MINTEQ2 Geochemical Code: Provisionary Organic Data Base

**J. R. Morrey
K. M. Krupka
F. H. Dove**

October 1985

**Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830**

**Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute**

DISCLAIMER

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

PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161

NTIS Price Codes
Microfiche A01

Printed Copy

Pages	Price Codes
001-025	A02
026-050	A03
051-075	A04
076-100	A05
101-125	A06
126-150	A07
151-175	A08
176-200	A09
201-225	A010
226-250	A011
251-275	A012
276-300	A013

MINTEQ2 GEOCHEMICAL CODE:
PROVISIONARY ORGANIC DATA BASE

J. R. Morrey
K. M. Krupka
F. H. Dove

October 1985

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

ACKNOWLEDGMENTS

We express gratitude to several people who have cooperated in the preparation of this report. First, we thank G. Sposito and S. Mattigod of the University of California, Riverside, for making their code GEOCHEM and its thermochemical data base available to us. We also are indebted to J. Serne, J. Sonnichsen, J. Relyea, E. Jenne and R. Isaacson for valuable comments, and J. Downs-Berg for editing help.

FOREWORD

The program, entitled "Site Performance Assessment for the Disposal of Hanford Defense Waste," was initiated in FY 1985 to address the consequences of events and processes that might affect the waste disposal system. The program is part of the issue resolution for performance assessments as defined in the Hanford Waste Management Technology Plan (December 1984). The objectives of the program are threefold:

- to evaluate the effectiveness of various disposal options in protecting present and future humans and their environments from Hanford defense waste
- to develop and maintain the analytical techniques, models, and data bases necessary to assess postulated disposal actions on a systems performance basis
- to provide a technical basis for decisions concerning site selection, conceptual systems design, system tradeoff studies, development of criteria and standards, and research and development priorities.

One programmatic task is directed toward developing tools to understand the implications of potential aqueous transport of chemicals from a storage tank or other source to the environment. In this regard, efforts during FY 1985 have included the development of a capability to estimate the aqueous composition of sources and the solubility coefficients of contaminants with the presence of organics in solution.

EXECUTIVE SUMMARY

Organic components in aqueous radioactive chemical sources, surface waters, and ground waters could substantially alter the mobility of radioactive and other important nonradioactive elements released from a defense waste disposal system. It is therefore important to be able to predict, as accurately as possible, the effects of selected organic components on the solubilities of radionuclides and important nonradioactive elements.

Pacific Northwest Laboratory (PNL) has developed the computer code, MINTEQ2, for the U.S. Department of Energy (DOE). This geochemical code can be used to assess solubilities provided that appropriate thermochemical data for organic and inorganic aqueous species and solids are available for its use. The code accepts an assemblage of gaseous and solid phases in contact with an aqueous phase and calculates the thermochemical equilibrium between these phases. Unlike typical hydrologic flow and transport codes where the data base is entirely site specific (i.e., parameters particular to the specific site), MINTEQ2 requires an additional generic thermochemical data base. This report discusses the addition of provisional organic reactions and associated equilibrium constants to the generic data base that can be used by MINTEQ2 in scoping calculations or preliminary performance assessments.

Our organic thermochemical data set was compiled from a thermochemical data set published as part of the GEOCHEM computer code by staff at the University of California, Riverside. Included in the compilation are reactions with the following organic ligands that commonly complex with metal ions and generally increase the solubility (thus mobility) of metals in water: 1) acetates, 2) citrates, 3) ethylenediamines, 4) ethylenediaminetetraacetates, 5) diethylenetriaminepentaacetates, and 6) nitrilotetraacetates. Of these ligands, only acetate, citrate, and ethylenediaminetetraacetate have been identified as major organics in Hanford defense waste. The other two, diethylenetriaminepentaacetate and nitrilotetraacetate, have not been identified to date, but they have been included to represent two other classes of organics that might be expected to form in defense waste tanks.

The task of modifying and formatting the thermochemical data in the GEOCHEM data set to be acceptable for use in MINTEQ2 required the generation of a manipulative computer code, GEOMIN. This new code was subsequently used to transform the thermochemical data.

The data base for MINTEQ2 is provisional because we have made no attempt to verify the data reported in the GEOCHEM data set and because the GEOCHEM data set did not include reactions for radionuclides. It will be necessary to accumulate additional data on the organic complexation of radionuclides from other sources in the literature. Furthermore, in the interest of economy, the final organic data base ought to be defined and verified only after all of the important organic ligands have been identified in the waste inventory and the subsurface environment. In the meantime, however, using MINTEQ2 and the provisional organic data base to simulate problems associated with the Hanford defense waste will help to focus attention on needed additional reactions.

We recommend that MINTEQ2 be further developed to increase its chemical modeling capability to include adsorption processes and to increase its applicability to Hanford defense waste problems, such as modeling leaks from containment vessels and other waste sources and chemical processing to produce the waste.

CONTENTS

ACKNOWLEDGMENTS.....	iii
FOREWORD.....	v
EXECUTIVE SUMMARY.....	vii
1.0 INTRODUCTION.....	1.1
1.1 ESTABLISHMENT OF A 'BEST' THERMOCHEMICAL DATA BASE.....	1.3
2.0 BACKGROUND.....	2.1
2.1 GEOCHEMICAL EQUILIBRIUM CODES.....	2.1
2.2 THERMOCHEMICAL DATA BASE.....	2.3
2.2.1 Previous Thermochemical Data Base.....	2.3
2.2.2 Need for Additions of Organic Ligands.....	2.5
2.2.3 Source of Organic Thermochemical Data.....	2.5
3.0 EXPANDED THERMODYNAMIC DATA BASE.....	3.1
3.1 ORGANIC LIGANDS IN THE SPOSITO-MATTIGOD DATA BASE.....	3.2
3.2 GENERATION OF THE MINTEQ2-COMPATIBLE DATA BASE.....	3.2
3.2.1 Data Base Conversion.....	3.2
3.2.2 Identification Indices for Organic Ligands.....	3.4
3.3 DEFINITIONS AND THERMODYNAMIC STANDARDS.....	3.6
3.4 SELECTED ORGANIC LIGANDS.....	3.7
3.4.1 Acetates.....	3.8
3.4.2 Citrates.....	3.10
3.4.3 Diethylenetriaminepentaacetates.....	3.12
3.4.4 Ethylenediamines.....	3.14
3.4.5 Ethylenediaminetetraacetates.....	3.15
3.4.6 Nitrilotriacetates.....	3.17

3.4.7 Oxalates.....	3.19
4.0 RECOMMENDATIONS FOR FURTHER WORK.....	4.1
4.1 ADDING ORGANIC REACTIONS TO THE THERMODYNAMIC DATA BASE.....	4.2
4.2 ADDING PITZER PARAMETERS FOR ORGANIC INTERACTIONS.....	4.3
4.3 ADDING ADSORPTION REACTIONS.....	4.3
4.4 FURTHER MODIFICATIONS TO MINTEQA2.....	4.3
4.5 APPLICATIONS TO HANFORD DEFENSE WASTE PROBLEMS.....	4.4
5.0 REFERENCES.....	5.1
APPENDIX A - CURRENT LISTING OF DATA CONVERSION CODE, GEOMIN.....	A.1

FIGURES

2.1	Schematic of Chemical Modeling Capabilities of MINTEQ2.....	2.3
-----	---	-----

TABLES

2.1	Listing of Thermodynamic Data Base Before Additions.....	2.4
3.1	Organic Ligands Included in the GEOCHEM Database.....	3.3
3.2	Wiswesser Group Designations.....	3.5
3.3	Designations for Organic Ligands.....	3.6
3.4	Thermochemical Additions for Acetates.....	3.8
3.5	Thermochemical Additions for Citrates.....	3.10
3.6	Thermochemical Additions for Diethylenetriaminepentaacetates.....	3.12
3.7	Thermochemical Additions for Ethylenediamines.....	3.14
3.8	Thermochemical Additions for Ethylenediaminetetraacetates.....	3.15
3.9	Thermochemical Additions for Nitrilotriacetates.....	3.17
3.10	Thermochemical Additions for Oxalates.....	3.19
4.1	Additional Organic-Ligand Reactions Needed for MINTEQ2.....	4.2

1.0 INTRODUCTION

Complex aqueous chemistry is associated with many aspects of the management of defense wastes. Problems associated with reprocessing of nuclear fuels, transfer of wastes to tanks through connecting pipes or tank cars, storage of wastes in repositories, spills or leaks, and transport rates of radioactive and hazardous nonradioactive elements through geological formations all need to be well understood to ensure adequate waste management. With systems as complex as those generally found at nuclear installations, however, the chemistry is concomitantly complex enough to require computer codes to calculate, simulate, or model the consequences of possible unplanned scenarios.

The use of chemical codes can be particularly helpful in obtaining valuable insight while interpreting laboratory or field data. Using these codes to test conceptual models of the actual physical and chemical processes can help distinguish important from unimportant factors affecting the complex chemistry. For example, modeling can be used to test the hypothesis that a certain chemical equilibrium has been attained, or conversely, determine which solid phases are not in thermodynamic equilibrium with a particular aqueous system. Codes can be used to help distinguish the relative importance of adsorption and precipitation and can identify the redox state of the system if it is not experimentally known.

One important application of geochemical equilibrium codes is in helping predict chemical behavior in storage tanks. Defense wastes are currently stored in a variety of disposal systems (e.g., single or double-shell tanks, near-surface trenches, settling ponds, etc.). Assessment of the performance of these systems requires defining the composition of aqueous solutions that could, under selected scenarios, migrate to the accessible environment. An example is the performance assessment of dewatered and liquid wastes in single-shell tanks. One scenario might be the migration of water through a rupture in the tank, dissolution of some of the salt cake or sludge, migration back out, and transport into the surrounding sediments. Another might be the direct leakage of existing liquids out of the tanks. In either case, to predict the

migration of chemicals away from the source, we must know the initial chemical composition of the water solution at the source (source term).

The development of a source term is a critical step in the performance assessment of a waste disposal option. Although the importance of this release component is well established, source-term modeling is perhaps the least developed of the performance assessment analyses. Because the contaminant eventually received at the accessible environment is directly related to the released waste, source-term modeling can significantly influence predictions of the future consequence of a contaminant release.

The source term depends on several variables: the scenario selected for contaminant release; the waste inventory; the waste form; the contaminant release rates for liquid, solid, and gaseous phases; the ground-water chemistry; the temperature; the pH; and the redox environment. Often, considerable uncertainty exists regarding the actual waste inventory, contaminant release rates, and ground-water chemistry, particularly in the unsaturated zone above the water table.

The presence of organic ligands may increase contaminant solubility well beyond concentrations normally predicted by considering inorganic solubility equilibria. Multidentate ligands are effective in this regard, and EDTA, a hexadentate ligand, is particularly effective (Stumm and Morgan 1970). For example, at a pH of 8, 10^{-2} molal EDTA will increase the solubility of Fe(III) in equilibrium with ferric hydroxide by six orders of magnitude over what it would be without the presence of EDTA.

This report does not focus directly on predicting the aqueous-organic chemistry in storage tanks nor in other applications; instead, its focus is on efforts to accumulate organic thermochemical data that must be added to existing compiled thermochemical data for inorganics before reliable predictions can be made. An organic thermochemical data base is required to estimate the effect of organic chemical reactions on the complexation of other dissolved chemical species and the precipitation or dissolution (i.e., solubility) of contaminant-containing solid phases.

Pacific Northwest Laboratory has developed a provisional organic data base that can be used by the geochemical code MINTEQA2. The thermochemical data for reactions described herein have all been taken from a compilation that was tailored to study reactions in soil-water systems. Consequently, the original data set contains a large number of organic ligands common to soils, most of which are not expected in low-humus Hanford site soils. Therefore, only a few ligands are included in our data base. All such organic reactions must be considered provisional because no effort has been expended to verify their accuracy or adequacy. Verification can best follow after it has been determined which organic ligands are important in the assessment of disposal systems for Hanford defense waste.

1.1 ESTABLISHMENT OF A 'BEST' THERMOCHEMICAL DATA BASE

Quality assurance for the thermochemical data of the reactions presented in this report will require a substantial and sustained effort. The normal process of selecting the 'best' data for a given element requires the following sequence of efforts:

- An initial collection of thermochemical data for the aqueous species, solids, and redox couples should be obtained from as many technically reputable sources as possible, including the National Bureau of Standards (NBS), the U.S. Geological Survey (USGS), the data base being assembled by the International Union of Pure and Applied Chemistry (CODATA), and data from refereed scientific journals. This collection should include fundamental thermochemical data (e.g., Gibbs free energies of formation, enthalpies of formation, and entropies) and reference citations for each thermochemical value.
- The collected thermochemical data should be critically reviewed and the best data selected by examining the original sources and checking the derivations of the thermochemical parameters.
- The choices should be documented. The documentation should include the references, selection criteria, recalculations or estimations, and efforts to generate an internally consistent data base.

- Validation studies should be conducted to document the degree of agreement between modeling studies, using the best selected values, and analytical data from laboratory and field experiments and site-characterization studies.

The data base in its present form should be useful for scoping calculations, preliminary performance assessments, and perhaps most importantly, identifying technical areas needing more research and development. However, it should be clearly understood that thermochemical modeling studies based on a the provisional thermochemical data base may not be technically defensible. Until the source of each thermochemical value is known and careful evaluations have been conducted, one cannot judge the accuracy of the calculations leading to the formation of the data base.

2.0 BACKGROUND

Often overlooked is the effectiveness of chemical codes in helping the user obtain valuable insight while interpreting laboratory or field data. Using these codes to test conceptual models of the actual physical and chemical processes can help distinguish important from unimportant factors affecting the complex chemistry. For example, modeling can be used to test the hypothesis that a certain chemical equilibrium has been attained, or conversely, determine which solid phases are not in thermodynamic equilibrium with a particular aqueous system. Codes can be used to help to distinguish the relative importance of adsorption and precipitation and can identify the redox state of the system if it is not experimentally known.

2.1 GEOCHEMICAL EQUILIBRIUM CODES

A number of sophisticated computer codes have been written to model complex aqueous chemical equilibria (Kincaid, Morrey and Rogers 1984). These have been used with varying degrees of success to predict aqueous concentrations of chemical elements in aqueous fluids as they interact with complexing ligands, soils, and sediments under the influence of a given pH, Eh (redox potential), temperature, carbon dioxide pressure, and oxygen gas pressure (Kincaid and Morrey 1984). Some codes have also been used to predict the formation of mineral phases and changes in pH, Eh, temperature, and gas pressures; or to understand how the composition of an aqueous phase changes when the pH, or oxygen or carbon dioxide pressure are altered by external means; or when a ligand is added to the aqueous stream.

One of the more versatile chemical codes is MINTEQ, developed by Felmy, Girvin and Jenne (1984). They combined the code MINEQL, developed by Westall, Zachary, and Morel (1976), with the data base and other attributes of WATEQ2, developed by Ball, Nordstrom and Jenne (1980). MINTEQ now includes the most complete set of algorithms for adsorption and the most completely documented thermochemical data base of any of the codes for modeling geochemical equilibrium. It also has been extended to model the dissolution or precipitation of finite quantities of solids.

MINTEQ, however, has some limitations that led us to modify it, thereby generating a follow-on version called MINTEQ2. The modifications are summarized below:

- The use of MINTEQ2 was made easier by constructing a preprocessor code to minimize errors in creating input data files.
- Convergence reliability of MINTEQ2 was improved. The Newton-Raphson technique used in MINTEQ was supplemented by deDonder shifting and back substitution (Morrey and Shannon 1981).
- The code's reliability in modeling solid systems with finite quantities of soluble materials was improved.
- The Pitzer formulation (Pitzer 1981) for modeling situations where high ionic strengths prevail was added and verified.
- Conservation of water was built into the code to account for the mass of water contributed to the aqueous phase by the dissolution and precipitation of water-containing solid phases.

MINTEQ2 adopts the thermochemical data base of MINTEQ and is designed to accept an assemblage of gaseous and solid phases in contact with, but not necessarily in equilibrium with, an aqueous phase. The code then adjusts concentrations in the aqueous phase to conform to an equilibrium state between the gaseous, aqueous, and solid phases. Figure 2-1 outlines in simple block form the modeling capability of MINTEQ and the updated MINTEQ2 code. The analogy is a series of containers connected by valves. The valves in the figure, (----Ø---), can be either open, indicating an open chemical system with respect to the solid and/or gas phases (infinite quantity), or closed, indicating a closed system (finite quantity). By opening or closing the valves between phases, it is possible to equilibrate only the aqueous phase, the aqueous and gas phases, the aqueous and mineral phases, the aqueous and adsorbed phases, or combinations of these.

To operate MINTEQ2, input is required on the total initial concentrations of all aqueous chemical elements, gas pressures, and, for certain applications,

FIGURE 2.1. Schematic of Chemical Modeling Capabilities of MINTEQA2

identified solid phases. In addition, if adsorption is to be modeled, the adsorption algorithm is chosen and chemical equilibria describing the adsorption processes are added.

