associated uncertainties for use in geochemical speciation codes. The data in this report are part of the Aqueous Solutions Database (ASD), a computerized tabulation of values of selected thermodynamic properties for use by researchers studying nuclear waste disposal and other geoscientific topics. The current content of the ASD is shown in Table 1.1. The elements listed in the table include those contained in the inventory of light water reactor (LWR) processed waste, spent fuel and associated cladding, and uranium mill tailings. The critical evaluation procedures are described in Section 1.2.2 below; a synopsis of a guide to accessing the ASD is provided in Section 1.3.

This report is limited to a tabulation of values for the following four thermodynamic properties: $\Delta_f G^\circ$, $\Delta_f H^\circ$, S° and C_p° . The tables are for use in predicting the behavior of radionuclides in subsurface repositories: therefore geologic materials are included, but most gaseous substances are specifically excluded. There are excellent publications with data for aqueous ions, minerals and other solid geologic materials; this work emphasizes ion pairs and higher complexes. Important gaps in the tabulation are filled using correlation procedures with the emphasis on filling gaps in tabulations for the actinide elements. Calculations of equilibrium constants are outside the scope of this report; however, selected values as well as standard electrode potentials have been calculated to compare our results with other work.

Selected experimental data used to calculate property values are given in the "Comments" section of FORM1 for each element in Appendix II. For those values which we

Table 1-1. Current content of Aqueous Solutions Database. See Figure 1-1, p. 9, for definitions of the Status of Data. Elements identified with an asterisk (*) are not included in this report; all data can be obtained by telecommunication access.

Element	Number of Aqueous Species	Number of Solids	Status of Data
Aluminum	19	12	1
Americium	16	19	1
Arsenic *	12	11	1
Barium	8	9	3
Bromine	2	0	1
Calcium	8	34	1
Carbon	5	1	1
Cerium *	7	7	2
Cesium	12	9	2
Chlorine	2	0	1
Chromium	17	22	2
Copper *	12	48	2
Curium	13	10	3
Electron	2	0	1
Europium	18	22	2
Fluorine	3	0	1
Gadolinium *	6	7	3
Hafnium *	12	4	3
Hydrogen	2	0	1
Iodine	16	11	1
Iridium *	2	9	3
Iron	12	27	2
Key Values	46	0	1
Lanthanum	6	9	2
Lead	19	28	2
Magnesium	7	29	1
Manganese *	2	20	3
Molybdenum *	32	7	1
Neodymium *	8	9	3
Neptunium	46	21	1
Nickel	3	17	3
Nitrogen	3	0	1
Oxygen	5	0	1
Palladium	8	12	1
Phosphorus	5	0	1
Plutonium	26	12	1
Potassium	3	14	1
Protactinium	4	6	3
Radium	12	61	3
Ruthenium	29	14	2
Selenium	11	8	1
Silicon	8	22	1
Silver *	1	5	2
Sodium	2	12	1
Strontium	8	12	1
Sulfur	10	1	1
Technetium	10	17	2
Thallium *	2	4	2
Thorium	28	35	2
Tin	24	15	2
Uranium	44	68	1
Ytterbium *	7	7	3
Zinc *	2	8	3

have calculated, the method used such "as calculated by eq 7" is indicated. The same procedure is applied to values obtained from other critical evaluations. References to all sources of experimental and calculated data used in compiling the property values are given in the Comments section.

For the ASD, uncertainty is defined as upper and lower bounds about the selected best value. These bounds are given as a standard deviation, \pm , for example -502.90 ± 7.5 which gives values of -510.4 and -495.4 . As a general rule, uncertainties assigned by a researcher or by another evaluator to their data are accepted for the ASD tabulation. We assign uncertainties in property values by calculation of the propagation of error, as well as a critical evaluation of the quality of the experimental work.

1.2.2 Internal Consistency and Critical Evaluation of Data

The internal consistency of the data base is ensured by checking the fundamental relationship $\Delta_f G^\circ = \Delta_f H^\circ - 298.15 \Delta_f S^\circ = -RT \ln K^\circ$. The measure of agreement between values of an equilibrium constant calculated by two or more procedures is also verified. Tabulated values of the chemical thermodynamic properties are related so that a $\log K^\circ$ obtained in any number of ways (paths) will yield the identical value. Methods of computing $\log K^\circ$ include the net change in Gibbs energy of reaction, and the addition of two or more chemical reactions which yield the desired reaction. Examples of these comparisons are given in this report. It must be stressed, however, that data from previously published critical evaluations are accepted in this work. Some residual inconsistencies may result from inclusion of data from independent sources. These are corrected quickly using our data management system (68). All thermodynamic data from other sources which are used here are checked for consistency with our reference values in Appendix I. Consistency with our data base is thus assured.

The networks of interrelated calculations and the interdependence of measured formation constants and tabulated thermodynamic data are examined anew as new values are added to the data base. A change in the recommended value of $\Delta_f G^\circ$, $\Delta_f H^\circ$, or S° for a key substance which results in a change in $\log K^\circ$ greater than 0.09 units is propagated throughout the data base. This is done with the dual purpose of compiling the best data in the data base, and to ensure consistency in calculated values of $\log K^\circ$.

The scope and quality of these data and the structure of the computerized data management system facilitate the use of this tabulation in many applications. An example is the analysis of the sensitivity of calculated solubilities as correlated to uncertainties in values of the Gibbs energy of formation for the various species involved in the solubility process. Constraints on the level of internal consistency of this tabulation are commensurate with this objective, and are described in detail in Section 4 of this work.

Selection of the best experimental measurements from which we obtain newer thermodynamic values is based on a number of considerations. These include: reproducibility of the measurements; experimental method used by the authors; details given about the laboratory procedures; purity of chemicals used, and any further purification; temperature control; number of replicate

measurements for each measured value; standard deviation from the mean; uncertainty assigned by the investigator, and, comparison of experimental results with theoretical expectations. We also attach importance to characterization of the chemicals used, e.g. verification of the crystallinity of a solid by x-ray diffraction (68). It is recognized that inconsistencies are unavoidable in tabulations such as this which involve a myriad of numerical calculations. These inconsistencies are corrected as soon as they are brought to our attention.

Table 1-1 describes the status of each element in the tabulation, ranked according to the depth of critical evaluation. Figure 1-1 outlines the evaluation procedure and defines the categories of status of the data. The emphasis of this work has been on the actinides and fission products contained in high level wastes; therefore, the status of these elements is commonly 1 or 2. Our work has also emphasized the aqueous ions and other aqueous species, because these species represent by far the largest gap in the available data.

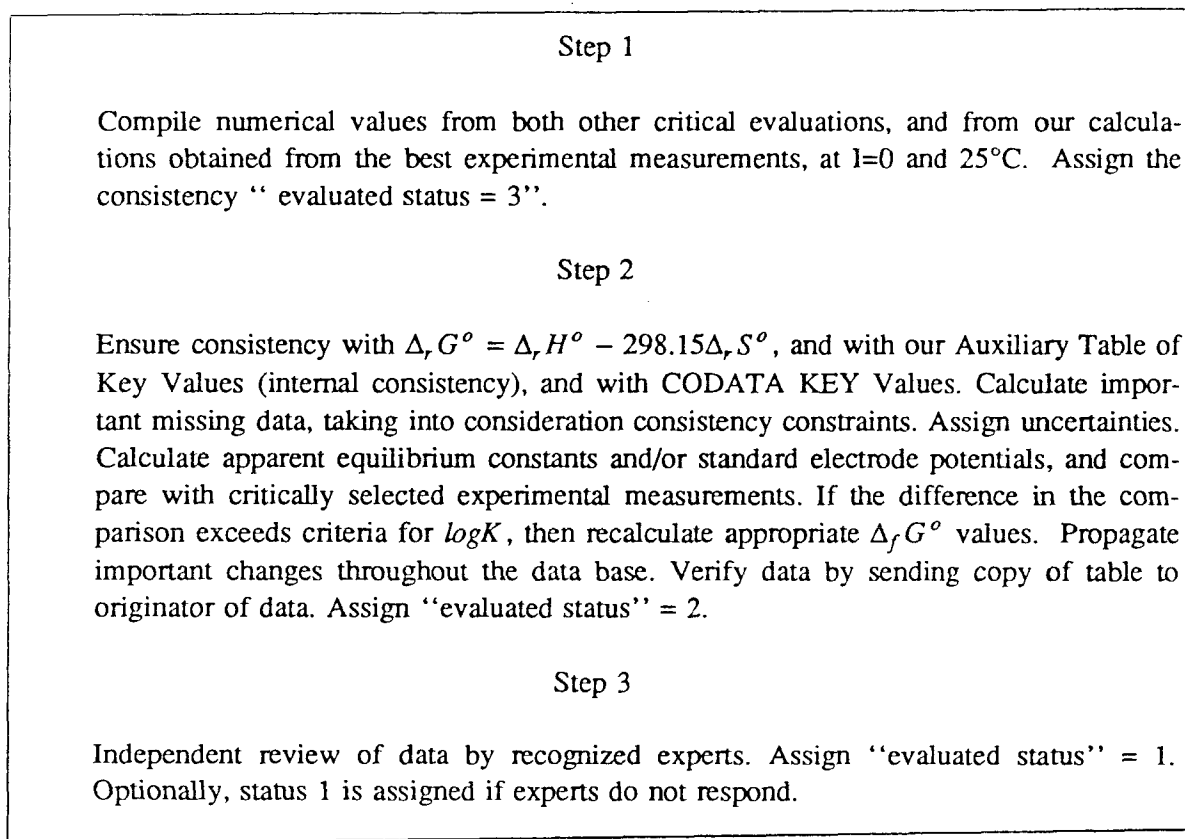


Figure 1-1. Critical evaluation procedure for selection and addition of new values of thermodynamic properties, for the ASD.

1.3 User's Guide for Telecommunication to the Aqueous Solutions Database

1.3.1 Introduction

A principal objective of this work is to provide a current, accessible data base with thermochemical property values that can be used in one or more geochemical speciation codes. A computerized data management system, the ASD, which will satisfy this goal, is under development. The format of the data base permits use of the data in a number of ways; the values of free energies in the tabulation can be used to calculate equilibrium constants for codes such as PHREEQE (4) or MINEQL (89). As discussed below, the data base may be accessed via several telecommunications networks using a modem and a terminal. Property values will be continually reevaluated and updated, so that users will have current information.

The ASD resides on the central VAX 8650 cluster at the Lawrence Berkeley Laboratory, and utilizes the DATATRIEVE data base management system, modified for this use. Several data formats are currently available for the individual user. For example, the user may request FORM1 for a specific element; FORM2.EQ, which is a listing of reactions for an element; or, a specified reaction, FORM2.SR, to obtain reaction stoichiometries, values of thermochemical constants, e.g., entropy of reaction, estimates of uncertainties, and sources of the data. See Sections 1.3.4 to 1.3.7 which follow.

It is important to note that the values of the reaction equilibrium constants in FORM2 and FORM2-SR are not always consistent with the data in the tables in FORM1. The FORM2 values are consistent with the thermodynamic property values in LBL-14996 (15), an earlier version of the ASD. In the ASD, both FORM1 and FORM2 have a "Comments" section which documents assumptions implicit in the choice of species to represent the chemistry of any element, possible alternative values, parameter values that have been recalculated in light of more recent laboratory work, sources of data, Debye-Huckel coefficients, and identifies to the user any controversial data in the system.

1.3.2 Log On and Log Off Procedures

Access to the Aqueous Solutions Database is obtained via the Federal Telecommunications System (FTS) or other telecommunication networks such as ARPANET. The exact procedure for communicating with the central LBL VAX 8650 cluster will differ from user to user. The sample procedures on the following pages illustrate communication with the LBL system via the FTS lines using an IBM/PC with DOS 2.0 and the "CROSSTALK" communications software package. It is assumed in Section 1.3.3 that the user has loaded the CROSSTALK disk in Drive A: of the IBM PC (or PC-compatible). On the following pages, computer prompts and responses are to the left of the prompt, ">", or ":"; the typical user responses are shown to the right of the prompts. A person with the VTERM communications package would use the following procedure to log on to the LBL computer cluster (csa):

A:> VTERM

(dial 8-451-4979; LBL csa will respond)

REQUEST: csa

(Hit carriage return 3 times; then answer prompts for user name and password. When the csa prompt is given, respond as shown in Section 1.3.3).

Log on Procedure

A:>XTalk (this loads CROSSTALK)

A:> NU 8-451-4979 (or execute command file 4 (LBL csa))

A:>GO

(Note: be certain modem type matches DPrefix (i.e., ATT for AT&T, ATDT for Hayes))

After the LBL csa system answers, the user is prompted as follows:

Request: CSA
(hit return 3 times)

Name:

Password:

CSA>DTR32

DTR>:Database
(follow the menu shown in Section 1.3.3 below)

Log off Procedure

DTR>exit

csa>logout

1.3.3 Menu for Telecommunication to Current Information

Menu

```
* * * * *
*           A Q U E O U S   S O L U T I O N S   D A T A B A S E
*
*   Enter  :form1, :form2, etc.  or  exit.
*
*   :FORM1   Tables of Gibbs energy of formation, enthalpy
*            of formation, entropy and heat capacity for
*            selected substances, 25 C, zero ionic strength.
*   :FORM1-SIMPLE  same as :FORM1 without typesetting (TROFF)
*   :FORM2   Tabulation of (1) enthalpy, entropy and heat
*            capacity changes, 25 C; (2) Debye-Huckel
*            coefficients, 25 C; (3) equilibrium quotients,
*            25-300 C, 0-3 ionic strength.
*   :FORM2-SR  Form2 for a specific reaction.
*   :REVIEW_COMM Enter review comments on database
*   :ADDREACT  Add a reaction to the reaction database
*   :COMPLOGK  Compute logK for new reactions in database
*
*   For more information call (415) 486-6865 or FTS 451-6865
* * * * *
```

The user accesses the data base and obtains hard copies on a user printer if desired. Hard copy can also be obtained from LBL.

Additional control functions (^ = control key):

- ^S = pause screen print
- ^Q = resume screen print
- ^C = cancel current printout: return to menu
- ^Z = exit DATATRIEVE: return to csa
- ^Y = interrupt: return to csa

Both upper case and lower case responses can be used, as shown in the Menu. Other information can be obtained which may not be listed in the Menu, for example :form2-eq shown on page 14.

1.3.4 Sample Session 1: Procedure for obtaining table of thermochemical values of $\Delta_f G^\circ$, $\Delta_f H^\circ$, S° , and C_p° for an element (:FORM1):

DTR> :form1

Enter Element Name: Strontium
(first page only is shown)

Aqueous Solutions Database	Lawrence Berkeley Laboratory	STRONTIUM Evaluated Status 1 October 1987
----------------------------------	------------------------------	--

PROPERTIES OF ELEMENTAL STRONTIUM:

Atomic Number: 38
Formula Mass: 87.62
Electronic Configuration: $5s^2$
Electronegativity: 1.0
Hydration Number:
Ionic Radius: 1.27 anstrom for Sr^{++}
Selected Average for Soils: 200 mg/kg
Concentration in Natural Waters: 5-15 mg/L in brines; 0.05 mg/L (Tuff)

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
α -Sr(s)	0.000	0.000	55.70	26.40	0012
			0.21		
SrO(s)	-559.960	-590.600	55.44	45.02	1112
	1.0	0.9	0.50		
Sr(OH) ₂ (s)	-882.175	-968.889	97.07	74.90	5555
	9.2	9.2	8.40		
SrF ₂ (s)	-1164.800	-1216.300	82.13	70.00	2222
α -SrCl ₂ (s)	-785.000	-833.850	114.85	75.60	1112
	0.8	1.0	0.42		
SrCl ₂ (aq)	-826.321	-885.060	81.70	-286.00	9119
	1.0	1.0	0.50		
SrCl ₂ ·2H ₂ O(s)	-1281.800	-1438.000	218.00	160.20	2222
	1.0				
SrCl ₂ ·6H ₂ O(s)	-2240.920	-2623.800	390.80		2220
	1.0				
SrSO ₄ (s), celestite	-1340.970	-1453.170	118.00		4440
	4.0	4.2	4.20		
SrSO ₄ (aq)	-1320.300	-1449.970	60.90	-313.00	9999
	5.0				
SrCO ₃ (s), strontianite	-1144.730	-1225.770	97.20	81.42	1113
	1.0	1.0	1.70		

1.3.5 Sample Session 2: Procedure for obtaining a list of reactions and index numbers for a given element:

DTR> :form2-eq

Enter element: Plutonium

RC	REACTION
PU1	$\text{PuO2}^{2+} + \text{H2O} = \text{PuO2OH}^+ + \text{H}^+$
PU10	$\text{PuO2}^{2+} + \text{F}^- = \text{PuO2F}^+$
PU11	$\text{PuO2}^{2+} + 2\text{F}^- = \text{PuO2F2}(\text{aq})$
PU12	$\text{PuO2}^{2+} + 3\text{F}^- = \text{PuO2F3}^-$
PU13	$\text{PuO2}^{2+} + 4\text{F}^- = \text{PuO2F4}^{--}$
PU14	$\text{PuO2}^{2+} + \text{Cl}^- = \text{PuO2Cl}^+$
PU15	$\text{Pu}^{4+} + \text{Cl}^- = \text{PuCl}^{3+}$
PU16	$\text{PuO2}^{2+} + 2\text{CO3}^{--} = \text{PuO2}(\text{CO3})2^{--}$
PU17	$\text{Pu}^{4+} + \text{CO3}^{--} = \text{PuCO3}^{2+}$
PU18	$\text{PuO2}^{2+} + \text{SO4}^{--} = \text{PuO2SO4}(\text{aq})$
PU19	$\text{Pu}^{4+} + \text{SO4}^{--} = \text{PuSO4}^{2+}$
PU2	$2\text{PuO2}^{2+} + 2\text{H2O} = (\text{PuO2})2(\text{OH})2^{2+} + 2\text{H}^+$
PU20	$\text{Pu}^{3+} + \text{SO4}^{--} = \text{PuSO4}^+$
PU21	$\text{PuF3}(\text{s}) = \text{Pu}^{3+} + 3\text{F}^-$
PU22	$\text{PuF4}(\text{s}) = \text{Pu}^{4+} + 4\text{F}^-$
PU23	$4\text{PuO2}(\text{s}) + 12\text{H}^+ = 4\text{Pu}^{3+} + 6\text{H2O} + \text{O2}(\text{g})$
PU24	$4\text{PuO2}(\text{s}) + 4\text{H}^+ + \text{O2}(\text{g}) = 4\text{PuO2}^+ + 2\text{H2O}$
PU25	$2\text{PuO2}(\text{s}) + 4\text{H}^+ + \text{O2}(\text{g}) = 2\text{PuO2}^{2+} + 2\text{H2O}$
PU26	$\text{Pu}(\text{OH})3(\text{s}) + 3\text{H}^+ = \text{Pu}^{3+} + 3\text{H2O}$
PU27	$\text{Pu}(\text{OH})4(\text{s}) + 4\text{H}^+ = \text{Pu}^{4+} + 4\text{H2O}$
PU28	$\text{Pu2O3}(\text{s}) + 6\text{H}^+ = 2\text{Pu}^{3+} + 3\text{H2O}$
PU29	$\text{PuO2}(\text{s}) + 4\text{H}^+ = \text{Pu}^{4+} + 2\text{H2O}$
PU3	$3\text{PuO2}^{2+} + 5\text{H2O} = (\text{PuO2})3(\text{OH})5^+ + 5\text{H}^+$
PU30	$\text{PuO2}(\text{OH})(\text{s}) + \text{H}^+ = \text{PuO2}^+ + \text{H2O}$
PU31	$\text{PuO2}(\text{OH})2(\text{s}) + 2\text{H}^+ = \text{PuO2}^{2+} + 2\text{H2O}$
PU32	$4\text{PuO2}^{2+} + 4\text{H}^+ = 4\text{Pu}^{3+} + 2\text{H2O} + 3\text{O2}(\text{g})$
PU33	$2\text{PuO2}^{2+} + 4\text{H}^+ = 2\text{Pu}^{3+} + 2\text{H2O} + \text{O2}(\text{g})$
PU34	$4\text{PuO2}^{2+} + 2\text{H2O} = 4\text{PuO2}^+ + 4\text{H}^+ + \text{O2}(\text{g})$
PU35	$4\text{PuO2}(\text{s}) + 6\text{H2O} = 4\text{Pu}(\text{OH})3(\text{s}) + \text{O2}(\text{g})$
PU36	$\text{PuO2}(\text{s}) + 2\text{H2O} = \text{Pu}(\text{OH})4(\text{s})$
PU37	$4\text{PuO2}(\text{s}) = 2\text{Pu2O3}(\text{s}) + \text{O2}(\text{g})$
PU38	$4\text{PuO2}(\text{s}) + \text{O2}(\text{g}) + 2\text{H2O} = 4\text{PuO2}(\text{OH})(\text{s})$
PU39	$2\text{PuO2}(\text{s}) + \text{O2}(\text{g}) + 2\text{H2O} = 2\text{PuO2}(\text{OH})2(\text{s})$
PU4	$\text{Pu}^{4+} + \text{H2O} = \text{PuOH}^{3+} + \text{H}^+$
PU5	$\text{Pu}^{4+} + 2\text{H2O} = \text{Pu}(\text{OH})2^{2+} + 2\text{H}^+$
PU50	$\text{Pu}^{4+} + \text{F}^- = \text{PuF}^{3+}$
PU51	$\text{Pu}^{4+} + 2\text{F}^- = \text{PuF2}^{2+}$
PU6	$\text{Pu}^{4+} + 3\text{H2O} = \text{Pu}(\text{OH})3^+ + 3\text{H}^+$
PU7	$\text{Pu}^{4+} + 4\text{H2O} = \text{Pu}(\text{OH})4(\text{aq}) + 4\text{H}^+$
PU8	$\text{Pu}^{4+} + 5\text{H2O} = \text{Pu}(\text{OH})5^- + 5\text{H}^+$
PU9	$\text{Pu}^{3+} + \text{H2O} = \text{PuOH}^{2+} + \text{H}^+$

1.3.6 Sample Session 3: Procedure for obtaining information on a specific reaction:

DTR> :form2-sr

Enter reaction code (rc): O3

(Note that $\hat{\Delta} = \Delta$, $\hat{r}H_o = \Delta_r H^\circ$; $A\gamma^z2 = A_\gamma \Delta z^2$)

```
*****
* Aqueous      *
* Solutions    *
* Database     *
*****
```

```
OXYGEN
WATER
rc = O3
August 1986
```

EQUILIBRIUM REACTION: H2O = OH- + H+

THERMOCHEMICAL PROPERTIES:

```
 $\hat{r}H_o$ , J mol-1      : 55815
 $\hat{S}_o$ , J mol-1 K-1   : - 80.67
 $\hat{C}_{p_o}$ , J mol-1 K-1 : - 231.40
 $A\gamma^z2$ , (kg mol-1)1/2 : 1.02
b, kg mol-1        :
log Ko              : -13.990
```

EQUILIBRIUM QUOTIENTS: I=ionic strength, mol kg-1

I/T	log Q							
	25 C	50 C	75 C	100 C	150 C	200 C	250 C	300 C
0.00	-13.99	-13.28	-12.71	-12.27	-11.64	-11.29	-11.19	-11.41
0.01	-13.91							
0.10	-13.78	-13.05	-12.47	-12.00	-11.33	-10.93	-10.72	-10.65
0.20								
0.50	-13.72	-12.97	-12.38	-11.90	-11.19	-10.73	-10.43	-10.19
1.00	-13.75	-13.00	-12.40	-11.92	-11.18	-10.68	-10.32	- 9.98
2.00								
3.00	-14.01	-13.23	-12.60	-12.07	-11.26	-10.66	-10.16	- 9.57

REFERENCES: Marshall;Franck;J.Phys.Chem.Ref.Data 1981,v.10,295.

COMMENTS: Values from Sweeton;Mesmer;Baes;J.Solution
Chem.1974,v.3,191,except for I=0 from Reference.

1.3.7 Sample Session 4: Procedure for obtaining values of $\Delta_r G^\circ \pm \sigma$, $\Delta_r H^\circ \pm \sigma$ for specific species; and $\log K^\circ \pm \sigma$ for specified reactions. Both Gibbs energy and enthalpy of reaction are in units of kJ/mol.

The following is a sample session:

```
DTR> :addreact
Determining next reaction number. . .
Ready to input reaction number 0056
Enter R for reactant or P for product: R
Enter substance name: NpO2+
Enter coefficient: 1
Enter Y for more terms for this reaction: Y
Enter R for reactant or P for product: R
Enter substance name: CO3--
Enter coefficient: 1
Enter Y for more terms for this reaction: Y
Enter R for reactant or P for product: P
Enter substance name: NpO2CO3-
Enter coefficient: 1
Enter Y for more terms for this reaction: N
Enter Y for additional reactions: N
Combining input with thermodynamic data . . .
```

```
DTR> ready rsandps
DTR> find rsandps with react_num=56
[3 records found]
DTR> print all current
```

REACT NUM	RP	GEO NAME	COEFF
56	R	NpO2+	1.00
56	R	CO3--	1.00
56	P	NpO2CO3-	1.00

```
DTR> ready rpgtemp
DTR> print all rpgtemp
```

REACT NUM	RP	GEO NAME	COEFF	FG	UNC FG	FH	UNC FH
56	R	NpO2+	1.00	-915.000	5.4	-978.200	4.6
56	R	CO3--	1.00	-527.730	0.3	-675.150	0.3
56	P	NpO2CO3-	1.00	-1470.020	1.0	-1599.900	1.0

```
DTR> :complogk
Enter reaction number: 56
DTR> ready logks
DTR> find all logks with react_num=56
[1 record found]
DTR> print all current
```

REACT NUM	LOGK	UNC LOGK
56	4.781	0.9635

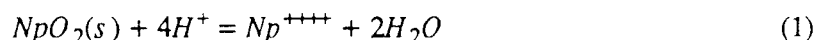
```
DTR> ready delrhs
DTR> find all delrhs with react_num=56
[1 record found]
DTR> print all current
```

REACT NUM	DELRH	UNC DELRH
56	53.450	

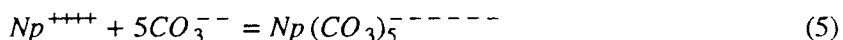
```
DTR> exit
```

2.0 ESTIMATION OF THERMODYNAMIC PROPERTY VALUES

When an oxide, e.g. $NpO_2(s)$, dissolves in acidic solution, the stoichiometric equation for the reaction is



Equation 1 is a simplified expression of a more complicated geochemical process and often may not reflect the experimentally measured solubility of the oxide. This is due to homogeneous chemical reactions coupled to the heterogeneous dissolution process which result in additional products. These coupled reactions depend on the properties of the water, for example, pH, pe and temperature. In natural waters, anions such as Cl^- , SO_4^{--} and HCO_3^- generally are present, and the pH might be sufficiently high to cause hydrolysis of Np^{++++} . Under these conditions, coupled chemical reactions will include the following equilibria



The result of equations 2 to 5, and any other homogeneous and heterogeneous reactions coupled to the dissolution of the oxide, will be an increased concentration of total dissolved Np in the water. The enhanced concentration must be calculated in assessing the performance of a HLW nuclear waste repository. Equations 2 to 4 are examples of ionic association (9,10). Techniques to estimate the values of the equilibrium constants and the thermodynamic properties of these ion pairs are described in Section 2.2. Finally, equation 5 describes the formation of an aqueous complex; a discussion of the properties of such higher complexes is found in Section 2.3.

2.1 Thermodynamics of Aqueous Hydrated Radionuclide Ions

The aqueous radionuclides described in this report are hydrated ions with positive charges ranging from +1 to +4. Their valences cover the range +3 to +6, with the +5 and +6 ions containing two bound oxygens. The coordination number is generally six, so that the aqueous

substances are assumed to have six waters of hydration bound to the central metal, or oxygenated metal.

2.1.1 Relation between $\Delta_f G^\circ$ and $\Delta_f H^\circ$

Values of $\Delta_f G^\circ$ and $\Delta_f H^\circ$ for the actinide ions were obtained from the IAEA publications (41,56,62) and from Morss (63). See Table 2-1. The values of $\Delta_f G^\circ$ and $\Delta_f H^\circ$ are correlated in a linear manner (36); see Figure 2-1. Two parallel lines are obtained, the first for the four trivalent ions; the second includes the +4, +5 and +6 valences. Lebedev explains the linear correlations as due to a constancy in the difference between the entropy of the aqueous ion and that of the actinide metal (36). The structure of the +3 ions differs from those of the +4, +5 and +6 species, which accounts for a separate correlation for the trivalent ions (36).

The Gibbs energy of formation and enthalpy of formation at 25°C (298.15 K) are mathematically related by the equation

$$\Delta_f G^\circ [M^{n+},aq] = \Delta_f H^\circ [M^{n+},aq] + 298.15(S^\circ [M,s] - (S^\circ [M^{n+},aq] + nS^\circ [e,aq])) \quad (6)$$

calculated for the electrochemical reaction $M^{n+} + ne = M(s)$. Equation 6 is a constraint on the internal consistency of the values for the thermodynamic properties in this data base; the equation is applied to all metals.

2.1.2 Entropy

Absolute values of molar entropy, S° , are compiled rather than entropy of formation. Entropy is not an independent property; it is linked to the Gibbs energy and enthalpy for any reaction by $\Delta_r G = \Delta_r H - T \Delta_r S$.

2.1.3 Heat Capacity

The close relationship between entropy and heat capacity is pointed out by Pitzer and Brewer (80,p.135):

$$S_T = \int_0^T C_p d(\ln T)$$

Values for the heat capacity for Np, Pu and U aqueous ions in this work were often compiled from those calculated by Lemire and Tremaine, and by Lemire, who used a modified Criss - Cobble equation (33,54). We obtained the magnitude of the heat

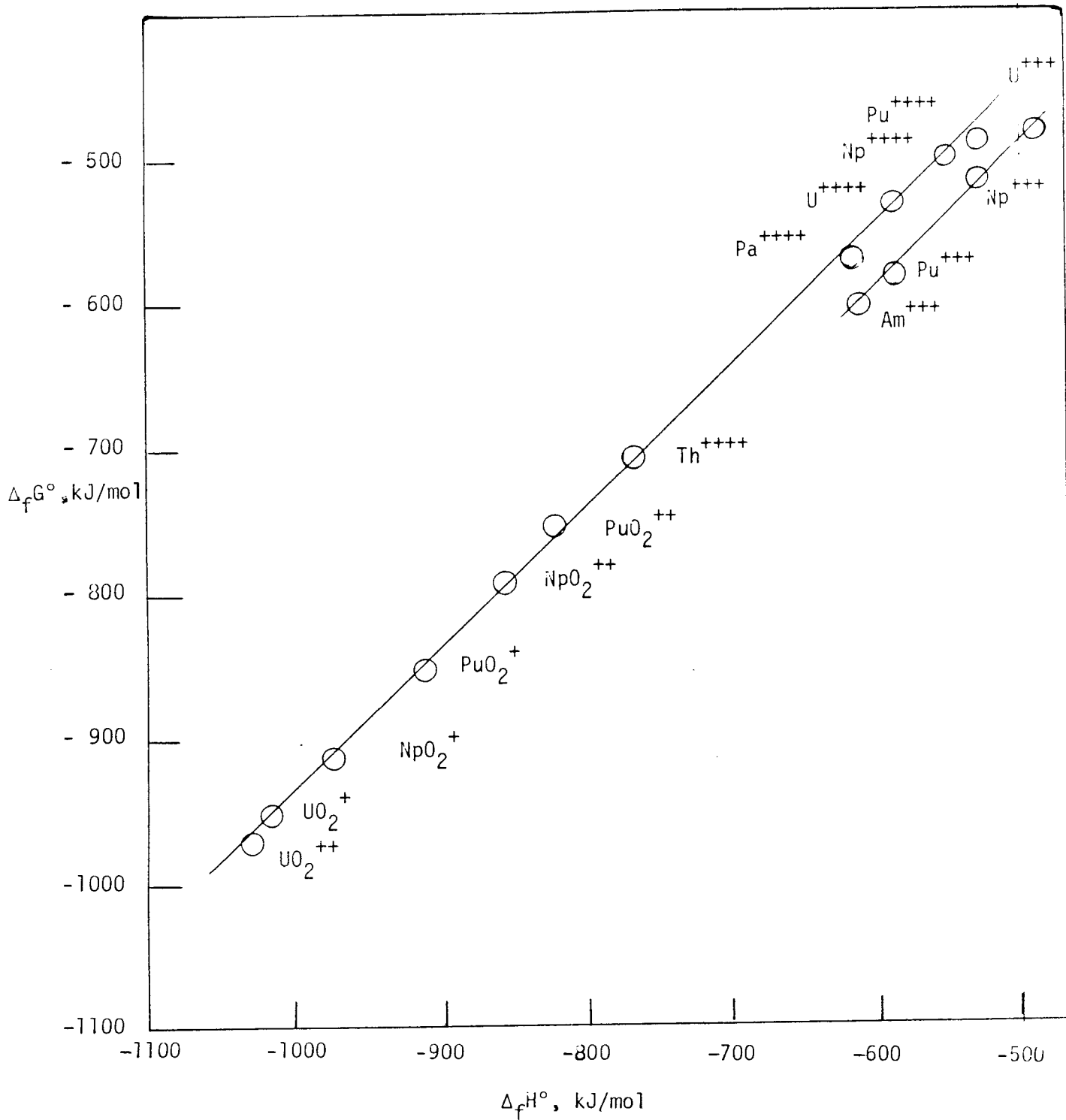


Figure 2-1. Plot of $\Delta_f G^\circ$ versus $\Delta_f H^\circ$ for selected aqueous actinide ions relevant to HLW disposal. UO_2^+ and PuO_2^+ disproportionate in aqueous solution. Data for the plot are given in Table 2-1; and in Appendix II and Reference 41, 63, 74, 76.

Table 2-1. Values of Gibbs energy of formation and enthalpy of formation for selected actinide aqueous cations, used in Figure 2-1. Data are from Appendix II.

Cation	$\Delta_f G^\circ, \text{kJ/mol}$	$\Delta_f H^\circ, \text{kJ/mol}$
Am ⁺⁺⁺	-599.1	-616.7
Np ⁺⁺⁺	-517.1	-527.2
Pu ⁺⁺⁺	-578.6	-592.0
U ⁺⁺⁺	-480.7	-489.1
Np ⁺⁺⁺⁺	-502.9	-556.1
Pa ⁺⁺⁺⁺	-565.0	-619.7
Pu ⁺⁺⁺⁺	-481.6	-536.4
Th ⁺⁺⁺⁺	-704.6	-769.0
U ⁺⁺⁺⁺	-530.9	-591.2
NpO ₂ ⁺	-915.0	-978.2
PuO ₂ ⁺	-849.8	-914.6
UO ₂ ⁺	-968.6	-1032.6
NpO ₂ ⁺⁺	-795.8	-860.6
PuO ₂ ⁺⁺	-756.9	-822.2
UO ₂ ⁺⁺	-952.7	-1019.2

capacity for other aqueous ions from research publications, and from the following correlation which we developed by linear regression using data from Brewer (82), Hovey et al. (45,83,84) and Spitzer et al. (32) shown in Table 2-2. The correlation is similar in form to that given by Naumov et al. (57). However, the values of our coefficients are different from those of Naumov et al.

$$Cp^{\circ} = 231.9 - 152.1z - (2/3)S^{\circ} \quad (7)$$

where z is the ionic charge. The correlation coefficient is $r^2 = 0.958$; and is considered satisfactory for calculating missing values of the heat capacity of positively charged aqueous ions. We have also applied eq 7 to the estimation of heat capacities for ion pairs and higher complexes which are positively charged.

Figure 2-2 is a plot of the residuals calculated as the difference between ionic heat capacities calculated by eq 7, and those shown in Table 2-2 which were used to develop our correlation. According to Figure 2-2, the uncertainty in values of Cp° calculated with eq 7 is about 30 J/mol/K. Equation 7 reproduces Cp° values for the aqueous ions of Na, K, Rb, Cs, Mg, Ca, Sr, Ba in Tanger and Helgeson (94) to about the same uncertainty, when their values of the molar entropies are used in eq 7.

Besides uncomplexed (aqueous) cations, we have also applied eq 7 to the estimation of heat capacities for ion pairs and higher complexes which are positively charged.

Our methods for calculating heat capacities of negatively charged ions and uncharged aqueous species are discussed in section 2.2.2.3.

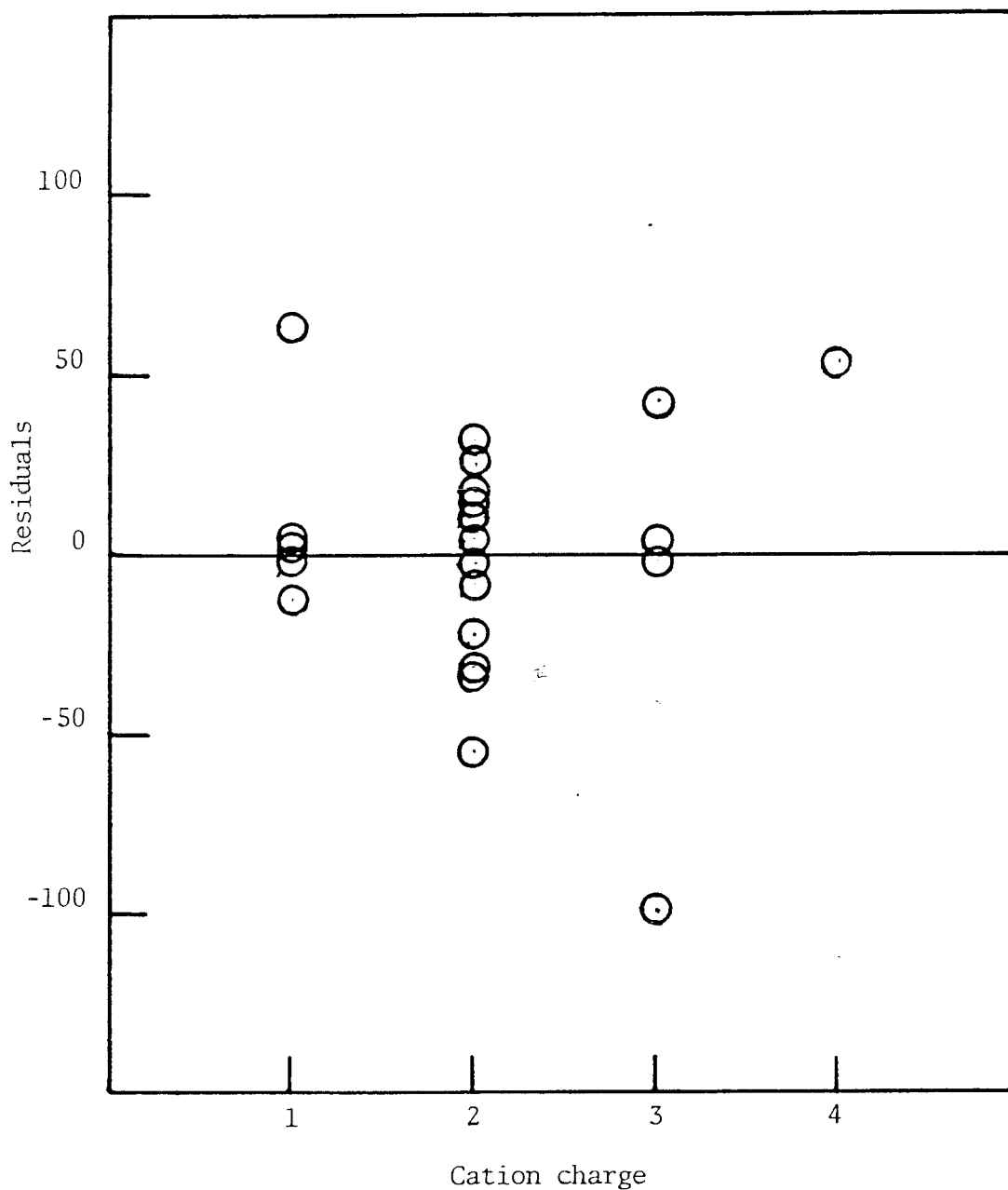


Figure 2-2. Plot of residuals based on linear regression of values of $Cp^\circ [M^{n+}]$ in Table 2-2. The figure gives an indication of the uncertainty associated with using eq 7 to estimate values of the heat capacity of cations, based on a correlation with the entropies of the cations. Estimated uncertainty is $\pm 30 \text{ J (mol-K)}^{-1}$.

Table 2-2. Values of S° and C_p° used in linear regression to develop correlation, eq 7, between entropy and heat capacity for positively charged aqueous ions. Heat capacity values from References 32, 33, 45, 82, 83.

