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MINTEQ--A COMPUTER PROGRAM FOR CALCULATING AQUEOUS GEOCHEMICAL EQUILIBRIA

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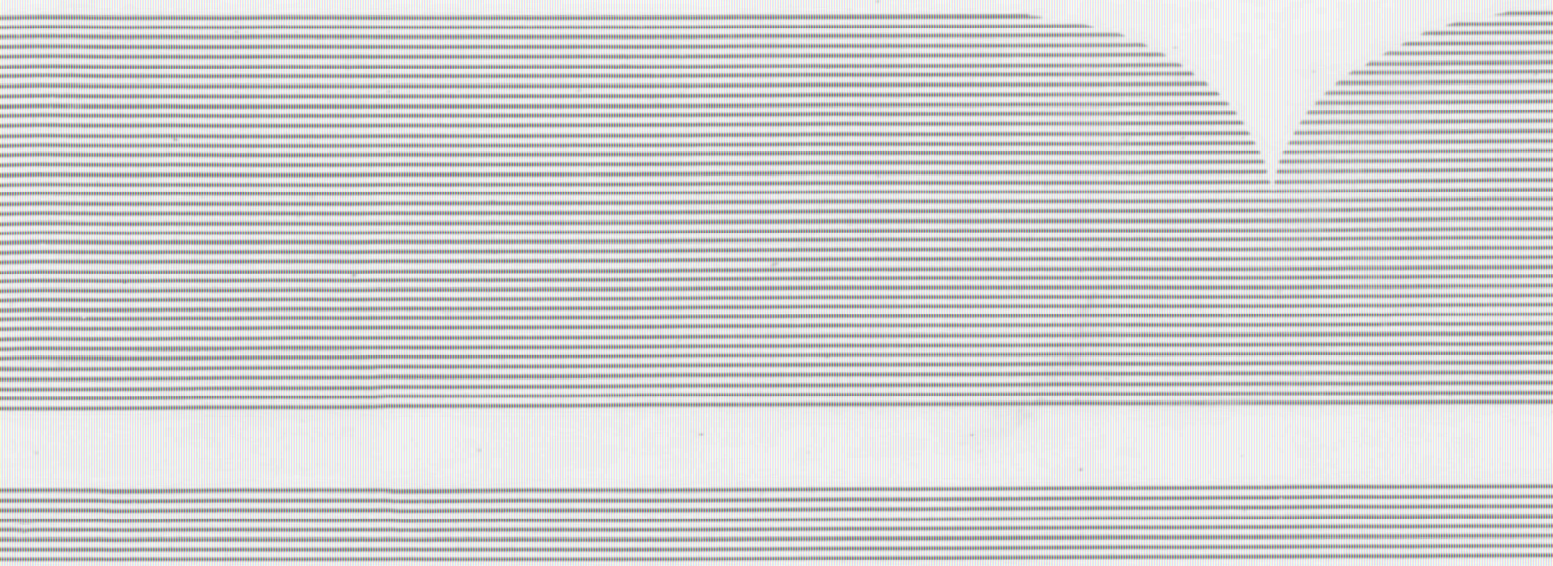
Richland, WA

Feb 84



U.S. DEPARTMENT OF COMMERCE
National Technical Information Service
NTIS®

EPA-600/3-84-032
February 1984

PB84-157148

MINTEQ--A COMPUTER PROGRAM FOR CALCULATING AQUEOUS GEOCHEMICAL EQUILIBRIA

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Contract No.
68-03-3089

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U.S. ENVIRONMENTAL PROTECTION AGENCY
ATHENS, GEORGIA 30613

TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)		
1. REPORT NO. EPA-600/3-84-032	2.	3. RECIPIENT'S ACCESSION NO. PB84 197148
4. TITLE AND SUBTITLE MINTEQ--A Computer Program for Calculating Aqueous Geochemical Equilibria		5. REPORT DATE February 1984 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) A.R. Felmy, D.C. Girvin, and E.A. Jenne		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Battelle Pacific Northwest Laboratories Richland WA 99352		10. PROGRAM ELEMENT NO. CCUL1A 11. CONTRACT/GRANT NO. 68-03-3089
12. SPONSORING AGENCY NAME AND ADDRESS U.S. Environmental Protection Agency--Athens GA Office of Research and Development Environmental Research Laboratory Athens GA 30613		13. TYPE OF REPORT AND PERIOD COVERED Final, 9/81-8/83 14. SPONSORING AGENCY CODE EPA/600/01
15. SUPPLEMENTARY NOTES		

16. ABSTRACT

MINTEQ is a computer program for computation of geochemical equilibria. MINTEQ was developed for incorporation into the Metals Exposure Analysis Modeling System (MEXAMS), a modeling system for the assessment of the fate and migration of selected priority pollutant metals in aquatic systems. MINTEQ combines the best features of two existing geochemical models MINEQL and WATEQ3. The mathematical structure was taken from MINEQL. The WATEQ3 features were added to this basic structure. The main features obtained from WATEQ3 are the well referenced thermodynamic data base, temperature correction of equilibrium constants using either the Van't Hoff relationship or analytical expressions for the equilibrium constants as a function of temperature and ionic strength correction using either the extended Debye-Huckel equation or the Davies equation. Six different adsorption algorithms: an "activity" Kd, an "activity" Langmuir equation, an "activity" Freundlich equation, an ion exchange algorithm, a constant capacitance surface complexation model, and the triple layer surface complexation model. In addition, a large number of user oriented features such as the ability to handle alkalinity inputs, an initial mass of solid, and different analytical inputs were incorporated.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED 20. SECURITY CLASS (This page) UNCLASSIFIED	21. NO. OF PAGES 98 22. PRICE

EPA Form 2220-1 (9-73)

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The MINTEQ computer code has been tested against other computer programs to verify its computational accuracy. Nevertheless, errors in the code are possible. The U.S. Environmental Protection Agency assumes no liability for either misuse of the model or for errors in the code. The user should perform verification checks of the code before using it.

FOREWORD

As environmental controls become more costly to implement and the penalties of judgment errors become more severe, environmental quality management requires more efficient analytical tools based on greater knowledge of the environmental phenomena to be managed. As part of this Laboratory's research on the occurrence, movement, transformation, impact, and control of environmental contaminants, the Technology Development and Applications Branch develops management or engineering tools to help pollution control officials achieve water quality goals.

Concern about environmental exposure to heavy metals has increased the need for techniques to predict the behavior of metals entering natural waters as a result of the manufacture, use, and disposal of commercial products. Previously, mathematical models have been developed to provide data on aquatic geochemistry, including metals speciation at equilibrium. The modeling technique described in this manual combines the best elements of two of these models and permits the user to examine what species of a metal are likely to be present under different chemical conditions in a water body. Because different species of a metal cause different biological effects, this model should help users better relate metals concentration and aquatic chemistry to observed effects.

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ABSTRACT

MINTEQ is a computer program for computation of geochemical equilibria. MINTEQ was developed for incorporation into the Metals Exposure Analysis Modeling System (MEXAMS) a modeling system for the assessment of the fate and migration of selected priority pollutant metals in aquatic systems.

MINTEQ combines the best features of two existing geochemical models, MINEQL and WATEQ3. The mathematical structure was taken from MINEQL. The WATEQ3 features were added to this basic structure. The main features obtained from WATEQ3 are the well referenced thermodynamic data base, temperature correction of equilibrium constants using either the Van't Hoff relationship or analytical expressions for the equilibrium constants as a function of temperature, and ionic strength correction using either the extended Debye-Huckel equation or the Davies equation. Six different adsorption algorithms were added: 1) an "activity" K_d, 2) an "activity" Langmuir equation, 3) an "activity" Freundlich equation, 4) an ion exchange algorithm, 5) a constant capacitance surface complexation model, and 6) the triple layer surface complexation model. In addition, a large number of user oriented features such as the ability to handle alkalinity inputs, an initial mass of solid, and different analytical input units were incorporated.

This report was submitted in fulfillment of Contract No. 68-03-3089 by Battelle, Pacific Northwest Laboratories under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from September 14, 1981 to August 31, 1983, and work was completed as of August 31, 1983.

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List of Abbreviations and Symbols

A - Davies equation A parameter

A_d - Debye-Huckel A parameter

a_i - Debye-Huckel ion size parameter

$a_{(i,j)}$ - stoichiometric coefficient of component j in species i

α_1 - constant used in computing log γ for neutral species

A^Z - ion of charge Z

B - conversion factor for coulombs of charge per square meter into moles of charge per liter

B_d - Debye-Huckel B parameter

b_i - Debye-Huckel parameter which allows for the decrease in solvent concentration in concentrated solutions

C - total dissolved concentration

C_i - concentration of species i

C_1 - capacitance between 'o' and 'b' planes in the triple layer model.

C_2 - capacitance between 'b' and 'd' planes in the triple layer model.

C' - capacitance of the double layer in the constant capacitance model.

C_s - concentration of solid in suspension

E_C - total excess equivalents of acid consumed by carbonate containing species over the stoichiometry of carbonate in each species.

E_N - noncarbonate alkalinity

ε - dielectric constant

ε_o - permittivity of free space.

F - Faraday's constant

f_i - carbonate alkalinity factor for species i

γ_i - activity coefficient for species i

I - ionic strength

$\underline{J}$ - Jacobian matrix

$^*K$ - equilibrium constant for adsorption reactions written in terms of the neutral sites (XOH) rather than the charged site (SO^-).

K_d - distribution coefficient

K_d^{act} - "activity" K_d

K_{ex} - equilibrium constant for ion exchange reactions

K_F - Freundlich constant

K_F^{act} - "activity" Freundlich constant

K_i - equilibrium constant for reaction i

K_L - Langmuir adsorption constant

K_L^{act} - "activity" Langmuir constant

K_r^o - equilibrium constant for reaction at 298.15°K

λ - F/RT

m - total number of aqueous species

M_i - mass of solid phase i

n - total number of components

$1/n$ - Freundlich constant

N_a - Avagadro's number

N_s - surface site density

ψ - electrostatic potential at a designated adsorption plane

q_i - noncarbonate alkalinity factor for species i

R - ideal gas constant

s - number of aqueous species plus number of solid phases

$\underline{S}$ - total mass adsorbed in molal units

$\overline{S}$ - free or unoccupied surface sites

S_A - specific surface area

σ - total charge at a designated adsorption plane

SI - saturation index

S_T - maximum quantity adsorbed in Langmuir isotherm

T_j - total analytical concentration of component j

X_j - activity of component j

Y_j - difference function (relaxed mass balance constraint) for component j

Z_i - charge on species i

Z(j,k) - Jacobian matrix of partial derivatives $\partial Y_j/\partial X_K$.

SECTION 1

INTRODUCTION

This report describes MINTEQ, a computer program for computation of geochemical equilibria. MINTEQ combines the best features of its precursors MINEQL (Westall et al. 1976) and WATEQ3 (Ball et al. 1981). Financial support for the development of MINTEQ has come from several sources. Development of the original WATEQ3 data base (Ball et al. 1981) was done by the United States Geological Survey (USGS). Development of the mathematical structure in MINEQL was supported under an earlier project funded by the Environmental Protection Agency (EPA). Incorporation of the WATEQ3 features and adsorption algorithms into the MINEQL mathematical structure was performed as part of EPA Contract No. 68-03-3089. The objective of this contract was to develop a predictive methodology for the assessment of the migration and fate of priority pollutant metals in aquatic systems. To meet this objective, MINTEQ was coupled with EXAMS, the Exposure Analysis Modeling System, through a user interactive program. The complete geochemical-transport modeling system is called MEXAMS, the Metals Exposure Analysis Modeling System. A separate report entitled MEXAMS - The Metals Exposure Analysis Modeling System provides guidelines for the use of MINTEQ. This report presents the chemical and mathematical concepts embodied in MINTEQ. Since the mathematical structure in MINTEQ is the same as in MINEQL, Westall's (1976) original notation will be used in this report.

MINTEQ provides a great deal of flexibility in the way the user defines the chemistry of the system being modeled. Although one does not need to

master the concepts presented in this report to effectively use MINTEQ, a basic understanding of the program will allow experienced users to solve a very broad range of chemical equilibrium problems. It is recommended that the user begin by reading the report entitled, MEXAMS - The Metals Exposure Analysis Modeling System.

This report is divided into three major sections. The first section describes the equations for computing equilibria with regard to aqueous speciation, adsorption and solid phases. The second section describes the numerical methods employed to solve the chemical equilbrium problem and the third section describes the thermochemical values which constitute the data base.

SECTION 2

CONCLUSIONS

The geochemical model MINTEQ is capable of calculating equilibrium aqueous speciation, adsorption, gas phase partitioning, solid phase saturation states and precipitation/dissolution. MINTEQ combines the best features of two geochemical precursors; MINEQL and WATEQ3. MINTEQ can solve a much broader range of chemical equilibrium problems than WATEQ3, is more user-oriented than MINEQL, contains a well referenced thermodynamic data base, and contains six different algorithms for calculating adsorption.

MINTEQ, like MINEQL, has a general mathematical approach to solving the chemical equilibrium problem. The general mathematical approach allows MINTEQ to solve a broad range of chemical equilibrium problems.

SECTION 3

RECOMMENDATIONS

The capabilities of MINTEQ would be extended if the thermodynamic data for aqueous species and solid phases of additional elements were added to the data base. Available data in the literature should be critically reviewed and the most accurate values incorporated into the MINTEQ data base. Furthermore, as more reliable thermodynamic data for important aqueous species and solid phases already in the model become available, they should be used to update the data base thereby increasing the overall competency of the model.

MINTEQ does not have a kinetic capability, it is only a thermodynamic equilibrium model. In many environmental systems the equilibrium assumption may not be valid. Kinetics of solid precipitation or dissolution may dominate the geochemistry of the system. Therefore, including kinetics of precipitation/dissolution and of oxidation-reduction would be an important extension.

The elementary ion association models used in MINTEQ for computing activity coefficients and aqueous speciation are not valid for high ionic strength solutions (i.e., ionic strengths equal to or greater than sea water). Higher order ion interaction models described by (Pitzer 1973; Pitzer and Mayorga 1973, Pitzer and Kim 1974) appear to be more reliable at high ionic strengths (Harvie and Weare 1980). Such models should be incorporated into MINTEQ for treating high ionic strength solutions where the ionic strength exceeds approximately 0.7 molal.

SECTION 4

MODEL THEORY

This section describes the formulation of the chemical equilibrium problem in MINTEQ. The equilibrium equations for aqueous speciation, adsorption and solid phases are described.

BASIC FORMULATIONS

The chemical equilibrium problem can be described by a set of mass balance equations, one for each component, and a set of mass action expressions, one for each species. The problem then reduces to solving the non-linear mass action expressions with the linear mass balance equations. This is commonly termed the equilibrium constant approach to the chemical equilibrium problem. There are other formulations of the chemical equilibrium problem that are also possible. As an example, at fixed temperature and pressure the chemical equilibrium problem can also be solved by a direct minimization of the Gibbs free energy or the Helmholtz free energy if the volume and temperature are specified [see Van Zeggeren and Storey (1970)].

The equilibrium constant approach is used in MINTEQ. A basic set of components is chosen and all mass action equations are written in terms of the components [Equation (1)],

$$\gamma_i C_i = K_i \sum_{j=1}^{n} X_j^{a(i,j)} \qquad (1)$$

where

γ_i = activity coefficient for species i

C_i = concentration of species i

K_i = equilibrium constant for reaction i

X_j = activity of component j

$a(i,j)$ = stoichiometric coefficient of component j in species i

n = number of components j.

The mass balance equations can then be written as a summation of the C_i terms (Westall et al. 1976),

$$T_j = \sum_{i=1}^{m} a(i,j)\, C_i \qquad (2)$$

where

T_j = total analytical concentration of component j

m = number of aqueous species.

Equation (2) can be reformulated to make the solution to the chemical equilibrium problem easier to solve by relaxing the mass balance constraint at intermediate iterations (Westall et al. 1976),

$$Y_j = \sum_{i=1}^{m} a(i,j)\, C_i - T_j \qquad (3)$$

where

Y_j = difference function for component j.

The solution is the set of all X_j terms such that all Y_j terms equal zero. The convergence criterion is described in Section 5.

The previous mathematical formulations are defined for systems without solid phases. Solid phases are handled in basically two ways. The first method treats the mass of each solid phase as an independent variable and thereby expands the basic set of unknowns (i.e., the X_j terms) to include a variable M_i for each solid phase. The mass balance equations can then be written,

$$Y_j = -T_j + \sum_{i=1}^{m} a(i,j)\, C_i - \sum_{i=m+1}^{s} a(i,j)\, M_i \qquad (4)$$

where s = number of solid phases plus number of aqueous species. The summation over the M_i terms then represents the mass of component j in solid phases.

This method is used in other geochemical models such as EQ3/EQ6 (Wolery 1979) and PHREEQE (Parkhurst et al. 1980).

The second method for handling solid phases is by what is termed a "transformation of basis." This is the method used in MINEQL and retained in MINTEQ. The transformation of basis reduces the number of independent variables which must be determined and also allows the treatment of different chemical reactions in a mathematically general way. This latter attribute allows MINEQL and MINTEQ to solve a wide range of chemical equilibrium problems. The mathematical description, given in Appendix One in Westall

et al. (1976), will not be reproduced here. Instead, the following example is presented to clarify the approach. Suppose there exists a four component system Ca^{2+}, H^+, CO_3^{2-} and H_2O, and the following reactions occur in aqueous solution.

$$Ca^{2+} + H_2O \rightleftarrows CaOH^+ + H^+ \quad , \qquad \log K_r^o = 12.6 \tag{5}$$

$$Ca^{2+} + H^+ + CO_3^{2-} \rightleftarrows CaHCO_3^+ \quad , \qquad \log K_r^o = 11.33 \tag{6}$$

$$Ca^{2+} + CO_3^{2-} \rightleftarrows CaCO_3^0 \quad , \qquad \log K_r^o = 3.15 \tag{7}$$

$$H_2O \rightleftarrows OH^- + H^+ \quad , \qquad \log K_r^o = -13.98 \tag{8}$$

where $\log K_r^o$ is the equilibrium constant for the stated reaction at 298.15°K.

If the solid calcite is now imposed as an equilibrium solid then one of the X_j terms in the calcite dissolution reaction, Equation (9), is eliminated computationally and all the reactions containing that component are rewritten with calcite [$CaCO_3(s)$] as a component (Westall et al. 1976),

$$Ca^{2+} + CO_3^{2-} \rightleftarrows CaCO_3(s) \quad , \quad \log K_r^o = 8.475 \tag{9}$$

As an example, suppose $X_{CO_3^{2-}}$ is eliminated then the reactions would be written as:

$$Ca^{2+} + H_2O \rightleftarrows CaOH^+ + H^+ \quad , \qquad \log K_r^o = 12.6 \tag{10}$$

$$CaCO_3(s) + H^+ \rightleftarrows CaHCO_3^+ \quad , \qquad \log K_r^o = 2.855 \qquad (11)$$

$$CaCO_3(s) \rightleftarrows CaCO_3^o \quad , \qquad \log K_r^o = -5.325 \qquad (12)$$

$$H_2O \rightleftarrows H^+ + OH^- \quad , \qquad \log K_r^o = -13.98 \qquad (13)$$

Since the activity of pure calcite is equal to one, the set of independent variables (X_j terms) is reduced by one. The transformation of basis is completely general and, for example, can be applied to species present at a fixed activity, gases at a fixed partial pressure, solids not present at unit activity, or redox reactions which establish a fixed relationship between components.

Activity Coefficients

The activity is related to the concentration by the activity coefficient (γ). MINTEQ corrects the equilibrium constants for ionic strength by a simple rearrangement of the mass action expressions, thus

$$C_i = \frac{(K_r^o)_i}{\gamma_i} \prod X_j^{a(i,j)} \quad . \qquad (14)$$

The resulting equilibrium constant is termed a "mixed constant" because the species formed in the reaction is in terms of concentration and the components are in terms of activities.

MINTEQ uses two alternate formulations for computing activity coefficients: 1) an extended Debye-Huckel equation which contains two

adjustable parameters (Truesdell and Jones 1974), and 2) the Davies equation (Davies 1962). The extended Debye-Huckel equation,

$$\log_{10} \gamma_i = \frac{-A_d Z_i^2 \sqrt{I}}{1 + B_d a_i \sqrt{I}} + b_i I \qquad (15)$$

where

A_d and B_d are the Debye-Huckel constants which depend upon the dielectric constant and temperature,

Z_i = charge on species i

a_i = ion size parameter

b_i = ion specific parameter which allows for the decrease in solvent concentration in concentrated solutions (Truesdell and Jones 1974)

I = ionic strength.

The A_d and B_d constants are computed as described in Truesdell and Jones (1974). The a_i and b_i parameters were taken directly from the WATEQ3 data base (Ball et al. 1981). The ionic strength is,

$$I = \frac{1}{2} \sum_{i=1}^{m} Z_i^2 C_i \quad . \qquad (16)$$

The a_i and b_i parameters are only available for the major ions and certain trace metals such as Cu and Mn. In cases where a_i and b_i are not available for the species formed in the reaction, MINTEQ defaults to the Davies equation for calculation of single ion activity coefficients,

$$\log \gamma_i = -A Z_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3\ I\right) \qquad (17)$$

Activity coefficients for neutral aqueous species are represented by (Helgeson 1969),

$$\log \gamma_i = \alpha_1 I.$$

MINTEQ sets α_1 to 0.1 for all neutral aqueous species.

The ion association models used in MINTEQ are not valid in high ionic strength solutions (brines). The ion-interaction models published by Pitzer (1973), Pitzer and Mayorga (1973) and Pitzer and Kim (1974) expand the basic Debye-Huckel equation by adding a series of ion interaction terms. These interaction terms are analogous to virial coefficients for non-ideal gases. Such ion interaction models should be added to MINTEQ before it can be accurately applied to high ionic strength solutions.

Activity of Water

The activity of water is calculated in MINTEQ by the relationship

$$X_{H_2O} = 1 - 0.017 \sum_{i=1}^{m} C_i \qquad (18)$$

where m is the total number of aqueous species. The expression is derived from Raoult's law and is valid only for dilute solutions. The constant 0.017 is

obtained from a plot of the activity of water versus number of solute ions (Garrells and Christ 1965).

Temperature Correction

The equilibrium constants in the MINTEQ data base are valid at 298°K or 25°C. MINTEQ corrects these equilibrium constants to temperatures other than 298°K by using either the Van't Hoff relationship or, whenever available, analytical expressions for log K_r^o as a function of temperature.