2.2 THERMOCHEMICAL DATA BASE

This report describes thermochemical data taken from the thermochemical data base associated with the chemical code GEOCHEM (Sposito and Mattigod 1980) reformatted into compatible form, and added to the already extensive thermochemical data base of the chemical equilibrium code, MINTEQA2. Adding these data will extend the capability of MINTEQA2 to model aqueous systems that contain certain organic ligands. Also, provisional data for the aqueous species and solids of certain metals in the data base of GEOCHEM can be made available for some elements that have not yet been added to the MINTEQA2 data base. In particular, reactions for some elements (i.e., beryllium, cerium, cobalt, lanthanum, mercury, scandium, selenium, thorium, titanium, and tin), are available from the GEOCHEM data set, but are not yet publicly available in the thermochemical data base for MINTEQA2.

2.2.1 Previous Thermochemical Data Base

Table 2.1 summarizes the contents of the thermochemical data base used by MINTEQA2 before the data from GEOCHEM were added. These data come in major part

TABLE 2.1. Listing of Thermodynamic Data Base Before Additions

Element (Redox State)	Number of Aqueous Species	Number of Solid Phases	Element (Redox State)	Number of Aqueous Species	Number of Solid Phases
Ag	35	17	Al	11	46
As(III)	5	5	As(V)	4	10
B	6	3	Ba	3	9
Br	13	7	C	41	41
Ca	10	52	Cd	34	23
Cl	45	51	Cr(III)	31	11
Cr(VI)	10	15	Cs	1	2
Cu(I)	9	14	Cu(II)	20	31
F	52	21	Fe(II)	10	22
Fe(III)	23	27	I	13	11
K	5	40	Li	2	1
Mg	10	49	Mn(II)	13	11
Mn(III)	1	6	Mo(VI)	10	23
N(III)	10	3	N(II)	2	0
N(IV)	13	6	Na	8	42
Ni	15	10	P	33	36
Pb	28	46	Pu(III)	9(a)	4(a)
Pu(IV)	17(a)	5(a)	Pu(V)	1(a)	1(a)
Pu(VI)	8(a)	0(a)	Rb	1	1
S(II)	54	28	S(VI)	42	42
S(IV)	10	7	SCN	28	6
Si	5	66	Sr	3	6
Tc(III)	1(a)	0(a)	Tc(IV)	4(a)	0(a)
Tc(V)	1(a)	0(a)	Tc(VI)	3(a)	0(a)
Tc(VII)	1	14(a)	U(III)	1(a)	2(a)
U(IV)	19(a)	34(a)	U(V)	2(a)	5(a)
U(VI)	24(a)	100(a)	V(II)	2	0
V(III)	7	7	V(IV)	9	8
V(V)	19	21	Zn	27	33

(a) Enhancements and revisions currently being completed and documented.

from the WATEQ3 data base (Ball, Nordstrom and Jenne 1980; Ball Jenne and Cantrell 1980; Truesdell and Jones 1974) and later additions (Krupka and Jenne 1982). Though these available data have been extensively documented and evaluated and have been made internally consistent, it should be emphasized that not all of these thermodynamical data still can be guaranteed correct. The selection of accurate and reliable thermochemical data is extremely important to the reliability of the chemical equilibrium calculations, and the efforts to achieve this goal should continue to be supported.

2.2.2 Need for Additions of Organic Ligands

The migration of chemical elements in the soil, sediment, and rock depends on reactions that render the elements mobile in the aqueous phase. Certain polar organics are both soluble in water and good chelating agents. They may increase the dissolved concentrations of certain metals via the formation of chelated complexes. Some of these chelating agents may also lower concentrations of metals in the aqueous phase by causing the precipitation of organic solid phases. An example is the oxalate ligand that forms stable metal oxalate solids. Some of these organics originate in soils; others have been used in the chemical processes at Hanford.

Four organic ligands have been identified in Hanford waste tanks (Delegard, Barney and Gallagher 1983): 1) ethylenediaminetetraacetic acid (EDTA), 2) hydroxyacetate, 3) citrate, and 4) N-2-hydroxyethylendiaminetriacetate (HEDTA); only two of these are included in MINTEQ2. In addition, other organics used in the PUREX process for waste fractionization can also be expected to be present: 1) di(2-ethylhexyl)phosphate (D2EHPA), 2) tributyl phosphate (TBP), and 3) gluconates (ERDA 1977, p. A-3). Therefore, we anticipate that these additional ligands will need to be added to the MINTEQ2 data base.

2.2.3 Source of Organic Thermochemical Data

The organic data base assembled by Sposito and Mattigod (1980) contains a large number of reactions with organic ligands because it was designed to predict complex aqueous chemistry of soils high in organic matter. Because the soils at Hanford generally do not contain large amounts of organic matter, particularly below the surface, including all of these organics in the MINTEQ2 data base currently seems unwarranted. Therefore, at least for the time being, we have chosen to limit consideration to those ligands most closely related to organics found in the Hanford waste tanks themselves. Nevertheless, should other organics be needed, they can be readily extracted from the GEOCHEM data base by using the code, GEOMIN.

3.0 EXPANDED THERMODYNAMIC DATA BASE

The thermodynamical data added to MINTEQ2 all come from the data base released by Sposito and Mattigod (1980) to be used in their chemical code, GEOCHEM. They have gleaned data from a wide range of reputable sources (Martell and Smith 1976, 77; Baes and Mesmer 1976; Robie, Hemingway and Fisher 1978; Sadiq and Lindsay 1979; Sposito 1977). Even though Sposito and Mattigod undoubtedly assembled these data with great care, the data cannot be guaranteed accurate nor internally consistent. The documentation for the GEOCHEM data base is not detailed enough to ensure that the proper procedure has been followed in each case in deriving the correct equilibrium constant. In most cases, of course, the data have been obtained from other sources. Most likely, some data have required manipulation to obtain an equilibrium constant, and so should be reviewed frequently and compared to new data on reactions of interest that appear in the chemical, geochemical, and soil chemical literature. It is very important to keep in mind that the calculational results can never be more accurate than the thermochemical data they contain.

Merging reactions from the GEOCHEM data base with reactions from the MINTEQ2 data base might also create internal inconsistencies. If reactions have been derived by combining other reactions, it is important that thermochemical data for the other reactions remain consistent throughout all the calculations. There is not enough documentary information to ensure that data from GEOCHEM will be internally consistent with those from MINTEQ2. If there are any discrepancies, they will have to be identified later in the program after it is determined which chemical elements and organic ligands are needed for the Hanford defense waste program.

The GEOCHEM data base does not contain separate enthalpies or entropies of reaction. Therefore, equilibrium constants from the source cannot be corrected for variation with respect to temperature. So in applying the data base to problems at different temperatures, it is implicitly assumed that the equilibrium constants for the additional organic complexes and solids are not temperature dependent. For certain reactions, this may be an untenable assumption.

3.1 ORGANIC LIGANDS IN THE SPOSITO-MATTIGOD DATA BASE (GEOCHEM)

The GEOCHEM data base includes a large number of chemical reactions and equilibrium constants for organic chelates. Table 3.1 gives a full listing of the ligands available in the GEOCHEM data base. The third column gives the index designation used by Sposito and Mattigod (1980); the fourth column is the index designation assigned for MINTEQ2 indices.

3.2 GENERATION OF THE MINTEQ2-COMPATIBLE DATA BASE

The GEOCHEM data base includes over 1700 reactions for organic and inorganic aqueous species and solids. The large number and the nondescriptive form of the entries for each reaction makes manual selection and reformatting difficult. In addition, a number of parameters needed for the MINTEQ2 data base are not included in the GEOCHEM data base. Consequently, a FORTRAN code called GEOMIN was written to select the data and calculate additional necessary parameters. Furthermore, including organic complexes and solids in the MINTEQ2 data base required the development of a protocol for unambiguously identifying them.

3.2.1 Data Base Conversion

GEOMIN is a FORTRAN code (see Appendix A for listing) that performs several functions in reading the GEOCHEM data base and converting the selected data to the format used in MINTEQ2:

- GEOMIN allows the user to select reactions to be retrieved, including metal species and ligands.
- GEOMIN calculates the charge on the species.
- GEOMIN separates aqueous complexation reactions from solubility reactions for minerals and related solids.
- GEOMIN assembles a MINTEQ2-compatible numerical index number for each reaction.
- GEOMIN assembles a name for the chemical species being formed by the reaction.

TABLE 3.1. Organic Ligands Included in the GEOCHEM Database

Ligand	Species	Index		Charge	Formula Weight
		GEOCHEM	MINTEQ2		
Acetate	Ac ⁻	15	OV1	-1	59.04
Acetylacetate	Acet ⁻	16	OV3	-1	117.08
Citrate	Cit ⁻³	17	XV3	-3	189.10
Oxalate	Ox ⁻²	18	VV0	-2	88.02
Salicylate	Sal ⁻²	19	RV1	-2	137.11
Tartrate	Tart ⁻²	20	VV2	-2	148.07
Ethylenediamine	En	21	ZZ2	0	60.11
Dipyridyl	Dip	22	NR2	0	156.19
Sulfosalicylate	Susal ⁻³	23	RS1	-3	215.16
Glycine	Gly ⁻	24	VZ0	-1	74.06
Glutamate	Glut ⁻²	25	VZ3	-2	145.11
Picolinate	Pic ⁻	26	RW3	-1	228.09
Nitrotriacetate	Nta ⁻³	27	NV3	-3	188.11
Ethylenediaminetetraacetate	Edta ⁻⁴	28	OVN	-4	281.21
1,2-diaminocyclohexane-tetraacetate	Dcta ⁻⁴	29	OV9	-4	342.30
Cysteine	Cyst ⁻²	30	SV2	-2	153.13
Nocardamine (desferri-ferrioxamine)	Noc ⁻³	31	ZZ0	-3	0.00
Phthalate	Phth ⁻²	32	RV2	-2	164.12
Arginine	Arg ⁻	33	VZ7	-1	174.20
Ornithine	Orn ⁻	34	VZ4	-1	131.15
Lysine	Lys ⁻	35	VZ6	-1	145.18
Hystidine	His ⁻	36	VZ7	-1	154.15
Aspartate	Asp ⁻	37	VZ8	-1	131.09
Serine	Ser ⁻	38	VZ1	-1	104.08
Alanine	Ala ⁻	39	VZ2	-1	88.09
Tyrosine	Tyr ⁻²	40	VZR	-2	179.17
Methionine	Met ⁻	41	VZS	-1	148.20
Valine	Val ⁻	42	VZB	-1	116.14
Threonine	Thr ⁻	43	VZQ	-1	118.11
Phenylalanine	Phe ⁻	44	VZT	-1	164.18
Isoleucine	Iso ⁻	45	VZD	-1	130.17
Leucine	Leu ⁻	46	VZC	-1	130.17
Proline	Pro ⁻	47	NV4	-1	113.12
Diethylenetriamine-pentaacetate	Dtpa ⁻⁵	58	VN5	-5	390.32
Maleate	Mal ⁻²	60	VV2	-2	114.06
Benzylsulfonate	Bes ⁻	61	125	-1	157.17
Formate	For ⁻	65	V0D	-1	45.02
Fulvate I	Ful1 ⁻	66	OVY	-1	450.00
Fulvate II	Ful2 ⁻	67	OVZ	-1	450.00
Ethylenedihydroxyphenylglycine	Edhg ⁻⁴	68	QZ0	-4	246.20

- GEOMIN generates a separate thermochemical data file in MINTEQ2 format.

3.2.2 Identification Indices for Organic Ligands

The thermochemical data base for MINTEQ2 up to now has not included any organics except humic and fulvic acids. To expand the data base to include a larger number of organic ligands, it was necessary to devise a reasonable identification scheme for any organic-ligand reaction that would be added in the execution of this task. To satisfy this requirement, we chose a coding based on the Wiswesser Line-Formation notation (Smith 1968). This notation has been used for some time to unambiguously identify organic structures and is gaining more popularity with the use of computers (Baker, Palmer and Nichols 1975). It is a method for expressing the structure of an organic compound as a linear string of symbols. The resulting notation is compact, unique, unambiguous, and particularly suitable for indexing and computer processing.

The scheme put forward in this document for naming the organics, though far from unambiguous, is at least consistent with the Wiswesser notation. It 1) provides an open-ended scheme for designating new organics and 2) provides some chemically specific descriptive information that could be searched in the data base. The coding is based on the Wiswesser Group Designations listed in Table 3.2.

These designations have been used to classify organics according to their two or three most important functional groups, listed according to their distance from the chelating or complexing group. When only two functional groups are specified, the third letter or number can be used as a sequence number or to designate the number of remaining non-hydrogen elements in the organic. As an example, consider ethylenediaminetetraacetate. The structure is

TABLE 3.2. Wiswesser Group Designations

Group	Letter Designation
Boron	B
Fluorine	F
Iodine	I
Phosphorous	P
Sulfur	S
Carbonyl	V
Hydroxy	Q
Chloro	G
Bromo	E
Carbon to 3 groups other than hydrogen	Y
Carbon to 4 groups other than hydrogen	X
Hydrogen-free nitrogen attached to less than 4 others	N
Nitrogen attached to more than three other groups	K
NH ₂ group	Z
-NR- group	M
Hydrogen-free oxygen, excluding Q and W cases	O
Ring system (such as benzene)	R

Accordingly, the notation would be OVN, indicating that an oxygen, O, closest to the chelating position is attached to a carbonyl group, V, that is in turn attached to a hydrogen-free nitrogen, N.

Following these criteria, we have assigned designations as given in Table 3.3. In Table 3.3 lower case "n" designates the number of carbons attached to the specific functional group. Thus ethyl alcohol would be Q2 (an OH group attached to two carbons) and acetone would be V11 (a carbonyl group attached to two separate methyl groups).

TABLE 3.3. Designations for Organic Ligands

Organic	Designation	Organic	Designation
Acetal	OY	Acid anhydride	VO or VOV
Acid Halide	GV, EV, etc.	Amino Acids	VZ, MV, NV, etc.
Carboxylic acids	OVn	Alcohols	Qn
Aldehydes	Vn	Amides	VZ, VM, or VN
Ureas	ZV, VM, or VN	Primary Amines	Zn
Secondary Amines	Mn	Tertiary Amines	Nn
Esters	OVn	Ethers	On
Alkyl Halides	Gn, En, etc.	Cycloalkyl Halides	Gn, En, etc.
Aryl Halides	GR, ER, etc.	Alkenes	Un
Ketones	Vnn	Azo Compounds	WN
Azoxy Compounds	WN	Hydroazo Compounds	WN
Isocyanates	NV	Isonitriles	Nn
Nitriles	Nn	Nitro Compounds	NW
Nitroso Compounds	NW	Phenols	RQ
Thiocyanates	NS	Isothiochanates	SN
Thio ethers	Sn	Thiols	SQ
Thiophenols	RS		

3.3 DEFINITIONS AND THERMODYNAMIC STANDARDS

The pressure-constant equilibrium constant for the reaction

is written as

$$K_{r,T} = (a_P/a_P^0) / ((a_B^b/a_B^0)^b (a_C^c/a_C^0)^c \dots)$$

where $K_{r,T}$ = the equilibrium constant for reaction r at temperature T

a_j = the activity of the product ($j=P$), or reactant ($j=A,B$) species;
the activity is in turn expressed as the product of an activity coefficient and a concentration for that species

a_j^0 = the activity of the j th species at standard state; this quantity is generally defined as unity (e.g., unit molality)

a, b = stoichiometric coefficients for the reaction.

When defined in this way, $K_{r,T}$ will always be dimensionless so that it will relate correctly to the thermodynamic quantity,

$$\Delta G_{Cr,T}^0 = -RT \ln K_{r,T} = \Delta H_{r,T}^0 - T\Delta S_{r,T}^0$$

where $\Delta G_{r,T}^0$ is the standard Gibbs free energy of reaction, R is the gas constant, T is the absolute temperature, $\Delta H_{r,T}^0$ is the standard enthalpy of reaction, and $\Delta S_{r,T}^0$ is the standard entropy of reaction. Usually, the standard state is taken to be unity. Therefore the equilibrium constant, $K_{r,T}$ is more frequently written as

$$K_{r,T} = a_p / (a_B^b a_C^c \dots)$$

According to Sposito and Mattigod (1980), the thermochemical data presented in their report are based on a standard state of moles per liter (molar). The units of the MINTEQ2 thermochemical data base are based on a more fundamentally useful concentration unit when the temperature is to be varied or when concentrations range widely [i.e., moles/1000 g of water (molal)]. However, for dilute solutions, the two standard states are equivalent to an adequate degree of approximation. Thus, if the equilibrium constant is obtained at sufficiently dilute concentration, or is extrapolated accurately to dilute concentration, the units for the two data bases will be consistent.

3.4 SELECTED ORGANIC LIGANDS

Tables 3.4 through 3.10 summarize the selected reactions and their equilibrium constants. The first column in each table given a unique identification code for the reaction. The second column gives the base-ten logarithm of the equilibrium constant for the reaction at 25°C and 1.0 atmosphere pressure. The third column gives the name of the product that has been generated by GEOMIN by concatenating names and charges of the reactants. The fourth

column defines the reaction. Reaction coefficients are positive if the component is a reactant and negative if the component is a product. For example, the reaction

should be interpreted to conventionally read

The designation (Aq) indicates that the product is aqueous and (So) indicates that the product is solid.

The following tables list all reactions added from the GEOCHEM data base that involve designated ligands.

