

EPA/600/3-91/021

March 1991

MINTEQA2/PRODEFA2, A GEOCHEMICAL ASSESSMENT MODEL  
FOR ENVIRONMENTAL SYSTEMS: VERSION 3.0 USER'S MANUAL

by

Jerry D. Allison<sup>+</sup>, David S. Brown, and Kevin J. Novo-Gradac<sup>\*</sup>

<sup>+</sup>Computer Sciences Corporation  
Environmental Research Laboratory  
Athens, Georgia 30605

Assessment Branch  
Environmental Research Laboratory  
Athens, Georgia 30605

<sup>\*</sup>Asci Corporation  
Environmental Research Laboratory  
Athens, Georgia 30605

ENVIRONMENTAL RESEARCH LABORATORY  
OFFICE OF RESEARCH AND DEVELOPMENT  
U.S. ENVIRONMENTAL PROTECTION AGENCY  
ATHENS, GEORGIA 30605

## DISCLAIMER

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the U.S. Environmental Protection Agency.

## FOREWORD

As environmental controls become more costly to implement and the penalties of judgment errors become more severe, environmental quality management requires more efficient management 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 Assessment Branch develops management or engineering tools to help pollution control officials achieve water quality goals.

The attention of environmental decision makers is increasingly being focused on the movement of pollutants into ground water. Of particular importance is the transport and speciation of metals. The MINTEQA2 model is a versatile, quantitative tool for predicting the equilibrium behavior of metals in a variety of chemical environments. Designed for convenient use by environmental scientists and engineers, the model should be a valuable tool for environmental risk assessment and hazard evaluation.

Rosemarie C. Russo, Ph.D.  
Director  
Environmental Research Laboratory  
Athens, Georgia

## ABSTRACT

MINTEQA2 is a geochemical equilibrium speciation model capable of computing equilibria among the dissolved, adsorbed, solid, and gas phases in an environmental setting. MINTEQA2 includes an extensive database of reliable thermodynamic data that is also accessible to PRODEFA2, an interactive program designed to be executed prior to MINTEQA2 for the purpose of creating the required MINTEQA2 input file.

This report describes how to use the MINTEQA2 model. The chemical and mathematical structure of MINTEQA2 and the structure of the database files also are described. The use of both PRODEFA2 and MINTEQA2 are illustrated through the presentation of an example PRODEFA2 dialogue reproduced from interactive sessions and the presentation of MINTEQA2 output files and error diagnostics. The content and format of database files also are explained.

## TABLE OF CONTENTS

DISCLAIMER .....	ii
FOREWORD .....	iii
ABSTRACT .....	iv
LIST OF FIGURES .....	vii
LIST OF TABLES .....	vii
ACKNOWLEDGMENT .....	viii
CHAPTER 1. INTRODUCTION .....	1
CHAPTER 2. CHEMICAL AND MATHEMATICAL CONCEPTS .....	3
Component and Species Definitions .....	3
Components .....	3
Type I Components as Species in Solution .....	3
Type II Other Species in Solution or Adsorbed .....	3
Type III Species with Fixed Activity .....	4
Type IV Finite Solids .....	4
Type V Possible (Undersaturated) Solids .....	4
Type VI Excluded Species .....	4
The Pre-Defined Set of Components .....	5
Oxidation/Reduction Reactions .....	5
General Problem Formulation .....	6
Example Problem without a Solid Phase .....	9
Example Problem with a Solid Phase and with a Gas Phase .....	13
Adjustments to Equilibrium Constants .....	16
Temperature Corrections of Equilibrium Constants .....	17
Activity Coefficient Corrections of Equilibrium Constants .....	18
Activity of H <sub>2</sub> O .....	20
Obtaining Total Dissolved Carbonate from Alkalinity .....	20
CHAPTER 3. ADSORPTION MODELS .....	24
Naming and Numbering Surface Species .....	24

Non-Electrostatic Adsorption Models .....	26
Activity $K_d$ Adsorption Model .....	26
Activity Langmuir Adsorption Model .....	27
Activity Freundlich Model .....	28
Ion Exchange Adsorption Model .....	29
Electrostatic Adsorption Models .....	30
General Implementation of Electrostatic Models in MINTEQA2 .....	32
Constant Capacitance and Diffuse-Layer Models .....	34
Triple-Layer Model .....	38
 CHAPTER 4. USING MINTEQA2 AND PRODEFA2 .....	 45
General Features and Organization of MINTEQA2 and PRODEFA2 .....	45
Running PRODEFA2 for the First Time .....	47
Detailed Explanation of PRODEFA2 Options .....	50
Main Menu Option 1: Edit Level I .....	50
Main Menu Option 2: Edit Level II .....	56
Main Menu Option 3: Edit Level III .....	67
Main Menu Option 4: Edit Level IV .....	70
Main Menu Option M: Multi-Problem Generator .....	74
Main Menu Option X: Exit .....	74
 CHAPTER 5. THE MINTEQA2 OUTPUT FILE AND ERROR DIAGNOSTICS .....	 75
Error Diagnostics .....	76
MINTEQA2 Error Codes and Messages .....	76
 REFERENCES .....	 81
 APPENDIX A. THE THERMODYNAMIC DATABASE USED BY MINTEQA2 .....	 83
The Component Database File .....	84
Format of Database Species Entries .....	86
Examples of Entries in the Thermodynamic Database Files .....	93
 APPENDIX B. NEWTON-RAPHSON APPROXIMATION METHOD .....	 96
 APPENDIX C. MINTEQA2 MODEL DISTRIBUTION .....	 97
 APPENDIX D. EXAMPLE MINTEQA2 FILES .....	 101

## LIST OF FIGURES

Figure 3.1.	Schematic representation of the surface charge/potential relationships used in the constant capacitance and diffuse-layer models. . . . .	36
Figure 3.2.	Schematic representation of surface species and charge/potential relationships in the triple-layer model. . . . .	41

## LIST OF TABLES

Table 2.1.	Reactions and log equilibrium constants for soluble species in a 0.001 M solution of $\text{CaCO}_3$ at 25 °C . . . . .	10
Table 2.2.	Stoichiometric matrix representing the 0.001 M $\text{CaCO}_3$ solution. . . . .	11
Table 2.3.	Mass action expressions applicable to the $\text{CaCO}_3$ solution using mixed equilibrium constants. . . . .	12

## ACKNOWLEDGMENT

The authors would like to thank Dr. John Westall, Oregon State University, Corvallis, OR, for openly sharing his wisdom on metal speciation modeling and for his criticisms and encouragement in the continued development of MINTEQA2 and PRODEFA2. The many discussions we've had at MINTEQA2 workshops sponsored by the Athens Environmental Research Laboratory (AERL) have contributed much to the enhancements in version 3.0.

We also extend thanks to Dr. Nick Loux of AERL for his shared insight in environmental geochemistry, especially in modeling real-world systems. The work of his colleagues, Ms. Claudia Chafin and Dr. Sayed Hassan of Technology Applications, Inc., in validating the diffuse-layer model iron-oxide database is also acknowledged. Mr. Bob Ambrose of AERL, Mr. Dave Disney, Ms. Catherine Green, Ms. Lisa Sealock of Computer Sciences Corporation, and Ms. Joyce Wool of Asci have contributed to the organization of MINTEQA2 into a form suitable for public distribution through the AERL Center for Exposure Assessment Modeling and have fostered its use by their by assistance in the presentation of MINTEQA2 workshops.

For helpful comments and suggestions arising from their review of this document, we thank Mr. Robert Ryans and Dr. George Bailey of AERL and Ms. Angelica Schnieder-Graziosi of Ismes-Italy, Rome.

Research contributing to the development of the MINTEQA2/PRODEFA2 model has been supported in part by the US EPA Office of Solid Waste.



## CHAPTER 1

### INTRODUCTION

Technical understanding of the physical, chemical, and biological processes controlling the behavior of pollutants in the environment has increased significantly in the past two decades. Many of the important advances are reflected in the quantitative mathematical models now being used to describe the influences of competing processes or reactions on the overall behavior of pollutants. A variety of mathematical models encompassing years of research are now available for predicting the behavior of pollutants in various environmental settings. The metal speciation model MINTEQA2, described in this manual, is a versatile, state-of-the-art example of the equilibrium solution chemistry programs now available.

MINTEQA2 is a geochemical equilibrium speciation model for dilute aqueous systems. The original MINTEQ (8) was developed at Battelle Pacific Northwest Laboratory (PNL) by combining the fundamental mathematical structure of MINEQL (23), a derivative of REDEQL (11), with the well-developed thermodynamic database of the U.S. Geological Survey's WATEQ3 model (1). MINTEQA2 is substantially different from the original MINTEQ in the features and options available, in the manner in which calculations are implemented, and in its thermodynamic database. Also, MINTEQA2 is complemented by PRODEFA2, an interactive program used to create input files. The original PRODEF also was a product of Battelle PNL and has undergone extensive modification and development as PRODEFA2. The model can be used to calculate the equilibrium composition of dilute aqueous solutions in the laboratory or in natural aqueous systems. It can be used to calculate the mass distribution between the dissolved, adsorbed, and multiple solid phases under a variety of conditions including a gas phase with constant partial pressure.

The data required to predict the equilibrium composition consists of a chemical analysis of the sample to be modeled giving total dissolved concentrations for the components of interest and any other relevant invariant measurements for the system of interest, possibly (but not necessarily) including  $P_h$ ,  $p_e$ , or the partial pressures of one or more gases. A measured value of  $P_h$  and/or  $p_e$  may be specified as equilibrium values or MINTEQA2 can calculate equilibrium values. Also, a mineral may be specified as presumed present at equilibrium, but subject to dissolution if equilibrium conditions warrant, or definitely present at equilibrium and not subject to complete dissolution.

MINTEQA2 has an extensive thermodynamic database that is adequate for solving a broad range of problems without need for additional user-supplied equilibrium constants. The standard database can be easily modified if it is found to be incomplete or inadequate for a particular problem. The empirical nature of the available metal adsorption data reflects the fact that natural adsorbent phases often occur as mixtures of impure amorphous substances that vary widely in chemical behavior from site to site. For this reason, adsorption data

are left to the discretion and problem-specific knowledge of the user. Seven adsorption models are available in MINTEQA2 to match the type of data available for specific problems.

The application of a geochemical equilibrium model to an environmental problem involves four steps:

- 1) Formulate one or more precise and relevant chemical questions that can be answered if one knows the equilibrium composition of the system. The formulation of the chemical questions must respect the inherent limitations in the site-specific data such as incomplete sampling or incomplete chemical analyses of samples.
- 2) Pose the chemical questions to the model in terms of those symbols and formats that it is programmed to understand and from which it may interpret a mathematical problem.
- 3) Cause the computer program that is the geochemical equilibrium model (in this case, MINTEQA2) to solve the mathematical problem.
- 4) Interpret the output from the model in terms of the original environmental problem.

The first step is almost always the most difficult; the ability to do this well is not obtained from reading a user manual. The authors anticipate the writing of a companion "applications" volume in which several case studies will be presented and the logic of step 1 will be emphasized. PRODEFA2 is designed to perform step 2 by asking questions about the chemical system to be modeled and building the appropriate MINTEQA2 input file from the answers. Step 3, the actual execution of MINTEQA2, is usually rather automatic, not requiring user intervention once initiated. Occasionally, computational problems will occur during execution that will require the user to make adjustments to the input file and re-execute MINTEQA2. This is discussed later in Chapter 5. Step 4 is performed as the user examines the MINTEQA2 output file and relates the result to the initial problem.

Chapter 2 is a presentation of the chemical and mathematical concepts employed in MINTEQA2 with the exception of those concepts that are peculiar to the adsorption models that are presented separately in Chapter 3. The mechanics of using PRODEFA2 and MINTEQA2 are presented in Chapter 4. Chapter 5 provides information about error conditions and their resolution.

## CHAPTER 2

### CHEMICAL AND MATHEMATICAL CONCEPTS

This chapter provides a brief review of the important concepts used to solve the general chemical equilibrium problem. The emphasis here is on how MINTEQA2 works, rather than how to work MINTEQA2 (the subject of chapter 4). After developing some definitions, we provide the relevant mass action and mole balance equations and describe their solution using an example problem first without, then with a solid phase. Other equations and algorithms used in MINTEQA2 for correcting equilibrium constants, computing total dissolved carbonate concentration from alkalinity, and obtaining other values are also presented. The material presented in this chapter also applies to adsorption reactions but the additional concepts that distinguish adsorption algorithms are presented in chapter 3.

#### Component and Species Definitions

**Components** - These are the basis entities or building-blocks from which all species in the system can be built. MINTEQA2 has an associated component database file containing more than 100 components (see Appendix A) from which the user selects only those needed in the specific problem of interest. The components used in MINTEQA2 form a pre-defined set, e.g., the component for calcium is  $\text{Ca}^{+2}$  and not some other species such as  $\text{CaOH}^+$ . The thermodynamic database, written in terms of these components, is searched automatically to retrieve only those species relevant to a specific problem. Components represent an accounting system and, while it is not required that they be actual chemical species, nearly all MINTEQA2 components except certain of those used to represent electrostatic terms in adsorption models are physically realizable species.

**Type I Components as Species in Solution** - These are the components themselves defined as actual chemical species. As mentioned above, in the general case, a component need not be an actual chemical species. The set of available components in MINTEQA2 happens to include components that are all bona fide chemical species (excepting the electrostatic components). Thus, all (non-electrostatic) components in a MINTEQA2 problem will also be defined as Type I species.

**Type II Other Species in Solution or Adsorbed** - These are all dissolved species other than those that are Type I. These may be complexes or free ions, for example,  $\text{Cr}^{3+}$  (the component for  $\text{Cr}^{3+}$  is  $\text{Cr}(\text{OH})_2^+$ ). Insofar as components may be thought of as reactants, Type II species may be considered aqueous and adsorption reaction products.

**Type III Species with Fixed Activity** - Generally, these are either species that are present at fixed equilibrium activity or are mock species that define a fixed equilibrium activity relationship between two real species. In earlier MINTEQ documentation as well as in documentation on related models (8,23), Type III species were referred to as Fixed Solids because all Type III species are treated mathematically in the same way as a solid. This terminology was a source of confusion since Type III species are not necessarily solids. Examples of a Type III species are any solids that are explicitly constrained to be present at equilibrium (not subject to complete dissolution; an infinite solid), any components whose activities are explicitly constrained to a given equilibrium value (e.g. fixed pH or pe), any gases whose partial pressures are explicitly constrained to a given equilibrium pressure, or any mock species whose equilibrium activity is explicitly constrained to an equilibrium value (such as a redox couple that fixes the equilibrium activity ratio of two components that form a redox pair.)

**Type IV Finite Solids** - These are solid phases that are presumed present initially or precipitate from the solution. In the latter case, the appropriate components are depleted in the aqueous phase to "create" the precipitated solids. With MINTEQA2, it is also possible to specify one or more precipitated solids as present initially at some given amount (per liter basis). For those Type IV solids that are specified as present initially, the entire amount may dissolve if equilibrium demands it and the concentrations of the appropriate components will then be supplemented in the aqueous phase. The reader should realize that, in theory, it doesn't matter to MINTEQA2 whether the system totals for various components are specified at the outset as all dissolved or all bound in precipitated solid(s) of given amount(s). In practice, it helps to avoid phase rule violations (discussed later) if Type IV solids are entered with a concentration of zero. In that case, the total dissolved concentrations of the components of the solid represent total system concentrations. MINTEQA2 will shift mass from the dissolved to precipitated phases or vice versa as required by equilibrium.

**Type V Possible (Undersaturated) Solids** - These are solid phases that are defined in MINTEQA2; however, they are not oversaturated, do not physically exist, and thus have no direct impact on the chemical equilibrium problem. When the solution becomes oversaturated with respect to a particular possible solid, and if that solid is more oversaturated than any other possible solid composed of the same components, MINTEQA2 will precipitate that solid depleting the aqueous phase concentrations of the appropriate components. The newly precipitated solid is then re-assigned as a Type IV species. If any Type IV solid dissolves completely so that its entire mass is shifted to the aqueous phase, that solid is re-assigned as Type V. Note that in PRODEFA2 and in the listing of input data that MINTEQA2 includes in its output file, Type V solids are referred to as POSSIBLE solids. In the listing of equilibrated results however, Type V species are referred to as UNDERSATURATED solids.

**Type VI Excluded Species** - These are species that would ordinarily be Type I, II, III, or V but are assigned as Type VI to exclude them from mass balance calculations. Reasons for wanting to impose such exclusions are varied. For example, the mass of the component representing the electron ( $e^-$ ) is entered as zero in the database. For obvious reasons, one would not want to impose the condition of mass balance on  $e^-$ . Therefore, unless an equilibrium pe is imposed,  $e^-$  is excluded from mass balance calculations by designating it as Type VI. When MINTEQA2 reads the input file for a specific problem, it searches the database to find all species that can be reaction products of the specified reactants

(components). Of these possible species, all gases and redox couples are entered as Type VI unless they are explicitly designated in the input file as Type III. Unless a flag in the input file directs otherwise, all solid phases are treated as Type VI by default. All electrostatic components used in adsorption reactions are entered as Type VI in the input file because they are not real chemical entities; they have no mass. Finally, any species that the user wishes to explicitly exclude may be so designated in the input file. For example, a solid phase that is suspected to be unrealistic for kinetic reasons, but which would otherwise precipitate may be explicitly excluded. PRODEFA2 has the logic to properly assign species to the Type VI category as necessary and provides for explicitly assigning any species to Type VI as desired by the user.

### The Pre-Defined Set of Components

The pre-defined set of components available in MINTEQA2 (see Appendix A) includes naked ions such as  $\text{Na}^+$  and neutral and charged complexes (e.g.  $\text{H}_4\text{SiO}_4$ ,  $\text{Cr}(\text{OH})_2^+$ ). In general, the species chosen to serve as components are those that are expected to be the dominant dissolved species in natural waters, i.e.,  $\text{H}_4\text{SiO}_4$  as opposed to some other species of dissolved silica. Of course, for a specific problem, the species which represents the component may not always be the dominant equilibrium species. Whatever components are selected, it is only necessary that they linearly combine to produce every species in the system and that it be impossible to produce any component through another combination of components (multiple oxidation states of the same chemical element being exempted from this latter requirement; i.e, the fact that component  $\text{Fe}^{3+}$  can be produced from a combination of components  $\text{Fe}^{2+}$  and  $e^-$  is acceptable).

### Oxidation/Reduction Reactions

Redox reactions are represented in either of two ways in MINTEQA2. One way is the designation of separate components to represent the oxidation states of interest. For example, in the current database, there are separate components for  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . Thus, separate reactions can be written for each of these components; in fact, this has been done and those reactions are available in the thermodynamic database. Also, as mentioned earlier in defining Type III Species with Fixed Activity, mock species are defined to represent the activity ratio between two members of a redox couple. When such a species is assigned as Type III and the equilibrium  $p_e$  is also specified, mass is shifted from one member of the couple to the other in such a way as to cause their activity ratio to honor the Nernst Equation at the equilibrium  $p_e$  specified. The other way to represent different oxidation states requires only one oxidation state to be defined as a component. Then any reaction that would involve a different oxidation state of that same component is written to include the gain or loss of electrons and the  $\log K$  for the formation of the product is adjusted accordingly. Had this scheme been used for the iron system,  $\text{Fe}^{3+}$  might have been chosen as a component and  $\text{Fe}^{2+}$  would have been a Type II species with  $\text{Fe}^{3+}$  and  $e^-$  as reactants. While most of the redox chemistry in MINTEQA2 is represented by the components of separately defined oxidation states, the electron appears in many reactions as well.

## General Problem Formulation

Two general approaches are commonly used to formulate and solve multiple-component chemical equilibrium problems: 1) minimization of the system free energy under mass balance constraints or 2) simultaneous solution of the nonlinear mass action expressions and linear mass balance relationships. MINTEQA2 uses the latter approach, frequently referred to as the "equilibrium constant method". This method also is used in several other geochemical equilibrium programs including PHREEQE (15), EQ3NR (24), and MICROQL II (21). Van Zeggeren and Storey (20) have shown the two approaches to be mathematically equivalent.

To solve the chemical equilibrium problem, MINTEQA2 uses an initial guess for the activity of each component to calculate the concentration of each species according to mass action expressions written in terms of component activities. The total mass of each component is then calculated from the concentrations of every species containing that component. The calculated total mass for each component is then compared with the known input total mass for each component. If the calculated total mass and the known input total mass for any component differ by more than a pre-set tolerance level, a new estimate of the component activity is made and the entire procedure is repeated. The aqueous phase equilibrium composition is that set of species concentrations which gives a mass imbalance less than the tolerance level for every component.

After equilibrating the aqueous phase, MINTEQA2 computes the saturation index (SI) for each possible solid with respect to the solution. The solid with the most positive SI is allowed to precipitate by depleting the dissolved concentrations of those components comprising the solid in accordance with the known stoichiometry of each component. The reverse process occurs if an existing solid is found to be undersaturated with respect to the solution. In either case, it is necessary to re-equilibrate the solution after mass has been added to or depleted from the aqueous phase. Thus the aqueous solution is re-equilibrated just as before except with one less degree of freedom if precipitation has occurred or one more if dissolution has occurred. The entire computational loop of iterating to equilibrium, checking for precipitation or dissolution, and shifting mass from the aqueous to the solid phase or vice versa is repeated until equilibrium is achieved and there are no oversaturated possible solids and no undersaturated existing solids.

The number of degrees of freedom of the system is the number of independent variables. These would ordinarily include temperature, pressure, and all the component activities that can be independently varied. Several constraints are used in MINTEQA2 that modify the usual phase rule relationship. Because temperature and pressure are both specified to be invariant by the user, the phase rule expression that applies to MINTEQA2 calculations is

$$f = C - P \qquad 2.01$$

Where:

f = the number of degrees of freedom

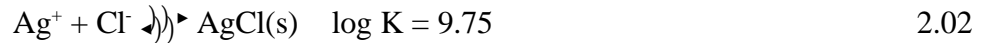
C = the number of components

$$P = NN(\text{III}) + NN(\text{IV})$$

NN(III) = the number of Type III Species with Fixed Activity

NN(IV) = the number of Type IV Finite Solid Species

MINTEQA2 calculates  $f$  at the outset of each problem and if  $f$  is greater than zero, proceeds with the calculations. One additional degree of freedom is lost for each new solid phase that forms, that is, each species that is re-assigned from Type V to Type IV. Conversely, each existing solid that dissolves (Type IV species re-assigned to Type V) adds one degree of freedom. Examples of constraints that result in reducing the number of degrees of freedom, that is, that contribute to  $P$  in equation 2.01, are the fixed activity of the component  $\text{H}_2\text{O}$  or of other components with fixed activities. As is evident above, each solid phase present (Type III or IV) also contributes to  $P$ . This follows from the solubility product constraint imposed by the presence of a solid phase. To see why the precipitation of a solid results in the loss of one degree of freedom, consider the example



By convention, the activity of the pure precipitated  $\text{AgCl(s)}$  is 1.0. Thus,

$$K = 10^{9.75} = \{\text{AgCl(s)}\} / \{\text{Ag}^+\} \{\text{Cl}^-\} \quad 2.03$$

or

$$\{\text{Ag}\} = 10^{-9.75} \{\text{Cl}\}^{-1}$$

Thus, when pure  $\text{AgCl(s)}$  exists  $\{\text{Ag}^+\}$  and  $\{\text{Cl}^-\}$  are no longer independent variables.