The analytical expressions for log K_r^o as a function of temperature are expressed as:

$$\log K_T = A + BT + C/T + D \log_{10}(T) + ET^2 + F/T^2 + G/\sqrt{T} \qquad (19)$$

where T is temperature in degrees Kelvin and A through G are empirically derived coefficients. When analytical expressions for log K with temperature are not available, the Van't Hoff relationship is used. The Van't Hoff relation (Lewis and Randall 1961) takes the form:

$$\log K_T = \log K_{Tr} - \frac{\Delta H_r^o}{2.3\ R} \left(\frac{1}{T} - \frac{1}{T_r}\right) \qquad (20)$$

where T_r is the reference temperature (298.15°K), ΔH_r^o is the enthalpy of reaction, T is the specified temperature and R is the ideal gas constant. Data for the enthalpy of reaction were taken from the WATEQ3 data base (Ball et al. 1981) and will be tabulated in Appendix A.

The Van't Hoff relation assumes that ΔH_r^o is independent of temperature. This assumption is not strictly valid so the Van't Hoff relationship may produce substantial errors at temperatures significantly different from 25°C. Unfortunately, data for $\Delta H_{r,298}^o$ or log K expressions as a function of temperatures are not available for all species in the MINTEQ data base. In such cases, the log $K_{r,298}$ is used at all temperatures. Because of these limitations, applications of MINTEQ should definitely be limited to temperatures less than 100°C.

Alkalinity Correction

Frequently, analytical data are available for total alkalinity but not total inorganic carbon. In such cases, MINTEQ can convert total alkalinity to total inorganic carbon. There are three important steps in the conversion.

The first step is to convert the input alkalinity expressed as carbonate to equivalents. This is simply done by multiplying the input alkalinity value by two since carbonate ion will consume two equivalents of acid per mole, Equation (21).

$$T'_{jj} = 2.0\ T_{CO_3^{2-}} \tag{21}$$

where jj represents CO_3^{2-}, $T_{CO_3^{2-}}$ is the titration alkalinity in molality, and T'_{jj} is the titration alkalinity in equivalents.

The next step is to subtract the difference between the equivalents of acid consumed by a carbonate containing species and the stoichiometry of carbonate in the species. As an example, the following species all would

consume two equivalents of acid per mole, CO_3^{2-}, $PbCO_3^0$, $MgCO_3^0$, and contain only one carbonate ion. This means each species consumes one excess equivalent of acid per mole. This difference must be subtracted from the total alkalinity in equivalents to obtain the correct total inorganic carbon. The number of equivalents of acid consumed per mole of a carbonate containing species is termed the carbonate alkalinity factor. The excess equivalents of acid consumed per mole of carbonate containing species is then,

$$E_C = \sum_{i=1}^{m} C_i \, [f_i - a(i,jj)] \tag{22}$$

where

E_C = excess equivalents of acid

f_i = carbonate alkalinity factor for species i

$a(i,jj)$ = molality of carbonate in species i.

The next step is to subtract the noncarbonate alkalinity. Noncarbonate alklinity results from such species as OH^-, $Al(OH)_4^-$, or HPO_4^{2-} which consume acid during the alkalinity titration but do not contain carbonate. The equivalents of acid consumed by nonarbonate containing species is,

$$E_N = \sum_{i=1}^{m} C_i \, q_i \tag{23}$$

where

E_N = equivalents of noncarbonate alkalinity

q_i = noncarbonate alkalinity factor for species i.

The noncarbonate alkalinity factor is the number of equivalents of H^+ consumed by a noncarbonate containing species if the solution were titrated to approximately pH 4.6.

The final step in computing total inorganic carbon is to add the mass of $H_2CO_3(aq)$. The overall conversion can be summarized,

$$T_{jj} = T'_{jj} - \sum_{i=1}^{m} C_i \left(f_i - a_{(i,jj)}\right) - \sum_{i=1}^{m} C_i q_i + C_{ii} \qquad (24)$$

where

T_{jj} = molality of inorganic carbon

f_i = carbonate alkalinity factor,

q_i = noncarbonate alkalinity factor

C_{ii} = mass of $H_2CO_3(aq)$.

ADSORPTION

MINTEQ contains six algorithms for treating adsorption: an "activity Kd," an "activity Langmuir" isotherm, an "activity Freundlich" isotherm, an ion exchange model and two surface complexation models, the constant capacitance surface complexation model (Huang and Stumm 1973; Schindler et al. 1976; Stumm et al. 1976), and the triple layer surface complexation model (Yates et al. 1974; Davis et al. 1978). This section presents a brief review of each model and an outline of the mathematical formalism used by each model. For further detail on the mathematical formalism of the constant capacitance model and the triple layer model see (Westall 1979a, 1979b; Westall 1980; Westall and Hohl 1980).

The K_d and the Langmuir and Freundlich Isotherms

In this section, the traditional concentration K_d and the Langmuir and Freundlich isotherms will be defined in terms of the total dissolved concentration of the adsorbate. These isotherms and the K_d will then be redefined in terms of the activity of the bare adsorbate ion and the limitations of this treatment of adsorption will be discussed.

The distribution coefficient K_d is defined as the ratio of the amount adsorbed to the amount remaining in solution. This can be conceptualized and written as any other reaction. An example for cadmium is,

$$\overline{S} + Cd_{total} \rightleftarrows \overline{SCd} \tag{25}$$

where $\overline{S}$ represents free or unoccupied surface sites, Cd_{total} = total dissolved cadmium remaining in solution, and $\overline{SCd}$ = adsorbed cadmium in molal units.

The mass action expression for Equation (25) is the common definition of the K_d,

$$\frac{\overline{SCd}}{Cd_{total}} = K_d \tag{26}$$

where the implicit assumption is made that $\overline{S}$ is in great excess with respect to Cd_{total} and the activity of $\overline{S}$ is set to one since with an assumed excess the variability of $\overline{S}$ is negligible.

Activity Langmuir Isotherm

The Langmuir equation can be formulated as,

$$S = \frac{K_L S_T C}{1 + K_L C} \tag{27}$$

where

S = the amount adsorbed in molality

K_L = the Langmuir adsorption constant

C = the total dissolved concentration in solution at equilibrium

S_T = the maximum quantity that can be adsorbed in molality.

Assuming that each adsorbing ion occupies only one adsorption site, then S_T is also equal to the total number of adsorption sites. The Langmuir isotherm has the advantage over the activity K_d in considering a mass balance on surface adsorption sites. The Langmuir equation as formulated in Equation (27) is simply a combination of a mass action expression for adsorption and a mass balance equation for surface sites,(a)

$$C + \overline{S} \rightleftarrows S \quad , \tag{28}$$

$$S_T = \overline{S} + S \quad , \tag{29}$$

(a) Note: In this formulation, competition between ions for surface sites can be readily included by formulating additional mass action expressions [Equation (28)] and then including the adsorbed species in the mass balance [Equation (29)].

where

$\overline{S}$ represents surface sites unoccupied by adsorbate.

If the adsorption data do not conform to a Langmuir plot, the Freundlich equation frequently provides a fit to the data. The Freundlich equation is formulated as,

$$S = K_F C^{1/n} \quad . \tag{30}$$

where K_F and $1/n$ are constants and C is the equilibrium total dissolved concentration. For cadmium adsorption then,

$$\overline{SCd} = K_F(Cd_{tot})^{1/n} \quad . \tag{31}$$

In this example, if the data conform to a Freundlich isotherm a plot of the logarithm of $\overline{SCd}$ versus the logarithm of the concentration of total Cd in solution at equilibrium (Cd_{tot}) would yield a straight line with slope $1/n$ and an intercept of log K_F. The Freundlich isotherm can then be thought of as an adsorption reaction where the stoichiometry of the adsorbing species equals $1/n$,

$$\overline{S} + 1/n\ (Cd_{tot}) \rightleftarrows \overline{SCd} \quad . \tag{32}$$

The mass action expression is then,

$$\frac{\overline{SCd}}{\overline{S}\,(Cd_{tot})^{1/n}} = K_F \quad . \tag{33}$$

There is no mass balance on surface sites and assuming an excess of sites with respect to the absorbate the activity of the free sites ($\overline{S}$) is set equal to one. There is one complication in use of the Freundlich isotherm in MINTEQ and that is in the stoichiometry of the adsorbing species. The stoichiometry of the adsorbing species in the mass action expression equals 1/n; however, the stoichiometry of the adsorbing species in the Cd mass balance equation equals one. Thus, to use the Freundlich isotherm in a geochemical model requires using separate stoichiometries for mass balance and mass action expressions.(a)

Equations (25) through (31) are written in terms of the total concentration of the adsorbate C_{tot} (or Cd_{tot}). Since C_{tot} involves all aqueous species, this formulation implicitly assumes that all species absorb with equal strength. There is abundant experimental evidence to support the hypothesis that only certain aqueous species react with the surface (Huang and Stumm 1973; Hohl and Stumm 1976; Davis and Leckie 1978). If C_{tot} is replaced with the activity of the aqueous species which dominates the adsorption reaction with the surface sites, say Cd^{2+} in the above examples, then the activity K_d is

$$K_d^{act} = \frac{\overline{SCd}}{\{Cd^{2+}\}} \quad . \tag{34}$$

(a) Only the UNIVAC and VAX versions of MINTEQ have this capability. Thus, the "activity" Freundlich isotherm cannot be used in the PDP 11/70 version unless $1/n \simeq 1.0$.

The activity Langmuir equation is

$$S = \overline{SCd} = \frac{K_L^{act} \, S_T \, \{Cd^{2+}\}}{1 + K_L^{act} \, \{Cd^{2+}\}} \tag{35}$$

and the activity Freundlich equation is,

$$S = K_F^{act} \, \{Cd^{2+}\}^{1/n} \tag{36}$$

where { } denote the activity of the adsorbing species, in this example Cd^{+2} ion, in bulk solution.

The dependency of the 'concentration' K_d and isotherms on adsorbate aqueous complexation and ionic strength effects has been removed by using the 'activity' representation in Equations (34) to (36). K_d^{act} and the activity isotherms are thus applicable over a wider range of natural water compositions than the standard concentration representations.

A number of limitations remain, however. These descriptions of adsorption do not consider: 1) a charge balance on surface sites and adsorbed species; 2) electrostatic interactions between the adsorbing ion and the charged surface; and 3) reaction of the solid with aqueous constituents other than the adsorbate ion, e.g., H^+ and major supporting electrolyte anions and cations. The effect of these factors varies with changes in solution composition. Thus failure to include these factors in describing adsorption limits the range of applicability of that description. The surface complexation models described below incorporate these effects and are thus more generally applicable.

To use "activity" Langmuir/Freundlich isotherms in MINTEQ the following procedure (see MEXAMS - The Metals Exposure Analysis Modeling Systems) should be followed. For the activity Langmuir isotherm, include a surface site (i.e., SOH1 or SOH2) as a component and specify a mass total (equal to S_T) for that component. Then enter the adsorption reaction as a type II inserted species with an equilibrium constant of K_L^{act}, and set the adsorption model (IADS) to one. For the activity Freundlich isotherm, include a surface site (i.e., SOH1 or SOH2) as a component and give it a type III designation. Include the adsorption reaction as a type II inserted species with an equilibrium constant of K_F^{act}, and set the adsorption model (IADS) to one. Finally, set the stoichiometry of the adsorbing component to 1/n and set the stoichiometry in the "B" matrix to 1.0.(a)

Ion Exchange

Ion exchange reactions are modeled in the same way as in the geochemical model PHREEQE (Parkhurst et al. 1980). The reader is referred to this document for details; only a brief summary will be presented here.

Ion exchange reactions involve the exchange of ions of like charge on the solid surface. As an example, K^+ ion could exchange for Na^+ ion on the surface of the exchanger S,

$$Na^+ + \overline{KS} \rightleftarrows K^+ + \overline{NaS} \qquad (37)$$

(a) Only the UNIVAC and VAX versions of MINTEQ have this capability. Thus, the "activity" Freundlich isotherm cannot be used in the PDP 11/70 version unless 1/n ≈ 1.0.

where $\overline{KS}$ represents exchanger bound potassium and $\overline{NaS}$ represents exchanger bound sodium.

MINTEQ, like PHREEQE, can model ion exchange reactions by maintaining a fixed activity ratio of the exchangeable species. Equations (38) and (39) present an example,

$$\frac{\{K^+\}\ \{\overline{NaS}\}}{\{Na^+\}\ \{\overline{KS}\}} = K_{ex} \tag{38}$$

$$K'_{ex} = K_{ex}\ \frac{\{\overline{KS}\}}{\{\overline{NaS}\}} = \frac{\{K^+\}}{\{Na^+\}} \quad . \tag{39}$$

The use of K'_{ex} assumes an infinite reservoir of exchanger at a constant solid phase composition [i.e., $\overline{KS}/\overline{NaS}$ remains fixed in Equation (39)]. This is equivalent to assuming that the concentration of exchangeable species on the surface is much greater than the concentration in solution. Therefore, even if the concentration of the exchangeable species in solution is changed, the activity ratio of the species in solution will re-adjust to the original fixed value due to the large reservoir of exchangeable species on the solid.

Surface Complexation Models

The "activity" Kd, "activity" Langmuir, "activity" Freundlich and ion exchange treatments described above all ignore electrostatic effects due to surface charge and the effect of solution chemistry on the solid. An electrical charge frequently exists on the surface of solid particles and creates an electrostatic potential which extends into solution. This

electrostatic potential can significantly influence the adsorption of charged species. In addition, pH and the concentration and composition of the electrolyte alter the distribution and availability of the surface hydroxyl groups which act as adsorption sites for the trace constituents, e.g., Cd. The surface complexation models described below include treatment of these effects.

Both of the surface complexation models of adsorption in MINTEQ, the constant capacitance model and the triple layer model, were developed for and have been primarily applied to crystalline oxides (Davis et al. 1978). These models have also been applied with considerable success to amorphous iron oxyhydroxides (Davis and Leckie 1978, Benjamin and Leckie 1981) and to clays (James and Parks 1982). Each model treats the oxide surface in contact with water as an array of hydroxyl groups designated as XOH, where X represent structural Si, Fe, Ti, Al, Mn or other atoms at the solid liquid interface. (Figures 1 and 2). These hydroxyl groups or adsorption "sites" can be treated as ligands which: 1) have specific acid/base characteristics, and 2) form complexes with supporting electrolyte ions, metal ions or other ion-pairs in solution. Adsorption reactions, i.e., the coordination of these solute ions with surface hydroxyl groups, are treated by analogy with complexaton in bulk solution. Thus, for an assumed stoichiometry of reaction, an association (adsorption) constant can be used to describe the adsorption reaction. The description which follows for surface sites, XOH, can be generalized to include additional surface sites, SOH or TOH, whose acid/base or cation/anion coordination behavior differ from those of XOH.

Examples of surface equilibria for oxides are typically written for protonation and deprotonation reactions as

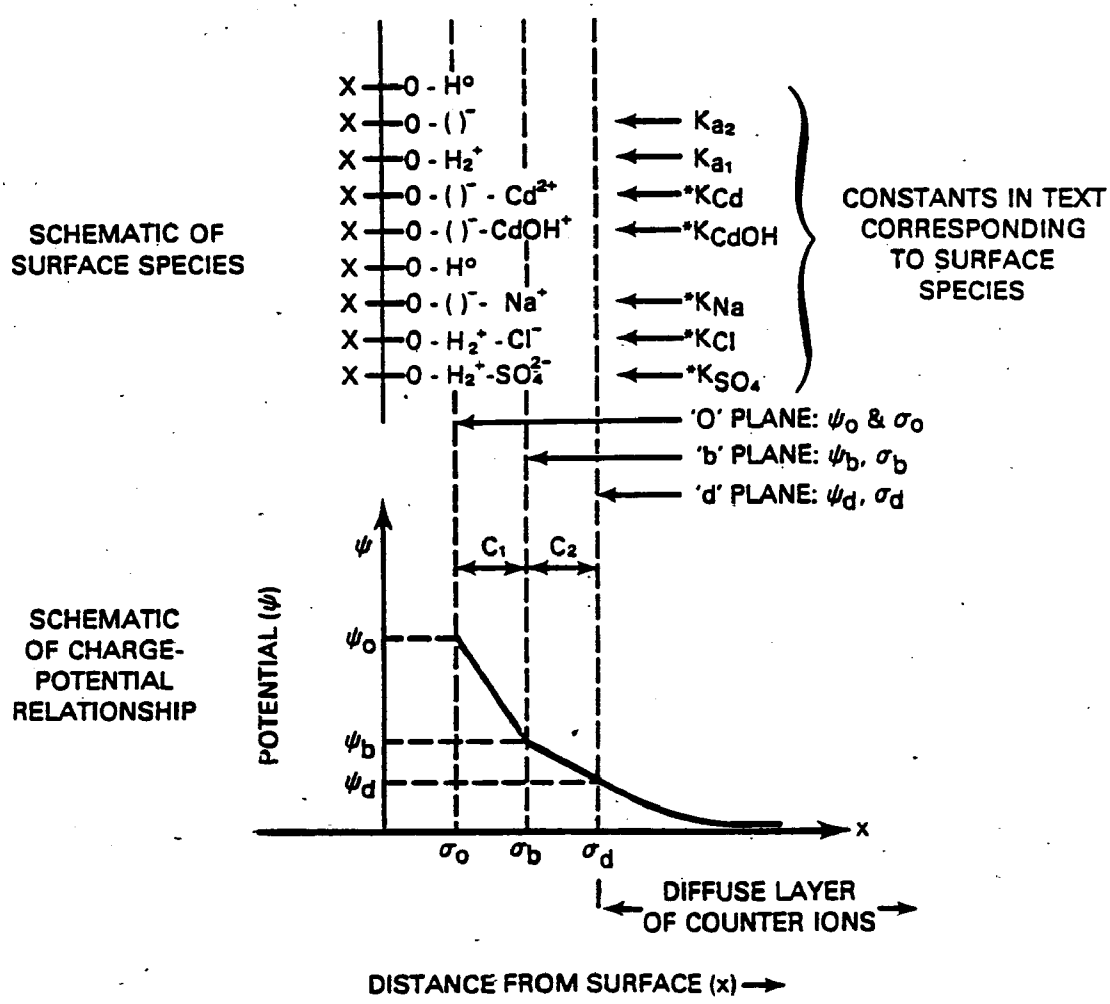


FIGURE 1. Schematic Representation of Surface Species and Surface Charge-Potential Relationship for the Triple Layer Model. Brackets in the 'zero' plane indicate deprotonated surface sites.

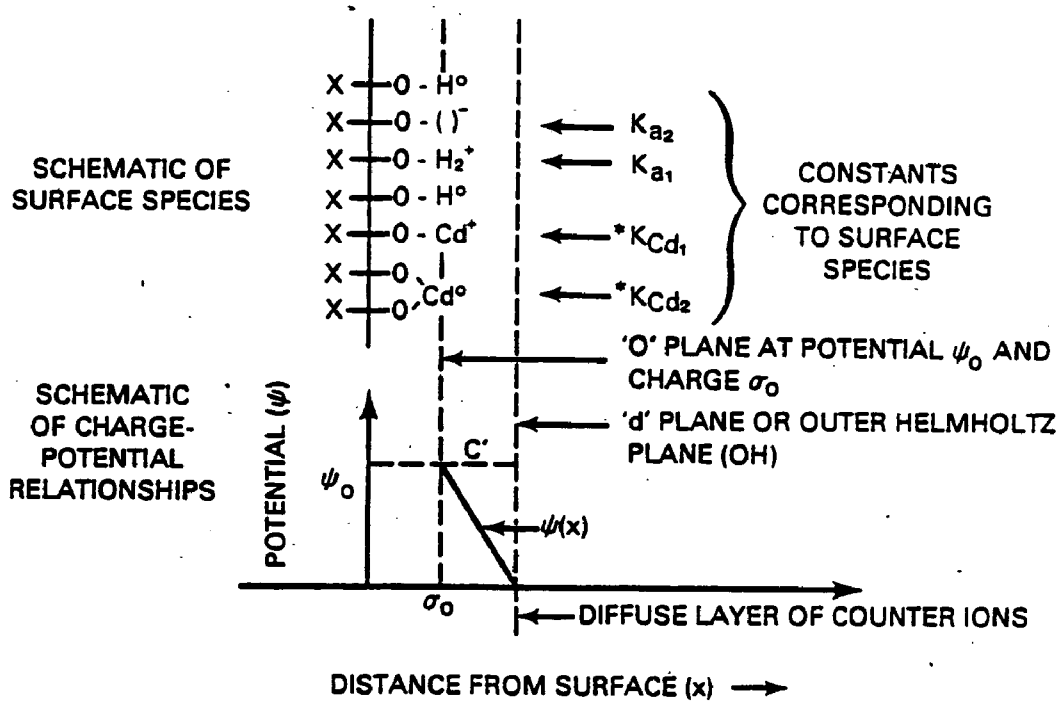


FIGURE 2. Schematic Representation of Surface Species and Surface Charge-Potential Relationship for the Constant Capacitance Layer Model. Brackets in the 'zero' plane indicate deprotonated surface sites.

$$XOH + H_s^+ \rightleftarrows XOH_2^+, \; K_{a_1} = \frac{\{XOH_2^+\}}{\{XOH_2\}\ \{H^+\}_s} \tag{40}$$

$$XOH = XO^- + H_s^+, \; K_{a_2} = \frac{\{XO^-\}\ \{H^+\}_s}{\{XOH\}} \tag{41}$$

respectively, and for adsorption of a divalent cation, M^{2+}, as

$$XOH + M_s^{2+} \rightleftarrows (XO^- - M^{2+})^+ + H_s^+, \; {}^*K_M = \frac{\{XO^- - M^{2+}\}\ \{H^+\}_s}{\{XOH\}\ \{M^{2+}\}_s} \tag{42}$$

where K_{a_1}, K_{a_2}, are the first and second surface acidity constants, ${}^*K_M$ is an adsorption constant, { } represents the activity of surface species XOH, XO^-, XOH_2^+, and $(XO^- - M^{2+})$ in moles per liter and $\{\ \}_s$ represents the activity of an ion in the electrical double layer. The subscript "s" (H_s^+, M_s^{2+}) indicates that the H^+ and M^{2+} ions are in the electric double layer rather than in the bulk solution. The asterisk on the adsorption constant is a convention which indicates that the adsorption reaction is written in terms of the neutral site XOH rather than a deprotonated site XO^-.

A fundamental difference between adsorption reactions at the solid-solution interface and aqueous coordination reactions in bulk solution is that a variable electrostatic interaction energy exists between the charged adsorbing ion and the surface charge on the solid (Figures 1 and 2). A difference in chemical potential of the charged ion develops near the surface due to the electrostatic potential, ψ, produced by the surface charge, σ. Because of these nonideal interactions, the activities of ions approaching the

surface are modified by the electrical work necessary to bring them from the bulk solution to a specific adsorption plane within the electric double layer. The activities near the surface are related to the activities in bulk solution by an exponential Boltzman factor which is a function of potential. For any ion A^Z, this relation is,

$$\{A^Z\}_s = \{A^Z\}_{aq} \exp(-ZF\psi/RT)$$

where 's' and 'aq' refer to activities in the electrostatic double layer and in bulk solution, respectively, Z is the charge on ion A, F is Faraday's constant, R is the ideal gas constant in joules, T is the absolute temperature, and ψ is the electrostatic potential on the surface or at the designated adsorption plane within the double layer.