3.4.1 Acetates

TABLE 3.4. Thermochemical Additions for Acetates

ID	Log(K ⁰ _{P,T})	Product	Reaction
1500V14	1.20	Ca(Ac) ⁺¹	(Aq) + Ca ⁺² + Ac ⁻
4600V14	1.30	Mg(Ac) ⁺¹	(Aq) + Mg ⁺² + Ac ⁻
8000V14	0.90	Sr(Ac) ⁺¹	(Aq) + Sr ⁺² + Ac ⁻
5000V14	-0.20	Na(Ac)	(Aq) + Na ⁺ + Ac ⁻
2810V14	4.20	Fe(Ac) ⁺²	(Aq) + Fe ⁺³ + Ac ⁻
2810V15	7.50	Fe(Ac) ₂ ⁺¹	(Aq) + Fe ⁺³ + 2 Ac ⁻
2810V16	10.50	Fe(Ac) ₃	(Aq) + Fe ⁺³ + 3 Ac ⁻
2800V14	1.40	Fe(Ac) ⁺¹	(Aq) + Fe ⁺² + Ac ⁻
4700V14	1.40	Mn(Ac) ⁺¹	(Aq) + Mn ⁺² + Ac ⁻
4700V15	2.20	Mn(Ac) ₂	(Aq) + Mn ⁺² + 2 Ac ⁻
2310V14	2.20	Cu(Ac) ⁺¹	(Aq) + Cu ⁺² + Ac ⁻
2310V15	3.50	Cu(Ac) ₂	(Aq) + Cu ⁺² + 2 Ac ⁻

TABLE 3.4. (Contd)

ID	$\text{Log}(K^0_{p,T})$	Product	Reaction
2310V16	3.90	$\text{Cu}(\text{Ac})_3^{-1}$	$(\text{Aq}) \leftarrow \text{Cu}^{+2} + 3 \text{Ac}^-$
2310V17	3.40	$\text{Cu}(\text{Ac})_4^{-2}$	$(\text{Aq}) \leftarrow \text{Cu}^{+2} + 4 \text{Ac}^-$
1000V14	0.90	$\text{Ba}(\text{Ac})^{+1}$	$(\text{Aq}) \leftarrow \text{Ba}^{+2} + \text{Ac}^-$
1600V14	2.60	$\text{Cd}(\text{Ac})^{+1}$	$(\text{Aq}) \leftarrow \text{Cd}^{+2} + \text{Ac}^-$
1600V15	3.60	$\text{Cd}(\text{Ac})_2$	$(\text{Aq}) \leftarrow \text{Cd}^{+2} + 2 \text{Ac}^-$
1600V16	4.20	$\text{Cd}(\text{Ac})_3^{-1}$	$(\text{Aq}) \leftarrow \text{Cd}^{+2} + 3 \text{Ac}^-$
1600V17	1.80	$\text{Cd}(\text{Ac})_4^{-2}$	$(\text{Aq}) \leftarrow \text{Cd}^{+2} + 4 \text{Ac}^-$
9500V14	1.80	$\text{Zn}(\text{Ac})^{+1}$	$(\text{Aq}) \leftarrow \text{Zn}^{+2} + \text{Ac}^-$
9500V15	2.90	$\text{Zn}(\text{Ac})_2$	$(\text{Aq}) \leftarrow \text{Zn}^{+2} + 2 \text{Ac}^-$
5400V14	1.20	$\text{Ni}(\text{Ac})^{+1}$	$(\text{Aq}) \leftarrow \text{Ni}^{+2} + \text{Ac}^-$
5400V15	2.10	$\text{Ni}(\text{Ac})_2$	$(\text{Aq}) \leftarrow \text{Ni}^{+2} + 2 \text{Ac}^-$
6000V14	2.40	$\text{Pb}(\text{Ac})^{+1}$	$(\text{Aq}) \leftarrow \text{Pb}^{+2} + \text{Ac}^-$
6000V15	4.10	$\text{Pb}(\text{Ac})_2$	$(\text{Aq}) \leftarrow \text{Pb}^{+2} + 2 \text{Ac}^-$
2000V14	1.60	$\text{Co}(\text{Ac})^{+1}$	$(\text{Aq}) \leftarrow \text{Co}^{+2} + \text{Ac}^-$
2000V15	2.40	$\text{Co}(\text{Ac})_2$	$(\text{Aq}) \leftarrow \text{Co}^{+2} + 2 \text{Ac}^-$
9002001	2.30	$\text{Ag}(\text{Ac})$	$(\text{So}) \leftarrow \text{Ag}^+ + \text{Ac}^-$
0200V14	0.60	$\text{Ag}(\text{Ac})$	$(\text{Aq}) \leftarrow \text{Ag}^+ + \text{Ac}^-$
0300V14	2.10	$\text{Al}(\text{Ac})^{+2}$	$(\text{Aq}) \leftarrow \text{Al}^{+3} + \text{Ac}^-$
4400V14	0.20	$\text{Li}(\text{Ac})$	$(\text{Aq}) \leftarrow \text{Li}^+ + \text{Ac}^-$
4300V14	2.90	$\text{La}(\text{Ac})^{+2}$	$(\text{Aq}) \leftarrow \text{La}^{+3} + \text{Ac}^-$
4300V15	4.80	$\text{La}(\text{Ac})_2^{+1}$	$(\text{Aq}) \leftarrow \text{La}^{+3} + 2 \text{Ac}^-$
1700V14	3.00	$\text{Ce}(\text{Ac})^{+2}$	$(\text{Aq}) \leftarrow \text{Ce}^{+3} + \text{Ac}^-$
1700V15	5.00	$\text{Ce}(\text{Ac})_2^{+1}$	$(\text{Aq}) \leftarrow \text{Ce}^{+3} + 2 \text{Ac}^-$
8930V14	3.00	$\text{UO}_2(\text{Ac})^{+1}$	$(\text{Aq}) \leftarrow \text{UO}_2^{+2} + \text{Ac}^-$
8930V15	5.30	$\text{UO}_2(\text{Ac})_2$	$(\text{Aq}) \leftarrow \text{UO}_2^{+2} + 2 \text{Ac}^-$
8930V16	7.20	$\text{UO}_2(\text{Ac})_3^{-1}$	$(\text{Aq}) \leftarrow \text{UO}_2^{+2} + 3 \text{Ac}^-$
3300V14	4.80	$(\text{Ac})\text{H}$	$(\text{Aq}) \leftarrow \text{Ac}^- + \text{H}^+$

3.4.2 Citrates

TABLE 3.5. Thermochemical Additions for Citrates

ID	$\log(K^0_{f,T})$	Product	Reaction
150XV34	4.70	$\text{Ca}(\text{Cit})^{-1}$	$(\text{Aq}) + \text{Ca}^{+2} + \text{Cit}^{-3}$
150XV35	9.50	$\text{Ca}(\text{Cit})\text{H}$	$(\text{Aq}) + \text{Ca}^{+2} + \text{Cit}^{-3} + \text{H}^{+}$
150XV36	12.30	$\text{Ca}(\text{Cit})\text{H}_2^{+1}$	$(\text{Aq}) + \text{Ca}^{+2} + \text{Cit}^{-3} + 2 \text{H}^{+}$
460XV34	3.40	$\text{Mg}(\text{Cit})^{-1}$	$(\text{Aq}) + \text{Mg}^{+2} + \text{Cit}^{-3}$
460XV35	8.20	$\text{Mg}(\text{Cit})\text{H}$	$(\text{Aq}) + \text{Mg}^{+2} + \text{Cit}^{-3} + \text{H}^{+}$
460XV36	12.00	$\text{Mg}(\text{Cit})\text{H}_2^{+1}$	$(\text{Aq}) + \text{Mg}^{+2} + \text{Cit}^{-3} + 2 \text{H}^{+}$
800XV34	4.10	$\text{Sr}(\text{Cit})^{-1}$	$(\text{Aq}) + \text{Sr}^{+2} + \text{Cit}^{-3}$
800XV35	20.80	$\text{Sr}(\text{Cit})\text{H}$	$(\text{Aq}) + \text{Sr}^{+2} + \text{Cit}^{-3} + \text{H}^{+}$
410XV34	1.20	$\text{K}(\text{Cit})^{-2}$	$(\text{Aq}) + \text{K}^{+} + \text{Cit}^{-3}$
500XV34	1.40	$\text{Na}(\text{Cit})^{-2}$	$(\text{Aq}) + \text{Na}^{+} + \text{Cit}^{-3}$
281XV34	11.50	$\text{Fe}(\text{Cit})$	$(\text{Aq}) + \text{Fe}^{+3} + \text{Cit}^{-3}$
281XV35	29.50	$\text{Fe}(\text{Cit})\text{H}^{+1}$	$(\text{Aq}) + \text{Fe}^{+3} + \text{Cit}^{-3} + \text{H}^{+}$
281XV36	30.40	$\text{Fe}(\text{Cit})\text{H}_2^{+2}$	$(\text{Aq}) + \text{Fe}^{+3} + \text{Cit}^{-3} + 2 \text{H}^{+}$
281XV37	21.40	$\text{Fe}_2(\text{Cit})_2(\text{OH})_2^{-2}$	$(\text{Aq}) + 2 \text{Fe}^{+3} + 2 \text{Cit}^{-3} + 2 \text{H}_2\text{O} - 2 \text{H}^{+}$
280XV34	4.40	$\text{Fe}(\text{Cit})^{-1}$	$(\text{Aq}) + \text{Fe}^{+2} + \text{Cit}^{-3}$
280XV35	9.00	$\text{Fe}(\text{Cit})\text{H}$	$(\text{Aq}) + \text{Fe}^{+2} + \text{Cit}^{-3} + \text{H}^{+}$
470XV34	5.40	$\text{Mn}(\text{Cit})^{-1}$	$(\text{Aq}) + \text{Mn}^{+2} + \text{Cit}^{-3}$
470XV35	9.60	$\text{Mn}(\text{Cit})\text{H}$	$(\text{Aq}) + \text{Mn}^{+2} + \text{Cit}^{-3} + \text{H}^{+}$
231XV34	5.90	$\text{Cu}(\text{Cit})^{-1}$	$(\text{Aq}) + \text{Cu}^{+2} + \text{Cit}^{-3}$
231XV35	9.80	$\text{Cu}(\text{Cit})\text{H}$	$(\text{Aq}) + \text{Cu}^{+2} + \text{Cit}^{-3} + \text{H}^{+}$
231XV36	13.40	$\text{Cu}(\text{Cit})\text{H}_2^{+1}$	$(\text{Aq}) + \text{Cu}^{+2} + \text{Cit}^{-3} + 2 \text{H}^{+}$
231XV37	-15.58	$\text{Cu}(\text{Cit})(\text{OH})^{-2}$	$(\text{Aq}) + \text{Cu}^{+2} + \text{Cit}^{-3} + \text{H}_2\text{O} - \text{H}^{+}$
231XV38	8.10	$\text{Cu}_2(\text{Cit})^{+1}$	$(\text{Aq}) + 2 \text{Cu}^{+2} + \text{Cit}^{-3}$
100XV34	2.90	$\text{Ba}(\text{Cit})^{-1}$	$(\text{Aq}) + \text{Ba}^{+2} + \text{Cit}^{-3}$
100XV35	8.20	$\text{Ba}(\text{Cit})\text{H}$	$(\text{Aq}) + \text{Ba}^{+2} + \text{Cit}^{-3} + \text{H}^{+}$
100XV36	11.90	$\text{Ba}(\text{Cit})\text{H}_2^{+1}$	$(\text{Aq}) + \text{Ba}^{+2} + \text{Cit}^{-3} + 2 \text{H}^{+}$
160XV34	3.80	$\text{Cd}(\text{Cit})^{-1}$	$(\text{Aq}) + \text{Cd}^{+2} + \text{Cit}^{-3}$
160XV35	5.40	$\text{Cd}(\text{Cit})_2^{-4}$	$(\text{Aq}) + \text{Cd}^{+2} + 2 \text{Cit}^{-3}$
160XV36	8.60	$\text{Cd}(\text{Cit})\text{H}$	$(\text{Aq}) + \text{Cd}^{+2} + \text{Cit}^{-3} + \text{H}^{+}$
160XV37	12.10	$\text{Cd}(\text{Cit})\text{H}_2^{+1}$	$(\text{Aq}) + \text{Cd}^{+2} + \text{Cit}^{-3} + 2 \text{H}^{+}$

TABLE 3.5. (Contd)

ID	Log($K^0_{P,T}$)	Product	Reaction
950XV34	5.00	$\text{Zn}(\text{Cit})^{-1}$	$(\text{Aq}) \leftarrow \text{Zn}^{+2} + \text{Cit}^{-3}$
950XV35	6.70	$\text{Zn}(\text{Cit})_2^{-4}$	$(\text{Aq}) \leftarrow \text{Zn}^{+2} + 2 \text{Cit}^{-3}$
950XV36	9.40	$\text{Zn}(\text{Cit})\text{H}$	$(\text{Aq}) \leftarrow \text{Zn}^{+2} + \text{Cit}^{-3} + \text{H}^+$
950XV37	12.40	$\text{Zn}(\text{Cit})\text{H}_2^{+1}$	$(\text{Aq}) \leftarrow \text{Zn}^{+2} + \text{Cit}^{-3} + 2 \text{H}^+$
540XV34	5.40	$\text{Ni}(\text{Cit})^{-1}$	$(\text{Aq}) \leftarrow \text{Ni}^{+2} + \text{Cit}^{-3}$
540XV35	9.70	$\text{Ni}(\text{Cit})\text{H}$	$(\text{Aq}) \leftarrow \text{Ni}^{+2} + \text{Cit}^{-3} + \text{H}^+$
540XV36	12.90	$\text{Ni}(\text{Cit})\text{H}_2^{+1}$	$(\text{Aq}) \leftarrow \text{Ni}^{+2} + \text{Cit}^{-3} + 2 \text{H}^+$
600XV34	4.00	$\text{Pb}(\text{Cit})^{-1}$	$(\text{Aq}) \leftarrow \text{Pb}^{+2} + \text{Cit}^{-3}$
600XV35	6.10	$\text{Pb}(\text{Cit})_2^{-4}$	$(\text{Aq}) \leftarrow \text{Pb}^{+2} + 2 \text{Cit}^{-3}$
600XV36	9.40	$\text{Pb}(\text{Cit})_3^{-7}$	$(\text{Aq}) \leftarrow \text{Pb}^{+2} + 3 \text{Cit}^{-3}$
600XV37	9.30	$\text{Pb}(\text{Cit})\text{H}$	$(\text{Aq}) \leftarrow \text{Pb}^{+2} + \text{Cit}^{-3} + \text{H}^+$
600XV38	4.90	$\text{Pb}(\text{Cit})\text{H}_2^{+1}$	$(\text{Aq}) \leftarrow \text{Pb}^{+2} + \text{Cit}^{-3} + 2 \text{H}^+$
600XV39	21.60	$\text{Pb}(\text{Cit})_2\text{H}_4$	$(\text{Aq}) \leftarrow \text{Pb}^{+2} + 2 \text{Cit}^{-3} + 4 \text{H}^+$
200XV34	5.00	$\text{Co}(\text{Cit})^{-1}$	$(\text{Aq}) \leftarrow \text{Co}^{+2} + \text{Cit}^{-3}$
200XV35	9.40	$\text{Co}(\text{Cit})\text{H}$	$(\text{Aq}) \leftarrow \text{Co}^{+2} + \text{Cit}^{-3} + \text{H}^+$
200XV36	12.40	$\text{Co}(\text{Cit})\text{H}_2^{+1}$	$(\text{Aq}) \leftarrow \text{Co}^{+2} + \text{Cit}^{-3} + 2 \text{H}^+$
020XV34	24.80	$\text{Ag}_2(\text{Cit})\text{H}$	$(\text{Aq}) \leftarrow \text{Ag}^+ + \text{Cit}^{-3} + \text{H}^+$
030XV34	25.70	$\text{Al}(\text{Cit})\text{H}^{+1}$	$(\text{Aq}) \leftarrow \text{Al}^{+3} + \text{Cit}^{-3} + \text{H}^+$
030XV35	22.80	$\text{Al}(\text{Cit})$	$(\text{Aq}) \leftarrow \text{Al}^{+3} + \text{Cit}^{-3}$
030XV36	19.40	$\text{Al}(\text{Cit})(\text{OH})^{-1}$	$(\text{Aq}) \leftarrow \text{Al}^{+3} + \text{Cit}^{-3} + \text{H}_2\text{O} - \text{H}^+$
220XV34	1.20	$\text{Cs}(\text{Cit})^{-2}$	$(\text{Aq}) \leftarrow \text{Cs}^+ + \text{Cit}^{-3}$
440XV34	1.50	$\text{Li}(\text{Cit})^{-2}$	$(\text{Aq}) \leftarrow \text{Li}^+ + \text{Cit}^{-3}$
110XV34	22.60	$\text{Be}(\text{Cit})\text{H}$	$(\text{Aq}) \leftarrow \text{Be}^{+2} + \text{Cit}^{-3} + \text{H}^+$
110XV35	26.10	$\text{Be}(\text{Cit})\text{H}_2^{+1}$	$(\text{Aq}) \leftarrow \text{Be}^{+2} + \text{Cit}^{-3} + 2 \text{H}^+$
110XV36	29.30	$\text{Be}(\text{Cit})\text{H}_3^{+2}$	$(\text{Aq}) \leftarrow \text{Be}^{+2} + \text{Cit}^{-3} + 3 \text{H}^+$
9143001	12.90	$\text{La}(\text{Cit})$	$(\text{So}) \leftarrow \text{La}^{+3} + \text{Cit}^{-3}$
430XV34	9.20	$\text{La}(\text{Cit})$	$(\text{Aq}) \leftarrow \text{La}^{+3} + \text{Cit}^{-3}$
430XV35	11.90	$\text{La}(\text{Cit})_2^{-3}$	$(\text{Aq}) \leftarrow \text{La}^{+3} + 2 \text{Cit}^{-3}$
430XV36	90.10	$\text{La}(\text{Cit})_3\text{H}_9^{+3}$	$(\text{Aq}) \leftarrow \text{La}^{+3} + 3 \text{Cit}^{-3} + 9 \text{H}^+$
170XV34	11.60	$\text{Ce}(\text{Cit})$	$(\text{Aq}) \leftarrow \text{Ce}^{+3} + \text{Cit}^{-3}$
170XV35	15.00	$\text{Ce}(\text{Cit})_2^{-3}$	$(\text{Aq}) \leftarrow \text{Ce}^{+3} + 2 \text{Cit}^{-3}$
170XV36	31.10	$\text{Ce}(\text{Cit})\text{H}_3^{+3}$	$(\text{Aq}) \leftarrow \text{Ce}^{+3} + \text{Cit}^{-3} + 3 \text{H}^+$