A system of  $n$  independent components that can combine to form  $m$  species is represented by a set of mass action expressions of the form

$$K_i = \{\text{S}_i\} \prod_j X_j^{-a_{ij}} \quad 2.04$$

Where:

$K_i$  = equilibrium constant for the formation of species  $i$

$\{\text{S}_i\}$  = activity of species  $i$

$X_j$  = activity of component  $j$

$a_{ij}$  = stoichiometric coefficient of component  $j$  in species  $i$

$\Pi$  = indicates the product over all components in species  $i$

The concentration of species  $i$ ,  $[\text{S}_i]$ , is related to the activity  $\{\text{S}_i\}$  by the activity coefficient,  $\gamma_i$

$$\{S_i\} = \gamma_i[S_i] \quad 2.05$$

Substituting this expression for  $\{S_i\}$  in equation 2.04 and rearranging gives

$$[S_i] = K_i/\gamma_i \prod_j X_j^{a_{ij}} \quad 2.06$$

Now, if we define  $K'_i$  such that

$$K'_i = K_i/\gamma_i \quad 2.07$$

then

$$C_i = [S_i] = K'_i \prod_j X_j^{a_{ij}} \quad 2.08$$

For notational convenience, we will use  $C_i$  and  $[S_i]$  interchangeably; both mean the concentration of species  $i$ . In equation 2.08, the activity coefficient term is incorporated into the equilibrium constant  $K'_i$  and ideal conditions (ionic strength = 0; activity coefficients = 1) correspond to the condition  $K'_i = K_i$ .

In logarithmic form, equation 2.08 becomes

$$\log C_i = \log K'_i + \sum_j a_{ij} \log X_j \quad 2.09$$

In addition to the mass action expressions, the set of  $n$  independent components is governed by  $n$  mass balance equations of the form

$$Y_j = \sum_i a_{ij} C_i - T_j \quad 2.10$$

Where:

$T_j$  = total dissolved concentration of component  $j$  (also referred to as the total analytical concentration because  $T_j$  is generally a known measured input parameter)

$Y_j$  = the difference between the *calculated* total dissolved concentration of component  $j$  and the *known analytical* total dissolved concentration of component  $j$

The solution (in the mathematical sense) is that set of component activities  $\mathbf{X}$  (using matrix notation for brevity) which results in the set of concentrations  $\mathbf{C}$  such that each individual of the set of mass balance differences  $\mathbf{Y}$  is equal to zero. In practice, it is only necessary to find  $\mathbf{X}$  such that each individual of  $\mathbf{Y}$  is made less than some tolerance value. The general procedure is to first guess  $\mathbf{X}$  (PRODEFA2 makes this guess and puts it in the input file), then calculate  $\mathbf{C}$  and  $\mathbf{Y}$ . If any individual of  $\mathbf{Y}$  exceeds (in absolute terms) its prescribed tolerance value, a new guess is made for  $\mathbf{X}$ ,  $\mathbf{C}$  and  $\mathbf{Y}$  are recalculated, and the test is repeated. This iterative procedure is continued until all the individuals of  $\mathbf{Y}$  are less than the tolerance value. Like MINEQL, MINTEQA2 uses the Newton-Raphson approximation method to estimate the new  $\mathbf{X}$  at each iteration (see Appendix B). The tolerance value or convergence criteria for MINTEQA2 is pre-set to  $10^{-4}$  times  $T_j$  for each component  $j$ .



### Example Problem without a Solid Phase

To illustrate the generalized mathematical formalisms used to solve chemical equilibrium problems, it is instructive to consider a simple problem in detail. The example problem formulation that follows is based on a simple calcium carbonate ( $\text{CaCO}_3$ ) solution. This solution has served as the classical example for many chemical equilibrium models and has been discussed in great detail elsewhere (7, 8, 21). A 0.001 molar solution of  $\text{CaCO}_3$  that has no access to atmospheric gases is considered. No solid phases are considered. Furthermore, no adsorbent phases are present, no redox reactions occur, and no Type III species are included.

The  $\text{CaCO}_3$  solution at equilibrium will contain ten soluble species:  $\text{Ca}^{2+}$ ,  $\text{CaOH}^+$ ,  $\text{CaCO}_3^0$ ,  $\text{CaHCO}_3^+$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{H}^+$ ,  $\text{OH}^-$ , and  $\text{H}_2\text{O}$ . (Note  $\text{CaCO}_3^0$  refers to the soluble complex, not the solid which is designated  $\text{CaCO}_3(\text{s})$ .) The set of 6 independent reactions involving these species is shown in Table 2.1. The choice of components to represent a given solution, in general, is not unique; however, the component set used in MINTEQA2 is pre-set (See Appendix A).

The required number of components is equal to the number of species minus the number of independent reactions. Thus, for this problem we need four components. Some general guidelines for choosing components are:

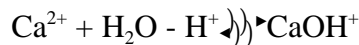
- 1) Always choose  $\text{H}_2\text{O}$  as a component; this is required in MINTEQA2 and, in fact,  $\text{H}_2\text{O}$  is chosen automatically.
- 2) Always choose  $\text{H}^+$  as a component; this is not required but, except for certain problems of academic interest,  $\text{H}^+$  should always be a component.
- 3) If redox transformations are involved in this problem, include the electron as a component. Remember that those database reactions that involve the electron as a component, such as  $\text{CH}_4(\text{g})$ , will not be brought into the problem if  $e^-$  is not a component. Even so, do not include  $e^-$  unless it's necessary.
- 4) For all other components, the choices are obvious; PRODEFA2 can provide a listing of all available components but there's only one that can represent  $\text{As}^{3+}$ , one that can represent  $\text{Ca}^{2+}$ , etc.

The four components that are applicable to the  $\text{CaCO}_3$  solution are  $\text{H}_2\text{O}$ ,  $\text{H}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{CO}_3^{2-}$ .  $\text{H}_2\text{O}$  is presumed to exist at constant activity. This is a good assumption for all dilute solutions because the mass of  $\text{H}_2\text{O}$  present is several orders of magnitude greater than the other components. The small mass of water consumed (or generated) by reactions with other components is justifiably neglected; there is no mole balance on  $\text{H}_2\text{O}$ .

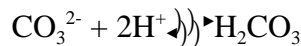
Table 2.1. Reactions and log equilibrium constants for soluble species in a 0.001 M solution of CaCO<sub>3</sub> at 25 °C .

Reactions	log K
$\text{H}_2\text{O} - \text{H}^+ \rightleftharpoons \text{OH}^-$	-14.0
$\text{CO}_3^{2-} + \text{H}^+ \rightleftharpoons \text{HCO}_3^-$	10.2
$\text{CO}_3^{2-} + 2\text{H}^+ \rightleftharpoons \text{H}_2\text{CO}_3$	16.5
$\text{Ca}^{2+} + \text{H}_2\text{O} - \text{H}^+ \rightleftharpoons \text{CaOH}^+$	-12.2
$\text{Ca}^{2+} + \text{CO}_3^{2-} + \text{H}^+ \rightleftharpoons \text{CaHCO}_3^+$	11.6
$\text{Ca}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CaCO}_3^0$	3.0

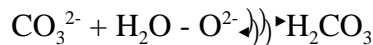
For any species, the stoichiometric coefficients for each component are given by the corresponding reaction written with the components all on the left side of the reaction and the species as the sole reaction product on the right side. For example,



Thus, the stoichiometric coefficient for the component H<sup>+</sup> in the species CaOH<sup>+</sup> is -1. Similarly for H<sub>2</sub>CO<sub>3</sub>



the stoichiometric coefficient for the component H<sup>+</sup> in the species H<sub>2</sub>CO<sub>3</sub> is +2. If MINTQA2's component list had been chosen differently (we have already observed that the selection of components in our pre-defined list is arbitrary) so that O<sup>2-</sup> were a component, then the reaction for H<sub>2</sub>CO<sub>3</sub> in the database would have been:



In that case, the components CO<sub>3</sub><sup>2-</sup>, H<sub>2</sub>O, and O<sup>2-</sup> would have stoichiometries 1, 1, and -1 respectively. Of course, the equilibrium constant for this reaction would be different from that of the former H<sub>2</sub>CO<sub>3</sub> reaction.

The stoichiometric coefficients and log equilibrium constants for all species in the CaCO<sub>3</sub> problem are shown in Table 2.2. Note that the equilibrium constants are for the formation of the species from the components with the corresponding stoichiometries and that these are thermodynamic database constants.

Before they are used in MINTEQA2, they will each be corrected by the species activity coefficient as in equation 2.07.

Table 2.2. Stoichiometric matrix representing the 0.001 M CaCO<sub>3</sub> solution.

Species	Components				K
	H <sub>2</sub> O	H <sup>+</sup>	Ca <sup>2+</sup>	CO <sub>3</sub> <sup>2-</sup>	
H <sub>2</sub> O	1	0	0	0	K <sub>1</sub>
H <sup>+</sup>	0	1	0	0	K <sub>2</sub>
Ca <sup>2+</sup>	0	0	1	0	K <sub>3</sub>
CO <sub>3</sub> <sup>2-</sup>	0	0	0	1	K <sub>4</sub>
OH <sup>-</sup>	1	-1	0	0	K <sub>5</sub>
HCO <sub>3</sub> <sup>-</sup>	0	1	0	1	K <sub>6</sub>
H <sub>2</sub> CO <sub>3</sub>	0	2	0	1	K <sub>7</sub>
CaOH <sup>+</sup>	1	-1	1	0	K <sub>8</sub>
CaHCO <sub>3</sub> <sup>+</sup>	0	1	1	1	K <sub>9</sub>
CaCO <sub>3</sub> <sup>o</sup>	0	0	1	1	K <sub>10</sub>

Note that Table 2.2 includes several identity relationships. The generalized nature of the computational algorithm is such that to make the species H<sup>+</sup> for example, requires that the stoichiometry of the component H<sup>+</sup> be one and that of all other components be zero.

The set of mass action constraints that apply to the reactions in Table 2.2 are given in Table 2.3. Note that because we are expressing species concentrations in terms of component activities, we must use the mixed equilibrium constants as given by equation 2.07.

---

Table 2.3. Mass action expressions applicable to the CaCO<sub>3</sub> solution using mixed equilibrium constants.

---

- (1)  $[\text{H}_2\text{O}] = \{\text{H}_2\text{O}\} K'_1$
  - (2)  $[\text{H}^+] = \{\text{H}^+\} K'_2$
  - (3)  $[\text{Ca}^{2+}] = \{\text{Ca}^{2+}\} K'_3$
  - (4)  $[\text{CO}_3^{2-}] = \{\text{CO}_3^{2-}\} K'_4$
  - (5)  $[\text{OH}^-] = \{\text{H}_2\text{O}\} \{\text{H}^+\}^{-1} K'_5$
  - (6)  $[\text{HCO}_3^-] = \{\text{CO}_3^{2-}\} \{\text{H}^+\} K'_6$
  - (7)  $[\text{H}_2\text{CO}_3] = \{\text{CO}_3^{2-}\} \{\text{H}^+\}^2 K'_7$
  - (8)  $[\text{CaOH}^+] = \{\text{Ca}^{2+}\} \{\text{H}_2\text{O}\} \{\text{H}^+\}^{-1} K'_8$
  - (9)  $[\text{CaHCO}_3^+] = \{\text{Ca}^{2+}\} \{\text{CO}_3^{2-}\} \{\text{H}^+\} K'_9$
  - (10)  $[\text{CaCO}_3^0] = \{\text{Ca}^{2+}\} \{\text{CO}_3^{2-}\} K'_{10}$
- 

Three mole balance expressions are required to complete the set of equations that define the CaCO<sub>3</sub> system (recall that mass balance is neglected on H<sub>2</sub>O). The mole balance expressions corresponding to equation 2.10 are generated by summing the concentrations of all species involving a particular component and subtracting the respective analytical input concentration for that component. The resulting expressions are:

$$Y_{\text{Ca}^{2+}} = [\text{Ca}^{2+}] + [\text{CaOH}^+] + [\text{CaHCO}_3^+] + [\text{CaCO}_3^0] - T_{\text{Ca}^{2+}} \quad 2.11$$

$$Y_{\text{CO}_3^{2-}} = [\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{H}_2\text{CO}_3] + [\text{CaHCO}_3^+] + [\text{CaCO}_3^0] - T_{\text{CO}_3^{2-}} \quad 2.12$$

$$Y_{\text{H}^+} = [\text{H}^+] + [\text{HCO}_3^-] + 2[\text{H}_2\text{CO}_3] + [\text{CaHCO}_3^+] \\ - [\text{CaOH}^+] - [\text{OH}^-] - T_{\text{H}^+} \quad 2.13$$

The ultimate goal is to solve these mole balance equations under the constraints of the mass action expressions in Table 2.3. To do this, the species concentration terms in those equations are replaced with their corresponding mass action expressions from the table. The final set of mole balance equations then becomes:

$$Y_{\text{Ca}^{2+}} = K'_3\{\text{Ca}^{2+}\} + K'_8\{\text{Ca}^{2+}\}\{\text{H}_2\text{O}\}\{\text{H}^+\}^{-1} + K'_9\{\text{Ca}^{2+}\}\{\text{H}^+\}\{\text{CO}_3^{2-}\} + K'_{10}\{\text{Ca}^{2+}\}\{\text{CO}_3^{2-}\} - T_{\text{Ca}^{2+}} \quad 2.14$$

$$Y_{\text{CO}_3^{2-}} = K'_4\{\text{CO}_3^{2-}\} + K'_6\{\text{H}^+\}\{\text{CO}_3^{2-}\} + K'_7\{\text{H}^+\}^2\{\text{CO}_3^{2-}\} + K'_9\{\text{Ca}^{2+}\}\{\text{H}^+\}\{\text{CO}_3^{2-}\} + K'_{10}\{\text{Ca}^{2+}\}\{\text{CO}_3^{2-}\} - T_{\text{CO}_3^{2-}} \quad 2.15$$

$$Y_{\text{H}^+} = K'_2\{\text{H}^+\} + K'_6\{\text{H}^+\}\{\text{CO}_3^{2-}\} + 2K'_7\{\text{H}^+\}^2\{\text{CO}_3^{2-}\} + K'_9\{\text{Ca}^{2+}\}\{\text{H}^+\}\{\text{CO}_3^{2-}\} - K'_8\{\text{H}_2\text{O}\}\{\text{Ca}^{2+}\}\{\text{H}^+\}^{-1} - K'_5\{\text{H}_2\text{O}\}\{\text{H}^+\}^{-1} - T_{\text{H}^+} \quad 2.16$$

These three equations are now expressed in terms of three unknowns,  $\{\text{H}^+\}$ ,  $\{\text{Ca}^{2+}\}$ , and  $\{\text{CO}_3^{2-}\}$ . The adjusted equilibrium constants, analytical component total dissolved concentrations, and the activity of  $\text{H}_2\text{O}$  are known. (Recall that the analytical input concentrations ( $T_{\text{Ca}^{2+}}$ ,  $T_{\text{CO}_3^{2-}}$ , and  $T_{\text{H}^+}$ ) are supplied by the user when the problem is specified and  $\text{H}_2\text{O}$  always has activity fixed at approximately 1.0). The mathematical solution is that set of component activities which gives  $Y_{\text{Ca}^{2+}}$ ,  $Y_{\text{CO}_3^{2-}}$ , and  $Y_{\text{H}^+}$  all equal to zero, or more practically, all less than some acceptably small error (convergence criteria). From final component activities, the equilibrium concentrations of all species can be calculated using the mass action expressions in Table 2.3.

### Example Problem with a Solid Phase and with a Gas Phase

Let us consider the same calcium carbonate system as before except with a solid phase, calcite, present at equilibrium. In that case, we would add the following reaction to Table 2.1



and the stoichiometric coefficients for  $\text{CaCO}_3(\text{s})$  in Table 2.2 would be the same as for the dissolved species  $\text{CaCO}_3^0$ . The appropriate mass action expression (equation 2.08) that would be added to Table 2.3 is

$$[\text{CaCO}_3^0] = \{\text{Ca}^{2+}\} \{\text{CO}_3^{2-}\} K'_{11} \quad 2.17$$

Now, because  $\text{CaCO}_3(\text{s})$  is a pure phase,

$$[\text{CaCO}_3(\text{s})] = \{\text{CaCO}_3(\text{s})\} = 1$$

and we can solve equation 2.17 for either  $\{\text{Ca}^{2+}\}$  or  $\{\text{CO}_3^{2-}\}$ ; let us choose  $\{\text{CO}_3^{2-}\}$ . Then,

$$\{\text{CO}_3^{2-}\} = \frac{1}{[\text{CaCO}_3^0] K'_{11}} \quad 2.18$$

$$K'_{11} \{Ca^{2+}\}$$

Thus, the three unknowns of equations 2.14 thru 2.16 have been reduced to only two by making use of the fact that a pure phase has activity of 1. If we make this substitution (equation 2.18) in the three mole balance equations, we obtain

$$Y_{Ca^{2+}} = K'_3 \{Ca^{2+}\} + K'_8 \{Ca^{2+}\} \{H_2O\} \{H^+\}^{-1} + K'_9 \{H^+\} (K'_{11})^{-1} + K'_{10} (K'_{11})^{-1} - T_{Ca^{2+}} \quad 2.19$$

$$Y_{CO_3^{2-}} = K'_4 (K'_{11} \{Ca^{2+}\})^{-1} + K'_6 \{H^+\} (K'_{11} \{Ca^{2+}\})^{-1} + K'_7 \{H^+\}^2 (K'_{11} \{Ca^{2+}\})^{-1} + K'_9 \{H^+\} (K'_{11})^{-1} + K'_{10} (K'_{11})^{-1} - T_{CO_3^{2-}} \quad 2.20$$

$$Y_{H^+} = K'_2 \{H^+\} + K'_6 \{H^+\} (K'_{11} \{Ca^{2+}\})^{-1} + 2K'_7 \{H^+\}^2 (K'_{11} \{Ca^{2+}\})^{-1} + K'_9 \{H^+\} (K'_{11})^{-1} - K'_8 \{H_2O\} \{Ca^{2+}\} \{H^+\}^{-1} - K'_5 \{H_2O\} \{H^+\}^{-1} - T_{H^+} \quad 2.21$$

Note that Equations 2.19 through 2.21 now contain only  $\{Ca^{2+}\}$  and  $\{H^+\}$  as unknowns. Carbonate ion activity has been eliminated as a component and the dimensions of the Jacobian matrix that must be calculated to estimate new component activities at each succeeding iteration during the Newton-Raphson iteration sequence have been reduced.

For more complicated systems that may contain a number of solids (Types III or IV), the process of eliminating variables is more complicated. A priority order of thermodynamic stabilities of each solid is established by comparing the appropriate ion activity products (IAP) with the corresponding formation constant after the aqueous phase has been equilibrated. The logarithmic ratio of these terms (saturation index) is calculated and used to establish the stability order for precipitation or dissolution of solids.

$$\text{Saturation Index} = \log \left( \frac{\text{IAP}}{K} \right) \quad 2.22$$

If the saturation index for a particular mineral is negative, the system is undersaturated with respect to that mineral. If the index is positive, the solution is supersaturated and, if the user has selected the appropriate precipitation option, MINTEQA2 will precipitate the solid in question until the equilibrium condition is satisfied, i.e., until:

$$\log \frac{IAP}{K} = 0 \quad 2.23$$

Undersaturation for a given mineral can arise from three situations: a) a less soluble mineral phase could be controlling the activities of one or more common ions, b) the component input concentrations are insufficient to exceed the formation constant, or c) free solution ion activities are limited by sorption reactions.

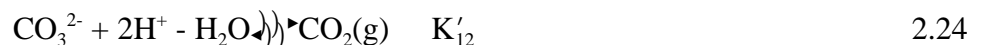
MINTEQA2 re-evaluates the saturation indices for each solid each time the aqueous phase is equilibrated. The user may choose to:

- 1) Allow no solids to precipitate regardless of saturation state,
- 2) Allow the precipitation of explicitly designated solids but only if they become oversaturated,
- 3) Allow all oversaturated solids to precipitate, or
- 4) Allow all oversaturated solids to precipitate except for those explicitly designated as excluded (Type VI).

In cases where precipitation is allowed, the entire computational loop of iterating to equilibrium, checking for precipitation or dissolution, and shifting mass from the aqueous to the solid phase or vice versa is repeated until equilibrium is achieved with no oversaturated Type V Possible Solids and no undersaturated Type IV Finite Solids.

Because the formation of solid phases changes the equilibrium species distributions, the inclusion of a large number of Type IV or V solids in MINTEQA2 executions requires that the species distribution equilibria problem be re-solved several times during the iteration sequence for precipitating solids. The difficulty of obtaining convergence is increased accordingly. For this reason, model systems should be spared unnecessary detail. The user should note that usually only a small number of solids control the free solution activities of species representing a given metal. It may be useful to perform a run with all solids prohibited from precipitating; examination of the saturation indices will provide information as to the dominant solids. The initial rule is, "If in doubt leave it out." The saturation index listings can be used to detect first-pass mistakes. All unprecipitated (supersaturated) solids will be represented by a positive saturation index. If any positive values are found, the user may then add the omitted solid and repeat the execution. In the final analysis, all controlling solids (those that actually precipitate) will be identified with saturation indices equal to zero.

Specifying a gas phase at a fixed partial pressure in the example  $\text{CaCO}_3$  system would have much the same effect mathematically as did the solid calcite phase. When a  $\text{CO}_2(\text{g})$  gas phase is present, the following reaction would apply



The corresponding mass action expression would be represented by

$$P_{\text{CO}_2} = \{\text{CO}_3^{2-}\} \{\text{H}^+\}^2 \{\text{H}_2\text{O}\}^{-1} K'_{12} \quad 2.25$$

where  $P_{\text{CO}_2}$  = the partial pressure of  $\text{CO}_2$  in atmospheres. For systems open to the atmosphere,  $P_{\text{CO}_2}$  is fixed at  $10^{-3.5}$  atmospheres. The new equilibrium constant would be:

$$K''_{12} = K'_{12}/P_{\text{CO}_2} \quad 2.26$$

Then,

$$\{\text{H}^+\} = [\{\text{CO}_3^{2-}\} K''_{12}]^{-1/2} \quad 2.27$$

If the solid phase is present as before, the expression for  $\{\text{CO}_3^{2-}\}$  (equation 2.18) can be substituted in equation 2.27 to give

$$\{\text{H}^+\} = [\{\text{Ca}^{2+}\} K'_{11} (K''_{12})^{-1}]^{1/2} \quad 2.28$$

This expression for  $\{\text{H}^+\}$  can be substituted into the mole balance equations (2.19 through 2.21) which are then expressed in terms of the only remaining unknown, namely  $\{\text{Ca}^{2+}\}$ .