In MINTEQ, the activity coefficients for ions are calculated using the Debye-Huckel or Davies equations. Since no adequate theory exists for calculation of the activity coefficients for surface species, the activity coefficients in MINTEQ for all surface species are set equal to one and the activities, { }, of all surface species are replaced by concentrations, [ ].

The major differences betwen the constant capacitance and the triple layer models, as normally formulated, are: 1) the set of surface species considered (e.g., whether surface-electrolyte species are considered), and 2) the description of the electric double layer, i.e., the definition and assignment of ions to "mean" planes of adsorption within the double layer and the mathematical form of the surface charge-potential relation, $\sigma = f(\psi)$.

The mass action and mass balance equations in both the constant capacitance and the triple layer models are similar. For mathematical simplicity in MINTEQ, the Boltzman factor in the mass action equations for surface species, e.g.,

$$[XOH_2^+] = [XOH] \{H\}_{aq} \exp(-F\psi/RT) \quad K_{a_1} ,$$

is treated as though it is just another chemical component. This new component is the coulombic or electrostatic component, $X(\sigma)$. From Equation (3) above, the mass balance equation used in MINTEQ to check convergence of each electrostatic component is,

$$Y(\sigma) = \sum_{i}^{m} a(i,\sigma)\, C_i - T(\sigma)$$

The electrostatic components are unique in that there is no measurable analytical value for total surface charge, $T(\sigma)$. A value for $T(\sigma)$ is calculated using the mathematical expression relating surface charge to potential, $\sigma = f(\psi)$, where $f(\psi)$ depends on the model of the electrical double layer used. Thus, $T(\sigma) = f(\psi)\, B$, where the factor B converts coulombs of charge per square meter into moles of charge per liter.

With this brief introduction, the constant capacitance and triple layer models will be described below for the case where adsorption occurs from a

solution containing Na^+, Cl^- and SO_4^{2-} as the major electrolyte ions and Cd^{2+} ion as the dilute adsorbate. Surface ligands consist of a single amphoteric surface site, XOH.

Constant Capacitance Model

With this model, all specifically adsorbed ions (H^+, OH^-, and Cd^{2+}) are considered to be located in the surface 'o' plane, contribute to the charge σ_o, and are subject to a potential, ψ_o, as shown in Figure 1. Ions which are not specifically adsorbed are excluded from the double layer and are assumed to be located in the diffuse layer. The dominant contribution to σ_o is from the potential determining ions H^+ and OH^-. It is assumed that the ions of the background electrolyte, Na^+, Cl^-, and SO_4^{2-} do not coordinate with the surface sites.

In the double layer, the surface charge-potential relationship used is the simple linear expression, $\sigma_o = C^1\psi_o$, where the capacitance of the double layer, C^1, is assumed to be constant. The surface hydrolysis and adsorption reactions together with the acidity and adsorption constants for the surface species as shown in Figure 1 are,

$$XOH + H_s^+ \rightleftarrows XOH_2^+ \qquad K_{a_1} = \frac{[XOH_2^+]}{[XOH]\{H^+\}} \exp(\lambda\psi) \qquad (43)$$

$$XOH = XO^- + H_s^+ \qquad K_{a_2} = \frac{[XO^-]\{H^+\}}{[XOH]} \exp(-\lambda\psi_o) \qquad (44)$$

$$XOH + Cd_s^{2+} = (XO^- - Cd^{2+})^+ + H_s^+ \qquad {}^*K_{Cd_1} = \frac{[XO^- - Cd^{2+}]\{H^+\}}{[XOH]\{Cd^{2+}\}} \exp(\lambda\psi_o) \qquad (45)$$

$$(XOH)_2 + Cd_s^{2+} = ((XO^-)_2 - Cd^{2+})^0 + 2H_s^+, \quad {}^*K_{Cd_2} = \frac{[(XO^-)_2 - Cd^{2+}]\{H^+\}^2}{[(XOH)_2]\{Cd^{2+}\}} \qquad (46)$$

where $\lambda = F/RT$, $\{\ \}_{aq} = \{\ \}$ represents the activity in the bulk solution, $(XOH)_2$ and $(XO^-)_2$ represents two adjacent XOH and XO^- sites, respectively, acting as a single surface ligand,(a) and [ ] represents the concentration of surface species.

In MINTEQ, the surface sites, XOH, are treated as a chemical component, X(XOH). The mass balance equation for surface sites is,

$$Y(XOH) = \sum (\text{all surface sites}) - T(XOH) \qquad (47)$$

where

$$\sum \left(\text{all}_{\text{surface sites}}\right) = [XOH] + [XO^-] + [XOH_2^+] + [XO^- \text{-}Cd^{2+}] + 2[(XO^-)_2 \text{-}Cd^{2+}]$$

is the sum of the concentrations of all of the surface sites as calculated from the mass action equations and T(XOH) is the analytical total concentration of surface sites in moles of sites per liter,

$$T(XOH) = N_S\ S_A\ C_S/N_A$$

Here, N_A is Avagadro's number, S_A is the specific surface area of the solid (m^2/g), C_S is the concentration of the solid in suspension (g/ℓ), and N_S is the analytically determined surface site density (number of sites/m^2).

In the case of the coulombic or electrostatic component, $X(\sigma_0)$, the equation describing the surface charge balance is,

(a) The UNIVAC and VAX versions, but not the PDP/11-70 version, of MINTEQ have the capability to model reactions with different stoichiometries in the mass action and mass balance equations.

$$Y(\sigma_o) = \sum \text{(charged species in 'o')} - T(\sigma_o) \qquad (48)$$

where the total surface charge (i.e., the net concentration of charged sites in the 'o' plane in moles/ℓ) calculated from the mass action equations is,

$$\sum \left(\begin{matrix}\text{charged} \\ \text{species in 'o'}\end{matrix}\right) = [XOH_2^+] - [XO^-] + [XO^- - Cd^{2+}].$$

Since no analytical value of $T(\sigma_o)$ is available, the model dependent charge-potential relation is used to define $T(\sigma_o)$ in moles of charge per liter as,

$$T(\sigma_o) = \sigma_o \; B = C \; \psi_o \; B \; ,$$

where $B = (S_A \; C_s)/F$. By analogy with all other components in the formulation of the equilibriuim problem, the sum of charged surface species in Equation (48), calculated from the mass action equations, must equal the electrostatically calculated charge $T(\sigma_o)$, Equation (49), when the problem is solved.

When using the constant capacitance model, the coulombic component $X(\sigma_o)$ (PSIO in the MINTEQ code), must be designated as Type VI (see users manual MEXAMS - The Metals Exposure Analysis Modeling Systems) since it has no mass in aqueous solution. The input to MINTEQ requires: 1) an initial guess for the value of the electrostatic component, e.g., for $\psi > 0$, let $\log [X(\sigma_o)] = -1.0$; 2) the same value for the capacitance (C^1) for a given ionic strength and electrolyte as that used to derive the adsorption constants; 3) analytical values for the surface site density (N_S), the specific surface area (S_A) and the concentration of the solid in suspension (C_s); and 4) acidity and adsorption constants for surface hydrolysis and complexation reactions, determined experimentally for a given ionic strength and electrolyte composition.

For this model, in which coordination of the background electrolyte ions with surface sites is ignored, both the capacitance, C^1, and the adsorption constants depend on the type and concentration of the background electrolyte, and are applicable only at the ionic strength and for the specific electrolyte for which the adsorption data were obtained. However, for applications where the background electrolyte is fixed and the concentration of strongly coordinated electrolyte ions remain unchanged, use of the constant capacitance model requires less experimental characterization than is required by the triple layer model (described below). If, however conditions include variable concentrations of strongly coordinating electrolyte ions, use of the constant capacitance model would require new adsorption constants, derived from experimental adsorption data, for each set of conditions, reminicent of the early Kd approach previously described. For these conditions, the experimental characterization required by the triple layer is less extensive than that required by the constant capacitance model. This is a direct consequence of the triple layer model's inclusion of known electrolyte/surface reactions.

Triple Layer Model

This model treats the solid solution interface as being composed of two constant capacitance layers bounded by a diffuse layer (Figure 2). Specifically, adsorbed H^+ and OH^- ions are located in the surface 'o' plane, contribute to the surface charge ψ_0, and experience an electrostatic potential, σ_0. All other specifically adsorbed ions, including major electrolyte ions, are located in the 'b' or inner Helmholtz plane and are bound pairwise to oppositely charged surface sites by either a specific chemical or an electrostatic energy or both. These ions contribute to the charge, σ_b, and are subject to an electrostatic potential, ψ_b. The outer Helmholtz plane or the

'd' plane is the inner boundary of the diffuse region of nonspecifically bound counter ions. From theoretical considerations of monovalent electrolytes, the potential, ψ_d, in the 'd' plane is related to the total charge in the diffuse region, σ_d, by the Gouy-Chapman equation

$$\sigma_d = -(\varepsilon\varepsilon_o RIT)^{1/2} \sinh (F\psi_d/2RT) \quad ,$$

where ε and I are respectively, the dielectric constant and the ionic strength of the solution and ε_o is the permittivity of free space [8.85×10^{-12} $(\text{coulombs})^2/\text{joule-meter}$]. As an approximation in MINTEQ, the Gouy-Chapmay equation is also used for nonsymmetric electrolytes (charge on cation not equal to charge on anion).

Regions of constant capacitance, C_1 and C_2, separate the 'o' and 'b' planes and the 'b' and 'd' planes, respectively. In the context of this model of the solid-solution interface, the surface charge-potential relations, based on electrostatic considerations, are:

in the surface or 'o' plane,

$$\sigma_o = C_1(\psi_o - \psi_b) \tag{50}$$

in the 'b' plane,

$$\sigma_b = C_1(\psi_b - \psi_o) + C_2(\psi_b - \psi_d) \tag{51}$$

and in the 'd' plane

$$\sigma_d = C_2(\psi_d - \psi_b) \quad . \tag{52}$$

The expressions for the surface hydrolysis reactions are identical to those given in Equations (43) and (44) for the constant capacitance model. The adsorption reactions and constants for the other surface species shown in Figure 2 are,

$$XOH + Na_s^+ = (XO^- - Na^+)^0 + H_s^+$$

$$^*K_{Na} = \frac{[XO^- - Na^+]\ \{H^+\}}{[XOH]\ \{Na^+\}} \exp\ (-\lambda(\psi_o - \psi_b))$$

$$XOH + Cl_s^- + H_s^+ = (XOH_2^+ - Cl^-)^0,$$

$$^*K_{Cl} = \frac{[XOH_2^+ - Cl^-]}{[XOH]\ \{CL^-\}\ \{H^+\}} \exp\ (\lambda(\psi_o - \psi_b))$$

$$XOH + Cd_s^{2+} = (XO^- - Cd^{2+})^+ + H_s^+,$$

$$^*K_{Cd} = \frac{[XO^- - Cd^{2+}]\ \{H^+\}}{[XOH]\ \{Cd^{2+}\}} \exp\ (-\lambda(\psi_o - 2\psi_b))$$

$$XOH + Cd_s^{2+} + H_2O = (XO^- - CdOH^+)^0 + 2H_s^+,$$

$$^*K_{CdOH} = \frac{[XO^- - CdOH^+]\ \{H^+\}^2}{[XOH]\ \{Cd^{2+}\}\{H_2O\}} \exp(-\lambda(\psi_o - \psi_b))$$

$$XOH + (SO_4^{2-})_s + H_s^+ = (XOH_2^+ - SO_4^{2-})^-,$$

$$^*K_{SO_4} = \frac{[XOH_2^+ - SO_4^{2-}]}{[XOH]\ \{SO_4^{2-}\}\ \{H^+\}} \exp\ (\lambda(\psi_o - 2\psi_b))$$

Here, three electrostatic components, $X(\sigma_o)$, $X(\sigma_b)$, and $X(\sigma_d)$, in addition to the surface site component, X(XOH), are added to the normal set of chemical components describing the aqueous equilibrium problem. Within the content of the triple layer model, no bidentate surface species $[(XO^-)_2 - Cd^{2+}]$ have been considered. The set of surface species shown in Figure 2, although not necessarily unique, usually provides an adequate fit of experimental adsorption data for mono- and divalent cations and anions.

As a consequence of the inclusion of surface-electrolyte coordination reactions and the multiple layer structure of the interface, the acidity and adsorption constants defined for the triple layer model are 'intrinsic' constants, i.e., they are applicable over a wide range of pH, electrolyte and dilute adsorbate (Cd^{2+}) concentrations. However, experimental data over a wide range of chemical conditions is needed to determine these intrinsic constants (Davis et al. 1978; James et al. 1978; Balistrieri and Murray, 1979, 1981, 1982).

The mass balance equation for the surface site component, X(XOH), is identical to Equation (47) except that,

$$\sum\left(\begin{matrix}\text{all}\\ \text{surface sites}\end{matrix}\right) = [XOH] + [XOH_2^+] + [XO^-] + [XOH_2^+ - Cl^-] + [XO^- - Na^+]$$
$$+ [XO^- - Cd^{2+}] + [XO^- - CdOH^+] + [XOH_2^+ - SO_4^{2-}]$$

For the electrostatic components $X(\sigma_0)$ and $X(\sigma_b)$, the surface charge balance equations are, respectively,

$$Y(\sigma_0) = \sum \text{(charged species in 'o')} - T(\sigma_0)$$

$$Y(\sigma_b) = \sum \text{(charged species in 'b')} - T(\sigma_b) \quad ,$$

where

$$\sum \left(\begin{matrix}\text{charged} \\ \text{species in 'o'}\end{matrix}\right) = [XOH_2^+] + [XOH_2^+ \text{-}Cl^-] - [XO^-] - [XO^- \text{-}Na^+]$$
$$- [XO^- \text{-}Cd^{2+}] - [XO^- \text{-}CdOH^+] + [XOH_2^+ \text{-}SO_4^{2-}]$$

and

$$\sum \left(\begin{matrix}\text{charged} \\ \text{species in 'b'}\end{matrix}\right) = [XO^- \text{-}Na^+] - [XOH_2^+ \text{-}Cl^-] + 2[XO^- \text{-}Cd^{2+}]$$
$$+ [XO^- \text{-}CdOH^+] - 2[XOH_2^+ \text{-}SO_4^{2-}]$$

The expressions for the T terms in these charge balance equations are $T(\sigma_0) = \sigma_0 B$, and $T(\sigma_b) = \sigma_b B$, where B is a constant defined on Page 31 and σ_0 and σ_b are defined by the Equations (50) and (51). The summations of the charged surface species in the 'o' and 'b' planes, calculated from mass action equations, must equal the electrostatically calculated charge, $T(\sigma_0)$, and $T(\sigma_b)$, respectively, when the equilibrium problem is solved. Since in this model there are no surface species assigned to the 'd' plane, the net charge in the diffuse layer, given by the Gouy-Chapman equation, must balance the electrostatic charge on the 'd' plane given by Equation (52). Thus, the charge balance equation for the electrostatic component, $X(\sigma_d)$, is,

$$Y(\sigma_d) = ((-8\epsilon\epsilon_o RTI)^{1/2} \sinh(F\psi_d/2RT)) - (C_2(\psi_d - \psi_b)).$$

As equilibrium is approached during the numerical solution of the problem, $Y(\sigma_d)$ and the values of Y for all components approach zero.

When using the MINTEQ code to solve problems with the triple layer model, an initial guess is supplied as input to the code for the electrostatic components $X(\sigma_o)$, $X(\sigma_b)$, and $X(\sigma_d)$ (PSIO, PSIB, and PSID, respectively in MINTEQ). These components are given a Type VI designation (see the users manual MEXAMS - The Metals Exposure Analysis Modeling System) because they have no mass in aqueous solution. Other input data is similar to that required for the constant capacitance model except that a second capacitance, C_2, is needed. It should be noted that the K values defined for the triple layer model are not conditional constants, as is the case for the constant capacitance model, but are invariant with respect to adsorbate concentration below a surface loading threshold which depends upon the adsorbate/surface combination (Benjamin and Leckie 1981) and within the experimental range of pH and ionic strength for which they were determined.

SOLID PHASES

Saturated Indices

The saturation indices are used to describe the apparent closeness to equilibrium of a solid phase and the aqueous solution with which it is in contact. For solid dissolution reactions, saturation indices can be formulated in the following straight-forward manner:

$$SI_i = \log (K_r)_i - \log \left(\sum_{j=1}^{n} X_j^{a(i,j)} \right) \quad (53)$$

where SI_i is the saturation index for species (solid) i.

The thermodynamic data base in MINTEQ was taken from WATEQ3 (Ball et al. 1981). All reactions involving solid phases were written as dissolution reactions in WATEQ3. The mathematical formalism in MINTEQ requires all reactions to be written as formation reactions. Therefore, all equilibrium constants for solid phases in WATEQ3 were multiplied by minus one to convert the log K_r values to association reactions. This also resulted in Equation (53) being rewritten as

$$SI_i = \log (K_r)_i + \log \left[\sum_{j=1}^{n} X_j^{a(i,j)} \right] \quad (54)$$

The Stable Phase Assemblage

This section describes how MINTEQ selects the thermodynamically stable solids from the array of all considered solids (i.e., Type V solids) described in MEXAMS - The Metals Exposure Analysis Modeling System. The procedure described here has been modified only slightly from the original MINEQL model. Equation (55) is the mathematical relation which details whether a solid will be present (i.e., in equilibrium),

$$\log (K_r)_i + \log \sum_{j=1}^{n} X_j^{a(i,j)} < 0.0 \quad . \quad (55)$$

This inequality simply means that at equilibrium all solids being considered must either be in equilibrium or undersaturated. To solve this inequality, MINTEQ first ranks all considered solids by their tendency to precipitate. The tendency to precipitate is estimated by dividing the saturation index by the number of ions in the solid formation reaction. Dividing by the number of ions is necessary because the saturation indices are a function of the manner in which the chemical reaction is written. In the example below, doubling the reaction stoichiometry doubles the saturation index. If the activities of Ca^{2+} and SO_4^{2-} are 1×10^{-3},

$$Ca^{2+} + SO_4^{2-} \rightleftarrows CaSO_4(s) \quad , \log K_r = 4.0 \; , \; SI = -2.0 \tag{56}$$

$$2\,Ca^{2+} + 2SO_4^{2-} \rightleftarrows 2CaSO_4(s) \; , \log K_r = 8.0 \; , \; SI = -4.0 \tag{57}$$

Dividing the saturation indices by the number of ions in the solid helps to eliminate this effect.

After the solids have been ranked, MINTEQ, like MINEQL, precipitates the solid with the highest ranking (i.e., equilibrates the solution with that solid). The solids are ranked again and the process repeated until Equation (55) is satisfied. If the selection process makes a wrong choice and the mass of a previously precipitated solid becomes negative, then MINTEQ will redissolve the amount of that solid phase which was precipitated and continue.

Effect of Solids on pH and pE

The dissolution or precipitation of solid phases can alter the pH or pE of the solution. MINTEQ can model the changes in pH or pE as solids dissolve or precipitate as long as the appropriate mass totals are known.

The mass total for H^+ ion is determined by use of a form of the electroneutrality condition called the "proton condition" which is defined as the excess or deficiency of protons over the "zero level" species (Stumm and Morgan 1970). The "zero level" species in MINTEQ are the components. If anionic components are in their unprotonated forms and all cationic components are the uncomplexed ions, then the proton condition corresponds directly to a mass total for hydrogen ion or the total ionizable hydrogen (Morel and Morgan 1972). If components are chosen which contain H^+, for example HS^- or HCO_3^-, then the proton condition does not have the physical interpretation of a total mass of hydrogen ion but is still computationally valid.

To correctly predict changes in pH during precipitation or dissolution, the initial proton excess or deficiency first must be determined and then entered as the total mass of H^+. To obtain the initial proton excess or deficiency, one enters the measured pH and models the solution in MINTEQ without permitting precipitation or dissolution of solids. The computed aqueous mass of H^+ is then the initial proton excess or deficiency. When this value is entered as the total mass of H^+, MINTEQ will compute the correct pH as precipitation or dissolution occurs.

Electrons do not exist in aqueous solution. Therefore, to allow the pE to vary during the precipitation or dissolution of solids, the mass totals for all components of redox reactions must be known in the absence of solids. This may require an initial modeling run at fixed pH and pE to obtain the mass totals for all components of redox couples. Then one merely reenters the electron as

Type VI (see the Users Manual for MEXAMS - The Metals Exposure Analysis Modeling System) and remodels the solution in the presence of solids. MINTEQ will recompute the correct pE during precipitation or dissolution.

One of the advantages to this method of computing pH and pE is that H^+ and the electron are treated identically to all other components and the new pH and pE are recomputed along with all other component activities.

Initial Mass of Solid

MINTEQ can accept input of a starting mass of solid. The initially specified mass is added to the mass computed by MINTEQ from equilibrium constraints. If the mass of solid (i.e., computed mass plus initial mass) should become negative, then MINTEQ will dissolve the initially specified mass of solid by adjusting the mass totals in the solid formation reaction and removing the equilibrium constraint.

SECTION 5

NUMERICAL METHOD

MINTEQ utilizes a Newton-Raphson iterative technique to solve the series of simultaneous nonlinear equations relating component activity to total mass. The technique is identical to that described by Westall et al. (1976) except for modifications required for the constant capacitance and triple layer adsorption models.

Given an initial estimate of all X_j values, MINTEQ computes all C_i terms by Equation (1). The difference function (i.e., relaxed mass balance constraint) defined by Equation (3) is then computed. The problem now reduces to one of finding new estimates for the X_j values. In the Newton-Raphson iteration technique, a new estimate for the set of components X_j is computed by first differentiating the set of relaxed mass balance equations, Equation (3), with respect to the components, X_k, to obtain the elements Z_{jk} of the n x n Jacobian matrix,

$$Z_{jk} = \frac{\partial Y_j}{\partial X_k} = a(i,j)\ a(i,k)\ C_i/X_k \qquad (58)$$

where j and k vary from 1 to n and

$$\frac{\partial T_j}{\partial X_k} = 0$$

except for electrostatic components. For a derivation of Equation (58) see Westall et al. 1976. The correction vector $\underline{\Delta x}$ is computed from the matrix equation,

$$\underline{\underline{Z}}\ \underline{\Delta x} = \underline{y}$$

where $\underline{\Delta x}$ is equal to $(\underline{x}_N - \underline{x}_{N+1})$, N is the iteration number and $\underline{\underline{Z}}$ is the Jacobian matrix of partial derivatives just computed. The system of linear equations represented by this matrix equation is then solved by gaussian elimination, and a new set of X_j terms are computed.