Cation	Residuals, J/mol/K	S° J/mol/K	C_p° J/mol/K
H ⁺	-	0	0
Li ⁺	-11.6	11.30	60.7
Na ⁺	1.5	58.41	42.4
K ⁺	0.5	101.04	13.0
NH ₄ ⁺	63.6	111.17	69.0
Mg ⁺⁺	-35.8	-138.1	-16
Ca ⁺⁺	4.6	-56.4	-30
Sr ⁺⁺	16.4	-31.5	-34.8
Ba ⁺⁺	32.2	8.4	-45.6
Co ⁺⁺	-32.1	-113.0	-29
Ni ⁺⁺	-54.7	-128.9	-41
Fe ⁺⁺	-3.1	-107	-4.2
Zn ⁺⁺	-21.8	-109.6	-21
Mn ⁺⁺	16.6	-67.76	-11
Cu ⁺⁺	-9.5	-97.1	-17
Al ⁺⁺⁺	-100	-308	-119
Cr ⁺⁺⁺	-0.5	-316.3	-14
La ⁺⁺⁺	-3.9	-209.2	-81
U ⁺⁺⁺	43.7	-174.9	-64
U ⁺⁺⁺⁺	52.4	-414	-48
UO ₂ ⁺⁺	11.7	-98.3	5
PuO ₂ ⁺⁺	24.6	-88	11
NpO ₂ ⁺	-1.8	-21	92

2.2 Thermodynamics of Complex Ions

2.2.1 Effect of Ionic Strength on $\log K^o$

Experimental data are obtained in media of varying ionic strength, and often differing supporting electrolytes. The formation constants of ion pairs are typically calculated at $I=0$ from laboratory measurements using both an extended Debye-Huckel equation for the range $0 < I < 3$ (5,13,15), and the Davies equation for $I < 0.1$ (9,13,15). The extended Debye-Huckel equation is written as eq 8:

$$\log K(I) = \log K^o + \frac{A_\gamma \Delta z^2 I^{1/2}}{1 + I^{1/2}} + bI \quad (8)$$

- $K(I)$ = apparent equilibrium constant at ionic strength I , $0 < I < 3$
 K^o = intrinsic equilibrium constant
 A_γ = 0.511 at 25°C; 0.596 at 100°C
 Δz^2 = $\Sigma(z_{products})^2 - \Sigma(z_{reactants})^2$
 b = a constant, $(m/kg)^{-1}$ (see Ref. 5)

The effect of changing ionic strength on $\log K(I)$ for formation of $(UO_2)_2(OH)_2^{++}$ and $NpO_2CO_3^-$ is shown in Figures 2-3 and 2-4.

The form of the Davies equation used here is

$$\log K(I) = \log K^o + A_\gamma \Delta z^2 \left[\frac{I^{1/2}}{1 + I^{1/2}} - 0.3I \right] \quad (9)$$

The Davies equation is widely used to calculate single ion activity coefficients for $0 < I < 0.2$; however, the error increases at ionic strengths exceeding about 0.1 from a few tenths of a percent to about 2 - 5% at $I = 0.2$. The Debye-Huckel slope, $A_\gamma = 0.511$, is used more often than 0.5 of the original equation in eq 9 and A_γ is used in this work.

We commonly use eq 8 in the form of eq 10 to calculate $\log K^o$, because a straight line is predicted thereby facilitating extrapolation to $I=0$ (13,15,69)

$$\log K(I) - \frac{A_\gamma \Delta z^2 I^{1/2}}{1 + I^{1/2}} = \log K^o + bI \quad (10)$$

At the intercept $I = 0$, $\log K(I)$ is equal to $\log K^o$, and the slope equals b . See Figures 2-3 and 2-4.

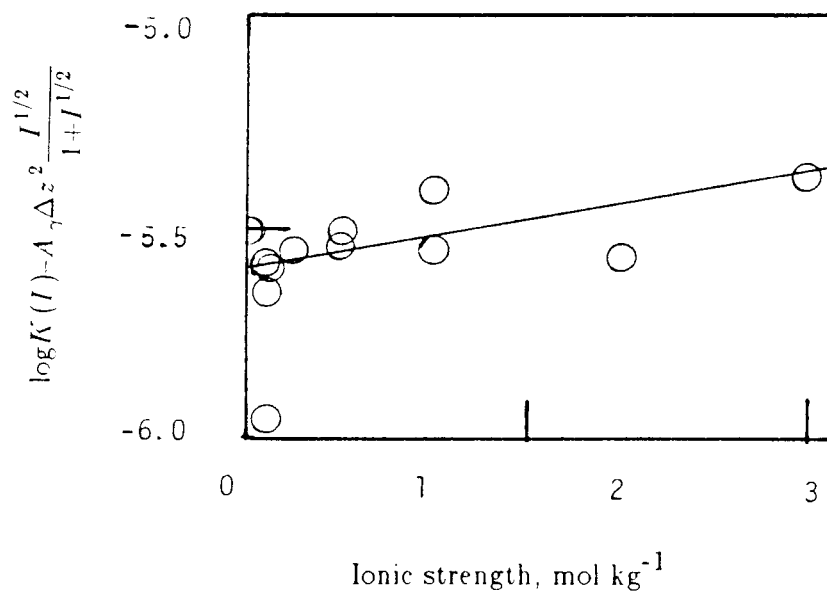


Figure 2-3. Variation in $\log K(I)$ function versus I , for the reaction $2\text{UO}_2^{++} + 2\text{H}_2\text{O} = (\text{UO}_2)_2(\text{OH})_2^{++} + 2\text{H}^+$. Experimental points are taken from Table 4-7, except for NaCl media; uranyl ion forms a complex with chloride ion. Extrapolation to $I = 0$ yields $\log K^0 = -5.66$, $b = 0.101$, $r^2 = 0.264$.

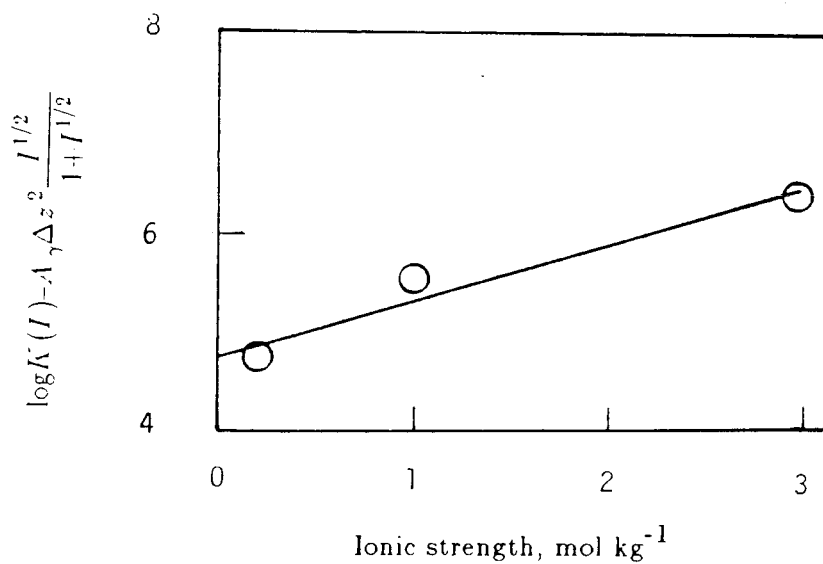


Figure 2-4. Effect of ionic strength on $\log K(I)$ for reaction $\text{NpO}_2^+ + \text{CO}_3^{--} = \text{NpO}_2\text{CO}_3^-$. At $I = 0$, $\log K^0 = 4.78$, $b = 0.55$, $r^2 = 0.980$. Data are taken from Table 4-11.

2.2.2 Calculation of Thermodynamic Property Values

In this section, techniques used to calculate selected thermodynamic properties of ion pairs from values of $\log K^\circ$ and correlations will be described.

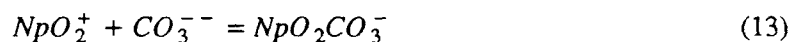
2.2.2.1 Free Energy of Formation

Values of $\Delta_f G^\circ$ are primarily calculated from measurements of equilibrium constants from the relationships

$$\Delta_r G^\circ = -RT \ln K^\circ \quad (11)$$

$$\Delta_r G^\circ = \sum \Delta_f G_p^\circ - \sum \Delta_f G_q^\circ \quad (12)$$

where $\Delta_f G_{p,q}^\circ$ are Gibbs energy of formation of the products (p) of a chemical process, and the reactants (q). Often $\ln K^\circ$ ($2.303 \log K^\circ$) is calculated at zero ionic strength from one or more measurements obtained at various ionic strengths using the Davies or Debye-Huckel equation. The desired $\Delta_f G^\circ$ is that of either a product or a reactant in the chemical process. For example, in the formation of the $NpO_2CO_3^-$ ion pair according to the reaction



$\log K(I=0.2) = 4.13 \pm 0.03$ (30). The intrinsic formation constant, $\log K^\circ$ is then calculated from the Davies equation, with $A_\gamma \Delta z^2 = -2.04$,

$$4.13 = \log K^\circ - 2.04 \left[\frac{0.447}{1.447} - 0.06 \right] \quad (9A)$$

so that $\log K^\circ = 4.64 \pm 0.03$, compared to $\log K^\circ = 4.78$ from Fig. 2-4. Using eq 11 and $\log K^\circ = 4.78$, we calculate $\Delta_r G^\circ = -27.289 \pm 0.17$ kJ/mol. From our tables, $\Delta_f G^\circ [NpO_2^+] = -915.0$ kJ/mol and $\Delta_f G^\circ [CO_3^{--}] = -527.73$ kJ/mol. Then, the numerical value of $\Delta_f G^\circ [NpO_2CO_3^-]$ calculated from eq 12 is:

$$-27.289 = \Delta_f G^\circ [NpO_2CO_3^-] - [-915.0 - 527.73]$$

so that $\Delta_f G^\circ [NpO_2CO_3^-] = -1470.02 \pm 5.4$ kJ/mol.

2.2.2.2 Enthalpy and Entropy of Reaction

Values of $\Delta_r H^\circ$ are obtained from calorimetric measurements, as well as from the slope of plots of $\log K(T)$ versus T^{-1} using the van't Hoff equation (80)

$$\frac{d \ln K}{dT} = \frac{\Delta_r H^\circ}{RT^2} \quad (14)$$

Data from calorimetric heats of solution or formation are preferred because the heat of reaction is directly measured. However, many values of $\Delta_r H^\circ$ are calculated from the van't Hoff equation. A larger uncertainty results from this approach due to a propagation of the uncertainty in the $\log K^\circ$ values at 25°C, to higher temperatures, added to the uncertainty associated with the higher temperature measurement.

Figure 2-5 is a plot of $\Delta_f G^\circ$ versus $\Delta_f H^\circ$ for selected actinide ion pairs. The data were obtained from Appendix II, and are listed in Table 2-3. The regression equation obtained from these data is used to estimate values of $\Delta_f H^\circ$ for this data base when experimental or other data are not available. For internal consistency, the entropy of the ion pair in the reaction $M+X=MX$ (charges omitted) is calculated from

$$S^\circ [MX] = (\Delta_r H^\circ - \Delta_r G^\circ)/(298.15) + (S^\circ [M^{n+},aq] + S^\circ [X^{m-},aq]) \quad (15)$$

2.2.2.3 Heat Capacity of Anions and Uncharged Aqueous Species

Previously, we have shown that heat capacities could be correlated with entropy for simple aqueous ions. Unfortunately, there is no general method of estimating the heat capacity of ion pairs. Lemire has used the Criss - Cobble method, but notes this approach is formally valid only for simple cations, anions, metal oxyanions and acid oxyanions (33, p.23). In addition, there is no good general procedure for calculating the heat capacity of uncharged aqueous ions (33). In one approach to this problem, Baes and Mesmer (34) approximate the heat capacity of a mononuclear hydroxide complex, $M(OH)_y^{(z-y)+}$ "as that of a monatomic cation of the same charge as the complex, and the same size as the hydrolyzing cation M^{z+} ". The rationale here is that the hydrated cation and its first hydrolysis product differ only by the protons lost in the reaction (34).

Table 2-3. Thermodynamic data for selected actinide ion pairs. See Appendix II and the references cited therein for the sources of these data.

Ion Pair	$\Delta_f G^\circ$ kJ/mol	$\Delta_f H^\circ$ kJ/mol	S° J/mol/K
NpO_2OH^+	-1004.0	-1102.99	24
$\text{NpO}_2\text{OH}(\text{aq})$	-1101.0	-1220.1	25
NpOH^{+++}	-734.0	-790.54	-167
NpOH^{++}	-714.3	-762.9	-75
NpO_2F^+	-1103.8	-1194.4	-14
$\text{NpO}_2\text{F}(\text{aq})$	-1207.9	-1284.7	100
NpO_2Cl^+	-926.0	-1015.54	0
$\text{NpO}_2\text{Cl}(\text{aq})$	-1044.0	-1129.89	80
$\text{NpO}_2\text{SO}_4^-$	-1656.1	-1856.4	91.9
NpF^{+++}	-834.3	-894.8	-247
NpCl^{+++}	-636.0	-703.47	-260
$\text{NpO}_2\text{SO}_4(\text{aq})$	-1558.9	-1753.5	42.8
NpSO_4^{++}	-1279.0	-1444.79	-195
$\text{NpO}_2\text{CO}_3^-$	-1470.0	-1599.9	200
UO_2Cl^+	-1094.0	-1186.5	-6
UO_2OH^+	-1156.26	-1258.2	16
PuCl^{+++}	-618.0	-686.3	-257
UOH^{+++}	-764.3	-828.0	-192
$\text{UO}_2\text{SO}_4(\text{aq})$	-1715.6	-1909.2	47.5
$\text{UO}_2\text{CO}_3(\text{aq})$	-1549.7	-1697.0	75.1
UO_2F^+	-1264.0	-1357.3	-19
UF^{+++}	-862.0	-907.01	-19
$\text{UO}_2\text{H}_2\text{PO}_4^+$	-2100.0	-2311.7	63
UHPO_4^{++}	-1689.0	-1837.2	-63
PuOH^{+++}	-715.9	-774.0	-167
PuO_2F^+	-1071.0	-1162.8	-10
PuOH^{++}	-770.3	-824.6	-88
UCI^{+++}	-677.0	-751.0	-283

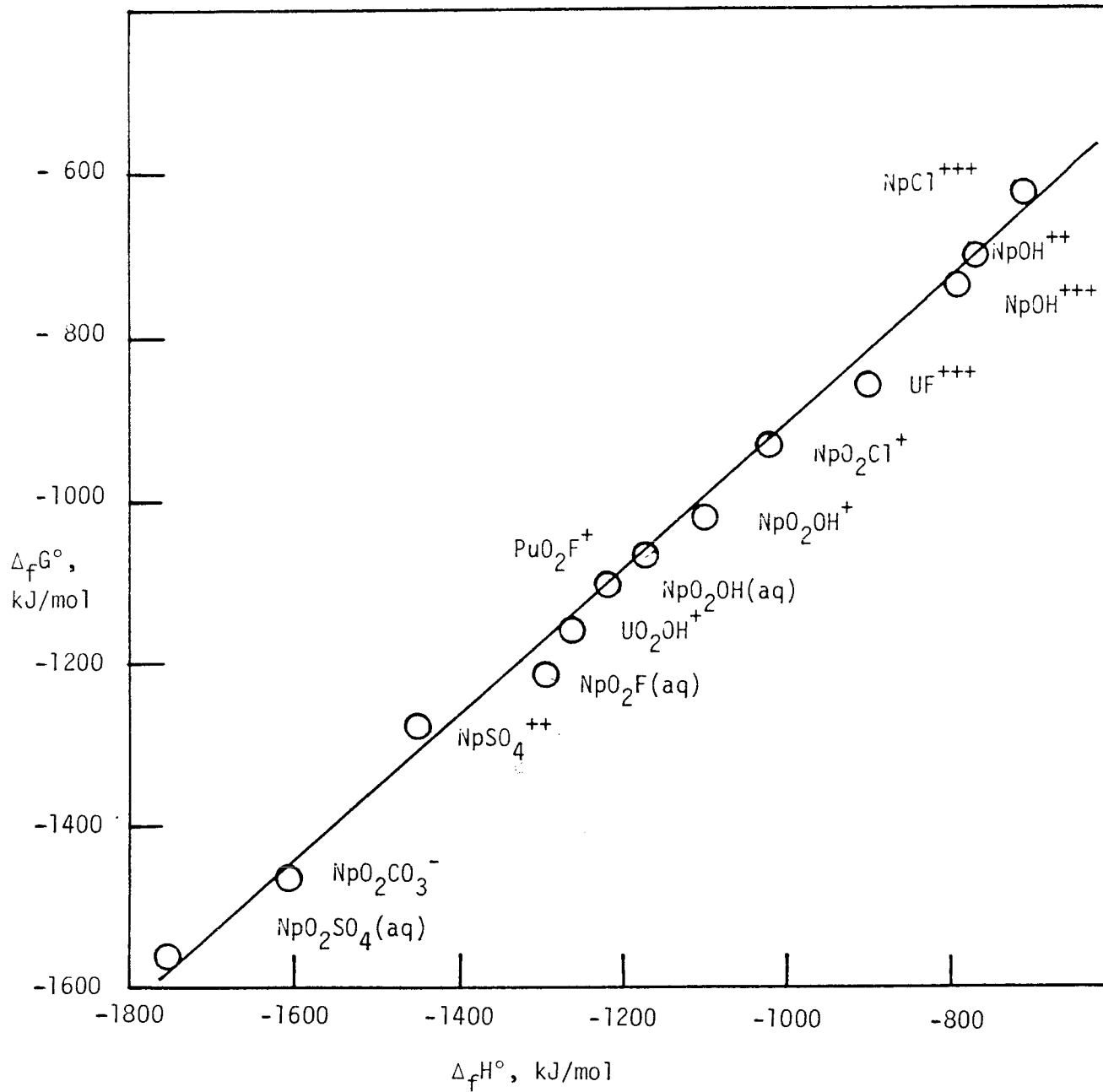


Figure 2-5. Plot of $\Delta_f G^\circ$ versus $\Delta_f H^\circ$ for selected actinide ion pairs. Data for the plot are given in Table 2-3.

An advantage of the Baes and Mesmer approach is that the Cp° of uncharged aqueous substances can be calculated, however it is not obvious that their method of estimating Cp° can be applied in general to all ion pairs. Also, the assumption of $\Delta_r Cp^\circ = 0$ for "reactions that produce no change in the number or in the magnitude of the ion charges" cannot be correct. Cobble et al. note that a value of $\Delta_r Cp^\circ = 0$ is highly unusual over an extended temperature range (21,p.4-11). In this work, we do not assume that $\Delta_r Cp^\circ = 0$.

In this data base eq 7 was used to estimate Cp° of positively charged ions when data were missing. Table 2-4 compares our calculated values of selected Cp° with those of Lemire (33), and Lemire and Tremaine (54). The comparison is quite good except for the chlorocomplexes for which our values are more negative.

For uncharged aqueous species, we assume that the heat capacity is the algebraic sum of the values of the partial molar heat capacity of the cation and anion, multiplied by the appropriate stoichiometric number. The correlation is

$$Cp^\circ = \Sigma Cp_{ca}^\circ \quad (7A)$$

where ΣCp_{ca}° is the algebraic sum of the heat capacity of the cation and anion, multiplied by the stoichiometric coefficients. See Table 2-5.

For negatively charged ion pairs and higher complexes, we have used the following correlation, for which the correlation coefficient $r^2 = 0.964$:

$$Cp^\circ = -7.17 - 133.15z + (2/3)S^\circ \quad (7B)$$

We developed eq 7B by correlating values of Cp° with S° for negatively charged ions, using the data in our data base as summarized in Table 2-6. Our calculated values of Cp° for selected negatively charged ions compare well with those tabulated by Brewer (82) as shown in Table 2-7. For reasons which are not clear, the agreement is poor for a similar comparison of those in Lemire (33) and Lemire and Tremaine (54). See Table 2-8. Our calculated value of Cp° for negatively charged species is about 150 J/mol/K more negative for $Al(OH)_4^-$ than that of Hovey and Tremaine (83,84). We have calculated Cp° for the chromium species $HCrO_4^-$ and $Cr_2O_7^{2-}$ using the heat capacity for CrO_4^{2-} predicted by eq 7B. These compare very well with those calculated from the measurements by Palmer et al. (18) for the reactions $CrO_4^{2-} + H^+ = HCrO_4^-$ and $2CrO_4^{2-} + 2H^+ = Cr_2O_7^{2-} + H_2O$. See Table 2-7. This table also shows our predicted heat capacity for $Cr(OH)_4^-$, calculated from eq 7B. Equation 7B reproduces Cp° values for the anions of F, Cl, Br, I and hydroxyl, nitrate, bisulfide and sulfate to within ± 30 J/mol/K of those in Tanger and Helgeson (94), when using their values of the entropies for these anions.

Table 2-4. Ionic heat capacities for selected cation higher complexes, calculated from eq 7, compared with those in Lemire and Tremaine (54), and Lemire (33). Units of C_p° are J/mol/K. The reference (Ref.) is either (33) or (54).

Cation	C_p° , eq 7	C_p° , Ref.
UOH^{+++}	-96	-54
$(UO_2)_2(OH)_2^{++}$	-60	-42
$PuCl^{+++}$	-53	266
NpO_2Cl^+	80	432
$Pu(H_2PO_4)^{++}$	-114	-82
PuF^{+++}	-113	-69
USO_4^{++}	109	121
$PuSO_4^+$	113	113
UO_2Cl^+	84	427
$U(OH)_3^+$	67	74
$PuCO_3^{++}$	123	134
$(NpO_2)_3(OH)_5^+$	2	16
NpF_2^{++}	-6	17
NpO_2F^+	89	86

Table 2-5. Comparison of values of heat capacity for uncharged aqueous species, calculated from eq 7A, with those (C_p° ,Ref) from references cited (Ref.).

Species	C_p° ,eq 7A	C_p° ,Ref.	Ref.
$AlCl_3(aq)$	-495	-499.3	45
$HCl(aq)$	-125.5	-127	35
$LiOH(aq)$	-80	-78	55
$KOH(aq)$	-127	-128	55
$UO_2SO_4(aq)$	-273	354	54
$K_3Fe(CN)_6(aq)$	-211	-206	32
$K_4Fe(CN)_6(aq)$	-467	-460	32
$PbCl_2(aq)$	-334	-256	42
$CaCl_2(aq)$	-281	-275,-208,-278	43,81
$MgCl_2(aq)$	-267	-265,-252	43,81
$SrCl_2(aq)$	-286	-288	81
$NaCl(aq)$	-83	-85	43
$NiCl_2(aq)$	-292	-295	43
$Al(NO_3)_3(aq)$	-335	-335.3	45
$MgSO_4(aq)$	-294	-288	99
$K_2SO_4(aq)$	-252	-252,-255	17,55
$Cr(NO_3)_3(aq)$	-230	-230	32
$LaCl_3(aq)$	-457	-465	32

Table 2-6. Entropy and heat capacity values used to develop correlation, eq 7B. Data are from References 44 and 55, and Appendix II.

Anion	Residuals, J/mol/K	S° J/mol/K	Cp° J/mol/K
F ⁻	-23	-13.18	-117
Cl ⁻	-15	56.73	-125.5
Br ⁻	-8	82.84	-132.2
I ⁻	-20	106.7	-120.5
NO ₃ ⁻	-68	146.94	-72
ClO ₄ ⁻	-113	182.0	-27
OH ⁻	0.2	-10.71	-140.5
HCO ₃ ⁻	-86	98.43	-54.04
CO ₃ ²⁻	0.0	-49.96	-273.5
IO ₃ ⁻	-66	118.4	-74
H ₂ PO ₄ ⁻	-106	90.37	-34
HPO ₄ ²⁻	-19	-33.47	-254
PO ₄ ³⁻	89	-220.3	-496
HSO ₄ ⁻	-99	124.26	-41.8
Fe(CN) ₆ ⁴⁻	-158	270.3	-249
Fe(CN) ₆ ³⁻	-21	95.0	-519
SO ₄ ²⁻	5	18.83	-278

Table 2-7. Comparison of Cp°, eq 7B, with values from Brewer (82) and other references shown. Entropy data from Brewer, except for ClO₄⁻, Al(OH)₄⁻ and chromium species. R = 8.3144 J/mol/K used to calculate Brewer's data.

Anion	S° J/mol/K	Cp°, Brewer	Cp°, eq 7B
I ₃ ⁻	236.9	0	18
HS ⁻	70.7	-83.1	-93
HSO ₄ ⁻	134.7	-83.1	-50
SO ₃ ²⁻	-34.9	-332.6	-297
S ₂ O ₃ ²⁻	33.3	-249	-251
S ₂ O ₈ ²⁻	244.4	-108	-111
S ₄ O ₆ ²⁻	260.2	-50.7	-100
NO ₂ ⁻	-123.0	-91.5	-222
NO ₃ ⁻	146.6	-72	-43
CNS ⁻	144.3	-40	-44
HCOO ⁻	91.5	-88.1	-79
CH ₃ COO ⁻	86.5	27	-83
ClO ₄ ⁻	182.0	-27 ^{***}	-19
Al(OH) ₄ ⁻	111.3	96.5 ^{***}	-66
Cr(OH) ₄ ⁻	-109	---	-213
CrO ₄ ²⁻	50.2	-323 [*]	-240
HCrO ₄ ⁻	184	-9 ^{**}	-18
Cr ₂ O ₇ ²⁻	261.9	-92 ^{**}	-99

* Ref. 57; ** Ref. 18; *** Refs. 20 and 45..

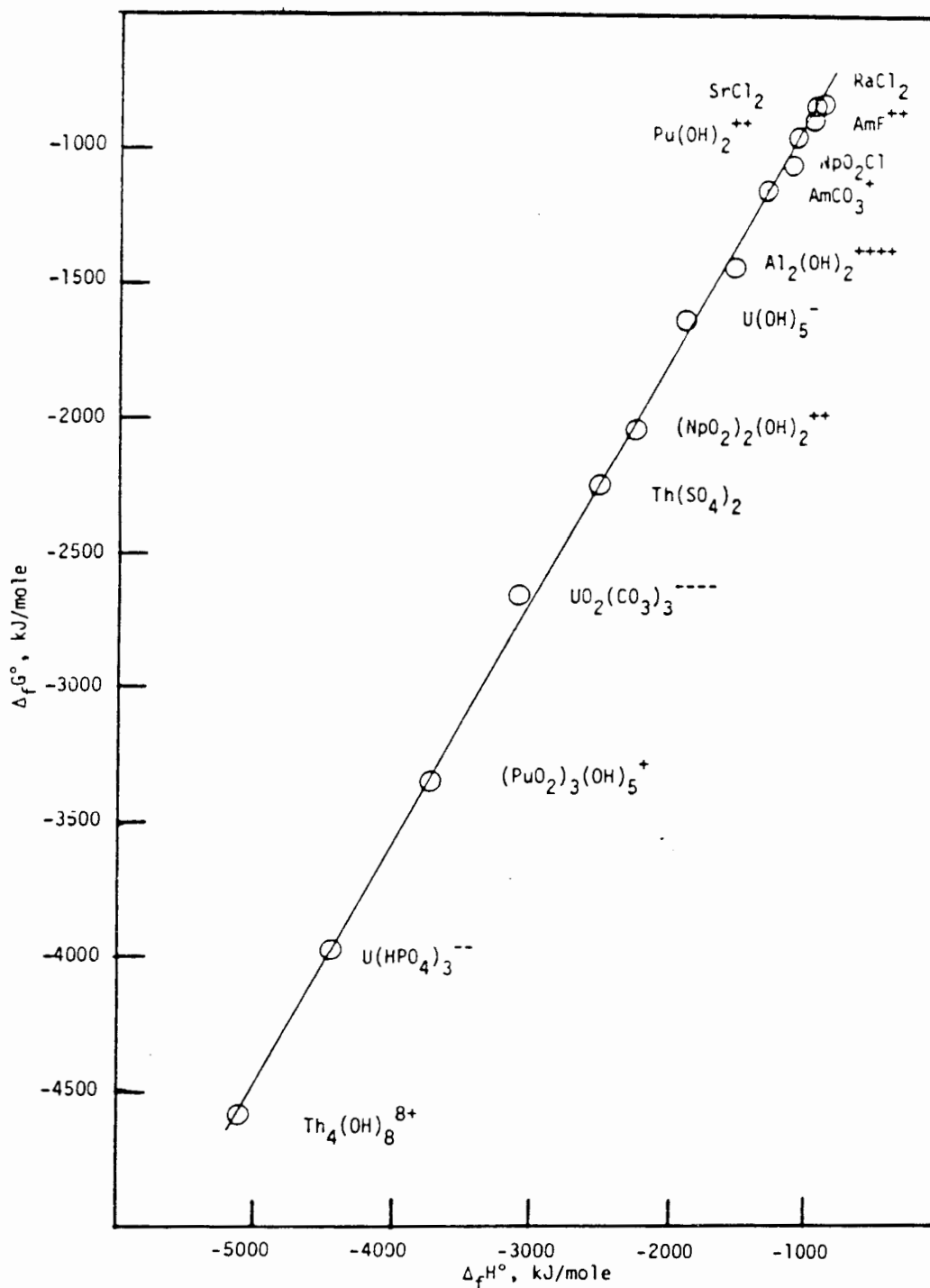


Figure 2-6. Linear relationship between $\Delta_f G^\circ$ and $\Delta_f H^\circ$, for selected higher complexes. Data are from Appendix II.

Table 2-8. Comparison of values of C_p° calculated using eq 7B, with values from Lemire and Tremaine (54) and Lemire (33,95). Units of heat capacity are J/mol/K.

Anion	S° , J/mol/K	C_p° , eq 7B	C_p° , Reference
$\text{Pu}(\text{OH})_5^-$	96	-76	-66
PuO_2F_3^-	79	-87	-273
$\text{PuO}_2\text{F}_4^{--}$	85	-217	-75
$\text{PuO}_2(\text{CO}_3)_2^{--}$	175	-157	-379
UO_2F_3^-	69	-94	-255
$\text{UO}_2\text{F}_4^{--}$	76	-223	-56
UF_5^-	71	-93	-125
UF_6^{--}	84	-217	14
$\text{UO}_2(\text{CO}_3)_2^{--}$	51.4	-239	10
$\text{UO}_2(\text{CO}_3)_3^{----}$	27.7	-521	290
$\text{UO}_2(\text{HPO}_4)_2^{--}$	126	-189	354
$\text{UO}_2(\text{H}_2\text{PO}_4)_3^-$	105	-70	43
$\text{U}(\text{HPO}_4)_3^{--}$	105	-203	194
$\text{U}(\text{HPO}_4)_4^{----}$	21	-526	302
$\text{Np}(\text{OH})_5^-$	96	-76	-67
$\text{U}(\text{OH})_5^-$	71	-93	-169
$\text{Pu}(\text{HPO}_4)_4^{----}$	46	-509	405
$\text{NpO}_2\text{SO}_4^-$	91.9	-79	-281
$\text{Np}(\text{CO}_3)_5^{-----}$	160	-699	771
$\text{NpO}_2\text{CO}_3^-$	200	-7	-20

2.3 Thermodynamics of Higher Complexes

The designation higher complexes refers to a cation associated with more than one ligand; the term also applies to polynuclear complexes with two or more metal cations. Examples are $(UO_2)_2(OH)_2^{++}$ and $PuO_2F_3^-$. In this work, correlation methods were used extensively to calculate missing values of thermodynamic properties in a consistent manner. The selected correlations which were used are described in the following paragraphs.

2.3.1 Correlation Between $\Delta_f G^\circ$ and $\Delta_f H^\circ$

Lebedev found a linear relation between $\Delta_f G^\circ$ and $\Delta_f H^\circ$ for the aqueous actinide ions in the trivalent, tetravalent, pentavalent and hexavalent oxidation states (36). We have found a similar linear relation for the plot of $\Delta_f G^\circ$ versus $\Delta_f H^\circ$ for higher complexes. See Figure 2-6.

2.3.2 Correlation Between $\Delta_f G^\circ$, $\Delta_f H^\circ$ and Number of Ligands

A second correlation developed here is based on our observation that $\Delta_f G^\circ$ and $\Delta_f H^\circ$ change in a linear fashion with the number of ligands added to the cation during formation of higher complexes (68,86).

Figure 2-7 is a plot of the variation in $\Delta_f G^\circ$ as a function of the number of ligands for selected actinides and geologic substances. Figure 2-8 is a similar plot with $\Delta_f H^\circ$ as the thermodynamic property, using data shown in Table 2-9. Data for Figure 2-7 are in Table 2-10, except for the neptunium carbonates. Values of the various entropies were calculated from $\Delta_f G^\circ = \Delta_f H^\circ - 298.15\Delta_f S^\circ$ for each reaction to ensure self-consistency.

2.3.3 Heat Capacity

Values for the heat capacity of higher complexes in this work are generally compiled from publications such as Lemire (33). There are some guidelines for estimating the heat capacity of hydrolysis reactions (34) and other reactions based on a correlation between entropy and heat capacity of the cations (57). In the absence of other data, we have used eq 7 for the heat capacity of a positively charged ion; the algebraic sum of the partial molar heat capacity of anion and cation, multiplied by the stoichiometric coefficient (eq 7A) for uncharged species; and eq 7B to estimate C_p° for negatively charged ionic species.

Table 2-9. Change in enthalpy of formation and silicic acid ionization with number of ligands for selected aqueous species, used in Figure 2-8. Data are from References 38, 51, 57, 77 and this work.

Ion	$\Delta_f H^\circ$	Ion	$\Delta_f H^\circ$
Al ⁺⁺⁺	-531.0	U ⁺⁺⁺⁺	-591.2
AlF ⁺⁺	-860.8	UOH ⁺⁺⁺	-828.0
AlF ₂ ⁺	-1190.8	U(OH) ₂ ⁺⁺	-1077.4
AlF ₃ (aq)	-1523.9	U(OH) ₃ ⁺	-1337.2
AlF ₄ ⁻	-1857.5	U(OH) ₄ (aq)	-1614.0
AlF ₅ ⁻⁻	-2192.8	U(OH) ₅ ⁻	-1893.9
AlF ₆ ⁻⁻⁻	-2533.0	Th ⁺⁺⁺⁺	-769.0
Si(OH) ₄ (aq)	-1460.1	ThSO ₄ ⁺⁺	-1658.5
SiO(OH) ₃ ⁻	-1434.5	Th(SO ₄) ₂ (aq)	-2556.4
SiO ₂ (OH) ₂ ⁻⁻	-1397.5	Th(SO ₄) ₃ ⁻⁻⁻	-3448.1
SiO ₃ OH ⁻⁻⁻	-1380.0		
SiO ₄ ⁻⁻⁻⁻	-1352.7	Th(SO ₄) ₄ ⁻⁻⁻⁻	-4351.5
La ⁺⁺⁺	-707.1		
LaSO ₄ ⁺	-1562.5		
La(SO ₄) ₂ ⁻	-2465.4		
Th ⁺⁺⁺⁺	-769.0		
ThF ⁺⁺⁺	-1106.7		
ThF ₂ ⁺⁺	-1442.6		
ThF ₃ ⁺	-1778.6		
ThF ₄ (aq)	-2115.0		

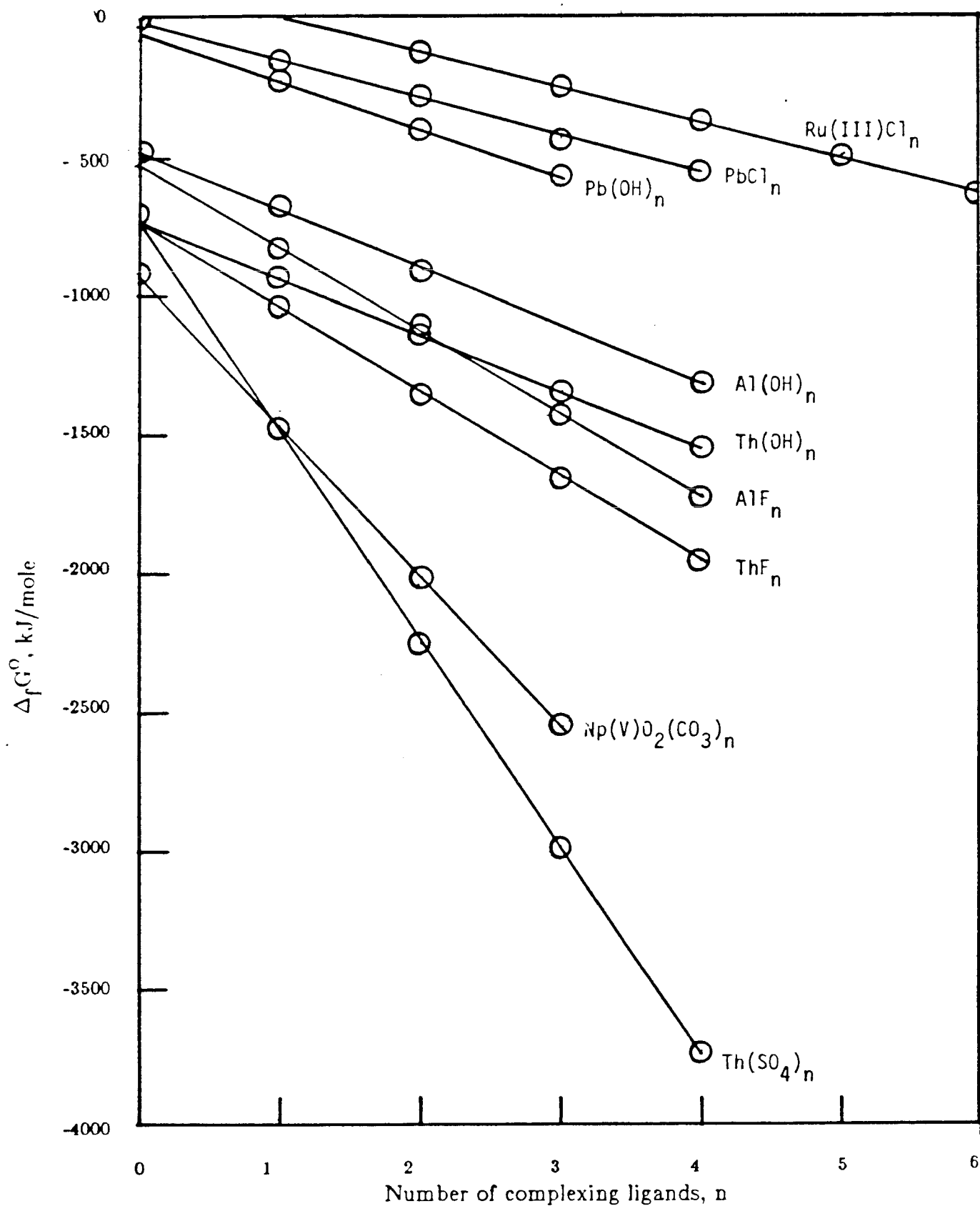


Figure 2-7. Plot of $\Delta_f G^\circ$ versus number of ligands, n , for selected higher complexes. Data from Appendix II and References 5, 14, 20, 30, 42, 51, 57, 92 and 100.

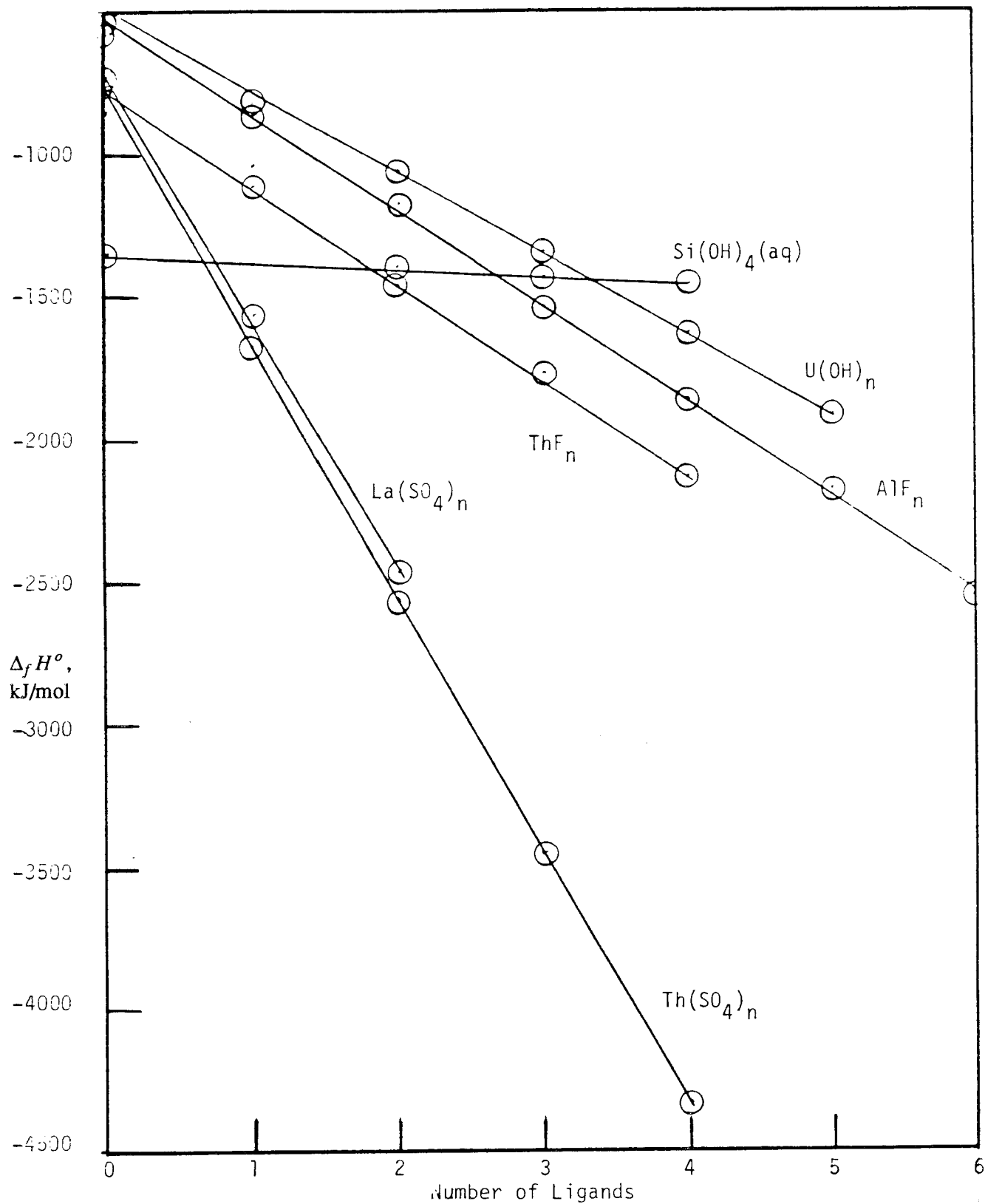


Figure 2-8. Correlation between $\Delta_f H^\circ$ and number of ligands, n , for higher complexes, or number of H^+ released during ionization. Data from References 38, 51, 57, 77 and this work.