TABLE 3.5. (Contd)

IO	Log($K_{F,T}^0$)	Product	Reaction
850XV34	16.80	Th(Cit) ⁺¹	(Aq) $\leftarrow$ Th ⁺⁴ + Cit ⁻³
850XV35	25.70	Th(Cit) ₂ ⁻²	(Aq) $\leftarrow$ Th ⁺⁴ + 2 Cit ⁻³
893XV34	9.30	UO ₂ (Cit) ⁻¹	(Aq) $\leftarrow$ UO ₂ ⁺² + Cit ⁻³
893XV35	26.60	UO ₂ (Cit)H	(Aq) $\leftarrow$ UO ₂ ⁺² + Cit ⁻³ + H ⁺
680XV34	1.10	Rb(Cit) ⁻²	(Aq) $\leftarrow$ Rb ⁺ + Cit ⁻³
330XV34	6.40	(Cit)H ⁻²	(Aq) $\leftarrow$ Cit ⁻³ + H ⁺
330XV35	11.20	(Cit)H ₂ ⁻¹	(Aq) $\leftarrow$ Cit ⁻³ + 2 H ⁺
330XV36	14.30	(Cit)H ₃	(Aq) $\leftarrow$ Cit ⁻³ + 3 H ⁺

3.4.3 Diethylenetriaminepentaacetates

TABLE 3.6. Thermochemical Additions for Diethylenetriaminepentaacetates

IO	Log(K)	Product	Reaction
150VN54	10.80	Ca(Dtpa) ⁻³	(Aq) $\leftarrow$ Ca ⁺² + Dtpa ⁻⁵
150VN55	16.90	Ca(Dtpa)H ⁻²	(Aq) $\leftarrow$ Ca ⁺² + Dtpa ⁻⁵ + H ⁺
150VN56	12.80	Ca ₂ (Dtpa) ⁻¹	(Aq) $\leftarrow$ 2 Ca ⁺² + Dtpa ⁻⁵
460VN54	9.30	Mg(Dtpa) ⁻³	(Aq) $\leftarrow$ Mg ⁺² + Dtpa ⁻⁵
460VN55	16.40	Mg(Dtpa)H ⁻²	(Aq) $\leftarrow$ Mg ⁺² + Dtpa ⁻⁵ + H ⁺
800VN54	11.90	Sr(Dtpa) ⁻³	(Aq) $\leftarrow$ Sr ⁺² + Dtpa ⁻⁵
281VN54	28.00	Fe(Dtpa) ⁻²	(Aq) $\leftarrow$ Fe ⁺³ + Dtpa ⁻⁵
281VN55	31.60	Fe(Dtpa)H ⁻¹	(Aq) $\leftarrow$ Fe ⁺³ + Dtpa ⁻⁵ + H ⁺
281VN56	31.90	Fe(Dtpa)(OH) ⁻³	(Aq) $\leftarrow$ Fe ⁺³ + Dtpa ⁻⁵ + H ₂ O - H ⁺
280VN54	16.50	Fe(Dtpa) ⁻³	(Aq) $\leftarrow$ Fe ⁺² + Dtpa ⁻⁵
280VN55	21.90	Fe(Dtpa)H ⁻²	(Aq) $\leftarrow$ Fe ⁺² + Dtpa ⁻⁵ + H ⁺
280VN56	22.70	Fe(Dtpa)(OH) ⁻⁴	(Aq) $\leftarrow$ Fe ⁺² + Dtpa ⁻⁵ + H ₂ O - H ⁺
280VN57	26.00	Fe(Dtpa)(OH) ₂ ⁻⁵	(Aq) $\leftarrow$ Fe ⁺² + Dtpa ⁻⁵ + 2 H ₂ O - 2 H ⁺
470VN54	15.60	Mn(Dtpa) ⁻³	(Aq) $\leftarrow$ Mn ⁺² + Dtpa ⁻⁵
470VN55	20.20	Mn(Dtpa)H ⁻²	(Aq) $\leftarrow$ Mn ⁺² + Dtpa ⁻⁵ + H ⁺
470VN56	17.70	Mn ₂ (Dtpa) ⁻¹	(Aq) $\leftarrow$ 2 Mn ⁺² + Dtpa ⁻⁵
231VN54	21.60	Cu(Dtpa) ⁻³	(Aq) $\leftarrow$ Cu ⁺² + Dtpa ⁻⁵
231VN55	26.30	Cu(Dtpa)H ⁻²	(Aq) $\leftarrow$ Cu ⁺² + Dtpa ⁻⁵ + H ⁺

TABLE 3.6. (Contd)

ID	Log(K)	Product	Reaction
231VN56	32.50	$\text{Cu}(\text{Dt pa})\text{H}_2^{-1}$	$(\text{Aq}) \leftarrow \text{Cu}^{+2} + \text{Dt pa}^{-5} + 2 \text{H}^+$
231VN57	30.50	$\text{Cu}_2(\text{Dt pa})^{-1}$	$(\text{Aq}) \leftarrow 2 \text{Cu}^{+2} + \text{Dt pa}^{-5}$
100VN54	10.80	$\text{Ba}(\text{Dt pa})^{-3}$	$(\text{Aq}) \leftarrow \text{Ba}^{+2} + \text{Dt pa}^{-5}$
160VN54	19.20	$\text{Cd}(\text{Dt pa})^{-3}$	$(\text{Aq}) \leftarrow \text{Cd}^{+2} + \text{Dt pa}^{-5}$
160VN55	23.30	$\text{Cd}(\text{Dt pa})\text{H}^{-2}$	$(\text{Aq}) \leftarrow \text{Cd}^{+2} + \text{Dt pa}^{-5} + \text{H}^+$
160VN56	29.70	$\text{Cd}(\text{Dt pa})\text{H}_2^{-1}$	$(\text{Aq}) \leftarrow \text{Cd}^{+2} + \text{Dt pa}^{-5} + 2 \text{H}^+$
160VN57	22.20	$\text{Cd}_2(\text{Dt pa})^{-1}$	$(\text{Aq}) \leftarrow 2 \text{Cd}^{+2} + \text{Dt pa}^{-5}$
950VN54	18.40	$\text{Zn}(\text{Dt pa})^{-3}$	$(\text{Aq}) \leftarrow \text{Zn}^{+2} + \text{Dt pa}^{-5}$
950VN55	23.80	$\text{Zn}(\text{Dt pa})\text{H}^{-2}$	$(\text{Aq}) \leftarrow \text{Zn}^{+2} + \text{Dt pa}^{-5} + \text{H}^+$
950VN56	30.20	$\text{Zn}(\text{Dt pa})\text{H}_2^{-1}$	$(\text{Aq}) \leftarrow \text{Zn}^{+2} + \text{Dt pa}^{-5} + 2 \text{H}^+$
950VN57	22.80	$\text{Zn}_2(\text{Dt pa})^{-1}$	$(\text{Aq}) \leftarrow 2 \text{Zn}^{+2} + \text{Dt pa}^{-5}$
540VN54	20.30	$\text{Ni}(\text{Dt pa})^{-3}$	$(\text{Aq}) \leftarrow \text{Ni}^{+2} + \text{Dt pa}^{-5}$
540VN55	25.90	$\text{Ni}(\text{Dt pa})\text{H}^{-2}$	$(\text{Aq}) \leftarrow \text{Ni}^{+2} + \text{Dt pa}^{-5} + \text{H}^+$
540VN56	32.10	$\text{Ni}(\text{Dt pa})\text{H}_2^{-1}$	$(\text{Aq}) \leftarrow \text{Ni}^{+2} + \text{Dt pa}^{-5} + 2 \text{H}^+$
540VN57	25.70	$\text{Ni}_2(\text{Dt pa})^{-1}$	$(\text{Aq}) \leftarrow 2 \text{Ni}^{+2} + \text{Dt pa}^{-5}$
360VN54	28.90	$\text{Hg}(\text{Dt pa})^{-3}$	$(\text{Aq}) \leftarrow \text{Hg}^{+2} + \text{Dt pa}^{-5}$
60VN55	33.70	$\text{Hg}(\text{Dt pa})\text{H}^{-2}$	$(\text{Aq}) \leftarrow \text{Hg}^{+2} + \text{Dt pa}^{-5} + \text{H}^+$
600VN54	18.80	$\text{Pb}(\text{Dt pa})^{-3}$	$(\text{Aq}) \leftarrow \text{Pb}^{+2} + \text{Dt pa}^{-5}$
600VN55	23.30	$\text{Pb}(\text{Dt pa})\text{H}^{-2}$	$(\text{Aq}) \leftarrow \text{Pb}^{+2} + \text{Dt pa}^{-5} + \text{H}^+$
600VN56	22.20	$\text{Pb}_2(\text{Dt pa})^{-1}$	$(\text{Aq}) \leftarrow 2 \text{Pb}^{+2} + \text{Dt pa}^{-5}$
200VN54	19.30	$\text{Co}(\text{Dt pa})^{-3}$	$(\text{Aq}) \leftarrow \text{Co}^{+2} + \text{Dt pa}^{-5}$
200VN55	21.90	$\text{Co}(\text{Dt pa})_2^{-8}$	$(\text{Aq}) \leftarrow \text{Co}^{+2} + 2 \text{Dt pa}^{-5}$
200VN56	24.00	$\text{Co}(\text{Dt pa})\text{H}^{-2}$	$(\text{Aq}) \leftarrow \text{Co}^{+2} + \text{Dt pa}^{-5} + \text{H}^+$
200VN57	30.50	$\text{Co}(\text{Dt pa})\text{H}_2^{-1}$	$(\text{Aq}) \leftarrow \text{Co}^{+2} + \text{Dt pa}^{-5} + 2 \text{H}^+$
200VN58	22.80	$\text{Co}_2(\text{Dt pa})^{-1}$	$(\text{Aq}) \leftarrow 2 \text{Co}^{+2} + \text{Dt pa}^{-5}$
D20VN54	9.80	$\text{Ag}(\text{Dt pa})^{-4}$	$(\text{Aq}) \leftarrow \text{Ag}^+ + \text{Dt pa}^{-5}$
030VN54	18.60	$\text{Al}(\text{Dt pa})^{-2}$	$(\text{Aq}) \leftarrow \text{Al}^{+3} + \text{Dt pa}^{-5}$
030VN55	23.20	$\text{Al}(\text{Dt pa})\text{H}^{-1}$	$(\text{Aq}) \leftarrow \text{Al}^{+3} + \text{Dt pa}^{-5} + \text{H}^+$
030VN56	27.90	$\text{Al}(\text{Dt pa})(\text{OH})^{-3}$	$(\text{Aq}) \leftarrow \text{Al}^{+3} + \text{Dt pa}^{-5} + \text{H}_2\text{O} - \text{H}^+$
330VN54	10.60	$(\text{Dt pa})\text{H}^{-4}$	$(\text{Aq}) \leftarrow \text{Dt pa}^{-5} + \text{H}^+$
330VN55	19.10	$(\text{Dt pa})\text{H}_2^{-3}$	$(\text{Aq}) \leftarrow \text{Dt pa}^{-5} + 2 \text{H}^+$
330VN56	23.40	$(\text{Dt pa})\text{H}_3^{-2}$	$(\text{Aq}) \leftarrow \text{Dt pa}^{-5} + 3 \text{H}^+$

3.4.4 Ethylenediamines

TABLE 3.7. Thermochemical Additions for Ethylenediamines

ID	Log(K)	Product	Reaction
330VN57	26.00	$(\text{Dtpa})\text{H}_4^{-1}$	$(\text{Aq}) \leftarrow \text{Dtpa}^{-5} + 4 \text{H}^+$
330VN58	27.80	$(\text{Dtpa})\text{H}_5$	$(\text{Aq}) \leftarrow \text{Dtpa}^{-5} + 5 \text{H}^+$
460ZZ24	0.30	$\text{Mg}(\text{En})^{+2}$	$(\text{Aq}) \leftarrow \text{Mg}^{+2} + \text{En}$
80ZZ24	4.20	$\text{Fe}(\text{En})^{+2}$	$(\text{Aq}) \leftarrow \text{Fe}^{+2} + \text{En}$
280ZZ25	7.50	$\text{Fe}(\text{En})_2^{+2}$	$(\text{Aq}) \leftarrow \text{Fe}^{+2} + 2 \text{En}$
280ZZ26	9.50	$\text{Fe}(\text{En})_3^{+2}$	$(\text{Aq}) \leftarrow \text{Fe}^{+2} + 3 \text{En}$
470ZZ24	2.60	$\text{Mn}(\text{En})^{+2}$	$(\text{Aq}) \leftarrow \text{Mn}^{+2} + \text{En}$
470ZZ25	4.70	$\text{Mn}(\text{En})_2^{+2}$	$(\text{Aq}) \leftarrow \text{Mn}^{+2} + 2 \text{En}$
470ZZ26	5.60	$\text{Mn}(\text{En})_3^{+2}$	$(\text{Aq}) \leftarrow \text{Mn}^{+2} + 3 \text{En}$
231ZZ24	10.50	$\text{Cu}(\text{En})^{+2}$	$(\text{Aq}) \leftarrow \text{Cu}^{+2} + \text{En}$
231ZZ25	19.50	$\text{Cu}(\text{En})_2^{+2}$	$(\text{Aq}) \leftarrow \text{Cu}^{+2} + 2 \text{En}$
160ZZ24	5.50	$\text{Cd}(\text{En})^{+2}$	$(\text{Aq}) \leftarrow \text{Cd}^{+2} + \text{En}$
160ZZ25	10.00	$\text{Cd}(\text{En})_2^{+2}$	$(\text{Aq}) \leftarrow \text{Cd}^{+2} + 2 \text{En}$
160ZZ26	12.00	$\text{Cd}(\text{En})_3^{+2}$	$(\text{Aq}) \leftarrow \text{Cd}^{+2} + 3 \text{En}$
950ZZ24	5.60	$\text{Zn}(\text{En})^{+2}$	$(\text{Aq}) \leftarrow \text{Zn}^{+2} + \text{En}$
950ZZ25	10.30	$\text{Zn}(\text{En})_2^{+2}$	$(\text{Aq}) \leftarrow \text{Zn}^{+2} + 2 \text{En}$
950ZZ26	12.00	$\text{Zn}(\text{En})_3^{+2}$	$(\text{Aq}) \leftarrow \text{Zn}^{+2} + 3 \text{En}$
540ZZ24	7.60	$\text{Ni}(\text{En})^{+2}$	$(\text{Aq}) \leftarrow \text{Ni}^{+2} + \text{En}$
540ZZ25	14.00	$\text{Ni}(\text{En})_2^{+2}$	$(\text{Aq}) \leftarrow \text{Ni}^{+2} + 2 \text{En}$
540ZZ26	18.50	$\text{Ni}(\text{En})_3^{+2}$	$(\text{Aq}) \leftarrow \text{Ni}^{+2} + 3 \text{En}$
360ZZ24	23.30	$\text{Hg}(\text{En})_2^{+2}$	$(\text{Aq}) \leftarrow \text{Hg}^{+2} + 2 \text{En}$
200ZZ24	5.80	$\text{Co}(\text{En})^{+2}$	$(\text{Aq}) \leftarrow \text{Co}^{+2} + \text{En}$
200ZZ25	10.60	$\text{Co}(\text{En})_2^{+2}$	$(\text{Aq}) \leftarrow \text{Co}^{+2} + 2 \text{En}$
200ZZ26	13.70	$\text{Co}(\text{En})_3^{+2}$	$(\text{Aq}) \leftarrow \text{Co}^{+2} + 3 \text{En}$
201ZZ24	46.70	$\text{Co}(\text{En})_3^{+3}$	$(\text{Aq}) \leftarrow \text{Co}^{+3} + 3 \text{En}$
020ZZ24	4.50	$\text{Ag}(\text{En})^{+1}$	$(\text{Aq}) \leftarrow \text{Ag}^+ + \text{En}$
020ZZ25	7.50	$\text{Ag}(\text{En})_2^{+1}$	$(\text{Aq}) \leftarrow \text{Ag}^+ + 2 \text{En}$

TABLE 3.7. (Contd)