The convergence criteria used in MINTEQ is identical to the criteria in MINEQL which is,

$$\frac{|Y_j|}{\max Y_j} < \varepsilon \qquad (59)$$

where max Y_j is the maximum of the terms comprising Y_j and ε equals 1×10^{-3} in MINTEQ. In the absence of solids, maximum Y_j equals T_j.

In the case of the constant capacitance and triple layer adsorption models $\partial T_j/\partial X_j \neq 0$ for the electrostatic components since the total charge depends upon the potential. The derivatives for the electrostatic terms have been computed by Westall (1979b) and are summarized in Table 1.

TABLE 1. DERIVATIVES FOR THE CONSTANT CAPACITANCE AND TRIPLE LAYER ADSORPTION MODELS (WESTALL 1979b)

Constant Capacitance Model

$$Z_{\psi_o,\psi_o} = \sum(\psi_o,\psi_o) + C_1 \frac{RT}{FX_{\psi_o}} \cdot B$$

Triple Layer Model

$$Z\psi_o,\psi_o = \sum (\psi_o,\psi_o) + C_1 \frac{RT}{FX_{\psi_o}} \cdot B$$

$$Z\psi_o,\psi_b = \sum (\psi_o,\psi_b) - C_1 \frac{RT}{FX_{\psi_b}} \cdot B$$

$$Z\psi_b,\psi_o = \sum (\psi_b,\psi_o) - C_1 \frac{RT}{FX_{\psi_o}} \cdot B$$

$$Z\psi_b,\psi_b = \sum (\psi_b,\psi_b) + (C_1 + C_2) \frac{RT}{FX_{\psi_b}} \cdot B$$

$$Z\psi_b\psi_d = - C_2 \frac{RT}{FX_{\psi_d}} \cdot B$$

$$Z\psi_d\psi_b = - C_2 \frac{RT}{FX_{\psi_d}} \cdot B$$

$$Z\psi_d\psi_d = [+8(\varepsilon\varepsilon_o RTI)^{1/2} \frac{F}{2RT} \cosh \frac{F\psi d}{2RT} + C_2] \frac{RT}{FX_{\psi_d}} \cdot B$$

Modified Line Search

The Newton-Raphson numerical method usually converges rapidly. Unfortunately, there are cases when the method does not converge. One of the most common instances of nonconvergence results from extremely poor starting estimates for the component activities. This frequently occurs for such components as Fe^{3+} or U^{4+} where the actual component activity is a small fraction of the mass total. In such cases the default starting estimate of one hundredth the mass total may be 20 or 30 orders of magnitude too high. Another common case of nonconvergence is when an aqueous solution contains two major components with essentially all of the mass of each component tied up in a common complex. In such cases, the ionic strength also varies with the major components activities and the numerical problem may become unstable.

For both of these cases of nonconvergence, the problem can usually be solved by making more accurate guesses for the component activities. Unfortunately, this may be a time consuming process. To help solve these problems, a modified line search has been included.

The modified line search is based on the fact that at convergence the component activities at the current iteration are approximately equal to the activities at the previous iteration (i.e., $X^N \simeq X^{N+1}$).[a] The line search uses this fact to modify the component activities (X_j terms) computed by the Newton-Raphson method. To understand the method, let X represent the component activity before Newton-Raphson correction and Y the value after Newton-Raphson correction. This means that at convergence, X = Y. The modified line search then simply monitors the progress of the iteration scheme and uses previous X-Y points to project new values for the component activities. The new values for

(a) The principal idea behind the modified line search was originally suggested by Dr. John R. Morrey, Battelle, Pacific Northwest Laboratories.

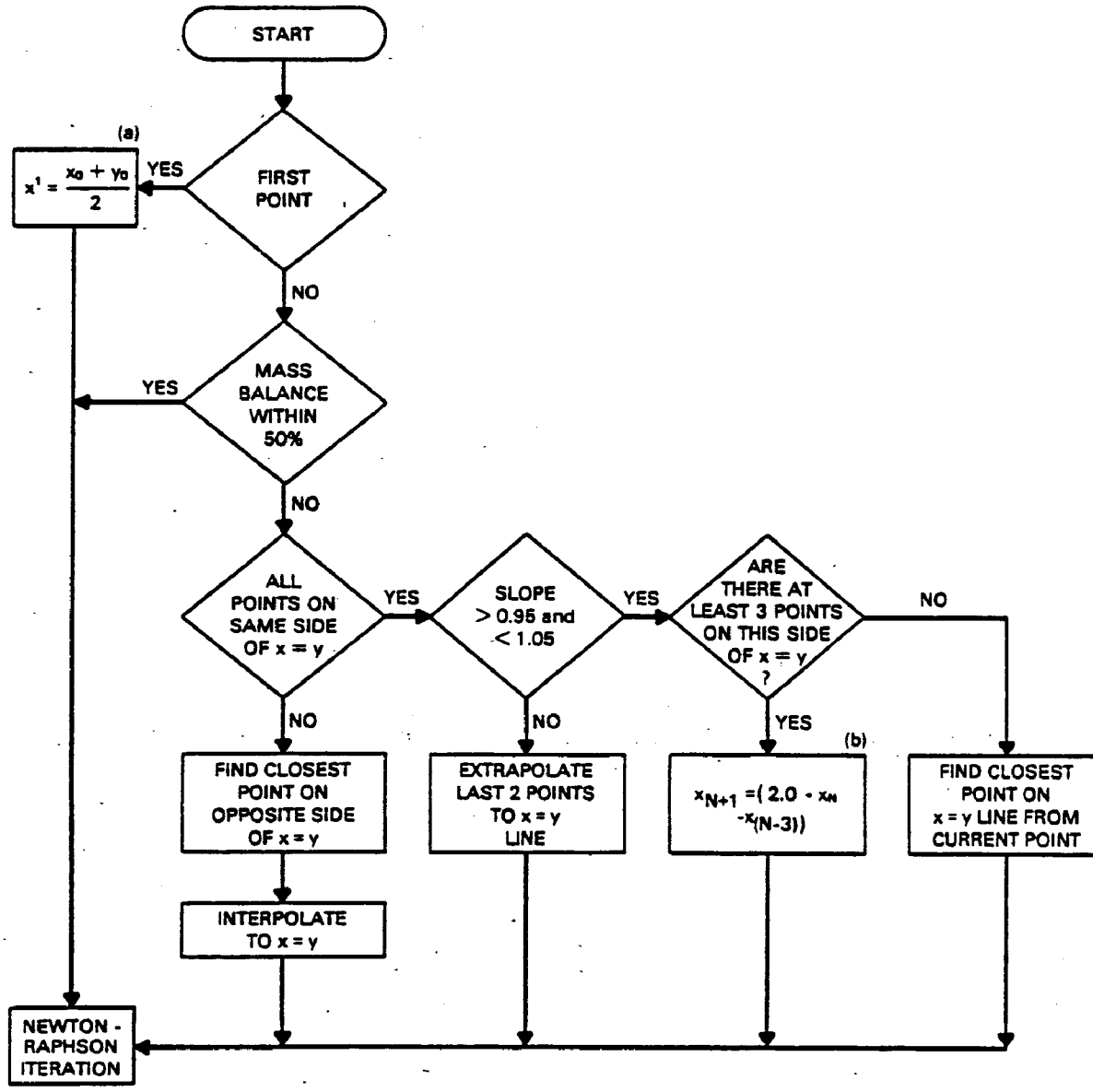
the component activities are obtained by either extrapolation or interpolation to the X = Y convergence line. The overall principal of the method is to refine the component activities to be close enough to the final solution values that the Newton-Raphson method will converge. The new values for the component activities are then used as the new starting estimates for the Newton-Raphson iteration. Figure 3 presents a logic diagram of the method.

An example convergence pattern for Fe^{3+} is shown in Figure 4. Figure 4 is a schematic of the following discussion. An initial estimate of the logarithm of the activity of Fe^{3+} (X_0) was made of -4.00. The Newton-Raphson iteration then produced a new estimate (Y_0) of -4.35. Since this is the first point, a new X_1 was computed,

$$X_1 = \frac{X_0 + Y_0}{2} = -4.18 \quad .$$

Newton-Raphson iteration then yields Y_1 = -4.52. Since both points are on the same side of X = Y, and the computed slope is 0.96 and since there are only two points on this side of the line, the model chooses the closest point on the X = Y line [i.e., $X_2 = (X_1 + Y_1)/2.0 = -4.35$]. Newton-Raphson iteration produces Y_2 = -4.70. The point (X_2,Y_2) is on the same side of the X = Y line as the previous points, and the computed slope between the last two points equals 1.01. Now, however, there are three points on the same side of X = Y and the algorithm extrapolates, $X_3 = 2 * X_2^{(a)} = -8.70$. Newton-Raphson then returns a value of Y_3 = -9.00. Since this is also on the same side of the X = Y line and the slope is still approximately equal to one, the model

(a) In comparing Figure 3 X_{N-3} equals zero for the first extrapolation.



(a) ALL x VALUES ARE LOGARITHMS

(b) SUBTRACTING THE VALUE OF THE THIRD PREVIOUS ITERATION HELPS PREVENT OVER EXTRAPOLATION

FIGURE 3. Logic Diagram for Modified Line Search

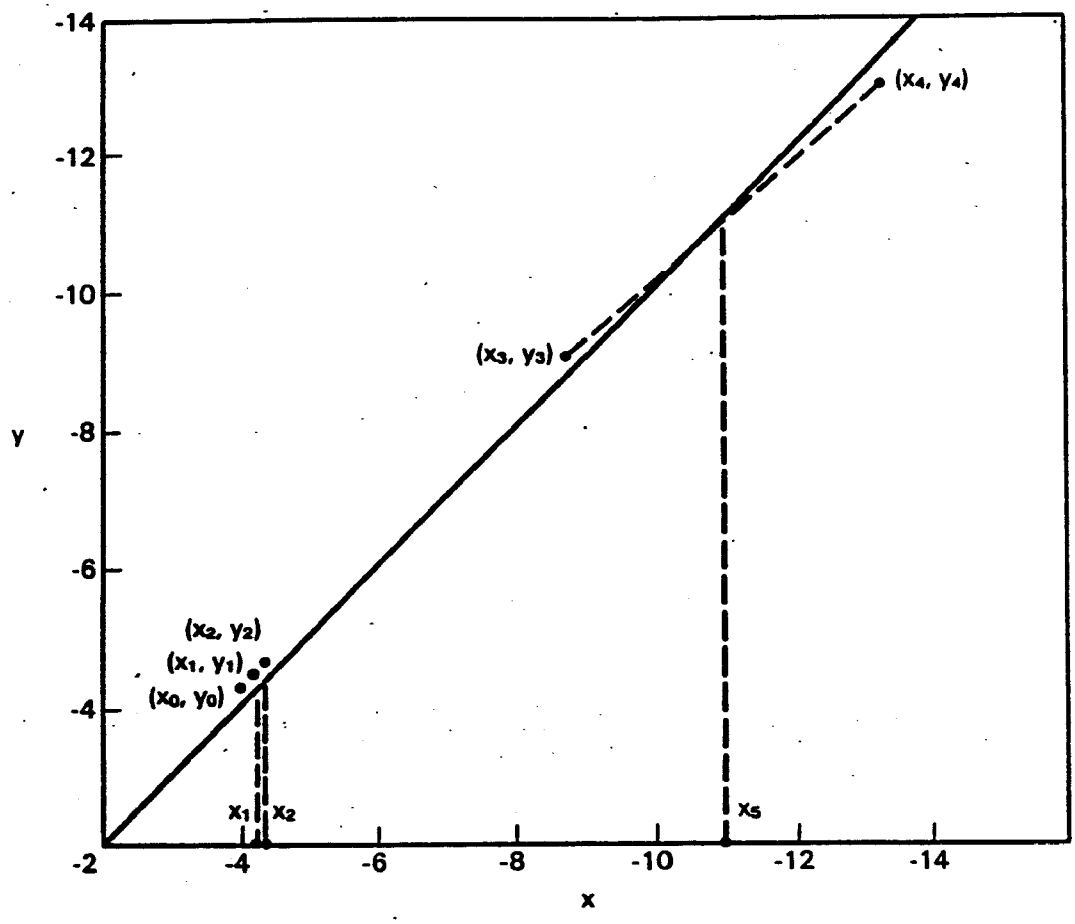


FIGURE 4. Example Convergence Pattern for Fe^{3+} Using the Modified Line Search. All values as logarithm.

extrapolates again $X_4 = 2X_3 - X_0 = -13.40$. Newton-Raphson then returns $Y_4 = -13.1$. The point (X_4,Y_4) is now on the other side of X = Y and the model interpolates a new point $[X_5 = (-slope \cdot X_4 + Y_4)/(1.0 - slope)] = -10.9$. Newton-Raphson then returns -11.1 which satisfies the mass balance criteria within 50% and the line search is complete.

It should be remembered that the line search utilized in MINTEQ was tested on only a few sample problems. The method is not intended to be used unless the user has been unable to get the Newton-Raphson method to converge. In such cases the method may prove useful but the users are advised that this option should be used at their own peril.

SECTION 6

THERMODYNAMIC DATA BASE

INTRODUCTION

The use of mass action expressions in MINTEQ requires the use of equilibrium constants ($\log K_r^o$) at a reference temperature of 298.15°K and zero ionic strength for entry into the data base. Equilibrium constants are extrapolated by MINTEQ to temperatures other than 298°K by use of the Van't Hoff relation which requires the enthalpy of reaction ($\Delta H^o_{r,298}$), when analytical expressions for $\log K_r^o$ are not available.

The equilibrium constants can be determined directly from solubility, potentiometric, ion exchange or other analytical methodologies (Rossotti 1981), or computed from calculated Gibbs free energies of reaction by the relationship,

$$\log K_{r,298} = \frac{\Delta G^o_{r,298}}{2.303\ RT}$$

where $\Delta G^o_{r,298} = \Sigma \Delta G^o_{f,298}$ (products) - $\Sigma G^o_{f,298}$ (reactants). The free energy of formation ($\Delta G^o_{f,298}$) is related to the heat of formation and entropy by,

$$\Delta G^o_{f,298} = \Delta H^o_{f,298} - 298.15\ \Delta S^o_{298} \quad .$$

Calorimetric measurements of the heat of solution and heat capacity can be used to compute, ΔH_f^o and ΔS_{298}^o, respectively. The enthalpy of reaction is readily computed,

$$\Delta H_{r,298}^o = \sum \Delta H_{f,298}^o \text{ (products)} - \sum \Delta H_{f,298}^o \text{ (reactants)}$$

Data for ΔH_f^o can be obtained from calorimetric measurements of the heat of solution or $\Delta H_{r,298}^o$ can be calculated from the experimentally determined variation of log K_r^o with temperature.

DATA IN MINTEQ

The selection of accurate and reliable thermodynamic data is extremely important to the reliability of chemical equilibrium model calculations (Nordstom et al. 1979). MINTEQ contains the WATEQ3 data base (Ball et al. 1981; Ball et al. 1980;(a) Truesdell and Jones 1974) which is the most thoroughly documented and evaluated thermodynamic data base used in any available geochemical model. However, when more recent and reliable experimental data, or data for reactions not present in the data base, become available, they should be included in the MINTEQ data base. The data base also contains some tabulated values for the minimum and maximum values for some equilibrium constants to assist in evaluating alternative thermodynamic data.

The thermodynamic data for MINTEQ will be listed in Appendix A. The included references refer to the selected values for log K_r^o and $\Delta H_{r,298}^o$. The

(a) A few clay minerals with either exchangeable cations in the chemical formula or variable component stoichiometrics as a function of pH were not included.

references do not give the primary source of the data but are intended as indexes to the tabulations which give the specific reactions and data sources.

ACCESSORY DATA

In addition to thermodynamic data, the MINTEQ data base also contains necessary supplementary data for each species. The data are summarized in Table 2. Most of these parameters have been previously described in this document or the accompanying User's Guide MEXAMS - The Metals Exposure Analysis Modeling System.

All Debye-Huckel parameters were taken directly from the WATEQ3 data base (Ball et al. 1981), the majority of which were in turn obtained from the tabulation in Truesdell and Jones (1974). Many of the Debye-Huckel parameters in the WATEQ3 data base for aqueous species of Cu, Mn and Zn were estimated.

TABLE 2. SUPPLEMENTARY DATA IN THE MINTEQ DATA BASE FOR EACH SPECIES

- Charge
- Gram formula weight
- Carbonate alkalinity factor
- Extended Debye Huckel parameters
- Name
- ID Number

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APPENDIX A

REACTIONS AND THERMODYNAMIC DATA

This appendix contains a listing of the thermochemical data in MINTEQ. The references are for the equilibrium constants and enthalpy of reaction data.

Footnotes for Tables A-1, A-2, A-3.

(a) reaction written in terms of $H^+(aq)$ and $H_2O(aq)$.

(b) reaction written in terms of $CO_3^{2-}(aq)$ rather than $HCO_3^-(aq)$. For the reaction:

$$H^+ + CO_3^{2-} \rightleftharpoons HCO_3^-$$

log K = 10.33, ΔH_r^o = -3.617 taken from Ball et al. (1981) to maintain consistency with that data base. Log K is the same as in NBS 270 series.[a]

(c) reaction written in terms of $PO_4^{3-}(aq)$ rather than $HPO_4^{2-}(aq)$. For the reaction:

$$H^+ + PO_4^{3-} \rightleftharpoons HPO_4^{2-}$$

log K = 12.346, ΔH_r^o = -3.53 taken from NBS 270-3 and identical to the values in Ball et al. (1981).

(d) reaction written in terms of $PO_4^{3-}(aq)$ rather than $H_2PO_4^-(aq)$. For the reaction:

$$2H^+ + PO_4^{3-} \rightleftharpoons H_2PO_4^-$$

log K = 19.553, ΔH_r^o = -4.52 taken from NBS 270-3[b] and identical to the values in Ball et al. (1981).

(e) reaction written in terms of Cu^{+1} rather than Cu^{+2} and e^-. For the reaction:

$$Cu^+ \rightleftharpoons Cu^{+2} + e^-$$

log K = -2.72 and ΔH_r^o = -1.65 from NBS 270-4, which is also the same values used in Ball et al. (1981).

(f) addition of WATEQ3 reactions 544 and 542 in Ball et al. (1981).

(g) reaction written in terms of $CO_3^{2-}(aq)$ rather than $H_2CO_3(aq)$. Thermodynamic data taken from NBS 270-3.

(h) reaction written in terms of $HS^-(aq)$ rather than $S^{2-}(aq)$. ΔG_f^o and ΔH_f^o for $HS^-(aq)$ from NBS 270-3.

(a) The NBS 270 series referred to here consists of NBS technical notes 270-3 (Wagman et al. 1968), 270-4 (Wagman et al. 1969), 270-6 (Parker et al. 1971), and 270-8 (Wagman et al. 1981).

(b) ΔG_f^o for $H_2PO_4^-(aq)$ in NBS 270-3 is in error and should be -270.17 kcal.

(i) reaction written in terms of $H_3AsO_4^o(aq)$ rather than $AsO_4^{3-}(aq)$. For the reaction:

$$AsO_4^{3-} + 3H^+ \rightleftharpoons H_3AsO_4^o$$

log K = 20.6, ΔH_r^o = -3.43 from NBS 270-3.

Data Sources for Tables A-1, A-2, A-3.

1. Ball et al. (1980)

2. Ball et al. (1981)

3. Plummer et al. (1976)

4. Truesdell and Jones (1974)

5. Recomputed by Krupka et al. [(a)] who reference Dongarra and Langmuir (1980) for the equilibrium constants.

6. Computed by Krupka et al. [(a)] who reference NBS 270-8 (Wagman et al. 1981).

7. Recomputed as part of this study using the data of Robie et al. (1978). The calculations are consistent with the accepted ancillary data of Krupka and Jenne (1981).

8. Recomputed as part of this study. ΔG_f^o and ΔH_f^o taken from Helgeson et al. (1978).

9. Recomputed as part of this study. $\Delta G_r^o = 65.9$ taken from Truesdell and Jones (1974) for:

   $$Al_2Si_4O_{10}(OH)_2 + 12\ H_2O \leftrightharpoons 2Al(OH)_4^- + 4H_4SiO_4^o + 2H^+.$$

   Reaction rewritten in terms of $Al^{3+}(aq)$ consistent with the ancillary data of Krupka et al. (1982).

10. Recomputed as part of this study. ΔG_f^o computed from log K in Baes and Mesmer (1976) written with $CO_2(g)$. ΔH_f^o taken from Robie et al. (1978). All ancillary data taken from NBS 270-3 except $Cu^{2+}(aq)$ and Cu(0) from Robie et al. (1978).

11. Krupka and Jenne (1982).

(a) Krupka, K. M., E. A. Jenne, and W. J. Deutsch (DRAFT). "Validation of the WATEQ4 Geochemical Model for Uranium." PNL-4333. Pacific Northwest Laboratory, Richland, Washington.