Note that PRODEFA2 computes the adjusted equilibrium constant from the user-specified partial pressure. The database log K is 18.16 and if

$P_{\text{CO}_2} = 10^{-3.5}$  atm, then the adjusted log K is computed from

$$\log K''_{12} = 18.16 - (-3.5) = 21.66 \quad 2.29$$

It is possible to over-constrain a system (eliminate all degrees of freedom) by entering too many fixed species. If, for instance, a user simultaneously fixed  $P_{\text{CO}_2}$  and  $\{\text{H}^+\}$  in the  $\text{CaCO}_3$  problem above and then if a solid phase is precipitated (by MINTEQA2 in computing the equilibrium or by the user specifying an initial solid), there would be no remaining variables in the mole balance equations and the system would be over-constrained. MINTEQA2 would report a phase rule violation and execution would end with an error.

In introducing the  $\text{CaCO}_3$  problem originally, the gas phase reactions were excluded. If this problem had been executed using MINTEQA2, the user would have been reminded of this exclusion in the output listing for Type VI Excluded Species.

### Adjustments to Equilibrium Constants

The equilibrium constants in equations 2.14 through 2.16 are functions of the system temperature and ionic strength. The values supplied in MINTEQA2's thermodynamic database are referenced to 25°C and an ionic strength of zero. If the temperature is not at 25°C, a new set of equilibrium constants must be calculated before solving the equations. The ionic strength affects activity coefficients which in turn affect the adjusted



equilibrium constants (equation 2.07). MINTEQA2 allows the option of specifying a fixed ionic strength or of recalculating the ionic strength from the new estimates of species concentrations at each iteration.

Temperature Corrections of Equilibrium Constants

MINTEQA2 incorporates two schemes for adjusting the equilibrium constants for temperature. If the necessary data are available in the thermodynamic database, MINTEQA2 uses a power function of the form

$$\log K_T = A + BT + C/T + D \text{Log}(T) + ET^2 + F/T^2 + GT^{1/2} \tag{2.30}$$

Where:

T = temperature (K°)

A,B,...,G = empirical constants stored in the thermodynamic database

Only 25 of the more than 1000 species in the database have these constants available.

For any species that does not have the constants needed for equation 2.30, the equilibrium constant is corrected for temperature variations from 25°C by the van't Hoff equation

$$\log K_T = \log K_{T_r} - \frac{\Delta H_r^\circ}{2.303R} \left( \frac{1}{T} - \frac{1}{T_r} \right) \tag{2.31}$$

Where:

T<sub>r</sub> = reference temperature, 298.16°K

log K<sub>T<sub>r</sub></sub> = logarithm of the equilibrium constant at the reference temperature

R = molar gas constant

T = temperature of the system to be modeled (Kelvin)

ΔH<sub>r</sub><sup>°</sup> = standard enthalpy change of the reaction

Caution should be used in attempting to apply MINTEQA2 to high temperature systems. The van't Hoff equation implicitly assumes the enthalpies of reaction to be independent of temperature. This assumption is not always valid and significant errors can result at temperatures far above 25°C. For this reason, MINTEQA2

calculations should be restricted to a temperature range below 100°C. Applications to high temperature geothermal systems should definitely not be attempted unless empirical temperature correction data are available.

If the standard enthalpy change is not available in the database, MINTEQA2 uses the uncorrected log K's (25°C). Users are encouraged to become familiar with the database and to evaluate the impacts of these limitations on their systems. Missing enthalpy data can be permanently added to the database or, alternatively, temporarily entered into a given model execution using instructions provided by PRODEFA2. The latter option is convenient for testing a given system's sensitivity for individual reaction enthalpies.

Activity Coefficient Corrections of Equilibrium Constants

Activity coefficients for all species are functions of solution ionic strength (I) and vary as species distributions alter the ionic strength. Unless a fixed ionic strength is specified, successive sets of activity coefficients are calculated for all solution species with each iteration. These are used to generate corrected values of the equilibrium constants (see equation 2.07) that appear in the mole balance expressions (equation 2.10). Initial activity guesses for the input components are provided in the input file for a given problem. These initial component activity guesses are used to "crudely" estimate the concentrations of each dissolved species so that the solution ionic strength can be calculated. Each succeeding iteration provides improved estimates of species concentrations and activity corrections. The solution ionic strength is used in either the modified Debye-Hückel equation (19) or the Davies equation (3) to calculate activity coefficients ( $\gamma$ ) for all charged species. If the user selects the modified Debye-Hückel equation, it will be used for those species that have the necessary parameters in the database. For any species lacking the necessary parameters, the Davies equation will be used to estimate the activity coefficient for that species. If the user selects the Davies equation at the outset, it will be used throughout the problem because it requires no species-specific data other than charge. The activity coefficients are used in equation 2.07 to compute adjusted equilibrium constants.

The modified Debye-Hückel expression used to calculate the activity coefficients is

$$\log \gamma_i = -\frac{A_d Z_i^2 I^{1/2}}{1 + B_d a_i I^{1/2}} + b_i I \tag{2.32}$$

Where:

$A_d$  and  $B_d$  = constants that depend on the dielectric constant and temperature

$Z_i$  = the charge on each species i

$a_i$  = ion size parameter

$b_i$  = ion specific parameter that accounts for the decrease in solvent concentration in concentrated solutions

$I$  = solution ionic strength

The ionic strength ( $I$ ) is calculated from

$$I = \frac{1}{2} \sum_{i=1}^m Z_i^2 C_i \quad 2.33$$

Where:

$C_i$  = concentration of ion species  $i$

$m$  = number of charged species present in the solution

$Z_i$  = charge on species  $i$

The modified Debye-Hückel relation above is used only when the parameters  $a_i$  and  $b_i$  are available in the database. The current database contains  $a_i$  and  $b_i$  parameters for many major inorganic ion species and a few important trace metals. The values used were taken largely from the WATEQ3 data compilation (1). Where data are not available or if the user selects it, the Davies equation will be used.

The Davies equation as implemented in MINTEQA2 is

$$\log \gamma_i = -AZ_i^2 \left( \frac{I^{1/2}}{1+I^{1/2}} \right) - 0.24I_i \quad 2.34$$

in which the variables are defined as in equation 2.32.

With the exception of  $H_2O$ , activity coefficients of neutral species are calculated using the development of Helgeson (10),

$$\log \gamma_i = \alpha_1 I \quad 2.35$$

where the constant  $\alpha_1$  is set equal to 0.1 in MINTEQA2.

Users are cautioned that the activity correction models presented here are generally not intended for use at ionic strengths greater than 0.5. At higher ionic strengths, as in marine conditions (ionic strength = 0.7 m), these correction equations may still provide usable results; this should be verified for the specific system to be modeled. Alternatively, one should consider adding expanded versions of the Debye-Hückel equation, which

include terms to account for ion interactions occurring in more concentrated solutions. The work of Pitzer and coworkers (16-18) provides some useful alternative equations.

Successive sets of log K values that reflect the temperature corrections (van't Hoff) and activity coefficient corrections (Debye-Hückel or Davies) above are computed and substituted into the mole balance expressions. If no solids are specified, the Jacobian matrix relating changes in mass balance to changes in component activities is used to calculate that set of component activities that will simultaneously minimize the mass imbalance for all species. The procedure used is an iterative Gaussian elimination and back substitution with a convergence test following each iteration.

### Activity of H<sub>2</sub>O

The activity of water is estimated from

$$\{H_2O\} = 1 - 0.017 \sum_{i=1}^n C_i \quad 2.36$$

where the  $C_i$ 's represent the concentrations of individual ion species. Equation 2.36 is applicable only in dilute solutions and is based on a derivation using Raoult's law. The proportionality constant (0.017) is derived from a plot of H<sub>2</sub>O activity versus the number of solute ions (9).

### Obtaining Total Dissolved Carbonate from Alkalinity

Most geochemical equilibria of the natural environment are in some way dependent upon the total dissolved carbonate concentration,  $T_{CO_3^{2-}}$ . Water analyses frequently provide an alkalinity measurement rather than an analytical measurement of dissolved carbonate. MINTEQA2 can compute  $T_{CO_3^{2-}}$  from alkalinity. Implicit in the method used to compute  $T_{CO_3^{2-}}$  are the assumptions that the titration used to determine alkalinity was to the CO<sub>2</sub> equivalence point and that there exists no solid phase in the titrated solution possessing additional acid-neutralizing capacity, all solids having been dissolved. This last assumption means that no solids should be allowed in a MINTEQA2 run that uses alkalinity. If modeling of solid phases is desired, do a preliminary model run without solids solely for calculating  $T_{CO_3^{2-}}$ , then use that calculated value in further modeling with solids rather than alkalinity.

Alkalinity as used here means that the value supplied represents the acid-neutralizing capacity of the solution as determined by titrating the solution to the CO<sub>2</sub> equivalence point. This corresponds to an operational definition implemented in MINTEQA2 which is: The alkalinity is given by the negative of the TOTH expression when the components are the principal components at the CO<sub>2</sub> equivalence point. Beyond this, the exact definition of alkalinity as used in a particular problem depends upon the content of the database file, ALK.DBS. The content of that file is entirely the responsibility of the user; it is not to be thought of as a database file, but

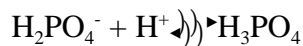
rather as an auxiliary input file. The definition of alkalinity as the negative of the equation for TOTH and the use of ALK.DBS are illustrated below.

In general, the principal components of an aqueous solution at the CO<sub>2</sub> equivalence point are H<sub>2</sub>O, H<sup>+</sup>, and the most abundant soluble species of each chemical entity. MINTEQA2 has a pre-defined set of components not all of which are the principal components at the CO<sub>2</sub> equivalence point, but this does not invalidate the applicability of the operational definition of alkalinity. It simply means that the alkalinity expression will incorporate species that may also be components. Practically, the procedure for determining the alkalinity factors needed for carbonate containing species in THERMO.DBS and for entries in ALK.DBS is to write (outside of MINTEQA2) the TOTH expression derived using the principal components at the CO<sub>2</sub> equivalence point. The negative of the coefficient for each species as it occurs in the TOTH equation is the alkalinity factor for that species. Stated differently, the contribution of each species in solution to the alkalinity is given by the negative of the stoichiometry of H<sup>+</sup> in that species times the species concentration. The only species that are implicitly included as contributors to the entered alkalinity is the Type I species (CO<sub>3</sub><sup>2-</sup>) and those Type 2 species for which there is a non-zero entry for the alkalinity factor in THERMO.DBS (such as for HCO<sub>3</sub><sup>-</sup>). For these species, it is not necessary for the user to know the alkalinity factor; the appropriate factor is already in THERMO.DBS. If other species are to be included as contributors to alkalinity, the ID number and the proper alkalinity factor, as given by the TOTH expression derived using the principal components at the CO<sub>2</sub> equivalence point, must be entered in ALK.DBS. Entries for species containing CO<sub>3</sub><sup>2-</sup> MUST NOT be included in that file. Suppose for example that the sample you wish to model and for which you've measured the alkalinity contains appreciable dissolved phosphate. You may wish to account for the phosphate contribution to the measured alkalinity so as to arrive at a more correct value for total dissolved carbonate. The procedure for doing this is:

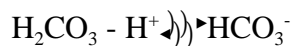
- 1) Determine the principal components at CO<sub>2</sub> equivalence point:



- 2) Write out a mole balance equation for H<sup>+</sup> including all species for which the stoichiometry of the component H<sup>+</sup> is non-zero. This is done by first writing the reactions to produce all the species using the components above as reactants. For example,



and



The stoichiometries of H<sup>+</sup> in HCO<sub>3</sub><sup>-</sup> and H<sub>3</sub>PO<sub>4</sub>, respectively, are 1 and -1. The complete TOTH expression then is

$$\text{TOTH} = [\text{H}^+] - [\text{OH}^-] - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}] + [\text{H}_3\text{PO}_4] - [\text{HPO}_4^{2-}] - 2[\text{PO}_4^{3-}] \quad 2.37$$

3) Noting that the  $pK_1$  for  $H_3PO_4$  is 2.2, we might choose to omit that species altogether due to its negligible concentration above pH 4. Retaining it here for illustration, entries in ALK.DBS would be:

```

3305802 -1.00
3305800 1.00
  580 2.00
3300020 1.00
  330 -1.00

```

where the 7-digit and 3-digit numbers are species ID numbers and the rightmost digit in each ID number is in column 7 and the first line in the file holds the first entry. The ID numbers correspond to species:

```

3305802 = H3PO4
3305800 = HPO42-
  580 = PO43-
3300020 = OH-
  330 = H+

```

The alkalinity equation to which the value input for alkalinity corresponds is  $alk = -TOTH$  or:

$$alk = -[H^+] + [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] - [H_3PO_4] + [HPO_4^{2-}] + 2[PO_4^{3-}] \quad 2.38$$

In most natural systems, the phosphate species are at much lesser concentration than the carbonate and can be neglected. In any case, the user controls the alkalinity equation by preparing ALK.DBS.

If this same file is used in a MINTEQA2 run for which component ID # 580 ( $PO_4^{3-}$ ) is not included, then those entries in ALK.DBS that involve component 580 are simply ignored and the alkalinity equation that would be used is:

$$alk = -[H^+] + [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] \quad 2.39$$

Let the contribution of non-carbonate containing species to the input alkalinity be called non-carbonate alkalinity. Then, the dissolved total inorganic carbon  $T_{CO_3^{2-}}$  is given by

$$T_{CO_3^{2-}} = alk - excrb - noncrb + [H_2CO_3] \quad 2.40$$

where

$alk$  = input alkalinity value converted to eq/L.

$excrb$  = total number of excess equivalents of acid consumed per mole of carbonate containing species, (summed over all such species). For each carbonate species, the alkalinity factor gives the total number of equivalents of acid consumed per mole. Therefore, the excess equivalents for each such species is

given by the difference between the alkalinity factor and the stoichiometry of  $\text{CO}_3^{2-}$  in that species times the number of moles, that is, times the concentration (per liter basis).

$\text{noncrb}$  = total number of equivalents of non-carbonate alkalinity (summed over all species contributing to non-carbonate alkalinity). For each non-carbonate species, the alkalinity factor is the number of equivalents of acid consumed per mole. Therefore, the number of equivalents of non-carbonate alkalinity for each such species is the alkalinity factor times the species concentration (per liter basis).

Since the alkalinity as given by equation 2.40 is a function of the speciation and thus, so is  $T_{\text{CO}_3^{2-}}$ , MINTEQA2 re-computes the  $T_{\text{CO}_3^{2-}}$  with each iteration. The user is reminded that the measured alkalinity assumes that there is no additional acid-neutralizing capacity in the form of solids. The measured alkalinity value cannot be used to compute an accurate value of  $T_{\text{CO}_3^{2-}}$  if solid phases are specified or allowed to precipitate. If the problem being modeled involves solids, use the alkalinity value in a preliminary run with no solid phases present or allowed. Then, in subsequent runs with solid phases, use the computed total dissolved carbonate concentration ( $T_{\text{CO}_3^{2-}}$ ) from that preliminary run rather than the measured alkalinity.

## CHAPTER 3

### ADSORPTION MODELS

Seven options are currently available in MINTEQA2 for modeling surface reactions. These include: 1) the activity  $K_d$  model, 2) the activity Langmuir model, 3) the activity Freundlich model, 4) the ion exchange model, 5) the constant capacitance model, 6) the triple-layer model, and 7) the diffuse-layer model. Thermodynamic database files of surface reactions are generally not provided for these models as for aqueous and solid species; the user must provide the set of surface reactions and their equilibrium constants. An exception is a database of several surface reactions relevant to the diffuse-layer model for trace metal adsorption onto an iron oxide surface. Mathematical formalisms and input data requirements of the individual adsorption models are discussed in separate sections below.

In the implementation of adsorption models in MINTEQA2, five different surfaces may be simultaneously defined for a single program execution. Each surface may have up to two types of sites. Only one adsorption model may be specified in a single execution ) e.g., it is not possible to define one surface undergoing adsorption in accordance with the Freundlich model and another surface undergoing Langmuir adsorption in the same MINTEQA2 run. The general modeling approach is to create a component to represent a particular type of site on a particular surface and then to write reactions between other components and that site. The reactions are introduced to MINTEQA2 through its input file and the solution is equilibrated with the surface species treated mathematically as aqueous species except with certain peculiarities pertinent to the adsorption model specified. When the equilibrium composition is determined, the equilibrated mass distribution between the dissolved, sorbed, and solid phases is computed and reported. When comparing MINTEQA2 equilibrated results with experimental  $K_d$  values, the MINTEQA2 adsorbed and precipitated species should be grouped together because these two phases are not experimentally distinguishable. There is no intrinsic difference within MINTEQA2 that distinguishes one surface from another nor one site on a surface from another. The user establishes the difference between any two surfaces and between the two sites on a surface by specifying the surface concentration and other surface specific parameters, such as specific surface area, and by specifying the reactions that each site may undergo.

#### Naming and Numbering Surface Species

Developing a coherent notational scheme for the naming of surface sites and the species that pertain to them is a difficult task. The notation frequently used in the literature for the electrostatic models seems to be primarily applicable to oxide surfaces. Nevertheless, it does provide a coherent system and we have used "SOH" to designate a surface site throughout this chapter. Within MINTEQA2, a more elaborate but generic scheme is



used both for naming and numbering surface species. The explanation that follows is not intended as a guide on how to name or number surface reactions. In fact, PRODEFA2 is aware of the rules described below so that specifying surfaces, sites, the parameters that define them, and the reactions in which they are involved is rather automatic. MINTEQA2 does not really care about the names; they are for the benefit of the user in organizing the problem and interpreting the results. ID numbers do have significance within MINTEQA2. The cardinal rule is: Do not change the component or species ID numbers assigned by PRODEFA2.

As for all MINTEQA2 components, the pre-defined adsorption components have 3 digits ) they span the range 811 through 859. The middle digit designates the surface number (1-5) and the meaning of the rightmost digit is:

- 1 = surface site 1
- 2 = surface site 2
- 3 = electrostatic component for the o-plane
- 4 = electrostatic component for the  $\beta$ -plane
- 5 = electrostatic component for the d-plane
- 6 = not used
- 7 = not used
- 8 = not used
- 9 = not used

Thus, component 834 represents the electrostatic component for the  $\beta$ -plane for the surface number 3, etc. (It is not really necessary to have defined surfaces 1 and 2 in order to have a surface with the number 3 although PRODEFA2, which would ordinarily be used to design the input file, will define the surfaces beginning with number 1. Also, as will be seen below, the electrostatic component for the  $\beta$ -plane is relevant to the triple-layer model only; this component would never be used for any of the other models.) The 3-digit ID number of a site and the 3-digit ID number of another component that reacts with that site are combined by suffixing the former with the latter and then an arbitrary digit is suffixed to that result to give a 7-digit number to represent the reaction product. For example, 8123301 would represent a surface species resulting from a reaction between site 2 on surface 1 and  $H^+$  (whose 3-digit number is 330). The rightmost digit (1) is arbitrary and is there to insure that the 7-digit number is unique (there could be other reactions between this site and  $H^+$ ).

The names assigned to those surface species that are reaction products are left to the discretion of the user (PRODEFA2 will query for the name). However, the names of the surface components themselves are pre-determined. These names are of the form ADSnTYP1, ADSnTYP2, ADSnPSI0, ADSnPSIB, ADSnPSID where n refers to surface number. For example, ADS1TYP1 corresponds to site 1 on surface 1 (component ID number 811), ADS4PSID corresponds to the electrostatic component representing the d-plane on surface number 4.

For the explanation and discussion of the adsorption models that follows, we have used the simpler notation of SOH to designate a surface site and electrostatic terms are referred to in accepted notation of  $\sigma$  and  $\psi$  to represent surface charge and potential, respectively.

## Non-Electrostatic Adsorption Models

The seven adsorption models in MINTEQA2 are conveniently grouped into those that involve electrostatic terms and those that do not. The non-electrostatic models have been in common use and certain conventions as to their use have become accepted (14). The specifics of each model and departures from accepted model conventions in MINTEQA2 are explained below.

### Activity $K_d$ Adsorption Model

The activity  $K_d$  adsorption model implemented in MINTEQA2 differs in two respects from the usual definition of the  $K_d$  model. For an adsorbing metal M,  $K_d$  is conventionally defined as the ratio of the concentration of metal bound on the surface to total dissolved metal concentration at equilibrium. That is,

$$K_d = \frac{[\text{SOH}\cdot\text{M}]}{[\text{M}]_T} \quad 3.01$$

where  $[\text{SOH}\cdot\text{M}]$  represents the concentration of adsorption sites occupied by an ion M or surface-bound metal and  $[\text{M}]_T$  is the total dissolved equilibrium concentration of M.

In the MINTEQA2 activity  $K_d$  model,

$$K_d^{\text{act}} = \frac{\{\text{SOH}\cdot\text{M}\}}{\{\text{M}\}} \quad 3.02$$

where  $\{\text{M}\}$  is the free activity of M in the equilibrium solution. Following convention and because there is no generally accepted method of computing activity coefficients for unreacted or reacted adsorption sites, we define those coefficients as unity so that  $\{\text{SOH}\cdot\text{M}\} = [\text{SOH}\cdot\text{M}]$ . Then in terms of concentrations, equation 3.02 becomes

$$K_d^{\text{act}} = \frac{[\text{SOH}\cdot\text{M}]}{\gamma_m[\text{M}]} \quad 3.03$$

where  $\gamma_m$  is the activity coefficient of dissolved species M and  $K_d^{\text{act}}$  may be thought of as the equilibrium constant of the surface reaction



SOH represents unreacted surface sites and is present at a fixed activity (or fixed concentration if we insist that the activity coefficient pertaining to SOH is unity). Taking the activity of SOH as 1.0 equation 3.03 may be

thought of as a mass action expression for reaction 3.04. This is implemented in MINTEQA2 by assigning the component representing unreacted sites, SOH, as a Type III species. The constraint is that there is an unlimited supply of fresh unreacted sites; the surface cannot approach saturation no matter how much M adsorbs. The reader will note that this constraint also renders competition between different metals ( $M_1, M_2, \dots$ ) meaningless. Equation 3.02 defines the equilibrium constant actually used for an activity  $K_d$  reaction in MINTEQA2; the reader will observe that this is a unitless ratio. However, PRODEFA2 calculates this value from the more common expression of  $K_d$  in l/kg and solid concentration in kg/l (e.g., the number of kg of soil with which one liter of solution is equilibrated).

### Activity Langmuir Adsorption Model

In the Langmuir adsorption model, the number of surface sites available for adsorption must be specified at the outset. The surface reaction can be written identically as for the activity  $K_d$  model



and where we again express the equilibrium constant in terms of activities

$$K_L^{\text{act}} = \frac{\{\text{SOH}\cdot\text{M}\}}{\{\text{M}\} \{\text{SOH}\}} \quad 3.06$$

If, as is the case for every adsorption model in MINTEQA2, we arbitrarily assign the value of unity to the activity coefficients pertaining to unreacted and reacted surface sites, we can re-write the mass action equation 3.06 as

$$K_L^{\text{act}} = \frac{[\text{SOH}\cdot\text{M}]}{\gamma_m[\text{M}] [\text{SOH}]} \quad 3.07$$

To see the correspondence between this implementation of the Langmuir model and the defining equation to which that model is commonly ascribed, we note that the mass balance equation written for the surface sites is

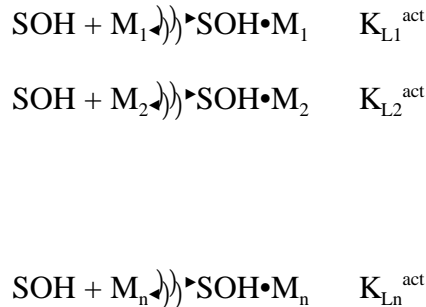
$$[\text{SOH}]_T = [\text{SOH}\cdot\text{M}] + [\text{SOH}] \quad 3.08$$

where  $[\text{SOH}]_T$  = total concentration of surface sites available. The combined mass balance and mass action expressions yield the Langmuir relationship in terms of activities

$$[\text{SOH}\cdot\text{M}] = \frac{K_L^{\text{act}} [\text{SOH}]_T \gamma_m[\text{M}]}{1 + K_L^{\text{act}} \gamma_m[\text{M}]} \quad 3.09$$

To express 3.09 in terms of concentrations, replace  $K_L^{act}$  with  $K_L$  and let  $\gamma_m = 1$ .