ID	Log(K)	Product	Reaction
230ZZ24	10.80	$\text{Cu}(\text{En})_2^{+1}$	$(\text{Aq}) + \text{Cu}^+ + 2 \text{En}$
230ZZ25	10.20	$\text{Cu}(\text{En})(\text{OH})$	$(\text{Aq}) + \text{Cu}^+ + \text{En} + \text{H}_2\text{O} - \text{H}^+$
330ZZ24	9.70	$(\text{En})\text{H}^{+1}$	$(\text{Aq}) + \text{En} + \text{H}^+$
330ZZ25	16.50	$(\text{En})\text{H}_2^{+2}$	$(\text{Aq}) + \text{En} + 2 \text{H}^+$

3.4.5 Ethylenediaminetetraacetates

TABLE 3.8. Thermochemical Additions for Ethylenediaminetetraacetates

ID	Log(K)	Product	Reaction
1500VN4	10.70	$\text{Ca}(\text{Edta})^{-2}$	$(\text{Aq}) + \text{Ca}^{+2} + \text{Edta}^{-4}$
1500VN5	13.90	$\text{Ca}(\text{Edta})\text{H}^{-1}$	$(\text{Aq}) + \text{Ca}^{+2} + \text{Edta}^{-4} + \text{H}^+$
4600VN4	8.80	$\text{Mg}(\text{Edta})^{-2}$	$(\text{Aq}) + \text{Mg}^{+2} + \text{Edta}^{-4}$
4600VN5	12.60	$\text{Mg}(\text{Edta})\text{H}^{-1}$	$(\text{Aq}) + \text{Mg}^{+2} + \text{Edta}^{-4} + \text{H}^+$
8000VN4	11.00	$\text{Sr}(\text{Edta})^{-2}$	$(\text{Aq}) + \text{Sr}^{+2} + \text{Edta}^{-4}$
8000VN5	16.20	$\text{Sr}(\text{Edta})\text{H}^{-1}$	$(\text{Aq}) + \text{Sr}^{+2} + \text{Edta}^{-4} + \text{H}^+$
4100VN4	0.80	$\text{K}(\text{Edta})^{-3}$	$(\text{Aq}) + \text{K}^+ + \text{Edta}^{-4}$
5000VN4	1.70	$\text{Na}(\text{Edta})^{-3}$	$(\text{Aq}) + \text{Na}^+ + \text{Edta}^{-4}$
2810VN4	25.10	$\text{Fe}(\text{Edta})^{-1}$	$(\text{Aq}) + \text{Fe}^{+3} + \text{Edta}^{-4}$
2810VN5	26.40	$\text{Fe}(\text{Edta})\text{H}$	$(\text{Aq}) + \text{Fe}^{+3} + \text{Edta}^{-4} + \text{H}^+$
2810VN6	21.00	$\text{Fe}(\text{Edta})(\text{OH})^{-2}$	$(\text{Aq}) + \text{Fe}^{+3} + \text{Edta}^{-4} + \text{H}_2\text{O} - \text{H}^+$
2810VN7	10.90	$\text{Fe}(\text{Edta})(\text{OH})_2^{-3}$	$(\text{Aq}) + \text{Fe}^{+3} + \text{Edta}^{-4} + 2 \text{H}_2\text{O} - 2 \text{H}^+$
2800VN4	14.30	$\text{Fe}(\text{Edta})^{-2}$	$(\text{Aq}) + \text{Fe}^{+2} + \text{Edta}^{-4}$
2800VN5	17.10	$\text{Fe}(\text{Edta})\text{H}^{-1}$	$(\text{Aq}) + \text{Fe}^{+2} + \text{Edta}^{-4} + \text{H}^+$
4700VN4	13.90	$\text{Mn}(\text{Edta})^{-2}$	$(\text{Aq}) + \text{Mn}^{+2} + \text{Edta}^{-4}$
4700VN5	17.00	$\text{Mn}(\text{Edta})\text{H}^{-1}$	$(\text{Aq}) + \text{Mn}^{+2} + \text{Edta}^{-4} + \text{H}^+$
2310VN4	18.80	$\text{Cu}(\text{Edta})^{-2}$	$(\text{Aq}) + \text{Cu}^{+2} + \text{Edta}^{-4}$
2310VN5	21.80	$\text{Cu}(\text{Edta})\text{H}^{-1}$	$(\text{Aq}) + \text{Cu}^{+2} + \text{Edta}^{-4} + \text{H}^+$
2310VN6	21.32	$\text{Cu}(\text{Edta})(\text{OH})^{-3}$	$(\text{Aq}) + \text{Cu}^{+2} + \text{Edta}^{-4} + \text{H}_2\text{O} - \text{H}^+$
1000VN4	10.20	$\text{Ba}(\text{Edta})^{-2}$	$(\text{Aq}) + \text{Ba}^{+2} + \text{Edta}^{-4}$
1000VN5	15.40	$\text{Ba}(\text{Edta})\text{H}^{-1}$	$(\text{Aq}) + \text{Ba}^{+2} + \text{Edta}^{-4} + \text{H}^+$
1600VN4	16.50	$\text{Cd}(\text{Edta})^{-2}$	$(\text{Aq}) + \text{Cd}^{+2} + \text{Edta}^{-4}$

TABLE 3.8. (Contd)

ID	Log(K)	Product	Reaction
1600VN5	19.40	$\text{Cd}(\text{Edta})\text{H}^{-1}$	$(\text{Aq}) + \text{Cd}^{+2} + \text{Edta}^{-4} + \text{H}^{+}$
9500VN4	16.50	$\text{Zn}(\text{Edta})^{-2}$	$(\text{Aq}) + \text{Zn}^{+2} + \text{Edta}^{-4}$
9500VN5	19.50	$\text{Zn}(\text{Edta})\text{H}^{-1}$	$(\text{Aq}) + \text{Zn}^{+2} + \text{Edta}^{-4} + \text{H}^{+}$
9500VN6	18.60	$\text{Zn}(\text{Edta})(\text{OH})^{-3}$	$(\text{Aq}) + \text{Zn}^{+2} + \text{Edta}^{-4} + \text{H}_2\text{O} - \text{H}^{+}$
5400VN4	18.60	$\text{Ni}(\text{Edta})^{-2}$	$(\text{Aq}) + \text{Ni}^{+2} + \text{Edta}^{-4}$
5400VN5	21.80	$\text{Ni}(\text{Edta})\text{H}^{-1}$	$(\text{Aq}) + \text{Ni}^{+2} + \text{Edta}^{-4} + \text{H}^{+}$
5400VN6	20.40	$\text{Ni}(\text{Edta})(\text{OH})^{-3}$	$(\text{Aq}) + \text{Ni}^{+2} + \text{Edta}^{-4} + \text{H}_2\text{O} - \text{H}^{+}$
3600VN4	24.20	$\text{Hg}(\text{Edta})^{-2}$	$(\text{Aq}) + \text{Hg}^{+2} + \text{Edta}^{-4}$
3600VN5	27.90	$\text{Hg}(\text{Edta})\text{H}^{-1}$	$(\text{Aq}) + \text{Hg}^{+2} + \text{Edta}^{-4} + \text{H}^{+}$
3600VN6	14.50	$\text{Hg}(\text{Edta})(\text{OH})^{-3}$	$(\text{Aq}) + \text{Hg}^{+2} + \text{Edta}^{-4} + \text{H}_2\text{O} - \text{H}^{+}$
6000VN4	18.00	$\text{Pb}(\text{Edta})^{-2}$	$(\text{Aq}) + \text{Pb}^{+2} + \text{Edta}^{-4}$
6000VN5	20.80	$\text{Pb}(\text{Edta})\text{H}^{-1}$	$(\text{Aq}) + \text{Pb}^{+2} + \text{Edta}^{-4} + \text{H}^{+}$
2000VN4	16.30	$\text{Co}(\text{Edta})^{-2}$	$(\text{Aq}) + \text{Co}^{+2} + \text{Edta}^{-4}$
2000VN5	19.30	$\text{Co}(\text{Edta})\text{H}^{-1}$	$(\text{Aq}) + \text{Co}^{+2} + \text{Edta}^{-4} + \text{H}^{+}$
2010VN4	39.80	$\text{Co}(\text{Edta})^{-1}$	$(\text{Aq}) + \text{Co}^{+3} + \text{Edta}^{-4}$
2010VN5	41.20	$\text{Co}(\text{Edta})\text{H}$	$(\text{Aq}) + \text{Co}^{+3} + \text{Edta}^{-4} + \text{H}^{+}$
0200VN4	8.40	$\text{Ag}(\text{Edta})^{-3}$	$(\text{Aq}) + \text{Ag}^{+} + \text{Edta}^{-4}$
0200VN5	15.30	$\text{Ag}(\text{Edta})\text{H}^{-2}$	$(\text{Aq}) + \text{Ag}^{+} + \text{Edta}^{-4} + \text{H}^{+}$
2150VN4	26.80	$\text{Cr}(\text{Edta})^{-1}$	$(\text{Aq}) + \text{Cr}^{+3} + \text{Edta}^{-4}$
2150VN5	29.20	$\text{Cr}(\text{Edta})\text{H}$	$(\text{Aq}) + \text{Cr}^{+3} + \text{Edta}^{-4} + \text{H}^{+}$
2150VN6	19.00	$\text{Cr}(\text{Edta})(\text{OH})^{-2}$	$(\text{Aq}) + \text{Cr}^{+3} + \text{Edta}^{-4} + \text{H}_2\text{O} - \text{H}^{+}$
0300VN4	16.30	$\text{Al}(\text{Edta})^{-1}$	$(\text{Aq}) + \text{Al}^{+3} + \text{Edta}^{-4}$
0300VN5	18.80	$\text{Al}(\text{Edta})\text{H}$	$(\text{Aq}) + \text{Al}^{+3} + \text{Edta}^{-4} + \text{H}^{+}$
0300VN6	13.60	$\text{Al}(\text{Edta})(\text{OH})^{-2}$	$(\text{Aq}) + \text{Al}^{+3} + \text{Edta}^{-4} + \text{H}_2\text{O} - \text{H}^{+}$
2200VN4	1.40	$\text{Cs}(\text{Edta})^{-3}$	$(\text{Aq}) + \text{Cs}^{+} + \text{Edta}^{-4}$
4400VN4	4.00	$\text{Li}(\text{Edta})^{-3}$	$(\text{Aq}) + \text{Li}^{+} + \text{Edta}^{-4}$
1100VN4	12.70	$\text{Be}(\text{Edta})^{-2}$	$(\text{Aq}) + \text{Be}^{+2} + \text{Edta}^{-4}$
7500VN4	26.90	$\text{Sc}(\text{Edta})^{-1}$	$(\text{Aq}) + \text{Sc}^{+3} + \text{Edta}^{-4}$
7500VN5	16.10	$\text{Sc}(\text{Edta})(\text{OH})^{-2}$	$(\text{Aq}) + \text{Sc}^{+3} + \text{Edta}^{-4} + \text{H}_2\text{O} - \text{H}^{+}$
8600VN4	20.00	$\text{TiO}(\text{Edta})^{-2}$	$(\text{Aq}) + \text{TiO}^{+2} + \text{Edta}^{-4}$
7900VN4	24.60	$\text{Sn}(\text{Edta})^{-2}$	$(\text{Aq}) + \text{Sn}^{+2} + \text{Edta}^{-4}$
4300VN4	19.20	$\text{La}(\text{Edta})^{-1}$	$(\text{Aq}) + \text{La}^{+3} + \text{Edta}^{-4}$

TABLE 3.8. (Contd)

ID	Log(K)	Product	Reaction
4300VN5	21.40	La(Edta)H	(Aq) + La ⁺³ + Edta ⁻⁴ + H ⁺
1700VN4	20.10	Ce(Edta) ⁻¹	(Aq) + Ce ⁺³ + Edta ⁻⁴
8500VN4	28.30	Th(Edta)	(Aq) + Th ⁺⁴ + Edta ⁻⁴
8500VN5	21.30	Th(Edta)(OH) ⁻¹	(Aq) + Th ⁺⁴ + Edta ⁻⁴ + H ₂ O - H ⁺
8930VN4	12.90	UO ₂ (Edta) ⁻²	(Aq) + UO ₂ ⁺² + Edta ⁻⁴
8930VN5	20.70	UO ₂ (Edta)H ⁻¹	(Aq) + UO ₂ ⁺² + Edta ⁻⁴ + H ⁺
8930VN6	21.60	(UO ₂) ₂ (Edta)	(Aq) + 2 UO ₂ ⁺² + Edta ⁻⁴
3300VN4	10.20	(Edta)H ⁻³	(Aq) + Edta ⁻⁴ + H ⁺
3300VN5	16.40	(Edta)H ₂ ⁻²	(Aq) + Edta ⁻⁴ + 2 H ⁺
3300VN6	19.00	(Edta)H ₃ ⁻¹	(Aq) + Edta ⁻⁴ + 3 H ⁺
3300VN7	21.10	(Edta)H ₄	(Aq) + Edta ⁻⁴ + 4 H ⁺
3300VN8	22.60	(Edta)H ₅ ⁺¹	(Aq) + Edta ⁻⁴ + 5 H ⁺
3300VN9	24.40	(Edta)H ₆ ⁺²	(Aq) + Edta ⁻⁴ + 6 H ⁺

3.4.6 Nitritotriacetates

TABLE 3.9. Thermochemical Additions for Nitritotriacetates

ID	Log(K)	Product	Reaction
150NV34	8.20	Ca(Nta) ⁻¹	(Aq) + Ca ⁺² + Nta ⁻³
460NV34	7.20	Mg(Nta) ⁻¹	(Aq) + Mg ⁺² + Nta ⁻³
800NV34	6.90	Sr(Nta) ⁻¹	(Aq) + Sr ⁺² + Nta ⁻³
500NV34	2.40	Na(Nta) ⁻²	(Aq) + Na ⁺ + Nta ⁻³
281NV34	18.60	Fe(Nta)	(Aq) + Fe ⁺³ + Nta ⁻³
281NV35	27.10	Fe(Nta) ₂ ⁻³	(Aq) + Fe ⁺³ + 2 Nta ⁻³
281NV36	14.60	Fe(Nta)(OH) ⁻¹	(Aq) + Fe ⁺³ + Nta ⁻³ + H ₂ O - H ⁺
281NV37	6.30	Fe(Nta)(OH) ₂ ⁻²	(Aq) + Fe ⁺³ + Nta ⁻³ + 2 H ₂ O - 2 H ⁺
280NV34	10.60	Fe(Nta) ⁻¹	(Aq) + Fe ⁺² + Nta ⁻³
280NV35	-00.10	Fe(Nta)(OH) ⁻²	(Aq) + Fe ⁺² + Nta ⁻³ + H ₂ O - H ⁺
470NV34	9.20	Mn(Nta) ⁻¹	(Aq) + Mn ⁺² + Nta ⁻³
231NV34	14.50	Cu(Nta) ⁻¹	(Aq) + Cu ⁺² + Nta ⁻³
231NV35	17.10	Cu(Nta) ₂ ⁻⁴	(Aq) + Cu ⁺² + 2 Nta ⁻³

TABLE 3.9. (Contd)

ID	Log(K)	Product	Reaction
231NV36	4.90	$\text{Cu}(\text{Nta})(\text{OH})^{-2}$	$(\text{Aq}) + \text{Cu}^{+2} + \text{Nta}^{-3} + \text{H}_2\text{O} - \text{H}^+$
100NV34	6.50	$\text{Ba}(\text{Nta})^{-1}$	$(\text{Aq}) + \text{Ba}^{+2} + \text{Nta}^{-3}$
160NV34	11.90	$\text{Cd}(\text{Nta})^{-1}$	$(\text{Aq}) + \text{Cd}^{+2} + \text{Nta}^{-3}$
160NV35	15.40	$\text{Cd}(\text{Nta})_2^{-4}$	$(\text{Aq}) + \text{Cd}^{+2} + 2 \text{Nta}^{-3}$
950NV34	12.40	$\text{Zn}(\text{Nta})^{-1}$	$(\text{Aq}) + \text{Zn}^{+2} + \text{Nta}^{-3}$
950NV35	14.20	$\text{Zn}(\text{Nta})_2^{-4}$	$(\text{Aq}) + \text{Zn}^{+2} + 2 \text{Nta}^{-3}$
540NV34	13.10	$\text{Ni}(\text{Nta})^{-1}$	$(\text{Aq}) + \text{Ni}^{+2} + \text{Nta}^{-3}$
360NV34	14.50	$\text{Hg}(\text{Nta})^{-1}$	$(\text{Aq}) + \text{Hg}^{+2} + \text{Nta}^{-3}$
360NV35	8.80	$\text{Hg}(\text{Nta})(\text{OH})^{-2}$	$(\text{Aq}) + \text{Hg}^{+2} + \text{Nta}^{-3} + \text{H}_2\text{O} - \text{H}^+$
600NV34	13.60	$\text{Pb}(\text{Nta})^{-1}$	$(\text{Aq}) + \text{Pb}^{+2} + \text{Nta}^{-3}$
200NV34	12.40	$\text{Co}(\text{Nta})^{-1}$	$(\text{Aq}) + \text{Co}^{+2} + \text{Nta}^{-3}$
030NV34	14.80	$\text{Al}(\text{Nta})$	$(\text{Aq}) + \text{Al}^{+3} + \text{Nta}^{-3}$
030NV35	20.80	$\text{Al}(\text{Nta})_2^{-3}$	$(\text{Aq}) + \text{Al}^{+3} + 2 \text{Nta}^{-3}$
030NV36	9.40	$\text{Al}(\text{Nta})(\text{OH})^{-1}$	$(\text{Aq}) + \text{Al}^{+3} + \text{Nta}^{-3} + \text{H}_2\text{O} - \text{H}^+$
110NV34	9.00	$\text{Be}(\text{Nta})^{-1}$	$(\text{Aq}) + \text{Be}^{+2} + \text{Nta}^{-3}$
860NV34	14.20	$\text{TiO}(\text{Nta})^{-1}$	$(\text{Aq}) + \text{TiO}^{+2} + \text{Nta}^{-3}$
430NV34	13.20	$\text{La}(\text{Nta})$	$(\text{Aq}) + \text{La}^{+3} + \text{Nta}^{-3}$
430NV35	20.90	$\text{La}(\text{Nta})_2^{-3}$	$(\text{Aq}) + \text{La}^{+3} + 2 \text{Nta}^{-3}$
170NV34	13.50	$\text{Ce}(\text{Nta})$	$(\text{Aq}) + \text{Ce}^{+3} + \text{Nta}^{-3}$
170NV35	21.40	$\text{Ce}(\text{Nta})_2^{-3}$	$(\text{Aq}) + \text{Ce}^{+3} + 2 \text{Nta}^{-3}$
850NV34	17.10	$\text{Th}(\text{Nta})^{+1}$	$(\text{Aq}) + \text{Th}^{+4} + \text{Nta}^{-3}$
850NV35	-17.20	$\text{Th}(\text{Nta})(\text{OH})_2^{-1}$	$(\text{Aq}) + \text{Th}^{+4} + \text{Nta}^{-3} + 2 \text{H}_2\text{O} - 2 \text{H}^+$
893NV34	11.50	$\text{UO}_2(\text{Nta})^{-1}$	$(\text{Aq}) + \text{UO}_2^{+2} + \text{Nta}^{-3}$
330NV34	10.50	$(\text{Nta})\text{H}^{-2}$	$(\text{Aq}) + \text{Nta}^{-3} + \text{H}^+$
330NV35	13.70	$(\text{Nta})\text{H}_2^{-1}$	$(\text{Aq}) + \text{Nta}^{-3} + 2 \text{H}^+$
330NV36	15.90	$(\text{Nta})\text{H}_3$	$(\text{Aq}) + \text{Nta}^{-3} + 3 \text{H}^+$