2.3.4 Correlations between Equilibrium Constants and Ligand Number

There are a number of correlations that are used to calculate values of equilibrium constants for ion pairs. Good examples have been summarized by Baes and Mesmer (5,34), Langmuir (12), and Kerrisk (37). Langmuir has shown correlations of $\log K$ for the formation of ion pairs with electronegativity of the cation; $\log K$ of carbonate complexes with oxalate complexes of divalent cations; and, of $\log K$ versus ligand number (n) for cumulative formation constants of monomeric complexes of Th^{++++} , up to $n = 4$. Plots of $\log K$ versus n are generally nonlinear (68).

In Figure 2-9 we have plotted the cumulative formation constants for selected complexes as a function of ligand number. As seen, the plots are nonlinear, and cannot be extrapolated with confidence. On the other hand, plots of $\Delta_f G^\circ$ versus the number of ligands are linear for the higher complexes shown in Figure 2-7. This result suggests that the formation constant of a higher complex can be calculated by using an interpolated or an extrapolated value of $\Delta_f G^\circ$ at the desired ligand number in calculating a $\Delta_r G^\circ$ for the reaction of interest.

2.4 Summary

The Aqueous Solutions Database contains values of the following four thermodynamic properties: $\Delta_f G^\circ$, $\Delta_f H^\circ$, S° , and C_p° for solids, simple ions, ion pairs and higher complexes of elements occurring in nuclear waste, natural waters and geologic materials. This tabulation is based on other critical evaluations including CODATA (52), the National Bureau of Standards (51), the IAEA series (41, 56, 62), Lemire and Tremaine (54), Lemire (33) and our on critical review of experimental work. Reliable experimental data are not available for many potentially important radionuclide species. Correlation methods that were used to estimate values of missing data were described.

Table 2-10. Gibbs energy of formation for selected cation-ligand complexes, versus number of ligands, n , where n ranges from 0 to the maximum value, n_{\max} ; however values for $n = 0$ were not included. All data were taken from Appendix II; data in Appendix II were obtained from References 14, 91, 92, 100 and other references cited. Average correlation coefficient, $r^2 = 0.9999$. m = slope, b = intercept, the quantity $\Delta_f G [M]$ is the Gibbs free energy of formation of the cation. Note that $\Delta_f G [M]$ is generally more positive than the extrapolated value, at $n = 0$ (b).

$M-X_n$	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	-204.08
Eu-OH	3	-576.2	-574.63	-196.3
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 ₄	3	-686.2	-685.62	-741.7
Th-SO ₄	5	-704.6	-718.62	-757.13

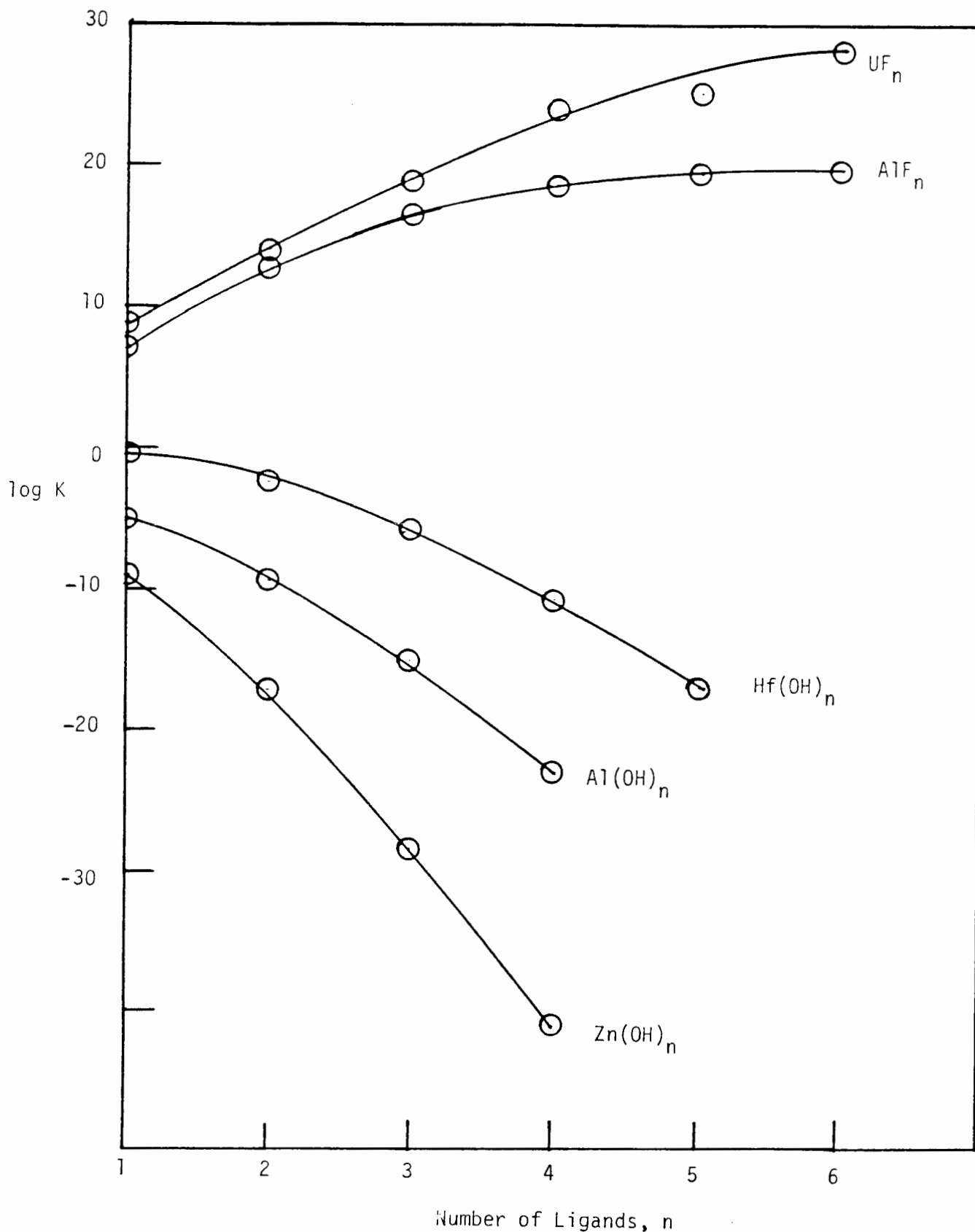


Figure 2-9. Plot of cumulative formation constant or hydrolysis constant versus number of ligands for typical complex ions. Data from This Work, Lemire and Tremaine (54), Baes and Mesmer (34) and Smith and Martell (19).

For all substances in the data base, thermodynamic properties are related by the fundamental equation (80):

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ \quad (i)$$

and heat capacity is correlated with entropy for anions and cations. The value of the intrinsic equilibrium constant for any reaction is related to the thermodynamic properties of the reactants and products by the relationship:

$$\Delta_r G^\circ = -RT \ln K^\circ \quad (11)$$

where

$$\Delta_r G^\circ = \sum \Delta_f G_p^\circ - \sum \Delta_f G_q^\circ \quad (12)$$

For simple aqueous ions, the $\Delta_f G^\circ$ can be estimated from linear correlations between $\Delta_f G^\circ$ and $\Delta_f H^\circ$. This relationship can be expressed in terms of an electrochemical reaction wherein an ion is reduced to the corresponding element (cf. eq 6). Heat capacities are estimated using a correlation between heat capacity, absolute entropy and ionic charge (cf. eq 7). For uncharged aqueous species, heat capacity is approximated from a correlation based on algebraically summing the values for the individual cation and anion.

The effect of ionic strength on formation constants was assessed using the extended Debye-Huckel and Davies equations (cf. eqs 8,9). Estimates of enthalpies of formation were made from a linear correlation between $\Delta_f G^\circ$ and $\Delta_f H^\circ$ (cf. Figure 2-6). Values of entropy and heat capacities of ion pairs were estimated in the manner described previously for simple ions.

Correlation methods were used extensively to obtain thermodynamic property values for higher complexes for this data base. The Gibbs energy of formation and enthalpy of formation of higher complexes change linearly with added ligand. The quantities $\Delta_f G^\circ$ and $\Delta_f H^\circ$ for the higher complexes are also related in a linear fashion. The entropy of each complex is calculated from $\Delta_r G^\circ = \Delta_r H^\circ - 298.15 \Delta_r S^\circ$ for each reaction.

3.0 THERMODYNAMIC PROPERTY TABLES

This section contains a discussion of the content of the tabulation of thermodynamic properties of radionuclides important to sensitivity analyses. The numerical values in these tables are consistent with thermodynamic relationships; consistent in the reproducibility of commonly accepted equilibrium constants; and, consistent in reproducing the best experimentally measured equilibrium constants.

Self-consistent values of selected thermodynamic properties are tabulated for the waste radionuclides Am, Ra, Th, Np, Pa, Pu and U, as well as other elements in geologic materials. These tables are organized according to the following format.

3.1 Property Values Tabulated in FORM1

The thermodynamic properties in this format are the Gibbs energy and enthalpy of formation, entropy and heat capacity. The magnitude of each property is given in units of joules (J). Figure 3-1 is an example of this format.

The mnemonic in the upper right hand corner identifies the radionuclide; status of the tabulation; and, date of the most current information. If the numerical quantities are evaluated, but not consistent then "status 2" is printed. When the information is compiled but not critically evaluated and consistent, then the term "status 3" is used.

The heading PROPERTIES OF ELEMENTAL lists selected properties of the gas, liquid or solid element. The THERMODYNAMIC PROPERTIES OF SUBSTANCES tabulates values of the intrinsic thermodynamic properties at 25°C and zero ionic strength (I).

3.1.1 Substance

Data for crystalline solids (s), amorphous solids (am), gases (g), liquids (l), aqueous uncharged neutral species (aq), and aqueous ions are included in this tabulation.

3.1.2 Property

The standard state value of the following four properties are tabulated: Gibbs energy of formation; enthalpy of formation; entropy; and heat capacity. The values are related so that for any chemical reaction, within ± 1 kJ/mol,

$$\Delta_r G^\circ = \Delta_r H^\circ - 298.15\Delta_r S^\circ \quad (19)$$

PROPERTIES OF ELEMENTAL AMERICIUM:

Atomic Number: 95

Formula Mass: 241.06

Electronic Configuration: $5f^7 7s^2$

Electronegativity: 1.3

Hydration Number: 12.8 (F.David,1986)

Ionic Radius: 0.975 angstrom

Selected Average for Soils:

Concentration in Natural Waters:

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Am(g)	242.000	284.000 4.0	194.40	20.79	1111
Am(s)	0.000	0.000	55.40 2.00	25.50 1.0	0011
Am ₂ O ₃ (s)	-1614.200 8.0	-1692.000 8.0	158.00		9110
AmO ₂ (s)	-880.060 2.5	-932.200 2.5	86.00		9110
AmF ₃ (s)	-1523.394 8.1	-1588.300 8.0	127.60 4.00	100.00	3339
AmF ₃ (aq)	-1500.000 4.0	-1590.000	56.00	-439.00	9999
AmF ₄ (s)	-1627.000 29.0	-1719.600 29.0	148.50 4.00	113.00	3339
AmCl ₃ (s)	-910.857 1.8	-977.800 1.3	164.80 6.30	123.00	1339
AmBr ₃ (s)	-786.592 8.6	-809.600 7.0	205.00 16.70	148.00	3339
AmI ₃ (s)	-613.793 9.4	-612.000 7.0	234.30 20.90	166.00	3339
Am(OH) ₃ (s)	-1168.000 3.0	-1272.000 25.0	209.00	150.00	1999
Am(OH) ₃ (aq)	-1159.215 10.0	-1380.000	-183.00	-509.00	2999

Figure 3-1. First page of a FORM1 printout, itroff format, using americium as the example. This is the format used in Appendix I and II. The number of zeros added by the computer system does not reflect the number of significant figures in the property values.

3.1.3 Standard Deviation

The uncertainty at 25°C and zero ionic strength in the magnitude of each property value is given immediately beneath the property value; with a \pm being understood. This uncertainty is generally taken from the referenced publication, and normally reflects a standard deviation of $\pm 1 \sigma$. For example, Baes and Mesmer (5) tabulated an uncertainty which is one standard deviation. Exceptions are the data from Robie et al. (58) where the standard deviation is $\pm 2 \sigma$. Fuger and Oetting assign uncertainties which "represent the best estimates of the overall uncertainties in the values at the 95% confidence level" (41,p.3).

3.1.4 References and Comments

A reference column (Ref.) identifies the literature source cited for each property value; the numbers in each column range from 0 to 9. Delimiters are not used. In the Ref. column, the numbers refer to the source of the values for $\Delta_f G^\circ, \Delta_f H^\circ, S^\circ, Cp^\circ$ in consecutive order, from left to right. Zero is always used to indicate missing data; 9 is always used to identify this work. As example of these comments is a portion of the Comments section for Am:

Comments:

Reference 1 is L.R.Morss,1985;2=Phillips,1982;3=IAEA,Part8,1983;4=Kerrisk,1984; 6=F.David:J.Less-Common Metals 1986,v.121,27; 7=Bidoglio: Radiochim. Radioanal.Letters 1982,v.53,45;8=R.Lundqvist:Acta Chem.Scand. 1982,v.A36,741. 9=This work. SmOH^{++} used as model for AmOH^{++} in estimating enthalpy and entropy. Enthalpy of $\text{Am}_2\text{O}_3(s)$ is from L.Morss; D.C.Sonnenberger: J.Nucl.Mater. 1985,v.130,266. Gibbs energy of $\text{AmOHCO}_3(s)$ from R.J.Silva: UCRL-91821, Lawrence Livermore National Laboratory,Livermore,CA (Jan.12,1985). Data for AmF^{+2} and AmF_2^+ from K.L.Nash and J.M.Cleveland: Radiochimica Acta 1984,v.37,19. For $\text{Am}^{++++} + e = \text{Am}^{+++}$, $E^\circ = 2.62$ v. Reference is L.R.Morss; J.Fuger: J.Inorg.Nucl.Chem. 1981,v.43, 2059. D.Rai; R.G.Strickert; D.A.Moore; J.L. Ryan: Radiochim. Acta 1983,v.33,201 measure for $\text{Am}(\text{OH})_3(s)$, $\log K_{sp} = -17.5 \pm 0.3$; $\log K \leq -8.2$ for $\text{Am}^{++++} + \text{H}_2\text{O} = \text{AmOH}^{++} + \text{H}^+$. We calculate $\log K(I=1.0) = -8.70$ for this hydrolysis reaction, using $b=0.3$ (value for NdOH^{++} , from Baes, Mesmer, 1976). Nair et al.: Radiochim. Acta 1982, v.32, 37 find $\log K(I=1.0) = -7.03$ for this hydrolysis reaction. Lundqvist, Ref.8, measures $\log K(I=1.0) = -7.5$; and Caceci; Choppin: Radiochim. Acta 1983, v.33, 101 find $\log K(I=0.7) = -7.54$ in 0.7M NaCl solution, at 21°C, for this first hydrolysis reaction. Considering difficulty in measuring Am^{+++} hydrolysis, agreement is probably satisfactory for one unit of $\log K(I=1.0)$. Values for $\text{AmF}_3(\text{aq})$ calculated in this work from the linear change in $\Delta_f G$ with number of F^- ligands; and $\Delta_f H$ from the linear relation between $\Delta_f G$ and $\Delta_f H$; also, $\text{Am}(\text{OH})_2^+$; $\text{Am}(\text{OH})_3(\text{aq})$. Values of $\log K^\circ$ for both $\text{AmH}_2\text{PO}_4^{++}$ and the 1:2 complex $\text{Am}(\text{H}_2\text{PO}_4)_2^+$ from Lebedev et al.: Radiokhimiya 1979,v.21,692. Kerrisk (1984) is LA-10040-MS (July 1984)

3.2 Auxiliary Data

The auxiliary data used in this work include the critically evaluated enthalpies and entropies from CODATA, and our evaluation. The tabulated ionic heat capacities were obtained from Brewer (82), Hovey et al. (83,84), or the references given.

3.2.1 CODATA Key Values

We have obtained values of the enthalpy of formation and entropy to the extent possible from the CODATA tabulation of Key Values (47,52). In general, uncertainties are less than ± 1.0 kJ/mol for $\Delta_f H^\circ$ and ± 1.0 J/mol/K for S° . The CODATA publication Bulletin 28 (April 1978) contains a bibliography of 176 references to sources of the experimental measurements used in arriving at the recommended Key Values. A Footnotes section describes the method of calculation for the enthalpy and entropy values listed.

3.2.2 Master Species

One of the intended uses of the Aqueous Solutions Database is in the preparation of well-documented, internally-consistent sets of data for use in geochemical speciation and reaction codes such as PHREEQE (4) and MINEQL (89). These codes require specification of $\log K$ values for reactions that involve "basis" or "master" species. Values of the thermodynamic properties of the master species were obtained from the NBS Tables (51), the JANAF Tables (71), Naumov et al. (57), and our evaluation (Section 1.2.2). Examples of these master substances are NpO_2^+ , Ra^{++} , Th^{++++} and CO_3^{--} . The uncertainties are generally larger than those of the CODATA values; for example, σ of $\Delta_f G^\circ [NpO_2^+, aq] = \pm 5.4$ kJ/mol.

Appendix I is a current list of master species and associated thermodynamic property values that has been defined for use with these codes. In the future, as the scope of applications of this data base expands, additional species may be added to this table. Values of master species are consistent with the CODATA Key Values, and are consistent in reproducing critically selected experimentally measured equilibrium constants. These auxiliary data and other data are stored on the LBL 8650 computer cluster, using the DATATRIEVE data base management system.

3.3 Apparent Equilibrium Constants at High Temperatures and Salinities in FORM2

The data contained in the Aqueous Solutions Database are used to calculate intrinsic equilibrium constants (25°C and I=0). Equilibrium constants at other temperatures ($K(T)$) and salinities ($K(I)$) are calculated with eq 20 (46) and eq 8 (13), respectively. The change in the value of the equilibrium constant with temperature is calculated from eq 20, when the heat capacity change can be assumed constant over the entire temperature range, $0 < T < 300^\circ\text{C}$ (46).

$$R \ln K(T) = \Delta_r S^\circ - \frac{\Delta_r H^\circ}{T} + \Delta_r C_p^\circ \left[\frac{298.15}{T} - \ln \frac{298.15}{T} - 1 \right] \quad (20)$$

At 25°C, eq 8 is used to calculate the effect of ionic strength on equilibrium constants

$$\log K(I) = \log K^\circ + \frac{A_\gamma \Delta z^2 I^{1/2}}{1 + I^{1/2}} + bI \quad (8)$$

over the range $0 < I < 3$.

Data on $\Delta_r S^\circ$, $\Delta_r H^\circ$ and $\Delta_r C_p^\circ$ for use in eq 20 are computed from data in these tables. Values of $A_\gamma \Delta z^2$ and b for eq 8 must be obtained from other publications. For example, Phillips, et al. (15) contains tabulations of $A_\gamma \Delta z^2$ and b values for a large number of reactions. An alternative to the use of eq 8 is to calculate individual ion activity coefficients by using the methods described by Garrels and Christ (70), Truesdell and Jones (88), and Pitzer (75). These approaches are incorporated in the PHREEQE (4), MINEQL (89) and PHREEQE* (90) computer codes.

Sample session 1.3.6 is an example of FORM2. The user should note that the data in FORM1 are continually updated to reflect newer values; however, values in FORM2 are not currently recalculated using the most recent FORM1 data. The data in FORM2 are consistent with the thermodynamic property values published earlier (15).

4.0 QUALITY CONTROL

A reliable thermodynamic data base is essential in predicting the performance of a HLW repository. Central to reliability is the imposition of integrity constraints. The twofold constraints are self-consistency within the data base, and consistency in reproducing critically selected experimental measurements.

4.1 Self-Consistency

Self-consistency is defined in two ways: for each substance the relationship $\Delta_r G^\circ = \Delta_r H^\circ - 298.15\Delta_r S^\circ$ will hold to within 1000 J/mol; and, an intrinsic equilibrium constant or standard potential will have a single value irrespective of the number of equations added or subtracted in arriving at the final, desired reaction. Self-consistency is reflected by consistency with geochemical reaction processes as discussed in the next section.

4.2 Consistency with Reaction Processes

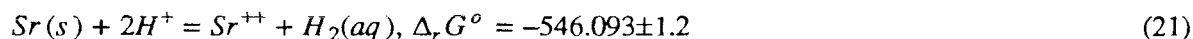
Reaction processes include both chemical reactions and electrode reactions. The equilibrium constant for each reaction is calculated from the various Gibbs energy values of individual substances taken from the tables. The constraint on quality control here is that the desired reaction which we identify as the net reaction, will have one value of $\log K^\circ$ regardless of the number of differing reactions added to form the final, net reaction.

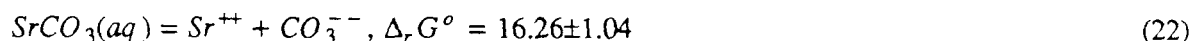
4.2.1 Program FPLOTT

The Hewlett-Packard program FPLOTT graphs mathematical equations and prints tables based on these equations. We have modified the program; the new procedure, named FPLOTT1, calculates thermodynamic quantities for individual chemical reactions. An additional feature is the calculation of the net change in Gibbs energy, enthalpy, entropy and heat capacity for each reaction, and the value of $\Delta_r H^\circ - 298.15\Delta_r S^\circ$ for each chemical reaction. This permits a precise calculation of self-consistency for the various reactions in a geochemical process. The program calculates values of $\log K(T)$ using enthalpy and entropy values, so that there may be a difference between $\log K^\circ$ calculated from $\Delta_r G^\circ$, and $\log K^\circ$ calculated from $\Delta_r H^\circ - 298.15\Delta_r S^\circ$.

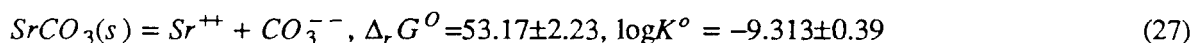
4.2.2 Chemical Equilibria

An example of consistency with reaction processes and application of the program FPLOTT1 is the following series of reactions which are added to give the net reaction, the dissolution of strontianite. The units of $\Delta_r G^\circ$ are kJ/mole.





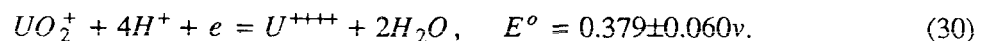
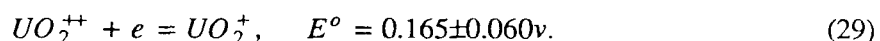
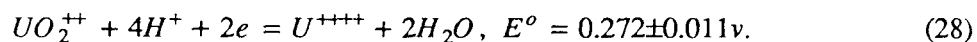
The net reaction is obtained by addition of eq 21 through eq 26,



Calculated directly for eq 27, $\Delta_r G^\circ = 53.170 \pm 1.31$ kJ/mol and $\log K^\circ = -9.313 \pm 0.23$. The value $\log K^\circ = -9.313$ compares with the value of $\log K^\circ = -9.13$ which was measured experimentally in NaCl media by Millero et al. (39); and with $\log K^\circ = -9.266 \pm 0.004$ measured by Busenberg, Plummer and Parker (40). Our propagated uncertainty was calculated as the square root of the sum of the squares of the individual standard deviations of the individual values of $\Delta_f G^\circ$.

4.2.3 Oxidation/Reduction Potentials

An example of self-consistency in oxidation/reduction reactions is a calculation of the standard potentials for the following three uranium couples



The $\Delta_r G^\circ$ for these reactions are: -52.458 kJ/mol, -15.900 kJ/mol and -36.558 kJ/mol, respectively. Adding eq 29 and eq 30 gives $\Delta_r G^\circ = -52.458 \pm 5.8$ kJ/mol, in agreement with $E^\circ = 0.272 \pm 0.030$ v. for eq 28. Newer measurements indicate a more negative $E^\circ = 0.25$ v. (87). However, we retain $E^\circ = 0.272$ v. until the newer data have been critically evaluated.

4.2.4 FPLO2 Program

The Hewlett-Packard program, FPLLOT, was modified to calculate standard potentials (E°), as well as changes in Gibbs energy of reaction, enthalpy, entropy and heat capacity. It serves the identical purpose as that of FPLLOT1 but is used for electrode reactions. Table 4-1 compares standard potentials computed from our Tables in Appendix II with selected reactions in Bard et al. (64).

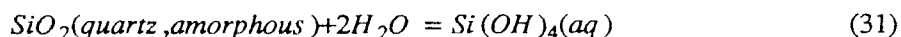
4.3 Reproducibility of Selected Experimental Measurements and Other Work

Values of $\log K$ are commonly measured by a number of methods including conductivity changes; potentiometry involving addition of OH^- to acidic solutions of a dissolved metal; spectrophotometry in which changes in absorption at specific wavelengths are monitored; distribution of an ion pair between two immiscible solvents; and, electroanalytical methods such as polarography.

The examples of experimental studies described in the following sections were chosen to represent a broad range of chemical behavior and experimental techniques. They represent a small subset of the total number of experimental works consulted during the compilation of the Aqueous Solutions Database.

4.3.1 Silica Solubility

The solubilities of quartz and amorphous silica have been measured by a number of researchers (48,49) at various temperatures. We calculated $\log K$ for solubility of silica using our values for SiO_2 and the CODATA tables for $\text{H}_2\text{O}(l)$, using eq 20, according to the dissolution reaction,



Our results compare with those calculated by Fournier (48) for quartz and Fournier and Marshall (49) for the amorphous form, both at saturation vapor pressures. However, we have assumed that: (a) equation 31 is valid over the temperature range 75 to 350°C; (b) that the data at 25°C can be used to extrapolate to 350°C using eq 20. Fournier, and Fournier and Marshall, do not assume a constant number of hydrated waters for the

Table 4-1. Standard electrode potentials for selected redox couples at 25°C and I = 0. E° calculated from data in Appendix II. The value of the faraday used in this table is 96,487 coulombs/mol. Differences are due to differing values for $\Delta_f G^\circ$. In this table, the quantity Δ is defined as

$$\Delta = \Delta_r G^\circ - [\Delta_r H^\circ - \Delta_r S^\circ], \text{ J/mol.}$$

Ideally, $\Delta = 0$.

Electrode Reaction	Δ	$E^\circ(\text{volt})$ This Work	$E^\circ(\text{volt})$ Ref. 64
$\text{O}_2(\text{aq}) + 4\text{H}^+ + 4\text{e} = 2\text{H}_2\text{O}$	124	1.272±0.0001	--
$2\text{H}^+ + 2\text{e} = \text{H}_2(\text{aq})$	0	-0.092±0.005	--
$\text{Na}^+ + \text{e} = \text{Na}(\text{s})$	22	-2.714±0.001	-2.714
$\text{K}^+ + \text{e} = \text{K}(\text{s})$	250	-2.925±0.001	-2.925
$\text{Cs}^+ + \text{e} = \text{Cs}(\text{s})$	340	-3.027±0.002	-2.923
$\text{Ag}^+ + \text{e} = \text{Ag}(\text{s})$	20	0.7991±0.001	0.7991
$\text{NpO}_2^+ + 4\text{H}^+ + 5\text{e} = \text{Np}(\text{s}) + 2\text{H}_2\text{O}$	150	-0.913±0.011	--
$\text{PuO}_2^{++} + 4\text{H}^+ + 6\text{e} = \text{Pu}(\text{s}) + 2\text{H}_2\text{O}$	490	-0.488±0.012	--
$\text{Ca}^{++} + 2\text{e} = \text{Ca}(\text{s})$	60	-2.865±0.004	-2.84
$\text{Sr}^{++} + 2\text{e} = \text{Sr}(\text{s})$	0	-2.922±0.004	-2.89
$\text{Cu}^{++} + 2\text{e} = \text{Cu}(\text{s})$	80	0.339±0.0005	0.340
$\text{Pb}^{++} + 2\text{e} = \text{Pb}(\text{s})$	10	-0.124±0.0005	-0.125
$\text{UO}_2^{++} + 4\text{H}^+ + 6\text{e} = \text{U}(\text{s}) + 2\text{H}_2\text{O}$	110	-0.826±0.004	--
$\text{Zn}^{++} + 2\text{e} = \text{Zn}(\text{s})$	0	-0.763±0.001	-0.7626
$\text{Fe}^{++} + 2\text{e} = \text{Fe}(\text{s})$	70	-0.474±0.005	-0.44
$\text{Fe}^{+++} + 3\text{e} = \text{Fe}(\text{s})$	100	-0.059±0.003	-0.037
$\text{Th}^{++++} + 4\text{e} = \text{Th}(\text{s})$	441	-1.826±0.014	-1.83
$\text{F}_2(\text{g}) + 2\text{e} = 2\text{F}^-$	19	2.920±0.007	2.87
$\text{Cl}_2(\text{g}) + 2\text{e} = 2\text{Cl}^-$	120	1.360±0.001	1.358
$\text{I}_2(\text{s}) + 2\text{e} = 2\text{I}^-$	10	0.5355±0.0083	0.5355
$\text{O}_2(\text{g}) + 2\text{H}_2\text{O} + 4\text{e} = 4\text{OH}^-$	252	0.401±0.001	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±0.005	-0.848

reaction 31. Results are in Table 4-2.

Table 4-2. Comparison of calculated solubility for 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 -3.39	-3.10 -3.16	-2.68 -2.76	-2.36 -2.43	-2.11 -2.16	-1.94 -1.91	-1.9 -1.71	48 This work
logK(amorphous)	-2.37 -2.59	-2.23 -2.43	-1.99 -2.15	-1.81 -1.91	-1.67 -1.71	-1.59 -1.54	-1.54 -1.39	49 This work

At 25°C, $\log K^o(\text{quartz}) = -3.96 \pm 0.36$, comparing with -4 tabulated by Baes and Mesmer (5); and, $\log K^o(\text{amorphous}) = -2.98 \pm 0.46$, comparing with -2.74 in Ref. 49.

The solubility reaction in eq 31 can be complicated by coupled reactions such as the ionization of silicic acid. Data for silicic acid ionization are discussed in the next section.

4.3.2 Silicic Acid Ionization

The next table compares our calculated values for the first ionization constant of $\text{Si}(\text{OH})_4(\text{aq})$ with Busey and Mesmer (50).

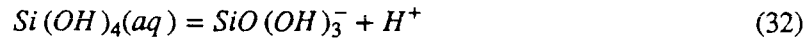


Table 4-3. Comparison of calculated apparent ionization constants for silicic acid with experimental data at high temperatures, at I = 0.

T,°C	log K(T)	
	This Work	Ref. 50
0	-10.26	-10.28
25	-9.82±0.30	-9.82
50	-9.50	-9.50
75	-9.27	-9.27
100	-9.12	-9.10
150	-8.96	-8.90
200	-8.95	-8.85
250	-9.02	-8.96
300	-9.15	-9.22

Values of $\log K(I)$ for reaction 32 were calculated using an extended Debye-Huckel equation (eq 8) over the range 0 - 3.0m using $b = -0.06$ and $A\sqrt{I}z^2 = 1.02$ (13). See Table 4-4.

Table 4-4. Comparison of calculated ionization constants for silicic acid calculated in this work with experimental data. T = 25°C.

I, mol/kg	$\log K(I)$ This Work	$\log K(I)$ Ref.50
0	-9.82±0.30	-9.83
0.1	-9.58	-9.59
0.5	-9.43	-9.44
1.0	-9.37	-9.38
2.0	-9.34	-9.35
3.0	-9.35	-9.36

4.3.3 Nickel/Fluoride Electrode System

An example of consistency in reproducing other experimental or calculated values of standard potentials is the comparison given in Table 4-5. The comparison is between our predicted values for the change in standard potential of the nickel/fluoride electrode system, with that calculated from the Gibbs energies in Barner and Scheuerman (53), for temperatures up to 300°C.

Assuming the $Ni(s)/NiF_2(s)$ couple is reversible, then $E^o = 0.211 \pm 0.006v.$ for the electrode reaction



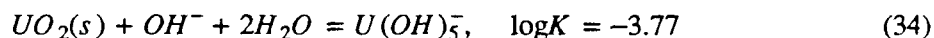
A table of standard potentials as a function of temperature was generated using FPLO2. At 25°C, values from the NBS tables of Wagman et al. (51) yield $E^o = 0.241v.$ for this reaction. The difference between our standard potential and that calculated from the data in the NBS tables is 0.030v.; this is due to our selection of the Gibbs energy of formation value for F^- from the 1977 CODATA Key Values (-281.75 kJ/mol) which differs from the NBS value for F^- (-278.65 kJ/mol)(51).

Table 4-5. Electrode potentials for the nickel-fluoride couple. *E° is this work; **E° is calculated from data in Barner and Scheuerman (53); ΔE° = *E° - **E°.

T°C	*E°,v.	**E°,v.	ΔE°
0	0.186	--	--
25	0.211±0.006	0.263	-0.036
50	0.237	0.269	-0.032
75	0.268	0.297	-0.027
100	0.302	0.334	-0.034
150	0.377	0.409	-0.032
200	0.462	0.501	-0.039
250	0.555	0.596	-0.041
300	0.656	0.705	-0.049
350	0.764	--	--

4.3.4 U⁺⁺⁺⁺ - OH⁻ System

Baes and Mesmer (5) interpreted the solubility measurements of Gayer and Leider (59) for UO₂(s) in alkaline media according to the reaction



On the assumptions of a mononuclear species and UO₂(s) as the solid phase they calculated $\log K^\circ = -16.0$ for formation of U(OH)₅⁻ according to the hydrolysis reaction U⁺⁺⁺⁺ + 5H₂O = U(OH)₅⁻ + 5H⁺. Using this value and assuming a regular progression of the intermediate equilibria, they estimated $\log K^\circ$ for U(OH)₂⁺⁺, U(OH)₃⁺, and U(OH)₄(aq). See Table 4-6. The parenthesis around the values of $\log K^\circ$ for the 1:2, 1:3 and 1:4 species are from Baes and Mesmer, and reflect the uncertainty in the existence of these species. Langmuir (61) used a similar approach. His data were adopted by Lemire and Tremaine (54); however, Langmuir's values are not all identical to those of Baes and Mesmer.

In both approaches, the magnitude of $\log K^\circ$ for formation of U(OH)₅⁻ determines the hydrolysis constants for the 1:2, 1:3, 1:4 species. In fact, only the first hydrolytic species has been experimentally identified and, both the existence of U(OH)₅⁻ and its hydrolysis constant have been questioned (7,60). For example, solubility measurements of UO₂(am) have been interpreted on the basis of both U(OH)₃⁺ and U(OH)₄(aq) as the soluble species, rather than U(OH)₅⁻ by Bruno et al. (60,87). It should be recalled that one of the questioned species, U(OH)₅⁻, exists only in highly alkaline solutions (e.g., pH>12); therefore when using computer codes for predicting radionuclide behavior we do not include this substance in natural waters where the pH does not exceed 9 or 10. On the other hand, an anionic hydrolytic species cannot be excluded on the basis that experimental measurements such as solubility of UO₂(s,am) do not give unequivocal results. For example, Cobble et al. (21) include the anionic iron

complexes $Fe(OH)_3^-$ and $Fe(OH)_4^{2-}$ as likely hydrolytic species in alkaline waters used to produce electrical power; other anionic species such as $Zr(OH)_5^-$ are included in Baes and Mesmer (5).

Bruno et al. have calculated a new standard potential for the U(VI)/U(IV) couple (87), $E^\circ = 0.260v.$ or $0.248v.$ depending on the method for correction to zero ionic strength. The first value is based on calculations using specific interaction theory; the second uses the Pitzer equations. We currently retain $0.272 \pm 0.011v.$, virtually identical to that in the IAEA series (41) pending critical evaluation of these newer results. A recent publication by Lemire (95) has revised values of free energy of formation, entropy and heat capacity for a number of species including $U(OH)_4(aq)$ and $U(OH)_5^-$, which differ from the data in Appendix I (uranium table).

4.3.5 UO_2^{++} Hydrolysis

Sylva and Davidson (22) studied the hydrolysis of UO_2^{++} at $25^\circ C$ in $0.10M KNO_3$ solutions at $25.0 \pm 0.1^\circ C$ (22); the total initial UO_2^{++} concentration ranged from $0.185 \times 10^{-3}M$ to $1.853 \times 10^{-3}M$. Titrations were carried out by addition of base in $0.1M KNO_3$ solutions which served to maintain a constancy in ionic strength. The number of data points taken during titration ranged from 42 to 65; the pH values were measured to three decimal places and ranged from 3.208 to 5.911. The experimental data were interpreted by fitting to 18 models, using the computer code MINIQUAD 75. The UO_2^{++} hydrolysis behavior is complex due partly to formation of dimeric and higher complexes. Therefore a trial-and-error approach was used consisting of various combinations of possible species, together with previously published models.

Criteria for selection of the best model were the simultaneous existence of: (a) standard deviations for all the constants of ca. 10%; and (b) a value of the goodness of fit parameter (R) of about 0.001. The best fit was obtained from a model based on the following hydrolytic species: UO_2OH^+ , $(UO_2)_2(OH)_2^{++}$, $(UO_2)_3(OH)_4^{++}$, $(UO_2)_3(OH)_5^+$ and $(UO_2)_4(OH)_7^+$. Only UO_2OH^+ is an ion pair; the remaining substances are polymeric hydrolytic products. Table 4-7 summarizes the results obtained by Sylva and Davidson (22) and other measurements (23) for the hydrolytic behavior of UO_2^{++} at $25^\circ C$. UO_2^{++} has a strong tendency to form dimers and polynuclear species; so that their work provides evidence for the 1:1 species (5). Adequate models of the behavior of UO_2^{++} in natural waters, which are expected to contain low concentrations of total uranium might consist of UO_2OH^+ as the principal hydrolytic product. We used these data to calculate values of Gibbs energy of formation for the hydrolytic species, after correcting to $I = 0$, using eq 10. See for example Figure 2-3.

Table 4-6. Standard hydrolysis products of U^{++++} , 25°C and $I = 0$. Values for This Work calculated from data in Appendix II. Uncertainties for the 1:2, 1:3 and 1:4 interpolated values calculated from $(1.81^2+0.39^2)^{1/2}$.

Hydrolysis Reaction	This Work	log K°		
		Bruno	Lemire(54)	Baes(5)
$U^{++++} + H_2O = UOH^{+++} + H^+$	-0.65±1.81		-1±1	-0.65±0.04
$U^{++++} + 2H_2O = U(OH)_2^{++} + 2H^+$	-4.27±1.85		-2±4	(-2.6)
$U^{++++} + 3H_2O = U(OH)_3^+ + 3H^+$	-7.87±1.85	-1.1(I=0.5)	-5±4	(-5.8)
$U^{++++} + 4H_2O = U(OH)_4(aq) + 4H^+$	-11.48±1.85	-5.4(I=0.5)	-9±14	(-10.3)
$U^{++++} + 5H_2O = U(OH)_5^- + 5H^+$	-15.09±0.39		-13±1	-16.0±0.1
Other Reactions				
$UO_2(s) + OH^- + 2H_2O = U(OH)_5^-$	-5.75±0.24		-3.77	-3.77
$UO_2(s) + 4H^+ = U^{++++} + 2H_2O$	-4.65±0.24	-1.6	-4.6±0.4	-1.8

Table 4-7. Selected apparent hydrolysis products of UO_2^{++} , 25°C.