The so-called competitive Langmuir model for the competing metals  $M_1, M_2, \dots$  is derived in a similar manner with additional reactions defined:



All that is required to model such competition in MINTEQA2 is to define these separate reactions on the surface.

The only difference between the Langmuir and activity  $K_d$  treatments is that the Langmuir equation accounts for the finite concentration of surface sites. It is also important to remember that the  $K_L$  used is an "activity"  $K_L$  rather than the conventional concentration-based constant.

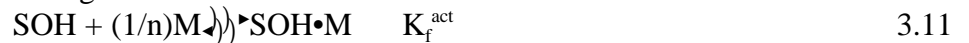
A meaningful way to employ commonly available "concentration"  $K_L$  data is to model the experimental supernatant solution in which the  $K_L$  was determined and replot the data in terms of the MINTEQA2 activities of the sorbate. To do this, the Langmuir isotherm is first rewritten in the linear form.

$$\frac{[M]}{[\text{SOH}\cdot M]} = \frac{1}{K_L} \frac{[M]}{[\text{SOH}]_T} + \frac{[M]}{[\text{SOH}]_T} \tag{3.10}$$

If the Langmuir isotherm accurately describes the system, a plot of  $[M]/[\text{SOH}\cdot M]$  will yield a straight line of slope  $1/[\text{SOH}]_T$  and intercept  $1/K_L[\text{SOH}]_T$ . Conventionally, the constant  $K_L$  is obtained by dividing the slope by the intercept. The  $K_L^{act}$  can be derived from an analogous plot in which the MINTEQA2 sorbate activities  $\{M\}$  are plotted in place of the sorbate concentration terms  $[M]$ .

### Activity Freundlich Model

The mass action equation representing the Freundlich model can be written



$$K_f^{act} = \frac{\{\text{SOH}\cdot M\}}{\{M\}^{1/n} \{\text{SOH}\}} \tag{3.12}$$

Like the activity  $K_d$  model, an unlimited supply of unreacted sites is assumed and the activity and concentration of surface species are considered to be equal. Imposing the condition  $\{\text{SOH}\} = 1.0$ .

$$[\text{SOH}\cdot\text{M}] = K_f^{\text{act}} \{\text{M}^{m+}\}^{1/n} \quad 3.13$$

$[\text{SOH}\cdot\text{M}]$  = equilibrium concentration of reacted sites or surface-bound metal

$\{\text{M}\}$  = equilibrium activity of the free metal species M

$1/n$  = mass action stoichiometric coefficient pertaining to M

This is similar to the activity  $K_d$  relationship except that the stoichiometric coefficient of the reacting species M is  $1/n$ . For the special case where  $n = 1$ , the Freundlich and activity  $K_d$  mass action equations are identical. Note that the mass balance stoichiometry for M is 1.0, just as it is for the activity  $K_d$  model. It is only the mass action stoichiometry that is  $1/n$ .

$K_f^{\text{act}}$  may be derived from conventional concentration  $K_f$  data in a manner similar to obtaining  $K_d^{\text{act}}$  from conventional  $K_d$  data. The logarithmic form of the Freundlich mass action equation (3.13) is

$$\log [\text{SOH}\cdot\text{M}] = \log K_f^{\text{act}} + 1/n \log \{\text{M}\} \quad 3.14$$

If the Freundlich model is applicable to a given system, a plot of  $\log [\text{SOH}\cdot\text{M}]$  versus  $\log \{\text{M}\}$  will yield a straight line of slope  $1/n$  and intercept  $\log K_f^{\text{act}}$ . Experimental isotherms usually involve concentration rather than activity plots. The  $K_f$  values from these plots can be converted to  $K_f^{\text{act}}$ 's by using MINTEQA2 to speciate the equilibrium solution at each point along the adsorption isotherm and re-plotting the isotherm in terms of  $\log \{\text{M}\}$  rather than  $\log [\text{M}]$ . The resulting intercept will be the  $K_f^{\text{act}}$  required by MINTEQA2. Alternatively, one can simply guess the activity coefficient of the adsorbing metal M for each concentration along the curve.

### Ion Exchange Adsorption Model

Ion exchange sorption is defined as the process by which an ion from solution is exchanged for one on the solid surface. The relative abilities of solute ion species to compete for surface sites is governed by intrinsic factors and their solution activities. The ion exchange model assumes that the surface site is initially occupied by an exchangeable ion that is released into solution during the exchange process. The ion exchange reaction and its corresponding mass action equation can be expressed as



$$K_{\text{ex}} = \frac{\{\text{M}_1\} \{\text{SOH}\cdot\text{M}_2\}}{\{\text{M}_2\} \{\text{SOH}\cdot\text{M}_1\}} \quad 3.16$$

where  $M_1$  is the ion initially occupying the exchange site,  $M_2$  is the replacing ion to be adsorbed, and  $\text{SOH}\cdot M_1$ ,  $\text{SOH}\cdot M_2$  are surface sites occupied by the respective ions. As for the previous models, no attempt is made to calculate activity coefficients for the occupied sites; they are arbitrarily taken as unity and  $K_{\text{ex}}$  is written in terms of concentrations by replacing activity of each species in equation 3.16 with the product of concentration and activity coefficient.

Earlier versions of MINTEQ implemented the ion exchange model in such a way as to require an infinite supply of solid of constant composition. This condition implied a fixed solution phase activity ratio between the two exchanging ions. Also, there was no mass balance on the ion that initially occupied the surface and was expelled during the exchange reaction. Beginning with MINTEQA2 version 3.00, these features are no longer model constraints; the model conforms to conventional and accepted usage as given by equations 3.15 and 3.16.

Selectivity coefficients ( $K_{\text{ex}}$ 's) can be derived from the literature for most common ions such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , etc., but are seldom available for trace metals. In using the ion exchange algorithm, users must supply the reaction stoichiometries and selectivity constants and specify the ion that initially occupies the exchange sites. Note also that reaction stoichiometries may be related to ion charge. For example, a single  $\text{Ca}^{2+}$  ion may replace two  $\text{Na}^+$  ions and thus occupy two sites.

### Electrostatic Adsorption Models

All four adsorption models discussed thus far neglect the electrostatic influences of charged surfaces on the solution and the counter influences of changes in surface charge due to solution composition. Many colloidal particles carry a significant surface charge that creates electrostatic potentials extending into the suspending solutions. Solution ions with charge of the same polarity as the surface are repelled and ions of opposite charge are attracted. Because of this, the electrostatic potentials associated with charged surfaces may greatly influence the adsorptive behavior of charged species. This influence is incorporated in electrostatic adsorption models by including terms in the mass action equations that modify the activities of sorbate ions approaching charged surfaces by the electrical work necessary to penetrate the zone of electrostatic potentials ( $\psi$ 's) extending away from the surface.

Several models are available to account for these effects in various degrees of detail. Readers are referred to Westall and Hohl's (22) excellent review for clear comparisons of the presently available surface complexation/ electrostatic models. The discussion that follows will be limited to brief descriptions of the three surface complexation model options provided in MINTEQA2: the constant capacitance, diffuse-layer, and triple-layer models. These three models are closely related in many ways. Each treats adsorption as a surface complexation reaction (that is, the reaction is treated as analogous to a solution phase complexation reaction governed by a mass action equation) and each accounts for the electrostatic potentials at the charged surface. They differ primarily in the types of surface species that are allowed within specific physical locations or layers extending away from the surface and in the parameters of the electrostatic model that each employs.

The surface complexation models available in MINTEQA2 were developed to describe surface reactions in amorphous metal oxide systems (2,4,5) and have also been applied to clay systems (12). The large body of experimental evidence that has accumulated from laboratory bench studies of pure oxide systems indicates that

surface complexation models can predict adsorption behavior (6). Few data exist for applying these models to natural systems where complex mixtures of impure amorphous oxides, clays, and humic materials provide the reactive surfaces. Recent work by Loux et.al. (13) demonstrated good model agreement with experimental results on an aquifer material spiked with trace metal cations. The adsorbing surface was modeled as amorphous iron oxide using MINTEQA2 with the diffuse-layer model using surface reactions and their associated stability constants as given by Dzombak (6). In general, freshly prepared laboratory oxide systems often behave differently from the aged, impure mixtures found in the environment. The interactions are such that properties of the mixture as a whole are not necessarily those obtained by summing the properties of the individual components. Care must be used in selecting input parameters for natural systems using MINTEQA2's surface complexation models.

The constant capacitance, diffuse-layer, and triple-layer models all treat trace metal surface reactions as complexation reactions analogous to the formation of complexes in solution. Surface sites are represented as SOH groups where S's are metals associated with the solid structure and located at the solid-liquid interface. Some ions, such as H<sup>+</sup>, OH<sup>-</sup>, and a variety of trace metal ions are presumed to be specifically adsorbed at the surface via complexation with the surface sites. In all three models, a charge ( $\sigma$ ) associated with the surface is assumed to be balanced by a charge ( $\sigma_d$ ) associated with a diffuse layer of counterions. These charges are such that  $\sigma + \sigma_d = 0$ . In the constant capacitance and diffuse-layer models, all specifically adsorbed ions contribute to the surface charge ( $\sigma$ ). However, in the triple-layer model, the net charge due to adsorption is the sum of the charges associated with two adsorbing planes rather than one. The innermost of the two planes (the  $\alpha$ -plane) specifically adsorbs H<sup>+</sup> and OH<sup>-</sup> and is characterized by charge  $\sigma_\alpha$ . The other plane ( $\beta$ -plane) has charge  $\sigma_\beta$  resulting from the adsorption of other ions. The net surface charge is given by  $\sigma = \sigma_\alpha + \sigma_\beta$  and is balanced by the charge in the diffuse layer such that  $\sigma + \sigma_d = 0$ . Because the electrical potential gradients extending away from the surface are the direct result of the surface charge, the specifically adsorbed potential determining ions also govern distributions of counterions in the diffuse layer.

Activities of ions in solution and near the surface are influenced by the presence of electrostatic potentials arising from the surface charge. The activity difference between ions near the surface and those far away is the result of electrical work in moving the ions across the potential gradient between the charged surface and the bulk solution. The activity change between these zones is related to the ion charge ( $z$ ) and the electrical potential ( $\psi$ ) near the surface and can be expressed using the exponential Boltzmann expression,

$$\{X_s^z\} = \{X^z\} [e^{-\psi F/RT}]^z \tag{3.17}$$

Where:

$z$  = charge of ion X

$\{X_s^z\}$  = activity of an ion X of charge  $z$  near the surface

$\{X^z\}$  = corresponding activity of X in bulk solution outside the influence of the charged surface

$e^{-\psi F/RT}$  = Boltzmann factor

F = Faraday constant

R = ideal gas constant

T = absolute temperature

### General Implementation of Electrostatic Models in MINTEQA2

The general algorithm is similar for all three of the electrostatic models. Specific details for each model are discussed separately below. As mentioned above, for the constant capacitance and diffuse-layer models, there is only one layer or plane within which specifically adsorbed ions define the surface charge  $\sigma$ . Accordingly, that plane is commonly referred to as the o-plane and the surface charge and potential are denoted  $\sigma_o$  and  $\psi_o$ . We will retain that notation here as well as the notation  $\sigma_d$  and  $\psi_d$  for their counterparts in the diffuse layer. We point out, however, that the o-plane is defined differently in the triple-layer model and those parameters subscripted with "o" in that model should not be regarded as equivalent to the o-plane parameters of the former two models. Also, with regard to the constant capacitance and diffuse-layer models, we may refer to  $\sigma_o$  and  $\psi_o$  as "surface" charge and "surface" potential. This is not true of the triple-layer model because there are two planes ("o" and "β") associated with the surface. Thus, the charge at the beginning of the diffuse layer is defined in terms of  $\sigma_o + \sigma_\beta$ .

The Boltzmann factor of equation 3.17 (with the potential  $\psi$  subscripted to indicate the layer to which it applies) is incorporated as a scaling factor by assigning it a component ID number and writing the surface reaction so as to include it as a reactant of appropriate stoichiometry. The reader should realize that this is only a mathematical way to incorporate the parameters of the desired model into an existing computational scheme. The mass action equations for surface reactions will contain those fake components (which we shall refer to as electrostatic components) that are really the Boltzmann factors. Also, because they are not real chemical entities, there is no analytical total to ascribe as input for the electrostatic components, rather the total charge is calculated via expressions that are unique to each model and are mathematically related to the potential. Still, we will refer below to  $T_\sigma$  referenced to a specific plane as the total charge for that plane but note that we do not imply a measured input value as was the case with earlier references to T. Also, MINTEQA2 will seek to perform mass balance calculations on all components. It is necessary, therefore, to direct otherwise for the electrostatic components by designating them as Type VI (excluded from mass balance). Charge balance equations that are analogous to mass balance (see equation 2.10) are defined for the electrostatic components and have the form

$$Y_\sigma = \sum_i a_{i\sigma} C_i - T_\sigma \quad 3.18$$

where  $a_{i\sigma}$  is the stoichiometry of the electrostatic component pertaining to  $\sigma$  in species  $i$ .

The overall sense of the electrostatic calculations for a given plane is this:



- 1) Calculate the total charge  $T_\sigma$  from the potential on the plane by using a functional relationship appropriate for the model (see below). Initial guesses for the potential of each plane are provided in the input file.
- 2) Calculate the total charge on the plane by a different method, namely, by summing the charges of all species specifically adsorbed on that plane. Operationally, this becomes a summation of the charge contribution from all species in which the stoichiometry of the component representing the plane is non-zero.

$$\sum_i a_i C_i$$

- 3) Obtain the difference in the total charge pertaining to the plane as in equation 3.18. Test whether the difference is less than some small tolerance value. If not, adjust the potential for that plane and repeat. Of course, the potentials are adjusted simultaneously with the activities of other components.

Calculations involving the surface sites themselves are exactly as described for other real chemical entities by the mass action equations (2.08) and mass balance equations (2.10).

As for all MINTEQA2 adsorption models, the activity coefficients of both the reacted and unreacted surface sites are always taken as unity. The artificial contrivance whereby we have created components to represent the Boltzmann factors demands that we create activity coefficients for them as well. Imaginary though they be, we make them innocuous by setting them to unity.

All surface reactions in MINTEQA2 are written in terms of the neutral surface site SOH (components 8n1 or 8n2;  $n = 1, 2, \dots, 5$ ) and the equilibrium constants appropriate for MINTEQA2 are formation constants. The constants for many reactions found in the literature are intrinsic constants, which sometimes are referenced to the protonated surface site  $\text{SOH}_2^+$  (for adsorbing anions) and to the deprotonated site  $\text{SO}^-$  (for adsorbing cations). Such reactions must be re-written in terms of MINTEQA2 components and their equilibrium constants adjusted accordingly before use in MINTEQA2. The surface reactions, which are generally model specific, must be provided to MINTEQA2 through its input file; there is no permanent database of adsorption reactions. Version 3.00 includes a separate file containing surface reactions that are applicable to the diffuse-layer model for an iron oxide surface. To be used, that file (FEO-DLM.DBS) must be appended to a previously prepared input file. Instructions for doing this are provided in PRODEFA2. For other surface reactions that the user may wish to create for an input file, PRODEFA2 is capable of computing the correct stoichiometry for the electrostatic components. In fact, this is done automatically without user intervention. The user may be asked to supply an initial activity guess for the electrostatic components (for use in item 1 above). Specifically, a seed value representing the negative of the exponent in the Boltzmann factor of equation 3.17 is requested and a guess of zero will usually work.

The analytical input concentration for the surface site,  $T_{SOH}$ , is expressed in moles of sites per liter and is calculated from

$$T_{SOH} = \frac{N_s S_A C_s}{N_A} \tag{3.19}$$

Where:

$N_s$  = the analytically determined surface site density (number of sites/m<sup>2</sup>)

$S_A$  = specific surface area of the solid (m<sup>2</sup>/g)

$C_s$  = concentration of solid in the suspension (g/L)

$N_A$  = Avogadro's number (6.02 X 10<sup>23</sup>)

$N_s$ ,  $S_A$ , and  $C_s$  are requested from the user by PRODEFA2. From these parameters,  $T_{SOH}$  is calculated.

### Constant Capacitance and Diffuse-Layer Models

The constant capacitance and diffuse-layer models have many similarities. Both define specific adsorption of all ions on the "o" plane. Also, their mass action and charge balance equations are identical (except for the numerical value of the equilibrium constants). The difference in these two models is in the function relating total surface charge  $\sigma_o$  to surface potential  $\psi_o$ . For the diffuse-layer model,

$$T_{\sigma_o} = 0.1174 I^{1/2} \sinh(Z\psi_o F/2RT) \tag{3.20}$$

where  $Z$  is the valency of the symmetrical electrolyte (which we take as unity),  $I$  is ionic strength, and all other parameters are defined as in equation 3.17. This expression is used in evaluating equation 3.18.

The constant capacitance model is a special case of the diffuse-layer model for solutions of high ionic strength and surfaces of low potential. In such systems, equation 3.20 can be approximated by

$$T_{\sigma_o} \approx C\psi_o \tag{3.21}$$

where  $C$  is a constant capacitance term. Equation 3.21 is used to evaluate equation 3.18 for the constant capacitance model. Although the models are similar in implementation, the capacitance term  $C$  is often treated as a fitting parameter rather than as a measured characteristic of the system and the constant capacitance model can be applied to systems of all ionic strengths. Outside the range of ionic strength where the approximation of equation 3.21 is valid, the constant capacitance and diffuse-layer models are not the same.

As mentioned, the assignment of specifically adsorbed species to the o-plane, the mass action equations, and the charge balance equations for the constant capacitance and diffuse-layer models are the same. Figure 3.1 shows a conceptual structure of an oxide surface as represented by either of these two models. The discussion of surface reactions that follows applies to either model.

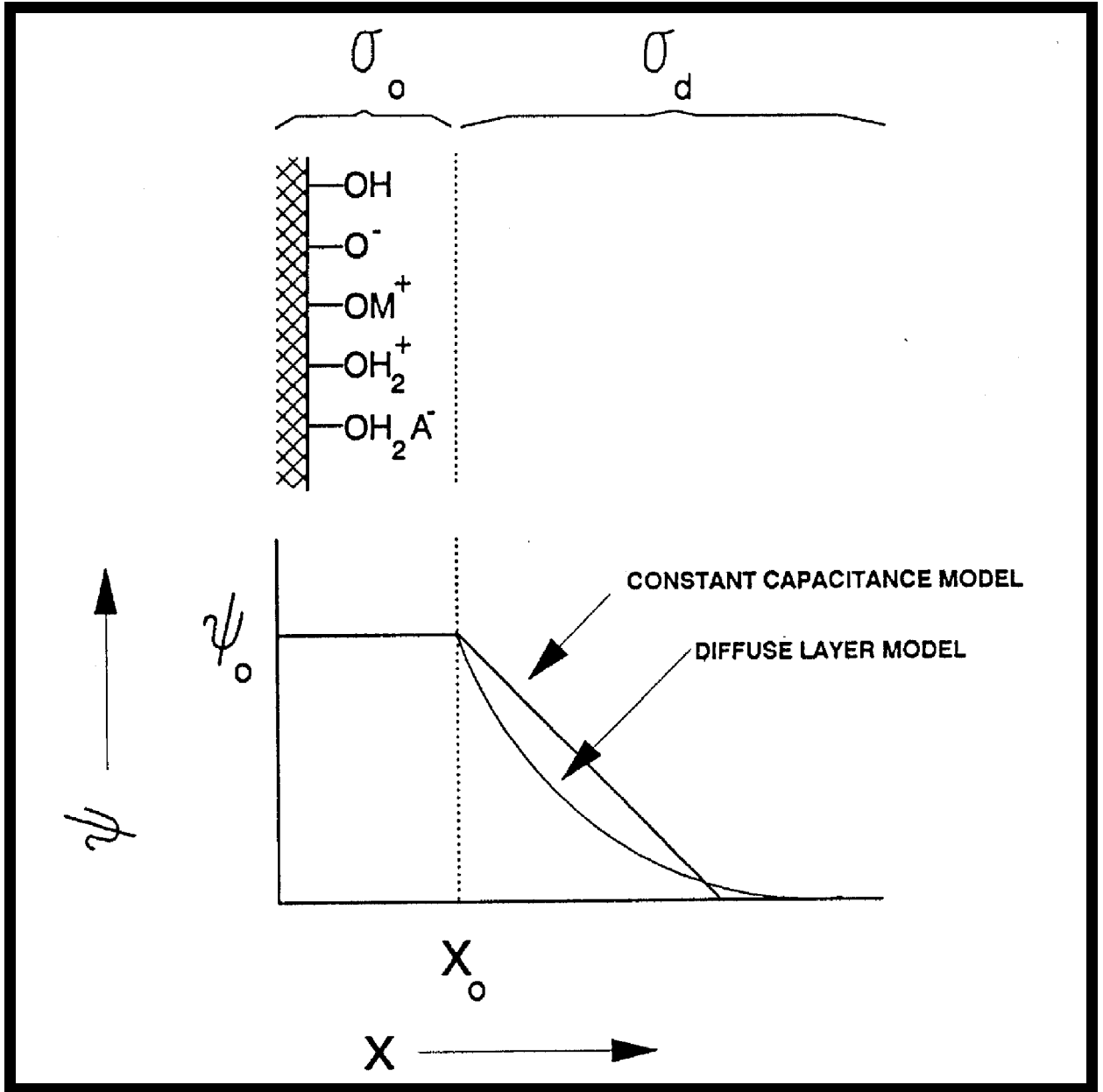


Figure 3.1. Schematic representation of the surface charge/potential relationships used in the constant capacitance and diffuse-layer models.