3.4.7 Oxalates

TABLE 3.10. Thermochemical Additions for Oxalates

ID	Log(K)	Product	Reaction
9115001	8.00	Ca(Ox)	(So) + Ca ⁺² + Ox ⁻²
150VV04	3.60	Ca(Ox)	(Aq) + Ca ⁺² + Ox ⁻²
9146001	3.70	Mg(Ox)	(So) + Mg ⁺² + Ox ⁻²
460VV04	2.90	Mg(Ox)	(Aq) + Mg ⁺² + Ox ⁻²
9180001	6.70	Sr(Ox)	(So) + Sr ⁺² + Ox ⁻²
800VV04	1.90	Sr(Ox)	(Aq) + Sr ⁺² + Ox ⁻²
281VV04	8.90	Fe(Ox) ⁺¹	(Aq) + Fe ⁺³ + Ox ⁻²
281VV05	15.70	Fe(Ox) ₂ ⁻¹	(Aq) + Fe ⁺³ + 2 Ox ⁻²
281VV06	20.40	Fe(Ox) ₃ ⁻³	(Aq) + Fe ⁺³ + 3 Ox ⁻²
470VV04	3.20	Mn(Ox)	(Aq) + Mn ⁺² + Ox ⁻²
470VV05	4.90	Mn(Ox) ₂ ⁻²	(Aq) + Mn ⁺² + 2 Ox ⁻²
231VV04	6.40	Cu(Ox)H ⁺¹	(Aq) + Cu ⁺² + Ox ⁻² + H ⁺
231VV05	5.10	Cu(Ox)	(Aq) + Cu ⁺² + Ox ⁻²
231VV06	9.70	Cu(Ox) ₂ ⁻²	(Aq) + Cu ⁺² + 2 Ox ⁻²
9110001	6.20	Ba(Ox)	(So) + Ba ⁺² + Ox ⁻²
100VV04	1.70	Ba(Ox)	(Aq) + Ba ⁺² + Ox ⁻²
9116001	7.20	Cd(Ox)	(So) + Cd ⁺² + Ox ⁻²
160VV04	3.40	Cd(Ox)	(Aq) + Cd ⁺² + Ox ⁻²
160VV05	5.50	Cd(Ox) ₂ ⁻²	(Aq) + Cd ⁺² + 2 Ox ⁻²
9195001	8.20	Zn(Ox)	(So) + Zn ⁺² + Ox ⁻²
950VV04	4.20	Zn(Ox)	(Aq) + Zn ⁺² + Ox ⁻²
950VV05	6.90	Zn(Ox) ₂ ⁻²	(Aq) + Zn ⁺² + 2 Ox ⁻²
950VV06	5.70	Zn(Ox)H ⁺¹	(Aq) + Zn ⁺² + Ox ⁻² + H ⁺
950VV07	11.10	Zn(Ox) ₂ H ₂	(Aq) + Zn ⁺² + 2 Ox ⁻² + 2 H ⁺
540VV04	4.60	Ni(Ox)	(Aq) + Ni ⁺² + Ox ⁻²
540VV05	8.00	Ni(Ox) ₂ ⁻²	(Aq) + Ni ⁺² + 2 Ox ⁻²
540VV06	9.40	Ni(Ox) ₃ ⁻⁴	(Aq) + Ni ⁺² + 3 Ox ⁻²
9160001	9.20	Pb(Ox)	(So) + Pb ⁺² + Ox ⁻²
200VV04	4.10	Co(Ox)	(Aq) + Co ⁺² + Ox ⁻²
200VV05	6.60	Co(Ox) ₂ ⁻²	(Aq) + Co ⁺² + 2 Ox ⁻²

TABLE 3.10. (Contd)

ID	Log(K)	Product	Reaction
200VV06	5.70	$\text{Co}(\text{Ox})\text{H}^{+1}$	$(\text{Aq}) \leftarrow \text{Co}^{+2} + \text{Ox}^{-2} + \text{H}^{+}$
200VV07	10.90	$\text{Co}(\text{Ox})_2\text{H}_2$	$(\text{Aq}) \leftarrow \text{Co}^{+2} + 2 \text{Ox}^{-2} + 2 \text{H}^{+}$
9102001	10.40	$\text{Ag}_2(\text{Ox})$	$(\text{So}) \leftarrow 2 \text{Ag}^{+} + \text{Ox}^{-2}$
020VV04	2.60	$\text{Ag}(\text{Ox})^{-1}$	$(\text{Aq}) \leftarrow \text{Ag}^{+} + \text{Ox}^{-2}$
215VV04	6.40	$\text{Cr}(\text{Ox})^{+1}$	$(\text{Aq}) \leftarrow \text{Cr}^{+3} + \text{Ox}^{-2}$
030VV04	12.50	$\text{Al}(\text{Ox})_2^{-1}$	$(\text{Aq}) \leftarrow \text{Al}^{+3} + 2 \text{Ox}^{-2}$
030VV05	16.40	$\text{Al}(\text{Ox})_3^{-3}$	$(\text{Aq}) \leftarrow \text{Al}^{+3} + 3 \text{Ox}^{-2}$
110VVD4	4.20	$\text{Be}(\text{Ox})$	$(\text{Aq}) \leftarrow \text{Be}^{+2} + \text{Ox}^{-2}$
110VV05	6.30	$\text{Be}(\text{Ox})_2^{-2}$	$(\text{Aq}) \leftarrow \text{Be}^{+2} + 2 \text{Ox}^{-2}$
750VV04	18.20	$\text{Sc}(\text{Ox})_3^{-3}$	$(\text{Aq}) \leftarrow \text{Sc}^{+3} + 3 \text{Ox}^{-2}$
860VV04	10.30	$\text{TiO}(\text{Ox})$	$(\text{Aq}) \leftarrow \text{TiO}^{+2} + \text{Ox}^{-2}$
860VV05	15.70	$\text{TiO}(\text{Ox})_2^{-2}$	$(\text{Aq}) \leftarrow \text{TiO}^{+2} + 2 \text{Ox}^{-2}$
430VV04	5.20	$\text{La}(\text{Ox})^{+1}$	$(\text{Aq}) \leftarrow \text{La}^{+3} + \text{Ox}^{-2}$
430VV05	9.40	$\text{La}(\text{Ox})_2^{-1}$	$(\text{Aq}) \leftarrow \text{La}^{+3} + 2 \text{Ox}^{-2}$
430VV06	12.20	$\text{La}(\text{Ox})_3^{-3}$	$(\text{Aq}) \leftarrow \text{La}^{+3} + 3 \text{Ox}^{-2}$
170VV04	6.80	$\text{Ce}(\text{Ox})^{+1}$	$(\text{Aq}) \leftarrow \text{Ce}^{+3} + \text{Ox}^{-2}$
170VV05	10.70	$\text{Ce}(\text{Ox})_2^{-1}$	$(\text{Aq}) \leftarrow \text{Ce}^{+3} + 2 \text{Ox}^{-2}$
170VV06	11.60	$\text{Ce}(\text{Ox})_3^{-3}$	$(\text{Aq}) \leftarrow \text{Ce}^{+3} + 3 \text{Ox}^{-2}$
893VV04	5.20	$\text{UO}_2(\text{Ox})$	$(\text{Aq}) \leftarrow \text{UO}_2^{+2} + \text{Ox}^{-2}$
893VV05	9.60	$\text{UO}_2(\text{Ox})_2^{-2}$	$(\text{Aq}) \leftarrow \text{UO}_2^{+2} + 2 \text{Ox}^{-2}$
893VV06	12.90	$\text{UO}_2(\text{Ox})_3^{-4}$	$(\text{Aq}) \leftarrow \text{UO}_2^{+2} + 3 \text{Ox}^{-2}$
330VV04	4.20	$(\text{Ox})\text{H}^{-1}$	$(\text{Aq}) \leftarrow \text{Ox}^{-2} + \text{H}^{+}$
330VV05	5.10	$(\text{Ox})\text{H}_2$	$(\text{Aq}) \leftarrow \text{Ox}^{-2} + 2 \text{H}^{+}$

4.0 RECOMMENDATIONS FOR FURTHER WORK

Thermochemical data in this report coupled with the improved geochemical code MINTEQ2 provide a provisional capability to assess some important effects of organic ligands on the aqueous chemistry of Hanford defense waste. We recommend their use to make preliminary assessments of the effect of organics on the solubilization or precipitation of inorganics that are found in Hanford defense wastes. The thermochemical data should also be used in computer modeling sensitivity exercises to determine which organic reactions could have a significant impact on Hanford defense waste management. Specific applications of MINTEQ2 could include assessment of the effects of known or hypothesized concentrations of organics in double-shell slurry and single-shell tank wastes. Knowledge of the effects of organics on these waste streams and the detailed knowledge on overall chemistry that MINTEQ2 provides will greatly help source term development efforts and subsequent calculations of waste migration in the Hanford sediments, both of which are essential elements of performance assessment analyses.

These exercises will help establish priorities in verifying the thermochemical data. Obviously, the careful evaluation of all possible metal/organic reactions would require many man-years of effort. However, most of these reactions will not be important because the organic ligand will not be in sufficient supply to make much of a difference. Others will, however, and must be identified.

We emphasize that the thermochemical data presented in this report are classified as provisional for several reasons: 1) they have not been individually documented; 2) we cannot be assured that they are internally consistent with the existing MINTEQ2 reactions; and 3) in some cases, the reaction has had to be inferred indirectly. After the preliminary analyses have been made, important reactions have been identified, and priorities have been established, additional resources should be allocated to verify the accuracy of these important reactions as they apply to the Hanford defense waste scenario.

4.1 ADDING ORGANIC REACTIONS TO THE THERMODYNAMIC DATA BASE

Notably absent from the organic data base described in this report are chemical reactions for the major radionuclides and reactions of several apparently important ligands for all of the elements. By operating MINTEQ2 in the mode described above, some of these may be legitimately ignored. However, some are certainly expected to play important roles. For the important reactions, free energies of reactions with pertinent metal species should be added. Table 4.1 summarizes the possible future need for additional data (indicated by x) for reactions involving organic ligands.

TABLE 4.1. Additional Organic-Ligand Reactions Needed for MINTEQ2

Element	Ligand ^(a)							
	<u>Ox-</u>	<u>Edta-4</u>	<u>Cit-3</u>	<u>Hyac-1</u>	<u>Hedta-3</u>	<u>Tbp</u>	<u>Gluc</u>	<u>D2ehpa</u>
Cobalt				x	x	x	x	x
Copper				x	x	x	x	x
Manganese				x	x	x	x	x
Cadmium				x	x	x	x	x
Lead				x	x	x	x	x
Lanthanum				x	x	x	x	x
Cerium				x	x	x	x	x
Cesium				x	x	x	x	x
Strontium				x	x	x	x	x
Mercury				x	x	x	x	x
Lanthanum				x	x	x	x	x
Uranium				x	x	x	x	x
Plutonium	x	x	x	x	x	x	x	x
Neptunium	x	x	x	x	x	x	x	x

(a) Edta-4 = ethylenediaminetetraacetate; Cit-3 = citrate; Hyac-1 = hydroxyacetate; Hedta-3 = hydroxyethylenediaminetriacetate; Tbp = tributyl phosphate, Gluc = gluconate; D2ehpa = Di(2-Ethylhexyl)phosphate.

4.2 ADDING PITZER PARAMETERS FOR ORGANIC INTERACTIONS

To accurately calculate activity coefficients of organic ligands in high-ionic-strength aqueous media, ion interaction parameters (Pitzer 1980, 1981) are needed for these ligands and for plutonium and neptunium. Because most of these probably will not be found in the literature, some effort must be extended to formulate a generalization for the organic parameters and perhaps for the plutonium and neptunium parameters.

4.3 ADDING ADSORPTION REACTIONS

Application of MINTEQ2 to assess disposal of defense waste will require knowledge of the important adsorption reactions for Hanford soils. Therefore, the literature on Hanford soils should be examined to extract thermochemical data for adsorption reactions between the metallic species and adsorption sites on the soils.

4.4 FURTHER MODIFICATIONS TO MINTEQ2

We believe that MINTEQ2 is now developed to the point that it could model most of the aqueous chemical problems at Hanford provided the appropriate thermochemical data were available. However, as is always the case with computer codes of this complexity, we can expect to discover deficiencies with usage that will need correction. These corrections are not expected to be a major effort, but rather will be part of an ongoing maintenance program.

Extension of MINTEQ2's capability to model adsorption at high ionic strengths will require some development of theory. Little work has yet been reported on modeling adsorption processes in concentrated aqueous media. Thus, a major scientific developmental effort is justified to develop adequate modeling capabilities. Fortunately, however, applications involving high ionic strengths may only be needed relatively close to the source and then only if adsorption surfaces are prevalent. Therefore, a lack of an adsorption capability at high ionic strength will not preclude most foreseeable applications of the code.

4.5 APPLICATIONS TO HANFORD DEFENSE WASTE PROBLEMS

Code validation is the most important and the most difficult of the tasks yet to be completed before the predicted results of MINTEQ2 can stand scientific scrutiny. Many validation studies can be conducted using data from relatively inexpensive laboratory experiments. The aqueous compositions predicted by MINTEQ2 can be compared with easily measurable quantitative aqueous analyses of solutions in contact with appropriate minerals, gases, and adsorption media.

It would also be desirable to compare the predictions given by MINTEQ2 with field experiments. One possibility is to use MINTEQ2 to calculate appropriate distribution coefficients for use in transport codes to predict migration away from waste tanks that have developed leaks. The distribution coefficient is generally assumed to be a constant through all of the chemical gradients that are dictated by the problem being modeled. This assumption is often untenable because the distribution function for a given element is generally highly dependent on other elements, minerals, Eh and pH. However, by using MINTEQ2, one could calculate redox conditions and obtain more appropriate spatially- and time-dependent distribution coefficients. These could then be used in place of a single distribution coefficient for each element.

If appropriate field data were available, calibration experiments could be performed to condition the geochemical transport model to predict experimental values. For example, if at time t and distance x from the source, element e had an aqueous concentration c , the adsorption parameters, mineral assemblages, pH, and Eh could be adjusted so that the predicted concentration would be the same as measured. If this were done for each element and at a number of spatial distances, the model would be calibrated and ready to predict events beyond the range of experimental knowledge.