Medium	log K(I)				Ref.
	UO_2OH^+	$(UO_2)_2(OH)_2^{++}$	$(UO_2)_3(OH)_5^+$	$(UO_2)_3(OH)_4^{++}$	
0.1m NaClO ₄		-6.2			5
	-6.08	-5.78	-16.59		15
0.1m NaNO ₃		-6.2			5
0.1m KNO ₃	-6.1	-5.84			5
0.1M KNO ₃	-5.50	-5.89	-16.46	-12.31	22
0.024M NaClO ₄		-5.64	-15.94		23
0.105M NaClO ₄		-5.85	-16.32		23
0.254M NaClO ₄		-5.89	-16.46		23
0.506M NaClO ₄		-5.97			23
	-6.10	-5.95	-16.91		15
1.005M NaClO ₄		-6.06	-16.67		23
	-5.99	-6.03	-17.03		15
2.003M NaClO ₄		-6.16	-16.79		23
	-5.69	-6.10	-17.14		15
0.5m KNO ₃	-5.7	-5.92	-16.22		5
1M NaCl	-5.6	-6.20	-16.96	-12.33	5
1M NaClO ₄		-5.91	-16.43		5
3M NaClO ₄		-6.02	-16.54		5
	-5.35	-6.13	-17.19		15
3M NaCl		-6.64	-18.07	-12.54	5

4.3.6 Hydrolysis of Am^{+++}

Caceci and Choppin used a solvent extraction method to measure the first hydrolysis constant of both $AmOH^{++}$ and $EuOH^{++}$ (24). Apparent stability constants were determined by extraction of an organoamericium chelate into benzene, from 0.7M NaCl solutions containing oxalate, and buffered with 0.05M hydroxylamine (pH6), or hydrazine (pH8). No hydrolysis was expected at pH6, so that the formation constants of the oxalate complexes were measured. The concentration in the organic phase was calculated from the activity of $^{241}Am^{+++}$, using a NaI(Tl) gamma well counter. Their and other results (25-27) are given in Table 4-8.

Table 4-8. Apparent hydrolysis constants for $Am^{+++} + H_2O = AmOH^{++} + H^+$.

Medium	log K(1)	Method	Reference
I=0	-8.0±1.9	Calculated	This work
0.7M NaCl	-7.54±0.2(21) ^o C	Extraction	24
1.0M NaClO ₄	-7.03±0.05		25
I=0	≤-8.2(22) ^o C	Solubility	27
1.0M NaClO ₄	-7.5±0.3	Potentiometric	26
1.0M NaClO ₄	-8.73	Calculated	This work

4.3.7 Am-F Complexes

Nash and Cleveland studied formation of the AmF^{++} ion pair using an ion-exchange method, over the temperature range 5-45°C (31). The measured substance was ^{241}Am , in 0.1M NaClO₄ media using a Ge(Li) gamma spectrometer. Values of $\Delta_r H^\circ$ and $\Delta_r S^\circ$ for the formation reaction were calculated using the van't Hoff equation:

$$\frac{d \ln K}{dT} = \frac{\Delta_r H}{RT^2} \quad (15)$$

and

$$\log K = \frac{A}{T} + B \quad (35)$$

where $\Delta_r H^\circ = -2.303RA$; $\Delta_r S^\circ = 2.303RB$. Results are summarized in Table 4-9.

Table 4-9. Tabulation of thermodynamic values for the formation of AmF^{++} and AmF_2^+ (31).

Medium	logK(I)	logK(I)	$\Delta_r H, kJ/mol$	$\Delta_r S, J/mol/K$
	AmF^{++}	AmF_2^+	AmF^{++}	AmF^{++}
0.1M $NaClO_4$	2.59±0.02	2.17±0.06	22.9±1.6	126±5
0.5M $NaClO_4$	3.39, 2.72			
1.0M $NaClO_4$	2.49±0.02	-	27.6±2.1	140±5

4.3.8 Hydrolysis of NpO_2^+

Lierse, Treiber and Kim studied the hydrolysis of NpO_2^+ in 1M $NaClO_4$ (28) by a method in which freshly prepared and uncharacterized $^{237}NpO_2OH(am?)$ was dissolved in $HClO_4$ and transferred to a solution of 1M $NaClO_4$ under Ar. Carbonate free 6.6M NaOH was added to obtain pH 13. The system was equilibrated for two days, and equilibrium was assumed after this time. The solid was separated, and the Np concentration determined radiometrically. Their results for the reaction $NpO_2^+ + OH^- = NpO_2OH(aq)$, as well as the solubility of $NpO_2OH(am?)$ are shown in Table 4-10.

Table 4-10. Apparent formation constants of the ion pair, $*NpO_2OH(aq)$ and solubility of $NpO_2OH(am)$.

Medium	**logK _{sp}	logK(I)	Method	Ref.
I=0	-9.77	-8.95	Calculated	This work
0.1M Cl^-	<-9.2	-8.85	Solubility	5
I=0.1	-9.2	-	Titration	in 28
0.2, 20°C	-9.0	-10.1	Solubility	in 28
I=0.2	-9.43	-9.00	Calculated	This work
0.02, 23°C	-9.73	-8.91	Potentiometry	93
1.0M $NaClO_4$	-	-9.12	Solubility	29
1.0M $NaClO_4$	-8.81	-11.43	Titration	28
0.2M $NaClO_4$	-	-9.59	Extraction	30
0.1M $NaClO_4$	-9.51	-8.97	Calculated	This work
1.0M $NaClO_4$	-9.17	-9.19	Calculated	This work
I=2.0	-8.98	-9.43	Calculated	This work
I=3.0	-8.84	-9.67	Calculated	This work

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

** Reaction: $NpO_2OH(am) = NpO_2^+ + OH^-$.

In Table 4-10, $\log K_{sp}$ is the solubility product of $NpO_2OH(am?)$. Our $\log K^o$'s were calculated from our data for NpO_2^+ , H_2O and the Davies equation for $\log K(I=0.1)$.

4.3.9 NpO_2^+ - Carbonate Complexes

Bidoglio, Tanet and Chatt studied the complexation of NpO_2^+ with carbonate under conditions simulating a geologic repository (30). Complexation was investigated using a solvent extraction technique involving a mixture of trioctyl methylammonium chloride and 2-thenoyl trifluoroacetone in benzene. The short-lived ^{239}Np was used, and the gamma emissions counted by either a NaI(Tl) crystal detector, or a liquid scintillation counter. Both the ion pair $NpO_2CO_3^-$ and the higher complex $NpO_2(CO_3)_2^{--}$ were identified. Formation constants for both substances are summarized in Table 4-11.

Table 4-11. Apparent formation constants of NpO_2^+ - carbonates, from Reference 30.

I, mol/kg	$\log K_{11}(I)$	$\log K_{12}(I)$	$\log K_{13}(I)$	Method	Ref.
0.05	5.9 ± 0.5	-	16.3 ± 0.5	Electrochemical	in 30
0.2	4.13 ± 0.03	7.06 ± 0.05	-	Extraction	in 30
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 30
1.0	4.31	7.27	-	Calculation	This work
3.0	5.09	8.15 ± 0.25	10.46 ± 0.08	Solubility	in 30
3.0	5.14	8.09	-	Calculation	This work

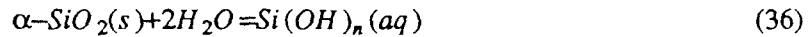
In Table 4-11, $\log K_{11}$ refers to the 1:1 ion pair and $\log K_{12}$ refers to the 1:2 higher complex. Our $\log K_{11}$ and $\log K_{12}$ were calculated from our thermodynamic tables, and from the Davies equation for $I=0.2$ and the extended Debye-Huckel equation for the range $0 < I < 3.0$.

5.0 UNCERTAINTY IN EQUILIBRIUM CONSTANTS

The term uncertainty refers to the numerical value of the standard deviation ($\pm 1\sigma$), in the equilibrium constant or the value of the thermodynamic property at 25°C. In this sense, the definition "is strictly an allowance assigned to a measured value to take into account two major components of error: (a) the systematic error, and (b) the random error attributed to the imprecision of the measurement process" (65). Uncertainty is also used here in a more general manner to denote an uncertain stoichiometry in a chemical reaction related to a geochemical process; to quantify an extrapolation procedure such as calculation of an equilibrium constant in solutions with high ionic strength, based on the values at zero ionic strength; and, to describe substances such as $U(OH)_5^-$ when a question exists on the existence of these substances in geochemical calculations related to solubility (1,68).

5.1 Uncertainty in Thermodynamic Tables

An example of uncertainty in the stoichiometry of a geochemical process is the dissolution of silica. Fournier (48) and Fournier and Marshall (49) characterize the solubility of quartz in hot water by the equation:

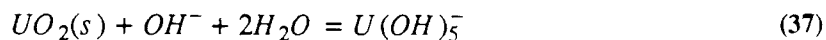


where n is the average number of water molecules bound to one SiO_2 molecule, i.e., the hydration number. Because the thermodynamic information is not available for fractional n , we use $n = 4$ so that the soluble product is silicic acid. In fact, the stoichiometry may be close to $n = 4$ as shown by the comparison of our calculated solubility, with the experimental measurements in Table 4-2. However, the hydration number is not necessarily an integer (48).

Another example is that in which an ionic species may be prevalent only in certain solutions. For example, $\text{Al}(\text{OH})_4^-$ forms significantly only in alkaline media; the neutral substance $\text{Al}(\text{OH})_3(aq)$ has not been verified in solutions with a neutral pH (73). Other substances such as the polynuclear species $\text{Th}_2(\text{OH})_3^{++++}$ and $\text{Th}_6(\text{OH})_{14}^{10+}$ are found in solutions containing chloride, but not in perchlorate (5).

5.2 Contested Substances

A further uncertainty is that associated with the interpretation of solubility measurements, for example the solubility of uraninite, $\text{UO}_2(s)$. In this case, there are two questions: 1. what is the actual solubility in basic media; 2. what is the stoichiometric equation describing the solubility process? The uncertainty arises due to the low solubility of uraninite in alkaline solutions, as well as the readiness with which $\text{UO}_2(s)$ is oxidized to the more soluble hexavalent form (68). As discussed in Section 4.3.4, Baes and Mesmer interpreted the solubility measurements by Gayer and Leider (5) in terms of the following reaction,



The Gibbs energy of formation of $U(OH)_5^-$ could then be calculated from the equilibrium constant for this reaction. Furthermore, the $\log K^\circ$ for this reaction together with the hydrolysis constant to form the 1:1 substance, UOH^{+++} , permitted an estimation of the hydrolysis constants for the other postulated hydrolysis products, $U(OH)_2^{++}$, $U(OH)_3^+$, and $U(OH)_4(aq)$. The assumption by Baes and Mesmer is a regularity in change in $\log K$ with addition of an OH^- ligand (5). Recent publications by Ryan and Rai (7) and Bruno et al. (60) have challenged the evidence supporting the existence of the $U(OH)_5^-$ species. This controversy over the aqueous model for U^{+++} is a source of uncertainty that should be accounted for in calculations of solubility and speciation. More discussion is given in Reference 68.

5.3 Propagation of Standard Deviation

This data base is given as a tabulation of Gibbs energy of formation, enthalpy of formation, entropy and heat capacity of individual substances. The first three quantities are related by the expression $\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ$ so that the individual standard deviations are also related. An additional relationship is $\Delta_r G^\circ = -RT \ln K^\circ$, where $\Delta_r G^\circ$ is obtained from the individual values of the Gibbs energy of formation. The following procedures are used to propagate the standard deviations in the table of thermodynamic properties in calculating the final value of $\Delta_r G^\circ \pm \sigma$; and, to calculate the uncertainty in the Gibbs energy of formation using the standard deviation of $\Delta_r H^\circ$ and S° . These procedures are used if and only if uncertainties have not been assigned to the thermodynamic quantities by authors of publications containing the values.

When the results of replicate experimental measurements follow a random distribution, the following relation is commonly applied to calculate a propagated uncertainty (33, 67).

$$\sigma^2 = (\sigma_1^2 + \sigma_2^2 + \dots + \sigma_n^2) \quad (38)$$

In a chemical reaction such as formation of an OH^- ion pair, the equilibrium is written



where M^{++} is a divalent metal ion. Then

$$\Delta_r G = \Delta_f G [MOH^+] - (\Delta_f G [M^{++}] + \Delta_f G [OH^-]) \quad (40)$$

$$\sigma^2 = (\sigma_{MOH})^2 + (\sigma_M)^2 + (\sigma_{OH})^2 \quad (41)$$

For reactions involving several ligands, each standard deviation is multiplied by a stoichiometric coefficient.

The uncertainty in the equilibrium constant is calculated by the relation $\sigma(\log K) = \sigma(\Delta_r G^\circ)/5708.93$, at 25°C (33). (Gibbs energy is in units of joules). For example, Table 5-1 is a compilation of propagated uncertainties associated with various values of $\log K$ for 7 reactions involving neptunium.

Uncertainties in $\Delta_f G^\circ$ are propagated from the uncertainties in the values of related quantities $\Delta_f H^\circ$ and S° by the following relationship used by Robie et al. (58)

$$\sigma_G^2 = \sigma_H^2 + (298.15\sigma_S^2 + \Sigma(298.15n_i\sigma_{S_i})^2) \quad (42)$$

where σ_H = uncertainty in $\Delta_f H^\circ$, σ_S = uncertainty in S° , and the σ_{S_i} are uncertainties in the entropies of the reference elements, and n_i are the number of moles of each element in the chemical formula of the substance.

Propagated uncertainties can be calculated for data in the Aqueous Solutions Database using DATATRIEVE interfaced to the computerized procedures ADDREACT and COMPLOGK. These procedures are described in Sections 5.3.1 and 5.3.2.

5.3.1 ADDREACT Interface to DATATRIEVE

The procedure ADDREACT (Section 1.3.7) automatically assigns a unique reaction number to a specific chemical equation and merges the numerical values of the various $\Delta_f G^\circ$ and $\Delta_f H^\circ$ with their associated uncertainties. The result is a tabulation of reactants and products, stoichiometric coefficients, $\Delta_f G^\circ$ and $\Delta_f H^\circ$ for each reactant and product, and the uncertainty in $\Delta_f G^\circ$ for each reactant and product. These data are then used to calculate $\Delta_r G^\circ$, $\Delta_r H^\circ$ and $\log K^\circ$ for the reaction, and a propagated uncertainty for each quantity using the computerized procedure, COMPLOGK.

5.3.2 COMPLOGK Interface to DATATRIEVE

The procedure COMPLOGK calculates values of $\log K^\circ$, the magnitude of $\Delta_r H^\circ$ and further calculates a propagated uncertainty as the square root of the sum of the squares of the uncertainties in the individual values of each $\Delta_f G^\circ$ and those of $\Delta_f H^\circ$, according to eq 38. See Table 5-1, as an example.

Table 5-1. Propagated uncertainties calculated according to eq 38 for selected reactions involving neptunium, using ADDREACT and COMPLOGK.

Reaction	$\log K^\circ \pm \sigma$ This work	$\log K^\circ \pm \sigma$ Lemire (33)
$\text{Np}^{++++} + \text{H}_2\text{O} = \text{NpOH}^{+++} + \text{H}^+$	-1.06 ± 1.83	-1.0 ± 1.0
$\text{Np}^{++++} + 2\text{H}_2\text{O} = \text{Np(OH)}_2^{++} + 2\text{H}^+$	-2.83 ± 2.79	-2.8 ± 2.6
$\text{Np}^{++++} + 3\text{H}_2\text{O} = \text{Np(OH)}_3^+ + 3\text{H}^+$	-5.83 ± 3.63	-5.8 ± 3.5
$\text{Np}^{++++} + 4\text{H}_2\text{O} = \text{Np(OH)}_4(\text{aq}) + 4\text{H}^+$	-9.53 ± 3.63	-9.6 ± 3.5
$\text{Np}^{++++} + 5\text{H}_2\text{O} = \text{Np(OH)}_5^- + 5\text{H}^+$	-14.29 ± 7.07	$-14.3 \pm 3.5, -7.0$
$\text{NpO}_2(\text{s}) + 4\text{H}^+ = \text{Np}^{++++} + 2\text{H}_2\text{O}$	-7.82 ± 1.04	-7.8 ± 1.4
$\text{NpO}_2(\text{s}) + \text{OH}^- + 2\text{H}_2\text{O} = \text{Np(OH)}_5^-$	-8.11 ± 7.02	

6.0 SUMMARY

In summary, a consistent tabulation of values for thermodynamic properties of the actinide and other elements important to assessing the performance of nuclear waste repositories has been developed. The content of the tables covers about 40 elements, with emphasis on radionuclides associated with high level waste materials. The resulting computerized data base system facilitates management of thermodynamic tables to meet the following eight major specifications:

- i. All numerical values result from a critical evaluation of selected experimental measurements, published in refereed journals. Besides our assessments, critical evaluations include standard reference data such as CODATA.
- 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 Al and Si are also needed, and are included in Appendix II.
- iii. All values of the Gibbs energy of formation 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 were filled by interpolation, correlation or theoretically based extrapolation.
- v. The ASD is consistent with: the CODATA tables; the fundamental relationship $\Delta_r G^\circ = \Delta_r H^\circ - 298.15\Delta_r S^\circ$ 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 via telecommunication.
- viii. Utility programs were developed to facilitate the use of the data in geochemical codes for sensitivity and uncertainty analysis.

While satisfactory for this purpose, additional research is needed to improve the data base for performance assessment and other applications. The newer research is described in the following section.

7.0 RECOMMENDATIONS FOR ADDITIONAL RESEARCH

After completion of this work, some recommendations are appropriate from the standpoint of an improved thermodynamic tabulation for application to nuclear waste disposal. Future activities should include the following research.

1. Experimental measurements with the objective of generating laboratory data specifically for nuclear waste disposal. A substantial quantity of the data in the Appendixes was obtained from publications of research not directly related to nuclear waste. The data were commonly obtained in aqueous solutions of one supporting electrolyte, for example sodium perchlorate. However, natural waters contain other dissolved ions such as chloride and carbonate. Laboratory measurements of apparent equilibrium constants in solutions containing a mixture of dissolved ions will better reflect the solubility, speciation and uncertainties in these measurements, and thus be more suitable for performance assessment studies.
2. Laboratory data which confirm the presence or absence of aqueous species in pure solutions, and in solutions mimicing natural groundwaters, preferably at expected ambient concentrations. The solubility of waste radionuclides is enhanced when aqueous species are formed, thus it is important to know which species to include, or exclude, in a thermodynamic table. There is current research in this area (78,85).
3. Measurements of apparent formation constants of radionuclides and other important elements, with chloride ions in saline media. The measurements should cover the range 0 to 6m NaCl (or saturation). Bucher et al. (78) discuss the questionable data now available for chloride complexes of U, Np, Pu and Am. For example, the equilibrium constant for $M^{++++} - Cl^-$ systems must be larger than those of the $M^{+++} - Cl^-$ systems; however the present data indicate the opposite.
4. Development of a user-friendly computerized data base readily accessible by telecommunications, centered around prompts to the user. The data base should be compatible with computer codes such as MINEQL, PHREEQE and EQ3/EQ6 for easy transferal of the data to the code. See for example the data base for the MINEQL pre-processor in Figure 7-1.
5. Generation of ionic activity coefficients covering a wide range of ionic strength, including 6m NaCl solutions. A table of trace activity coefficients would be prepared for aqueous species important to waste disposal. The tabulation would permit calculation of apparent equilibrium constants for predicting the solubility of radionuclides in ambient groundwaters in contact with tuff minerals (72).
6. Use of the data base and preprocessors in sensitivity analysis. Figure 7-2 shows possible applications.

Ion	Notation	logK°	Enthalpy	Uncertainty
SrOH+	was	-11.820	0.000	0.199
	is	-13.124	14.539	
FeOH++	was	-2.190	10.400	0.408
	is	-2.190	9.921	
UO2OH+	was	-5.300	0.000	0.642
	is	-5.751	10.992	
(UO2)2(OH)2++	was	-5.680	0.000	1.144
	is	-5.546	9.885	
(UO2)3(OH)5+	was	-15.650	0.000	1.652
	is	-15.546	25.275	
UO2CO3(aq)	was	10.070	0.000	0.644
	is	10.183	-3.358	
UO2(CO3)2--	was	16.980	0.000	0.519
	is	17.336	2.438	
UO2(CO3)3----	was	21.400	0.000	0.532
	is	21.861	-10.098	
UO2F+	was	5.100	0.000	0.653
	is	5.177	-0.657	
UO2F2(aq)	was	8.960	0.000	0.687
	is	8.899	-0.813	
UO2F3-	was	11.350	0.000	0.739
	is	11.395	-0.753	
UO2F4--	was	12.570	0.000	0.808
	is	12.490	-0.980	
UO2Cl+	was	0.240	0.000	1.449
	is	1.764	-0.053	
UO2SO4(aq)	was	2.730	0.000	0.795
	is	2.938	5.163	
UO2(SO4)2--	was	4.220	0.000	0.804
	is	4.246	6.190	
UOH+++	was	-0.650	0.000	1.449
	is	-0.706	11.718	
U(OH)2++	was	-2.260	0.000	3.523
	is	-2.305	17.725	
U(OH)3+	was	-4.890	0.000	3.523
	is	-4.955	22.655	
U(OH)4(aq)	was	-8.550	0.000	3.524
	is	-8.481	24.766	
U(OH)5-	was	-13.180	0.000	

Figure 7-1. Selected portion of data base for preprocessor linking the ASD with the MINEQL code. Table shows original data, "was", and the ASD values, "is". Enthalpy is the enthalpy of reaction, in kcal/mol; and, uncertainty is the propagated uncertainty in $\log K^\circ$ calculated as described in Section 5.3.

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

1. Reads ΔG values and σ 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 7-2. Functions of the thermodynamic data base system in the preprocessor for sensitivity analysis. $\Delta G = \Delta_f G^\circ$; σ = standard deviation; LHS = Latin Hypercube Sampling procedure.

8.0 LITERATURE CITED

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Appendix I. Key Values

Heat capacity of anions and uncharged aqueous species calculated from eq 7B and eq 7A; for cations, the following equation was used only for Appendix I and II:

$$C_p^\circ[M^{n+}] = 229.2 - 150.3 z^{-(2/3)} \text{ S}^\circ$$

when reference in table is Ref. 9. Standard state is one atmosphere.

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 ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
O ₂ (g)	0.000	0.000	205.04 0.01	29.38 0.0	2555
O ₂ (aq)	16.530 0.2	-12.138 0.2	108.90 0.80	224.00 25.0	9777
H ₂ (g)	0.000	0.000	130.57 0.03	28.82	2557
H ₂ (aq)	17.780 0.9	-4.040 0.8	57.37 2.50	175.00 25.0	9777
H ₂ O(g)	-228.572 0.1	-241.814 0.0	188.72 0.04	33.61	2557
H ₂ O(l)	-237.129 0.1	-285.830 0.1	69.95 0.08	75.29	2557
e ⁻ ,electron	0.000	0.000	65.28 0.01	14.42 0.1	0066
Si(OH) ₄ (aq)	-1308.000 1.7	-1460.140 1.7	180.00 4.20	145.40	9921
H ⁺	0.000 0.0	0.000 0.0	0.00 0.00	0.00 0.0	2222
NH ₄ ⁺	-79.310 0.1	-133.260 0.3	111.17 0.75	69.00	2557
Li ⁺	-292.620 0.2	-278.455 0.1	11.30 0.35	60.70	9557
Na ⁺	-261.905 0.1	-240.300 0.1	58.41 0.20	42.40	2557
K ⁺	-282.224 0.1	-252.170 0.1	101.04 0.25	13.00 4.1	9557
Rb ⁺	-283.980 0.2	-251.120 0.1	120.46 0.40	-2.00	2559

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Cs ⁺	-292.020 0.2	-258.040 0.1	132.84 0.40	-10.00	2559
Tl ⁺	-32.430 0.2	5.360 1.2	125.50 4.00	-5.00	2229
Cu ⁺	49.980 0.1	71.670 0.1	40.60 0.40	52.00	2229
Ag ⁺	77.107 0.1	105.750 0.1	73.38 0.40	30.00	2559
NpO ₂ ⁺	-915.000 5.4	-978.200 4.6	-21.00 8.00	92.00	4448
Hg ₂ ⁺⁺	153.607 0.1	166.820 0.2	65.52 0.80		9550
Hg ⁺⁺	164.700 0.1	170.160 0.2	-36.32 0.80		9550
Fe ⁺⁺	-91.550 1.0	-92.730 0.8	-107.00 2.50	-4.00 33.0	1197
Mg ⁺⁺	-454.800 1.7	-466.850 1.3	-138.10 1.70	-16.00 8.0	2227
Ca ⁺⁺	-552.870 0.8	-543.100 0.8	-56.40 0.40	-30.00	9557
Sr ⁺⁺	-563.830 0.8	-550.900 0.5	-31.50 2.00	-34.80	333*
Ba ⁺⁺	-555.360 2.0	-532.500 2.0	8.40 2.00	-45.60	333*
Ra ⁺⁺	-561.500 10.0	-527.600	54.00	-107.00	2229
Cu ⁺⁺	65.520 0.1	65.690 0.8	-97.10 1.20	-17.00	955*
Sn ⁺⁺	-27.200 0.8	-8.900 0.8	-15.80 4.00	-60.00	9559
Pb ⁺⁺	-23.970 0.1	0.920 0.3	17.70 0.80	-83.00	9559
Ni ⁺⁺	-45.600 0.9	-54.000 0.9	-128.90 0.90	-42.00	222*
Mn ⁺⁺	-230.300 0.9	-221.160 0.1	-67.76 0.85	-11.00 3.0	9777

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
UO ₂ ⁺⁺	-952.700 2.1	-1019.200 2.5	-98.30 4.00	5.00	9558
PuO ₂ ⁺⁺	-756.900 7.1	-822.200 6.7	-88.00 8.00	11.00	4448
Zn ⁺⁺	-147.230 0.2	-153.390 0.2	-109.60 0.70	-21.00	955*
Al ⁺⁺⁺	-489.530 1.4	-531.000 4.0	-308.00 15.00	-119.00 10.0	9***
Fe ⁺⁺⁺	-17.280 1.0	-50.110 0.8	-279.00 4.10	-35.00 0.1	*999
Th ⁺⁺⁺⁺	-704.600 5.4	-769.000 2.5	-423.00 17.00	-89.00 11.0	4449
Pa ⁺⁺⁺⁺	-565.000 17.0	-619.700 13.0	-397.00 42.00	-106.00	4449
F ⁻	-281.750 0.7	-335.350 0.7	-13.18 0.54	-117.00 4.0	9557
Cl ⁻	-131.228 0.1	-167.080 0.1	56.73 0.16	-125.50	2557
Br ⁻	-103.960 0.2	-121.500 0.2	82.84 0.20	-132.20 4.2	2557
I ⁻	-51.669 0.8	-56.900 0.8	106.70 0.20	-120.50 4.2	9557
OH ⁻	-157.244 0.1	-230.025 0.1	-10.71 0.20	-140.50 4.0	2557
NO ₃ ⁻	-110.780 0.4	-206.860 0.4	146.94 0.04	-72.00 4.0	9777
SO ₄ ⁻⁻	-744.530 0.4	-909.600 0.4	18.83 0.50	-278.00 6.7	2557
CO ₃ ⁻⁻	-527.730 0.3	-675.150 0.3	-49.96 0.80	-273.50 4.0	9777

Comments:

Reference 0 = no data; 1 = Cobble et al.,1982; 2 = Wagman et al.,1982; 3 = Busenberg et al.,1984,1986; 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 O₂(aq),H₂(aq),we calculated $\Delta_f G$ using $\Delta_f H$ and S from L.Brewer:"Thermodynamic Data for Flue-Gas Desulfurization",in"Flue Gas Desulfurization", LBL-12342, CONF-801176, Lawrence Berkeley Laboratory (Sept.1981). Heat capacity of O₂(aq) and H₂(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⁺⁺,Hg₂⁺⁺ compare well with Hepler;Olofsson:Chem.Rev.1975, v.75,585 GHS values for Sr⁺⁺ from E.Busenbergl;L.N.Plummer; V.B.Parker:Geochim.Cosmochim.Acta 1984,v.48,2021. $\Delta_f G[\text{UO}_2^{++}]$ was calculated here using CODATA values of $\Delta_f H$ and S;Cp[UO₂⁺⁺] from R.J.Lemire;P.R.Tremaine: J.Chem.Eng.Data 1980, v.25, 361. $\Delta_f H[\text{Fe}^{+++}]$ calculated from free energy and entropy. * $\Delta_f G[\text{Fe}^{+++}]$ from Flynn:Chem.Rev.1984,v.84,31. For Cl⁻, L'vov; Rakhmievich; I.A.Dibrov: Russ.J.Phys.Chem.

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Appendix II. Thermodynamic Tables

The elements are in alphabetical order in this Appendix. Heat capacity of solids calculated from correlation $C_p^\circ = 20.7 + 0.621S^\circ$, when Reference = 9. Gibbs energy of formation of crystalline solids correlated with enthalpy of formation by the equation $\Delta_f G^\circ = 25.152 + 0.938\Delta_f H^\circ$, when Reference = 9.

In Comments portion of tables, the symbol denoting standard state conditions, $^\circ$, is often omitted. For example, $\log K^\circ$ is also $\log K$, and $\Delta_f G^\circ$ is $\Delta_f G$. Heat capacity of solids calculated from correlation $C_p^\circ = 20.7 + 0.621 S$, when Ref. = 9. Heat capacity of cations calculated from $C_p^\circ = 229.2 - 150.3 z - (2/3) S^\circ$, when Ref. = 9.

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0. No data. Values are missing.

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PROPERTIES OF ELEMENTAL ALUMINUM:

Atomic Number: 13
 Formula Mass: 26.9815
 Electronic Configuration:
 Electronegativity: 1.5
 Hydration Number: 11.9 (Hinton,1971)
 Ionic Radius: 0.51 angstrom
 Selected Average for Soils: 71,000 ppm
 Concentration in Natural Waters: Al present in nearly
 all natural waters.

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Al(s)	0.000	0.000	28.35 0.08	24.31	8558
α -Al ₂ O ₃ (s),corundum	-1582.300 1.3	-1675.700 1.3	50.94 0.10	79.03	8558
AlO(OH)(s),boehmite	-916.072 2.1	-990.675 2.1	48.45 0.21	65.43	8888
AlO(OH)(s),diaspore	-921.432 8.0	-999.944 8.0	35.34 0.04	53.21	8888
Al(OH) ₃ (s),gibbsite	-1156.500 1.2	-1294.630 1.2	68.44 0.14	91.76	8888
Al ₂ SiO ₅ (s),kyanite	-2445.120 1.7	-2596.010 1.7	82.30 0.13	121.60	2222
Al ₂ SiO ₅ (s),andalusite	-2443.720 1.7	-2591.900 1.7	91.39 0.14	122.60	2222
Al ₂ SiO ₅ (s),sillimanite	-2440.900 1.7	-2587.770 1.7	95.79 0.14	123.20	2222
Al ₂ Si ₂ O ₅ (OH) ₄ (s),kaolinite	-3802.496 4.0	-4122.615 3.9	205.15 0.47	245.94 0.4	8888
Al ₂ Si ₂ O ₅ (OH) ₄ (s),dickite	-3798.770 3.8	-4133.302 3.8	197.06 3.20	239.36 0.7	8888
Al ₂ Si ₂ O ₅ (OH) ₄ (s),halloysite	-3783.194 3.0	-4114.854 2.9	203.33 3.20	244.93 0.8	8888
Al ₂ Si ₄ O ₁₀ (OH) ₂ (s),pyrophyllite	-5268.625 4.4	-5642.319 4.4	239.33 1.02	294.13 0.3	8888

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
AlF ₃ ·3H ₂ O(s)	-2051.000 2.0	-2296.000	209.00		9990
Al ⁺⁺⁺	-489.530 1.4	-531.000 1.4	-308.00 15.00	-119.00 10.0	4443
AlOH ⁺⁺	-698.310 1.3	-767.050 2.0	-166.00 10.00	40.00	1119
Al(OH) ₂ ⁺	-905.160 1.3	-1011.680 1.3	-59.59	105.00	9999
Al(OH) ₃ (aq)	-1104.430 1.3	-1256.310 1.3	21.57	-540.00	9999
Al(OH) ₄ ⁻	-1305.600 1.4	-1500.940 2.7	111.30 3.70	96.50	3933
Al ₂ (OH) ₂ ⁺⁺⁺⁺	-1409.100 1.7	-1555.400 8.1	-361.00 29.00	-130.00	1919
Al ₃ (OH) ₄ ⁵⁺	-2337.140 0.6	-2785.600 1.0	-405.70 54.00	-252.00	1919
Al ₁₃ O ₄ (OH) ₂₄ ⁷⁺	-12438.100 0.3	-13772.500 8.0	-133.30 30.00	-734.00	1919
AlF ⁺⁺	-811.820 0.2	-860.770	-165.30	39.00	6669
AlF ₂ ⁺	-1123.900 0.3	-1190.800	-58.60	118.00	6669
AlF ₃ (aq)	-1427.040 0.3	-1523.900	7.50	-470.00	6669
AlF ₄ ⁻	-1720.270 0.4	-1857.520	39.70	-114.00	6669
AlF ₅ ⁻⁻	-2008.300 1.0	-2192.800	46.90	-238.00	6669
AlF ₆ ⁻⁻⁻	-2291.100 1.0	-2533.000	20.90	-394.00	6669
Al(OH)F ⁺	-1012.700 1.5	-1114.800	-111.50	153.00	7799
Al(OH) ₂ F(aq)	-1213.100 1.5	-1341.100	35.21	-517.00	7799
Al(OH) ₃ F ⁻	-1409.900 1.5	-1553.500	216.00	4.00	7799

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Al(OH)F ₂ (aq)	-1320.000 1.5	-1467.200	-95.40	-493.00	7799
Al(OH) ₂ F ₂ ⁻	-1517.900 2.5				7000

Comments:

Ref.1=Baes;Mesmer,1976; 2=Robie,1988; 3=Hovey;Tremaine,1986 and Hovey;Hepler;Tremaine,1988; 4=Robie et al.,1978; 5=CODATA,1978; 6=Naumov et al.,1974; 7=Sanjuan;Michard,1987; 8=Robinson et al.,1982; 9=This work. $\Delta_f G^\circ$ of all hydrolysis species except Al(OH)₂⁺, Al(OH)₃(aq) and Al(OH)₄⁻ calculated from values of logK^o in Ref.1; S° of Al₂(OH)₂⁺⁺⁺⁺, Al₃(OH)₄⁵⁺, Al₁₃O₄(OH)₂₄⁷⁺ calculated from data in Ref.1, assuming values of $\Delta_f S^\circ$ at 1mKCl are also values at I=0. $\Delta_f H^\circ$ values calculated from G=H-TS, for these species. $\Delta_f H^\circ$ [Al(OH)₂⁺] obtained from interpolation of plot of $\Delta_f H^\circ$ versus nOH⁻. Both Gibbs Energy and enthalpy of Al(OH)₃(aq) obtained by interpolation of plots of Gibbs energy and enthalpy versus nOH⁻. Values of Cp^o calculated from correlations, when reference is 9. May;Helmke;Jackson;Geochim.Cosmochim.Acta 1979,v.43,861 measure $\Delta_f G^\circ$ = -698.3kJ/mol for AlOH⁺⁺, -905.8 for Al(OH)₂⁺, -1311.7 for Al(OH)₄⁻. Couturier et al.,1984 tabulate Gibbs energy and enthalpy of formation for acidic and basic solutions: for Al⁺⁺⁺, AlOH⁺⁺, Al(OH)₂⁺, $\Delta_f G^\circ$ = -489.5,-483.7; -698.3,-692.5; -1311.3,-1305.4 kJ/mol,respectively. For $\Delta_f H^\circ$: -525.1,-529.7; -760.6,-765.3; -1490.7,-1495.4 kJ/mol, respectively. Brown et al: J.Chem.Soc.Dalton Trans. 1985,p.1967 measure log K₁₁(I=0.1)=-5.33, logK₁₂(I=0.1)=-10.91; logK₃₄(I=0.1)=-13.13 compared to our calculated -5.41, -9.93 and -13.73, respectively, using Gibbs energy values in this work,and the Davies equation.Sanjuan;Michard (1987) find that low values in alkaline media can be related to a new solid phase, bayerite or nordstrandite, in the presence of initial gibbsite, based on infrared spectra of solids. Our values for the Al-OH-F species were obtained from Sanjuan and Michard, 1987,cited above. Their values were obtained in part from Couturier,et al.,1986. Our uncertainties for the AlF_n series are partly from Smith and Martell,1976. Data for AlF₃.3H₂O(s) are from Bard et al., 1985, p.570. Hedlund;Sjoberg;Ohman: Acta Chem.Scand. 1987, v.A41, 197 find evidence for species which have tentative formulae Al₂(OH)₂CO₃⁺⁺, and Al₃(OH)₃CO₃⁺⁺⁺⁺, in 0.1M and 3.0M Na(Cl). Hovey;Tremaine,1986 is Geochim.Cosmochim.Acta 1986, v.50, 453. B.S. Hemingway, Adv. Phys. Geochem., S.K. Saxena, ed., Vol.2, Springer(1982),p. 298 calculates the following values of $\Delta_f G^\circ$: Al⁺⁺⁺=-489.8±4.0; AlOH⁺⁺=-701.4±4; Al(OH)₂⁺=-903.4±4.0; Al(OH)₄⁻=-1305.0±1.3 from solubility of nordstrandite. Ref. 2 = R.A. Robie, Private Communication, April 8, 1988.