Surface reactions are represented by mass action expressions with Boltzmann factors represented as components (see equation 3.17). Stoichiometries of those components are included in the definition of surface reactions provided to MINTEQA2. Several examples of such reactions and their corresponding mass action expressions are given below to illustrate the use of Boltzmann factors. Consider the protonation reaction



where  $\text{H}_s^+$  denotes a hydronium ion near the surface. The corresponding mass action expression is

$$K = \frac{\{\text{SOH}_2^+\}}{\{\text{SOH}\} \{\text{H}_s^+\}} \quad 3.23$$

As mentioned previously, the surface species are presumed to have activity coefficients equal to unity and the terms  $\{\text{SOH}_2^+\}$  and  $\{\text{SOH}\}$  need no further conversion; however, the activity of the surface hydronium ions must be corrected for the energy expended in moving them to the charged surface where the reaction occurs. This is accomplished by expressing  $\{\text{H}_s^+\}$  in terms of the bulk solution hydronium ion activity  $\{\text{H}^+\}$ . In this case,  $z = 1$  and equation 3.17 is written

$$\{\text{H}_s^+\} = \{\text{H}^+\} e^{-\psi_o F/RT} \quad 3.24$$

The mass action expression used in MINTEQA2 is obtained by substituting this expression into Equation 3.23.

$$K = \frac{\{\text{SOH}_2^+\}}{\{\text{SOH}\} \{\text{H}^+\} [e^{-\psi_o F/RT}]} \quad 3.25$$

With the Boltzmann factor incorporated as a component, the stoichiometry for this reaction in MINTEQA2 corresponds to:



For the corresponding de-protonation reaction



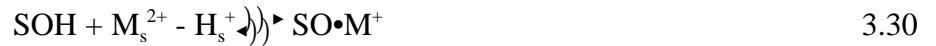
and its mass action expression

$$K = \frac{\{\text{SO}^-\} \{\text{H}^+\} [e^{-\psi_o F/RT}]}{\{\text{SOH}\}} \quad 3.28$$

The stoichiometry in MINTEQA2 corresponds to:



For multivalent species, both charge and stoichiometry of the adsorbing ion must be considered in writing the mass action expression. Consider the surface reaction involving the divalent cation  $M^{2+}$



The corresponding mass action expression is

$$\begin{aligned} K &= \frac{\{\text{SO} \cdot M^+\} \{\text{H}_s^+\}}{\{\text{SOH}\} \{M_s^{2+}\}} \\ &= \frac{\{\text{SO} \cdot M^+\} \{\text{H}^+\} [e^{-\psi_o F/RT}]}{\{\text{SOH}\} \{M^{2+}\} [e^{-\psi_o F/RT}]^2} \\ &= \frac{\{\text{SO} \cdot M^+\} \{\text{H}^+\}}{\{\text{SOH}\} \{M^{2+}\} [e^{-\psi_o F/RT}]} \end{aligned} \quad 3.31$$

In this case, the Boltzmann factor in the numerator can be canceled and the stoichiometry in MINTEQA2 corresponds to:



Mass action expressions for other surface reactions are formulated in a similar manner.

In addition to the surface reactions with their equilibrium constants and the parameters of equation 3.19, the constant capacitance model requires an input value for the capacitance,  $C$ . This is the capacitance (farads/m<sup>2</sup>) between the o-plane and the diffuse layer of counterions.

### Triple-Layer Model

The triple-layer model is generally more complex than the constant capacitance and diffuse-layer models. In the MINTEQA2 implementation of the triple-layer model, only protonation and deprotonation of surface sites are assigned to the o-plane. Other specifically adsorbed ions are assigned to the  $\beta$ -plane and determine the charge  $\sigma_\beta$  and potential  $\psi_\beta$  in that zone. Non-specifically adsorbed ions are envisioned as residing in the diffuse layer or 'd' plane and are influenced by  $\psi_d$  potentials. The capacitance between the o-plane and the  $\beta$ -plane is

denoted  $C_1$  and between the  $\beta$ -plane and d-plane,  $C_2$ . Both are treated as user-supplied constants in MINTEQA2. Background electrolytes are allowed to adsorb. Also, note that the potential gradients in the inner and outer zones are linear, but potentials decay exponentially in the diffuse layer zone. A schematic diagram of the triple-layer model surface is shown in Figure 3.2.

The input parameters for the triple-layer model are similar to those for the constant capacitance model except that two capacitance terms and three electrostatic components are required. As with the other electrostatic models, the first of these components (id number 8n3) pertains to the charge and potential on the o-plane. The second (id number 8n4) pertains to the charge and potential on the  $\beta$ -plane and the third (id number 8n5) to the d-plane.

Total charges associated with the triple-layer model o-,  $\beta$ -, and d- planes are related to the potential differences between planes.

$$T_{\sigma_o} = C_1 (\psi_o - \psi_\beta) \quad 3.33$$

$$T_{\sigma_\beta} = C_1 (\psi_\beta - \psi_o) + C_2 (\psi_\beta - \psi_d) \quad 3.34$$

$$T_{\sigma_d} = C_2 (\psi_d - \psi_\beta) \quad 3.35$$

Where:

$T_{\sigma_o}$ ,  $T_{\sigma_\beta}$ , and  $T_{\sigma_d}$  = total charges associated with the o-,  $\beta$ -, and d-planes

$C_1$  and  $C_2$  = capacitances associated with the zones between the o- and  $\beta$ -planes and  $\beta$ - and d-planes, respectively

$\psi_o$ ,  $\psi_\beta$ , and  $\psi_d$  = electrostatic potentials at the o-,  $\beta$ -, and d-planes

The total charge on the o- and  $\beta$ -planes are used in equation 3.18 along with the summation of species that are specifically adsorbed on each plane and have non-zero stoichiometry in the appropriate electrostatic component.

Recalling that the d-plane has no specifically adsorbed ions and thus has zero stoichiometry in all species, we replace equation 3.18 for that plane only with

$$Y_{\sigma_d} = \sigma_d - T_{\sigma_d} \quad 3.36$$

where the diffuse layer charge ( $\sigma_d$ ) for a monovalent symmetric electrolyte is given by the Gouy-Chapman relationship

$$\sigma_d = - (\epsilon \epsilon_o RIT)^{1/2} \sinh(F\psi_d/2RT) \quad 3.37$$

Where:

$\epsilon$  = dielectric constant

$\epsilon_0$  = permittivity in free space ( $8.85 \times 10^{-12}$  (coulombs)<sup>2</sup>/joule-m

I = ionic strength

MINTEQA2 also uses Equation 3.37 as an approximation for non-symmetric electrolytes.



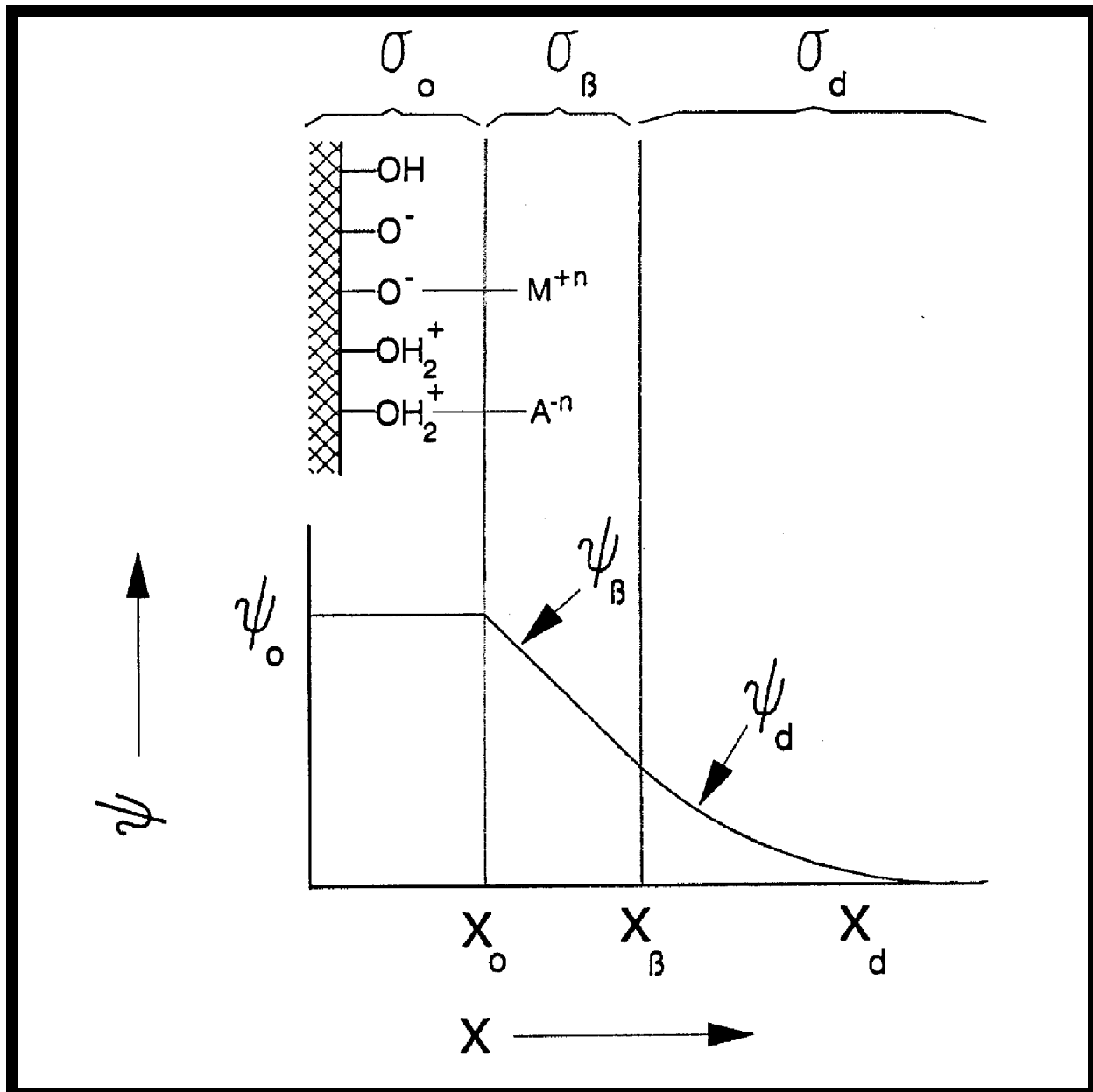


Figure 3.2. Schematic representation of surface species and charge/potential relationships in the triple-layer model.

Surface reactions in the triple-layer model are represented in a manner similar to the other two electrostatic models except that mass action expressions must have the proper stoichiometry for the electrostatic component representing the  $\beta$ -plane as well as the o-plane. No stoichiometry is needed for the d-plane because no specific adsorption occurs on that plane.

The following surface reactions and mass action expressions illustrate the determination of stoichiometric coefficients for those components. For the surface protonation and de-protonation reactions, the triple-layer model results are identical to those obtained for the constant capacitance and diffuse-layer models in equations 3.26 and 3.29 (although one could expect the numerical value of the equilibrium constants to be different). For the monovalent metal ion  $M^+$



With the substitution for  $\text{H}_s^+$

$$\{\text{H}_s^+\} = \{\text{H}^+\} [e^{-\psi_o F/RT}] \quad 3.39$$

(see equation 3.17) and a similar substitution for the metal ion near the surface (except the effective potential refers to the  $\beta$ -plane because that is where  $M^+$  is specifically adsorbed)

$$\{\text{M}_s^+\} = \{\text{M}^+\} [e^{-\psi_\beta F/RT}] \quad 3.40$$

the mass action expression is

$$K = \frac{\{\text{SO}\cdot\text{M}\} \{\text{H}^+\} [e^{-\psi_o F/RT}]}{\{\text{SOH}\} \{\text{M}^+\} [e^{-\psi_\beta F/RT}]} \quad 3.41$$

The reaction written in terms of MINTEQA2 components and including the electrostatic components is



For a surface reaction involving a divalent metal,  $M^{2+}$



the substitution of equation 3.39 together with

$$\{\text{M}_s^{2+}\} = \{\text{M}^{2+}\} [e^{-\psi_\beta F/RT}]^2 \quad 3.44$$

provides the mass action expression

$$K = \frac{\{\text{SO}\cdot\text{M}^+\} \{\text{H}^+\} [e^{-\psi_o F/RT}]}{\{\text{SOH}\} \{\text{M}^{2+}\} [e^{-\psi_\beta F/RT}]^2} \quad 3.45$$

The corresponding MINTEQA2 reaction is



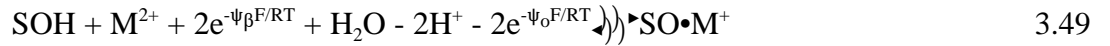
The combined hydrolysis/sorption reaction for an  $\text{M}^{2+}$  ion is expressed



and the corresponding mass action expression is written

$$K = \frac{\{\text{SO}\cdot\text{MOH}\} \{\text{H}^+\}^2 [e^{-\psi_o F/RT}]^2}{\{\text{SOH}\} \{\text{M}^{2+}\} \{\text{H}_2\text{O}\} [e^{-\psi_\beta F/RT}]^2} \quad 3.48$$

The corresponding MINTEQA2 reaction is



For the reaction of a monovalent anion ( $\text{A}^-$ ), a neutral surface species can result



With the substitution

$$\{\text{A}_s^-\} = \{\text{A}^-\} [e^{-\psi_\beta F/RT}]^{-1} \quad 3.51$$

the mass action expression is

$$K = \frac{\{\text{SOH}_2\cdot\text{A}\} [e^{-\psi_\beta F/RT}]}{\{\text{SOH}\} \{\text{A}^-\} \{\text{H}^+\} [e^{-\psi_o F/RT}]} \quad 3.52$$

and the MINTEQA2 reaction is written



Finally, for a divalent anion,



the mass action expression is

$$K = \frac{\{\text{SOH}_2 \bullet \text{A}^-\} [\text{e}^{-\psi_\beta F/RT}]^2}{\{\text{SOH}\} \{\text{A}^{2-}\} \{\text{H}^+\} [\text{e}^{-\psi_o F/RT}]} \quad 3.55$$

The MINTEQA2 reaction is written



The reader is reminded to write adsorption reactions in terms of MINTEQA2 components and to adjust the equilibrium constants accordingly before entering the reaction through PRODEFA2. The electrostatic components are of no concern in this procedure. PRODEFA2 will add the appropriate electrostatic components at the correct stoichiometry when the reaction is entered.

## CHAPTER 4

### USING MINTEQA2 AND PRODEFA2

The purpose of this chapter is to inform the reader how to use MINTEQA2 from an operational point of view. There is another level of understanding how to use the model -- a level that embodies knowledge of chemical, geological, and other physical parameters of the system to be modeled and from which a chemical question or problem is developed. Before addressing that level, it is necessary to learn to pose the chemical problem to the model. Largely, this consists of learning to use the interactive program PRODEFA2 to create input files for MINTEQA2. An effective way of becoming familiar with PRODEFA2 and the options it provides is to run through several interactive sessions and note the changes in the resulting files as you change your responses to the prompts. The following pages provide a "walk through" of a PRODEFA2 session. Because of the many options available and numerous branching of prompts; however, it is not practical to include every permutation of possible prompts and responses. Therefore, before beginning the "walk through," some general facts about both programs are discussed. These are points that would certainly become apparent after several sessions. Knowing about them beforehand will help the new user to anticipate the flow of logic and many of the prompts.

Appendix C describes the content of the distribution diskettes and general computer system requirements. There are several test files included on the diskettes that are helpful as learning aids. These are named TESTxx.HLP (PRODEFA2 dialogue file), TESTxx.INP (MINTEQA2 input file), and TESTxx.LST (MINTEQA2 output file). The "xx" represents additional numbers or characters of the name. The PRODEFA2 dialogue files (.HLP) provide a record of the prompts and responses that occurred during the interactive session in which the MINTEQA2 input files (.INP) were created and the MINTEQA2 output files (.LST) show the results when those files were executed with MINTEQA2. A useful approach to becoming familiar with PRODEFA2 is to print a particular .HLP file, and with the printout in hand, to run PRODEFA2 and respond to the prompts as shown on the printout. You should choose a different name for the input file you are creating so that the .INP file is not superseded and compare the new file with the .INP file. The .INP and .LST files for a problem using the triple-layer adsorption model are reproduced in Appendix D.

#### General Features and Organization of MINTEQA2 and PRODEFA2

The following features will become obvious after using the programs several times, but it is helpful to know them in advance:

- The two programs are completely separate. The sequence of their execution is generally PRODEFA2 followed by MINTEQA2. Execution of the former begins when the user types "PRODEFA2" at the

DOS (or DCL) prompt. MINTEQA2 is executed by typing "MINRUN" and answering the filename prompts.

- Both programs use the same thermodynamic database files (their names are listed in Appendix C). These files contain the pre-defined set of components and the reactions in which those components serve as reactants.
- Because the model has its own database, the primary information that must be conveyed through the input file to model a particular system is the total dissolved concentration or fixed activity of each component of the system. Components are selected from the pre-defined set by specifying either the first letter of the component name or the 3-digit component ID number. In general, it is not necessary to identify the species that are reaction products of the selected components. MINTEQA2 will search the database to find the species that can be formed from the specified components. Exceptions are specifying that a particular species is to be excluded, specifying the disposition of a particular solid with regards to oversaturation (explained below), or for any database species, specifying a different equilibrium constant than that provided in the thermodynamic database. When it is necessary to do so, aqueous species that are reaction products are identified by specifying the components that represent the major cation and major anion. Solids are identified to PRODEFA2 by specifying the component that represents the major cation and the main mineral group to which the solid belongs (e.g. carbonate, sulfide). Alternatively, one may specify the 7-digit ID number for any aqueous or solid species if it is known. Menus and prompts within PRODEFA2 allow all of these things to be done with relative ease.
- New components may be defined by editing the component database file, COMP.DBS. Of course, new components are of little use unless reactions incorporating them as reactants are also provided. New reactions between new or existing components may be permanently added to the database files (see Appendix A) or may be added for a particular execution by including them in the input file. PRODEFA2 will prompt for the information needed to do this.
- MINTEQA2 solves the equilibrium problem iteratively by computing mole balances from estimates of component activities, that is, activities of the free species represented by the components (see Chapter 2). Hence, it is necessary to provide an initial estimate or guess for the activity of each component. PRODEFA2 makes this guess automatically for every component as equal to the component total dissolved concentration but also provides the means for the user to change the guess.
- It is possible for the user to insist that certain conditions prevail at equilibrium. For example, it may be desired to equilibrate the solution to a specified pH. This is done by specifying that the activity of  $H^+$  is fixed as dictated by the selected pH. The pe may be fixed in a similar manner. It is also possible to insist that a given solid is present at equilibrium. This is done by specifying it as an INFINITE solid in PRODEFA2. Likewise, the equilibrium partial pressure of a gas may be specified.
- The user has four options with regard to allowing oversaturated solids to precipitate (not including the infinite solids option above). 1) No solids are allowed to precipitate, 2) No solids are allowed except for

those explicitly specified in the input file, 3) All oversaturated solids are allowed, or 4) All oversaturated solids are allowed except for those explicitly excluded in the input file.

- The process of picking the correct set of solids so that equilibrium is attained without phase-rule violations is also an iterative procedure within MINTEQA2. This means that a particular solid may precipitate and then may dissolve in a later iteration. The user can assist the model in arriving at the proper set of solids by designating those presumed to be present at equilibrium as FINITE solids. PRODEFA2 provides the means of doing this.

- There are four choices for units of concentration for the input data:

1) Molal (approximately the same as molar for the dilute systems appropriate for MINTEQA2), 2) mg/l, 3) PPM (parts per million), or 4) meq/l (milliequivalents per liter). PRODEFA2 can convert from one to another so that you may, for example, enter a portion of the total dissolved concentration data in molal and then convert to mg/l. Regardless of the units chosen for input data, the units of concentration used for the MINTEQA2 output data are always molal.

- At start-up, PRODEFA2 asks for the name of the MINTEQA2 input file to be created. It also asks for the name of an existing MINTEQA2 input file to use as a seed file or "template." If the user does not wish to use a seed file, program defaults are used for all system variables and program flags and the single component H<sup>+</sup> is entered automatically. If a seed file is used, all system variables, program flags, and species definitions become identical to those of the seed file. Note that the seed file itself is not modified by this procedure unless the filename selected for the MINTEQA2 file to be created and the seed file's name are the same.

- PRODEFA2 is divided into four distinct sections called *edit levels*. After inquiring for file names, PRODEFA2 goes automatically to EDIT LEVEL I to display the settings and parameters of the default problem or the seed problem represented by a seed file if one has been specified. Upon the users acceptance of the EDIT LEVEL I settings, a main menu screen is displayed from which the user may choose to enter any of the four edit levels, to use the current problem as a seed for another similar problem to be included in the same MINTEQA2 input file, or to exit the program. Upon returning from any edit level, this MAIN MENU is always displayed.

### Running PRODEFA2 for the First Time

The following pages provide a basic introduction to PRODEFA2 by "walking-through" a short session where only the problem title is changed. This session also demonstrates the "default problem" built-in to PRODEFA2. After that session, each edit level is explored separately in greater detail. If you have never used PRODEFA2 or MINTEQA2 before, you should first read the information supplied with your copy of the MINTEQA2 and PRODEFA2 software. The program is currently distributed in a compacted form which requires that you stringently adhere to the installation procedure. You should read the documentation distributed with the software thoroughly since it will also contain information on changes that have been made to the code

since the release of this manual as well as corrections to this document. Once you have loaded your copy of MINTEQA2 onto your computer you should then proceed through the short example that follows.

The steps presented below will familiarize you with the basic operation of the PRODEFA2 preprocessor and the files that it creates. This practice session will terminate with the preparation of an input file that you can then run through MINTEQA2. This final step is recommended as an initial test of your installation of the MINTEQA2 routine and datasets.

In order to execute PRODEFA2, you must change to the MINTEQA2 sub-directory and type PRODEFA2 at the prompt. PRODEFA2 will begin by prompting you for the name of the MINTEQA2 input file you will create during this session. PRODEFA2 allows you to create an input file by beginning with the standard default values or by using an existing MINTEQA2 input file as a seed file. The following is a sample listing of the opening dialogue with PRODEFA2. Lines that are indented and appear in the smaller characters represent what actually appears on your computer screen. Items that are underlined are examples of entries made by the program user.

```

*
*          P R O D E F A 2          *
*
*          Version 3.00 09-01-90      *
*
*  PRODEFA2 is an interactive program used to build  *
*  input files for MINTEQA2 v3.00.          *
*

```

---

If you encounter errors, please print the file named SAMPLE.QUE  
or copy it to a diskette and send along with a description of the  
problem you were attempting to model to: Jerry D. Allison,  
USEPA Environmental Research Lab, College Station Rd., Athens, GA      30613.

In responding to prompts, use: Y or y = Yes, N or n = No,  
R or r = Return to previous prompt (where applicable).

Enter the name of the MINTEQA2 input file to be created.  
Use up to 8 characters PLUS from 0 to 3 characters for an  
extension.

ENTER FILENAME (enter "X" to exit PRODEFA2) > TESTA.INP

If you want to use an existing MINTEQA2 input file as a "seed" file to be  
copied into PRODEFA2 and modified, enter the filename. Otherwise:  
-- Enter an R to return to the previous question, or  
-- Simply press ENTER to start a new file from scratch.

ENTER filename, R, or press ENTER >

The MINTEQA2 input file to be created is called TESTA.INP. No seed file is specified, so PRODEFA2's default values will be used for all system parameters and program flags and the component H<sup>+</sup> will be entered automatically with a total concentration of 1.000e-07 m. Had an existing filename been entered at the second prompt, the parameters, flags, and species entries of that file would be entered automatically. Note that in the VAX environment, the name of the existing file must be different from the name of the file to be created. When the two names are identical in a PC environment, the existing file is overwritten by the one being created.



An accessory file called LAST.DAT is periodically updated throughout the PRODEFA2 session so that if an abnormal termination occurs, some portion of the work will be recoverable.