5.0 REFERENCES

- Baes, C. F. and R. E. Mesmer. 1976. The Hydrolysis of Cations. John Wiley and Sons, New York.
- Baker, P. A., G. Palmer, and P. W. L. Nichols. 1975. "The Wiswesser Line Formula Notations," in Chemical Information Systems, J. E. Ash and E. Hyde, Eds., Ellis Horwood, Chichester, Chapter 9.
- Ball, J. W., D. K. Nordstrom and E. A. Jenne. 1980. "Additional and Revised Thermochemical Data and Computer Code for WATEQ2--A Computerized Chemical Model for Trace and Major Element Speciation and Mineral Equilibria of Natural Waters." U.S. Geol. Survey, Water Res. Invest. 78-116.
- Ball, J. W., E. A. Jenne, and M. W. Cantrell. 1981. WATEQ3: A Geochemical Model with Uranium Added. U.S. Geol. Survey, Open-File Report 81-1183.
- Delegard, C. H. G. S. Barney and S. A. Gallagher. 1983. Effects of Hanford High-Level Waste Components on the Solubility and Sorption of Co, Sr, Np, Pu, and Am. RHO-RE-SA-18P, Rockwell Hanford Operations, Richland, Washington.
- ERDA. 1977. Alternatives for Long-Term Management of Defense High-Level Radioactive Waste, Hanford Reservations, Richland, Washington, Energy Research and Development Administration, Washington, D.C.
- Felmy, A. R., D. C. Girvin, and E. A. Jenne. 1984. MINTEQ: A Computer Program for Calculating Aqueous Geochemical Equilibria. EPA Contract No. 68-03-3089, Athens Environmental Research Laboratory, Athens, Georgia.
- Helgeson, H. C. 1969. "Thermodynamics of Hydrothermal Systems at Elevated Temperatures and Pressures." Am. J. Sci. 267:729-804.
- Kincaid, C. T., J. R. Morrey and J. E. Rogers. 1984. Geohydrochemical Models for Solute Migration. Volume I: Process Description and Computer Code Selection, Palo Alto, California, Electric Power Research Institute, EA-3417.
- Kincaid, C. T., and J. R. Morrey. 1984. Geohydrochemical Models for Solute Migration. Volume II: Preliminary Evaluation of Selected Computer Codes for Modeling Aqueous Solutions and Solute Migration in Soils and Geologic Media. Palo Alto, California, Electric Power Research Institute, EA-____.
- Krupka, K. M. and E. A. Jenne. 1982. WATEQ3 Geochemical Model: Thermodynamic Data for Several Additional Solids. PNL 4276, Pacific Northwest Laboratory, Richland, Washington.
- Martell, A. E. and R. M. Smith. 1976-77. Critical Stability Constants. 4 Vols. Plenum Press, New York.

APPENDIX A

CURRENT LISTING OF DATA CONVERSION CODE, GEOMIN

APPENDIX A

CURRENT LISTING OF DATA CONVERSION CODE, GEOMIN

```

READ GEOCHEM DATA BASE AND TRANSFORM TO MINTEQ2 DATA BASE
*****DEFINITIONS*****
L = LTH REACTION
J = JTH COMPONENT IN LTH REACTION
K = KTH REACTION OF CARD 5
IDYT(L) = MINTEQ2 IDENTIFICATION
TYP(L) = TYPE OF REACTION (AQ, SOLID, REDOX, ETC.)
CK(L) = LOG(K)
NCOMP(L) = NUMBER OF COMPONENTS IN LTH REACTION
CH(L) = CHARGE ON PRODUCT OF LTH REACTION
II(J,L) = GEOCHEM INDEX NUMBER OF JTH REACTANT IN LTH REACTION
IT(J,L) = TYPE OF JTH COMPONENT IN LTH REACTION (1=METAL, 2=LIGAND)
INS(J,L) = STOICHIOMETRIC COEFFICIENT OF JTH REACTANT IN LTH REACTION
LCK(K) = 10LOGK FOR KTH REACTION IN CARD 5
INSA(J,K) = STOICHIOMETRIC COEFFICIENT OF JTH REACTANT IN KTH REACTION
IDSEL(M,I) = GEOCHEM INDEX OF COMPONENT TO SELECT (M=1 METAL, M=2 LIGAND)
MINTRA(M,I) = MINTEQ2 INDEX CORRESPONDING TO GEOCHEM INDEX I (M=1 METAL
MINCLA(M,I) = MINERAL CLASSIFICATION INDEX FOR MINTEQ
COMNAM(M,I) = NAME CORRESPONDING TO ITH GEOCHEM INDEX (M=1 METAL
COMSYM(M,I) = CHEMICAL SYMBOL FOR THE ITH GEOCHEM INDEX
GFWM(M,I) = GRAM FORMULA WEIGHT OF ITH SPECIES OF MTH TYPE
GFWC(L) = MOLECULAR WEIGHT OF LTH PRODUCT
NCHA(M,I) = NUMBER OF CHARACTERS IN COMSYM(M,I)
*****END DEFINITIONS*****
      IMPLICIT REAL*8(A-H,O-Z)
      CHARACTER*8 COMNAM,SPECIES,TYP,COMSYM,NAM3
      CHARACTER*1 NAM1,NAM2,NUMB(10),ISIM(12)
      CHARACTER*2 HOL(20),IASC(12)
      CHARACTER*7 IDYT(1000)
      CHARACTER*1 IDYY(7,1000)
      EQUIVALENCE (IDYT(1),IDYY(1,1))
      CHARACTER*7 MINTRA(2,99)
      CHARACTER*18 NAMED,NAM0
      DIMENSION MINCLA(2,99)
      DIMENSION NAM1(18),NAM2(8)
      EQUIVALENCE (NAM2(1),NAM3),(NAM1(1),NAM0)
      DIMENSION II(7,1000),IT(7,1000),INS(7,1000),T(7,1000)
      DIMENSION LCK(9),INSA(4,9),SPECIES(2)
      DIMENSION IDSEL(2,99),COMNAM(2,99),COMSYM(2,99),
      INCHA(2,99),V(2,99),ICH(2,99),GFW(2,99)
      DIMENSION NAMED(1000),TYP(5),CK(1000),CH(1000)
      1,GFWC(1000),NCOMP(1000)
      DATA (HOL(I),I=1,20)/' 1',' 2',' 3',' 4',' 5',' 6',' 7',' 8',

```

```

1' 9', '10', '11', '12', '13', '14', '15', '16', '17', '18', '19', '0' /
DATA (MINTRA(1,I), I=1,35) / '150', '460', '800', '410', '500', '281',
1' 280', '470', '231', '100', '160', '950', '540', '360', '600', '200',
2' 201', '020', '215', '030', '220', '440', '110', '750', '860', '790',
3' 792', '430', '170', '080', '850', '893', '230', '361', '680' /
MINTRA(1,50) = '330'
MINTRA(1,51) = '002'
DATA (MINTRA(2,I), I=1,68) / '140', '732', '180', '270', '130', '380',
1' 494', '733', '580', '581', '582', '771', '735', '143', '0V1', '0V3',
2' 'XV3', 'VV0', 'RV1', 'VV2', 'ZZ2', 'NR2', 'RS1', 'VZ0', 'VZ3', 'RW3',
3' 'NV3', 'OVN', 'OV9', 'SV2', 'ZZ0', 'RV2', 'VZ7', 'VZ4', 'VZ6', 'VZ7',
4' 'VZ8', 'VZ1', 'VZ2', 'VZR', 'VZS', 'VZB', 'VZQ', 'VZT', 'VZD', 'VZC',
5' 'NV3', '091', '733', '734', '492', '480', '910', '062', '904', '760',
6' 494', 'VN5', '761', 'VV2', '125', '181', ' ', ' ', ' ', 'VOD', 'OVY',
7' 'OVZ', 'QZ0' /
MINTRA(2,98) = '001'
MINTRA(2,99) = '330'
DATA (COMNAM(1,I), I=1,35) / 'Ca+2', 'Mg+2', 'Sr+2', 'K+', 'Na+', 'Fe+3',
1' 'Fe+2', 'Mn+2', 'Cu+2', 'Ba+2', 'Cd+2', 'Zn+2', 'Ni+2', 'Hg+2', 'Pb+2',
2' 'Co+2', 'Co+3', 'Ag+', 'Cr+3', 'Al+3', 'Cs+', 'Li+', 'Be+2', 'Sc+3',
3' 'TiO+2', 'Sn+2', 'Sn+4', 'La+3', 'Ce+3', 'Au+', 'Th+4', 'UO2+2', 'Cu+',
4' 'CH3Hg+', 'Rb+' /
COMNAM(1,50) = 'H+'
COMNAM(1,51) = 'H2O'
COMNAM(1,90) = 'UNDEF'
DATA (GFW(1,I), I=1,35) / 40.08, 24.31, 87.62, 39.10, 22.99, 55.85,
155.85, 54.94, 63.55, 137.34, 112.4, 65.38, 58.71, 200.59, 207.2, 58.99,
258.99, 107.90, 52.00, 26.98, 132.91, 6.94, 9.01, 44.56, 63.90,
3118.69, 118.69, 138.91, 140.12, 196.97, 232.03, 270.03, 63.546, 22.59,
485.48 /
GFW(1,50) = 1.01
GFW(1,51) = 18.02
GFW(1,90) = 0
DATA (ICH(1,I), I=1,35) / 2, 2, 2, 1, 1, 3, 2, 2, 2, 2, 2, 2, 2, 2, 2, 2, 3, 1, 3, 3, 1,
11, 2, 3, 2, 2, 4, 3, 3, 1, 4, 2, 1, 1, 1 /
ICH(1,50) = 1
ICH(1,51) = 0
ICH(1,90) = 0
DATA (COMSYM(1,I), I=1,35) / 'Ca', 'Mg', 'Sr', 'K', 'Na', 'Fe',
1' 'Fe', 'Mn', 'Cu', 'Ba', 'Cd', 'Zn', 'Ni', 'Hg', 'Pb',
2' 'Co', 'Co', 'Ag', 'Cr', 'Al', 'Cs', 'Li', 'Be', 'Sc',
3' 'TiO', 'Sn', 'Sn', 'La', 'Ce', 'Au', 'Th', 'UO2', 'Cu',
4' 'CH3Hg', 'Rb' /
COMSYM(1,50) = 'H'
COMSYM(1,51) = '(H2O)'
COMSYM(1,90) = 'UNDEF'
DATA (NCHA(1,I), I=1,35) / 2, 2, 2, 1, 2, 2, 2, 2, 2, 2, 2, 2, 2, 2, 2, 2, 2, 2, 2, 2,
12, 2, 2, 2, 2, 3, 2, 2, 2, 2, 2, 2, 3, 2, 5, 2 /
NCHA(1,50) = 1
NCHA(1,51) = 5
NCHA(1,90) = 5

```



```

25,6,0,0,0,7,7,7,7,5,9,7,9,9,7,0,0,9,9,9,9/
DATA (MINCLA(2,J),J=1,68)/10,10,1,2,10,3,10,10,10,10,10,10,
110,10,10,1,1,1,2,2,2,3,3,3,3,4,4,3,3,5,4,4,4,4,4,4,4,4,
24,4,7,4,4,4,2,10,10,10,8,5,2,3,6,1,5,6,4,4,7,10,10,2,2,2/
DATA (SPECIES(I), I=1,2)/'METALS ', 'LIGANDS '/
DATA (TYP(I),I=1,5)/'Solid ', 'Aqueous ', 'Redox ', 'Mxd.Sol.',
1'Sol.Rdx.'/
DATA (NUMB(I),I=1,10)/'1','2','3','4','5','6','7','8','9','0'/
OPEN(UNIT=9,FILE='OUTPUT.DAT',TYPE='NEW',RECL=132)
OPEN(UNIT=10,FILE='THERMO.DAT',TYPE='OLD')
OPEN(UNIT=7,FILE='GEOMOR.DAT',TYPE='NEW',RECL=132)
OPEN(UNIT=8,FILE='COMMOR.DAT',TYPE='NEW',RECL=80)
ENTER GEOCHEM INOICES FOR METALS AND LIGANDS TO SELECT HERE
WRITE(6,3)
WRITE(9,3)
3 FORMAT(' ENTER NUMBER OF METALS TO RETRIEVE')
READ(5,4) NMET
4 FORMAT(I5)
WRITE(6,5) NMET
WRITE(9,5) NMET
5 FORMAT(' ENTER GEOCHEM INDICES FOR ',I3,' METALS- ONE PER LINE')
DO 6 I=1,NMET
READ(5,4) IDSEL(1,I)
6 WRITE(9,4) IDSEL(1,I)
WRITE(6,7)
WRITE(9,7)
7 FORMAT(' ENTER NUMBER OF LIGANDS TO RETRIEVE')
READ(5,4) NLIG
WRITE(6,8) NLIG
WRITE(9,8) NLIG
8 FORMAT(' ENTER GEOCHEM INDICES FOR ',I3,' LIGANDS- ONE PER LINE')
DO 9 I=1,NLIG
READ(5,4) IDSEL(2,I)
9 WRITE(9,4) IDSEL(2,I)
NALL=1
ENTER CODES FOR METALS AND LIGANDS TO SELECT ABOVE
DO 50 L=1,1000
IDYT(L)='00000000'
CK(L)=0
NCOMP(L)=0
CH(L)=0
NAMER(L)=' '
DO 50 J=1,7
II(J,L)=0
IT(J,L)=0
T(J,L)=0
50 INS(J,L)=0
WRITE(6,10) ' METALS ',(COMNAM(1,IDSEL(1,I)),I=1,NMET)
WRITE(9,10) ' METALS ',(COMNAM(1,IDSEL(1,I)),I=1,NMET)
10 FORMAT('/' ',A8,' PULLED:'15('/' ',7(A8,2X)))
WRITE(6,10) ' LIGANDS ',(COMNAM(2,IDSEL(2,I)),I=1,NLIG)

```

```

        WRITE(9,10) ' LIGANDS ',(COMNAM(2,IDSEL(2,I)),I=1,NLIG)
CARD #1
    READ(10,11)NCM,NCL
    11 FORMAT(2I3)
        ICA=0
        ICS=1000
        IE=NCM
        LE=NMET
        DO 200 M=1,2
            IC=0
            WRITE (6,1300)
            WRITE (9,1300)
1300  FORMAT(15X,' SPECIES ',2X,6X,' INOEX',5X,'CHARGE',1X,'DIAMETER',
            11X,'FORMULA'/' ',25X,'GEOCHEM MINTEQ',8X,'ANGSTROM',' WEIG
            2HT')
            DO 100 I=1,IE
CARD #2
CARD #3
    READ(10,12) III,ICHA,V(M,III)
    12 FORMAT(I2,I3,F7.2)
        IF(ICA.NE.ICH(M,III)) WRITE (6,999) COMNAM(M,II(M,III)),
        1ICHA,ICH(M,III)
999  FORMAT(' CHARGE MISMATCH FOR ',A8,':',2I5)
        CHA=ICHA
        WRITE(6,13) COMNAM(M,III),III,MINTRA(M,III),
        1ICH(M,III),V(M,III),GFW(M,III)
        WRITE(9,13) COMNAM(M,III),III,MINTRA(M,III),
        1ICH(M,III),V(M,III),GFW(M,III)
    13 FORMAT(16X,A8,2X,I5,5X,A3,2X,I5,2X,F7.2,2X,F8.2)
        DO 40 L=1,LE
    40  IF(IDSEL(M,L).EQ.III) GO TO 60
        GO TO 100
    60  IC=IC+1
        WRITE(8,131) MINTRA(M,II(M,III)),COMNAM(M,II(M,III)),CHA,
        1V(M,III),GFW(M,III)
    131 FORMAT(' ',A3,1X,A8,F4.1,F7.1,13X,F9.4)
    100 CONTINUE
        WRITE(6,130) IC,SPECIES(M)
        WRITE(9,130) IC,SPECIES(M)
    130 FORMAT(/28X,' DATA TRANSFER WILL BE FOR ',I4,1X,A8/)
        IE=NCL
        LE=NLIG
    200 CONTINUE
CARD #4
    READ(10,14)NMAT,WK,PCO2CT
    14 FORMAT(I5,F5.2,F5.1)
        WRITE(6,1400)
        WRITE(9,1400)
1400  FORMAT(' ID LOG(K) PRODUCT
        1 REACTION')
        ICOUNT=0

```



```

      DO 300 KK=1,NMAT
ARD #5  READ(10,16) (II(M,1000),M=1,2),(LCK(K),(INSA(J,K),J=1,3),K=1,9)
      16 FORMAT(2I2,9(I4,2I1,I2))
      LE=NMET
      DO 245 M=1,2
      DO 240 L=1,LE
      IF(IOSEL(M,L).EQ.II(M,1000)) GO TO 260
240 CONTINUE
245 LE=NLIG
      GO TO 300
260 ISPEC=1
      DO 290 K=1,9
      IF(K.EQ.4) ISPEC=2
      DO 265 J=1,3
      IF(INSA(J,K).NE.0) GO TO 270
265 CONTINUE
      GO TO 290
270 IF(ISPEC.EQ.2) THEN
      ICA=ICA+1
      IC=ICA
      ELSE
      ICS=ICS-1
      IC=ICS
      END IF
      ICOUNT=ICOUNT+1
      NCOMP(IC)=3
      II(1,IC) = II(1,1000)
      II(2,IC) = II(2,1000)
      IH0H=3
      II(3,IC)=50
      IT(3,IC)=1
      IF(INSA(3,K).LT.0) II(3,IC)=99
      DO 271 M=1,2
      IF(II(M,IC).EQ.99) THEN
      IH0H=M
      INSA(M,K)=INSA(3,K)
      NCOMP(IC)=2
      END IF
271 CONTINUE
      IT(1,IC)=1
      IT(2,IC)=2
      IF(II(IH0H,IC).EQ.99) THEN
      IT(IH0H,IC)=2
      INSA(IH0H,K)=-INSA(IH0H,K)
      END IF
      DO 272 J=1,3
      T(J,IC) = INSA(J,K)
272 INS(J,IC)=INSA(J,K)
      IF(K.LE.3) THEN
      IDYT(IC)=MINTRA(1,II(1,IC))