PROPERTIES OF ELEMENTAL AMERICIUM:

Atomic Number: 95

Formula Mass: 241.06

Electronic Configuration: $5f^7 7s^2$

Electronegativity: 1.3

Hydration Number: 12.8 (F.David,1986)

Ionic Radius: 0.975 angstrom

Selected Average for Soils:

Concentration in Natural Waters:

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Am(g)	242.000	284.000 4.0	194.40	20.79	1111
Am(s)	0.000	0.000	55.40 2.00	25.50 1.0	0011
Am ₂ O ₃ (s)	-1614.200 8.0	-1692.000 8.0	158.00		9110
AmO ₂ (s)	-880.060 2.5	-932.200 2.5	86.00		9110
AmF ₃ (s)	-1523.394 8.1	-1588.300 8.0	127.60 4.00	100.00	3339
AmF ₃ (aq)	-1500.000 4.0	-1590.000	56.00	-439.00	9999
AmF ₄ (s)	-1627.000 29.0	-1719.600 29.0	148.50 4.00	113.00	3339
AmCl ₃ (s)	-910.857 1.8	-977.800 1.3	164.80 6.30	123.00	1339
AmBr ₃ (s)	-786.592 8.6	-809.600 7.0	205.00 16.70	148.00	3339
AmI ₃ (s)	-613.793 9.4	-612.000 7.0	234.30 20.90	166.00	3339
Am(OH) ₃ (s)	-1168.000 3.0	-1272.000 25.0	209.00	150.00	1999
Am(OH) ₃ (aq)	-1159.215 10.0	-1380.000	-183.00	-509.00	2999

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
AmH ₂ (s)	-143.000 15.0	-184.000 15.0	48.00 4.00	38.00 3.0	1111
AmOCl(s)	-904.162 3.3	-953.500 2.5	102.50 7.10	84.00	3339
AmOBr(s)	-860.000 8.7	-890.000 7.0	117.10 16.70	73.00	1119
Am(OH)(CO ₃)(s)	-1414.300 1.6	-1535.000 25.0	131.00	102.00	4999
Am ₂ (CO ₃) ₃ (s)	-2996.160 2.0	-3221.000 25.0	295.00	204.00	4999
Am ⁺⁺⁺	-599.100 3.8	-616.700 1.3	-199.00 13.00	-88.00	9669
Am ⁺⁺⁺⁺	-347.000 9.0	-406.000 6.0	-408.00	-100.00	1119
AmO ₂ ⁺	-741.000 6.8	-805.000 5.0	-21.00 8.00	93.00	9669
AmO ₂ ⁺⁺	-587.000 5.1	-652.000 2.0	-88.00 8.00	-12.00	9669
AmOH ⁺⁺	-790.560 10.0	-844.800	-87.90	-13.00	2999
Am(OH) ₂ ⁺	-976.885 10.0	-1110.000	-122.00	160.00	2999
AmF ⁺⁺	-899.400 2.1	-933.040 2.0	-88.20 5.00	-12.00	9999
AmF ₂ ⁺	-1196.000 2.2	-1269.000 2.0	-54.40	115.00	9999
AmCl ⁺⁺	-737.410 2.0	-799.400 15.0	-173.00	44.00	2999
AmCl ₂ ⁺	-870.650 2.0	-983.000 40.0	-165.00	190.00	2999
AmSO ₄ ⁺	-1367.200 2.0	-1505.000 15.0	-31.00	100.00	2999
Am(SO ₄) ₂ ⁻	-2119.400 2.4	-2391.000 40.0	92.00	-79.00	2999
AmHCO ₃ ⁺⁺	-1217.550 1.4	-1337.000 15.0	-99.00	-5.00	7999

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Am(HCO ₃) ₂ ⁺	-1826.410 1.5	-2060.000 40.0	-37.00	104.00	7999
AmCO ₃ ⁺	-1164.100 2.0	-1277.000 15.0	-76.40	130.00	8999
Am(CO ₃) ₂ ⁻	-1734.700 2.0	-1957.000 40.0	0.90	-140.00	8999
AmH ₂ PO ₄ ⁺⁺	-1713.800				9000
Am(H ₂ PO ₄) ₂ ⁺	-2838.400				9000

Comments:

Reference 1 is L.R.Morss,1985;2=Phillips,1982;3=IAEA,Part8,1983;4=Kerrisk,1984; 6=F.David:J.Less-Common Metals 1986,v.121,27; 7=Bidoglio: Radiochim. Radioanal.Letters 1982,v.53,45;8=R.Lundqvist:Acta Chem.Scand. 1982,v.A36,741. 9=This work. SmOH⁺⁺ used as model for AmOH⁺⁺ in estimating enthalpy and entropy. Enthalpy of Am₂O₃(s) is from L.Morss; D.C.Sonnenberger: J.Nucl.Mater. 1985,v.130,266. Gibbs energy of AmOHCO₃(s) from R.J.Silva: UCRL-91821, Lawrence Livermore National Laboratory,Livermore,CA (Jan.12,1985). Data for AmF⁺⁺ and AmF₂⁺ from K.L.Nash and J.M.Cleveland: Radiochimica Acta 1984,v.37,19. For Am⁺⁺⁺⁺ + e = Am⁺⁺⁺, E⁰ = 2.62 v. Reference is L.R.Morss; J.Fuger: J.Inorg.Nucl.Chem. 1981,v.43, 2059. D.Rai; R.G.Strickert; D.A.Moore; J.L. Ryan: Radiochim. Acta 1983,v.33,201 measure for Am(OH)₃(s), log K_{sp} = -17.5±0.3; log K ≤ -8.2 for Am⁺⁺⁺ + H₂O = AmOH⁺⁺ + H⁺. We calculate logK(I=1.0)=-8.70 for this hydrolysis reaction,using b=0.3 (value for NdOH⁺⁺,from Baes;Mesmer,1976). Nair et al.:Radiochim. Acta 1982, v.32, 37 find log K(I=1.0) = -7.03 for this hydrolysis reaction. Lundqvist, Ref.8, measures log K(I=1.0)= -7.5; and Caceci; Choppin: Radiochim. Acta 1983, v.33, 101 find log K(I=0.7) = -7.54 in 0.7M NaCl solution, at 21°C, for this first hydrolysis reaction. Considering difficulty in measuring Am⁺⁺⁺ hydrolysis, agreement is probably satisfactory for one unit of log K(I=1.0). Values for AmF₃(aq) calculated in this work from the linear change in $\Delta_f G$ with number of F⁻ ligands; and $\Delta_f H$ from the linear relation between $\Delta_f G$ and $\Delta_f H$; also,Am(OH)₂⁺;Am(OH)₃(aq). Values of log K^o for both AmH₂PO₄⁺⁺ and the 1:2 complex Am(H₂PO₄)₂⁺ from Lebedev et al.: Radiokhimiya 1979,v.21,692. Kerrisk (1984) is LA-10040-MS (July 1984)

PROPERTIES OF ELEMENTAL BARIUM:

Atomic Number: 56
 Formula Mass: 137.34
 Electronic Configuration:
 Electronegativity: 0.9
 Hydration Number: 10.7
 Ionic Radius: 1.35 angstrom, Coordination No. = 6.
 Selected Average for Soils: 430 mg/kg.
 Concentration in Natural Waters: 49 µg/L in drinking water.

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Ba(s)	0.000	0.000	62.42 0.80	28.09	1111
BaO(s)	-520.390 2.1	-548.100 2.1	72.10 0.40	47.28	1111
Ba(OH) ₂ ·8H ₂ O(s)	-2792.800 3.0	-3342.200	427.00		2220
Ba(OH) ₂ (aq)	-875.300 3.0	-995.400	-8.40		7770
BaCl ₂ (s)	-810.400 0.5	-858.600	123.68	75.14	2222
BaCl ₂ (aq)	-823.210 0.5	-871.950	122.60		2220
BaCl ₂ ·2H ₂ O(s)	-1296.320 1.0	-1460.130 1.0	202.90 0.50	161.96	2222
BaCO ₃ (s),witherite	-1132.210 2.2	-1210.850 2.2	112.13 2.10	85.35	1111
BaCO ₃ (aq)	-1067.850 2.2	-1222.600	-143.30	-319.00	4449
BaSO ₄ (s),barite	-1362.200 1.3	-1473.200 1.0	132.21 0.80	101.75	1111
BaSO ₄ (aq)	-1318.400 0.5				9000
Ba(IO ₃) ₂ (s)	-864.700	-1027.200	249.40	187.40	2222

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Ba ₅ (IO ₆) ₂ (s)		-3945.960			0600
Ba ⁺⁺	-555.360 2.0	-532.500 2.0	8.40 2.00	-45.60	4445
BaOH ⁺	-721.600 1.0	-754.300 1.0	56.10		9930
BaCl ⁺	-691.200 5.0				9000
BaHCO ₃ ⁺	-1136.680 2.2	-1245.700	10.00	72.20	4449
BaB(OH) ₄ ⁺	-1722.200 3.0				8000

Comments:

Reference 1=Robie et al.,1978;2=Wagman et al.,1982;3=Naumov et al.,1974. 4=E.Busenberg;L.N.Plummer: Geochim.Cosmochim.Acta 1986,v.50,2225. 5=J.K.Hovey;L.G.Hepler;P.R.Tremaine:J.Solution Chem. 1986,v.15,977. 6=C.F.V.Mason;J.D.Farr;M.G.Bowman:J.Inorg.Nucl.Chem. 1980,v.42,799. Ref. 7 = Bard et al., 1985; 8 = R.L.Bassett, 1980. Ionic radius from Shannon and Prewitt; selected average from soils from Lindsay; concentration in natural waters Standard Methods, 15th ed. Our selected $\Delta_f G^\circ[\text{Ba}^{++}]$ gives $E^\circ = -2.88$ v. $\Delta_f G^\circ = -560.74$ kJ/mole from Ref. 1 . gives $E^\circ = -2.91$ v., agreeing with -2.92 ± 0.01 v. in Bard et al. $\Delta_f G^\circ[\text{BaCl}^+, \text{aq}]$ calculated from value of formation constant, $I=0$ and 18°C, given in Smith and Martell, 1976. $\Delta_f G^\circ$ for both BaOH⁺ and BaSO₄(aq) calculated from log K data in F.J.Millero; D.R.Schreiber: Am.J.Sci. 1982,v.282,1508. We calculate $\Delta_f H^\circ = -13.2$ kJ/mol for dissolution reaction BaCl₂(s) = Ba⁺⁺ + 2Cl⁻, comparing with -14.30 measured by A.S.Monaenkova; G.I.Alekseev; A.F.Vorob'ev: Russ.J.Phys.Chem. 1983,v.57,1323.

PROPERTIES OF ELEMENTAL BROMINE:

Atomic Number: 35

Formula Mass: 79.9090

Electronic Configuration: 3s2 3p6 3d10 4s2 4p5

Electronegativity: 2.8

Hydration Number: 2.6 (Br⁻)

Ionic Radius: 1.94 angstrom

Selected Average for Soils: 5 mg/kg (ppm)

Concentration in Natural Waters: < 1 mg/L in drinking
water: brines 400 mg/L

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Br ₂ (l)	0.000	0.000	152.21 0.04	75.69	0012
Br ⁻	-103.960 0.2	-121.500 0.2	82.84 0.20	-132.20 4.2	2113

Comments:

Reference 1 = CODATA,1978; 2 = Wagman et al.,1982; 3 = L.Brewer, 1981.

PROPERTIES OF ELEMENTAL CESIUM:

Atomic Number: 102
 Formula Mass: 132.9054
 Electronic Configuration:
 Electronegativity: 0.75
 Hydration Number: 1.5
 Ionic Radius: 1.69 angstrom
 Selected Average for Soils: 6 mg/kg
 Concentration in Natural Waters: <10 ug/L

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Cs(s)	0.000	0.000	85.23 0.40	32.17	5551
Cs ₂ O(s)	-308.140 1.2	-345.770 1.2	146.86 0.44	75.98 0.2	1111
CsOH(s)	-370.690 0.9	-416.726 0.8	98.74 4.20	67.86	3333
Cs(OH).H ₂ O(s)		-754.040			0100
CsOH(aq)	-449.250	-488.270	122.30		1110
CsF(s)	-525.500 1.0	-553.500 1.0	92.80 0.10	51.09	1111
CsF(aq)	-570.810	-590.910	119.20		1110
CsCl(s)	-414.530 0.8	-443.040 0.8	101.17 0.20	52.47	1111
CsCl(aq)	-423.240	-425.530	189.54	-146.90	1111
CsI(s)	-340.580 1.0	-346.600 1.0	123.05 0.20	52.80	1111
CsI(aq)	-343.590	-313.470	244.30	-152.70	1111
CsI ₃ (s)	-354.330	-361.900	235.10		1110
CsI ₄ (s)	-357.700	-365.700	290.80		1110
Cs ₂ SO ₄ (s)	-1323.580 0.8	-1443.020 0.8	211.92	134.89	1111
Cs ₂ SO ₄ (aq)	-1328.560	-1425.820	286.20		1110

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
CsHSO ₄ (s)		-1158.100			0100
CsHSO ₄ (aq)	-1047.930	-1145.620	264.80		1110
Cs ₂ CO ₃ (s)	-1054.300	-1134.930 0.6	204.47	123.85	1111
Cs ₂ CO ₃ ·3H ₂ O(s)		-2048.100			0100
Cs ₂ CO ₃ (aq)	-1111.850	-1193.700	209.20		1110
Cs ⁺	-292.020 0.2	-258.040 0.1	132.84 0.40	-10.00	1559
CsSO ₄ ⁻	-1030.380				4000
CsHCO ₃ (aq)	-878.780	-950.270	224.30		1110

Comments:

Reference 1=Wagman et al.,1982;5= CODATA, 1978. Uncertainties for Cs₂O(s) from J.L.Settle;G.K.Johnson; W.N.Hubbard: J.Chem.Thermodynamics 1974,v.6,2663. H.F.Floto;D.W.Osborne: Ibid.,p.135. 3 = Robie et al., 1978. 4 = Phillips, 1982.

PROPERTIES OF ELEMENTAL CHLORINE:

Atomic Number: 17

Formula Mass: 35.4530

Electronic Configuration: 2s² 2p⁶ 3s² 3p⁵

Electronegativity: 3.0

Hydration Number: 1 (Cl⁻), 0.3 (ClO₄⁻)

Ionic Radius: 1.83 angstrom

Selected Average for Soils: 100 mg/kg

Concentration in Natural Waters: 0.15 to 1000 mg/L. Brines 180,000 mg/L

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Cl ₂ (g)	0.000	0.000	222.97 0.01	33.91	5552
Cl ⁻	-131.228 0.1	-167.080 0.1	56.73 0.16	-125.50	2557
ClO ₄ ⁻	-8.520 0.4	-129.330 0.4	182.00	-27.00	2226

Comments:

Reference 2=Wagman et al.,1982; 5 = CODATA, 1978. S.N.L'vov;Ya.D.Rakhmievich;I.A.Dibrov: Russ.J.Phys.Chem. 1984, v.58, 2240 measured (emf) S = 75.6 J/mol/K and Cp = -61.0 J/mol/K. Reference 6 = Abraham;Marcus:J.Chem.Soc.,Faraday Trans. 1986,v.82, 3255. Ref. 7=L. Brewer, 1981.

PROPERTIES OF ELEMENTAL CHROMIUM:

Atomic Number: 24

Formula Mass:

Electronic Configuration:

Electronegativity: 1.6 (Cr⁺⁺⁺)

Hydration Number:

Ionic Radius: 0.615 angstrom (Cr⁺⁺⁺); 0.30 (CrO₄⁻)

Selected Average for Soils: 100 ppm

Concentration in Natural Waters: 3-40 μ-g/L

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Cr(g)	352.590	395.390 4.0	174.18 0.40	20.79	3333
Cr ⁺ (g)		1056.500			0100
Cr ⁺⁺ (g)		2654.300			0100
Cr ⁺⁺⁺ (g)		5648.400			0100
Cr ⁺⁺⁺⁺ (g)		10439.000			0100
Cr ⁺⁺⁺⁺⁺ (g)		17497.000			0100
Cr ⁶⁺ (g)		26246.000			0100
Cr ⁷⁺ (g)		41802.000			0100
CrO(g)	154.580	188.280 41.8	239.16 6.30	31.32	3333
CrO ₂ (g)	-87.380	-75.300 41.8	269.10 12.60	43.40	3333
CrO ₃ (g)	-273.470	-292.900 41.8	266.10 16.70	56.02	3333
H ₂ CrO ₄ (g)		-736.400			0100
H ₂ CrO ₄ (aq)	-760.700	-840.900 2.0	293.00 13.00	-238.00	1119
CrF(g)		21.000			0100
CrF ₂ (g)		-414.200			0100
CrF ₃ (g)		-907.900			0100

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
CrCl ₂ (g)	-148.100	-128.400	312.90		1110
(CrCl ₂) ₂ (g)		-464.400			0100
CrCl ₃ (g)	-297.100	-297.100	351.50		1110
CrCl ₄ (g)	-407.900	-426.800	366.10		1110
CrBr ₂ (g)	-119.200	-71.100	337.31		1110
(CrBr ₂) ₂ (g)		-351.500			0100
CrI ₂ (g)	71.100	133.900	352.08		1110
CrI ₄ (g)	-50.000	13.000	469.00		1110
CrO ₂ Cl ₂ (g)	-501.700	-538.100	329.70	84.50	1114
CrO ₂ Cl ₂ (l)	-510.900	-579.500	221.70		1110
Cr(s)	0.000	0.000	23.80	23.35	1114
			0.30		
Cr ₂ O ₃ (s),escolaite	-1058.100	-1139.700	81.20	118.74	1114
	8.4	8.4	1.30		
CrO ₂ (s)	-548.100	-598.300	54.40		1110
CrO _{2.40} (s)		-587.000			0100
CrO _{2.62} (s)		-582.000			0100
CrO ₃ (s)	-510.400	-589.500	66.90		1110
		2.0	13.00		
Cr(OH) ₂ (s)	-576.100	-658.900	81.20		2220
	8.0	12.0	12.00		
Cr(OH) ₃ (s)	-846.800	-975.710	95.40		2220
	8.4	13.0	13.00		
Cr(OH) ₃ (am)	-837.600				1000
CrF ₂ (s)	-736.400	-778.200	83.70		1110
CrF ₃ (s)	-1087.800	-1158.900	93.89	78.74	1114
			0.40		
CrF ₄ (s)	-1158.900	-1246.800	138.00		1110
CrCl ₂ (s)	-356.100	-395.470	115.31	71.17	4444
		1.7	0.20		
CrCl ₃ (s)	-486.200	-556.500	122.90	91.80	1114
CrBr ₂ (s)	-288.700	-302.100	134.00		1110

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
CrI ₂ (s)	-163.000	-156.900	155.00		1110
CrI ₃ (s)	-205.000	-205.000	197.00		1110
CrICl ₂ (s)		-418.000			0100
CrIBr ₂ (s)		-330.000			0100
MgCr ₂ O ₄ (s)	-1671.500	-1786.100	106.02 0.80	126.70	1112
FeCr ₂ O ₄ (s),chromite	-1352.600	-1453.600 2.0	146.02 1.70	133.64	2222
Ag ₂ CrO ₄ (s)	-634.700 1.7	-724.710	217.60 1.30	142.00	2222
Cr ⁺⁺	-146.400	-143.500 21.0	-100.00	-4.00	1119
Cr ⁺⁺⁺	-203.900 13.0	-211.700 13.0	-316.30 21.00	-10.00	2229
CrO ₄ ⁻⁻⁻⁻	-737.600				1000
CrO ₄ ⁻⁻⁻	-727.600	-881.100 1.7	50.20 4.00	-247.00	1119
HCrO ₄ ⁻	-764.800 2.1	-878.200 2.0	184.10 4.00	-17.00	1119
Cr ₂ O ₇ ⁻⁻	-1301.200	-1490.300 2.0	261.90	-105.00	1119
CrOH ⁺⁺	-418.400 8.0	-445.900 13.0	-153.10	31.00	2229
Cr(OH) ₂ ⁺	-606.700 8.0	-736.400	-134.00	168.00	1119
Cr(OH) ₄ ⁻	-987.400 1.0	-1247.000	-109.00	-213.00	1119
CrCl ⁺⁺	-338.600 8.0				2000
CrCl ₂ ⁺	-465.800 13.0	-546.000	-87.60		2220
Cr(OH)Cl ₂ (aq)	-662.700				1000
CrO ₃ Cl ⁻	-664.800	-754.800	205.00		1110
CrBr ⁺⁺	-283.300	-339.300	-175.70		1110

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$	S° J mol ⁻¹ K ⁻¹	C_p°	Ref.
HCrPO ₇ ²⁻	-1660.600				1000
H ₂ CrPO ₇ ⁻	-1675.700				1000

Comments:

1=Dellien et al.; 2=Naumov et al.; 3=JANAF; 4=Wagman et al. Reference 1 is I.Dellien;F.M.Hall;L.G.Hepler: Chem.Rev. 1976, v.76, 283. Uncertainties from Naumov et al. Palmer et al.:J.Solution Chem.1987,v.16,443 measure for the reactions $\text{CrO}_4^{2-} + \text{H}^+ = \text{HCrO}_4^-$, $\Delta_r S=145\text{J/mol/K}$ and $\Delta_r C_p=231\text{J/mol/K}$; for $2\text{CrO}_4^{2-} + 2\text{H}^+ = \text{CrO}_7^{2-} + \text{H}_2\text{O}$, $\Delta_r S= 269\text{J/mol/K}$; $\Delta_r C_p=463\text{J/mol/K}$.

PROPERTIES OF ELEMENTAL ELECTRON:

Atomic Number:

Formula Mass:

Electronic Configuration:

Electronegativity:

Hydration Number:

Ionic Radius:

Selected Average for Soils:

Concentration in Natural Waters:

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
e ⁻	0.000	0.000	65.28 0.01	14.42 0.1	0012
e ⁻ (aq)	-157.000	-136.400 6.7	69.80 22.50		3330

Comments:

Ref. 1 = A.G.Ryabukhin: Russ.J.Phys.Chem. 1977,v.51,573. Ref.2= A.G.Ryabukhin: Russ.J.Phys.Chem. 1980,v.54,1197. Ref.3 = B.Hickel; K.Sehested: J.Phys. Chem. 1985, v.89, 5271. Note that JANAF Tables: J.Phys.Chem.Ref.Data 1982,v.11,795 has for e⁻(g), $\Delta_f G = \Delta_f H = 0$; $S = 20.87$ J/mol/K, $C_p = 20.79$ J/mol/K. For electrode reactions which are heterogeneous, we use properties of e⁻(gas), with the symbol e⁻. (e⁻, electron, in Key Values.)

PROPERTIES OF ELEMENTAL EUROPIUM:

Atomic Number:

Formula Mass: 151.96

Electronic Configuration:

Electronegativity: 1.1

Hydration Number:

Ionic Radius: 0.950 angstrom (Eu⁺⁺⁺(aq)).

Selected Average for Soils:

Concentration in Natural Waters:

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Eu(c)	0.000	0.000	77.81	27.66	1112
EuO(s)	-563.400 5.7	-592.200 5.5	83.64	48.74	1115
Eu ₃ O ₄ (s)	-2141.000 14.0	-2270.500 12.0	209.20 8.80		1110
Eu ₂ O ₃ (s),monoclinic	-1555.700 3.7	-1650.800 2.6	144.10 3.70	122.20	1112
Eu ₂ O ₃ (s),cubic	-1564.900 4.7	-1661.900 3.8	137.80 2.30	123.80	1112
Eu(OH) ₃ (s)	-1198.900 7.9	-1336.500 8.3	119.90		1110
EuF ₃ (s)		-1571.000 11.0			0400
EuF ₃ ·0.5H ₂ O(s)	-1632.400 12.0				1000
EuCl ₂ (s)	-774.800 7.9	-822.500 6.7	141.00 3.30		1110
EuCl ₃ (s)	-855.800 4.3	-935.800 4.0	144.10	98.29	1113
EuCl ₃ ·6H ₂ O(s)	-2363.400 7.8	-2784.500 4.3	409.10 3.00	366.90	1112
EuOCl(s)	-854.400 8.4	-911.100 7.3	101.80 3.70		1110

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Eu(OH) _{2.5} Cl _{0.5} (s)	-1161.400 7.8				1000
Eu(OH) ₂ Cl(s)	-1129.900 7.8				1000
EuBr ₃ (s)	-716.000 33.0	-779.000 33.0	182.80		1410
Eu(BrO ₃) ₃ ·9H ₂ O(s)		-3494.900 7.8			0100
Eu(IO ₃) ₃ ·2H ₂ O(s)	-1499.700 5.7	-1861.800 8.0	426.60 27.00		1110
EuSO ₄ (s)	-1335.100 7.3	-1471.000 9.1	64.10 55.00		1110
Eu ₂ (SO ₄) ₃ ·8H ₂ O	-5341.700 17.0	-6139.200 19.0	672.00	610.90	1112
Eu ₂ (CO ₃) ₃ (s)		-3092.500 11.0			0100
Eu ₂ (CO ₃) ₃ ·3H ₂ O	-3599.400 30.0	-4000.400 11.0	449.90 100.00		1110
EuS(s)	-443.100 7.9	-447.300 7.2	95.77	50.18	1113
Eu ⁺⁺	-542.500 6.8	-527.700 7.6	-10.00 11.00	-65.00	1119
Eu ⁺⁺⁺	-576.200 5.3	-604.800 4.2	-214.00 3.10	-78.00	1119
Eu(OH) ⁺⁺	-766.300 6.9				1000
Eu(OH) ₂ ⁺	-965.800 16.0				1000
EuF ⁺⁺	-877.000 6.2				1000
EuF ₂ ⁺	-1172.700 13.0				1000
EuCl ⁺⁺	-710.500 7.5	-772.400	-151.00	29.00	2229
EuCl ₂ ⁺	-838.500 9.4				1000

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
EuCl ₃ (aq)	-967.700	-1106.200	-54.00	-402.00	2222
EuBr ⁺⁺	-681.700 6.7				1000
EuBr ₂ ⁺	-783.800 8.1				1000
Eu(BrO ₃) ⁺⁺	-582.000 7.3				1000
Eu(IO ₃) ⁺⁺	-714.800 7.8	-814.900 8.7	-22.90 36.00	-56.00	1119
Eu(NO ₃) ⁺⁺	-691.300 7.0				1000
Eu(SO ₄) ⁺	-1341.200 5.5	-1497.400 6.0	-69.40 20.00	125.00	1119
Eu(SO ₄) ₂ ⁻	-2094.600 6.9	-2398.800 8.2	6.90 30.00	-136.00	1119
Eu(CO ₃) ⁺	-1150.500 7.2				1000
Eu(CO ₃) ₂ ⁻	-1709.200 9.0				1000

Comments:

Reference 1 is J.A.Rard: Chemistry and Thermodynamics of Europium and Some of Its Simpler Inorganic Compounds and Aqueous Species: Chem.Rev. 1985, v.85, 555. Table reviewed by J.A.Rard, Dec.5,1985. Ref. 2 is Wagman et al.,1982; Ref. 3 is Barin et al.,1977; Reference 4 is L.R.Morss: "Yttrium,Lanthanum, and the Lanthanide Elements", in, "Standard Potentials in Aqueous Solution", A.J.Bard; R.Parsons;J.Jordan,eds., Marcel Dekker, Inc.,New York (1985), p.587. Ref. 5 = Robie et al., 1978. Cantrell;Byrne: J.Solution Chem. 1987,v.16,555 measure log K for both EuCO₃⁺ and Eu(CO₃)₂⁻ from which we EuCO₃⁺ and log K₁₂ for Eu(CO₃)₂⁻ from which we calculate $\Delta_f G^\circ = -1148.92$, and -1706.45 kJ/mol, respectively.

PROPERTIES OF ELEMENTAL FLUORINE:

Atomic Number: 9
 Formula Mass: 18.9984
 Electronic Configuration: 1s² 2s² 2p⁵
 Electronegativity: 3.95
 Hydration Number: 1.8 (F⁻)
 Ionic Radius: 1.35 angstrom
 Selected Average for Soils: 200 mg/kg
 Concentration in Natural Waters: 2-37 mg/L in Basalt,
 tuff, granite waters

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
F ₂ (g)	0.000	0.000	202.69 0.04	31.30	5552
HF(g)	-273.200	-273.300 0.7	173.67 0.04	29.13	2552
HF(aq)	-299.930 0.5	-321.282 0.7	94.98 0.50	39.00	1911
F ⁻	-281.750 0.7	-335.350 0.7	-13.18 0.54	-117.00 4.0	9557
HF ₂ ⁻	-584.800		104.80	-66.00	1011

Comments:

Reference 1 = Lemire and Tremaine: J.Chem.Eng.Data 1980, v.25, 361. Ref 2 = Wagman et al.,1982; 5 = CODATA, 1978.
 $\Delta_f G^\circ$ [HF,aq] compares within uncertainty of that calculated from logK = -3.18 for HF(aq) ionization: G.Hefter: J.Solution Chem.
 1984, v. 13, 457. Ref. 7=L. Brewer. Ref.9 = This work.

PROPERTIES OF ELEMENTAL HYDROGEN:

Atomic Number: 1
Formula Mass: 1.008
Electronic Configuration:
Electronegativity: 2.15
Hydration Number: 3.9 (H⁺)
Ionic Radius:
Selected Average for Soils:
Concentration in Natural Waters:

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
H ₂ (g)	0.000	0.000	130.57 0.03	28.82	1112
H ₂ (aq)	17.780 0.9	-4.040 0.8	57.37 2.50	175.00 25.0	9333
H ⁺	0.000 0.0	0.000 0.0	0.00 0.00	0.00 0.0	2222

Comments:

Reference 1 = CODATA, 1978; 2 = Wagman et al., 1982; Reference 3 = L.Brewer, 1981; 9 = This work.

PROPERTIES OF ELEMENTAL IODINE:

Atomic Number: 53

Formula Mass: 126.905

Electronic Configuration: $4s^2 4p^6 4d^{10} 5s^2 5p^5$

Electronegativity: 2.55

Hydration Number: 0.9 (I^-)Ionic Radius: 2.22 angstrom (I^-)

Selected Average for Soils: 0.1 to 40 mg/kg

Concentration in Natural Waters: 1.23 mg/L (lake water); 10 mg/L (brine)

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
I ₂ (s)	0.000	0.000	117.94 0.80	54.44	5591
I ₂ (aq)	16.400	22.600 0.4	137.20 1.70	330.00 33.0	111*
I ₂ (g)	19.327	62.421 0.1	260.57 0.06	36.90	1551
HI(g)	1.780 0.8	26.360 0.8	206.48 0.04	29.15	9551
HIO(g)	-85.800	-98.300	187.40		***0
CH ₃ I(g)	14.700	13.000	254.12	44.10	1111
I ₂ O ₅ (s)	-7.887 10.0	-158.070	115.00 30.00	129.00 50.0	9999
HIO ₃ (s)	-134.750 1.0	-231.840 0.4	110.77	90.71	9*99
AgIO ₃ (s)	-93.700 0.4	-171.100 1.0	149.40 4.10	102.93	1111
Ba(IO ₃) ₂ (s)	-864.700	-1027.200	249.40	187.40	1111
Ba ₅ (IO ₆) ₂ (s)		-3945.960			0*00
Sr ₅ (IO ₆) ₂ (s)		-3975.140			0*00
AgI(s),iodargyrite	-66.190 1.7	-61.840 1.7	115.50 1.70	56.82	1111
AgI(aq)	25.520	50.380	184.10	-120.50	1111

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	Cp° J mol ⁻¹ K ⁻¹	Ref.
HgI ₂ (s),coccinite	-101.700 2.5	-105.400 1.7	180.00 6.30		1110
HgI ₂ (aq)	-75.300	-79.500	176.00		1110
H ₅ IO ₆ (s)			162.30 0.30	171.20 0.3	00**
H ₅ IO ₆ (aq)	-541.550 1.0	-759.400 4.0	268.90		*1*0
IO ₄ ⁻	-58.500	-151.500	222.00		1110
H ₃ IO ₆ ⁻	-486.230	-756.000	95.30		*1*0
H ₄ IO ₆ ⁻	-524.420 0.5	-759.400 4.6	212.00 16.70		*1*0
IO ₃ ⁻	-128.000 0.5	-221.550 2.2	118.40	-74.00	**1*
HIO ₃ (aq)	-137.550 1.0	-217.030 1.0	159.40 1.30	-40.00	****
IO ⁻	-38.500	-107.500	-5.40	90.00	111*
HIO(aq)	-99.100	-138.100	95.40	-74.00	111*
I ₂ O ⁻	-82.220 0.2				*000
I ₂ OH ⁻	-164.870 0.2	-209.330	201.40	-6.00	***9
H ₂ IO ⁺	-107.790 1.1	-193.940	-62.80	121.00	1999
I ⁻	-51.669 0.8	-56.900 0.8	106.70 0.20	-120.50 4.2	955*
I ₃ ⁻	-51.400	-51.500 1.9	239.30 4.00	18.00	1119

Comments:

Reference 1=Wagman et al.,1982;5=CODTA, 1978;9=This work;0=No reference; References with * are as follows: Cp[I₂(aq)] is from J.R.Cobble et al.,1982. Brewer (1981) tabulates GHSCp data for I₂(aq) respectively:16.4,22.45,136.3,291. GHS values for HIO₃(g) are from C.-C. Lin: J.Inorg.Nucl.Chem.1980,v.42,1093 and Ibid.,1981,v.43,3229. Enthalpy of HIO₃(s) is from A.Finch;P.N.Gates;M.A.Jenkinson: J.Inorg.Nucl. Chem. 1980,v.42,1506. Values of GSCp for HIO₃(s) calculated in this work. Enthalpy of both Ba₅(IO₆)₂(s),Sr₅(IO₆)₂(s), from C.F.V.Mason; J.D.Farr;M.G.Bowman:J.Inorg.Nucl.Chem.1980,v.42,799. Values of GS for H₃IO₆⁻,H₄IO₆⁻,H₅IO₆(aq) calculated from data given in F.A.Cotton;G.Wilkinson: "Advanced Inorganic Chemistry", John Wiley & Sons,Inc.,New York (1980),p.561, and in R.M.Kren;H.W.Dodgen; C.J.Nyman:Inorg.Chem. 1968,v.7,446. For IO₃⁻, GHSCp data obtained as follows: $\Delta_f G^\circ$ calculated from standard potential measurements by W.O.Lundberg;C.S.Vestling;J.E.Ahlberg: J.Am.Chem.Soc. 1937, v.59, 264 (Chem.Abstr.,v.31,2523) for: IO₃⁻ + 6H⁺ + 6e = 0.5I₂(s) + 3H₂O, E° = 1.195v. Gibbs energy from Wagman et al.,1982, and from C.-H.Wu; M.M.Birkey;L.G.Hepler: J.Phys.Chem. 1963, v.67, 1202 yield respectively, 1.209v. and 1.201v., both too positive. Enthalpy of IO₃⁻ calculated here using our G value, and the S tabulated by Wagman et al.,1982. Heat capacity of IO₃⁻ is from A.Roux;G.M.Musbally;G.Perron;J.E.Desnoyers; P.P.Singh;E.M.Woolley;L.G.Hepler:Can.J.Chem. 1978,v.56,24. Cp[HIO₃,aq] is

from E.M.Woolley;L.G.Hepler: Can.J.Chem. 1977, v.55, 158. Cp of HIO(aq) is 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 (1982). $\Delta_f G^\circ[\text{I}_2\text{O}^-]$ calculated from Y.-T.Chia: "Chemistry of +1 Iodine in Alkaline Solution", UCRL-8311, Lawrence Berkeley Laboratory,Berkeley,CA (1958). Gibbs energy of HIO(aq) calculated from HIO(g) = HIO(aq) data in C.-C.Lin: J.Inorg.Nucl.Chem. 1981,v.43,3229. GHS data for H_2IO^+ calculated using measurements by J.D.Burger;H.A.Liebhafsky: Anal.Chem. 1973, v.45, 600. Heat capacity of I^- from L.Brewer: "Thermodynamic Data for Flue-Gas Desulfurization Processes",in,"Flue Gas Desulfurization", L.Brewer,ed.,LBL-12342,Lawrence Berkeley Laboratory (1981). Cp[I_3^-] calculated from measurements by D.A.Palmer;R.W.Ramette;R.E.Mesmer: J.Solution Chem. 1984, v.13, 673. 1984, v.13, 673. J.Paquette;B.L.Ford: Can.J.Chem. 1985, v.63, 2444 calculate $\log K = -10.6$ from reaction $\text{HIO} = \text{IO}^- + \text{H}^+$, and $\log K = -1.4$ for equilibrium $\text{H}_2\text{IO}^+ = \text{HIO} + \text{H}^+$. For their $\log K = -10.6$, $\Delta_f G^\circ$ is 60.51 kJ/mol, comparing well with 60.66 kJ/mol calculated using our tabulated data. For $\text{I}_2\text{O}_5(\text{s})$, $\Delta_f H^\circ$ is from calorimetric measurements by P.J.Cerutti;H.C.Ko;K.K.McCurdy;L.G.Hepler: Can.J.Chem. 1978, v.50, 3084; by Cerutti et al.:Can.J.Chem. 1978, v.56, 3084; both S and Cp are from the values calculated by A.K.Gorbachev; F.K.Andryushchenko;S.P.Lugovol;Russ.J.Phys.Chem. 1984, v.58, 988. We calculated $\Delta_f G^\circ$ from $\Delta_f G^\circ = \Delta_f H^\circ - 298.15\Delta_f S^\circ$. E.E.Mercer;D.T.Farrar:Can.J.Chem. 1968, v.46, 2679 measure following $\Delta_f H$ values: $\text{IO}_4^- = -162.3 \pm 1.7$, $\text{H}_5\text{IO}_6(\text{aq}) = -790.36 \pm 4$, $\text{H}_4\text{IO}_6^- = -799.48 \pm 4$ kJ/mol, based on calorimetric measurements. C.E.Crouthamel;A.M.Hayes;D.S.Martin:J.Am.Chem.Soc. 1951, v.73, 82 measure $\log K$ for reactions: $\text{H}_5\text{IO}_6(\text{aq}) = \text{H}_4\text{IO}_6^- + \text{H}^+$, $\log K = -3.29$; $\text{H}_4\text{IO}_6^- = \text{H}_3\text{IO}_6^{--} + \text{H}^+$, $\log K = -6.70$. Data for $\text{H}_5\text{IO}_6(\text{s})$ from L.A.K.Staveley;R.D.Weir: J.Chem.Thermodynamics 1986, v.18, 477.

PROPERTIES OF ELEMENTAL IRON:

Atomic Number: 26

Formula Mass: 55.847

Electronic Configuration:

Electronegativity: 1.8(Fe⁺⁺⁺), 1.7(Fe⁺⁺)Hydration Number: 10.5(Fe⁺⁺⁺), 12.0(Fe⁺⁺)Ionic Radius: Fe⁺⁺(0.61); Fe⁺⁺⁺(0.55) angstrom

Selected Average for Soils: 38,000 ppm

Concentration in Natural Waters: <1 mg/L.

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Fe(s)	0.000	0.000	27.28 0.13	24.98	1111
FeO(s)	-251.156 2.2	-272.043 2.1	59.80 1.70	49.92	1111
Fe _{0.947} O(s), wustite	-244.579 0.5	-265.416 0.6	58.46 0.56	48.40 0.2	8888
Fe ₃ O ₄ (s), magnetite	-1014.137 0.8	-1117.262 0.9	146.01 0.50	151.08 0.2	8888
α -Fe ₂ O ₃ (s), hematite	-745.269 1.0	-827.148 1.1	87.48 0.31	103.80 0.1	8888
γ -Fe ₂ O ₃ (s), maghemite	-711.420 5.0				9000
Fe _{0.877} S(s), pyrrhotite	-106.860	-106.320 1.7	60.79 0.21	49.88	6666
FeS(s), troilite	-101.333 1.5	-100.960 1.5	60.33 0.17	50.50	1111
FeS ₂ (s), pyrite	-160.229 1.7	-171.544 1.7	52.93 0.13	62.17	1111
FeS ₂ (s), marcasite	-158.421 2.1	-169.450 2.1	53.89 0.11	62.43	1111
Fe ₂ S ₃ (s)	-280.750	-280.000	152.29 13.00	47.80	3333
Fe ₇ S ₈ (s)	-748.500				6000

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
FeSO ₄ ·7H ₂ O(s),melanterite	-2509.870 1.3	-3014.570 0.6	409.20 1.30	394.47	2222
FeSO ₄ (s)	-824.980	-928.800 8.4	120.96 1.30	100.40	6666
Fe ₂ (SO ₄) ₃ (s)	-2246.100	-2582.900 1.7	307.50 8.40	289.80	6666
FeSe _{0.96} (s)	-68.760	-66.900	69.20	54.76	9444
FeSe(s)	-75.730	-75.310 1.3	70.60 0.40	54.76	333*
FeSe ₂ (s),ferroselite	-144.780	-121.960	86.82 0.21	72.89	**33
Fe ₂ (SeO ₃) ₃ (s)	-1332.300				*000
Fe ₂ (SeO ₃) ₃ ·2H ₂ O(s)	-1835.900 13.0				3000
Fe ₂ (OH) ₂ SeO ₃ (s)	-1385.500				*000
FeSiO ₃ (s),ferrosilite	-1117.457 0.9	-1194.286 1.5	95.95 2.20	84.33 3.0	8888
Fe ₂ SiO ₄ (s),fayalite	-1378.980 1.4	-1478.170 1.3	151.00 0.20	131.90 0.2	****
Fe(OH) ₂ (s)	-493.040	-573.210	92.50		3330
Fe(OH) ₃ (am)	-714.630 11.0	-844.330	96.20 13.00		3330
α-FeO(OH)(s),goethite	-488.550 0.8	-559.330 0.7	60.38 0.63	69.04	1113
β-FeO(OH)(s),akaganeite	-678.860 5.0				9000
γ-FeO(OH)(s),lepidocrocite	-471.200 1.0				*000
Fe ⁺⁺	-91.550 1.0	-92.730 0.8	-107.00 2.50	-4.00 33.0	669*
Fe ⁺⁺⁺	-17.280 1.0	-50.110 0.8	-279.00 4.10	-35.00 0.1	6999
FeOH ⁺	-275.540 0.5	-250.550	-14.48	88.00	7959

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$	S° J mol ⁻¹ K ⁻¹	C_p°	Ref.
Fe(OH) ₂ (aq)	-448.220		-126.70		7050
Fe(OH) ₃ ⁻	-625.970		117.20		7050
Fe(OH) ₄ ^{- -}	-777.480		37.82		7050
FeOH ⁺⁺	-241.910 0.2	-294.430	-104.50	-1.00	7779
Fe(OH) ₂ ⁺	-459.170		-18.91		7050
Fe(OH) ₃ (aq)	-651.040		-333.10		7050
Fe(OH) ₄ ⁻	-842.490		114.30		7050
Fe ₂ (OH) ₂ ⁺⁺⁺⁺	-491.980 3.0	-619.400	-284.20		7770
Fe ₃ (OH) ₄ ⁵⁺	-964.390				7000

Comments:

Ref.1=Robie et al.,1978;2=Wagman et al.,1982;3=Naumov et al.,1974;4=Barin et al.,1977; 5=Vasilenko et al.,Russ.J.Phys.Chem.1983,v.57,625;6=Cobble et al.,1982; 7=Baes;Mesmer,1976;8=Robinson et al.,1982;9=This work. Data for FeSe₂ gotten by averaging values for sulfide and telluride from Ref.4. Gibbs energy for Fe₂(SeO₃)₃ and Fe₂(OH)₂SeO₃ calculated from log K values in H.R.Geering;E.E.Cary;L.H.P.Jones;W.H.Allaway;Soil Sci.Soc.Am.Proc. 1968, v.32, 35. Data for Fe⁺⁺ and Fe⁺⁺⁺ from Cobble;Murray;Turner; K.Chen:"High-Temperature Thermodynamic Data for Species in Aqueous Solution",NP-2400, San Diego State Univ.,San Diego, CA (May 1982). Also, from C.M.Flynn: Chem.Rev. 1984, v.84, 31. See also J.W.Larson; P.Cerutti;H.K.Garber;L.G.Hepler: J.Phys.Chem. 1968, v.72, 2902. Our Gibbs energies for Fe⁺⁺ and Fe⁺⁺⁺ give E°=-0.473v. for Fe⁺⁺+e=Fe(s), which compares well with the commonly accepted value. Similarly, we calculate E°=-0.062v. for Fe⁺⁺⁺+3e=Fe(s). Our values for hydrolysis free energy values calculated from data in Baes;Mesmer, 1976. Gibbs energy of formation for lepidocrocite is from K.M.Krupka;E.A.Jenne: "WATEQ3 Geochemical Model: Thermodynamic Data for Several Additional Solids", PNL-4276, Pacific Northwest Laboratory, Richland,WA (Sept.1982). Vasil'ev et al. Measure for Fe⁺⁺, $\Delta_f H^\circ=-91.0$ kJ/mol, $S^\circ=-143.93$ J/mol/K: Russ.J.Inorg.Chem. 1985, v.30, 957. Vasil'ev et al. given $\Delta_f H^\circ[\text{FeSO}_4 \cdot 7\text{H}_2\text{O},s] = -3014.58$ kJ/mol, Ibid.,p.959. P.H.Tewari;A.B.Campbell:J.Phys.Chem. 1976, v.80, 1844 measure $\Delta_f G^\circ=-15.7 \pm 0.3$ kJ/mol for reaction FeS(s)+2H⁺=Fe⁺⁺+H₂S(g), so that we calculate $\Delta_f G^\circ[\text{FeS},s]$. Khoe et al.,J.Chem.Soc.Dalton Trans.1986,1901 measure for the Fe⁺⁺⁺-(OH)_n system at I=1.0: logK₁₁=-2.72;logK₁₂=-6.29;logK₂₂=-3.20;logK₃₄=-6.98 which compare with our -2.77, -6.43, -2.63 and -5.79, respectively. Gibbs energy for both $\gamma\text{-Fe}_2\text{O}_3(s)$ and $\beta\text{-FeO(OH)}(s)$ are from Flynn (1984). Flynn also provides logK° values from which we calculated Gibbs energies of Fe(OH)₃(s)=-706.8±11, $\gamma\text{-FeO(OH)}(s) = -473.41 \pm 3$ kJ/mol. Cp[F⁺⁺] is from L. Brewer, 1981. Data for fayalite from Robie; Finch; Hemingway: Am. Mineral. 1982, v.67,463 (R.A. Robie, Private Communication, April 8, 1988). Khoe notes that data for Fe(III)-OH were obtained in perchlorate and nitrate media: logK₁₁, logK₁₂, logK₂₂ (NO₃⁻); logK₃₄ (ClO₄⁻). Therefore, the effect of different ionic media must be considered (Private Communication, April 11, 1988).