As previously mentioned, PRODEFA2 has four sections called edit levels. By default, you will automatically be placed in EDIT LEVEL I after responding to the filename prompts

```
_____ EDIT LEVEL I _____ PROB # 1 _____  
1 Title 1:  
2 Title 2:  
3 Temperature (Celsius): 25.00  
4 Units of concentration: MOLAL  
5 Ionic strength: TO BE COMPUTED  
6 Inorganic carbon is not specified.  
7 Terminate if charge imbalance exceeds 30% ? NO  
8 Oversaturated solids ARE NOT ALLOWED to precipitate. EXCEPTIONS: Solids  
  listed in this file as TYPE -III (Infinite), -IV (Finite) or -V (Possible).  
9 The maximum number of iterations is: 40  
10 The method used to compute activity coefficients is: Davies equation  
11 Level of output: INTERMEDIATE  
12 The pH is: TO BE COMPUTED  
13 Neither pe nor Eh has been specified.  
14 Adsorption phenomena are not to be modeled.  
15 Display on-screen status messages during MINTEQA2 execution? YES  
99 Choose a different file to modify OR return to output filename prompt.  
  
To change any of the above entries or to explore other possible values,  
enter the number to the left of the entry. Enter zero when you are finished.  
ENTER CHOICE >
```

In EDIT LEVEL I, a screen of information is displayed on your computer, as shown above. In this example, PRODEFA2's default settings for system parameters, and program flags are displayed. If you had selected a previously existing input file as the starting point, its values would be displayed instead. In order to change any of the entries on this screen, enter the number to the left of the entry and respond to the questions presented. For example, to change the first line of title information for the run, enter a "1" as shown below. The program will then prompt you to enter the first line of the title for this problem.

```
ENTER CHOICE > 1  
  
Enter problem title (1 of 2 lines),  
OR press ENTER to omit title,  
OR enter "R" to return to previous prompt:  
This exercise illustrates PRODEFA2's "default problem".
```

After any option is selected and changes are specified, the EDIT LEVEL I screen is updated to reflect the changes. The remainder of the EDIT LEVEL I options are discussed in a subsequent section. To exit EDIT LEVEL I enter a "0" at the "ENTER CHOICE >" prompt in the EDIT LEVEL I menu.

After exiting from EDIT LEVEL I, the MAIN MENU is displayed. From the MAIN MENU the user may choose to enter any of the four edit levels, to use the current problem as a seed for a another similar problem to be included in the same MINTEQA2 input file, or to exit the program. Upon returning from any edit level, this MAIN MENU is always displayed. The options presented in each edit level will be the subject of the remainder of this chapter. For the moment, let us exit PRODEFA2.

```
_____ MAIN MENU: SELECT OPTION _____ PROB # 1 _____  
  
1 = EDIT LEVEL I (Change ionic strength, pH, Eh, temperature, adsorption
```

```

parameters, number of iterations, precipitation options, etc.)

2 = EDIT LEVEL II (Specify components, gas, redox, aqueous, and mineral
species, adsorption sites and reactions, add new species of all types)

3 = EDIT LEVEL III (Check, individually edit all entries)

4 = EDIT LEVEL IV (Sweep a range of pH, pE, or dissolved concentration;
Designate an auxiliary MINTEQA2 output file to receive equilibrated
mass distribution data.)

M = MULTI-PROBLEM GENERATOR

X = EXIT (Write the current problem to the new MINTEQA2 input file
and EXIT PROGRAM)

ENTER CHOICE > X

```

This causes the file "testa.inp" to be written to the directory that you are currently connected to and PRODEFA2 reminds you of the filename as you exit the program.

```

A Problem File Named TESTA.INP Has Now Been Generated.
It Can Be Modified By This Same Program By Recalling It As The Old File.

```

The contents of the file TESTA.INP are shown below. Note that the default values for system parameters, program flags, and species entries in PRODEFA2 really define a default chemistry problem, namely, to calculate the pH of a solution that is 1.0E-07 molal in H<sup>+</sup>. The file TESTA.INP created above is thus a legitimate MINTEQA2 input file. You might like to use MINRUN to submit this problem to MINTEQA2.

This exercise illustrates PRODEFA2's "default problem".

```

25.00 MOLAL 0.000
0 0 1 0 0 0 0 0 1 1 1 0 0
0 0 0
330 1.000E-07 -7.00 /H+1

```

## Detailed Explanation of PRODEFA2 Options

The primary options available in PRODEFA2 are explained and illustrated below. The specific settings associated with each option are not necessarily default values; most were chosen for illustration only. Default values in program start-up are discussed above. Others are mentioned where appropriate.

### Main Menu Option 1: Edit Level I

EDIT LEVEL I displays the current settings of system parameters such as temperature as well as program flag settings such as the number of iterations allowed. The user may change any of these settings by selecting the option number and responding to the resulting prompts.

This section contains a more detailed explanation of EDIT LEVEL I options and suggestions for using them. For most options, the explanation provided by PRODEFA2 will prove adequate. You are encouraged to experiment with all of the options available to become familiar with the capabilities of the program. Below is a sample of the display that appears when you enter EDIT LEVEL I.

- 1 Title 1:
- 2 Title 2:
- 3 Temperature (Celsius): 25.00
- 4 Units of concentration: MOLAL
- 5 Ionic strength: TO BE COMPUTED
- 6 Inorganic carbon is not specified.
- 7 Terminate if charge imbalance exceeds 30% ? NO
- 8 Oversaturated solids ARE NOT ALLOWED to precipitate. EXCEPTIONS: Solids listed in this file as TYPE -III (Infinite), -IV (Finite) or -V (Possible).
- 9 The maximum number of iterations is: 40
- 10 The method used to compute activity coefficients is: Davies equation
- 11 Level of output: INTERMEDIATE
- 12 The pH is: TO BE COMPUTED
- 13 Neither pe nor Eh has been specified.
- 14 Adsorption phenomena are not to be modeled.
- 15 Display on-screen status messages during MINTEQA2 execution? YES
- 99 Choose a different file to modify OR return to output filename prompt.

---

To change any of the above entries or to explore other possible values, enter the number to the left of the entry. Enter zero when you are finished.  
 ENTER CHOICE >

### Edit Level I Options 1 and 2: Titles

These two entries allow you to enter a two line title for the MINTEQA2 run. The titles will appear in PART 1 of the MINTEQA2 output file and serve as a reminder of the purpose of the run.

### Edit Level I Option 3: Temperature

Many of the parameters used in MINTEQA2 are temperature dependent and we recommend that you set this value to the actual conditions. MINTEQA2 will automatically correct as many values as possible to the temperature that you specify. See Chapter 2 for a description of temperature corrections to equilibrium constants.

### Edit Level I Option 4: Units of Concentration

Values for component total dissolved concentrations are later requested in whatever units are specified here. When the units parameter is changed, values that are already present in the input file are converted to the new units. The available choices for units are listed below as they appear in PRODEFA2.

Select units for concentration. Because these are dilute solutions, you can approximate molal concentrations with molar concentrations with negligible error.

- 1 = molal
- 2 = mg/l
- 3 = ppm
- 4 = meq/l

ENTER CHOICE >

### Edit Level I Option 5: Ionic Strength

Two choices are available, the ionic strength can either be computed by MINTEQA2 from the solution chemistry or it can be fixed at a molal value specified by the user. Fixing the ionic strength will generally improve convergence times since changes in ionic strength also change the activity coefficients and hence the solution composition. When the ionic strength is fixed, it becomes independent of the solution chemistry. Fixing the ionic strength implies that there are certain rather inert ions present in large enough concentration for their impact on ionic strength, and hence on activity coefficients, to be important. However, because these ions are not very reactive, they need not be included as actual components. Examples are  $\text{Na}^+$  and  $\text{Cl}^-$  in many surface water problems (though it is not true that they should always be represented solely by fixing the ionic strength). An example of the dialogue when Option 5 is selected is shown below.

```
Should the ionic strength be fixed? (Y,N,H) > Y
Enter fixed ionic strength (molal) > .01
```

### Edit Level I Option 6: Inorganic Carbon

MINTEQA2 needs the total dissolved concentration of each component for use in the mole balance equations. Frequently, the dissolved total for carbonate ( $\text{CO}_3^{2-}$ ) is not available but alkalinity is. PRODEFA2 allows you to enter the alkalinity in your choice of several commonly used units. The alkalinity value is stored in the data location ordinarily used for total dissolved carbonate and a special program flag is set in the input file so that MINTEQA2 will know to treat this value as alkalinity. MINTEQA2 computes the total dissolved carbonate concentration from the alkalinity value by the method described in Chapter 2. You should read that portion of Chapter 2 carefully before using this option. When the alkalinity option is not used, total dissolved carbonate concentration may be entered just as any other component. Alternatively, you may set the total dissolved carbonate concentration to zero and specify that carbonate is in equilibrium with a fixed partial pressure of  $\text{CO}_2(\text{g})$  in EDIT LEVEL II. The PRODEFA2 dialogue for entering alkalinity is shown below.

```
Do you want to specify dissolved inorganic carbon
in this problem ? (Y,N) > Y

When alkalinity is specified, no solids are allowed. (set EDIT LEVEL I Option 8
to zero and specify no TYPE III,IV, or V solids.)
Also, the titration used to determine alkalinity is assumed to be to the
pH that is the equivalence point of the solution). Otherwise the alkalinity,
factors in the database will not be applicable.

You have the option of specifying alkalinity as a measure of
dissolved inorganic carbon. Alternatively, you may specify dissolved
inorganic carbon explicitly. Your choice will generally depend upon the way
carbonate concentration is expressed in the chemical analysis of the
sample you are modeling.

Do you want to specify alkalinity ? (Y,N) > Y

Select alkalinity units:
0 = Return to previous question
1 = mg/l  $\text{CO}_3^{2-}$ 
2 = mg/l  $\text{CaCO}_3$ 
3 = eq/l
ENTER CHOICE > 2

Enter alkalinity in mg/l  $\text{CaCO}_3$  > 0.500E+02
```

Alternatively, if you choose to entered total dissolved carbonate directly, the dialogue is:

```
Do you want to specify alkalinity ? (Y,N) > N

Do you want to enter total inorganic carbon as total dissolved concentration
of the MINTEQA2 component for inorganic carbon CO3-2 ? (Y,N) > Y

Enter total inorganic carbon as total dissolved concentration of
CO3-2 in MOLAL > 0.3500E-03
```

The same result could have been achieved by entering total carbonate as you would any other component in EDIT LEVEL II.

#### Edit Level I Option 7: Termination on Charge Imbalance

Generally, it is not important for MINTEQA2 to terminate if the charge balance exceeds 30%. There are some cases when a large charge imbalance would indicate improper data, however. When a large charge imbalance occurs, the user should consider whether it results from omitting a relatively inert species such as  $\text{Na}^+$  or from omitting a more reactive species such as  $\text{SO}_4^{2-}$ . In the former case the equilibrium composition will be affected very little (provided the effect on ionic strength is accounted for by fixing it as if  $\text{Na}^+$  were present), but in the latter, the omission might be important.

#### Edit Level I Option 8: Precipitation

This entry allows you to turn precipitation on or off for the solids in the database except those which you explicitly specify as "POSSIBLE" or "EXCLUDED." These special designations for solids can be made in EDIT LEVEL II. Sometimes, it is better to not allow any precipitation for the first run of a complex system and then to incorporate precipitation into a second run. When precipitation is not allowed, MINTEQA2 will still compute the saturation indices for all the solids. Indices greater than zero indicate oversaturation with respect to the solution and indices less than zero indicate undersaturation. The indices are printed in the output file and may be used to decide which of the solids may be important in your problem.

In a model run with solid precipitation not permitted, many solids may be listed as oversaturated at equilibrium. It is important to realize that if a solid is listed as oversaturated, it may not actually precipitate when precipitation is permitted in a subsequent run. For a given cation, the most oversaturated solid will precipitate first. After it does so, others that were also oversaturated with respect to the pre-precipitation solution may not be oversaturated. When precipitation is allowed, it is generally best to also set the number of iterations to a large number (100 or 200) depending on the number of solids you expect to precipitate. MINTEQA2 allows you to obtain the saturation indices each time the solution is provisionally equilibrated during the program execution by specifying the solids print option as shown below. (Here, the term "provisional equilibration" means that the solution is equilibrated but not with the complete or correct set of solids.) Generally, print option 1 is sufficient. With print option 1, provisional equilibration results are not written to the MINTEQA2 output file. Print option 2 causes provisional as well as final equilibrated results to be written to the output file.

Are all oversaturated solids to be allowed to precipitate? (Y,N,H) > Y

Select the solids output print option:  
0 = Return to previous question  
1 = Only after the final answer is reached  
2 = Each time a mineral precipitates or dissolves  
ENTER CHOICE >

### Edit Level I Option 9: Maximum Number of Iterations

The default number of iterations is 40. Generally this is sufficient for relatively simple problems or those that do not allow solids to precipitate. More iterations may be necessary if the problem is very complex and/or poor activity guesses are provided for the species present. Also, if you suspect that multiple solids will precipitate, then a larger number of iterations will be required.

Select maximum number of iterations:  
0 = 40 iterations  
1 = 10 iterations  
2 = 100 iterations  
3 = 200 iterations  
ENTER CHOICE > 0

### Edit Level I Option 10: Calculation of Activity Coefficients

There are two choices for calculating activity coefficients, the modified Debye-Hückel equation or the Davies equation (consult Chapter 2 for details). It should be noted that only a fraction of the species present in the database have the necessary constants for the modified Debye-Hückel equation. When the Debye-Hückel equation is selected, the Davies equation will be substituted for those species lacking the required constants. By selecting option "1" you will cause all the activity coefficients to be calculated in a consistent manner by with Davies equation.

Select an activity coefficient algorithm:  
0 = Extended Debye-Huckel  
1 = Davies Equation  
ENTER CHOICE >

### Edit Level I Option 11: MINTEQA2 Output File Options

You can control the amount of information written to the MINTEQA2 output file. Option 1 is the most complete and Option 3 provides the least information. You should experiment with these to determine how much of the information you really need to obtain. In general, Option 2 provides the best combination of brevity and completeness. Care should be used in selecting Option 1 and simultaneously choosing the solids print Option 2 (see EDIT LEVEL I OPTION 8) and using the sweep option (see EDIT LEVEL IV OPTION 1). Very large output files may result.

Select the output option:  
0 = Return to previous question  
1 = FULL output file  
2 = INTERMEDIATE (omit some of the thermodynamic data read from the database uncorrected log K values, gfw, etc.)  
3 = ABBREVIATED (mass distribution at equilibrium only)  
ENTER CHOICE >

### Edit Level I Option 12: pH

The hydronium ion concentration can be entered as a measured pH, or as total hydrogen. Each of these options also allows you the choice of fixing the pH or letting MINTEQA2 calculate the equilibrium value. If you choose to let MINTEQA2 calculate the value.

```
Select pH option:  
1 = Measured pH  
2 = Measured total hydrogen  
3 = Neither  
ENTER CHOICE > 1  
  
Enter pH > 6.600  
  
Should H+1 Be Independently Fixed? (Y,N) > Y
```

### Edit Level I Option 13: pe or Eh

Redox potential can be entered as either Eh or pe. If you choose to enter either value you will also be asked whether to fix the electron activity, that is, whether to consider the pe or Eh entered an equilibrium value. Systems containing redox chemistry can be very sensitive to the initial activity guesses made for the electron (if the pe is to be calculated) or for the components of redox couples (if pe is fixed). Be prepared to assist MINTEQA2 by making improved guesses.

```
Select redox potential option:  
E = You want to specify Eh  
P = You want to specify pE  
N = You prefer not to specify either  
H = You want more explanation  
ENTER CHOICE > E  
  
Enter Eh (millivolts) > -0.1560  
  
Should E- (ENTERED AS EH) Be Independently Fixed? (Y,N) > Y
```

### Edit Level I Option 14: No Adsorption Modeling

This is not a real option, but rather a display line that lets you see which adsorption model has been implemented in this file. You can change the sorption model in EDIT LEVEL TWO, described below.

### Edit Level I Option 15: On Screen Status Messages

MINTEQA2 is capable of generating status screens during execution as a means of reporting on progress in a problem. It is sometimes useful to display these screens if an error is occurring, but writing them out does slow the calculations considerably, causing significantly longer execution times. If you are working in an AT environment it is recommended that you turn this option off. You can perform timing tests on your problems to determine if the time savings is significant on your machine.

## Edit Level I Option 99: Change Seed File or Change Name of File to be Created

This option allows you to abandon any work up to the point it is selected and choose a different existing file to use as a seed file. Once you arrive at the prompt that allows this adjustment, you have the option of returning to the very first prompt of the PRODEFA2 session and specifying a different filename for the MINTEQA2 input file to be created, or to exit the program.

## Main Menu Option 2: Edit Level II

EDIT LEVEL II is used to specify the chemistry of the system. Total dissolved concentrations or fixed activities of components are specified by selecting the appropriate option from the EDIT LEVEL II menu. Infinite solids, gases, redox couples, finite solids, and other possible solids may also be specified. Many of the options involving aqueous species and solids provide a facility for searching the database if the user is uncertain whether that species is included. New species may be defined by following the prompts. EDIT LEVEL II also provides for choosing an adsorption model, specifying its parameters, and defining adsorption reactions. (There are no adsorption reactions in the standard database; see Chapter 3.) The menu screen for EDIT LEVEL II appears below.

```

_____ SELECT OPTION _____
1 = Specify AQUEOUS COMPONENTS: TOTAL CONCENTRATIONS or FIXED ACTIVITIES
2 = Specify AQUEOUS SPECIES not in the database, search the database,
   or alter a database AQUEOUS SPECIES equilibrium constant
3 = Specify an ADSORPTION MODEL and REACTIONS
4 = Specify GASES at FIXED partial pressures
5 = Specify REDOX COUPLES with FIXED activity ratios
6 = Specify INFINITE SOLID phases
7 = Specify FINITE SOLID phases
8 = Specify POSSIBLE SOLID phases
9 = Specify EXCLUDED SPECIES of any type
R = RETURN to MAIN MENU

All choices allow you to browse and return without changing anything;
Most allow you to search or view a directory of the relevant database.
ENTER CHOICE > 1
```

Each of these selections will prompt you for information in approximately the same way and you will find some repetition in the discussion of the different options that follow.

## Edit Level II Option 1: Specify an Aqueous Component

This option is used to select the basic components that you will need in the MINTEQA2 input file. Components are the building blocks for all other species in the database. A complete list of all components and their ID numbers can be found in Appendix A. When a component is selected, you must specify either its total dissolved concentration or the fixed activity of the free component.

Components are identified to PRODEFA2 by specifying the first letter of the component name or the 3-digit component ID number. In the example below,  $\text{Ca}^{+2}$  is selected from the list of components starting with the



letter "C." For  $\text{Ca}^{+2}$  this ID number would be 150 as shown below. To signal that you are finished entering components, enter a zero. You may toggle between the first letter mode of entry and the ID number mode by entering -1 as directed. Note that the names of some components are written as acids. For example, an entry of "S" in the first letter mode will produce a numbered list of components that begin with the letter "S" but the component for silicon will not be among them. That component,  $\text{H}_4\text{SiO}_4$ , is listed under "H". Also, when you enter a total dissolved concentration, an activity guess is made by PRODEFA2 unless the entered concentration is zero. In that case you will be asked to supply the activity guess (read the prompt carefully; you may be asked for the "log activity" which should be taken to mean the common logarithm of the free component activity). For components that you specify as having fixed activity, you will likewise be asked to specify the fixed activity. Note that activities, whether fixed or guessed, are always in units of molal (approximately molar) regardless of the concentration units specified in EDIT LEVEL I.

```

_____
EDIT LEVEL II _____ PROB # 1_
_____
DEFINE COMPONENT SPECIES _____

```

```

Specify components for which you know the:
1 = TOTAL DISSOLVED CONCENTRATION
2 = FIXED EQUILIBRIUM ACTIVITY
R = Return to previous options menu (EDIT LEVEL II)
ENTER CHOICE > 1

```

```

- Enter the FIRST LETTER for the COMPONENT:
  To identify the component you want, enter the first letter in its
  chemical symbol (inorganic) or name (organic),
OR enter a minus one (-1) to switch to component entry by ID number,
OR enter a zero (0) to terminate component entry.
  ENTER your choice > c
  1 CO3-2    2 CN-    3 Ca+2    4 Cd+2    5 Cl-1
  6 Cr+2    7 Cr(OH)2+    8 CrO4-2    9 Cu+1    10 Cu+2
  11 Citrate

```

```

Select the number of the appropriate component (0 = NONE) > 3

```

```

Enter the TOTAL DISSOLVED CONCENTRATION (MOLAL) of COMPONENT:
Ca+2    ID # 150 > 0.10000E-03

```

```

- Enter the FIRST LETTER for the COMPONENT:
  To identify the component you want, enter the first letter in its
  chemical symbol (inorganic) or name (organic),
OR enter a minus one (-1) to switch to component entry by ID number,
OR enter a zero (0) to terminate component entry.
  ENTER your choice > 0

```

```

Specify components for which you know the:
1 = TOTAL DISSOLVED CONCENTRATION
2 = FIXED EQUILIBRIUM ACTIVITY
R = Return to previous options menu (EDIT LEVEL II)
ENTER CHOICE > R

```

### Edit Level II Option 2: Specify an Aqueous Species

There are two reasons for selecting this option. One is to change the equilibrium constant associated with a particular species from the database value to some other that you have reason to believe more appropriate. The other reason is to search the database to see whether a particular species is included and, if it is not, to define that species as an added reaction. The series of prompts that assist you in defining the new aqueous species are similar to those encountered in defining a new solid or an adsorption reaction in other EDIT LEVEL II options.

You should have the reaction already written out in terms of MINTEQA2 components so that you can provide the stoichiometry and you should have the log K for the reaction as written as well as the species charge and molar mass. Other entries (enthalpy, Debye-Hückel constants, alkalinity factor) can be entered as zero if you do not have good values.