TABLE A.1. Thermochemical Data for Aqueous Complexes (Default Type II)

									REFERENCE	WATEQ REACTION NUMBER
2		1,000 893	1,000 180							
8937320	KUO2SO4 AQ	5,100	2,789			0, 0,0	0,0	366,0894	2	590
2		1,000 893	1,000 732							
8937321	KUO2SO4)2-2	6,100	4,183			-2, 0,0	0,0	462,1518	2	591
2		1,000 893	2,000 732							
8935800	KUO2HPO4 AQ	-2,100	20,814			0, 0,0	0,0	366,0872	2	592
3		1,000 893	1,000 580	1,000 330						
8935801	KUO2HPO4)2	-11,599	42,988			-2, 0,0	0,0	461,9865	5	---
3		1,000 893	2,000 580	2,000 330						
8935802	KUO2H2PO4+1	-5,700	22,643			1, 0,0	0,0	367,0151	2	594
3		1,000 893	1,000 580	2,000 330						
8935803	KUO2H2PO4)2	-16,5	44,78			0, 0	0	464,002	2	595
3		1,000 893	2,000 580	4,000 330						
8935804	KUO2H2PO4)3	-28,6	66,245			-1, 0	0	568,989	2	596
3		1,000 893	3,000 580	6,000 330						
8937700	KUO2H3SIO4		-2,4			1, 0	0	365,135	2	689
3		1,000 893	1,000 770	-1,000 330						
7317300	KS2 -2	11,4	-14,520			-2, 0,0	0,0	64,128	1	582
3		1,000 730	1,000 731	-1,000 330						
7317301	KS3 -2	10,4	-13,282			-2, 0,0	0,0	96,192	1	583
3		1,000 730	2,000 731	-1,000 330						
7317302	KS4 -2	9,7	-9,829			-2, 0,0	0,0	128,256	1	584
3		1,000 730	3,000 731	-1,000 330						
7317303	KS5 -2	9,3	-9,595			-2, 0,0	0,0	160,320	1	585
3		1,000 730	4,000 731	-1,000 330						
7317304	KS6 -2		-9,881			-2, 0,0	0,0	192,384	1	586
3		1,000 730	5,000 731	-1,000 330						

TABLE A.1. (contd)

Species line	Component line	Charge / data	Reference	WATEQ Reaction Number
	2 1.000 142 1.000 330			
8913300 KUOH +3 11.715 -0.656	3 1.000 891 1.000 2 -1.000 330	3. 0.0 0.0 255.0364	2	545
8913301 KU(OH)2 +2 17.730 -2.270	3 -2.000 330 1.000 891 2.000 2	2. 0.0 0.0 272.0437	2	546
8913302 KU(OH)3 +1 22.645 -4.935	3 1.000 891 3.000 2 -3.000 330	1. 0.0 0.0 289.0511	2	547
8913303 KU(OH)4 AQ 24.700 -8.498	3 1.000 891 4.000 2 -4.000 330	0. 0.0 0.0 306.0586	2	548
8913304 KU(OH)5 -1 27.575 -13.120	3 1.000 891 5.000 2 -5.000 330	-1. 0.0 0.0 323.0659	2	549
8912700 KUF +3 5.050 8.659	2 1.000 891 1.000 270	3. 0.0 0.0 257.0274	2	556
8912701 KUF2 +2 7.200 14.457	2 1.000 891 2.000 270	2. 0.0 0.0 276.0258	2	557
8912702 KUF3 +1 7.150 19.115	2 1.000 891 3.000 270	1. 0.0 0.0 295.0242	2	558
8912703 KUF4 AQ 4.600 23.640	2 1.000 891 4.000 270	0. 0.0 0.0 314.0226	2	559
8912704 KUF5 -1 4.050 25.238	2 1.000 891 5.000 270	-1. 0.0 0.0 333.0210	2	560
8912705 KUF6 -2 3.300 27.718	2 1.000 891 6.000 270	-2. 0.0 0.0 352.0194	2	561
8911800 KUCL +3 9.933 1.338	2 1.000 891 1.000 180	3. 0.0 0.0 273.4820	2	564
8917320 KUSO4 +2 3.700 5.461	2 1.000 891 1.000 732	2. 0.0 0.0 334.0906	2	565
8917321 KU(SO4)2 AQ 7.600 9.749	2 1.000 891 2.000 732	0. 0.0 0.0 430.1522	2	566
8915800 KUHPO4 +2 7.500 24.443	3 1.000 891 1.000 580 1.000 330	2. 0.0 0.0 334.0084	2	567
8915801 KU(HPO4)2AQ 1.700 46.833	3 1.000 891 2.000 580 2.000 330	0. 0.0 0.0 429.9877	2	568
8915802 KU(HPO4)3-2 -7.000 67.564	3 1.000 891 3.000 580 3.000 330	-2. 0.0 0.0 525.9671	2	569
8915803 KU(HPO4)4-4 -26.500 88.483	3 1.000 891 4.000 580 4.000 330	-4. 0.0 0.0 621.9465	2	570
8933300 KUO2OH +1 10.210 -5.090	3 1.000 893 1.000 2 -1.000 330	1. 0.0 0.0 287.0352	5	---
8933301 KUO2)2OH2+2 10.230 -5.645	3 2.000 893 2.000 2 -2.000 330	2. 0.0 0.0 574.0703	2	575
8933302 KUO2)3OH5+1 25.075 -15.593	3 3.000 893 5.000 2 -5.000 330	1. 0.0 0.0 895.1203	2	576
8931400 KUO2CO3 AQ 0.840 10.071	2.00 2 1.000 893 1.000 140	0. 0.0 0.0 330.0372	2	581
8931401 KUO2CO3)2-2 3.480 17.008	4.00 2 1.000 893 2.000 140	-2. 0.0 0.0 390.0465	2	582
8931402 KUO2CO3)3-4 -0.780 21.384	6.00 2 1.000 893 3.000 140	-4. 0.0 0.0 450.0559	2	583
8932700 KUO2F +1 -0.450 5.105	2 1.000 893 1.000 270	1. 0.0 0.0 289.0262	2	585
8932701 KUO2F2 AQ -0.900 8.920	2 1.000 893 2.000 270	0. 0.0 0.0 308.0246	2	586
8932702 KUO2F3 -1 -0.850 11.364	2 1.000 893 3.000 270	-1. 0.0 0.0 327.0230	2	587
8932703 KUO2F4 -2 -1.100 12.607	2 1.000 893 4.000 270	-2. 0.0 0.0 346.0214	2	588
8931800 KUO2CL +1 1.233 0.220		1. 0.0 0.0 305.4808	2	589

TABLE A.1. (contd)

										REFERENCE	WATEQ REACTION NUMBER
2	1,000	20	1,000 732								
0204920 KAGNO3 AQ	0,0000		-0,2900					0, 0,0	0,0	169,8720	1	435
2	1,000	20	1,000 492								
0204910 KAG(NO2)2 -	0,0000		2,2200					-1, 0,0	0,0	199,8790	1	436
2	1,000	20	2,000 491								
0201302 KAGHR3 -2	0,0000		8,7100					-2, 0,0	0,0	347,5800	1	473
2	1,000	20	3,000 130								
0203002 KAGI3 -2	-27,0300		13,3700					-2, 0,0	0,0	488,5810	1	474
2	1,000	20	3,000 300								
0203003 KAGI4 -3	0,0000		14,0000					-3, 0,0	0,0	615,4850	1	475
2	1,000	20	4,000 300								
0207302 KAG(B4)2 -3	0,0000		0,9910					-3, 22,0	0,0	364,3800	1	587
4	1,000	20	2,000 730	-2,000 330				6,000 731				
0207303 KAGS4S5 -3	0,0000		8,6800					-3, 24,0	0,0	396,4440	1	588
4	1,000	20	2,000 730	-2,000 330				7,000 731				
0207304 KAG(H8)34-2	0,0000		10,4310					-2, 15,0	0,0	269,1960	1	589
4	1,000	20	2,000 730	-1,000 330				3,000 731				
0201410 KAG FULVATE	0,0000		2,3990					-1, 0,0	0,0	757,8680	1	531
2	1,000	20	1,000 141									
0201420 KAG HUMATE	0,0000		2,3990					-1, 0,0	0,0	2187,8670	1	532
2	1,000	20	1,000 142									
3300600 KH2ASO3 -	6,5600		-9,2200					-1, 0,0	0,0	124,9358	1	478
2	1,000	60	-1,000 330									
3300601 KHASO3 -2	14,1990		-21,33					-2, 0,0	0,0	123,9278	1	479
2	1,000	60	-2,000 330									
3300602 KASO3 -3	20,2500		-34,7440					-3, 0,0	0,0	122,9198	1	480
2	1,000	60	-3,000 330									
3300610 KH4ASO3 +	0,0000		-0,3050					1, 0,0	0,0	126,9510	1	481
2	1,000	60	1,000 330									
3300611 KH2ASO4 -	-1,6900		-2,2430					-1, 0,0	0,0	140,9350	1	482
2	1,000	61	-1,000 330									
3300612 KHASO4 -2	-0,9200		-9,0010					-2, 0,0	0,0	139,9270	1	483
2	1,000	61	-2,000 330									
3300613 KASO4 -3	3,4300		-20,5970					-3, 0,0	0,0	138,9190	1	484
2	1,000	61	-3,000 330									
3301400 KHCO3 -	-3,0170		10,3300					-1, 5,4	0,0	61,0178	1	68
1,00 2	1,000 140		1,000 330									
3301401 KH2CO3 AQ	-2,2470		16,681					0, 0,0	0,0	62,0258	1(0)	35
2	1,000 140		2,000 330									
3307320 KHSO4 -	4,9100		1,9870					-1, 4,5	0,0	97,0690	4	89
2	1,000 732		1,000 330									
3302700 KHF AQ	3,4000		3,1690					0, 0,0	0,0	20,0068	1	202
2	1,000 270		1,000 330									
3302701 KHF2 -	4,5500		3,7490					-1, 3,5	0,0	39,0040	1	203
2	2,000 270		1,000 330									
3302702 KH2F2 AQ	0,0000		6,7680					0, 0,0	0,0	40,0120	1	537
2	2,000 270		2,000 330									
3305000 KHPO4 -2	-3,5500		12,3460					-2, 5,0	0,0	95,9790	4	15
2	1,000 580		1,000 330									
3305001 KH2PO4 -	-4,5200		19,5530					-1, 5,4	0,0	96,9870	4	16
2	1,000 580		2,000 330									
3307300 KH2S AQ	-5,500		6,9940					0, 0,0	0,0	34,0790	4	91
2	1,000 730		1,000 330									
3307301 KS -2	12,1000		-12,9100					-2, 5,0	0,0	32,0640	4	92
2	1,000 730		-1,000 330									
3301410 KH FULVATE	0,0000		4,2700					-1, 0,0	0,0	651,0080	1	523
2	1,000 141		1,000 330									
3301420 KH HUMATE	0,0000		4,2700					-1, 0,0	0,0	2001,0070	1	524

TABLE A.1. (contd)

										REFERENCE	RATEQ REACTION NUMBER
2,00 2		1,000 6nn		1,000 140							
6003305	KPb(OH)4 -2	0,0000		-39,6999				-2, 0,0	0,0 375,2190	1	469
3		1,000 6nn		4,000 2		-4,000 330					
6007321	KPb(SO4)2-2	0,0000		3,4700				-2, 0,0	0,0 399,5130	1	470
2		1,000 6nn		4,000 732							
6001402	KPbHCO3 +	0,0000		13,200				1, 0,0	0,0 268,2870	1(B)	517
1,00 3		1,000 6nn		1,000 140		1,000 330					
5401300	KNiBR +	0,0000		0,5000				1, 0,0	0,0 138,6140	1	483
2		1,000 54n		1,000 130							
5401000	KNICL +	0,0000		0,3998				1, 0,0	0,0 94,1630	1	484
2		1,000 540		1,000 180							
5402700	KNIF +	0,0000		1,3000				1, 0,0	0,0 77,7080	1	485
2		1,000 54n		1,000 270							
5403300	KNIOH +	12,4200		-9,8600				1, 0,0	0,0 75,7170	1	486
3		1,000 540		1,000 2		-1,000 330					
5403301	KNI(OH)2 AQ	0,0000		-19,0000				0, 0,0	0,0 92,7240	1	487
3		1,000 54n		2,000 2		-2,000 330					
5403302	KNI(OH)3 -	0,0000		-30,0000				-1, 0,0	0,0 109,7320	1	488
3		1,000 540		3,000 2		-3,000 330					
5407320	KNiSO4 AQ	1,5200		2,2900				0, 0,0	0,0 154,7710	1	489
2		1,000 540		1,000 732							
5401001	KNICL2 AQ	0,0000		0,9600				0, 0,0	0,0 129,6160	1	518
2		1,000 540		2,000 180							
5401400	KNiHCO3 +	0,0000		12,470				1, 0,0	0,0 119,7270	1(B)	519
1,00 3		1,000 540		1,000 140		1,000 330					
5401401	KNICO3 AQ	0,0000		6,4700				0, 0,0	0,0 110,7190	1	520
2,00 2		1,000 54n		1,000 140							
5401402	KNI(CO3)2-2	0,0000		10,1100				-2, 0,0	0,0 178,7280	1	521
2,00 2		1,000 540		2,000 140							
5407321	KNI(SO4)2-2	0,0000		1,0200				-2, 0,0	0,0 250,8330	1	522
2		1,000 540		2,000 732							
0201300	KAGBR AQ	0,0000		4,2400				0, 0,0	0,0 187,7720	1	421
2		1,000 2n		1,000 130							
0201301	KAGBR2 -	0,0000		7,2800				-1, 0,0	0,0 267,6760	1	422
2		1,000 2n		2,000 130							
0201000	KAGCL AQ	-2,0000		3,2700				0, 0,0	0,0 143,3210	1	423
2		1,000 20		1,000 180							
0201001	KAGCL2 -	-3,9300		5,2700				-1, 0,0	0,0 178,7740	1	424
2		1,000 20		2,000 180							
0201002	KAGCL3 -2	0,0000		5,2900				-2, 0,0	0,0 214,2270	1	425
2		1,000 20		3,000 180							
0201003	KAGCL4 -3	0,0000		5,5100				-3, 0,0	0,0 249,6790	1	426
2		1,000 2n		4,000 180							
0202700	KAGF AQ	-2,8300		0,3600				0, 0,0	0,0 126,8660	1	427
2		1,000 2n		1,000 270							
0207300	KAGHS AQ	0,0000		14,85nn				0, 0,0	0,0 140,9390	1	428
2		1,000 2n		1,000 730							
0207301	KAG(HS)2 -	0,0000		10,45nn				-1, 0,0	0,0 174,0110	1	429
2		1,000 2n		2,000 730							
0203000	KAGI AQ	0,0000		6,0000				0, 0,0	0,0 234,7720	1	430
2		1,000 2n		1,000 380							
0203001	KAGI2 -	0,0000		10,6000				-1, 0,0	0,0 361,6760	1	431
2		1,000 2n		2,000 380							
0203300	KAGOH AQ	0,0000		-12,0000				0, 0,0	0,0 124,8750	1	432
3		1,000 2n		1,000 2		-1,000 330					
0203301	KAG(OH)2 -	0,0000		-24,0000				-1, 0,0	0,0 141,8820	1	433
3		1,000 2n		2,000 2		-2,000 330					
0207320	KAGSO4 -	1,4900		1,2900				-1, 0,0	0,0 203,9290	1	434

TABLE A.1. (contd)

									REFERENCE	WATEQ REACTION NUMBER
2	1.000	10H	1.000	380						
1603001	KCUI2 AQ	0.0000	3.5900			0, 0.0	0.0	366.2000	1	454
2	1.000	100	2.000	380						
1601400	KCUHCO3 +	0.0000	12.400			1, 0.0	0.0	173.4170	1(b)	514
1.00 3	1.000	100	1.000	140	1.000	330				
1601401	KCUCO3 AQ	0.0000	5.3990			0, 0.0	0.0	172.4890	1	515
2.00 2	1.000	10H	1.000	140						
1607321	KCU(SO4)2-2	0.0000	3.5000			-2, 0.0	0.0	288.4610	1	516
2	1.000	100	2.000	732						
1601410	KCU FULVATE	0.0000	3.5000			0, 0.0	0.0	762.3990	1	529
2	1.000	100	1.000	141						
1601420	KCU HUMATE	0.0000	3.5000			0, 0.0	0.0	2112.3990	1	530
2	1.000	10H	1.000	142						
6001000	KPBCL +	0.5000	1.6000			1, 0.0	0.0	242.6430	1	341
2	1.000	0HH	1.000	180						
6001001	KPBCL2 AQ	1.0000	1.8000			0, 0.0	0.0	278.0960	1	342
2	1.000	0H0	2.000	180						
6001002	KPBCL3 -	2.1700	1.6990			-1, 0.0	0.0	313.5490	1	343
2	1.000	0H0	3.000	180						
6001003	KPBCL4 -2	3.5500	1.3800			-2, 0.0	0.0	349.0020	1	344
2	1.000	0H0	4.000	180						
6001400	KPB(CO3)2-2	0.0000	10.6400			-2, 0.0	0.0	327.2080	1	345
4.00 2	1.000	0HH	2.000	140						
6002700	KPBF +	0.0000	1.2500			1, 0.0	0.0	226.1880	1	346
2	1.000	0HH	1.000	270						
6002701	KPBF2 AQ	0.0000	2.5600			0, 0.0	0.0	245.1860	1	347
2	1.000	0HH	2.000	270						
6002702	KPBF3 -	0.0000	3.4200			-1, 0.0	0.0	264.1850	1	348
2	1.000	0HH	3.000	270						
6002703	KPBF4 -2	0.0000	3.1000			-2, 0.0	0.0	283.1830	1	349
2	1.000	0HH	4.000	270						
6003300	KPBOH +	0.0000	-7.7100			1, 0.0	0.0	224.1970	1	350
3	1.000	0HH	1.000	2	-1.000	330				
6003301	KPB(OH)2 AQ	0.0000	-17.1200			0, 0.0	0.0	241.2040	1	351
3	1.000	0HH	2.000	2	-2.000	330				
6003302	KPB(OH)3 -	0.0000	-28.0600			-1, 0.0	0.0	258.2120	1	352
3	1.000	0HH	3.000	2	-3.000	330				
6003303	KPB2OH +3	0.0000	-6.3600			3, 0.0	0.0	431.3870	1	353
3	2.000	0HH	1.000	2	-1.000	330				
6004920	KPBNO3 +	0.0000	1.1700			1, 0.0	0.0	269.1940	1	354
2	1.000	0HH	1.000	492						
6007320	KPBSO4 AQ	0.0000	2.7500			0, 0.0	0.0	303.2510	1	355
2	1.000	0HH	1.000	732						
6007300	KPB(HS)2 AQ	0.0000	15.2700			0, 0.0	0.0	273.3330	1	356
2	1.000	0H0	2.000	730						
6007301	KPB(HS)3 -	0.0000	16.5700			-1, 0.0	0.0	306.4050	1	357
2	1.000	0HH	3.000	730						
6003304	KPB3(OH)4+2	20.5000	-23.8000			2, 0.0	0.0	689.5990	1	358
3	3.000	0HH	4.000	2	-4.000	330				
6001300	KPBOH +	2.0000	1.7700			1, 0.0	0.0	287.0940	1	455
2	1.000	0HH	1.000	130						
6001301	KPBOH2 AQ	0.0000	1.4400			0, 0.0	0.0	366.9980	1	456
2	1.000	0HH	2.000	130						
6003000	KPBI +	0.0000	1.9400			1, 0.0	0.0	334.0940	1	457
2	1.000	0HH	1.000	380						
6003001	KPBI2 AQ	0.0000	3.1990			0, 0.0	0.0	460.9980	1	458
2	1.000	0HH	2.000	380						
6031401	KPBCO3 AQ	0.0000	7.2400			0, 0.0	0.0	267.1990	1	468

TABLE A.1. (contd)

													REFERENCE	RATEQ REACTION NUMBER
	2	1,000	950	1,000	732									
9507321	KZN(SO4)2-2	0.0000		3,2800					-2.	0.0	0.0	257.4930	1	264
	2	1,000	950	2,000	732									
9501300	KZNOH +	0.0000		-0.5000					1.	0.0	0.0	145.2740	1	447
	2	1,000	950	1,000	130									
9501301	KZNOH2 AQ	0.0000		-0.9000					0.	0.0	0.0	225.1700	1	448
	2	1,000	950	2,000	130									
9503000	KZNI +	0.0000		-2.9100					1.	0.0	0.0	192.2740	1	449
	2	1,000	950	1,000	300									
9503001	KZNI2 AQ	0.0000		-1.6900					0.	0.0	0.0	319.1700	1	450
	2	1,000	950	2,000	300									
9501400	KZNHCO3 +	0.0000		12.400					1.	0.0	0.0	126.3570	1(B)	511
1.00	3	1,000	950	1,000	140	1,000	330							
9501401	KZNCO3 AQ	0.0000		5.3000					0.	0.0	0.0	125.3790	1	512
2.00	2	1,000	950	1,000	140									
9501402	KZN(CO3)2-2	0.0000		9.6300					-2.	0.0	0.0	185.3500	1	513
4.00	2	1,000	950	2,000	140									
1601000	KCOCL +	0.5900		1.9000					1.	0.0	0.0	147.6530	1	294
	2	1,000	160	1,000	180									
1601001	KCOCL2 AQ	1.2400		2.6000					0.	0.0	0.0	183.3860	1	295
	2	1,000	160	2,000	180									
1601002	KCOCL3 -	3.9000		2.3990					-1.	0.0	0.0	218.7590	1	296
	2	1,000	160	3,000	180									
1602700	KCOF +	0.0000		1.1000					1.	0.0	0.0	131.3980	1	297
	2	1,000	160	1,000	270									
1602701	KCOF2 AQ	0.0000		1.5000					0.	0.0	0.0	150.3960	1	298
	2	1,000	160	2,000	270									
1601402	KCO(CO3)3-4	0.0000		6.2200					-4.	0.0	0.0	292.4200	1	299
6.00	2	1,000	160	3,000	140									
1603300	KCOOH +	13.1000		-10.0000					1.	0.0	0.0	129.4070	1	300
	3	1,000	160	1,000	2	-1,000	330							
1603301	KCO(OH)2 AQ	0.0000		-20.3500					0.	0.0	0.0	146.4140	1	301
	3	1,000	160	2,000	2	-2,000	330							
1603302	KCO(OH)3 -	0.0000		-33.3000					-1.	0.0	0.0	163.4220	1	302
	3	1,000	160	3,000	2	-3,000	330							
1603303	KCO(OH)4 -2	0.0000		-47.3500					-2.	0.0	0.0	180.4290	1	303
	3	1,000	160	4,000	2	-4,000	330							
1603304	KCO2OH +3	18.8490		-9.3900					3.	0.0	0.0	241.0074	1	304
	3	2,000	160	1,000	2	-1,000	330							
1601003	KCOOHCL AQ	4.5550		-7.4840					0.	0.0	0.0	164.8600	1	305
	4	1,000	160	1,000	2	-1,000	330	1,000	180					
1604920	KCUNO3 +	-5.2000		0.3990					1.	0.0	0.0	174.4040	1	306
	2	1,000	160	1,000	492									
1607320	KCOSO4 AQ	1.0500		2.4600					0.	0.0	0.0	200.4610	1	307
	2	1,000	160	1,000	732									
1607300	KCUHS +	0.0000		10.1700					1.	0.0	0.0	145.4720	1	308
	2	1,000	160	1,000	730									
1607301	KCU(HS)2 AQ	0.0000		16.5300					0.	0.0	0.0	178.5430	1	309
	2	1,000	160	2,000	730									
1607302	KCU(HS)3 -	0.0000		18.7100					-1.	0.0	0.0	211.6150	1	310
	2	1,000	160	3,000	730									
1607303	KCU(HS)4 -2	0.0000		20.9000					-2.	0.0	0.0	244.6870	1	311
	2	1,000	160	4,000	730									
1601300	KCUOH +	-0.0140		2.1700					1.	0.0	0.0	192.3040	1	451
	2	1,000	160	1,000	130									
1601301	KCUOH2 AQ	0.0000		2.8990					0.	0.0	0.0	272.2080	1	452
	2	1,000	160	2,000	130									
1603000	KCU3 +	-2.5700		2.1500					1.	0.0	0.0	239.3040	1	453

TABLE A.1. (contd)