PROPERTIES OF ELEMENTAL LANTHANUM:

Atomic Number:
 Formula Mass: 138.91
 Electronic Configuration:
 Electronegativity: 1.1
 Hydration Number: 7.5 (La⁺⁺⁺)
 Ionic Radius: 1.061 angstrom (La⁺⁺⁺)
 Selected Average for Soils:
 Concentration in Natural Waters:

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
La(s)	0.000	0.000	56.90 0.80	27.11	2222
La ₂ O ₃ (s),hexagonal	-1705.800	-1793.700 0.8	127.32 0.20	108.78	2222
La(OH) ₃ (s)	-1278.000	-1410.000	117.80	14.12	8888
La(OH) ₃ (am)	-1286.200 4.2	-1410.000	144.80		3330
LaF ₃ ·H ₂ O(s)		-1987.400			0200
LaCl ₃ (s)	-997.510	-1071.100 1.3	145.60 13.00	108.80	3332
LaCl ₃ ·7H ₂ O(s)	-2712.900	-3178.600	462.80 2.10	431.00	2222
La ₂ (SO ₄) ₃ (s)		-3941.300			0200
La ₂ (CO ₃) ₃ (s)	-3141.600				2000
La ⁺⁺⁺	-686.200 2.1	-707.100 2.1	-209.20 13.00	-81.00	3339
LaOH ⁺⁺	-872.310				6000
LaF ⁺⁺	-979.500				2000
LaCl ⁺⁺	-813.800				7000
LaSO ₄ ⁺	-1435.300	-1562.500			9900
La(SO ₄) ₂ ⁻	-2180.970	-2464.600			9900
LaCO ₃ ⁺	-1258.100				3000

Comments:

Reference 2=Wagman et al., 1982; 3=Naumov et al., 1974; 6=Baes;Mesmer,1976; 7=Smith;Martell,1976; 8=L.R.Morss: Yttrium, Lanthanum, and the Lanthanide Elements, in "Standard Potentials in Aqueous Solution",A.J.Bard; R. Parsons; J. Jordan, eds., Marcel Dekker, Inc., New York (1985), p. 587. Cp for La(OH)₃(s) from R.D.Chirico;E.F. Westrum: J. Chem. Thermodynamics

1980, v. 12, 71. Data for LaSO_4^+ and $\text{La}(\text{SO}_4)_2^-$ from Simpson:J.Solution Chem.1987,v.16,411. We have assumed values at $I=1.0$ are the same as those at $I=0$.

PROPERTIES OF ELEMENTAL LEAD:

Atomic Number: 27
 Formula Mass: 207.1900
 Electronic Configuration:
 Electronegativity: 1.6
 Hydration Number: 12
 Ionic Radius: 1.18 angstrom (Pb^{++})
 Selected Average for Soils: 10 ppm
 Concentration in Natural Waters: 20 $\mu\text{g/L}$

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

Substance	$\Delta_f G^\circ$ kJ mol^{-1}	$\Delta_f H^\circ$ kJ mol^{-1}	S° $\text{J mol}^{-1} \text{K}^{-1}$	C_p° $\text{J mol}^{-1} \text{K}^{-1}$	Ref.
Pb(s)	0.000	0.000	64.80 0.30	26.44	5552
PbO(s)(yellow),massicot	-188.573 0.7	-218.070 0.6	68.70 0.21	45.77	1111
PbO(s)(red),litharge	-189.202 0.9	-219.409 0.8	66.32 0.84	45.77	1111
PbO ₂ (s),plattnerite	-215.314 3.0	-274.470 3.0	71.80 0.42	61.17	1111
Pb ₃ O ₄ (s),minium	-601.358 6.3	-718.686 6.3	211.96 6.70	154.93	1111
Pb(OH) ₂ (s)	-452.200 4.1				2000
Pb(OH) ₂ (aq)	-400.960 4.1				*000
PbClOH(s),laurionite	-480.300 4.0				3000
Pb ₃ (CO ₃) ₂ (OH) ₂ (s)	-1711.000 4.0				3000
PbO.0.3H ₂ O(s)	-258.610				9000
PbF ₂ (s)	-630.901	-676.970 4.2	112.90 8.40	72.26	6666
PbF ₂ (aq)	-582.000 0.1	-666.900	-17.20	-317.00	2229

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
PbCl ₂ (s),cotunnite	-314.100 0.7	-359.000 0.3	136.00 2.10	73.15	1111
PbCl ₂ (aq)	-297.700 0.1	-318.500	218.10	-334.00	4449
PbFCl(s),matlockite	-484.800	-533.500 1.3	114.60		3330
Pb ₂ (CO ₃)Cl ₂ (s)	-952.300 4.0				3000
PbBr ₂ (s)	-261.900 0.4	-278.700	161.50 2.00	80.12	3333
PbI ₂ (s)	-176.300	-178.070	175.18 0.21	79.16	3333
PbS(s),galena	-96.075 0.8	-97.709 1.0	91.38 1.30	49.50	1111
PbSO ₄ (s),anglesite	-813.140 1.0	-919.940 0.9	148.49 0.40	103.21	2552
PbSO ₄ (aq)	-783.200 4.0				3000
PbO.PbSO ₄ (s)	-1032.100				9000
PbCO ₃ (s),cerrusite	-625.337 1.5	-699.150 1.2	131.00 3.30		1110
PbCO ₃ (aq)	-589.210 0.6				*000
PbCl ₂ .PbCO ₃ (s)	-952.210 10.0				9000
Pb ₃ (PO ₄) ₂ (s)	-2363.900		353.10	256.27	9922
PbSe(s),clausthalite	-101.577 2.1	-102.925 2.2	102.51 2.10	50.20	1112
PbSeO ₃ (s),molybdomenite	-447.220 10.0	-532.600 10.0	128.40	99.49	9444
PbSeO ₄ (s),kerstenite	-504.900	-609.200	167.80		2220
PbSiO ₃ (s)	-1062.100	-1145.700	109.60 1.30	90.04	2222
Pb ₂ SiO ₄ (s)	-1252.600	-1363.100	186.60	137.15	2222

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
PbMoO ₄ (s),wulfenite	-951.110 0.9	-1051.860 0.9	166.10 2.10		1110
Pb ⁺⁺	-23.970 0.1	0.920 0.3	17.70 0.80	-83.00	9559
PbOH ⁺	-217.550 2.1	-240.140	89.30	19.00	***9
Pb(OH) ₃ ⁻	-575.630 4.0				*000
Pb ₂ OH ⁺⁺⁺	-249.700				*000
Pb ₃ (OH) ₄ ⁺⁺	-888.600	-1037.600	234.00		2220
Pb ₃ (OH) ₅ ⁺	-1212.980				7000
Pb ₄ (OH) ₄ ⁺⁺⁺⁺	-936.300	-1066.100	234.00		2220
Pb ₆ (OH) ₈ ⁺⁺⁺⁺	-1800.200	-2089.900	498.00		2220
PbF ⁺	-311.700				3000
PbF ₃ ⁻	-884.100				3000
PbCl ⁺	-163.300 0.2	-163.700	109.40	6.00	4449
PbCl ₃ ⁻	-427.100 0.2	-503.100	210.00	-1.00	4449
PbCl ₄ ⁻⁻	-557.100 0.3				4000
PbHCO ₃ ⁺	-642.200				9000
Pb(HCO ₃) ₂ (aq)	-1247.800				9000
Pb(CO ₃) ₂ ⁻⁻	-1137.470 0.6				*000

Comments:

Reference 1=Robie et al.,1978;2=Wagman et al.,1982;3=Naumov et al.,1974; 4=Seward,1984;
5=CODATA,1978;7=Sylva,1980;9=This work. 6 = Baes;Mesmer, 1976.

Gibbs energy for PbCl⁺, PbCl₂(aq) and PbCl₃⁻ calculated using log K values given in F.J.Millero;R.H.Byrne: Geochim. Cosmochim.Acta 1984,v.48,1145 differ from those in Ref. 4: T.M. Seward: Geochim. Cosmochim. Acta 1984, v. 48, 121. $\Delta_f G^\circ$ for Pb(OH)₂(aq), Pb(OH)₃⁻, Pb₂OH⁺⁺⁺ calculated using log K values in C.F. Baes; R.E.Mesmer: The Hydrolysis of Cations (1976); $\Delta_f G^\circ$ for Pb₃(OH)₅⁺ calculated from log K in R.N. Sylva; P.L. Brown: J.C.S. Dalton 1980, 1577; for PbCO₃(aq) and Pb(CO₃)₂⁻⁻, from H. Bilinski; P. Schindler: Geochim. Cosmochim. Acta 1982, v. 46, 921. Gibbs energies for bicarbonates from Phillips, 1982. Grenthe;Hietnan;Salvatore:Acta Chem.Scand. 1987,v.A41,349 find for Pb⁺⁺ + 2CO₃⁻⁻ = Pb(CO₃)₂⁻⁻, log K° = 10.4, comparing with our calculated 10.11. Lozar et al., Thermochim.Acta 1984,v.79,171 measure $\Delta_f G^\circ$ as follows: PbCl⁺, -164.82; PbCl₂(aq), -296.44; PbCl₃⁻, -433.084 kJ/mol.

PROPERTIES OF ELEMENTAL MAGNESIUM:

Atomic Number:

Formula Mass: 24.312

Electronic Configuration:

Electronegativity: 1.2

Hydration Number: 5.1 (Mg⁺⁺)

Ionic Radius: 0.72 angstrom for coordination no. = 6.

Selected Average for Soils: 5000 mg/kg.

Concentration in Natural Waters: Varies, Mg is a common constituent.

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Mg(s)	0.000	0.000	32.68 0.10	24.89	2222
MgCl ₂ (s),chloromagnesite	-591.780 0.5	-641.320 0.5	89.54 0.80	71.04	3333
MgCl ₂ ·2H ₂ O(s)	-1118.100 0.8	-1279.700 0.8	180.00 2.10	159.00	3333
MgCl ₂ ·4H ₂ O(s)	-1623.500 0.8	-1899.000 0.8	264.00 3.00	241.00	3333
MgCl ₂ ·6H ₂ O(s),bischofite	-2115.010 0.8	-2499.060 0.8	366.10 4.00	317.00	3333
MgO(s),periclase	-568.961 0.3	-601.239 0.3	26.95 0.17	37.34	8888
MgCO ₃ (s),magnesite	-1029.477 1.4	-1113.225 1.3	65.08 0.71	76.23 0.3	8888
MgCO ₃ ·3H ₂ O(s),nesquehonite	-1723.750 0.5	-1977.260 0.3	195.67 0.60		1110
Mg(OH) ₂ (s),brucite	-834.337 0.4	-925.307 0.4	63.18 0.66	77.64 0.1	8888
MgSiO ₃ (s),clinoenstatite	-1457.995 1.2	-1544.844 1.2	67.76 1.80	81.57 0.2	8888
MgSiO ₃ (s),enstatite	-1457.411	-1544.696	66.29 0.34	82.20 0.1	8888
MgSiO ₃ (s),protoenstatite	-1449.182	-1531.885	81.67 4.80	79.99 6.0	8888

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Mg ₂ SiO ₄ (s),forsterite	-2053.843 1.3	-2172.729 1.3	95.51 3.60	118.10 0.3	8888
Mg ₃ Si ₂ O ₅ (OH) ₄ (s)	-4032.365 3.5	-4482.037 3.5	221.34 1.13	273.86 0.8	8888
Mg ₃ Si ₄ O ₁₀ (OH) ₂ (s),talc	-5514.937 4.3	-6200.218 4.3	260.80 1.33	322.66 0.7	8888
Mg ₇ Si ₈ O ₂₂ (OH) ₂ (s),anthophyllite	-11332.884	-12058.366 13.0	537.00 1.02	663.62 0.8	8888
Mg ₄₈ Si ₃₄ O ₈₅ (OH) ₆₂ (s),antigorite	-66113.823	-71397.109			8888
MgSe(s)	-268.690	-272.790	61.50	47.97	9444
MgSeO ₃ .6H ₂ O(s)	-2266.500	-2701.600	321.70		3330
MgSeO ₃ (s)	-928.100 6.0	-943.100 4.0	86.20 6.00	88.50	6666
MgSeO ₃ (am)		-887.000 4.0			0300
MgSeO ₃ (aq)	-841.000				7000
MgSeO ₄ (s)		-968.510			0200
MgSeO ₄ (aq)	-908.888				7000
MgSeO ₄ .H ₂ O(s)		-1295.450			0200
MgSeO ₄ .4H ₂ O(s)		-2189.910			0200
MgSO ₄ (s)	-1165.790 2.0	-1279.970 2.0	91.60 1.00	96.48	3333
MgSO ₄ .7H ₂ O(s),epsomite	-2871.240 0.9	-3388.700 1.2	372.00 4.00		1110
MgSO ₄ .H ₂ O(s),kieserite	-1428.700 4.0	-1602.100	126.40 4.00		2220
MgSO ₄ .6H ₂ O(s)	-2631.800	-3087.000	348.10	348.10	2222
Mg ⁺⁺	-454.800 1.7	-466.850 1.3	-138.10 1.70	-16.00 8.0	2225
MgOH ⁺	-627.600 2.0				3000
MgCl ₂ (aq)	-717.100 2.0				2000

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
MgSO ₄ (aq)	-1211.800 2.0	-1368.900	-52.30		3330
MgCO ₃ (aq)	-1002.500 2.0				3000
MgB(OH) ₄ ⁺	-1618.000 3.0				*000

Comments:

Reference 1=Robie et al.,1978;2=Wagman et al.,1982;3=Naumov et al.,1974; 4 = Barin et al., 1977; 5 = Brewer, 1981; 6 = Pashinkin et al.: Russ.J.Phys.Chem. 1971, v.45, 909 and from Malkova et al.: Russ.J.Phys.Chem. 1976, v.50, 1312 for heat capacity. Reference 8 is Robinson et al., 1982. S of antigorite is 3606.08 J/mol/K. Heat capacity of antigorite is 4436.510 J/mol/K. Uncertainties for silicates obtained from Ref.1, except those for anthophyllite are from Naumov et al.,Ref.3. Ref. 7 is Sposito, and $\Delta_f G^\circ$ [MgSeO₄,aq] calculated from log K of formation,using value from G.Sposito: Thermodynamic Formation Constants for Selenium Species at 298.15 K, Private Communication, May 12,1986. * Value for MgB(OH)₄⁺ from L.Bassett, 1980.

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	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Np(s)	0.000	0.000	50.30 1.00	29.62 0.6	4444
Np ₂ O ₅ (s)	-2013.000 14.0	-2147.250 15.0	163.00 23.00	129.00	1911
NpO ₂ (s)	-1021.800 2.5	-1074.000 2.5	80.30 0.40	66.21	1911
NpO ₃ .H ₂ O(s)	-1247.000 8.0	-1379.000 4.6	146.00 33.00	112.00	3339
NpO ₂ (OH) ₂ (s)	-1236.000 12.0	-1377.010 12.0	118.00 20.00	112.00	1911
NpO ₂ (OH)(am)	-1128.000 5.5	-1224.100 6.0	101.00 8.00	86.00	1911
Np(OH) ₄ (s)	-1447.000 20.0	-1621.365 20.0	139.00 25.00	131.00	1911
NpF ₄ (s)	-1783.630	-1874.000 13.0	152.72 4.10	116.06	2222
NpF ₃ (s)	-1460.310	-1528.830 5.0	124.68 4.00	98.32	2222
NpCl ₄ (s)	-896.208	-984.100 1.7	201.67 4.10	120.46	2222
NpCl ₃ (s)	-831.699	-898.500 2.5	161.50 8.40	104.39	2222
NpBr ₄ (s)	-737.644	-771.100 1.7	242.67 12.50	128.62	2222

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
NpBr ₃ (s)	-706.031	-730.500 2.1	196.65 17.00	109.24	2222
NpO ₂ (NO ₃) ₂ (s)		-1190.000			0400
NpO ₂ (NO ₃) ₂ ·H ₂ O(s)		-1505.000			0400
NpO ₂ (NO ₃) ₂ ·6H ₂ O(s)	-2429.200 5.4	-3009.100 5.0	516.30 4.60		3330
NpOCl ₂ (s)	-967.760	-1037.600 13.0	141.00 8.40		2220
NaNpO ₂ CO ₃ ·3.5H ₂ O(s)	-2601.000 10.0		314.00 50.00	269.00	1011
Np(C ₂ O ₄) ₂ (s)	-1975.000 21.0				3000
Np(HPO ₄) ₂ (s)	-2858.000 14.0	-3121.300	200.00 20.00	224.00	1911
Na ₂ Np ₂ O ₇ (s)		-2893.500 9.9			0400
NpO ₂ ⁺⁺	-795.800 5.4	-860.600 4.6	-94.00 8.00	-8.00	4449
NpO ₂ ⁺	-915.000 5.4	-978.200 4.6	-21.00 8.00	92.00	4449
Np ⁺⁺⁺⁺	-502.900 7.5	-556.100 4.2	-389.10 21.00	-112.00	4449
Np ⁺⁺⁺	-517.100 3.3	-527.200 2.1	-179.10 6.40	-102.00	4449
NpO ₂ OH ⁺	-1004.000 5.0	-1102.990 6.0	24.00 50.00	63.00	1919
(NpO ₂) ₂ (OH) ₂ ⁺⁺	-2029.380 10.0	-2246.210 10.0	-14.00 50.00	-62.00	1919
(NpO ₂) ₃ (OH) ₅ ⁺	-3474.000 17.0	-3897.550 17.0	116.00 50.00	2.00	1919
NpO ₂ (OH)(aq)	-1101.000 5.0	-1220.100	25.00 60.00	-48.00	1919
NpOH ⁺⁺⁺	-734.000 9.0	-790.540 40.0	-167.00 40.00	-110.00	1919
Np(OH) ₂ ⁺⁺	-961.000 15.0	-1050.400 15.0	-44.00 80.00	-42.00	1919

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Np(OH) ₃ ⁺	-1181.000 20.0	-1313.705 20.0	44.00 110.00	50.00	1919
Np(OH) ₄ (aq)	-1397.000 20.0	-1699.900	75.00 130.00	-695.00	1919
Np(OH) ₅ ⁻	-1607.000 40.0	-1863.350	96.00 170.00	-76.00	1919
NpOH ⁺⁺	-714.300 4.0	-762.900 4.0	-75.00 30.00	-21.00	1919
NpO ₂ F ⁺	-1103.800 5.7	-1194.400 7.0	-14.00 80.00	88.00	1919
NpO ₂ F ₂ (aq)	-1403.800 6.0	-1527.735 6.0	40.00 80.00	-249.00	1919
NpO ₂ F(aq)	-1207.900 6.0	-1284.700 9.0	100.00 100.00	-24.00	6919
NpF ⁺⁺⁺	-834.300 8.0	-894.800 8.0	-247.00 50.00	-56.00	1919
NpO ₂ Cl ⁺	-926.000 6.0	-1015.540 5.0	0.00 150.00	79.00	1919
NpO ₂ Cl ₂ (aq)	-1055.000 5.0	-1175.300 5.0	73.80	-266.00	9999
NpO ₂ Cl(aq)	-1044.000 8.0	-1129.892 10.0	80.00 200.00	-33.00	1919
NpCl ⁺⁺⁺	-636.000 9.0	-703.475 9.0	-260.00 150.00	-48.00	1919
NpCl ₂ ⁺⁺	-765.000 9.0	-795.795 10.0	40.00 200.00	-98.00	1919
NpO ₂ SO ₄ (aq)	-1558.900 1.0	-1753.500 0.5	42.80 2.00	-293.00	7779
NpO ₂ (SO ₄) ₂ ⁻⁻	-2311.400 1.0	-2653.800 1.0	119.70 6.00	-201.00	7779
NpO ₂ SO ₄ ⁻	-1656.100 1.0	-1856.400 8.0	91.90 50.00	-79.00 3.0	8889
NpSO ₄ ⁺⁺	-1279.000 10.0	-1444.790 10.0	-195.00 50.00	59.00	1919
Np(SO ₄) ₂ (aq)	-2048.000 10.0	-2334.600	-27.00 70.00	-689.00	1919

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
NpO ₂ (CO ₃)(aq)	-1360.000 5.0	-1540.000 5.0	-36.00	-289.00	9999
NpO ₂ (CO ₃) ₂ ⁻	-1953.800 2.0	-2221.700 2.0	116.10 30.00	-203.00 30.0	7779
NpO ₂ (CO ₃) ₃ ⁻⁻⁻⁻	-2505.200 2.0	-2927.900 2.0	38.10 9.00	-535.00	7779
NpO ₂ CO ₃ ⁻	-1470.020 1.0	-1599.900 1.0	200.00 200.00	-7.00	5919
NpO ₂ (CO ₃) ₂ ⁻⁻⁻	-2009.600 1.0	-2298.800 1.0	110.00 200.00	-348.00	5919
NpO ₂ (CO ₃) ₃ ⁻⁻⁻⁻⁻	-2547.000 1.0	-2977.700 1.0	80.00 50.00	-648.00	1919
Np(CO ₃) ₅ ⁻⁻⁻⁻⁻	-3361.000 14.0	-3912.310 15.0	160.00 200.00	-735.00	1919
NpO ₂ HPO ₄ (aq)	-1932.000 8.0	-2159.000	10.00 200.00	-269.00	1919
NpO ₂ H ₂ PO ₄ ⁺	-1940.000 8.0	-2184.900	-50.00 200.00	112.00	1919
NpO ₂ HPO ₄ ⁻	-2025.000 6.0	-2221.200	180.00 200.00	-20.00	1919
NpO ₂ H ₂ PO ₄ (aq)	-2049.000 6.0	-2292.700	20.00 200.00	59.00	1919
NpH ₂ PO ₄ ⁺⁺	-1661.000 10.0	-1854.200	-146.00 200.00	26.00	1919
Np(H ₂ PO ₄) ₂ ⁺	-2799.000 10.0	-3195.300	-180.00 200.00	199.00	1919
Np(H ₂ PO ₄) ₃ (aq)	-3941.000 20.0	-4549.600	-245.00 200.00	-218.00	1919
NpHPO ₄ ⁺⁺	-1666.000 20.0	-1840.900	-150.00 200.00	29.00	1919
Np(HPO ₄) ₂ (aq)	-2817.000 20.0	-3175.900	-120.00 200.00	-641.00	1919
Np(HPO ₄) ₃ ⁻⁻	-3962.000 20.0	-4478.200	0.00 200.00	-280.00	1919
Np(HPO ₄) ₄ ⁻⁻⁻⁻	-5107.000 20.0	-5792.400	80.00 200.00	-508.00	1919
Np(HPO ₄) ₅ ⁻⁻⁻⁻⁻	-6246.000 20.0	-7100.500	160.00 200.00	-735.00	1919

Comments:

Ref.1=Lemire (1984); 2=IAEA,Part8,1983; 3=IAEA,Part 3,1978; 4=Morss (1985); 5=Bidoglio; 6=Choppin. 7=Ullman; 8=Halperin. 9=this work, as discussed below. The existence of $\text{Np}(\text{OH})_5^-$ is tacitly questioned since $\text{U}(\text{OH})_5^-$ (a basis for $\text{Np}(\text{OH})_5^-$) was questioned by Ryan; Rai: Polyhedron 1983, v.2, 947. We choose to include $\text{Np}(\text{OH})_5^-$ in our table, citing the rationale by R.J.Lemire: "...Neptunium...", AECL-7817, Atomic Energy of Canada, Ltd. (March 1984). Thus, although there is no unequivocal evidence for the formation of anionic Np(IV) hydrolysis species, this species is included "in the expectation that, within the noted estimated uncertainties, these may serve a guide to the probable behaviour of Np(IV) in solution...". Also, "stability of $\text{Np}(\text{OH})_5^-$ is especially likely to be overstated if the noted value is used, as little experimental evidence was found for increased solubility of U(IV) in basic solutions...". Lemire (1984) assigns uncertainty to $\text{Np}(\text{OH})_5^-$ for $\Delta_f G^\circ$ of +40, -20 kJ/mol. Note Baes and Mesmer (1976) tabulate hydrolysis constants for other anionic pentahydroxy species, $\text{Hf}(\text{OH})_5^-$, $\text{Zr}(\text{OH})_5^-$ (log K = -17.2, -16.0). However, the large uncertainty in $\Delta_f G^\circ[\text{Np}(\text{OH})_5^-]$ renders any conclusions on the solubility calculations involving this species highly tenuous. For example, the propagated uncertainty for the reaction $\text{NpO}_2(\text{s}) + 2\text{H}_2\text{O} + \text{OH}^- = \text{Np}(\text{OH})_5^-$ is $\log K^\circ = -8.11 + 7.03, -8.11 - 3.50$. See Reference 68 in This Work for a more complete evaluation of $\text{U}(\text{OH})_5^-$.

PROPERTIES OF ELEMENTAL NICKEL:

Atomic Number:

Formula Mass:

Electronic Configuration:

Electronegativity:

Hydration Number:

Ionic Radius:

Selected Average for Soils:

Concentration in Natural Waters:

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Ni(s)	0.000	0.000	29.87	26.07	2222
NiO(s),bunsenite	-211.700	-239.740	37.99	44.31	3333
	0.5	0.4	0.17		
NiF ₂ (s)	-604.170	-651.400	73.60	64.06	2222
	1.2				
NiF ₂ (aq)	-603.300	-719.200	-156.50		2220
NiF ₂ ·4H ₂ O(s)	-1581.000				2000
NiS(s),millerite	-85.240	-87.860	53.01	47.11	1111
	4.4	6.3	0.40		
NiS ₂ (s)	-124.890	-131.380	71.96	70.63	1111
		17.0	8.00		
Ni ₃ S ₂ (s),heazelwoodite	-210.470	-216.310	133.89	117.73	1111
		5.0	0.40		
Ni ₃ S ₄ (s)	-291.992	-301.250	186.48	164.81	1111
		21.0	17.00		
NiSO ₄ (s)	-763.250	-872.950	103.80	97.61	3333
		1.7	0.80		
NiSO ₄ ·6H ₂ O(s)	-2224.720	-2682.600	334.47	327.90	3333
		2.1	0.21		
NiSO ₄ ·7H ₂ O(s)	-2461.990	-2976.120	378.94	364.60	3333
		2.1	0.21		
NiSe ₂ (s),kullerudite	-139.650	-108.800	103.50	75.48	4444

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
NiSe _{1.05} (s)	-73.180	-74.900	75.19	53.39	9444
NiSe _{1.143} (s)	-73.950	-79.700	77.15	55.07	9444
NiSe _{1.25} (s)	-72.510	-83.050	80.08	56.86	9444
NiSeO ₃ (s)	-598.160	-547.700 6.0	100.40 8.00	97.34	9**4
NiSeO ₃ .2H ₂ O,ahlfeldite	-915.460 4.0	-1109.180 4.0	197.10		3330
NiSeO ₄ (aq)					0000
Ni ⁺⁺	-45.600 0.9	-54.000 0.9	-128.90 0.90	-42.00	222*

Comments:

Ref.1=JANAF;2=Wagman et al.,1982;3=Naumov et al.,1974;4=Barin et al.,1977; 9=This work. *Data on enthalpy and entropy of NiSeO₃(s) are from A.S.Pashinkin et al.:Russ.J.Phys.Chem. 1971, v.45, 909. $\Delta_f G^\circ$ for NiSe_{1.05}(s), NiSe_{1.43}(s), NiSe_{1.25}(s) calculated here for internal consistency. C_p° [Ni⁺⁺] from Spitzer et al., 1978.

PROPERTIES OF ELEMENTAL NITROGEN:

Atomic Number: 7

Formula Mass: 14.0067

Electronic Configuration: $1s^2 2s^2 2p^3$

Electronegativity: 3.0

Hydration Number: 0.2 (NH_4^+), 0 (NO_3^-)Ionic Radius: 1.48 angstrom for NH_4^+

Selected Average for Soils: 1400 mg/kg (1400 ppm)

Concentration in Natural Waters: 10-100 ug/L; 5.6 mg/L (Tuff)

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
$\text{N}_2(\text{g})$	0.000	0.000	191.5 45.77 0.01	29.12	1554
$\text{NH}_3(\text{g})$	-16.450	-45.940 0.4	192.67 0.08	35.06	1551
$\text{NH}_3(\text{aq})$	-26.500	-80.290 0.2	111.30 0.80 4.0	86.40 4.0	3333
$\text{NH}_4\text{OH}(\text{aq})$	-263.650	-366.121 0.2	181.20 0.80 3.3	150.50 3.3	1114
NH_4^+	-79.310 0.1	-133.260 0.3	111.17 0.75	69.00	1554
NO_3^-	-110.780 0.4	-206.860 0.4	146.94 0.04	-72.00 4.0	9454

Comments:

Ref.1=Wagman et al.,1982; 3=Naumov et al.,1974; 4=Brewer,1981; 5 = CODATA, 1978.

PROPERTIES OF ELEMENTAL OXYGEN:

Atomic Number: 8
 Formula Mass: 15.9994
 Electronic Configuration: $1s^2 2s^2 2p^4$
 Electronegativity: 3.5
 Hydration Number: 6.1 for OH^-
 Ionic Radius: 1.40 angstrom
 Selected Average for Soils: 490,000 mg/kg
 Concentration in Natural Waters: 8.24 mg/L for $\text{Cl}^- = 0$

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
$\text{O}_2(\text{g})$	0.000 0.0	0.000 0.0	205.04 0.03	29.38	5555
$\text{O}_2(\text{aq})$	16.530 0.2	-12.138 0.2	108.90 0.80	224.00 25.0	9222
$\text{H}_2\text{O}(\text{g})$	-228.572 0.1	-241.814 0.0	188.72 0.04	38.61	1552
$\text{H}_2\text{O}(\text{l})$	-237.129 0.1	-285.830 0.1	69.95 0.08	75.29	1551
OH^-	-157.244 0.1	-230.025 0.1	-10.71 0.20	-140.50 4.0	1552
$\text{OH}(\text{aq})$, radical	13.900	-4.990 2.5	64.80 8.00		3220
$\text{O}^-(\text{aq})$	81.600	37.400 8.3	-16.60 17.00	-116.40 2.5	3222
$\text{O}_2^-(\text{aq})$		-53.211 8.3	41.57 33.00		0220
$\text{O}_3^-(\text{aq})$	48.900				3000

Comments:

Ref. 1 = Wagman et al., 1982; 2 = Brewer, 1981; 3 = Koppenol; Liebman: J.Phys.Chem. 1984, v.88, 99.
 N.E.Khomutov; A.Sh.Groisman: Russ.J.Phys.Chem. 1984, v.58, 1078. have published equilibrium data on $\text{O}_2(\text{g})/\text{O}_2(\text{aq})$. 5 = CODATA, 1987 or 1978.

PROPERTIES OF ELEMENTAL PALLADIUM:

Atomic Number: 46

Formula Mass: 106.4

Electronic Configuration:

Electronegativity: 2.0

Hydration Number:

Ionic Radius: 0.64 angstrom for M-O distance

Selected Average for Soils:

Concentration in Natural Waters:

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Pd(s)	0.000	0.000	37.57 0.20	25.98	4444
PdO(s)	-84.900 2.1	-115.500 2.1	38.90 12.00	31.40	3334
PdO ₂ (s)	-100.000				9000
Pd(OH) ₂ (s)	-302.400 0.3	-368.200	149.90	114.00	9399
Pd(OH) ₂ (aq)	-271.500 1.1	-355.200	90.10	-279.00	9999
Pd(OH) ₄ (s)	-481.200 8.0	-649.500	146.00	40.00 40.0	3939
PdF ₂ (s)	-301.300 2.1	-350.000 4.0	77.00 0.20	66.94	9996
PdCl ₂ (s)	-117.100 1.2	-163.000	108.80	75.27	3339
PdCl ₂ (aq)	-130.000 2.1	-199.000 2.0	26.50	-250.00	9999
PdOHCl(aq)	-218.000				9000
PdCl ₂ .H ₂ O(s)	-550.000 2.0	-481.000 3.0			9500
PdCl ₂ .2H ₂ O(s)	-900.000 2.0	-778.200 3.0			9500
PdCl ₂ .3H ₂ O(s)	-1270.000 3.0	-1075.300 3.0			9500

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
PdCl ₂ .4H ₂ O(s)	-1600.000 3.0	-1372.300 3.0			9500
PdCl ₂ .5H ₂ O(s)	-2000.000 4.0	-1669.400 4.0			9500
PdCl ₂ .6H ₂ O(s)	-2350.000 4.0	-1966.500 4.0			9500
Pd(NH ₃) ₂ Cl ₂ (s)	-498.000	-422.600			9300
PdBr ₂ (s)		-104.200			0400
PdI ₂ (s)	-58.580	-58.580	159.00		3330
Pd(SCN) ₂ (s)	234.300				4000
Pd(SCN) ₂ (aq)	314.300				4000
PdS(s),braggite	-68.060	-75.000	46.00	43.40	9446
PdS ₂ (s)	-74.500	-81.200	79.00	65.90	4446
Pd ₄ S(s)	-67.000	-67.000	180.00	114.90	4446
PdSe(s)	-50.670	-58.600	53.10		9770
PdTe(s)		-46.000	65.60	51.30	0776
H ₂ PdCl ₄ (aq)		-551.900			0400
K ₂ PdCl ₆ (s)	-1029.300	-1158.900	397.50		3330
K ₂ PdCl ₄ (s)		-1083.700			0300
Pd ⁺⁺	176.500 1.3	172.900	-108.10	1.00	4999
PdOH ⁺	-48.600 0.6	-81.970	25.40	62.00	9999
PdCl ⁺	16.800 2.0	-50.000	-144.00	175.00	9999
PdCl ₃ ⁻	-280.000 4.2	-370.000	133.00	-51.00	9999
PdCl ₄ ⁻⁻	-416.000 4.2	-523.000	253.00	-111.00	9999
PdCl ₆ ⁻⁻	-432.300 2.1	-601.100	272.00	-99.00	9949
PdBr ₃ ⁻	-204.200				4000

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$	S° J mol ⁻¹ K ⁻¹	C_p°	Ref.
PdBr ₄ ⁻⁻	-318.000	-384.900	247.00		4440
PdBr ₆ ⁻⁻	-335.100				4000
PdI ₄ ⁻⁻	-171.500				3000
PdI ₆ ⁻⁻	-184.100				3000
PdCN ⁺	289.000				4000
Pd(CN) ₄ ⁻⁻	628.000				4000
Pd(SCN) ₄ ⁻⁻	410.500				4000
PdI ₂ (SCN) ⁻	23.900				4000
Pd(NO ₂) ₄ ⁻⁻	-83.700				3000
Pd(NH ₃) ₄ ⁺⁺	-104.600				3000
Pd(N ₃) ₂ Cl ₂ ⁻⁻	557.000				4000
PdCl ₃ (C ₂ H ₄) ⁻	-210.300	-370.300	176.00		4440

Comments:

0 = No data; 3 = Goldberg and Hepler,1968; 4 = Wagman et al.,1982; 5 = Burylev,1976; 6 = Barin et al.,1977; 7 = Buketov et al.,1964; 9 = This work. $\Delta_f G[\text{PdO}_2, \text{s}]$ calculated from correlation between $\Delta_f G[\text{MO}, \text{s}]$ and $\Delta_f G[\text{MO}_2, \text{s}]$. $S[\text{Pd}(\text{OH})_2, \text{s}]$ calculated from $\Delta_f G = \Delta_f H - 298.15\Delta_f S$; $C_p[\text{Pd}(\text{OH})_2, \text{s}]$ from correlation of $C_p[\text{M}(\text{OH})_2, \text{s}]$ and M - O distance. Enthalpy of $\text{Pd}(\text{OH})_2(\text{aq})$ calculated on assumption of linear change in $\Delta_f H[\text{M}(\text{OH})_2, \text{aq}]$ with number of OH⁻ ligands; entropy calculated from enthalpy and free energy; heat capacity of both $\text{Pd}(\text{OH})_2(\text{aq})$ and $\text{PdCl}_2(\text{aq})$ estimated eq 7A. Heat capacity of $\text{Pd}(\text{OH})_4(\text{s})$ was obtained from a plot of values of properties for $\text{Pd}(\text{OH})_2(\text{s})$ versus those for $\text{Pd}(\text{OH})_4(\text{s})$: a straight line could be drawn through the three points, and interpolated to find C_p . Enthalpy of $\text{Pd}(\text{OH})_4(\text{s})$ was recalculated so that self-consistency is <1000 J/mol. Heat capacity of $\text{PdCl}_2(\text{s})$ was obtained from a correlation between $C_p[\text{MCl}_2, \text{s}]$ and $S[\text{MCl}_2, \text{s}]$. Gibbs energy of formation of hydrated chloride series $\text{PdCl}_2 \cdot x\text{H}_2\text{O}(\text{s})$ was estimated by analogy with the comparable Ni hydrated chlorides using values from the NBS Tables. $C_p[\text{Pd}^{++}, \text{aq}]$ calculated from the correlation, eq 7. $C_p[\text{PdOH}^+]$ obtained from correlation, eq 7. Data for the $\text{Pd}^{++} - \text{Cl}^-$ complexes calculated from Ryhl:Acta Chem.Scand.1972,v.26,2961. $C_p[\text{Pd}^{++} - \text{Cl}^-]$ complexes calculated from eq 7, 7A, 7B. The values for the Pd(IV) chloride complex, PdCl_6^{--} recalculated for self-consistency, except heat capacity calculated from eq 7A. Values of $\Delta_f G[\text{Pd}(\text{OH})_2, \text{aq}, \text{s}]$ calculated from equilibria in Baes and Mesmer. Davies equation was used to calculate $I = 0.1$ values to $I = 0$. $\text{PdF}_2(\text{s})$ data from Barin et al. Enthalpy tabulation of $\text{PdCl}_2 \cdot x\text{H}_2\text{O}(\text{s})$ from Burylev. Enthalpy and entropy of $\text{PdSe}(\text{s})$ and $\text{PdTe}(\text{s})$ are from Buketov. Enthalpy and entropy for Pd^{++} were recalculated from Goldberg and Hepler values to maintain self-consistency. PdOH^+ values calculated from Baes and Mesmer, and for self-consistency with the hydrolysis reaction $\text{Pd}^{++} + \text{H}_2\text{O} = \text{PdOH}^+ + \text{H}^+$.