In identifying the species of interest, the user is asked for both the major cation and anion in a manner that is similar to EDIT LEVEL II OPTION 1 above. The database is searched for complexes that contain both components. If any matches are found, the reactions that contain them and their products are displayed on the screen. You may select any of these reactions. If no match is found or the species you want is not among those found, you are given an opportunity to add a new reaction. Note that you may skip the database search when a new species is to be added, but do this ONLY if you are sure the species is not in the database already. It is generally best to first search the database by choosing the search option (1) first. An example dialogue for adding a reaction is shown below.

```
Specify AQUEOUS SPECIES ? (Y,N) > Y
Choose an option:
0 = Return to the previous question.

1 = Search the thermodynamic database for the species you want.
  If it is in the database, display its log K and enthalpy values for
  you to change if desired. If not in the database, assist you in
  defining and adding the species.

2 = Assist you in defining and adding a species that you already know
  is not in the thermodynamic database.
  ENTER CHOICE > 1
```

The idea of the next series of prompts is to identify the species you want to PRODEFA2. The 7-digit ID number could be used for an existing species (assuming you want to check or change its equilibrium constant).

```
_____
EDIT LEVEL II _____ PROB # 1_
_____
DEFINE AQUEOUS SPECIES _____
```

```
Is the ID # known for AQUEOUS SPECIES ? (Y,N) > N
Define MAJOR cation component
- Enter the FIRST LETTER for the COMPONENT:
  To identify the component you want, enter the first letter in its
  chemical symbol (inorganic) or name (organic),
OR enter a minus one (-1) to switch to component entry by ID number,
OR enter a zero (0) to terminate component entry.
  ENTER your choice > c
  1 Ca+2    2 Cd+2    3 Cr+2    4 Cr(OH)2+    5 Cu+1
  6 Cu+2
Select the number of the appropriate component (0 = NONE) > 3
Define MAJOR anion component
- Enter the FIRST LETTER for the COMPONENT:
  To identify the component you want, enter the first letter in its
  chemical symbol (inorganic) or name (organic),
OR enter a minus one (-1) to switch to component entry by ID number,
OR enter a zero (0) to terminate component entry.
  ENTER your choice > c
  1 CO3-2    2 CN-    3 Cl-1    4 CrO4-2    5 Citrate
Select the number of the appropriate component (0 = NONE) > 3
```

Once you have completed choosing the major ions, the computer will search the entire database for entries that contain those two major components. In this case, no matches were found. Had one or more species been found that included both of these components, a numbered menu would appear from which to choose. If none were the species of interest, you would be given opportunity to define a new species just as the case where no matching species was found, as in this example. The dialogue which informs you that no matches were detected and proceeds to prompt you for information for the new species follows.

```

PATIENCE..Thermodynamic database file 7 is being searched !

No NEAR match found in the database for ID 2101800

Do you want to define a new species comprised at least partly of those
constituents you have already specified ? (Y,N) > Y

Is ID = 2101800 acceptable for a new AQUEOUS SPECIES ? (Y,N,H) > Y
Now Add Reaction Not Yet In Data Base For AQUEOUS SPECIES

Enter Name For AQUEOUS SPECIES .-> CrCl+

Enter Charge On Species > 1.00

Enter Debye-Huckel A Parameter > 0.00

Enter Debye-Huckel B Parameter > 0.00

Enter Alkalinity Factor > 0.00

Enter Molecular Wt. (GFW) > 87.5

    THE REACTION THUS FAR CREATED IS :

    0.000 Cl-1  +  0.000 Cr+2  <----->  CrCl+

--- Specify MASS ACTION and MASS BALANCE stoichiometry ---

Enter the stoichiometric coefficient for Cl-1
Remember that REACTANTS have positive stoichiometry while PRODUCTS have
negative stoichiometry. ENTER stoichiometry > 1.

    THE REACTION THUS FAR CREATED IS :

    1.000 Cl-1  +  0.000 Cr+2  <----->  CrCl+

--- Specify MASS ACTION and MASS BALANCE stoichiometry ---

Enter the stoichiometric coefficient for Cr+2
Remember that REACTANTS have positive stoichiometry while PRODUCTS have
negative stoichiometry. ENTER stoichiometry > 1.

Are there any other components in this reaction ? (Y,N,H) > N

    THE REACTION THUS FAR CREATED IS :

    1.000 Cl-1  +  1.000 Cr+2  <----->  CrCl+

Should Cl-1          Be Independently Fixed? (Y,N,H) > N
Should Cr+2          Be Independently Fixed? (Y,N,H) > N

For The Request That Follows, K Must Be Consistent With Molal Concentrations.

Enter Log K      For Reaction To Form CrCl+      > 5.6
Enter  Enthalpy For Reaction To Form CrCl+      > -20.2

ID # 2101800 CrCl+          Chosen. Current LOG10(KEQ)= 0.56000E+01

```



aqueous species as shown in EDIT LEVEL II OPTION 2. For the electrostatic models, note that the components that represent electrostatic terms are entered with the proper stoichiometry automatically.

\_\_\_\_\_ ADSORPTION STATUS \_\_\_\_\_

The following binding-site types are defined for 0 surface(s):

---- NO SURFACES CURRENTLY DEFINED ----

\_\_\_\_\_ ADSORPTION OPTIONS \_\_\_\_\_

Select an option:

- 1 = ADD a NEW SURFACE with a site
- 2 = ADD a NEW SITE on a currently defined surface
- 3 = ADD a NEW REACTION at a currently defined site
- 4 = ATTACH an auxiliary database of adsorption reactions
- 5 = DELETE a currently defined site
- R = RETURN without changing anything

Enter Choice: > 1

Enter the site type number (1 or 2) > 1

\_\_\_\_\_ SPECIFICATION OF ADSORPTION REACTIONS ON Site Type 1 \_\_\_\_\_  
\_\_\_\_\_ SURFACE NUMBER ONE \_\_\_\_\_

\*\*\*\* PROCEED TO DEFINE REACTION # 1 \*\*\*\*

Select An Aqueous Metal Or Ligand To Make Up ID For ADSORP'N PRODUCT

- Enter the FIRST LETTER for the COMPONENT:

To identify the component you want, enter the first letter in its chemical symbol (inorganic) or name (organic).

OR enter a minus one (-1) to switch to component entry by ID number,

OR enter a zero (0) to terminate component entry.

ENTER your choice > c

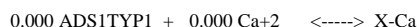
- |            |            |          |        |         |
|------------|------------|----------|--------|---------|
| 1 CO3-2    | 2 CN-      | 3 Ca+2   | 4 Cd+2 | 5 Cl-1  |
| 6 Cr+2     | 7 Cr(OH)2+ | 8 CrO4-2 | 9 Cu+1 | 10 Cu+2 |
| 11 Citrate |            |          |        |         |

Select the number of the appropriate component (0 = NONE) > 3

Is ID = 8111500 acceptable for a new ADSORBED SPECIES ? (Y,N) > Y  
Now Add Reaction Not Yet In Data Base For ADSORBED SPECIES

Enter Name For ADSORP'N PRODUCT . > X-Ca

THE REACTION THUS FAR CREATED IS :

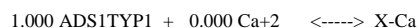


--- Specify MASS ACTION and MASS BALANCE stoichiometry ---

Enter the stoichiometric coefficient for ADSITYP1

Remember that REACTANTS have positive stoichiometry while PRODUCTS have negative stoichiometry. ENTER stoichiometry > 1.00

THE REACTION THUS FAR CREATED IS :



--- Specify MASS ACTION and MASS BALANCE stoichiometry ---

Enter the stoichiometric coefficient for Ca+2

Remember that REACTANTS have positive stoichiometry while PRODUCTS have negative stoichiometry. ENTER stoichiometry > 1.00

Are there any other components in this reaction ? (Y,N) > N

THE REACTION THUS FAR CREATED IS :

1.000 ADSITYP1 + 1.000 Ca+2 <----> X-Ca  
 For The Request That Follows, K Must Be Consistent With Molal Concentrations.

Enter Log K For Reaction To Form X-Ca > 0.50000E+00

Enter Enthalpy For Reaction To Form X-Ca > 0.00000E+00

ID # 8111500 X-Ca Chosen. Current LOG10(KEQ)= 0.50000E+00

Any MORE ADSORPTION REAC`NS for Site Type 1? (Y,N) > N  
 \_\_\_\_\_ ADSORPTION STATUS \_\_\_\_\_

The following binding-site types are defined for 1 surface(s):

Surface	Site Type Number	Component Number	Site Conc (moles/l)
1	1	811	Infinite Supply

\_\_\_\_\_ ADSORPTION OPTIONS \_\_\_\_\_

Select an option:

- 1 = ADD a NEW SURFACE with a site
  - 2 = ADD a NEW SITE on a currently defined surface
  - 3 = ADD a NEW REACTION at a currently defined site
  - 4 = ATTACH an auxiliary database of adsorption reactions
  - 5 = DELETE a currently defined site
  - R = RETURN without changing anything
- Enter Choice: > R

Note that a currently defined site and all added reactions in which it is involved may be deleted by choosing Option 5.

### Edit Level II Option 4: Specify a Fixed Gas Species

When this option is chosen, you are prompted with a complete list of the gases present in MINTEQA2's database. You then make a selection and enter the fixed equilibrium partial pressure of the gas. You are allowed to change the log K if you desire; otherwise, it is automatically corrected to the partial pressure you have specified (in atm). All gases are automatically defined as EXCLUDED species in MINTEQA2 unless explicitly entered here.

\_\_\_\_\_ EDIT LEVEL II \_\_\_\_\_ PROB # 1\_  
 \_\_\_\_\_ DEFINE GASEOUS SPECIES \_\_\_\_\_

Specify FIXED GASES ? (Y,N) > Y  
 1-CH4 (g) 2-CO2 (g) 3-O2 (g) 4-Hg (g)  
 5-Hg2 (g) 6-Hg(CH3)2(g) 7-HgBr (g) 8-HgCl (g)  
 9-HgF (g) 10-HgI (g) 11-HgBr2 (g) 12-HgF2 (g)  
 13-HgI2 (g)

Enter the number corresponding the gas you want. Enter zero to abort the specification of a gas.  
 ENTER CHOICE > 2

PATIENCE..Thermodynamic database file 9 is being searched !  
 1 3301403 CO2 (g) <- 1.0 CO3-2 + 2.0 H+1 + -1.0 H2O

Enter the non-zero partial pressure (atm) of CO2 (g) > 0.10000E-02  
 Corrected log K is 21.160

Want To Change Log K For CO2 (g) From 0.2116E+02 ? (Y,N) > N

Specify FIXED GASES ? (Y,N) > N

### Edit Level II Option 5: Specify a Redox Couple

When this option is selected, PRODEFA2 will scan the list of components that have thus far been selected. For each of those components, if a redox couple exists in the thermodynamic database, that couple will be displayed in a numbered menu from which you may choose those you want to include in the MINTEQA2 problem. If no components have been specified that have a corresponding reduced or oxidized form that is also available as a MINTEQA2 component, no such numbered menu will be displayed. Therefore, if you plan to implement redox chemistry, specify the components of interest first in EDIT LEVEL II OPTION 1. It is also a good idea to specify the pe or Eh either as a guess at the equilibrium value (if the true pe or Eh is to be computed) or as a fixed value (if the solution is to be equilibrated to a given pe or Eh). In the example that follows, either Fe<sup>+2</sup>, Fe<sup>+3</sup>, or both could be specified as components first. If neither is specified, the Fe redox couple would not appear on the numbered menu.

```

_____
EDIT LEVEL II _____ PROB # 1_
_____
DEFINE REDOX SPECIES _____

Specify FIXED-RATIO REDOX ? (Y,N) > Y
1-FE+3/FE+2 2-CR+2/CR(OH)2

This menu displays only those redox couples for which you have already
specified at least one aqueous component. Enter the index corresponding
to the couple you want. Enter zero to abort redox specification.
ENTER CHOICE > 1

PATIENCE..Thermodynamic database file 8 is being searched !
1 2812800 FE+3/FE+2 <- 1.0 Fe+3 + -1.0 Fe+2 + 1.0 E-1

Want To Change Log K For FE+3/FE+2 From 0.1303E+02 ? (Y,N) > N
Want To Change Enthalpy For FE+3/FE+2 From -0.1000E+02 ? (Y,N) > N
_____
EDIT LEVEL II _____ PROB # 1_
_____
DEFINE REDOX SPECIES _____

Specify FIXED-RATIO REDOX ? (Y,N) > N

```

Note that had the electron not already been entered as a component (by specifying the pe or Eh in EDIT LEVEL I OPTION 13 or by simply selecting it as a component in EDIT LEVEL II OPTION 1 above), PRODEFA2 would have entered it as a component with total dissolved concentration of zero and inquired whether to fix its activity (at the program default value of log activity = -16.0).

### Edit Level II Option 6: Specify an Infinite Solid

An infinite solid is one that is not subject to complete dissolution. As such, the solution is required to be at equilibrium with the infinite solid. All precipitated solids, whether infinite or finite, reduce the degrees of freedom by 1 (see Chapter 3). As was shown above for EDIT LEVEL II OPTION 2 (Specify Aqueous Species), PRODEFA2 provides means of searching the database to see whether a particular solid is present, allowing you to specify an equilibrium constant different from the database value if desired, and allowing you to define a new solid species if the one you seek is not found in the database. The method of identifying the solid species you

want is the primary difference between the aqueous species procedure and that shown below (which applies to INFINITE, FINITE and POSSIBLE solids). In general, the major cation and major mineral group as given by a numbered menu are specified. For solids that are known to be included in the database, the 7-digit ID number may be specified instead.

```

_____
                EDIT LEVEL II                PROB # 1_
_____
                DEFINE MINERAL SPECIES      _____

Specify INFINITE SOLIDS ? (Y,N) > Y

Choose an option:
0 = Return to the previous question.

1 = Search the thermodynamic database for the species you want.
  If it is in the database, display its log K and enthalpy values for
  you to change if desired. If not in the database, assist you in
  defining and adding the species.

2 = Assist you in defining and adding a species that you already know
  is not in the thermodynamic database.
  ENTER CHOICE > 1

Is the ID # known for MINERAL ? (Y,N) > N
1 Elemental          10 Sulfide          11 Cyanide
12 Selenide          14 Antimonide         20 Oxide or Hydroxide
30 Multiple Oxide    40 Bromide             41 Chloride
42 Fluoride          43 Iodide              50 Carbonate
51 Nitrate           52 Borate              60 Sulfate
61 Selenate or Selenite 70 Phosphate           72 Arsenate
73 Vanadate          80 Orthosilicate       82 Chain Silicate
84 Framework Silicate 86 Sheet Silicate

Enter the number corresponding to the class to which this mineral belongs.
ENTER CHOICE (0 = none) > 10

***** Specify the major cation or cation donor *****

- Enter the FIRST LETTER for the COMPONENT:
  To identify the component you want, enter the first letter in its
  chemical symbol (inorganic) or name (organic),
  OR enter a minus one (-1) to switch to component entry by ID number,
  OR enter a zero (0) to terminate component entry.
  ENTER your choice > f
1 Fe+2      2 Fe+3

Select the number of the appropriate component (0 = NONE) > 1

PATIENCE..Thermodynamic database file 19 is being searched !
1 1028000 FES PPT <- -1.0 H+1 + 1.0 Fe+2 + 1.0 HS-1

2 1028001 GREIGITE <- -4.0 H+1 + 2.0 Fe+3 + 1.0 Fe+2
+ 4.0 HS-1
3 1028002 MACKINAWITE <- -1.0 H+1 + 1.0 Fe+2 + 1.0 HS-1

4 1028003 PYRITE <- -2.0 H+1 + -2.0 E-1 + 1.0 Fe+2
+ 2.0 HS-1

Enter the number aligned with the species you want. (0 = None of above) > 4

Should HS-1 Be Independently Fixed? (Y,N) > N

Want To Change Log K For PYRITE From 0.1848E+02 ? (Y,N) > N

Want To Change Enthalpy For PYRITE From -0.1130E+02 ? (Y,N) > N

```

Remember that each solid specified, as well as each gas, each redox couple, each finite solid, and each component with fixed activity reduces the number of degrees of freedom for solving this problem by 1. If the



degrees of freedom is reduced to zero, phase-rule violation will occur in MINTEQA2 (see Chapter 2 for details). PRODEFA2 checks the degrees of freedom upon attempting to exit the program and warns if it is zero at the outset due to the presence of more fixed species than variable components. It may be necessary to remove some constraints such as one or more infinite solids if such a warning occurs.

#### Edit Level II Option 7: Specify a Finite Solid

A finite solid is presumed present at equilibrium and, as an aid to MINTEQA2 in picking the correct set of solids, is noted as such by specifying it here. Unlike the infinite solid above, a solid designated as finite may dissolve if equilibrium conditions warrant. It is entered in the same manner as the infinite solid, with the exception that you may specify an amount present (in moles present in one liter of solution). The amount can be entered as zero because you really do not know how much is present at equilibrium, if any; it is MINTEQA2's job to figure that out! If you choose to enter a non-zero amount, be aware that the total system concentration of the components of the solid will be changed unless you also deplete the total dissolved concentrations of those components by a corresponding amount (with proper respects to the stoichiometry of each component of the solid). To see how this works, do a simple MINTEQA2 run using the default values for all EDIT LEVEL I parameters except the pH which is fixed at 7.0. In EDIT LEVEL II, specify  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  as components, each with total dissolved concentration of  $1.000\text{e-}03$  m, not fixed. Using this option, specify calcite as a finite solid with a concentration of zero. Submit this problem to MINTEQA2 and save the output file. Next use PRODEFA2 to create a second file using that first one as a seed file. Change nothing except in EDIT LEVEL III, change the total dissolved concentration of both  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  to zero, and change the concentration of the finite solid calcite to  $1.000\text{e-}3$ . Exit and submit this problem to MINTEQA2. Compare the output file from the second run with the first. You will see that the equilibrated results are identical. Now imagine what the results would have been if, in the second run, you had changed the amount of calcite from zero to  $1.000\text{e-}03$ , but had not changed the total dissolved concentration of the constituent components. In that case, the results could not be the same because the total system concentration of both  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  would be  $2.000\text{e-}03$  m; the problem would be fundamentally different.

#### Edit Level II Option 8: Specify a Possible Solid

POSSIBLE SOLIDS are solids that are permitted to precipitate if equilibrium conditions warrant. All database solids become POSSIBLE SOLIDS when the precipitation flag in EDIT LEVEL I OPTION 8 is so set. In that case there is no need for this option. However, the other setting of the EDIT LEVEL I flag dictates that all solids be EXCLUDED SPECIES except those explicitly designated as POSSIBLE SOLIDS through this option. Note that within MINTEQA2, when a POSSIBLE SOLID precipitates it is re-defined as a FINITE SOLID. Conversely, when a FINITE SOLID dissolves, it is re-defined as a POSSIBLE SOLID. Chapter 2 provides more details. The manner of identifying POSSIBLE SOLIDS is identical to that for INFINITE SOLIDS above and is not repeated here.

## Edit Level II Option 9: Specify an Excluded Species

This option allows you to exclude any type of species from mole balance. In the case of solids, one setting of the precipitation flag in EDIT LEVEL I provides for all database solids to be excluded from precipitating (the equivalent of defining them as EXCLUDED SPECIES). Another provides for all to be permitted to precipitate if equilibrium conditions warrant. This option can be used in conjunction with the latter EDIT LEVEL I option to explicitly exclude certain solids (see EDIT LEVEL II OPTION 8). Any aqueous species may also be excluded including any component as an aqueous species. The user will note that certain species appear in the list of EXCLUDED SPECIES automatically when MINTEQA2 is executed. These include the electron unless its activity is fixed, all electrostatic components of the adsorption models, all database gases and redox couples not explicitly defined as SPECIES WITH FIXED ACTIVITY. EXCLUDED solids do not appear in the list unless explicitly defined as EXCLUDED SPECIES in MINTEQA2.

The procedure for explicitly excluding a species amounts to little more than identifying it to PRODEFA2. The procedures for doing that are basically the same as for identifying species of the various types as shown above. The same questions and rules follow here as well, except a little less information is required. Please refer to the options above for examples of the selection dialogue. An example of excluding a component follows.

```

_____
EDIT LEVEL II _____ PROB # 1_
_____ DEFINE Excluded Species _____

-- This section allows you to specify component, aqueous, mineral, or
adsorbed, species that you want to be excluded from mass balance
calculations. Note that all redox and gas species except those you entered
above are excluded automatically as are components used for
electrostatic potentials.

Specify EXCLUDED SPECIES ? (Y,N) > Y
1-COMPONENT SPECIE 2-AQUEOUS SPECIES 3-MINERAL SPECIES
4-ADSORBED SPECIES 5-REDOX SPECIES 6-GASEOUS SPECIES

Enter the number that corresponds to the desired class > 3

Is the ID # known for EXCLUDED SPECIES ? (Y,N) > N
1 Elemental 10 Sulfide 11 Cyanide
12 Selenide 14 Antimonide 20 Oxide or Hydroxide
30 Multiple Oxide 40 Bromide 41 Chloride
42 Fluoride 43 Iodide 50 Carbonate
51 Nitrate 52 Borate 60 Sulfate
61 Selenate or Selenite 70 Phosphate 72 Arsenate
73 Vanadate 80 Orthosilicate 82 Chain Silicate
84 Framework Silicate 86 Sheet Silicate

Enter the number corresponding to the class to which this mineral belongs.
ENTER CHOICE (0 = none) > 10

***** Specify the major cation or cation donor *****

- Enter the FIRST LETTER for the COMPONENT:
To identify the component you want, enter the first letter in its
chemical symbol (inorganic) or name (organic),
OR enter a minus one (-1) to switch to component entry by ID number,
OR enter a zero (0) to terminate component entry.
ENTER your choice > f
1 Fe+2 2 Fe+3

Select the number of the appropriate component (0 = NONE) > 1

PATIENCE..Thermodynamic database file 19 is being searched !
```

```

1 1028000 FES PPT <- -1.0 H+1 + 1.0 Fe+2 + 1.0 HS-1
2 1028001 GREIGITE <- -4.0 H+1 + 2.0 Fe+3 + 1.0 Fe+2
+ 4.0 HS-1
3 1028002 MACKINAWITE <- -1.0 H+1 + 1.0 Fe+2 + 1.0 HS-1
4 1028003 PYRITE <- -2.0 H+1 + -2.0 E-1 + 1.0 Fe+2
+ 2.0 HS-1

Enter the number aligned with the species you want. (0 = None of above) > 1

Specify EXCLUDED SPECIES ? (Y,N) > N

```

### Main Menu Option 3: Edit Level III

EDIT LEVEL III functions as a "line editor" in displaying by category or TYPE of data (see Chapter 2) line by line entries of those species that have been explicitly entered through EDIT LEVEL II. The order of data presentation is: 1) COMPONENTS, 2) TYPE II - AQUEOUS SPECIES, 3) TYPE III - SPECIES WITH FIXED ACTIVITY, 4) TYPE IV - FINITE SOLIDS, 5) TYPE V - POSSIBLE SOLIDS, and 6) TYPE VI - EXCLUDED SPECIES. Finally, any new species for which the reaction has been entered in PRODEFA2 (referred to as TYPE VII in this listing) is displayed. Note that TYPE I - COMPONENTS AS SPECIES IN SOLUTION are omitted because displaying the components themselves is sufficient here. Also, if no species have been explicitly entered for a particular type, that listing is omitted. For all the data types, the user is given opportunity to change entered values or to delete an entry altogether.