											REFERENCE	MATEQ REACTION NUMBER
2.00 2		1.000 231	1.000 140									
2311401	KCU(CO3)2-2	0.0000	9.8300					-2.	0.0	0.0	183.5640	1	210
4.00 2		1.000 231	2.000 140									
2311000	KCUCL +	0.6500	0.4300					1.	4.0	0.0	98.9990	1	211
2		1.000 231	1.000 180									
2311001	KCUCL2 AQ	10.5000	0.1600					0.	0.0	0.0	134.4520	1	212
2		1.000 231	2.000 180									
2311002	KCUCL3 -	13.6900	-2.2900					-1.	4.0	0.0	169.9850	1	213
2		1.000 231	3.000 180									
2311003	KCUCL4 -2	17.7000	-4.5900					-2.	5.0	0.0	205.3500	1	214
2		1.000 231	4.000 180									
2312700	KCUF +	1.6200	1.2600					1.	0.0	0.0	82.5440	1	215
2		1.000 231	1.000 270									
2313300	KCUOH +	0.0000	-8.0000					1.	4.0	0.0	80.5530	1	216
3		1.000 231	1.000 2	-1.000 330									
2313301	KCU(OH)2 AQ	0.0000	-13.6800					0.	0.0	0.0	97.5600	1	217
3		1.000 231	2.000 2	-2.000 330									
2313302	KCU(OH)3 -	0.0000	-26.8990					-1.	0.0	0.0	114.5680	1	218
3		1.000 231	3.000 2	-3.000 330									
2313303	KCU(OH)4 -2	0.0000	-39.6000					-2.	0.0	0.0	131.5750	1	219
3		1.000 231	4.000 2	-4.000 330									
2313304	KCU2(OH)2+2	17.5590	-10.3590					2.	0.0	0.0	161.1060	1	220
3		2.000 231	2.000 2	-2.000 330									
2317320	KCUSO4 AQ	1.2200	2.3100					0.	0.0	0.0	159.6070	1	221
2		1.000 231	1.000 732										
2317300	KCU(HS)3 -	0.0000	25.8990					-1.	0.0	0.0	162.7610	1	222
2		1.000 231	3.000 730										
2311402	KCUHCO3 +	0.0000	13.000					1.	0.0	0.0	124.5630	1(B)	510
1.00 3		1.000 231	1.000 140	1.000 330									
2311410	KCU FULVATE	0.0000	6.1990					0.	0.0	0.0	713.5460	1	527
2		1.000 231	1.000 141										
2311420	KCU HUMATE	0.0000	6.1990					0.	0.0	0.0	2063.5450	1	528
2		1.000 231	1.000 142										
9501000	KZNCL +	7.7900	0.4300					1.	4.0	0.0	100.8230	1	251
2		1.000 950	1.000 180										
9501001	KZNCL2 AQ	8.5000	0.4500					0.	0.0	0.0	136.2760	1	252
2		1.000 950	2.000 180										
9501002	KZNCL3 -	9.5600	0.5000					-1.	4.0	0.0	171.7290	1	253
2		1.000 950	3.000 180										
9501003	KZNCL4 -2	10.9600	0.1990					-2.	5.0	0.0	207.1820	1	254
2		1.000 950	4.000 180										
9502700	KZNF +	2.2200	1.1500					1.	0.0	0.0	84.3680	1	255
2		1.000 950	1.000 270										
9503300	KZNOH +	13.3990	-8.9600					1.	0.0	0.0	82.3770	1	256
3		1.000 950	1.000 2	-1.000 330									
9503301	KZN(OH)2 AQ	0.0000	-16.8990					0.	0.0	0.0	99.3840	1	257
3		1.000 950	2.000 2	-2.000 330									
9503302	KZN(OH)3 -	0.0000	-28.3990					-1.	0.0	0.0	116.3920	1	258
3		1.000 950	3.000 2	-3.000 330									
9503303	KZN(OH)4 -2	0.0000	-41.1990					-2.	0.0	0.0	133.3990	1	259
3		1.000 950	4.000 2	-4.000 330									
9501004	KZNUHCL AQ	0.0000	-7.4800					0.	0.0	0.0	117.8300	1	260
4		1.000 950	1.000 2	-1.000 330	1.000 180								
9507300	KZN(HS)2 AQ	0.0000	14.9400					0.	0.0	0.0	131.5130	1	261
2		1.000 950	2.000 730										
9507301	KZN(HS)3 -	0.0100	16.1000					-1.	0.0	0.0	164.5850	1	262
2		1.000 950	3.000 730										
9507320	KZNSO4 AQ	1.3000	2.3700					0.	0.0	0.0	161.4310	1	263

TABLE A.1. (contd)

										REFERENCE	WATEQ REACTION NUMBER
2	1,000 281	3,000 180									
2813301 KFEOH2 +	0,0000	-5,6700				1, 5,4	0,0	89,8618		1	182
3	1,000 281	2,000 2	-2,000 330								
2813302 KFEOH3 AQ	0,0000	-13,6000				0, 0,0	0,0	106,8698		1	183
3	1,000 281	3,000 2	-3,000 330								
2813303 KFEOH4 -	0,0000	-21,6000				-1, 5,4	0,0	123,8768		1	184
3	1,000 281	4,000 2	-4,000 330								
2815001 KFEH2PO4 +2	0,0000	24,980				2, 5,4	0,0	152,8348		1(D)	156
3	1,000 281	1,000 568	2,000 330								
2812700 KFEF +2	2,6990	6,1990				2, 5,0	0,0	74,8458		1	165
2	1,000 281	1,000 270									
2812701 KFEF2 +	4,0000	10,0000				1, 5,0	0,0	93,8438		1	166
2	1,000 281	2,000 270									
2812702 KFEF3 AQ	5,3990	14,000				0, 0,0	0,0	112,8428		1	167
2	1,000 281	3,000 270									
2817321 KFE(SO4)2 -	4,6000	5,4200				-1, 0,0	0,0	247,9700		1	333
2	1,000 281	2,000 732									
2811410 KFE FULVATE	0,0000	9,3990				1, 0,0	0,0	785,8478		1	525
2	1,000 281	1,000 141									
2811420 KFE HUMATE	0,0000	9,3990				1, 0,0	0,0	2855,8468		1	526
2	1,000 281	1,000 142									
2813304 KFE2(OH)2+4	11,5000	-2,9500				4, 0,0	0,0	145,7888		1	334
3	2,000 281	2,000 2	-2,000 330								
2813305 KFE3(OH)4+5	14,3000	-6,3000				5, 0,0	0,0	235,5708		1	335
3	3,000 281	4,000 2	-4,000 330								
4407320 KL1804 -	0,0000	0,6400				-1, 5,0	0,0	103,8000		4	126
2	1,000 440	1,000 732									
8003300 KNHOH +	14,495	-13,170				1, 5,0	0,0	184,6278		4(A)	129
3	1,000 800	1,000 2	-1,000 330								
1003300 KBAOH +	15,495	-13,350				1, 5,0	0,0	154,3478		4(A)	130
3	1,000 100	1,000 2	-1,000 330								
4701000 KMNCL +	0,0000	0,6070				1, 5,0	0,0	90,3910		1	170
2	1,000 470	1,000 180									
4701001 KMNCL2 AQ	0,0000	0,0410				0, 0,0	0,0	125,8440		1	171
2	1,000 470	2,000 180									
4701002 KMNCL3 -	0,0000	-,30500				-1, 5,0	0,0	161,2970		1	172
2	1,000 470	3,000 180									
4703300 KMNOH +	14,3990	-10,5900				1, 5,0	0,0	161,2970		1	173
3	1,000 470	1,000 2	-1,000 330								
4703301 KMN(OH)3 -1	0,0000	-34,8000				-1, 5,0	0,0	105,9600		1	174
3	1,000 470	3,000 2	-3,000 330								
4702700 KMNF +	0,0000	0,8500				1, 5,0	0,0	73,9360		1	175
2	1,000 470	1,000 270									
4707320 KMNSO4 AQ	2,1700	2,2600				0, 0,0	0,0	150,9990		1	176
2	1,000 470	1,000 732									
4704920 KMN(NO3)2AQ	-0,3960	0,6000				0, 0,0	0,0	178,9470		1	177
2	1,000 470	2,000 492									
4701400 KMNHCO3 +	0,0000	11,600				1, 5,0	0,0	115,9550		1(B)	178
1,00 3	1,000 470	1,000 140	1,000 330								
2301000 KCUCL2 -	-0,42	5,5				-1, 4,0	0,0	134,452		1(F)	206
2	1,000 230	2,000 180									
2301001 KCUCL3 -2	0,20	5,70				-2, 5,0	0,0	169,905		1(F)	207
2	1,000 230	3,000 180									
2307300 KCU(SO4)2 -2	0,0	3,39				-3, 23,0	0,0	320,058		1(F)	485
4	1,000 230	2,000 730	6,000 731	-2,000 330							
2307301 KCUSO4S5 -1	0,0	2,66				-3, 25,0	0,0	352,122		1(F)	486
4	1,000 230	2,000 730	7,000 731	-2,000 330							
2311400 KCUCO3 AQ	0,0000	6,7300				0, 0,0	0,0	123,5550		1	209

TABLE A.1. (contd)

									REFERENCE	RATEQ REACTION NUMBER
1.00 3		1.000 500		1.000 100		1.000 330				
5007320	KNASO4 -	1.1200		0.7000			-1.	5.4 0.0 119.0510	1	71
2		1.000 500		1.000 732						
5005800	KNAHPO4 -	0.0000		12.636			-1.	5.4 0.0 118.9690	1(C)	30
3		1.000 500		1.000 580		1.000 330				
5002700	KNAF AQ	0.0000		-0.9560			0.	0.0 0.0 41.9880	2	540
2		1.000 500		1.000 270						
4107320	KKSO4 -	2.2500		0.0500			-1.	5.4 0.0 135.1630	1	72
2		1.000 410		1.000 732						
4105800	KKHPO4 -	0.0000		12.640			-1.	5.4 0.0 135.0810	1(C)	32
3		1.000 410		1.000 580		1.000 330				
0303300	KALOH +2	11.0990		-4.9900			2.	5.4 0.0 43.9880	1	80
3		1.000 30		1.000 2		-1.000 330				
0303301	KAL(OH)2 +	0.0000		-10.1000			1.	5.4 0.0 68.9960	1	81
3		1.000 30		2.000 2		-2.000 330				
0303302	KAL(OH)4 -	44.0000		-23.0000			-1.	4.5 0.0 95.0110	1	82
3		1.000 30		4.000 2		-4.000 330				
0302700	KALF +2	0.0000		7.0100			2.	5.4 0.0 45.9790	4	83
2		1.000 30		1.000 270						
0302701	KALF2 +	20.0000		12.7500			1.	5.4 0.0 64.9780	4	84
2		1.000 30		2.000 270						
0302702	KALF3 AQ	2.5000		17.0200			0.	0.0 0.0 83.9760	4	85
2		1.000 30		3.000 270						
0302703	KALF4 -	0.0000		19.7200			-1.	4.5 0.0 102.9750	4	86
2		1.000 30		4.000 270						
0307320	KALSO4 +	2.1500		3.0200			1.	4.5 0.0 123.0430	1	87
2		1.000 30		1.000 732						
0307321	KAL(SO4)2 -	2.8400		4.9200			-1.	4.5 0.0 219.1040	1	88
2		1.000 30		2.000 732						
0303303	KAL(OH)3 AQ	0.0000		-16.0000			0.	0.0 0.0 78.0030	1	336
3		1.000 30		3.000 2		-3.000 330				
2803300	KFEOH +	13.1990		-9.5800			1.	5.0 0.0 72.8540	1	2
3		1.000 280		1.000 2		-1.000 330				
2803301	KFEOH3 -1	30.3000		-31.0000			-1.	5.0 0.0 106.8690	1	3
3		1.000 280		3.000 2		-3.000 330				
2807320	KFESO4 AQ	3.2300		2.2500			0.	0.0 0.0 151.9080	1	8
2		1.000 280		1.000 732						
2805000	KFEH2PO4 +	0.0000		22.253			1.	5.4 0.0 152.8340	4(D)	120
3		1.000 280		1.000 580		2.000 330				
2803302	KFEOH2 AQ	20.5650		-20.5700			0.	0.0 0.0 89.8610	4	105
3		1.000 280		2.000 2		-2.000 330				
2805001	KFEHPO4 AQ	0.0000		15.950			0.	0.0 0.0 151.8260	4(C)	138
3		1.000 280		1.000 580		1.000 330				
2807300	KFE(HS)2 AQ	0.0000		8.9500			0.	0.0 0.0 121.9900	1	476
2		1.000 280		2.000 730						
2807301	KFE(HS)3 -	0.0000		10.9870			-1.	0.0 0.0 155.0620	1	477
2		1.000 280		3.000 730						
2813300	KFEOH +2	10.5990		-2.1900			2.	5.0 0.0 72.8540	1	1
3		1.000 281		1.000 2		-1.000 330				
2815000	KFEHPO4 +	-7.500		17.780			1.	5.4 0.0 151.8260	1(C)	139
3		1.000 281		1.000 580		1.000 330				
2817320	KFESO4 +	3.9100		3.9200			1.	5.0 0.0 151.9080	1	4
2		1.000 281		1.000 732						
2811000	KFECL +2	5.0000		1.4800			2.	5.0 0.0 91.3000	1	5
2		1.000 281		1.000 180						
2811001	KFECL2 +	0.0000		2.1300			1.	5.0 0.0 126.7530	1	6
2		1.000 281		2.000 180						
2811002	KFECL3 AQ	0.0000		1.1300			0.	0.0 0.0 162.2060	1	7

TABLE A.1. (contd)

													REFERENCE	RATEQ REACTION NUMBER
3300020	K OH-		15.345	-13.998					-1.	5.5	0.0	17.0074	4	152
2	1.000	2	-1.000	330										
3307700	KH3SIO4 -		8.9350	-9.9300					-1.	4.0	0.0	95.1070	4	13
2	1.000	770	-1.000	330										
3307701	KH2SIO4 -2		29.7140	-21.6190					-2.	5.4	0.0	94.0990	4	14
2	1.000	770	-2.000	330										
7702700	KSIF6 -2		-16.2600	30.1000					-2.	5.0	0.0	142.0760	1	201
4	1.000	770	6.000	270	4.000	330	-4.000	2						
3300900	KH2BO3 -1		3.2240	-9.2400					-1.	2.5	0.0	60.0250	4	25
2	1.000	90	-1.000	330										
0902700	KBF(OH)3 -		1.6500	-0.3990					-1.	2.5	0.0	88.8510	1	161
2	1.000	90	1.000	270										
0902701	KBF2(OH)2 -		1.63500	7.63000					-1.	2.5	0.0	82.8220	1(A)	162
4	1.000	90	2.000	270	-1.000	2	1.000	330						
0902702	KBF3OH -		-1.5000	13.66700					-1.	2.5	0.0	84.8130	1(A)	163
4	1.000	90	3.000	270	-2.000	2	2.000	330						
0902703	KBF4 -		-1.7950	20.27400					-1.	2.5	0.0	86.0040	1(A)	164
4	1.000	90	4.000	270	-3.000	2	3.000	330						
3304900	KNH3 AQ		12.4000	-9.2520					0.	0.0	0.0	17.0300	4	26
2	1.000	490	-1.000	330										
4907320	KNH4SO4 -		0.0000	1.1180					-1.	5.0	0.0	114.1000	4	131
2	1.000	490	1.000	732										
4603300	KMGOH +		15.955	-11.79					1.	6.5	0.0	41.3190	1(A)	24
3	1.000	460	1.000	2	-1.000	330								
4602700	KMGF +		4.6740	1.0200					1.	4.5	0.0	43.3100	4	22
2	1.000	460	1.000	270										
4601400	KMGCO3 AQ		2.0220	2.9800					0.	0.0	0.0	84.3210	1	73
2.00 2	1.000	460	1.000	140										
4601401	KMGHCO3 +		-2.430	11.400					1.	4.0	0.0	85.3290	1(B)	74
1.00 3	1.000	460	1.000	140	1.000	330								
4607320	KMGSO4 AQ		1.5990	2.2500					0.	0.0	0.0	120.3730	1	75
2	1.000	460	1.000	732										
4605800	KMGPO4 -		3.1000	6.5090					-1.	5.4	0.0	119.2830	4	123
2	1.000	460	1.000	580										
4605801	KMGH2PO4 +		-1.140	21.066					1.	5.4	0.0	121.2990	4(D)	124
3	1.000	460	1.000	580	2.000	330								
4605802	KMGHPO4 AQ		-0.230	15.220					0.	0.0	0.0	120.2910	4(C)	33
3	1.000	460	1.000	580	1.000	330								
1503300	KCAOH +		14.535	-12.598					1.	6.0	0.0	57.0870	4(A)	76
3	1.000	150	1.000	2	-1.000	330								
1501400	KCAHCO3 +		1.7900	11.330					1.	6.0	0.0	101.0970	4(B)	77
1.00 3	1.000	150	1.000	140	1.000	330								
1501401	KCACO3 AQ		4.0300	3.1500					0.	0.0	0.0	100.0890	1	78
2.00 2	1.000	150	1.000	140										
1507320	KCASO4 AQ		1.4700	2.3090					0.	0.0	0.0	136.1410	1	23
2	1.000	150	1.000	732										
1505800	KCAHPO4 AQ		-0.230	15.085					0.	0.0	0.0	136.0590	4(C)	34
3	1.000	150	1.000	580	1.000	330								
1505801	KCAPO4 -		3.1000	6.4590					-1.	5.4	0.0	135.0510	4	121
2	1.000	150	1.000	580										
1505802	KCAH2PO4 +		-1.120	20.960					1.	5.4	0.0	137.0670	4(D)	122
3	1.000	150	1.000	580	2.000	330								
1502700	KCAF +		3.7980	0.9400					1.	5.0	0	59.0780	1	160
2	1.000	150	1.000	270										
5001400	KNACO3 -		8.9110	1.2680					-1.	5.4	0.0	82.9990	4	69
2.00 2	1.000	500	1.000	140										
5001401	KNAHCO3 AQ		0.0000	10.0800					0.	0.0	0.0	84.0070	4(B)	70

TABLE A.2. Thermochemical Data for Redox Reactions and Gases (Default Type VI)

													REFERENCE	WATEQ REACTION NUMBER
2812000	FE+3/FE+2	-10.0	13.032										1	1
3	1.000	281	-1.000	280	1.000	1								
4700020	KMNO4 -	176.6200	-127.0240				-1.	5.0	0.0	118.9350			1	179
4	1.000	470	4.000	2	-8.000	330	-5.000	1						
4700021	KMNO4 -2	136.0200	-118.4400				-2.	5.0	0.0	118.9350			1	180
4	1.000	470	4.000	2	-8.000	330	-4.000	1						
4914920	NO2/NO3	-43.76	28.57										1	400
5	1.000	492	-1.000	491	2.000	330	2.000	1	-1.000	2				
4984920	NH4/NO3	-187.055	119.077										1	127
5	-1.000	490	1.000	492	-3.000	2	10.000	330	8.000	1				
0600610	AS03/AS04	-50.015	19.444										1	487
5	1.000	61	2.000	1	2.000	330	-1.000	60	-1.000	2				
8900930	U+3/UO2+2	-10.05	0.420										2(F)	---
5	1.000	893	3.000	1	4.000	330	-1.000	890	-2.000	2				
8910930	U+4/UO2+2	-34.43	9.216										2	542
5	1.000	895	2.000	1	4.000	330	-1.000	891	-2.000	2				
8920930	UO2+/UO2+2	-3.50	2.785										2	573
3	1.000	893	1.000	1	-1.000	892								
4714700	MN+3/MN+2	25.700	-25.507										1	169
3	1.000	470	-1.000	1	-1.000	471								
2302310	CU+1/CU+2	1.65	2.72										1	208
3	1.000	251	1.000	1	-1.000	250								
7307320	HS-/SO4-2	-60.14	33.66										4(A)	90
5	1.000	732	9.000	330	8.000	1	-1.000	730	-4.000	2				
3381404	CH4(GAS)	-61.0	41.00									16.0432	4(B)	94
4	1.000	140	8.000	1	10.000	330	-3.000	2						
3381403	CU2(GAS)	-11.55	18.16									41.0100	4(G)	137
3	1.000	140	2.000	330	-1.000	2								
3300021	O2(AQ) SATO		-45.54									31.9988	4	136
3	2.000	2	-4.000	330	-4.000	1								
3300022	O2(AQ) CALC	155.65	-85.98									31.9988	4	151
3	2.000	2	-4.000	330	-4.000	1								
8913505	KUO(OH)15+9 0		-17.229				9.	0.0	0.0	1683.2846			2	550
3	6.000	891	15.000	2	-15.000	330								
3300023	O2(GAS)	156.65	-85.120										4	93
3	2.000	002	-4.000	330	-4.000	001								

TABLE A.3. Thermochemical Data for Minerals and Solids (Default Type V or VI)

									REFERENCE	RATED REACTION NUMBER
2889100	URANINITE	18.630	4.700	.000	.000			270.0278	2	551
3	-4.000 330	1.000 891	2.000 2							
2889101	UO2 (AM)	26.230	-.934	.000	.000			270.0278	2	552
3	-4.000 330	1.000 891	2.000 2							
3089103	U4O9 (C)	101.235	3.384	.000	-3.000			1096.1196	2	553
4	-18.000 330	-2.000 1	4.000 891	9.000 2						
3089101	U3O8 (C)	116.020	-21.107	.000	-34.589			842.0822	2	554
4	-16.000 330	-4.000 1	3.000 891	8.000 2						
8089100	U8IO4 (C)	14.540	7.620	.000	.000			330.1121	2	555
3	-4.000 330	1.000 891	1.000 770							
4289100	UF4 (C)	18.980	18.000	.000	.000			314.0226	2	562
2	1.000 891	4.000 270								
4289101	UF4,2.5H2O	.588	27.579	.000	.000			359.0606	2	563
3	1.000 891	4.000 270	2.500 2							
7089100	UHPO4)2,4H2O	-3.840	51.584	.000	.000			582.0486	2	571
4	1.000 891	2.000 580	2.000 330	4.000 2						
7015000	NINGYOITE	2.278	53.906	.000	.000			584.0822	2	572
4	1.000 891	1.000 150	2.000 580	2.000 2						
2089300	UO3 (C)	19.315	-7.719	.000	.000			286.0272	2	577
3	-2.000 330	1.000 893	1.000 2							
2089301	GUMMITE	23.815	-10.403	.000	.000			286.0272	2	578
3	-2.000 330	1.000 893	1.000 2							
2089302	B-UO2(OH)2	15.730	-5.544	.000	.000			304.0424	2	579
3	-2.000 330	1.000 893	2.000 2							
2089303	SCHOEPITE	12.045	-5.404	.000	.000			322.0576	2	580
3	-2.000 330	1.000 893	3.000 2							
5089300	RUTHERFORDIN	1.448	14.439	.000	.000			330.0370	2	584
2	1.000 893	1.000 140								
7089300	(UO2)3(PO4)2	-94.900	49.037	129.134	.000			1000.0262	2	597
2	3.000 893	2.000 580								
7089301	H-AUTUNITE	3.680	47.931	.000	.000			732.0144	2	598
3	2.000 330	2.000 893	2.000 580							
7050000	NA-AUTUNITE	.460	47.409	.000	.000			775.9780	2	599
3	2.000 580	2.000 893	2.000 580							
7041000	K-AUTUNITE	-5.860	48.244	.000	.000			808.2024	2	600
3	2.000 410	2.000 893	2.000 580							
7049000	URAMPHITE	-9.700	51.749	.000	.000			766.0756	2	601
3	2.000 893	2.000 490	2.000 580							
7046000	SALEEITE	20.100	43.646	.000	.000			754.3104	2	602
3	2.000 893	1.000 460	2.000 580							
7015001	AUTUNITE	14.340	43.927	.000	.000			778.0784	2	603
3	2.000 893	1.000 150	2.000 580							
7080000	SR-AUTUNITE	13.050	44.457	.000	.000			817.6184	2	604
3	2.000 893	1.000 000	2.000 580							
7010000	URANOCIRCITE	10.100	44.031	.000	.000			867.3384	2	605
3	2.000 893	1.000 100	2.000 580							
7028000	BASSEITE	19.900	44.485	.000	.000			785.8454	2	606
3	2.000 893	1.000 280	2.000 580							
7023102	TORBERNITE	15.900	45.279	.000	.000			793.5444	2	607
3	2.000 893	1.000 231	2.000 580							
7060000	PHZNEVALSKIT	11.000	44.365	.000	.000			937.1063	2	608
3	2.000 893	1.000 000	2.000 580							
8015000	URANOPHANE	.000	-17.490	.000	.000			766.5176	2	610
4	-6.000 330	2.000 893	1.000 150	2.000 770						
5189300	UO2NO3)2	20.140	-12.369	.000	.000			394.0380	6	---
2	1.000 893	2.000 492								
5189301	UO2NO3,2H2O	6.060	-4.851	.000	.000			430.0690	6	---