PROPERTIES OF ELEMENTAL PHOSPHORUS:

Atomic Number: 15

Formula Mass: 30.9738

Electronic Configuration: 3s² 3p³

Electronegativity: 2.1

Hydration Number:

Ionic Radius:

Selected Average for Soils: 600 mg/kg

Concentration in Natural Waters:

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
P(s),white	0.000	0.000	41.09 0.25	23.84	0051
PO ₄ ⁻⁻⁻	-1018.700	-1277.400 4.2	-220.30 8.40	-496.00 20.0	1224
HPO ₄ ⁻	-1089.150	-1292.140 2.1	-33.47 4.10	-254.00 4.0	1224
H ₂ PO ₄ ⁻	-1130.280	-1296.290 2.1	90.37 1.30	-34.00 4.0	1224
H ₃ PO ₄ (aq)	-1142.540	-1288.340 2.1	158.10 4.20	94.00 4.0	1224

Comments:

Reference 1 = Wagman et al.,1982; 2 = Naumov et al.,1974; 5 = CODATA, 1976; Reference 4 is

J.W.Larson;K.G.Zeeb;L.G.Hepler: Can.J.Chem. 1982, v.60,2141. A.J. Read: J.Solution Chem. 1988, v.17,213 for H₃PO₄(aq) = H₂PO₄⁻ + H⁺ calculates $\Delta_f G^\circ = 12.3$ kJ/mol, $\Delta_f H^\circ = -11.7$ kJ/mol; $\Delta_f S^\circ = -80$ J/mol/K; $\Delta_f C_p^\circ = 44$ J/mol/K. These compare with our GHSCp: 12.26, -7.95; -67.73, -128, respectively.

PROPERTIES OF ELEMENTAL PLUTONIUM:

Atomic Number: 94

Formula Mass: 239.05

Electronic Configuration: $5f^6 7s^2$

Electronegativity: 1.3

Hydration Number:

Ionic Radius: 1.00 angstrom (Pu^{+++}); 0.90 angstrom (Pu^{++++})

Selected Average for Soils:

Concentration in Natural Waters:

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Pu(s)	0.000	0.000	54.46 0.42	31.19 0.3	3333
PuO ₂ (s)	-998.000 0.8	-1056.192 0.8	66.13 0.25	66.25	1111
β -Pu ₂ O ₃ (s)	-1580.000 21.0	-1656.000 21.0	163.00 0.60	117.00 0.5	3333
PuO ₂ (OH) ₂ (s)	-1209.900 8.0	-1356.900 8.0	104.00 13.00	112.00	9911
PuO ₂ (OH)(am)	-1056.000 8.0	-1158.160 8.0	87.00 8.00	86.00	1911
Pu(OH) ₄ (am)	⁻⁷⁴²⁶ -1436.000 29.0	-1615.120 29.0	107.00 21.00	131.00	3444 1911
Pu(OH) ₃ (s)	-1157.000 7.0	-1296.600 7.0	92.00 8.00	105.00	3911
PuF ₄ (s)	-1753.000 21.0	-1846.000 20.0	147.25 0.40	116.19 0.3	3333
PuF ₃ (s)	-1516.400 13.0	-1585.700 13.0	126.10 0.40	92.60	3331
PuCl ₄ (s)		-964.000 8.0			0300
PuO ₂ HPO ₄ (s)	-1918.000 13.0	-2103.210	154.00 8.00	159.00	1911
Pu(HPO ₄) ₂ (s)	-2818.000 8.0	-3085.190	187.00 17.00	224.00	1911

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Pu(SO ₄) ₂ (s)	-2012.504 41.8	-2238.440 41.8	184.10 21.00	182.00	3333
PuO ₂ ⁺⁺	-756.900 7.1	-822.200 6.7	-88.00 8.00	11.00	3311
PuO ₂ ⁺	-849.800 7.5	-914.600 5.9	-21.00 8.00	93.00	3339
Pu ⁺⁺⁺⁺	-481.600 3.3	-536.400 3.3	-389.00 20.00	-112.00	3339
Pu ⁺⁺⁺	-578.600 3.3	-592.000 2.1	-185.00 8.00	-98.00	3339
PuO ₂ OH ⁺	-961.900 8.0	-1062.600 8.0	26.00 80.00	62.00	1119
(PuO ₂) ₂ (OH) ₂ ⁺⁺	-1941.000 13.0	-2157.900 13.0	0.00 80.00	-71.00	1119
(PuO ₂) ₃ (OH) ₅ ⁺	-3333.000 21.0	-3756.300 21.0	140.00 80.00	-14.00	1119
PuO ₂ (OH)(aq)	-1032.000 13.0	-1131.504 12.0	96.00 200.00	-47.00	1119
PuOH ⁺⁺⁺	-715.900 20.0	-774.000 20.0	-167.00 40.00	-110.00	1119
Pu(OH) ₂ ⁺⁺	-942.700 20.0	-1033.700 20.0	-44.00 80.00	-42.00	1119
Pu(OH) ₃ ⁺	-1163.000 20.0	-1297.300 20.0	44.00 110.00	50.00	1119
Pu(OH) ₄ (aq)	-1376.000 20.0	-1570.600 20.0	75.00 130.00	-674.00	1119
Pu(OH) ₅ ⁻	-1582.000 20.0	-1839.900 20.0	96.00 170.00	-76.00	1119
PuOH ⁺⁺	-770.300 4.2	-824.600 4.2	-88.00 40.00	-12.00	1119
PuO ₂ F ⁺	-1071.000 8.0	-1162.800 8.0	-10.00 80.00	85.00	1119
PuO ₂ F ₂ (aq)	-1383.000 8.0	-1534.600 8.0	-44.00 80.00	-244.00	1119
PuO ₂ F ₃ ⁻	-1693.000 8.0	-1857.700 8.0	79.00 80.00	-87.00	1119

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
PuO ₂ F ₄ ²⁻	-1991.000 8.0	-2203.600 8.0	85.00 80.00	-215.00	1119
PuF ³⁺	-811.640 8.0	-849.920 8.0	-167.00 130.00	-109.00	9919
PuF ₂ ²⁺	-1131.100 10.0				9000
PuO ₂ Cl ⁺	-887.000 8.0	-978.100 8.0	4.00 130.00	76.00	1119
PuCl ³⁺	-618.000 4.0	-686.300 4.0	-257.00 130.00	-49.00	1119
PuO ₂ SO ₄ (aq)	-1481.730 1.0	-1715.700 1.0	46.90	-267.00	2299
PuO ₂ (SO ₄) ₂ ²⁻	-2271.070 1.0	-2598.400 1.0	174.10	-164.00	2299
PuSO ₄ ²⁺	-1259.000 8.0	-1433.500 8.0	-218.00 30.00	74.00	1119
PuSO ₄ ⁺	-1343.000 5.0	-1487.200 5.0	-50.00 30.00	112.00	1119
PuO ₂ CO ₃ (aq)	-1216.100 1.0				2000
PuO ₂ (CO ₃) ₂ ²⁻	-1898.000 13.0	-2149.500 13.0	175.00 130.00	-155.00	1119
PuO ₂ (CO ₃) ₃ ³⁻	-2445.700 1.0	-2886.200	-17.90	-527.00	2229
PuCO ₃ ²⁺	-1070.000 21.0	-1227.800 21.0	-293.00 200.00	124.00	9919

Comments:

Reference 1 is R.J.Lemire;P.R.Tremaine: J.Chem.Eng.Data 1980, v.25, 361. Ref. 2 = Ullman;Schreiner: Radiochim.Acta 1986, v.40, 179. Ibid.,to be published (1987). Ref. 3=L.R.Morss, 1986; Ref. 9 = This work. Refer to R.Silva;H.Nitsche: National Meeting American Chemical Society, Miami,FL April 29 - May 3,1985 where they reported log Q₁(0.5M) less than 13.0 for the reaction Pu⁴⁺ + CO₃²⁻ = PuCO₃²⁺. D.Rai and J.L.Ryan: Inorg.Chem. 1985 v.24,247 mention a reasonable value for formation of PuCO₃²⁺ is 10³². J.F.Kerrisk:LA-9484-PR, Los Alamos National Laboratory,Los Alamos,NM 87545 (October 1982) calculates log K = 9.9 from plots of formation constants versus number of ligands for OH⁻, F⁻, HPO₄²⁻,SO₄²⁻ and CO₃²⁻ ligands for U(IV),Pu(IV),Th(IV). We calculate log K = 10.4, and values for properties tabulated by correlating oxalate,carbonate and sulfate formation constants for actinides. The existence of Pu(OH)₅⁻ is tacitly questioned, since U(OH)₅⁻ (the basis for Pu(OH)₅⁻) was questioned by J.L.Ryan; D.Rai: Polyhedron 1983, v.2, 947. We choose to include Pu(OH)₅⁻ in our table although unequivocal data for a U(OH)₅⁻ anionic substance does not appear to exist, to maintain consistency with Np and U tables. Also, Baes and Mesmer (1976) list other anionic pentahydroxy species, e.g.,Hf(OH)₅⁻,Zr(OH)₅⁻ with compatible values for hydrolysis constants of log K= -17.2 and -16.0, respectively. Ryan and Rai (1983) found that UO₂(am) is less soluble in 0.045 - 10.0M NaOH containing added Zn(s) and dithionite than measured by Gayer and Leider: Can.J.Chem. 1957, v.35, 5. Inclusion of data for Pu(OH)₅⁻ within the assigned uncertainties "may serve as a guide to the probable behaviour of [Pu(OH)₅⁻] in solution...". See Lemire: "...Neptunium...",AECL-7817, Atomic Energy of Canada,Ltd.(March 1984). For ΔG_f° [Np(OH)₅⁻],Lemire assigns an

uncertainty of +40 kJ/mol, -20 kJ/mol. Morss (1986) questions the stoichiometry of $\text{Pu}(\text{OH})_4(\text{am})$. Data for PuF^{+++} recalculated to conform with $\log K^0 = 8.46$ in Morss (1986) and Nash (1984). PuF_2^{++} calculated from data in Ahrland, in, Katz et al. (1986), p.1498.

PROPERTIES OF ELEMENTAL POTASSIUM:

Atomic Number: 19

Formula Mass: 39.102

Electronic Configuration:

Electronegativity: 0.80

Hydration Number: 0.6 (K^+)

Ionic Radius: 1.38 angstrom.

Selected Average for Soils: 8300 ppm.

Concentration in Natural Waters: <20mg/L in most drinking waters.

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
K(s)	0.000	0.000	64.68 0.20	29.58	5552
KOH(s)	-378.930 0.5	-424.680 0.4	78.91 0.80	64.89	1111
KCl.MgCl ₂ .6H ₂ O(s),carnallite	-2529.230 4.0	-2944.700 4.0			4300
KCl.MgSO ₄ .3H ₂ O(s),kainite	-2325.710 4.0	-2640.100 4.0			4200
K ₂ SO ₄ (s),arcanite	-1319.660 0.5	-1437.700 0.5	175.56 0.30	130.04	1111
K ₂ SO ₄ .MgSO ₄ .6H ₂ O(s),picromerite(shoenite)	-3956.590 4.0	-4538.420 4.0			4300
K ₂ Ca ₂ Mg(SO ₄) ₄ .2H ₂ O(s),polyhalite	-5658.110 5.0				4000
K ₂ SO ₄ .MgSO ₄ .4H ₂ O(s),leonite	-3480.310 4.0	-3948.350 4.0			4300
KHCO ₃ (s),kalicinite	-866.760 4.0	-966.090 4.0	109.20 12.00		3330
KIO ₄ (s)	-361.350	-467.230	176.00	126.30 0.6	222*
K ₂ Se(s)		-395.000			0200
K ₂ Se(aq)	-437.200				2000
K ₂ SeO ₃ (s)		-982.000			0200

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
K ₂ SeO ₃ (aq)	-936.300 2.0	-1013.800	218.00		2220
K ₂ SeO ₄ (s)	-1002.800	-1110.020	222.00	142.64	222*
KTcO ₄ (s)		-1030.000	164.77	123.30	0222
K ⁺	-282.224 0.1	-252.170 0.1	101.04 0.25	13.00 4.1	9556

Comments:

Reference 1 = Robie et al.,1978; 2 = Wagman et al., 1982; 3 = Naumov et al.,1974; 4 = Bodine, 1986; 5 = CODATA, 1978; 6 = L.Brewer, 1981.

PROPERTIES OF ELEMENTAL PROTACTINIUM:

Atomic Number:
 Formula Mass: 231.0359
 Electronic Configuration:
 Electronegativity: 1.7 (Pa(V))
 Hydration Number:
 Ionic Radius:
 Selected Average for Soils:
 Concentration in Natural Waters:

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Pa(g)	617.000	660.000	197.90	22.90	4444
Pa(s)	0.000	0.000	55.00 1.00	34.00 1.0	4444
PaO ₂ (s)	-1044.000	-1109.000	77.00		4440
Pa ₂ O ₅ (s)			88.00		0040
PaF ₄ (s)	-1853.000	-1946.000 20.0	147.00	115.00	4444
PaCl ₄ (s)	-954.000	-1044.000 13.0	194.00	121.00	4444
PaCl ₅ (s)	-1032.000	-1143.000 15.0	238.00	156.00	4444
Pa ⁺⁺	22.000	49.000	22.00	-86.00	4449
Pa ⁺⁺⁺	-431.000	-439.000	-172.00	-107.00	4449
Pa ⁺⁺⁺⁺ (1M HCl)	-565.000 17.0	-619.700 13.0	-397.00 42.00	-106.00	5559
PaOOH ⁺⁺ (1M HCl)	-1050.000 17.0	-1113.000 17.0	-21.00 16.00		4440

Comments:

Ref. 4=L.R. Morss: "Thermodynamic Properties," in "The Chemistry of the Actinide Elements," 2nd ed., preprint, Nov. 6, 1985.
 Ref. 5 = Fuger; Oetting, 1976; 9 = This work.

PROPERTIES OF ELEMENTAL RADIUM:

Atomic Number: 97
 Formula Mass: 226.025
 Electronic Configuration:
 Electronegativity: 0.9
 Hydration Number:
 Ionic Radius: 0.14 nm
 Selected Average for Soils:
 Concentration in Natural Waters: Not detected.

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Ra(g)	129.700	159.000	176.47	20.79	3333
Ra ⁺ (g)		674.540			0300
Ra ⁺⁺ (g)		1659.790			0300
RaH(g)	-195.000	-223.000	227.00	30.30	3333
RaF(g)	-372.000	-348.000	234.00	50.00	3333
RaCl(g)	-233.000	-208.000	-265.00	38.00	3333
RaBr ₂ (g)	-502.000	-448.000	339.00	62.00	3333
RaI ₂ (g)	-418.000	-337.000	351.00	63.00	3333
RaI ₂ (aq)	-665.000	-640.000	271.00		3330
Ra(s)	0.000	0.000	71.00	30.00	111*
RaO(s)	-511.000	-523.000	76.20	46.40	3111
RaO ₂ (s)	-704.000	-598.000	3.70	64.00	3333
Ra(OH) ₂ (s)	-838.000	-950.000	117.00	89.20	3333
RaH ₂ (s)	-142.000	-151.000	78.40	44.80	3333
RaF ₂ (s)	-1197.000	-1201.000	100.00	73.60	3333
Ra(ClO ₃) ₂ (s)	-620.000	-787.000	180.00	167.00	3333
Ra(ClO ₄) ₂ (s)	-527.000	-845.000	190.00	172.00	3333
RaCl ₂ (s)	-841.000	-887.000	134.00	76.50	1131
RaCl ₂ ·2H ₂ O(s)	-1302.900	-1464.400	213.40	163.00	1111

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
RaCl ₂ ·4H ₂ O(s)		-2051.000			0400
RaCl ₂ ·6H ₂ O(s)		-2596.000			0400
RaBr ₂ (s)	-720.000	-770.000	153.00	81.00	3333
RaBr ₂ ·2H ₂ O(s)	-1238.000	-1385.000	224.00	171.00	3333
RaBr ₂ ·4H ₂ O(s)		-2006.000			0400
RaBr ₂ ·6H ₂ O(s)		-2527.000			0400
Ra(BrO ₃) ₂ (s)	-611.000	-711.000	256.00	172.00	3333
Ra(BrO ₃) ₂ ·H ₂ O(s)	-858.000	-1013.000	302.00	217.00	3333
RaI ₂ (s)	-594.000	-640.000	176.00	84.00	3333
RaI ₂ ·0.5H ₂ O(s)	-724.000	-796.000	199.00	106.00	3333
RaI ₂ ·4H ₂ O(s)		-1875.000			0400
RaI ₂ ·6H ₂ O(s)		-2403.000			0400
Ra(IO ₃) ₂ ·H ₂ O(s)	-1102.000	-1320.000	307.00	234.00	3333
Ra(IO ₃) ₂ (s)	-869.000	-1027.000	272.00	188.00	3333
Ra(HCO ₃) ₂ (s)		-1979.000			0300
RaCO ₃ (s)	-1142.000	-1222.000	123.00	85.00	3333
RaCO ₃ (aq)	-1103.700	-1200.300	67.00		2220
Ra(NO ₂) ₂ (s)		-774.000			0300
Ra(NO ₃) ₂ (s)	-796.100	-992.000	222.00	154.00	1333
Ra(NO ₃) ₂ (aq)	-784.000	-942.200	347.00		3133
Ra(NO ₃) ₂ ·4H ₂ O(s)		-2181.000			0400
Ra(NO ₃) ₂ ·6H ₂ O(s)		-2731.000			0400
Ra ₃ (PO ₄) ₂ (s)	-3974.000	-4170.000			3300
RaS(s)	-423.000	-446.000	85.00	52.00	3333
Ra(HS) ₂ (s)		-548.000			0300
RaSO ₃ (s)	-1089.000	-1180.000	133.00	96.00	3333
Ra(HSO ₄) ₂ (s)		-2326.000			0300
RaSO ₄ (s)	-1366.000	-1471.000	159.00	103.00	3393
RaSO ₄ (aq)	-1306.200	-1436.800	75.00		3330

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
RaSe(s)	-350.000	-360.000	92.00	53.00	3333
RaSeO ₃ (s)	-970.000	-1033.000	174.00	100.00	3333
RaSeO ₄ (s)	-1050.000	-1175.000	180.00	108.00	3333
RaTe(s)				54.00	0003
RaPo(s)				54.00	0003
Ra(N ₃) ₂ (s)	-170.000	-4.000	170.00		3330
Ra ₃ N ₂ (s)		-335.000			0300
RaC ₂ (s)		-80.000			0300
RaC ₂ O ₄ (s)		-1410.000			0300
Ra(CHO ₂) ₂ (s),formate		-1376.000			0300
Ra(CH ₃ CO ₂) ₂ (s)		-1498.000			0300
Ra(CN) ₂ (s)		-217.000			0300
RaCN ₂ (s),cyanamide		-234.000			0300
Ra(CNS) ₂ (s)		-406.000			0300
RaSiO ₃ (s),metasilicate	-1537.000	-1577.000	120.00	91.00	3333
Ra ₂ SiO ₄ (s)	-2268.000	-2268.000	195.00	136.00	3333
Ra(ReO ₄) ₂ (s)		-2167.000			0300
RaCrO ₄ (s)	-1330.000	-1440.000	160.00	118.00	3333
RaMoO ₄ (s)	-1470.000	-1570.000	157.00	118.00	3333
RaWO ₄ (s)	-1592.000	-1693.000	166.00	125.00	3333
RaV ₂ O ₆ (s)	-2450.000		253.00	184.00	*033
Ra ₂ V ₂ O ₇ (s)			290.00	226.00	0033
RaTiO ₃ (s)	-1548.000	-1640.000	123.00	103.00	3333
Ra ₂ TiO ₄ (s)	-2092.000	-2197.000	214.00	160.00	3333
RaZrO ₃ (s)	-1707.000	-1785.000	143.00	105.00	3333
Ra ⁺⁺	-561.500 10.0	-527.600	54.00	-107.00	3319
RaOH ⁺	-728.000	-757.000	46.40	48.00	3339
Ra(OH) ₂ (aq)	-895.000	-987.000	38.30	-388.00	3339
RaCl ₂ (aq)	-823.800	-861.900	167.00	-358.00	3339

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Ra(ClO ₄) ₂ (aq)	-580.000	-810.000	418.00	-161.00	3339
RaBr ₂ (aq)	-770.000	-770.000	213.00	-371.00	3339
RaC ₂ O ₄ (aq)	-1242.300				9000
Ra(CH ₃ COO) ₂ (aq),acetate	-931.380				9000

Comments:

Reference 1 is Wagman et al.,1982; 2=D.Langmuir;A.C.Riese:Geochim.Cosmochim. Acta 1985, v.49,1593;
3=R.T.Lowson:Thermochimica Acta 1985, v.91,185. Ref.4=D.S.Kaganyuk;V.I.Kyskin;I.V.Kazin:Radiokhimiya 1983, v.25, 67.
Ref. 9 is This Work. $C_p[\text{Ra}^{++}]$ calculated from eq 7. Lowson H-TS=53.18kJ/mole for solubility of RaSO₄(s) inconsistent with
G=59.97 and logK = -10.43. The logK value agrees with -10.37 (20 C) from Smith & Martell,1976; and -10.26 calculated by
Langmuir & Melchior: Geochim.Cosmochim.Acta 1985,v.49,2423. We choose to recalculate S(RaSO₄,s) as 159 J/mole/K, so that
H - TS = 59.80, agreeing within 0.17 of the G value. Values for oxalate and acetate (aq) calculated from log K values in
Kumok: Radiokhimiya 1979, v.20, 687. $\Delta_f G[\text{Ra}_2\text{V}_2\text{O}_6\text{,s}]$ from Yu.P.Chukova: Russ.J.Phys.Chem. 1984, v.58, 21.

PROPERTIES OF ELEMENTAL RUTHENIUM:

Atomic Number:

Formula Mass:

Electronic Configuration:

Electronegativity: 2.0 (Ru⁺⁺⁺)

Hydration Number:

Ionic Radius:

Selected Average for Soils:

Concentration in Natural Waters:

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Ru(g)	595.800	642.700	186.40	29.84	2211
RuO ₃ (g)	-55.800 9.1	-70.800 6.6	285.80 8.40	59.40	1113
RuO ₄ (g)	-148.500 4.1	-192.700 4.0	290.60 0.60	75.60	1113
RuCl ₃ (g)	16.700 26.0	16.900 33.0	363.70 33.00	55.80	1113
RuCl ₄ (g)	-63.400 17.0	-93.300 17.0	374.10 21.00	84.05	1113
Ru(s)	0.000	0.000	28.61	24.06	1111
Ru ₂ O ₅ (am)	-445.000 26.0				1000
RuO ₂ (s)	-253.100 8.2	-307.200 7.8	52.20 8.70	56.30	1113
RuO ₂ ·2H ₂ O(am)	-691.000 13.0				1000
RuO ₄ (s)	-159.500 4.6	-244.400 4.4	154.00 1.10	75.90	1112
RuO ₄ (aq)	-154.000 5.0	-238.100 4.7	156.70 1.10		1110
Ru(OH) ₃ ·H ₂ O(am)	-766.000 13.0				1000
RuF ₅ (s)	-940.900	-892.900	161.10	163.00	3333

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
$\alpha\text{-RuCl}_3(\text{s})$	-158.700 23.0	-221.200 33.0	153.30 32.00	115.00	1113
$\text{RuBr}_3(\text{s})$	-120.800 10.0	-147.800 12.0	166.50 53.00		1110
$\text{RuI}_3(\text{s})$	-53.500 9.2	-58.400 8.0	186.30 25.00		1110
$\text{RuS}_2(\text{s})$	-188.400 1.7	-199.500 1.7	55.20 1.70	66.53	1111
$\text{RuSe}_2(\text{s})$	-138.000 0.8	-146.400 0.8	85.40 0.80	70.25	1111
$\text{RuTe}_2(\text{s})$	-128.600 0.8	-140.000 0.8	89.60 0.80	74.06	1111
Ru^{++}	150.300 19.0				1000
Ru^{+++}	173.400 20.0				1000
RuO_4^-	-250.100 5.5	-332.400 18.0	224.90 79.00		1110
$\text{H}_2\text{RuO}_5(\text{aq})$	-391.200 5.0				1000
RuO_4^{--}	-306.600 6.6	-457.000 3.4	64.90 34.00		1110
HRuO_5^-	-325.400 7.1				1000
$\text{Ru}(\text{OH})_2^+$	-280.900 21.0				1000
$\text{Ru}(\text{OH})^{++}$	-51.000 21.0				1000
$\text{Ru}(\text{OH})_2^{++}$	-221.800 13.0				1000
$\text{Ru}_4(\text{OH})_{12}^{++++}$	-1877.000 58.0				1000
$\text{Ru}_4(\text{OH})_{10}^{5+}$	-1462.400 61.0				1000
$\text{Ru}_4(\text{OH})_8^{6+}$	-1056.000 62.0				1000

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$	S° J mol ⁻¹ K ⁻¹	C_p°	Ref.
$\text{Ru}_4(\text{OH})_6^{7+}$	-629.200 63.0				1000
$\text{Ru}_4(\text{OH})_4^{8+}$	-193.500 72.0				1000
RuCl^{++}	29.700 19.0				1000
RuCl^+	21.800 25.0				1000
RuCl_2^+	-110.600 20.0				1000
$\text{RuCl}_3(\text{aq})$	-245.000 20.0				1000
RuCl_4^-	-375.400 21.0				1000
RuCl_5^{--}	-505.000 23.0				1000
RuCl_6^{---}	-634.000 24.0				1000
$\text{Ru}(\text{OH})_2\text{Cl}^+$	-361.000 14.0				1000
$\text{Ru}(\text{OH})_2\text{Cl}_2(\text{aq})$	-494.700 14.0				1000
$\text{Ru}(\text{OH})_2\text{Cl}_3^-$	-624.900 14.0				1000
$\text{Ru}(\text{OH})_2\text{Cl}_4^{--}$	-762.400 14.0				1000
$\text{Ru}(\text{OH})_2\text{SO}_4(\text{aq})$	-976.500 13.0				1000
$\text{RuSO}_4(\text{aq})$	-607.600 19.0				1000
RuSO_4^+	-582.200 20.0				1000
$\text{Ru}(\text{SO}_4)_2^-$	-1333.000 21.0				1000

Comments:

Reference 1 is J.A.Rard: Chem.Rev. 1985, v.85, 1. Ref. 2 is Wagman et al.,1982; Ref. 3 is Barin et al.,1977. Table reviewed by J.A.Rard, Dec.5,1985. $\text{RuO}_4(\text{aq})$ and $\text{H}_2\text{RuO}_5 (= \text{RuO}_4 + \text{H}_2\text{O})$ are the same species.

PROPERTIES OF ELEMENTAL SELENIUM:

Atomic Number: 34
 Formula Mass: 78.96
 Electronic Configuration: 3d10 4s2 4p4
 Electronegativity: 2.48
 Hydration Number:
 Ionic Radius: 1.17 angstrom, covalent radius
 Selected Average for Soils: 0.3 mg/kg
 Concentration in Natural Waters: <10 µg/L

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Se(g)	187.030	227.070	176.72	20.82	2222
Se ₂ (g)	96.200	146.000	252.00	35.40	2222
SeO(g)	26.800	53.350	233.90	31.24	2244
H ₂ Se(g)	15.900	29.700	219.02	34.73	2222
	8.0	8.0	4.00		
H ₂ Se(aq)	22.200	19.200	163.60	103.30	2223
	8.0	8.0	4.00		
Se(s),hexagonal	0.000	0.000	42.27	25.06	1111
			0.05		
Se(s),monoclinic		6.700			0200
Se(am)	3.350	5.020	48.41	27.15	3333
			0.80		
SeO ₂ (s),selenolite	-171.540	-225.350	66.69	117.60	3333
		2.1	1.70		
SeO ₂ (aq)	-189.010	-221.630	137.90	118.80	9299
		1.3			
SeO ₃ (s)	-84.100	-166.900	72.40		3330
		6.3	12.00		
H ₂ SeO ₃ (s)		-524.670			0300
		2.1			
H ₂ SeO ₃ (aq)	-426.140	-507.480	207.90	194.10	2223
		1.3			

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
SeCl ₄ (s)	-246.705	-188.700	194.50	134.00	4444
SeBr ₄ (s)		-74.900 2.1			0500
Se ²⁻	129.290 8.4	64.010 8.4	-46.02 21.00	-379.50	3333
HSe ⁻	44.000 8.4	15.900 8.4	79.50 20.00	-151.90	2233
Se ₂ ²⁻	114.200				3000
SeO ₃ ²⁻	-369.800 2.0	-509.200 2.0	13.00 4.00	-282.80	2223
HSeO ₃ ⁻	-411.460 2.0	-514.550 2.0	135.10 4.00	-69.04	2223
SeO ₄ ²⁻	-441.300 2.0	-599.100	54.00 21.00	-323.80	2223
HSeO ₄ ⁻	-452.200 2.0	-581.600 4.0	149.40 8.00	-84.90	2223

Comments:

1=Robie et al.,1978;2=Wagman et al.,1982;3=Naumov et al.,1974; 4=Barin et al.,1977; 5=Epifanov et al.,1984; 9=This work.

Values for SeO₂(aq) calculated from equation for hydration of SeO₂(aq) where SeO₂(aq) + H₂O = H₂SeO₃(aq), for which $\Delta_f G = \Delta_f H = \Delta_f S = \Delta_f C_p = 0$.

PROPERTIES OF ELEMENTAL SILICON:

Atomic Number: 14

Formula Mass: 28.0855

Electronic Configuration: $3s^2 3p^2$

Electronegativity: 1.8

Hydration Number:

Ionic Radius: 1.17 angstrom covalent

Selected Average for Soils: 320,000 mg/kg

Concentration in Natural Waters: 11-92 mg/L in tuff,
basalt, granite waters

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Si(s)	0.000	0.000	18.81 0.08	19.94	7771
SiO ₂ (s), α -quartz	-856.288 1.1	-910.700 1.0	41.46 0.20	44.59	1771
SiO ₂ (s),cristobalite	-854.512 2.1	-908.346 2.0	43.40 0.13	44.18	1111
SiO ₂ (s),tridymite	-853.812 2.4	-907.488 2.4	43.93 0.42	44.60	1111
SiO ₂ (am)	-850.700 2.0	-903.490	46.90	44.40	3333
SiO ₂ (s),silica glass	-850.559 2.1	-903.200 2.1	47.40 0.21	37.94	1111
SiO ₂ (s),coesite	-850.850 2.1	-905.584 2.1	40.38 0.42	45.40	1111
SiO ₂ (aq)	-833.700 2.0	-888.500 2.0	40.10 4.00	-6.00	9999
SiO ₂ (soil)	-851.438				8000
H ₂ SiO ₃ (aq)	-1072.900	-1176.300	110.00	140.00	9999
Si(OH) ₄ (aq)	-1308.000 1.7	-1460.140 1.7	180.00 4.20	215.00	9999
SiO(OH) ₃ ⁻	-1251.910 1.7	-1434.540 1.7	77.83 4.00	51.10 11.0	9999
SiO ₂ (OH) ₂ ⁻⁻	-1177.150 2.0	-1397.540	-48.90	-80.00	9999

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
SiO ₃ (OH) ⁻⁻⁻⁻	-1120.500 3.0	-1380.000	-180.20	-230.00	9999
SiO ₄ ⁻⁻⁻⁻	-1027.200 3.0	-1352.700	-402.10	-380.00	2999
Si ₄ O ₆ (OH) ₆ ⁻⁻	-4207.447				4000
Si ₄ O ₈ (OH) ₄ ⁻⁻⁻⁻	-4081.820				4000
SiO ₃ ⁻⁻	-887.000 1.0				8000
NaAlSiO ₄ (s),nepheline	-1977.498 2.5	-2092.110 2.4	124.35 1.30	115.81	1111
Na[AlSi ₂ O ₆].H ₂ O(s),analcime	-3091.730 3.7	-3309.840 3.6	234.43 2.50	210.00	1112
NaAlSi ₃ O ₈ (s),low albite	-3711.723 3.4	-3935.120 3.4	207.40 0.40	205.10	1111
KAlSi ₃ O ₈ (s),microcline	-3742.330 3.4	-3967.690 3.4	214.20 0.44	202.40	1111
Ca[Al ₂ Si ₄ O ₁₂].4H ₂ O(s),laumontite	-6657.200 8.7				6000
Ca[Al ₂ Si ₄ O ₁₂].2H ₂ O(s),wairakite	-6183.100 8.0				6000
Ca[Al ₂ Si ₁₀ O ₂₄].8H ₂ O(s),clinoptilolite	-12743.600 13.0				6000
Mg[Al ₂ Si ₁₀ O ₂₄].8H ₂ O(s),Mg-clinoptilolite	-12654.500 13.2				6000
Na ₂ [Al ₂ Si ₁₀ O ₂₄].8H ₂ O(s),Na-clinoptilolite	-12720.200 15.8				6000
K ₂ [Al ₂ Si ₁₀ O ₂₄].8H ₂ O(s),K-clinoptilolite	-12827.300 12.9				6000
Ca[Al ₂ Si ₇ O ₁₈].6H ₂ O(s),heulandite	-9700.200 11.6				6000
Na[AlSi ₅ O ₁₂].3H ₂ O(s),mordenite	-6122.000 6.6				6000
K[AlSi ₅ O ₁₂].3H ₂ O(s),K-mordenite	-6176.400 5.1				6000

Comments:

Ref.1=Robie et al.,1978; 2=Naumov et al.,1974; 3=Wagman et al.,1982 4=Baes;Mesmer,1976; 6=Kerrisk: "Free Energy of Formation of Some Minerals in Nevada Tuff",LA-9225-PR, Los Alamos National Laboratory (April 1982),p.75. Ref. 7=CODATA, 1978; 8=Bard et al.,1985; 9 = This work. $C_p^\circ[\text{Si}(\text{OH})_4(\text{aq})]$ calculated from data in Cobble et al., p. 4-30. For SiO_2 (quartz) + $2\text{H}_2\text{O}(\text{l}) = \text{Si}(\text{OH})_4(\text{aq})$, $\Delta_f G^\circ = 22.987$ kJ/mol, $\Delta_f S^\circ = 22.01$ J/mol/K, $\Delta_f C_p^\circ = -49.79$ J/mol/K By definition: Gibbs energy, enthalpy, entropy and heat capacity of reaction are zero for hydration of aqueous substances, for example - $\text{SiO}_2(\text{aq}) + \text{H}_2\text{O} = \text{H}_2\text{SiO}_3(\text{aq})$.

PROPERTIES OF ELEMENTAL SODIUM:

Atomic Number: 11
 Formula Mass: 22.9898
 Electronic Configuration:
 Electronegativity: 0.9
 Hydration Number: 4 (Na⁺)
 Ionic Radius: 1.02 angstrom.
 Selected Average for Soils: 6300 ppm
 Concentration in Natural Waters: 1 to 500 mg/L.

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Na(s)	0.000	0.000	51.30 0.20	28.24	5552
NaCl(s),halite	-384.210 0.1	-411.260 0.1	72.12 0.20	50.51	1111
NaCl(aq)	-393.133 1.0	-407.270 1.0	115.50	-90.00	2222
NaHCO ₃ (s),nahcolite	-815.900 1.2	-913.500 1.2	102.10 1.60	87.60	3333
Na ₂ SO ₄ (s),thenardite	-1269.990 0.4	-1387.790 0.4	149.58 0.08	127.28	1111
Na ₂ SO ₄ ·10H ₂ O(s),mirabilite	-3646.540 3.0	-4327.250 4.0	591.90 0.60		1110
Na ₂ CO ₃ ·H ₂ O(s),thermonatrite	-1285.700 1.0	-1432.000 1.2	168.10 0.40	145.60	3333
Na ₂ CO ₃ ·10H ₂ O(s),natron(soda)	-3431.510 1.2	-4082.030 1.2	564.70 0.80	550.30	3333
Na ₃ H(CO ₃) ₂ ·2H ₂ O(s),trona	-2380.690				4000
Na ₂ SO ₄ ·3K ₂ SO ₄ (s),glaserite	-5240.600				6000
Na ₂ SO ₄ ·MgSO ₄ ·4H ₂ O(s),bloedite	-3429.820				4000
Na ₂ SO ₄ ·CaSO ₄ (s),glauberite	-2569.530				6000
2Na ₂ SO ₄ ·CaSO ₄ (s),labile salt	-4342.060				
Na ₂ CO ₃ ·CaCO ₃ ·2H ₂ O(s),pirssonite	-2660.120				4000
Na ⁺	-261.905 0.1	-240.300 0.1	58.41 0.20	42.40	2552

Comments:

Reference 1 = Robie et al., 1971; 2 = Wagman et al., 1982; 3 = Naumov et al., 1974; 4 = Bodine, 1986; 5 = CODATA, 1978; 6

= Harvie, 1980.

PROPERTIES OF ELEMENTAL STRONTIUM:

Atomic Number: 38

Formula Mass: 87.62

Electronic Configuration: $5s^2$

Electronegativity: 1.0

Hydration Number: 3.7 (Sr^{++})Ionic Radius: 1.27 anstrom for Sr^{++}

Selected Average for Soils: 200 mg/kg

Concentration in Natural Waters: 5-15 mg/L in brines; 0.05 mg/L (Tuff)

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
$\alpha\text{-Sr}(s)$	0.000	0.000	55.70 0.21	26.40	0012
$\text{SrO}(s)$	-559.960 1.0	-590.600 0.9	55.44 0.50	45.02	1112
$\text{Sr}(\text{OH})_2(s)$	-882.175 9.2	-968.889 9.2	97.07 8.40	74.90	5555
$\text{SrF}_2(s)$	-1164.800	-1216.300	82.13	70.00	2222
$\alpha\text{-SrCl}_2(s)$	-785.000 0.8	-833.850 1.0	114.85 0.42	75.60	1112
$\text{SrCl}_2(aq)$	-826.321 1.0	-885.060 1.0	81.70 0.50	-286.00	9119
$\text{SrCl}_2 \cdot 2\text{H}_2\text{O}(s)$	-1281.800 1.0	-1438.000	218.00	160.20	2222
$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}(s)$	-2240.920 1.0	-2623.800	390.80		2220
$\text{SrSO}_4(s)$, celestite	-1340.970 4.0	-1453.170 4.2	118.00 4.20		4440
$\text{SrSO}_4(aq)$	-1320.300 5.0	-1449.970	60.90	-313.00	9999
$\text{SrCO}_3(s)$, strontianite	-1144.730 1.0	-1225.770 1.0	97.20 1.70	81.42	1113
$\text{SrCO}_3(aq)$	-1107.820 1.0	-1204.300 1.0	45.40 4.20	-308.00	1119

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Sr(NO ₃) ₂ (s)	-780.020 1.0	-978.220	194.56	149.91	2222
SrSe(s)		-385.800			0200
SrSeO ₃ (s)	-969.400 4.0	-1047.700			3200
SrSeO ₄ (s)	-1039.100 7.0	-1156.210 6.3	112.90		3330
SrSiO ₃ (s)	-1561.640 4.0	-1645.980	96.70 0.84	88.53	3333
Sr ₂ SiO ₄ (s)	-2215.090 2.1	-2328.980 2.1	153.10 1.30	134.26	3333
Sr ⁺⁺	-563.830 0.8	-550.900 0.5	-31.50 2.00	-34.80	1116
SrOH ⁺	-726.040 0.8	-775.900 4.2	-8.74	85.00	9999
SrF ⁺	-851.500 0.8				9000
SrHCO ₃ ⁺	-1157.520 1.0	-1215.560 1.0	174.40 4.20	-37.00	1119
SrB(OH) ₄ ⁺	-1719.210 3.0				*000

Comments:

Reference 1= E.Busenberg;L.Niel Plummer;V.B.Parker:Geochim.Cosmochim.Acta 1984,v.48,2021. Reference 2=Wagman et al.,1982; 3=Naumov et al.,1974;4=Robie et al.,1978; 5 = JANAF Tables; 6 = J.K.Hovey;L.G.Hepler;P.R.Tremaine: J.Solution Chem. 1986, v.15, 977; 9 = This work. $\Delta_f G^\circ$ [SrCl₂,aq] calculated to -826.21 for consistency with H-TS. Ref.1 recommends -826.33J/mol for $\Delta_f G^\circ$ [SrCl₂,aq].NBS Tables for SrSO₄(aq) give inconsistent G = H - TS; also, log K calculated from NBS Tables is -0.76 for reaction Sr⁺⁺ + SO₄⁻⁻ = SrSO₄(aq), in disagreement with range 2.1 to 2.55 given in Smith and Martell; and Millero and Schreiber: Am.J.Sci. 1982, v.282, 1508. * From L.Bassett, 1980.