```

```

DO 273 KKK=5,3,-1
273 IDYY(KKK,IC)=IDYY(KKK-2,IC)
   IDYY(1,IC) =NUMB(MINCLA(1,II(2,IC)))
   IDYY(2,IC) =NUMB(MINCLA(2,II(2,IC)))
   IDYY(3,IC) = MINTRA(1,II(1,IC))
   IDYY(6,IC)=NUMB(10)
   IDYY(7,IC)=NUMB(K)
ELSE
   IDYT(IC)=MINTRA(1,II(1,IC))
   IDYT(1000)=MINTRA(2,II(2,IC))
   IDYY(4,IC)=IDYY(1,1000)
   IDYY(5,IC)=IDYY(2,1000)
   IDYY(6,IC)=IDYY(3,1000)
   IDYY(7,IC)=NUMB(K)
END IF
CK(IC)=0.1*LCK(K)
ME=NCOMP(IC)
DO 280 M=1,ME
  L=ME+1-M
  IF(INS(L,IC).EQ.0) THEN
    NCOMP(IC) = NCOMP(IC)-1
    IF(L.LE.NCOMP(IC)) THEN
      DO 275 N=L,NCOMP(IC)
        T(N,IC)=T(N+1,IC)
        INS(N,IC)=INS(N+1,IC)
        IT(N,IC)=IT(N+1,IC)
        II(N,IC)=II(N+1,IC)
275 IF(II(N,IC).EQ.50.OR.II(N,IC).EQ.99) IH0H=N
      ENO IF
    END IF
280 CONTINUE
    CH(IC)=0.
    GFWC(IC)=0.
    DO 281 J=1,NCOMP(IC)
      GFWC(IC)=GFWC(IC)+INS(J,IC)*GFW(IT(J,IC),II(J,IC))
281 CH(IC)=CH(IC)+INS(J,IC)*ICH(IT(J,IC),II(J,IC))
      NAM0='K'
      IE=2
      DO 284 J=1,NCOMP(IC)
        NAM3=COMSYM(IT(J,IC),II(J,IC))
        IS=IE
        IE=IE+NCHA(IT(J,IC),II(J,IC))
        IF(IE.GT.18) GO TO 285
        N=1
        DO 283 I=IS,IE
          NAM1(I)=NAM2(N)
283 N=N+1
          IF(INS(J,IC).GT.1) THEN
            IS=IE
            IE=IE+1
            NAM1(IS)=NUMB(IABS(INS(J,IC)))

```

```

      END IF
284 CONTINUE
      IF(CH(IC).EQ.0.0) GO TO 285
      IS=IE+1
      IF(IS.GT.17) GO TO 285
      ICHA=CH(IC)
      NAM1(IS)='- '
      IF(ICA.GT.0) NAM1(IS)='+'
      IS=IS+1
      NAM1(IS)=NUMB(IABS(ICA))
285 NAMED(IC)=NAMO
      IF(II(IHOH,IC).EQ.99) THEN
      NCOMP(IC)=NCOMP(IC)+1
      II(IHOH,IC)=51
      IT(IHOH,IC)=1
      INS(IHOH,IC)=IABS(INS(IHOH,IC))
      II(NCOMP(IC),IC)=50
      IT(NCOMP(IC),IC)=1
      INS(NCOMP(IC),IC)=-INS(IHOH,IC)
      END IF
      DO 2850 JJ=1,NCOMP(IC)
      ISIM(JJ)='- '
      IF(INS(JJ,IC).GT.0) ISIM(JJ)='+'
      IAB=IABS(INS(JJ,IC))
      IASC(JJ)=' '
      IF(IAB.NE.1) IASC(JJ)=HOL(IAB)
      ISIM(NCOMP(IC)+1)=' '
      IF(JJ.EQ.1) ISIM(JJ)=' '
2850 CONTINUE
      WRITE(6,17) IDYT(IC),CK(IC),(NAM1(JJ),JJ=2,18),
      1TYP(ISPEC),(ISIM(J),IASC(J),COMNAM(IT(J,IC),II(J,IC)),
      2J=1,NCOMP(IC))
      WRITE(9,17) IDYT(IC),CK(IC),(NAM1(JJ),JJ=2,18),
      1TYP(ISPEC),(ISIM(J),IASC(J),COMNAM(IT(J,IC),II(J,IC)),
      2J=1,NCOMP(IC))
      17 FORMAT(' ',A7,F7.2,1X,17A1,'(',A2,') --',6(A1,A2,1X,A8))
290 CONTINUE
300 CONTINUE
      WRITE(6,170) ICOUNT
      WRITE(9,170) ICOUNT
      170 FORMAT(/9X,I5,' SIMPLE SOLID OR AQUEOUS COMPLEXES TRANSF
      IERRED.'/)
      CARD #6
      READ(10,18)INREX
      18 FORMAT(9I5,A8)
      ISPEC=4
      ICOUNT=0
      DO 400 KK=1,INREX
      II(3,1000)=98
      IT(3,1000)=2
      II(4,1000)=50

```

```

      IT(4,1000)=1
CARO #7
      REAO(10,18) IRN,II(1,1000),II(2,1000),ITY,INS(3,1000),
1INS(4,1000),LOK,INS(1,1000),INS(2,1000),NAM3
      IHOH=3
      INS(3,1000)=-INS(3,1000)
      ISPEC=3
      IF(ITY.EQ.10) THEN
        IT(1,1000) = 2
        IT(2,1000) = 2
        INS(1,1000)=1
      END IF
      IF(ITY.LT.10.AND.ITY.GT.0) THEN
        IT(1,1000) = 1
        IT(2,1000) = 2
      END IF
      IF(ITY.GT.-10.AND.ITY.LT.0) THEN
        IT(1,1000) =1
        IT(2,1000) = 2
        ISPEC=5
      END IF
      IF(ITY.EQ.-10) THEN
        IT(1,1000)=1
        IT(2,1000)=1
        INS(1,1000)=1
      END IF
      LE=NMET
      DO 345 M=1,2
      DO 340 L=1,LE
        IF(IDSEL(IT(M,1000),L).EQ.II(M,1000)) GO TO 360
340 CONTINUE
345 LE=NLIQ
      GO TO 400
360 DO 365 J=1,3
365 IF(INS(J,1000).NE.0) GO TO 370
      GO TO 400
370 IF(ITY.GT.-10.AND.ITY.LT.0) THEN
      ICS=ICS-1
      IC=ICS
    ELSE
      ICA=ICA+1
      IC=ICA
    END IF
      ICOUNT=ICOUNT+1
      IF(ITY.GT.-10.AND.ITY.LT.0) THEN
        IDYT(IC)=MINTRA(IT(1,1000),II(1,1000))
        DO 373 KKK=5,3,-1
373 IDYY(KKK,IC)=IDYY(KKK-2,IC)
        IDYY(1,IC) =NUMB(MINCLA(1,II(2,1000)))
        IDYY(2,IC) =NUMB(MINCLA(2,II(2,1000)))
        IDYY(3,IC) = MINTRA(1,II(1,1000))

```

```

IDYY(6,IC)=NUMB(10)
IDYY(7,IC)=NUMB(1)
ELSE
IDYT(IC)=MINTRA(IT(1,1000),II(1,1000))
IDYT(1000)=MINTRA(IT(2,1000),II(2,1000))
IDYY(4,IC)=IDYY(1,1000)
IDYY(5,IC)=IDYY(2,1000)
IDYY(6,IC)=IDYY(3,1000)
IDYY(7,IC)=NUMB(1)
END IF
CK(IC)=0.1*LOK
GFWC(IC)=0.
NAMO='K
DO 310 I=2,9
310 NAM1(I)=NAM2(I-1)
DO 311 I=10,18
311 NAM1(I)=' '
NAMER(IC)=NAMO
NCOMP(IC)=4
IF(II(2,IC).EQ.99) THEN
IHOH=2
IT(2,1000)=2
END IF
DO 372 J=1,3
II(J,IC)=II(J,1000)
IT(J,IC)=IT(J,1000)
T(J,IC)=INS(J,1000)
372 INS(J,IC)=INS(J,1000)
ME=NCDMP(IC)
DO 380 M=1,ME
L=ME+1-M
IF(INS(L,IC).EQ.0) THEN
NCOMP(IC)=NCOMP(IC)-1
IF(L.LE.NCOMP(IC)) THEN
DO 375 N=L,NCOMP(IC)
T(N,IC)=T(N+1,IC)
INS(N,IC)=INS(N+1,IC)
IT(N,IC)=IT(N+1,IC)
II(N,IC)=II(N+1,IC)
375 IF(II(N,IC).EQ.50.OR.II(N,IC).EQ.99) IHOH=N
END IF
END IF
380 CONTINUE
GFWC(IC)=0.
DO 381 J=1,NCOMP(IC)
381 GFWC(IC)=GFWC(IC)+INS(J,IC)*GFW(IT(J,IC),II(J,IC))
IF(II(IHOH,IC).EQ.99) THEN
NCOMP(IC)=NCOMP(IC)+1
II(IHOH,IC)=51
IT(IHOH,IC)=1
INS(IHOH,IC)=IABS(INS(IHOH,IC))/2

```

```

      II(NCOMP(IC),IC)=50
      IT(NCOMP(IC),IC)=1
      INS(NCOMP(IC),IC)=-2*INS(IHOH,IC)
      END IF
      DO 3850 JJ=1,NCOMP(IC)
        ISIM(JJ)='- '
        IF(INS(JJ,IC).GT.0) ISIM(JJ)='+'
        IAB=IABS(INS(JJ,IC))
        IASC(JJ)=' '
        IF(IAB.NE.1) IASC(JJ)=HOL(IAB)
        ISIM(NCOMP(IC)+1) = ' '
        IF(JJ.EQ.1) ISIM(JJ)=' '
3850 CONTINUE
        WRITE(6,17) IDYT(IC),CK(IC),(NAM1(JJ),JJ=2,18),
        1TYP(ISPEC),(ISIM(J),IASC(J),COMNAM(IT(J,IC),II(J,IC)),
        2J=1,NCOMP(IC))
        WRITE(9,17) IDYT(IC),CK(IC),(NAM1(JJ),JJ=2,18),
        1TYP(ISPEC),(ISIM(J),IASC(J),COMNAM(IT(J,IC),II(J,IC)),
        2J=1,NCOMP(IC))
400 CONTINUE
        WRITE(6,190) ICOUNT
        WRITE(9,190) ICOUNT
190 FORMAT('/' ' ',9X,15,' REDOX REACTIONS TRANSFERRED.'/)
        READ(10,20)NMIX
        20 FORMAT(I4)
        ISPEC=3
        ICOUNT=0
        II(6,1000)=20
        II(7,1000)=12
        IT(6,1000)=1
        IT(7,1000)=2
        DO 500 KK=1,NMIX
ARD #9
        II(5,1000)=50
        IT(5,1000)=1
        READ(10,22) IRN,ITY,(II(J,1000),J=1,4),(INS(J,1000),J=1,5),
        1LOK,INS(6,1000),INS(7,1000),NAM3
        22 FORMAT(11I4,I6,2I4,A8)
        DO 410 J=1,6
410 IT(J,1000) = 1
        IF(ITY.EQ.0) THEN
          IT(3,1000) = 2
          IT(4,1000) = 2
        END IF
        IF(INS(5,1000).LT.0) THEN
          IT(5,1000) = 2
          II(5,1000) = 99
        END IF
        LE=NMET
        DO 445 M=1,4
        DO 440 L=1,LE

```

```

      IF(IDSEL(IT(M,1000),L).EQ.II(M,1000)) GO TO 460
440 CONTINUE
445 LE=NLIG
      GO TO 500
460 DO 465 J=1,4
465 IF(INS(J,1000).NE.0) GO TO 470
      GO TO 500
470 ICOUNT=ICOUNT+1
      ICS=ICS-1
      IC=ICS
      IDYT(IC)=MINTRA(1,II(1,1000))
      DO 473 KKK=5,3,-1
473 IDYY(KKK,IC)=IDYY(KKK-2,IC)
      IDYY(1,IC)=NUMB(MINCLA(1,II(2,1000)))
      IDYY(2,IC)=NUMB(MINCLA(2,II(2,1000)))
      IDYY(3,IC)=MINTRA(1,II(1,1000))
      IDYY(6,IC)=NUMB(10)
      IDYY(7,IC)=NUMB(1)
      CK(IC)=0.1*LOK
      DO 472 J=1,7
      II(J,IC)=II(J,1000)
      IT(J,IC)=IT(J,1000)
      T(J,IC)=INS(J,1000)
472 INS(J,IC)=INS(J,1000)
      NAMO='K'
      IE=2
      DO 484 J=1,NCOMP(IC)
      NAM3=COMSYM(IT(J,IC),II(J,IC))
      IS=IE
      IE=IE+NCHA(IT(J,IC),II(J,IC))
      IF(IE.GT.18) GO TO 485
      N=1
      DO 483 I=IS,IE
      NAM1(I)=NAM2(N)
      N=N+1
483 CONTINUE
      IF(INS(J,IC).GT.1) THEN
      IS=IE
      IE=IE+1
      NAM1(IS)=NUMB( IABS( INS(J,IC) ))
      END IF
484 CONTINUE
485 NAMED(IC)=NAMO
      NCOMP(IC)=7
      IHOH=5
      ME=NCOMP(IC)
      DO 480 M=1,ME
      L=ME+1-M
      IF(INS(L,IC).EQ.0) THEN
      NCOMP(IC)=NCOMP(IC)-1
      IF(L.LE.NCOMP(IC)) THEN

```

```

DO 475 N=L,NCOMP(IC)
T(N,IC)=T(N+1,IC)
INS(N,IC)=INS(N+1,IC)
IT(N,IC)=IT(N+1,IC)
II(N,IC)=II(N+1,IC)
475 IF(II(N,IC).EQ.50.OR.II(N,IC).EQ.99) IHOH=N
END IF
END IF
480 CONTINUE
GFWC(IC)=0.
DO 481 J=1,NCOMP(IC)
481 GFWC(IC)=GFWC(IC)+INS(J,IC)*GFW(IT(J,IC),II(J,IC))
IF(II(IHOH,IC).EQ.99) THEN
NCOMP(IC)=NCOMP(IC)+1
II(IHOH,IC)=51
IT(IHOH,IC)=1
INS(IHOH,IC)=IABS(INS(IHOH,IC))
II(NCOMP(IC),IC)=50
IT(NCOMP(IC),IC)=1
INS(NCOMP(IC),IC)=-INS(IHOH,IC)
END IF
DO 4850 JJ=1,NCOMP(IC)
ISIM(JJ)='- '
IF(INS(JJ,IC).GT.0) ISIM(JJ)='+ '
IAB=IABS(INS(JJ,IC))
IASC(JJ)=' '
IF(IAB.NE.1) IASC(JJ)=HOL(IAB)
ISIM(NCOMP(IC)+1) = ' '
IF(JJ.EQ.1) ISIM(JJ)=' '
4850 CONTINUE
WRITE(6,17) IDYT(IC),CK(IC),(NAMI(JJ),JJ=2,18),
1TYP(ISPEC),(ISIM(J),IASC(J),COMNAM(IT(J,IC),II(J,IC)),
2J=1,NCOMP(IC))
WRITE(9,17) IDYT(IC),CK(IC),(NAMI(JJ),JJ=2,18),
1TYP(ISPEC),(ISIM(J),IASC(J),COMNAM(IT(J,IC),II(J,IC)),
2J=1,NCOMP(IC))
500 CONTINUE
WRITE(6,230) ICOUNT
WRITE(9,230) ICOUNT
230 FORMAT(' ',9X,I5,' MIXED MINERALS TRANSFERRED'//)
ICB=1
ICE=ICA
ITOT=ICE
DO 600 M=1,2
WRITE(7,510) ITOT
510 FORMAT(/I5)
DO 550 IC=ICB,ICE
WRITE(7,171) IDYT(IC),NAMES(IC),CK(IC),CH(IC),GFWC(IC),NCOMP(IC),
2((T(J,IC),MINTRA(IT(J,IC),II(J,IC))),J=1,NCOMP(IC))
WRITE(7,172)
171 FORMAT(' ',A7,1X,A18,7X,F10.4,18X,F5.0,9X,F9.4/' ',6X,I1,3X,

```



```
      18(F7.3,1X,A3,3X))
172 FORMAT(/' DATA FROM GEOCHEM (SPOSITO & MATTIGOD)')
550 CONTINUE
      ICB=ICS
      ICE=999
      ITOT=1000-ICS
600 CONTINUE
      STOP
      END
```

DISTRIBUTION

No. of
Copies

No. of
Copies

OFFSITE

United Nuclear Industries

30 DOE Technical Information
Center

O. R. Pratt

G. Sposito
Department of Soils
University of California
Riverside
Riverside, CA 92502

33 Pacific Northwest Laboratory

D. W. Dragnich
J. L. Downs-Berg
M. J. Fayer
J. Fruchter
G. W. Gee
M. J. Graham
H. A. Haerer
J. N. Hartley
P. C. Hays
K. Krupka
J. R. Morrey (10)
S. Peterson
R. J. Serne
C. S. Simmons
J. A. Sottlemyre
G. P. Streile
R. Wildung
Technical Information (5)
Publishing Coordination (2)

ONSITE

Hanford Engineering Development
Laboratory

R. E. Lerch

7 Richland Operations Office

E. A. Bracken
M. Dayani
G. Drten
K. W. Bracken
M. W. Shupe
J. D. White
J. K. W. Wukelic

5 Rockwell Hanford Operations

R. E. Isaacson
J. F. Relyea
R. C. Routson
J. C. Sonnichsen
D. E. Wood