TABLE A.3. (cqntd)

									REFERENCE	WATEQ REACTION NUMBER
3	1.000 893	2.000 492	2.000 2							
5169302 UO2NO3,3H2O		2.485	-3.642	.000	.000			448.0840	6	---
3	1.000 893	2.000 492	3.000 2							
5169305 UO2NO3,6H2O		-4.770	-2.500	.000	.000			502.1300	6	---
3	1.000 893	2.000 492	6.000 2							
2003000 ALOH3(A)		27.045	-10.588	-9.690	.000			78.0073	4(A)	140
3	1.000 30	3.000 2	-3.000 330							
6003000 ALOHSO4		.000	3.430	3.390	3.070			140.0505	1	471
4	-1.000 330	1.000 30	1.000 732	1.000 2						
6003001 AL4(OH)10SO4		.000	-22.700	.000	.000			374.0616	1	472
4	-10.000 330	4.000 30	1.000 732	10.000 2						
6041000 ALUM K		-7.220	5.170	.000	.000			438.3597	1	338
4	1.000 410	1.000 30	2.000 732	12.000 2						
6041001 ALUNITE		-3.918	1.546	.000	.000			414.2141	4(A)	50
5	1.000 410	3.000 30	2.000 732	6.000 2	-6.000 330					
6015000 ANHYDRITE		3.769	4.637	.000	.000			136.1416	4	17
2	1.000 150	1.000 732								
5015000 ARAGONITE		2.615	8.360	.000	.000			100.0894	1	21
2	1.000 150	1.000 140								
5046000 ARTINITE		20.742	-9.000	.000	.000			196.6941	1	150
4	-2.000 330	2.000 460	1.000 140	5.000 2						
4210000 BAF2		-1.000	5.760	6.740	4.650			175.3368	1	398
2	1.000 100	2.000 270								
6010000 BARITE		-6.288	9.976	.000	9.773			233.4016	1	144
2	1.000 100	1.000 732								
2003001 BOEHMITE		20.138	-8.578	-8.065	.000			59.9884	4(A)	52
3	-3.000 330	1.000 30	2.000 2							
2046000 BRUCITE		25.848	-16.792	.000	.000			58.3268	4(A)	19
3	1.000 460	2.000 2	-2.000 330							
5015001 CALCITE		2.585	8.475	8.560	.000			100.0894	1	12
2	1.000 150	1.000 140								
6000000 CELESTITE		.470	6.465	.000	6.549			183.6816	1	143
2	1.000 000	1.000 732								
2077000 CHALCEDONY		-4.615	3.523	.000	.000			60.0848	4	97
2	-2.000 2	1.000 770								
8646000 CHRYSOTILE		52.485	-32.180	.000	.000			277.1349	4(A)	20
4	-6.000 330	3.000 460	2.000 770	1.000 2						
8246000 CLINOENSTITE		20.015	-11.330	-10.972	-11.632			100.3964	4(A)	29
4	-1.000 2	1.000 460	1.000 770	-2.000 330						
2077001 CRISTOBALITE		-5.500	3.587	.000	.000			60.0848	4	99
2	-2.000 2	1.000 770								
2003002 DIASPORE		24.630	-6.873	.000	.000			59.9884	4(A)	154
3	-3.000 330	1.000 30	2.000 2							
8215000 DIOPSIDE		32.280	-19.086	.000	.000			216.5600	4(A)	28
5	-2.000 2	1.000 150	1.000 460	2.000 770	-4.000 330					
5015002 DOLOMITE		8.298	17.000	.000	.000			184.4106	4	11
3	1.000 150	1.000 460	2.000 140							
6046000 EPSOMITE		-2.820	2.140	.000	.000			246.4807	1	340
3	1.000 460	1.000 732	7.000 2							
8646003 SEPIOLITE(C)		27.268	-15.913	.000	.000			323.9313	4(A)	36
4	-.500 2	2.000 460	3.000 770	-4.000 330						
2028100 FERRIHYDRITE		.000	-4.891	-1.557	-4.996			104.8692	4	112
3	-3.000 330	1.000 281	3.000 2							
2028101 FE3(OH)8		.000	-20.222	-17.112	-24.105			297.6002	1	419
4	-8.000 330	2.000 281	1.000 280	8.000 2						
4128100 FEOH)2.7CL.3		.000	3.040	.000	.000			110.4029	1	181
4	-2.700 330	1.000 281	2.700 2	.300 180						
1026000 FES PPT		.000	3.915	.000	.000			85.9110	4	119

TABLE A.3. (contd)

										REFERENCE	WATEQ REACTION NUMBER
	3	-1.000 3SH	1.000 280	1.000 730							
6828100	FE2(SO4)3	59.120	-3.500	.650	.000			395.8788		1	481
	2	2.000 2H1	3.000 732								
7815002	FCOSAPATITE	-39.398	114.400	.000	.000			967.3670		1	396
	6	9.496 150	.360 580	.144 460	4.000 580	1.200 140	2.400 270				
4215000	FLUORITE	-4.710	10.900	.000	.000			78.0768		1	62
	2	1.000 15H	2.000 270								
8046000	FORSTERITE	40.510	-20.290	.000	.000			236.8234		4(A)	27
	3	-4.000 33H	2.000 460	1.000 770							
2003003	GIBBSITE (C)	22.800	-8.770	-8.487	-9.440			78.0037		1	51
	3	-3.000 330	1.000 38	3.000 2							
2028102	GOETHITE	14.480	-.500	.000	.000			86.8536		1	110
	3	-3.000 330	1.000 281	2.000 2							
8628000	GREENALITE	.000	-20.010	.000	.000			365.7393		1	111
	4	-6.000 33H	3.000 280	2.000 770	1.000 2						
1028001	GREIGITE	.000	45.035	.000	.000			289.7970		1	118
	4	-4.000 33H	2.000 281	1.000 280	4.000 730						
6015001	GYPSUM	-.261	4.840	.000	.000			172.1722		4	18
	3	1.000 15H	1.000 732	2.000 2							
4150000	HALITE	-.918	-1.582	.000	.000			58.4428		4	64
	2	1.000 500	1.000 180								
2028105	HEMATITE	30.845	4.000	.000	.000			155.6919		4	108
	3	-6.000 33H	2.000 281	3.000 2							
5015003	HUNTITE	25.760	29.960	.000	.000			353.8536		4	117
	3	3.000 46H	1.000 150	4.000 140							
5046001	HYDROMAGNESIT	52.210	8.760	.000	.000			467.6736		4(A)	38
	4	5.000 460	4.000 140	-2.000 330	6.000 2						
6058000	JAROSITE NA	36.180	11.200	.000	.000			478.6978		1	284
	5	-6.000 33A	1.000 580	3.000 281	2.000 732	6.000 2					
6041002	JAROSITE K	31.280	14.800	.000	.000			494.8100		1	285
	5	-6.000 33H	1.000 410	3.000 281	2.000 732	6.000 2					
6028101	JAROSITE H	35.150	12.100	.000	.000			480.7320		1	337
	4	-5.000 33H	3.000 281	2.000 732	7.000 2						
1028002	MACNINAWITE	.000	4.640	.000	.000			87.9110		4	67
	3	-1.000 33H	1.000 280	1.000 730							
8450000	MAGADIITE	.000	14.300	.000	.000			532.6521		4	98
	4	-1.000 33H	-9.000 2	1.000 500	7.000 770						
2028104	MAGHEMITE	.000	-6.386	.000	.000			159.6922		4	109
	3	-6.000 33H	2.000 281	3.000 2							
5046002	MAGNESITE	0.169	8.029	6.279	7.779			84.3214		4	10
	2	1.000 46H	1.000 140								
3028000	MAGNETITE	30.460	-3.737	-3.567	-6.595			231.5386		1	107
	4	-8.000 33H	2.000 281	1.000 280	4.000 2						
6028000	MELANTERITE	-2.860	2.470	.000	.000			278.0157		1	339
	3	1.000 28H	1.000 732	7.000 2							
6050001	MIRABILITE	-18.987	1.114	.000	.000			322.1942		4	66
	3	2.000 50H	1.000 732	10.000 2							
3050000	NATRON	-15.745	1.511	.000	.000			286.1420		4	60
	3	2.000 50H	1.000 140	10.000 2							
5046003	NESQUEHONITE	5.789	5.621	5.133	4.546			138.3673		1	149
	3	1.000 46H	1.000 140	3.000 2							
8646001	PHLOGOPITE	66.300	-66.300	.000	.000			417.2865		1	44
	5	-10.000 33H	1.000 410	3.000 46H	1.000 5H	3.000 770					
1028003	PYRITE	-11.300	18.479	.000	.000			119.9750		4	114
	4	-2.000 33H	-2.000 1	1.000 280	2.000 73H						
2077002	QUARTZ	-6.220	4.000	.000	.000			60.0848		4	101
	2	-2.000 2	1.000 770								
8646004	SEPIOLITE(A)	.000	-18.760	.000	.000			323.9540		4(A)	153

TABLE A.3. (contd)

										REFERENCE	RATED REACTION NUMBER
4	-.500 2	2.000 460	3.000 770	-4.000 330							
5028000	SIDERITE	5.328	10.550	14.104	.000			115.8564		4	9
2	1.000 280	1.000 140									
2077003	SIO2(A,GL)	-4.440	3.010	.000	.000			60.0848		4	180
2	-2.000 2	1.000 770									
2077004	SIO2(A,PT)	-3.910	2.710	.000	.000			60.0848		1	395
2	-2.000 2	1.000 770									
4208000	SRF2	-1.250	8.540	9.120	.000			125.6168		1	399
2	1.000 800	2.000 270									
7028100	STRENGITE	2.030	26.400	29.123	26.235			186.8490		4	146
3	1.000 281	1.000 580	2.000 2								
5088000	STRONTIANITE	.690	9.250	11.789	.000			147.6294		1	142
2	1.000 800	1.000 140									
8646002	TALC	35.005	-23.055	-18.988	-23.088			379.2888		4(A)	37
4	-4.000 2	3.000 460	4.000 770	-6.000 330							
6050002	THENARDITE	.572	.179	.000	.000			142.0412		4	65
2	2.000 500	1.000 732									
5050001	THERMONATR	2.802	-.125	.000	.000			124.0043		4	61
3	2.000 500	1.000 140	1.000 2								
8215001	TREMOLITE	96.615	-56.546	.000	.000			812.4696		4(A)	31
5	-8.000 2	2.000 150	5.000 460	8.000 770	-14.000 330						
7028001	VIVIANITE	.000	36.000	.000	.000			501.6062		4	106
3	3.000 280	2.000 580	8.000 2								
5010000	WITHERITE	-.360	8.585	13.335	.000			197.3494		1	145
2	1.000 100	1.000 140									
2047000	PYROLUSITE	29.180	-15.861	.000	-16.038			86.9368		1	183
4	-4.000 330	-1.000 1	1.000 471	2.000 2							
2047001	BIRNESSITE	.000	-18.091	.000	.000			86.9368		1	184
4	-4.000 330	-1.000 1	1.000 471	2.000 2							
2047002	NSUTITE	.000	-17.504	.000	.000			86.9368		1	185
4	-4.000 330	-1.000 1	1.000 471	2.000 2							
3047100	BIXBYITE	15.245	.611	2.226	.430			157.8742		1	186
3	-6.000 330	2.000 471	3.000 2								
3047000	HAUSMANNITE	80.140	-61.540	.000	.000			228.8116		1	187
4	-8.000 330	-2.000 1	3.000 470	4.000 2							
2047003	PYROCHOITE	22.590	-15.088	.000	-15.381			88.9528		1	188
3	-2.000 330	1.000 470	2.000 2								
2047100	MANGANITE	.000	.238	.000	.000			87.9448		1	189
3	-3.000 330	1.000 471	2.000 2								
5047000	RHODOCHROSIT	2.079	10.410	11.019	9.993			114.9474		1	190
2	1.000 470	1.000 140									
4147000	MNCL2, 4H2O	-17.380	-2.718	.000	.000			197.9052		1	191
3	1.000 470	2.000 180	4.000 2								
1047000	MNS GREEN	5.790	-3.000	.000	.000			87.0020		1	192
3	-1.000 330	1.000 470	1.000 730								
6047000	MNSO4	15.480	-2.669	.000	.000			150.9996		1	182
2	1.000 470	1.000 732									
6047100	MN2(SO4)3	39.060	5.711	.000	.000			398.0600		1	134
2	2.000 471	3.000 732									
7047000	MN3(PO4)2	-2.120	25.027	.000	.000			354.7568		1	193
2	3.000 470	2.000 580									
3041000	A-CRYPTOMELN	.000	.000	.000	.000			775.7382		1	195
5	-34.000 330	16.000 471	.800 410	17.000 2	-7.400 470						
3010000	HOLLANDITE	.000	.000	.000	.000			817.4214		1	196
6	-32.000 330	14.000 471	.820 100	.570 280	16.000 2	-6.410 470					
3015000	TODOKOKITE	.000	.000	.000	.000			592.4641		1	198
6	-24.000 330	.393 150	.473 460	10.000 471	14.000 2	-3.866 470					
3044000	LITHIOPHORIT	.000	.000	.000	.000			1953.3934		1	199

TABLE A.3. (contd)

										REFERENCE	WATEQ REACTION NUMBER
6	-70,000	330	2,000	440	8,000	30	20,000	471	49,000 2 -8,000 470		
3815001	RANCIEITE		,000		,000		,000		466,1930	1	208
5	-10,000	330	,440	150	8,000	471	12,000	2	-3,440 470		
0023000	CU METAL		-17,130	8,760	,000	8,000			63,5460	1	223
2	1,000	230	1,000	1							
4123000	NANTOKITE		-9,900	6,760	,000	6,630			98,9990	1	224
2	1,000	230	1,000	180							
4223000	CUF		12,370	-7,000	,000	,000			82,5444	1	225
2	1,000	230	1,000	270							
2023000	CUPRITE		-6,245	1,550	1,870	,700			143,0914	1	226
3	-2,000	330	2,000	230	1,000	2					
1023000	CHALCOCITE		-49,350	34,619	34,920	30,900			159,1560	1	227
3	-1,000	330	2,000	230	1,000	730					
1023001	DJURLEITE		-47,881	33,920	,000	,000			154,9620	1	247
4	-1,000	330	,066	231	1,000	230	1,000	730			
1023002	ANILITE		-43,535	31,070	,000	,000			143,2695	1	535
4	-1,000	330	,250	231	1,500	230	1,000	730			
1023003	BLAUBLEI II		,000	27,279	,000	,000			121,0284	1	534
4	-1,000	330	,600	231	,800	230	1,000	730			
1023100	BLAUBLEI I		,000	24,162	,000	,000			101,9646	1	533
4	-1,000	330	,900	231	,200	230	1,000	730			
1023101	COVELLITE		-24,010	23,030	,000	22,170			95,6100	1	246
3	-1,000	330	1,000	231	1,000	730					
6023000	CU2SO4		4,560	1,950	,000	,000			223,1536	1	228
2	2,000	230	1,000	732							
3023000	CUPROUSFERIT		5,000	8,920	,000	6,000			151,3910	1	229
4	-4,000	330	1,000	230	1,000	201	2,000	2			
4123100	MELANOTHALLI		12,320	-3,730	,000	-4,450			134,4520	1	238
2	1,000	231	2,000	180							
5023100	CUCO3		,000	9,630	9,650	9,610			123,5552	1	231
2	1,000	231	1,000	140							
4223100	CUF2		13,320	,620	,000	,000			101,5420	1	232
2	1,000	231	2,000	270							
4223101	CUF2, 2H2O		3,650	4,550	,000	,000			137,5732	1	233
3	1,000	231	2,000	270	2,000	2					
2023100	CU(OH)2		15,250	-8,640	,000	-9,200			97,5606	1	234
3	-2,000	330	1,000	231	2,000	2					
4123101	ATACAMITE		18,690	-7,540	-7,240	-7,490			213,5669	1	237
4	-3,000	330	2,000	231	3,000	2	1,000	180			
5123100	CU2(OH)3NO3		17,350	-9,240	,000	-9,310			240,1186	1	238
4	-3,000	330	2,000	231	3,000	2	1,000	492			
6023100	ANTLERITE		,000	-8,290	,000	-8,900			354,7248	1	239
4	-4,000	330	3,000	231	4,000	2	1,000	732			
6023101	BROCHANTITE		,000	-15,340	-15,150	-15,500			452,2854	1	240
4	-6,000	330	4,000	231	6,000	2	1,000	732			
6023102	LANGITE		39,610	-16,790	,000	-17,400			470,3006	1	241
4	-6,000	330	4,000	231	7,000	2	1,000	732			
2023101	TENORITE		15,240	-7,620	-7,350	-7,490			79,5454	1	242
3	-2,000	330	1,000	231	1,000	2					
6023103	CUCUSO4		35,575	-11,930	,000	,000			239,1490	1	243
4	-2,000	330	2,000	231	1,000	2	1,000	732			
7023100	CU3(PO4)2		,000	36,050	,000	36,900			380,5000	1	244
2	3,000	231	2,000	580							
7023101	Cu3(PO4)2,3H		,000	35,120	,000	,000			434,6264	1	245
3	3,000	231	2,000	580	3,000	2					
6023104	CUSO4		10,140	-3,010	-2,650	-3,420			159,6036	1	247
2	1,000	231	1,000	732							
6023105	CHALCANTHITE		-1,440	2,040	2,900	2,135			249,6796	1	248

TABLE A.3. (contd)

								REFERENCE	MATEQ REACTION NUMBER
3	1,000 231	1,000 732	5,000 2						
2023102 DIOPTASE	8,960	-6,500	,000	,000			157,6449	1	420
3	-2,000 330	1,000 231	1,000 770						
3023100 CUPRICFERIT	38,690	-5,880	-5,350	,000			239,2376	1	249
4	-8,000 330	1,000 231	2,000 201	4,000 2					
1023102 CHALCOPYRITE	-35,480	35,270	,000	30,790			183,5130	1	250
4	-2,000 330	1,000 231	1,000 200	2,000 730					
4023000 CUOR	-13,880	8,210	,000	,000			143,4500	1	459
2	1,000 230	1,000 130							
4323000 CUI	-20,140	11,690	,000	,000			190,4505	1	460
2	1,000 230	1,000 380							
0095000 ZN METAL	36,780	-25,757	,000	-25,790			65,3800	1	265
2	1,000 950	2,000 1							
4195000 ZNCL2	17,480	-7,830	,000	-7,060			136,2860	1	267
2	1,000 950	2,000 180							
5095000 SMITHSONITE	4,360	10,000	10,810	9,820			125,3892	1	268
2	1,000 950	1,000 140							
5095001 ZNCO3, 1H2O	,000	10,660	,000	,000			143,4044	1	269
3	1,000 950	1,000 140	1,000 2						
4295000 ZNF2	13,080	1,520	,000	1,080			103,3768	1	270
2	1,000 950	2,000 270							
2095000 ZN(OH)2 (A)	,000	-12,450	-12,260	-12,480			99,3946	1	271
3	-2,000 330	1,000 950	2,000 2						
2095001 ZN(OH)2 (C)	,000	-12,200	,000	,000			99,3946	1	272
3	-2,000 330	1,000 950	2,000 2						
2095002 ZN(OH)2 (B)	,000	-11,750	-11,320	-11,890			99,3946	1	273
3	-2,000 330	1,000 950	2,000 2						
2095003 ZN(OH)2 (G)	,000	-11,710	-11,190	-11,840			99,3946	1	274
3	-2,000 330	1,000 950	2,000 2						
2095004 ZN(OH)2 (E)	,000	-11,500	-10,950	-11,620			99,3946	1	275
3	-2,000 330	1,000 950	2,000 2						
4195001 ZN2(OH)3CL	,000	-15,200	,000	,000			217,2349	1	276
4	-3,000 330	2,000 950	3,000 2	1,000 180					
4195002 ZN5(OH)8CL2	,000	-38,500	,000	,000			533,8644	1	277
4	-8,000 330	5,000 950	8,000 2	2,000 180					
6095000 ZN2(OH)2SO4	,000	-7,500	,000	,000			260,6322	1	278
4	-2,000 330	2,000 950	2,000 2	1,000 732					
6095001 ZN4(OH)6SO4	,000	-20,400	,000	,000			459,6214	1	279
4	-6,000 330	4,000 950	6,000 2	1,000 732					
5195000 ZNNO3)2,6H2O	-5,510	-3,440	,000	,000			297,4810	1	280
3	1,000 950	2,000 492	6,000 2						
2095005 ZNO(ACTIVE)	,000	-11,310	-11,570	-11,860			81,3794	1	281
3	-2,000 330	1,000 950	1,000 2						
2095006 ZINCITE	21,860	-11,140	-10,990	-11,540			81,3794	1	282
3	-2,000 330	1,000 950	1,000 2						
6095002 ZN3O(SO4)2	62,000	-19,020	,000	,000			404,2546	1	283
4	-2,000 330	3,000 950	2,000 732	1,000 2					
7095004 ZN3(PO4),4H	,000	32,040	,000	,000			458,1436	1	284
3	3,000 950	2,000 580	4,000 2						
1095000 ZNS (A)	-5,670	9,052	,000	,000			97,4400	1	285
3	-1,000 330	1,000 950	1,000 730						
1095001 SPHALERITE	-8,250	11,010	11,212	5,952			97,4400	1	286
3	-1,000 330	1,000 950	1,000 730						
1095002 WURTZITE	-5,060	9,682	10,182	8,552			97,4400	1	287
3	-1,000 330	1,000 950	1,000 730						
8295000 ZNSIO3	10,270	-2,930	,000	,000			141,4637	1	288
4	-2,000 330	-1,000 2	1,000 950	1,000 770					
8095000 WILLEMITE	33,370	-15,330	-13,350	,000			220,8431	1	289