PROPERTIES OF ELEMENTAL SULFUR:

Atomic Number: 16
 Formula Mass: 32.06
 Electronic Configuration: $3s^2 3p^4$
 Electronegativity: 2.44 (6)
 Hydration Number: 2.8 (SO_4^{--})
 Ionic Radius: 1.90 angstrom (S^{--}), 2.40 (SO_4^{--})
 Selected Average for Soils: 700 mg/kg (ppm) (7)
 Concentration in Natural Waters: 19-108 mg/L sulfate
 in tuff,basalt,granite waters

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
S(s),rhombic	0.000	0.000	32.05 0.05	22.64 0.1	0052
H ₂ S(g)	-33.560 0.7	-20.630 0.6	205.79 0.21	34.23	2222
H ₂ S(aq)	-27.865 0.4	-39.700 1.7	121.00 4.20	178.50 1.9	333*
HS ⁻	12.080 0.4	-17.600 1.2	62.80	-92.00 1.0	333*
S ⁻⁻	85.800 2.0	33.100 3.3	-14.60 12.50	-400.40	333*
S ₂ ⁻⁻	79.500 4.2	30.120 4.2	28.45 8.40	-428.90	3333
SO ₂ (g)	-300.194 0.2	-296.810 0.2	248.11 0.06	39.87 0.0	2552
SO ₂ (aq)	-300.676 0.4	-322.980 0.8	161.90 1.30	195.00 10.0	333*
SO ₃ ⁻⁻	-486.500 4.2	-635.500 4.2	-29.00 12.50	-268.20	333*
HSO ₃ ⁻	-527.730 4.2	-626.220 3.3	139.70 0.70	-10.00 4.0	222*
H ₂ SO ₃ (aq)	-537.810 0.2	-608.810 0.3	232.20 0.80	293.00 10.0	222*
SO ₄ ⁻⁻	-744.530 0.4	-909.600 0.4	18.83 0.50	-278.00 6.7	255*
HSO ₄ ⁻	-755.910	-888.760 2.1	124.26 1.30	-41.80	333*

Comments:

Reference 2=Wagman et al.,1982; 3= Naumov et al.,1974; 5=CODATA,1978. * Heat capacity data from Barbero;McCurdy;Tremaine: Can.J.Chem. 1982, v.60, 1872; J.A.Barbero;L.G.Hepler;K.G.McCurdy;P.R.Tremaine: Can.J.Chem. 1983, v.61, 2509. Our data for $\text{SO}_2(\text{g})$ and $\text{SO}_2(\text{aq})$ compare well with that in Goldberg;Parker: J.Res.Natl.Bur.Stand. 1985, v.90, 341. For $\text{HS}^- = \text{S}^{2-} + \text{H}^+$, $\log K^\circ = -17.6 \pm 0.3$, reported by S.Licht;J.Manassen: J.Electrochem.Soc. 1987, v.134, 918. This leads to $\Delta_f G^\circ[\text{S}^{2-}] = 112.44 \text{ kJ/mol}$.

PROPERTIES OF ELEMENTAL TECHNETIUM:

Atomic Number:

Formula Mass:

Electronic Configuration:

Electronegativity: 1.9(Tc(V)),2.3(Tc(VI))

Hydration Number:

Ionic Radius:

Selected Average for Soils:

Concentration in Natural Waters:

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Tc(g)		678.000	181.07	20.79	0222
Tc ₂ O ₇ (g)	-888.500 16.0	-987.400 10.0	449.40 13.00		1110
TcF ₆ (g)			371.28 0.75		0010
TcO ₃ Cl(g)			317.60		0010
Tc(s)	0.000	0.000	33.50	24.30	1111
Tc ₂ O ₇ (s)	-935.600 15.0	-1120.000 8.0	166.00 13.00	238.00	1113
TcO ₃ (s)	-461.000	-539.700	71.10	107.90	1333
TcO ₂ (s)	-450.510	-433.040	59.00	55.77	3333
TcO ₂ ·2H ₂ O(s)	-836.300 7.0				1000
Tc ₃ O ₄ (am?)	-863.800 3.8				1000
Tc ₄ O ₇ (am?)	-1324.000 21.0				1000
TcOH(am?)	-234.700 3.8				1000
Tc(OH) ₂ (am?)	-461.200 3.8				1000
Tc(OH) ₃ (am?)	-658.500 3.8				1000

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
TcF ₆ (s)			253.52 0.25		0010
TcS ₂ (s)	-216.000	-224.000	71.00		1000
TcS ₃ (s)	-263.000	-276.000	84.00		1000
Tc ₂ S ₇ (s)	-581.000	-615.000	176.00		1110
HTcO ₄ (s)	-589.800 10.5	-703.800 9.6	126.30		1110
NaTcO ₄ (s)	-877.000 10.1				1000
HTcO ₄ (aq)	-630.420	-724.000			9200
KTcO ₄ (s)	-919.200 10.0	-1022.200 5.5	164.78	123.30	111*
Tc ⁺⁺⁺	105.800 10.5				1000
TcO ⁺⁺	-100.600 10.5				1000
TcO(OH) ⁺	-331.300 10.5				1000
TcO(OH) ₂ (aq)	-556.000 10.5				1000
[TcO(OH) ₂] ₂ (aq)	-1149.200 21.3				1000
TcO ₄ ⁻⁻⁻	-508.000 11.2				1000
TcO ₄ ⁻⁻	-564.900 10.0				1000
HTcO ₄ ⁻	-614.600 10.5				1000
H ₂ TcO ₄ (aq)	-616.300 12.1				1000
TcO ₄ ⁻	-623.800 10.0	-716.300 4.5	199.00 1.30		1110

Comments:

Reference 1 is J.A.Rard: Critical Review of the Chemistry and Thermodynamics of Technetium and Some of Its Inorganic Compounds and Aqueous Species, UCRL-53440, Lawrence Livermore National Laboratory, Livermore, CA 94550 (Sept.15,1983). Reference 2 is Wagman et al.,1982; Ref. 3 is Barin et al.,1977. Table reviewed by J.A.Rard, Dec. 5,1985. C_p (KTcO₄,s) from Busey et al.:J.Chem.Thermodynamics 1972,v.4,77. Rard notes values are estimated for TcS₂,TcS₃,Tc₂S₇,TcO₃, and Tc(s). Also,existence of Tc₄O₇ is questionable; the little evidence for TcOH,Tc(OH)₂ and Tc₃O₄ is for surface films only. Gibbs energy of formation for HTcO₄(aq) is from Bibler,1985.

PROPERTIES OF ELEMENTAL THORIUM:

Atomic Number: 90
 Formula Mass: 232.0381
 Electronic Configuration:
 Electronegativity: 1.4
 Hydration Number:
 Ionic Radius: 1.00 angstrom
 Selected Average for Soils:
 Concentration in Natural Waters: .

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Th(g)	556.400	598.000 6.0	189.30 0.40	20.79	7777
ThO(g)	-50.200	-28.000 2.0	240.00	31.25	2722
ThO ₂ (g)	-506.700	-497.000 3.0	287.60	47.35	2222
ThF(g)			257.20	34.70	0077
ThF ₂ (g)	-663.000	-651.000	295.10	52.40	7777
ThF ₃ (g)	-1161.000	-1166.000 12.0	339.20	73.30	7777
ThF ₄ (g)	-1724.000	-1759.000 11.0	342.00	93.00	7777
ThCl(g)			269.10	36.50	0077
ThCl ₂ (g)			317.00	55.30	0077
ThCl ₃ (g)			369.60	78.00	0077
ThCl ₄ (g)	-932.000 3.0	-964.000 20.0	390.70	107.60	7777
ThBr(g)			281.00	37.50	0077
ThBr ₂ (g)			338.90	56.70	0077
ThBr ₃ (g)			405.10	80.80	0077
ThBr ₄ (g)	-783.000	-762.000 20.0	430.00	104.90	7777

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
ThI(g)			228.50	37.60	0077
ThI ₂ (g)			355.50	57.40	0077
ThI ₂ (s)		-352.000			0700
ThI ₃ (g)			429.80	81.80	0077
ThI ₄ (g)	-521.000	-466.000 8.0	469.00	106.00	7777
Th(s)	0.000	0.000	52.64 0.40	26.24	7777
ThO ₂ (s), thorianite	-1168.770 3.5	-1226.400 3.5	65.23 0.20	61.76 0.1	1111
Th(OH) ₄ (s)	-1599.100	-1772.300	143.50 12.00		5550
Th(OH) ₄ (aq)	-1562.700	-1834.300	-100.00		3330
ThF ₄ (s)	-1997.000 4.0	-2098.000 9.0	142.05 0.20	110.54 0.1	1711
ThF ₄ .2.5H ₂ O(s)	-2614.000 10.0	-2854.000 10.0	234.00 9.00		7770
ThOF ₂ (s)	-1592.400 11.0	-1669.400 10.5	101.00 9.00	86.00	6677
ThCl ₄ (s)	-1094.500 3.0	-1186.600 1.7	190.40 4.00	120.90	6666
ThCl ₄ .2H ₂ O(s)		-1836.300 8.4			0600
ThCl ₄ .4H ₂ O(s)		-2469.800 8.4			0600
ThCl ₄ .7H ₂ O(s)		-3375.700 8.4			0600
ThCl ₄ .8H ₂ O(s)		-3675.200 8.4			0600
ThOCl ₂ (s)	-1169.800 3.0	-1233.400 2.9	114.60 4.00	91.00	6666
ThBr ₄ (s)	-925.500 4.0	-964.400 2.1	228.03 8.40	125.20	6666
ThSiO ₄ (s), huttonite			106.70		0030

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
ThBr ₄ ·7H ₂ O(s)		-3162.300 8.4			0600
ThBr ₄ ·10H ₂ O(s)		-4071.900 8.4			0600
ThBr ₄ ·12H ₂ O(s)		-4767.500 8.4			0600
ThOBr ₂ (s)	-1076.500	-1129.700 13.0	129.70 13.00	93.50	6666
ThI ₃ (s)		-515.000			0700
ThI ₄ (s)	-662.000	-670.700 3.8	255.00	126.60	7777
ThOI ₂ (s)	-959.000	-997.000	145.00	94.00	7777
ThS(s)	-395.000 4.0	-399.000 4.0	69.81 0.35	47.72 0.2	7777
ThS _{1.03} (s)		-405.000 4.0			0700
ThS ₂ (s)	-621.000 40.0	-627.000 40.0	96.20 0.80	70.30 0.3	7777
Th ₂ S ₃ (s)	-1077.000 13.0	-1083.000	180.00 8.00		7770
Th ₂ S ₅ (s)		-1272.000 40.0	215.00		0770
Th ₇ S ₁₂ (s)		-4138.000 53.0	641.00		0770
Th(SO ₄) ₂ (s)	-2306.300 15.0	-2535.900 21.0	167.40 10.00	173.50 0.6	4444
Th(SO ₄) ₂ (aq)	-2249.300	-2556.400	-92.00	-630.00	8889
Th(HPO ₄) ₂ ·4H ₂ O(s)	-3985.300	-4476.800	372.00		3330
Th(HPO ₄) ₂ (aq)	-3013.300	-3189.500	-100.00		3330
Th(NO ₃) ₄ (s)	-1049.000 14.0	-1446.000 13.0	335.00 13.00		7770
Th(NO ₃) ₄ ·4H ₂ O(s)		-2707.000 13.0			0700
Th(NO ₃) ₄ ·5H ₂ O(s)	-2325.000 4.0	-3007.900 4.2	543.10 2.00	480.80	7777

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Th(C ₂ O ₄) ₂ ·6H ₂ O(s)	-3618.000 10.0				7000
ThH ₂ (s)	-105.600 1.0	-145.100 1.0	50.73 0.10	36.71 0.1	7777
Th ⁺⁺⁺⁺	-704.600 5.4	-769.000 2.5	-423.00 17.00	-89.00 11.0	7779
ThOH ⁺⁺⁺	-920.500 5.0	-1030.100	-343.00	8.00	2229
Th(OH) ₂ ⁺⁺	-1140.900	-1282.400	-218.00	74.00	2229
Th(OH) ₃ ⁺	-1349.300	-1541.400	-151.00	180.00	3339
Th ₂ (OH) ₂ ⁺⁺⁺⁺⁺	-1848.500	-2047.600	-615.00	-261.00	3339
Th ₄ (OH) ₈ ⁺⁺⁺⁺⁺	-4595.300	-5121.200	-724.00	-488.00	3339
Th ₆ (OH) ₁₅ ⁺⁺⁺⁺⁺	-7575.500	-8447.500	-669.00	-675.00	3339
ThF ⁺⁺⁺	-1029.700	-1106.700	-300.00	-21.00	2229
ThF ₂ ⁺⁺	-1343.900	-1442.600	-205.00	66.00	2229
ThF ₃ ⁺	-1649.300	-1778.600	-142.00	174.00	2229
ThF ₄ (aq)	-1947.200	-2115.000	-105.00	-543.00	2229
ThCl ⁺⁺⁺	-842.700	-936.000	-343.00	8.00	2229
ThCl ₂ ⁺⁺	-971.900	-1015.700	-3.53	-68.00	2889
ThCl ₃ ⁺	-1108.300	-1204.300	-2.93	81.00	2889
ThSO ₄ ⁺⁺	-1480.700	-1658.500	-230.00	82.00	2229
Th(SO ₄) ₃ ^{- -}	-2998.400	-3448.100	-4.62	-273.00	2889
Th(SO ₄) ₄ ^{- - - -}	-3731.400	-4351.500	-4.76	-543.00	2889
ThCO ₃ ⁺⁺	-1295.370				8000
ThH ₃ PO ₄ ⁺⁺⁺	-1864.900	-1994.600	2.62	-372.00	8889
ThH ₂ PO ₄ ⁺⁺⁺	-1867.700	-1997.900	0.97	-222.00	8889
Th(H ₂ PO ₄) ₂ ⁺⁺	-3029.700	-3350.700	8.06	-76.00	8889
ThHPO ₄ ⁺⁺	-1855.600	-1884.100	-251.00	96.00	3339
Th(HPO ₄) ₃ ^{- -}	-4192.200	-4683.400	84.43	-217.00	8889
ThC ₂ O ₄ ⁺⁺	-1431.800				3000
Th(C ₂ O ₄) ₂ (aq)	-2158.500				3000
Th(C ₂ O ₄) ₃ ^{- -}	-2873.600				3000

Comments:

Reference 1=Robie et al.,1978;2=Wagman et al.,1982;3=Langmuir and Herman,1980;4=IAEA, Part 3,1978;5=Naumov et al.,1974;6=IAEA, Part 8, 1983; 7=L.R.Morss, 1985; 8=NEA,1986.

References: D. Langmuir; J.S. Herman: *Geochim. Cosmochim. Acta* 1980, v. 44, 1753. L.R. Morss: "Thermodynamic Properties," in "The Chemistry of the Actinide Elements," 2nd ed., J.J. Katz; G.T. Seaborg; L.R. Morss, eds. preprint (August 1985).

PROPERTIES OF ELEMENTAL TIN:

Atomic Number: 50

Formula Mass: 118.69

Electronic Configuration: [Kr] 4d¹⁰5s²5p²Electronegativity: 1.8 (Sn⁺⁺)

Hydration Number:

Ionic Radius: 0.93 angstrom (Sn⁺⁺), 0.69 (Sn⁺⁺⁺⁺)

Selected Average for Soils: 10 mg/kg

Concentration in Natural Waters: .

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Sn(g)	267.300	301.200	168.38	21.26	2552
		1.7	0.02		
Sn(s),white	0.000	0.000	51.18	26.99	5552
			0.08		
β -Sn(s),gray	0.130	-2.090	44.14	25.77	2222
	0.4	0.4	0.06		
SnO(s)	-256.900	-285.930	57.17	44.31	2552
		0.7	0.30		
SnO ₂ (s),cassiterite	-519.600	-580.780	52.30	52.59	2552
	0.8	0.4	1.20		
Sn(OH) ₂ (s)	-491.600	-561.100	155.00		2220
Sn(OH) ₂ (aq)	-461.200	-543.300	113.80	-341.00	6919
	4.0				
Sn(OH) ₄ (s)		-1110.000			0200
SnCl ₂ (s)	-302.100	-349.800	122.60	78.05	444*
	1.0				
SnCl ₂ (aq)	-299.500	-329.700	172.00	-311.00	2229
	4.0				
SnOHCl(aq)	-392.000	-453.500	126.00	-326.00	2229
SnO(OH)F(aq)	-788.600				2000
SnCl ₂ ·2H ₂ O(s)		-921.300			0200
SnOHCl·H ₂ O(s)	-648.400				2000

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	Cp° J mol ⁻¹ K ⁻¹	Ref.
SnCl ₄ (l)	-440.100	-511.300	258.60	165.30	2222
SnS(s),herzenbergite	-98.300	-100.000	77.00	49.25	2222
	1.5	1.5	0.80		
SnS ₂ (s),stannic sulfide	-179.600	-153.500	87.45		4440
			0.20		
SnSO ₄ (s)	-1055.900	-1014.600	138.60		4440
SnSO ₄ (aq)	-779.000				*000
Sn(SO ₄) ₂ (s)	-1451.000	-1646.000	155.20		4440
Sn(SO ₄) ₂ (aq)	-1481.800				2000
SnSe(s)	-123.810	-94.500	92.46		44*0
		0.4	13.00		
SnSe ₂ (s)	-159.860	-124.700	118.00		4440
	10.0	12.0	2.50		
Sn ⁺⁺	-27.870	-7.610	-11.05	-60.00	8889
	0.1	1.2	4.00		
Sn ⁺⁺⁺⁺	1.630	30.500	-117.00	-293.00	8229
	0.1				
SnOH ⁺	-244.920	-264.600	89.70	19.00	6669
	2.0				
Sn(OH) ₃ ⁻	-643.800	-776.140	178.70	-21.00	6919
	0.5				
Sn ₂ (OH) ₂ ⁺⁺	-501.430				6000
	2.0				
Sn ₃ (OH) ₄ ⁺⁺	-990.800				6000
	0.5				
Sn(OH) ₃ ⁺	-712.100	-834.400	77.40	-67.00	1119
	2.0				
Sn(OH) ₅ ⁻	-1123.900	-1302.060	358.10	99.00	9779
	2.0				
Sn(OH) ₆ ⁻⁻	-1298.200	-1584.060	231.80	-118.00	9779
SnOH ⁺⁺⁺	-238.180	-260.400	-52.30	-186.00	1119
Sn(OH) ₂ ⁺⁺	-470.870	-543.070	13.04	-80.00	1119
Sn(OH) ₄ (aq)	-950.600	-1123.610	142.30	-855.00	1119

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
SnF ⁺	-332.170	-353.590	34.30	56.00	1119
SnCl ⁺	-168.490	-165.700	107.22	15.00	8889
	0.2	1.6	4.60		
SnCl ₃ ⁻	-432.630	-487.000	259.00	32.00	3919
	4.0				
SnCl ₄ ^{- -}	-560.600	-610.500	476.70	45.00	*999
SnSO ₄ ⁺⁺	-781.740				3000
	4.0				

Comments:

Reference 1=Jackson; Helgeson, 1985;2=Wagman et al.,1982;3=Naumov et al.,1974; 4=Barin et al.,1977;5=CODATA, 1978;6=Baes; Mesmer, 1976,1981: 9=This work.

7 = Eadington, 1982; 8 = Vasil'ev, 1976, 1979.: Values for SnSe₂(s) from Melekh et al.:Russ.J.Phys.Chem. 1971,v.45,1144. Gibbs energies of following calculated from values of hydrolysis constants given in Baes;Mesmer,1976, 1981: SnOH⁺, Sn(OH)₂(aq), Sn(OH)₃⁻, Sn₂(OH)₂⁺⁺,Sn₃(OH)₄⁺⁺⁺. Enthalpy and entropy of SnOH⁺ calculated from data in Baes;Mesmer,1981. Heat capacity and entropy of SnCl₂(s) obtained from Paukov;Stenin; G.I.Frolova:Russ.J.Phys.Chem. 1979, v.53, 1505. Gibbs energy of formation for SnCl₄^{- -},SnSO₄(aq),Sn(SO₄)₂^{- -} from data in Phillips, 1982. Entropy of SnO(s) is from the calorimetry measurements by V.N.Kostyukov et al.: Russ.J.Phys.Chem. 1978, v.52, 1071. The Gibbs energy for Sn⁺⁺⁺⁺ from emf measurements by V.P.Vasil'ev et al.:Izv.Vyssh.Uchebn.Zaved.,Khim.Khim.Tekhnol. 1979, v. 22, 1082 (Chem.Abstr. 1980, 91:199833f). Enthalpy of formation of both SnO(s) and SnO₂(s) are -280.71 and -577.63kJ/mol, measured by combustion calorimetry: E.G.Lavut;B.I.Timofeyev;V.M.Yuldasheva;E.A.Lavut;G.L.Galchenko: J.Chem.Thermodynamics 1981, v.13, 635. P.J.Eadington: Proc.First Intl.Conf.Hydrothermal Reactions (1982); Vasil'ev et al.:Russ.J.Inorg.Chem.1976,21,218;1985,30,957.

PROPERTIES OF ELEMENTAL URANIUM:

Atomic Number: 92
 Formula Mass: 238.0290 for U
 Electronic Configuration: $5f^3 6s^2 6p^6 6d^1 7s^2$
 Electronegativity: U(IV)=1.4; U(VI)=1.9
 Hydration Number: $UO_2^{++}=7.35$
 Ionic Radius: $U^{+++}=1.025$; $U^{++++}=0.93$; $UO_2^{++}=0.75$ angstrom.
 Selected Average for Soils:
 Concentration in Natural Waters: 3.3μ g/L in sea water.

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

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
U(s)	0.000	0.000	50.20	27.66	5557
			0.20	0.0	
UO ₂ (s),uraninite	-1031.700	-1084.900	77.03	63.60	1111
	1.0	1.0	0.20	0.0	
UO ₂ (am)	-1010.700				9000
	4.0				
UO ₃ (am),gummite	-1130.500	-1208.300	96.65		8880
α -U ₃ O ₈ (s)	-3369.700	-3574.800	282.59	238.36	1111
	3.0	2.5	0.50		
γ -UO ₃ (s)	-1145.900	-1223.800	96.11	81.67	1111
	2.0	2.0	0.40		
UO ₃ ·2H ₂ O(s)	-1632.000	-1827.200	171.00	200.20	1111
	2.0	2.1	4.00		
U ₄ O ₉ (s)	-4275.000	-4510.000	334.10	293.30	7777
		4.0	0.70		
β -UO ₂ (OH) ₂ (s)	-1394.000	-1534.700	123.00	85.79	1111
	4.0	4.0	13.00		
UO ₂ (OH) ₂ ·H ₂ O(s),schoepite	-1633.400	-1825.900	178.20		8880
UF ₆ (s)	-2068.500	-2197.000	227.60	166.77	4444
		1.7	1.30	0.2	
UF ₄ (s)	-1823.300	-1914.200	151.67	116.02	4444
		4.1	0.17	0.1	
UF ₄ ·2.5H ₂ O(s)	-2408.000	-5262.490	289.00	263.70	1111
	13.0	15.0	25.00		

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
UCl ₆ (s)	-962.000	-1092.000 13.0	285.80 1.70	175.70 4.1	4444
UOCl ₂ (s)	-996.200	-1066.900 2.5	138.32 0.20	95.06 0.4	4444
UO ₂ CO ₃ (s),rutherfordine	-1562.600 2.0	-1691.200 8.0	138.10 8.00	125.50	3333
β -UO ₂ SO ₄ (s)	-1685.915 2.5	-1845.100 0.8	163.17 8.00	144.90	3333
U(SO ₄) ₂ (s)	-2084.900 14.6	-2309.600 12.6	180.00 21.00		3330
UO ₂ HPO ₄ (s)	-2111.660 4.0				9000
(UO ₂) ₃ (PO ₄) ₂ (s)	-5176.000 17.0	-6008.200 17.0	406.00 21.00	357.00	1111
(UO ₂) ₂ (HPO ₄) ₂ (s)	-4218.000 13.0	-4577.300 13.0	331.00 17.00	298.00	1111
U(HPO ₄) ₂ ·4H ₂ O(s)	-3811.000 3.0	-4305.300 3.0	356.00 17.00	460.00	1111
USiO ₄ (s),coffinite	-1891.200	-1999.900	117.10		8880
(NH ₄) ₂ (UO ₂) ₂ (PO ₄) ₂ (s)	-4397.400	-4899.500	439.30		8880
H ₂ (UO ₂) ₂ (PO ₄) ₂ (s),H-autunite	-4217.500	-4457.300	330.00		8880
Na ₂ (UO ₂) ₂ (PO ₄) ₂ (s),Na-autunite	-4736.300	-5071.000	393.30		8880
K ₂ (UO ₂) ₂ (PO ₄) ₂ (s),K-autunite	-4782.300	-5121.200	405.80		8880
Mg(UO ₂) ₂ (PO ₄) ₂ (s),saleeite	-4648.400	-4974.800	343.10		8880
Ca(UO ₂) ₂ (PO ₄) ₂ (s),autunite	-4748.800	-5075.200	351.50		8880
Sr(UO ₂) ₂ (PO ₄) ₂ (s),Sr-autunite	-4757.200	-5083.600	364.00		8880
Ba(UO ₂) ₂ (PO ₄) ₂ (s),uranocircite	-4757.200	-5087.700	368.20		8880
Fe(UO ₂) ₂ (PO ₄) ₂ (s),bassetite	-4276.000	-4598.200	355.60		8880
Cu(UO ₂) ₂ (PO ₄) ₂ (s),torbernite	-4133.800	-4460.100	355.60		8880
Pb(UO ₂) ₂ (PO ₄) ₂ (s),przhevalskite	-4220.700	-4548.000	376.60		8880
K ₂ (UO ₂) ₂ (VO ₄) ₂ (s),carnotite	-4589.800	-4912.000	439.30		8880
Ca(UO ₂) ₂ (VO ₄) ₂ (s),tyuyamunite	-4560.600	-4870.100	384.90		8880

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
CaU(PO ₄) ₂ ·2H ₂ O(s),ningyosite	-3905.300	-4250.900	293.00		8880
Ca(UO ₂) ₂ (SiO ₃ OH) ₂ (s),uranophane	-4975.000				8000
Na ₂ U ₂ O ₇ (s)	-3002.000	-3203.800	275.86	227.30	7777
		4.4	0.83	0.7	
β-Cs ₂ U ₂ O ₇ (s)	-3003.300	-3226.600	327.80	231.20	7777
	5.0	4.5	0.70	0.5	
α-Li ₂ UO ₄ (s)		-1971.900			0700
		1.7			
α-Na ₂ UO ₄ (s)	-1778.300	-1897.000	166.02	146.60	7777
	2.0	4.0	0.30	0.3	
β-Na ₂ UO ₄ (s)		-1886.000			0700
		4.0			
K ₂ UO ₄ (s)		-1911.000			0700
		1.7			
Cs ₂ UO ₄ (s)	-1803.801	-1926.314	219.66	152.76	7777
	4.2	4.2	0.46	0.3	
Li ₄ UO ₅ (s)		-2641.000			0700
β-Na ₄ UO ₅ (s)		-2451.000			0700
		2.0			
MgU ₃ O ₁₀ (s)			338.60	305.60	0077
CaU ₂ O ₇ (s)		-3335.000			0700
Sr ₂ U ₃ O ₁₁ (s)		-5234.000			0700
		3.0			
MgUO ₄ (s)	-1749.213	-1856.900	131.90	128.10	7777
	1.3	1.3			
CaUO ₄ (s)	-1895.043	-2001.626	123.80	123.30	7777
	3.3	21.0	8.00		
α-SrUO ₄ (s)		-1985.000			0700
		2.0			
β-SrUO ₄ (s)		-1987.000			0700
		2.0			
BaUO ₄ (s)	-1887.200	-1997.100	153.97	125.27	7777
	2.1	2.1	0.30	0.3	
Sr ₂ UO ₅ (s)		-2626.000			0700
		2.0			

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
Ca ₃ UO ₆ (s)		-3302.000 3.0			0700
Sr ₃ UO ₆ (s)		-3263.000 4.0			0700
Ba ₃ UO ₆ (s)		-3210.600 5.8			0700
Ba ₂ MgUO ₆ (s)		-3245.300 4.8			0700
Ba ₂ CaUO ₆ (s)		-3295.600 5.3			0700
NiU ₃ O ₁₀ (s)		-3942.000	358.00		0770
LiUO ₃ (s)		-1522.100 1.7			0700
NaUO ₃ (s)	-1412.200 1.6	-1494.600 1.6	132.84 0.13	108.90 0.1	7777
KUO ₃ (s)		-1522.900 1.6			0700
RbUO ₃ (s)		-1520.900 1.7			0700
Na ₃ UO ₄ (s)	-1897.965 2.5	-2022.127 2.5	198.20 0.42	173.01 0.4	7777
CaU ₂ O ₆ (s)		-3210.000			0700
KUO ₂ PO ₄ ·3H ₂ O(s)	-3102.000 8.0				9000
NH ₄ UO ₂ PO ₄ ·3H ₂ O(s)	-2915.800 8.4				9000
UO ₂ ⁺⁺	-952.700 2.1	-1019.200 2.5	-98.30 4.00	5.00	7551
UO ₂ ⁺	-968.600 5.4	-1032.600 5.9	-25.00 8.00	98.00	2221
U ⁺⁺⁺⁺	-530.900 2.1	-591.200 3.3	-414.00 21.00	-48.00	2221
U ⁺⁺⁺	-480.700 4.6	-489.100 3.8	-174.90 6.40	-64.00	2221
UO ₂ OH ⁺	-1156.260 0.2	-1258.230 0.2	16.00 25.00	68.00	9919

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
UO ₂ (OH) ₂ (aq)	-1359.000 5.0	-1515.000	59.00 17.00	-276.00	1119
(UO ₂) ₂ (OH) ₂ ⁺⁺	-2347.350 0.5	-2566.510 0.7	-19.00 17.00	-58.00	9919
(UO ₂) ₃ (OH) ₄ ⁺⁺	-3739.500 2.0				6000
(UO ₂) ₃ (OH) ₅ ⁺	-3955.000 7.0	-4381.000 7.0	111.00 17.00	5.00	1119
(UO ₂) ₃ (OH) ₇ ⁻	-4343.000 20.0		299.00 80.00	59.00	1019
UOH ⁺⁺⁺	-764.320 2.0	-827.990 2.0	-192.00 40.00	-93.00	6919
U(OH) ₂ ⁺⁺	-980.800 20.0	-1077.390 20.0	-69.00 40.00	-25.00	9919
U(OH) ₃ ⁺	-1197.350 20.0	-1337.220 20.0	19.00 40.00	66.00	9919
U(OH) ₄ (aq)	-1413.870 20.0	-1614.050 20.0	50.00 40.00	-610.00	9919
U(OH) ₅ ⁻	-1630.380 20.0	-1893.860 20.0	71.00 40.00	-93.00	9919
UO ₂ F ⁺	-1264.000 3.0	-1357.300 3.0	-19.00 20.00	92.00	1119
UO ₂ F ₂ (aq)	-1567.000 3.0	-1693.300 3.0	35.00 20.00	-229.00	1119
UO ₂ F ₃ ⁻	-1863.000 3.0	-2028.400 3.0	69.00 20.00	-94.00	1119
UO ₂ F ₄ ⁻⁻	-2151.000 3.0	-2364.700 3.0	76.00 20.00	-221.00	1119
UF ⁺⁺⁺	-862.000 8.0	-907.010 8.0	-192.00 80.00	-93.00	1119
UF ₂ ⁺⁺	-1177.000 8.0	-1233.300 8.0	-63.00 200.00	-29.00	1119
UF ₃ ⁺	-1485.000 13.0	-1567.300 13.0	13.00 200.00	70.00	1119
UF ₄ (aq)	-1793.000 13.0	-1914.900 13.0	50.00 200.00	-516.00	1119

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
UF ₅ ⁻	-2084.000 17.0	-2249.600 17.0	71.00 200.00	-93.00	1119
UF ₆ ⁻⁻	-2379.000 17.0	-2589.500 17.0	84.00 200.00	-215.00	1119
UO ₂ Cl ⁺	-1094.000 8.0	-1186.500	-6.00 80.00	83.00	1119
UCI ⁺⁺⁺	-677.000 8.0	-751.000 8.0	-283.00 80.00	-32.00	1119
UO ₂ SO ₄ (aq)	-1715.610 0.2	-1909.200 0.7	47.50 3.00	-273.00	9999
UO ₂ (SO ₄) ₂ ⁻⁻	-2466.870 0.6	-2800.600 2.0	150.40 9.00	-173.00	9999
USO ₄ ⁺⁺	-1307.000 8.0		-272.00 30.00	110.00	1019
U(SO ₄) ₂ (aq)	-2076.000 17.0	-2378.600 17.0	-110.00 50.00	-604.00	1119
UO ₂ CO ₃ (aq)	-1549.730 1.0	-1697.050 1.0	75.10	-269.00	9999
UO ₂ (CO ₃) ₂ ⁻⁻	-2104.980 2.0	-2391.900 2.0	51.40	-239.00	9999
UO ₂ (CO ₃) ₃ ⁻⁻⁻⁻	-2660.230 2.0	-3086.750 2.0	27.70 8.00	-522.00	9999
(UO ₂) ₂ CO ₃ (OH) ₃ ⁻	-3132.300 10.0	-3631.000 30.0			9900
UO ₂ HPO ₄ (aq)	-2090.000 42.0	-2304.900 42.0	50.00 200.00		1110
UO ₂ (HPO ₄) ₂ ⁻⁻	-3237.000 42.0	-3622.900 42.0	126.00 200.00	-187.00	1119
UO ₂ H ₂ PO ₄ ⁺	-2100.000 3.0	-2311.700 3.0	63.00 200.00	37.00	1119
UO ₂ (H ₂ PO ₄) ₂ (aq)	-3245.000 4.0	-3242.600 4.0	84.00 200.00		1110
UO ₂ (H ₂ PO ₄) ₃ ⁻	-4385.000 4.0	-4970.600 4.0	105.00 200.00	-65.00	1119
UHPO ₄ ⁺⁺	-1689.000 21.0	-1837.200 21.0	-63.00 200.00	-29.00	1119

Substance	$\Delta_f G^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	S° J mol ⁻¹ K ⁻¹	C_p° J mol ⁻¹ K ⁻¹	Ref.
U(HPO ₄) ₂ (aq)	-2835.000 21.0	-3138.800 21.0	63.00 200.00		1110
U(HPO ₄) ₃ ⁻⁻⁻	-3974.000 21.0	-4455.900 21.0	105.00 200.00	-201.00	1119
U(HPO ₄) ₄ ⁻⁻⁻⁻	-5109.000 21.0	-5811.600 21.0	21.00 200.00	-529.00	1119
UO ₂ SiO(OH) ₃ ⁺	-2246.800				8000

Comments:

References are as follows: 1=R.J.Lemire;P.R.Tremaine:J.Chem.Eng.Data 1980,v.25,361; 2=IAEA,Part 2,1976;3=IAEA,Part3,1978;4=IAEA,Part 8,1983;5=CODATA; Ref. 6 = Baes; Mesmer, 1976; 7=L.R.Morss:"Thermodynamic Properties",in, "The Chemistry of the Actinide Elements",2nd ed.,Preprint (Nov.6,1985);8=D.Langmuir:Geochim.Cosmochim. Acta 1978, v.42, 547; 9 = This work. $\Delta_f G^\circ[(UO_2)_2CO_3(OH)_3^-]$ from L.Maya:Inorg.Chem.1982,v.21,2895. Species U(OH)₅⁻ has been questioned in two ways by Ryan and Rai: Polyhedron 1983, v.2, 947:(a) whether this anionic form exists in alkaline media,(b) logK for hydrolysis of -16.0 as calculated by Baes and Mesmer,1976. $\Delta_f G^\circ[(UO_2)_2(OH)_2^{++}]$ obtained by plotting experimental measurements of log K(I) versus I, according to extended Debye-Huckel equation, and extrapolating to zero ionic strength, to obtained log K°. From this value, the Gibbs energy of formation was calculated. Ryan and Rai (1983) found that uncharacterized UO₂(am) is less soluble in 0.045 to 10.0M NaOH solutions containing added Zn(s) and dithionite than measured by Gayer and Leider: Can.J.Chem. 1957, v.35, 5. Also, the solubility of carefully characterized UO₂(s) in pOH 1.5 and pOH 2.5 solutions, 25 to 300°C under wet H₂(g) by Tremaine;Chen;Wallace; W.A.Boivin: J.Solution Chem. 1981, v.10, 221 gave results "at least consistent with UO₂(s) + 2H₂O + OH⁻ = U(OH)₅⁻". We have calculated $\Delta_f G^\circ[U(OH)_5^-]$ from the measurements of Tremaine et al. (1981) on the solubility of uraninite; this value together with that for U(OH)⁺⁺⁺⁺ was plotted versus the number of OH⁻ ligands, and values for the 1:2, 1:3 and 1:4 postulated intermediate hydrolysis products were obtained by interpolation of this plot. Ullman;Schreiner:Radiochim.Acta 1986,v.40,179 and Ibid. (submitted,1987) report data from which we calculate or use for Gibbs energy and enthalpy of formation values for UO₂SO₄(aq);UO₂(SO₄)₂⁻⁻⁻,and 1:2,1:3 carbonates. Gibbs energy and enthalpy of formation for UO₂CO₃(aq) calculated from plot of these values for the 1:2 and 1:3 complexes, then extrapolating to n=1. IAEA,Part 3, gives $\Delta_f G^\circ[UO_2CO_3(aq)] = -1536.8 \pm 9.2$, and $\Delta_f H^\circ = -1691.2 \pm 8.9$, $S^\circ = 50 \pm 8$. Enthalpy of formation for (UO₂)₂CO₃(OH)₃⁻ from Ullman;Schreiner. $\Delta_f G^\circ[UO_2(am)]$ calculated from Bruno et., 1986. Gibbs energy for UO₂HPO₄(s), NH₄UO₂PO₄(s).3H₂O(s), and KUO₂PO₄.3H₂O(s) are from Naumov et al (1974). Gibbs energy of UO₂OH⁺ is from Caceci;Choppin: Radiochim.Acta 1983,v.33,207. F.David: J.Less-Common Metals 1986,v.121,27 gives $S^\circ[U^{++++}] = -183$, $S^\circ[U^{++++}] = -399$, $S^\circ[UO_2^{++}] = -26$, $S^\circ[UO_2^{++}] = -98$, all J/mol/K. His values for corresponding $\Delta_f H^\circ$ are: -489.1, -591.2, -1033, -1019.2, all kJ/mol. Our $\Delta_f G^\circ[UO_2^{++}]$ and $\Delta_f G^\circ[U^{++++}]$ give $E^\circ = 0.272$ v. for UO₂⁺⁺ + 4H⁺ + 2e = U⁺⁺⁺⁺ + 2H₂O, comparing with 0.329 v. by Sobkowski;Minc:J.Inorg.Nucl.Chem. 1961,v.23,81; and, 0.273v., by Nikolaeva: in Bruno et al.:Mat.Res.Soc.Symp.Proc. 1985,v.50,299; and, 0.329 v. by Guorong et al., Radiochim.Acta 1985,v.38,145. Parks and Pohl: Geochim.Cosmochim.Acta 1988, v.52,863 published careful experimental data on "Hydrothermal Solubility of Uraninite" from 100 to 300° C.

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J. G. Blencoe
N. H. Cutshall
T. O. Early
L. M. Ferris
R. M. Gove
G. K. Jacobs
A. D. Kelmers
D. C. Kocher
S. Y. Lee
R. E. Meyer
V. S. Tripathi

Westinghouse Hanford Operations
P.O. Box 800
Richland, WA 99352 (7)
Attn: S. M. Baker
G. S. Barney
J. H. LaRue
J. Myers
P. F. Salter
G. Solomon
M. I. Wood

Battelle Pacific Northwest Laboratory
P.O. Box 999
Richland, WA 99352 (9)
Attn: L. L. Ames
M. J. Apted
D. G. Coles
W. J. Gray
E. A. Jenne
K. Krupka
G. L. McVay
D. Rai
J. Serne

U. S. Department of Energy
Waste Management Project Office
Nevada Operations Office
Las Vegas, NV 89104
Attn: J. S. Szymanski

DIST-3

Dept. of Geology and Institute of Meteoritics
University of New Mexico
Albuquerque, NM 87131 (4)
Attn: D. Brookins
L. Crossey
R. Ewing
K. Keil

Environmental Engineering and Science
Department of Civil Engineering
Stanford University
Stanford, CA 94305 (2)
Attn: J. O. Leckie
D. Freyberg

National Science Foundation
Division of Earth Sciences
Washington, DC 20555
Attn: R. Buden

Sandia National Laboratories

1512 K. L. Erickson
3141 S. A. Landenberger (5)
3151 W. L. Garner
6230 W. C. Luth
6233 T. R. Gerlach
6233 W. H. Casey
6233 J. L. Krumhansl
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6400 D. J. McCloskey
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6416 J. S. Philbin
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6416 L. R. Shippers
6416 G. F. Wilkinson
8024 P. W. Dean

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