TABLE A.3. (contd)

											REFERENCE	RATED REACTION NUMBER
	3	-4.000 330	2.000 950	1.000 770								
6095003	ZINCOSITE		19.200	-3.010	.000	-3.930				161.4376	1	290
	2	1.000 950	1.000 732									
6095004	ZN8U4, 1H2O		10.640	.570	.000	.500				179.4528	1	291
	3	1.000 950	1.000 732	1.000 2								
6095005	BIANCHITE		.160	1.765	.000	1.020				269.5288	1	292
	3	1.000 950	1.000 732	6.000 2								
6095006	GOSLARITE		-3.300	1.960	.000	1.870				287.5440	1	293
	3	1.000 950	1.000 732	7.000 2								
4095008	ZN8N2, 2H2O		7.510	-5.210	.000	.000				261.2184	1	461
	3	1.000 950	2.000 130	2.000 2								
4395008	ZNI2		13.440	-7.030	.000	.000				319.1890	1	462
	2	1.000 950	2.000 380									
0016000	CD METAL		10.000	-13.490	.000	-13.640				112.4100	1	312
	2	1.000 160	2.000 1									
0016001	GAMMA CD		10.140	-13.590	.000	.000				112.4100	1	313
	2	1.000 160	2.000 1									
5016000	OTAVITE		.500	13.740	19.810	11.210				172.4192	1	315
	2	1.000 160	1.000 148									
4116000	CDCL2		4.470	.600	.000	.470				183.3160	1	316
	2	1.000 160	2.000 180									
4116001	CDCL2, 1H2O		1.820	1.710	.000	.000				201.3312	1	317
	3	1.000 160	2.000 180	1.000 2								
4116002	CDCL2,2.5H2O		-1.710	1.940	.000	.000				228.3536	1	318
	3	1.000 160	2.000 180	2.500 2								
4216000	CDF2		9.720	2.980	.000	.000				150.4068	1	319
	2	1.000 160	2.000 270									
2016000	CD(OH)2 (A)		20.770	-13.730	-13.610	-14.300				146.4246	1	320
	3	-2.000 330	1.000 160	2.000 2								
2016001	CD(OH)2 (C)		.000	-13.650	.000	.000				146.4246	1	321
	3	-2.000 330	1.000 160	2.000 2								
4116003	CDOHCL		7.407	-3.520	-3.300	.000				164.8783	1	322
	4	-1.000 330	1.000 160	1.000 2		1.000 180						
6016000	CD3(OH)4SO4		.000	-22.560	.000	.000				501.3168	1	323
	4	-4.000 330	3.000 160	4.000 2		1.000 732						
6016001	CD3OH2(SO4)2		.000	-6.710	.000	.000				563.3598	1	324
	4	-2.000 330	3.000 160	2.000 2		2.000 732						
6016002	CD4(OH)6SO4		.000	-28.400	.000	.000				647.7414	1	325
	4	-6.000 330	4.000 160	6.000 2		1.000 732						
2016002	MONTEPONITE		24.760	-15.120	.000	-15.740				128.4094	1	326
	3	-2.000 330	1.000 160	1.000 2								
7016000	CD3(PO4)2		.000	32.600	.000	.000				527.1728	1	327
	2	3.000 160	2.000 580									
8216000	CUB103		10.630	-4.960	-7.960	.000				188.4937	1	328
	4	-1.000 2	1.000 160	1.000 770		-2.000 330						
6016003	CUSO4		14.740	.100	.130	.050				208.4676	1	329
	2	1.000 160	1.000 732									
6016004	CUSO4, 1H2O		7.520	1.657	1.680	1.630				226.4828	1	330
	3	1.000 160	1.000 732	1.000 2								
6016005	CUSO4,2.7H2O		4.300	1.873	1.890	1.860				256.3079	1	331
	3	1.000 160	1.000 732	2.670 2								
1016000	GREENOCKITE		-16.360	15.930	.000	13.112				144.4700	1	332
	3	-1.000 330	1.000 160	1.000 730								
4016000	CDBR2, 4H2O		-7.230	2.420	.000	.000				344.2788	1	463
	3	1.000 160	2.000 130	4.000 2								
4316000	CDI2		-4.000	5.610	.000	.000				366.2190	1	464
	2	1.000 160	2.000 380									
0060000	PB METAL		-.400	-4.270	-4.070	-4.310				207.2000	1	360

TABLE A.3. (contd)

										REFERENCE	RATED REACTION NUMBER
2	1,000 600	2,000 1									
4160000	COTUNNITE	-5,600	4,770	4,970	4,670			278,1000		1	362
2	1,000 600	2,000 180									
4160001	MATLOCKITE	-7,950	9,430	,000	8,000			261,6514		1	363
3	1,000 600	1,000 180	1,000 270								
4160002	PHOSGENITE	,000	19,010	19,940	,000			545,3152		1	364
3	2,000 600	2,000 180	1,000 140								
5060000	CERUSSITE	-4,860	13,130	13,440	12,830			267,2092		1	365
2	1,000 600	1,000 140									
4260000	PBF2	,700	7,440	7,570	,000			245,1968		1	366
2	1,000 600	2,000 270									
2060000	MASSICOT	16,780	-12,910	-12,790	,000			223,1994		1	367
3	-2,000 330	1,000 600	1,000 2								
2060001	LITHARGE	16,380	-12,720	-12,640	-13,070			223,1994		1	368
3	-2,000 330	1,000 600	1,000 2								
2060002	PBO, .3H2O	,000	-12,980	,000	,000			229,1444		1	369
3	-2,000 330	1,000 600	1,330 2								
5060001	PB2OCO3	11,460	,500	,780	,000			498,4006		1	370
4	-2,000 330	2,000 600	1,000 2	1,000 140							
6060000	LARNAKITE	6,440	,280	6,300	,000			526,4570		1	371
4	-2,000 330	2,000 600	1,000 732	1,000 2							
6060001	PB3O2SO4	20,750	-10,400	,000	,000			749,6564		1	372
4	-4,000 330	3,000 600	1,000 732	2,000 2							
6060002	PB4O3SO4	35,070	-22,100	,000	,000			972,8558		1	373
4	-6,000 330	4,000 600	1,000 732	3,000 2							
7060001	CLPYROMORPH	,000	84,430	,000	34,510			1356,3672		1	376
3	5,000 600	3,000 580	1,000 180								
7060002	HXYPYROMORPH	,000	62,790	,000	,000			1337,9215		1	377
4	-1,000 330	5,000 600	3,000.580	1,000 2							
5060002	PB3O2CO3	20,430	-11,020	,000	,000			713,6080		1	378
4	-4,000 330	3,000 600	1,000 140	2,000 2							
7060003	PLUMBGUMMITE	,000	32,790	,000	,000			581,1391		1	379
5	-5,000 330	1,000 600	3,000 30	2,000 580	6,000 2						
7060004	HINSDALITE	,000	2,500	,000	,000			581,2174		1	380
6	-6,000 330	1,000 600	3,000 30	1,000 580	1,000 732	6,000 002					
7060005	TSUMEBITE	,000	9,790	,000	,000			677,9849		1	381
5	-3,000 330	2,000 600	1,000 251	1,000 580	6,000 2						
8260000	PBSIO3	9,260	-7,320	-6,120	-7,640			283,2837		1	382
4	-1,000 2	-2,000 330	1,000 600	1,000 770							
8060000	PB2SIO4	26,000	-19,760	-19,220	-20,050			506,4831		1	383
3	-4,000 330	2,000 600	1,000 770								
6060003	ANGLESITE	-2,150	7,790	7,670	,000			303,2576		1	384
2	1,000 600	1,000 732									
1060001	GALENA	-19,400	15,132	16,452	13,682			239,2600		1	385
3	-1,000 330	1,000 600	1,000 730								
2060003	PLATTNERITE	70,730	-49,300	-49,000	,000			239,1988		1	386
4	-4,000 330	-2,000 1	1,000 600	2,000 2							
3060000	PB2O3	,000	-61,040	,000	,000			462,3982		1	387
4	-6,000 330	-2,000 1	2,000 600	3,000 2							
3060001	MINIUM	102,760	-73,690	-70,000	,000			685,5976		1	388
4	-8,000 330	-2,000 1	3,000 600	4,000 2							
2060004	PB(OH)2 (C)	13,990	-8,150	,000	-13,630			241,2146		1	389
3	-2,000 330	1,000 600	2,000 2								
4160003	LAURIONITE	,000	-,625	-,175	,000			259,6003		1	390
4	-1,000 330	1,000 600	1,000 180	1,000 2							
4160004	PB2(OH)3CL	,000	-8,745	,000	,000			500,8749		1	391
4	-3,000 330	2,000 600	3,000 2	1,000 180							
5060003	HYDCERRUSITE	,000	17,460	,000	,000			775,6330		1	392

TABLE A.3. (contd)

								REFERENCE	RATED REACTION NUMBER
4	-2.000 330	3.000 600	2.000 140	2.000 2					
2060005 PB2O(OH)2		.000	-26.200	.000	-27.100		464.4140	1	393
3	-4.000 330	2.000 600	3.000 2						
4060000 PBBR2		-8.100	5.160	5.340	4.410		367.0000	1	465
2	1.000 600	2.000 130							
4060001 PBBRF		.000	8.490	.000	.000		306.1024	1	466
3	1.000 600	1.000 130	1.000 270						
4360000 PBI2		-15.160	8.070	.000	.000		461.0090	1	467
2	1.000 600	2.000 380							
6060004 PB4(OH)6SO4		.000	-21.100	.000	.000		1026.9014	1	394
4	-6.000 330	4.000 600	1.000 732	6.000 2					
5054000 NICO3		9.040	6.040	.000	.000		118.7092	1	410
2	1.000 540	1.000 140							
2054000 NI(OH)2		-30.450	-18.000	-10.590	-13.500		92.7146	1	411
3	-2.000 330	1.000 540	2.000 2						
6054004 NI4(OH)6SO4		.000	-32.000	.000	.000		432.9014	1	412
4	-6.000 330	4.000 540	1.000 732	6.000 2					
2054001 BUNSENITE		23.920	-12.450	.000	-12.590		74.6994	1	413
3	-2.000 330	1.000 540	1.000 2						
7054000 NI3(PO4)2		.000	31.500	.000	.000		366.0428	1	414
2	3.000 540	2.000 580							
1054000 MILLERITE		-2.500	8.042	8.132	.000		90.7600	1	415
3	-1.000 330	1.000 540	1.000 750						
6054001 RETGERSITE		-1.100	2.040	.000	.000		262.0488	1	416
3	1.000 540	1.000 732	6.000 2						
6054002 MORENOSITE		-2.940	2.360	.000	.000		280.0640	1	417
3	1.000 540	1.000 732	7.000 2						
8054000 NI2SIO4		33.360	-14.540	.000	.000		209.4831	1	418
3	-4.000 330	2.000 540	1.000 770						
0002000 AG METAL		-25.234	13.510	.000	.000		107.8680	1	437
2	1.000 2H	1.000 1							
4002000 BROMYRITE		-20.170	12.270	.000	.000		187.7720	1	438
2	1.000 2H	1.000 130							
4102000 CERARGYRITE		-15.652	9.750	.000	.000		143.3210	1	439
2	1.000 2H	1.000 180							
5002000 AG2CO3		-9.530	11.070	.000	.000		275.7452	1	440
2	2.000 2H	1.000 140							
4202000 AGF.4H2O		-4.270	-.550	.000	.000		198.9272	1	441
3	1.000 2H	1.000 270	4.000 2						
4302000 IODYRITE		-26.820	16.070	.000	.000		234.7725	1	442
2	1.000 2H	1.000 380							
2002000 AG2O		10.430	-12.580	.000	.000		231.7354	1	443
3	-2.000 330	2.000 20	1.000 2						
7002000 AG3PO4		.000	17.550	.000	.000		418.5754	1	444
2	3.000 2H	1.000 580							
1002000 ACANTHITE		-53.300	36.050	.000	.000		247.7960	1	445
3	-1.000 330	2.000 20	1.000 750						
6002000 AG2SO4		-4.250	4.920	.000	.000		311.7936	1	446
2	2.000 2H	1.000 732							
8450001 ANALCIME		22.840	-6.719	.000	.000		220.1550	7	---
5	1.000 540	1.000 30	2.000 770	-1.000 2	-4.000 330				
8603000 HALLOYSITE		39.750	-8.994	.000	.000		258.1620	7	---
4	2.000 3H	2.000 770	1.000 2	-6.000 330					
8603001 KAOLINITE		35.280	-5.726	.000	.000		258.1620	7	---
4	2.000 3H	2.000 770	1.000 2	-6.000 330					
8415000 LEUNNARDITE		85.360	-16.490	.000	.000		922.8670	7	---
5	-1.000 2	-16.000 330	2.000 150	8.000 770	4.000 30				
845A002 LOW ALBITE		17.400	-2.592	.000	.000		262.2250	7	---

TABLE A.3. (contd)

												REFERENCE	WATEQ REACTION NUMBER
	5	1,000 5H	1,000	30	3,000	770	-4,000	330	-4,000	2			
8450003	ANALBITE		20,000	-3,500	,000		,000				262,2250	7	---
	5	1,000 5H	1,000	30	3,000	770	-4,000	330	-4,000	2			
8641000	MUSCOVITE		59,340	-12,990	,000		,000				398,3110	7	---
	4	1,000 4H	3,000	30	3,000	770	-10,000	330					
8641001	ANNITE		65,720	-23,490	,000		,000				511,0900	8	---
	5	1,000 4H	3,000	280	1,000	30	3,000	770	-10,000	330			
8415001	ANORTHITE		70,660	-25,430	,000		,000				278,2110	7	---
	4	1,000 1H	2,000	30	2,000	770	-6,000	330					
8603002	PYROPHYLLITE		,000	1,598	,000		,000				360,3138	9	---
	4	2,00H 3H	4,000	770	-4,000	2	-6,000	330					
8415002	LAUMONTITE		50,450	-14,460	,000		,000				470,4410	8	---
	4	1,000 1H	2,000	30	4,000	770	-6,000	330					
8415003	WAIRAKITE		63,150	-18,670	,000		,000				434,4110	8	---
	5	1,000 1H	2,000	30	4,000	770	-8,000	330	-2,000	2			
5023101	MALACHITE		15,610	5,100	,000		3,940				221,1162	10	---
	4	2,000 2H	2,000	2	1,000	140	-2,000	330					
5023102	AZURITE		23,770	16,920	,000		,000				344,6716	10	---
	4	3,000 2H	2,000	2	2,000	140	-2,000	330					
3006000	ARSENOLITE		-14,330	2,001	2,859		2,728				395,6824	1	497
	2	4,000 6H	-6,000	2									
3006001	CLAUDETITE		-13,290	3,065	,000		3,021				395,6824	1	498
	2	4,000 6H	-6,000	2									
4306000	AsI3		-1,875	-4,155	,000		,000				455,6347	1	499
	4	1,000 6H	3,000	380	3,000	330	-3,000	2					
1006000	ORIPMENT		-82,890	60,971	,000		46,004				246,0350	1	500
	4	2,000 6H	3,000	730	3,000	330	-6,000	2					
1006001	REALGAR		-38,545	19,747	26,574		,000				106,9855	1	501
	5	1,000 6H	1,000	730	2,000	330	1,000	1	-3,000	2			
3006100	AS2O5		5,485	-6,099	,000		-9,478				229,8400	1	488
	2	2,000 6I	-3,000	2									
5295000	ZN(BO2)2		,000	-8,290	,000		,000				150,9893	1	266
	4	-2,000 2	-2,000	330	1,000	950	2,000	98					
5216000	CD(BO2)2		,000	-9,840	,000		,000				198,0188	1	314
	4	-2,000 2	-2,000	330	1,000	160	2,000	98					
5260000	PB(BO2)2		5,000	-7,610	,000		,000				292,8093	1	361
	4	-2,000 2	-2,000	330	1,000	600	2,000	98					
7047001	MnHPO4(C)		,000	25,400	,000		,000				150,9174	1(C)	194
	3	1,000 4?0	1,000	580	1,000	330							
7060006	PbHPO4		,000	23,900	,000		,000				303,1693	1(C)	374
	3	1,000 6H0	1,000	580	1,000	330							
7060007	Pb3(PO4)2		,000	44,500	,000		,000				811,5125	1(C)	375
	2	3,000 6HA	2,000	580									
0073100	SULFUR		4,200	2,110	,000		,000				32,0640	1(H)	402
	3	1,000 73H	-1,000	330	-2,000	1							
7203000	ALASO4,2H		,000	-4,000	,000		,000				165,9006	1(I)	489
	4	1,000 3H	1,000	61	2,000	2	-3,000	330					
7215000	CA3(ASO4)2H		,000	-22,300	,000		,000				506,1700	1(I)	490
	4	3,000 1?H	2,000	61	4,000	2	-6,000	330					
7223100	CU3(ASO4)2H		,000	-6,100	,000		,000				576,5660	1(I)	491
	4	3,000 2I1	2,000	61	2,000	2	-6,000	330					
7228100	FEASO4,2H		,000	-,400	,000		,000				230,7967	1(I)	492
	4	1,000 2I1	1,000	61	2,000	2	-3,000	330					
7247000	MN3ASO42H		,000	-12,500	,000		,000				586,7746	1(I)	493
	4	3,000 47H	2,000	61	8,000	2	-6,000	330					
7254000	NI3(ASO4)2H		,000	-15,700	,000		,000				459,1707	1(I)	494
	4	3,000 54H	2,000	61	8,000	2	-6,000	330					
7260000	PB3(ASO4)2		,000	-5,000	,000		,000				899,4079	1(I)	495

TABLE A.3. (contd)

													REFERENCE	RATED REACTION NUMBER
3	3,000 000	2,000	61	-6,000 330										
7295000	ZN3AS0422.5H	,000	-13,650	,000	,000			518,9862					1(I)	496
4	3,000 950	2,000	61	2,500 2	-6,000 330									
7210000	BA(AS04)2	-2,640	8,910	,000	,000			689,8582					1(I)	541
3	3,000 100	2,000	61	-6,000 330										
2015000	LIME	46,265	-32,797	0	0			0					11	---
3	-2,000 330	1,000 150		1,000 002										
2015001	PORTLANDITE	30,690	-22,675	0	0			0					11	---
3	-2,000 330	1,000 150		2,000 002										
2020000	HUBITITE	24,846	-11,687	0	0			0					11	---
3	-2,000 330	0,947 280		1,000 002										
2046001	PERICLASE	56,135	-21,510	0	0			0					11	---
3	-2,000 330	1,000 460		1,000 002										
3020001	HERCYNITE	78,360	-27,162	0	0			0					11	---
4	-8,000 330	1,000 280		2,000 030	4,000 002									
3046000	SPINEL	84,089	-36,333	0	0			0					11	---
4	-8,000 330	1,000 460		2,000 030	4,000 002									
3046001	MAG-FERRITE	66,639	-16,765	0	0			0					11	---
4	-8,000 330	1,000 460		2,000 201	4,000 002									
4250000	CRYOLITE	-10,994	31,490	0	0			0					11	---
3	1,000 030	3,000 500		6,000 270										
8215002	WOLLASTONITE	19,498	-12,990	0	0			0					11	---
4	-1,000 002	-2,000 330		1,000 770	1,000 150									
8215003	P-WOLLSTANIT	21,066	-13,646	0	0			0					11	---
4	-1,000 002	-2,000 330		1,000 770	1,000 150									
8015001	CA-OLIVINE	54,695	-37,649	0	0			0					11	---
3	-4,000 330	1,000 770		2,000 150										
8015002	LARNITE	57,238	-39,141	0	0			0					11	---
3	-4,000 330	1,000 770		2,000 150										
8015007	CA3SIO5	106,335	-73,867	0	0			0					11	---
4	-6,000 330	1,000 770		3,000 150	1,000 002									
8015003	MONTICELLITE	49,421	-30,272	0	0			0					11	---
4	-4,000 330	1,000 770		1,000 150	1,000 460									
8015005	AKERMINITE	76,445	-47,472	0	0			0					11	---
5	-1,000 002	-6,000 330		2,000 770	2,000 150	1,000 460								
8015004	MERWINITE	107,111	-68,543	0	0			0					11	---
4	-8,000 330	2,000 770		1,000 460	3,000 150									
8441000	KALSILITE	28,919	-12,838	0	0			0					11	---
4	-4,000 330	1,000 770		1,000 030	1,000 410									
8441001	LEUCITE	22,885	-6,425	0	0			0					11	---
5	-2,000 002	-4,000 330		2,000 770	1,000 030	1,000 410								
8441002	MICROCLINE	12,309	-8,616	0	0			0					11	---
5	-4,000 002	-4,000 330		3,000 770	1,000 030	1,000 410								
8441003	H SANIDINE	14,252	-1,062	0	0			0					11	---
5	-4,000 002	-4,000 330		3,000 770	1,000 030	1,000 410								
8450004	NEPHELINE	33,204	-14,218	0	0			0					11	---
4	-4,000 330	1,000 770		1,000 030	1,000 500									
8015006	GEHLENITE	116,125	-56,822	0	0			0					11	---
5	-10,000 330	2,000 030		1,000 770	2,000 150	3,000 002								
2028103	LEPIDOCHROCIT	0	-1,371	0	0			0					11	---
3	-3,000 330	1,000 201		2,000 002										
8650000	NA-NONTRONIT	0	14,504	12,122	16,886			0					11	---
6	-7,320 330	-2,680 002		0,330 030	2,000 201	0,330 500		3,670 770						
8641002	K-NONTRONITE	0	15,549	12,765	18,334			0					11	---
6	-7,320 330	-2,680 002		0,330 030	2,000 201	0,330 410		3,670 770						
8615000	CA-NONTRONIT	0	20,889	19,057	22,722			0					11	---
6	-7,320 330	-2,680 002		0,330 030	2,000 201	0,167 150		3,670 770						
8646005	MG-NONTRONIT	0	20,589	19,013	22,165			0					11	---
6	-7,320 330	-2,680 002		0,330 030	2,000 201	0,167 460		3,670 770						