As each screen is displayed, the user is given opportunity to edit specific entries by specifying the number displayed to the left of each entry. Upon selecting an entry for editing, that entry is isolated and a menu of change operations is displayed. The change commands are rather straightforward. The example below illustrates simple change commands.

```

-----
EDIT LEVEL III                                PROB # 1_
-----
Verify or change listing of COMPONENTS
-----

Entry  I.D.  Name      Total Conc.  Log Activity
1      330  H+1       1.00000E-07 -7.00000E+00
2      150  Ca+2      1.00000E-04 -4.00000E+00
3      180  Cl-1      0.00000E-01 -1.60000E+01
4      210  Cr+2      0.00000E-01 -1.60000E+01
8      280  Fe+2      1.00000E-05 -5.00000E+00

Enter entry # to change, add or delete (0 = NONE) > 1

```

1. You may edit parameters for any of the components present in a variety of ways, as shown here for entry

```

Entry  I.D.  Name      Total Conc.  Log Activity
1      330  H+1       1.00000E-07 -7.00000E+00

Select:
-1 = Delete this component
0 = Return; no more changes
1 = Change ID number
2 = Change name
3 = Change total concentration
4 = Change log activity guess
Enter Choice: > 0

```

Enter entry # to change, add or delete (0 = NONE) > 0

---

EDIT LEVEL III PROB # 1\_  
Verify or change listing of AQUEOUS SPECIES

Entry	I.D.	Name	Log K	Enthalpy
1	1501401	CaCO3 AQ	3.45000E+00	4.03000E+00

Enter entry # to change, add or delete (0 = NONE) > 1

Entry	I.D.	Name	Log K	Enthalpy
1	1501401	CaCO3 AQ	3.45000E+00	4.03000E+00

Select:

- 1 = Delete this species
  - 0 = Return; no more changes
  - 1 = Change the ID number
  - 2 = Change the name
  - 3 = Change the log K
  - 4 = Change the enthalpy
- Enter Choice: > 3

Enter Log K For Reaction To Form CaCO3 AQ > 3.150E+00

Entry	I.D.	Name	Log K	Enthalpy
1	1501401	CaCO3 AQ	3.15000E+00	4.03000E+00

Select:

- 1 = Delete this species
  - 0 = Return; no more changes
  - 1 = Change the ID number
  - 2 = Change the name
  - 3 = Change the log K
  - 4 = Change the enthalpy
- Enter Choice: > 0

---

EDIT LEVEL III PROB # 1\_  
Verify or change listing of FIXED SPECIES

Entry	I.D.	Name	Log K	Enthalpy
1	3301403	CO2 (g)	2.11600E+01	-5.30000E-01
2	2812800	FE+3/FE+2	1.30320E+01	-1.00000E+01
3	1028003	PYRITE	1.84790E+01	-1.13000E+01
4	811	ADS1TYP1	0.00000E-01	0.00000E-01

Enter entry # to change, add or delete (0 = NONE) > 0

No FINITE SOLIDS (TYPE 4) have been defined.  
No POSSIBLE SOLIDS (TYPE 5) have been defined.

---

EDIT LEVEL III PROB # 1\_  
Verify or change listing of EXCLUDED SPECIES

Entry	I.D.	Name
1	1028000	FES PPT
2	1	E-1

Enter entry # to change, add or delete (0 = NONE) > 0

Note that there is seldom a need to change the ID number associated with a species. If you had mistakenly entered  $K^+$  rather than  $Na^+$ , you could correct that mistake by changing the ID number from 410 to 500 and changing the names (although MINTEQA2 does not use the names read from the input file anyway, it uses the ID number and finds the name in the database files). EDIT LEVEL III has been designed to give you

maximum control over the data that finally appears in the output file. Use it to replace PRODEFA2 generated data such as "activity guesses" with your own. "Activity guesses" are the common logarithm of the free component species activity in molal. PRODEFA2 usually guesses that the free component activity is equal to the component's total dissolved concentration. This is usually an adequate guess. The exception is for any component that has not yet been entered when a species that requires it is explicitly entered in one of the other categories. In that case, PRODEFA2 enters the component automatically at a total dissolved concentration of zero and with a log activity guess of -16.0. EDIT LEVEL III allows you to change such entries if desired. DO NOT USE EDIT LEVEL III TO CREATE NEW COMPONENT ID NUMBERS.

The change command menu for added species includes the option of changing the mass action stoichiometry of any component and designating those components that have different mass balance stoichiometry. The mass balance stoichiometry is denoted "\*stoichiometry" for brevity. The example below illustrates this menu.

```

_____
                          EDIT LEVEL III                      PROB # 1_
_____ Verify or change listing of ADDED SPECIES _____

Entry  I.D.   Name   Log K  Enthalpy  Charge  gfw  Alk. Factor
  1  2101800  CrCl+   5.600 -20.20   1.0  87.500   0.00

      Stoichiometry: ( 1.000)180 ( 1.000)210
  2  8111500  X-Ca    0.500  0.00   0.0  0.000   0.00
      Stoichiometry: ( 1.000)811 ( 1.000)150

Enter entry # to change, add or delete (0 = NONE) > 2
Entry  I.D.   Name   Log K  Enthalpy  Charge  gfw  Alk. Factor
  2  8111500  X-Ca    0.500  0.00   0.0  0.000   0.00
      Stoichiometry: ( 1.000)811 ( 1.000)150

Select:
-1 = Delete this species
 0 = Return; no more changes
 1 = Change ID number
 2 = Change name
 3 = Change log K
 4 = Change enthalpy
 5 = Change charge
 6 = Change gram formula wt.
 7 = Change alkalinity factor
 8 = Change stoichiometry
Enter Choice: > 8

There are two groups of stoichiometry/component ID pairs for each reaction.
The main group, which allows up to 12 pairs, ordinarily represents the
stoichiometry of each component for both mass action and mass balance, these
being equal. Sometimes however, it is useful to specify a mass balance
stoichiometry for one or more components that is not equal to its mass
action counterpart. The second group of stoichiometry/component ID pairs,
which allows up to 3 pairs, represents the mass balance stoichiometry
for those components. The main group is labeled "Stoichiometry" in the
listing of added species while the second group, present only in special cases
such as a Freundlich adsorption reaction, is labeled "*Stoichiometry".

Select an option:
 0 = Return; no more changes
 1 = Change, add to, delete from Stoichiometry
 2 = Change, add to, delete from *Stoichiometry
Enter Choice: > 0
Entry  I.D.   Name   Log K  Enthalpy  Charge  gfw  Alk. Factor
  2  8111500  X-Ca    0.500  0.00   0.0  0.000   0.00
      Stoichiometry: ( 1.000)811 ( 1.000)150

Select:

```

-1 = Delete this species  
 0 = Return; no more changes  
 1 = Change ID number  
 2 = Change name  
 3 = Change log K  
 4 = Change enthalpy  
 5 = Change charge  
 6 = Change gram formula wt.  
 7 = Change alkalinity factor  
 8 = Change stoichiometry  
 Enter Choice: > 0

## Main Menu Option 4: Edit Level IV

EDIT LEVEL IV is concerned with certain utility functions rather than with chemistry. There are two primary options in EDIT LEVEL IV. One is to set certain parameters so that the MINTEQA2 run becomes a series of multiple runs as in a titration or "sweep." The total concentration or fixed activity of one (and only one) user selectable component may be designated as the sweep parameter. A starting value and incremental value may be specified along with the number of titration points or the value of the sweep parameter may be entered explicitly for up to 20 points. The second option allows the user to direct that the equilibrated mass distribution among dissolved, sorbed, and solid phases be written to a special file for up to three components. The format of that special file is such that it can be imported by popular spreadsheet programs. The components  $H^+$  and  $e^-$  are written automatically when this option is used; the three selectable components are in addition to these. Combined use of these two options can produce plottable results, say dissolved  $Cd^{2+}$  as a function of pH, in a single MINTEQA2 run. An example of the dialogue for these two options is shown below.

### Edit Level IV Option 1: Sweep Option

In the example that follows, a demonstration of how to set up an incremental sweep over the total dissolved concentration of the component  $Ca^{2+}$  is shown. The starting concentration is  $1.000e-05$ , the incremental concentration is  $1.000e-06$ , and there are six titration points in the sweep. The dialogue begins after having selected option 1 from the EDIT LEVEL IV menu.

SPECIFY THE SWEEP COMPONENT:

- Enter the FIRST LETTER for the COMPONENT:  
 To identify the component you want, enter the first letter in its chemical symbol (inorganic) or name (organic).  
 OR enter a minus one (-1) to switch to component entry by ID number,  
 OR enter a zero (0) to terminate component entry.  
 ENTER your choice > f  
 1 F-1    2 Fe+2    3 Fe+3    4 Formate    5 Fulvate  
 Select the number of the appropriate component (0 = NONE) > 2

Indicate what the values are to represent:  
 1 = Total Concentration  
 2 = Fixed Equilibrium Activity (values entered as negative log activity,  
 e.g., pH, pE, or in general, p[X])  
 R = Return to previous question,  
 ENTER CHOICE > 1

Enter the number of values. Range: 2 to 20 values;  
 An entry of one (1) or zero (0) ABORTS sweep.  
 Enter number of values > 6

Choose the method of entering the 6 Total Concentration values:  
 1 = Specify a starting value and a constant incremental value  
 2 = Specify the values explicitly  
 R = Return to previous question  
 ENTER CHOICE > 1

Enter the increment between desired values.  
 An entry of zero (0) ABORTS sweep.  
 Enter increment > 0.100E-05

```

_____ EDIT LEVEL IV _____ PROB # 1_
_____ SWEEP UTILITY _____

>>>>>> CURRENT SETTINGS for Sweep Component Fe+2 <<<<<<<<

Series of values represent: TOTAL CONCENTRATION
Number of values:      6
Starting value:        1.000E-05
Incremental value:     1.000E-06

_____ OPTIONS _____

1 = Change the SWEEP COMPONENT
2 = Change the NUMBER OF VALUES or the VALUES
3 = Change whether the values represent TOTAL DISSOLVED CONCENTRATION
   or FIXED EQUILIBRIUM ACTIVITY (values entered as negative log activity,
   e.g., pH, pE, or in general, p[X])
R = ACCEPT current settings and RETURN to EDIT LEVEL IV main menu
C = CANCEL current settings and RETURN to EDIT LEVEL IV main menu
ENTER CHOICE >

```

You can change the sweep component, the number of values, or the type of sweep from a total concentration to fixed activity or vice versa at any time during a PRODEFA2 session. Below is an example of changing the Ca<sup>2+</sup> component total dissolved concentrations to just four explicitly given values.

```

ENTER CHOICE > 2

_____ EDIT LEVEL IV _____ PROB # 1_
_____ SWEEP UTILITY _____

>>>>>> CURRENT SETTINGS for Sweep Component Fe+2 <<<<<<<

Series of values represent: TOTAL CONCENTRATION
Number of values:      6
Starting value:        1.000E-05
Incremental value:     1.000E-06

_____ OPTIONS _____

Enter the number of values. Range: 2 to 20 values;
An entry of one (1) or zero (0) ABORTS sweep.
Enter number of values > 4
Choose the method of entering the 4 Total Concentration values:
1 = Specify a starting value and a constant incremental value
2 = Specify the values explicitly
R = Return to previous question
ENTER CHOICE > 2

The current starting value is 1.000E-04.
Is this correct (Y/N) ? N

Enter the new starting total concentration > 5E-06

Enter the next 3 successive values separating them from one another
with commas or spaces > 6E-06, 7E-06, 8E-06

```

Note that you are given opportunity to re-affirm or change the original value for the sweep component's total dissolved concentration. That value becomes the starting value for the sweep and the next three values are entered explicitly. You may cancel the sweep entirely or accept the current settings as shown below.

```

_____ EDIT LEVEL IV _____ PROB # 1_
_____ SWEEP UTILITY _____

>>>>>> CURRENT SETTINGS for Sweep Component Fe+2 <<<<<<<

Series of values represent: TOTAL CONCENTRATION
Number of values: 4
----- VALUES -----
5.000E-06 6.000E-06 7.000E-06 8.000E-06

_____ OPTIONS _____

1 = Change the SWEEP COMPONENT
2 = Change the NUMBER OF VALUES or the VALUES
3 = Change whether the values represent TOTAL DISSOLVED CONCENTRATION
or FIXED EQUILIBRIUM ACTIVITY (values entered as negative log activity,
e.g., pH, pE, or in general, p[X])
R = ACCEPT current settings and RETURN to EDIT LEVEL IV main menu
C = CANCEL current settings and RETURN to EDIT LEVEL IV main menu
ENTER CHOICE > R

```

### Edit Level IV Option 2: Special Output File from MINTEQA2

The following section shows how to tell PRODEFA2 to create a spreadsheet importable file and how to specify the information you want. In this example, the file to be appended to (or created if it doesn't already exist) is TESTD.PRN. Each line within that file represents the equilibrated results from a separate MINTEQA2 run or from an individual sweep or titration point of a run where the sweep option is used. The first two entries on each line of the file are time and date ID numbers that allow you to associate the results with the run or sweep to which they pertain (those same ID numbers are written to PART 5 of the MINTEQA2 output file). When this option is used, the pH will be written automatically without having been designated as a component to be written. The same is true of pe if it is defined in your run. The equilibrated mass distribution for the other components selected (up to 3) is written to the special file just as it appears in PART 5 of the MINTEQA2 output file. Information on Fe<sup>2+</sup> and HS<sup>-</sup> is requested as shown in the example below.

```

_____ EDIT LEVEL IV _____ PROB # 1_
_____ SELECT OPTION _____

1 = Specify that the total concentration or fixed log activity of
one component only is to be systematically varied in a series of
otherwise identical problems.

2 = Specify that the equilibrated mass distribution (computed by
MINTEQA2) of up to three user selected components, pH, and
Eh (if applicable) be written to a user designated file in a
format appropriate for import by popular spreadsheet programs.

R = Return to MAIN MENU

ENTER CHOICE > 2

_____ EDIT LEVEL IV _____ PROB # 1_
_____ IMPORT UTILITY _____

```



- 1 = Filename to which the equilibrated data for spreadsheet import is to be written:
- 2 = Currently specified component(s) whose equilibrated mass distributions are to be written:
- C = Cancel current settings and reset so as to NOT generate importable output
- R = Return to previous menu without changing anything

ENTER CHOICE > 1

Enter the name of the file to which the importable MINTEQA2 output data is to be written. Use up to 8 characters plus an optional filename extension of up to 3 characters.

ENTER FILENAME > TESTD.PRN

---

EDIT LEVEL IV \_\_\_\_\_ PROB # 1\_

---

IMPORT UTILITY \_\_\_\_\_

---

- 1 = Filename to which the equilibrated data for spreadsheet import is to be written: TESTD.PRN
- 2 = Currently specified component(s) whose equilibrated mass distributions are to be written:
- C = Cancel current settings and reset so as to NOT generate importable output
- R = Return to previous menu without changing anything

ENTER CHOICE > 2

STEP 1 - ENTER THE NUMBER OF COMPONENTS whose equilibrated mass distributions are to be written (from 1 to 3; 0 to cancel) > 2

STEP 2 - Follow instructions to SPECIFY COMPONENT 1 of the 2 to be written to the importable ASCII file.

- Enter the FIRST LETTER for the COMPONENT:  
 To identify the component you want, enter the first letter in its chemical symbol (inorganic) or name (organic).  
 OR enter a minus one (-1) to switch to component entry by ID number,  
 OR enter a zero (0) to terminate component entry.

ENTER your choice > f

1 F-1      2 Fe+2      3 Fe+3      4 Formate      5 Fulvate

Select the number of the appropriate component (0 = NONE) > 2  
 \*\*\*\*\*

Component ID number 280, Fe+2 is now flagged for special output by MINTEQA2.

STEP 2 - Follow instructions to SPECIFY COMPONENT 2 of the 2 to be written to the importable ASCII file.

- Enter the FIRST LETTER for the COMPONENT:  
 To identify the component you want, enter the first letter in its chemical symbol (inorganic) or name (organic).  
 OR enter a minus one (-1) to switch to component entry by ID number,  
 OR enter a zero (0) to terminate component entry.

ENTER your choice > h

1 H2O      2 H3AsO3      3 H3AsO4      4 H3BO3      5 H+1  
 6 Hg2+2      7 Hg(OH)2      8 HS-1      9 HSe-1      10 HSeO3-1  
 11 H4SiO4      12 Hexam      13 Humate

Select the number of the appropriate component (0 = NONE) > 8

\*\*\*\*\*  
Component ID number 730, HS-1 is now flagged for special  
output by MINTEQA2.

\_\_\_\_\_ EDIT LEVEL IV \_\_\_\_\_ PROB # 1\_  
\_\_\_\_\_ IMPORT UTILITY \_\_\_\_\_

- 1 = Filename to which the equilibrated data for spreadsheet import  
is to be written: TESTD.PRN
- 2 = Currently specified component(s) whose equilibrated mass distributions  
are to be written: Fe+2 HS-1
- C = Cancel current settings and reset so as to NOT generate importable output
- R = Return to previous menu without changing anything
- ENTER CHOICE > R

### Main Menu Option M: Multi-Problem Generator

MINTEQA2 will also accept multiple problems that are submitted back-to-back in one input file. PRODEFA2 supports this feature and allows you to create input files which contain multiple problems. This feature is most useful when you need to make subtle changes to a standard input file in a fashion that the sweep option does not support. These back-to-back problems do not generate a time savings over running separate files (separate files have the advantage of flexibility and can be strung together with batch files for sequential execution.) The time savings which can be realized is the result of a shortened setup time for the additional problems in PRODEFA2.

### Main Menu Option X: Exit

Upon selecting the EXIT option, PRODEFA2 re-orders the list of TYPE III - SPECIES WITH FIXED ACTIVITY so that fixed components are last in the list. It also checks to be sure that the electron is excluded if it is not a FIXED SPECIES. Finally, as mentioned in the explanation above for EDIT LEVEL II OPTION 4 (infinite solids), PRODEFA2 determines the initial degrees of freedom. If found to be zero or less, the user is advised to add more components or remove some of the species from the TYPE III list. Finally, upon exiting PRODEFA2 reminds the user of the name of the MINTEQA2 input file just created.

## CHAPTER 5

### THE MINTEQA2 OUTPUT FILE AND ERROR DIAGNOSTICS

The MINTEQA2 output file is divided into six parts. Some of these parts may appear several times in one file depending on the combination of solid print option, general output file detail, and whether the sweep option is used. The designations of PARTS 1 through 6 are designed to lend organization rather than sequential ordering although there is logic in the ordering as well.

PART 1 - Reproduction and interpretation of the input file.

PART 2 - Detailed listing of species read from the database files including log K values, enthalpy, molar mass, charge, Debye-Hückel constants, etc.

PART 3 - Iteration information and detailed information for each species including calculated concentration, activity, adjusted log K values, etc.

PART 4 - Percentage distribution of components among dissolved and adsorbed species.

PART 5 - Provisional or equilibrated mass distribution, provisional or equilibrium ionic strength, equilibrium pH and pe, electrostatic surface potential and charge for electrostatic adsorption models.

PART 6 - Saturation indices of all database solids with respect to the solution.

The "provisional" designation in PART 5 pertains to the use of solids print option 2 where provisional results are written to the output file each time a solid precipitates. The final results will be designated "equilibrated" in the output file. Only equilibrated results are written when the solids print option is set to 1.

The FULL OUTPUT option in PRODEFA2 results in an output file that includes all six parts. The INTERMEDIATE OUTPUT option causes PART 2 to be omitted. The ABBREVIATED OUTPUT option causes PART 2, most of PART 3, and all of PART 6 to be omitted. Appendix D contains an example output file.

## Error Diagnostics

The README.1ST document included with the MINTEQA2 diskettes explains how to configure your system for properly executing MINTEQA2. If an error occurs while attempting to use MINRUN, consult that document to be sure you have set the CONFIG.SYS parameters as instructed.

Occasionally, errors occur during the execution of MINTEQA2 that are unrelated to the installation of the model. Whatever the cause, the output file will contain an error code of the form MVx.xx-yy where x.xx is the MINTEQA2 version number and yy refers to an error message code. All error message codes are written to the output file along with a suggested **REMEDY** and sometimes with an **ALTERNATIVE** remedy. The complete set of error message codes and their corresponding remedies are listed below along with additional explanation and remedial suggestions if appropriate.

### MINTEQA2 Error Codes and Messages

#### MV3.00-01

The number of COMPONENTS specified exceeds the maximum allowed, NXDIM.

**REMEDY:** Eliminate unnecessary components (those that are chemically non-reactive in this system, the reduced members of redox couples when the pe is very high or vice versa, etc.).

**ALTERNATIVE:** Re-compile MINTEQA2 with a larger value for parameter NXDIM in the file MINTEQA2.INC.

Too many components are specified in the MINTEQA2 input file. Eliminate those that would probably remain as free species at equilibrium anyway. If eliminating such components adversely affects the ionic strength, fix it at the appropriate value. The effect of Na<sup>+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and K<sup>+</sup> on the final equilibrium composition can frequently be adequately modeled by merely fixing the ionic strength.

#### MV3.00-02

The number of species read from the database exceeds the maximum allowed, NYDIM.

**REMEDY:** Eliminate unnecessary components (those that are chemically non-reactive in this system, the reduced members of redox couples when the pe is very high or vice versa, etc.). This will result in fewer species.

**ALTERNATIVE:** Re-compile MINTEQA2 with a larger value for parameter NYDIM in the file MINTEQA2.INC.

Same comment as for MV3.00-01.

#### MV3.00-03

A species included in the input file as TYPE 3, 4, 5, or 6 was not in the thermodynamic database.

**REMEDY:** Check to make sure that the ID numbers of TYPE 3, 4, 5, and 6 entries in the input file are valid.

If the input file ID numbers are all legitimate database species, check to be sure you have not inadvertently changed the database.

#### MV3.00-04

The number of adsorption parameters entered is insufficient for the adsorption model specified.

**REMEDY:** Check the input file to be sure that the solid sorbent concentration, specific surface area, and capacitance parameters are entered as appropriate for the model specified. PRODEFA2 inserts the appropriate parameters for each model.

Use PRODEFA2 to set-up input files for adsorption runs; do not try to insert adsorption parameters by using an editor. Also, do not attempt to change the adsorption model of an input file in PRODEFA2; that characteristic of a file cannot be changed with PRODEFA2.

#### MV3.00-05

The input file is interpreted to have a species TYPE greater than six.

**REMEDY:** This usually results from having used an editor to modify the input file outside PRODEFA2. Check for misplaced blank lines or the wrong number of entries specified for TYPE 3, 4, 5, or 6 in the input file.

There is no legitimate type number greater than six. If things are out of place in the input file, MINTEQA2 may misinterpret an input field.

#### MV3.00-06

A component ID listed in the input file is not a valid MINTEQA2 component ID number.

**REMEDY:** This error may be a typo resulting from using an editor to modify the input file. If it is not a typo but rather is an attempt to use a new component previously unknown to MINTEQA2, be aware that you must edit the component database file COMP.DBS and insert the new component therein. Consult the documentation file DATABASE.DOC for more info.

New components cannot be defined by specifying them in PRODEFA2. The component database COMP.DBS file must be edited to define a new component.

#### MV3.00-07 RESERVED - NOT CURRENTLY USED

#### MV3.00-08

As requested via an input option, execution is halted due to charge imbalance.

**REMEDY:** Obtain more accurate or complete analyses of total dissolved concentrations or reset the input option via PRODEFA2 to continue in spite of charge imbalance.

#### MV3.00-09 06

Computations have resulted in a singular matrix.

**REMEDY:** Check initial activity guesses. Poor guesses may lead to divergence rather than convergence. If this is a fixed pH or fixed pe run, use the sweep option starting at a pH or pe where you can make good guesses to compute the equilibria at a difficult pH or pe by specifying a small increment with each sweep.

This error is generated by the routine that estimates the change in component activities with each successive iteration. It indicates that the problem is not converging and results either from poor initial activity guesses or from an improperly posed chemical problem. Re-think the chemical problem in terms of a laboratory system and make sure it is formulated properly for MINTEQA2. If it seems to be a reasonable chemical problem, try making better initial activity guesses.

#### MV3.00-10 07

Computations have resulted in an estimate of zero for the activity of some component.

**REMEDY:** Check initial activity guesses. Poor guesses may lead to divergence rather than convergence. For fixed pH or fixed pe runs, use the sweep option starting at a pH or pe where you can make good guesses to compute equilibria at a difficult pH or pe by specifying a small increment with each sweep.

**ALTERNATIVE:** Eliminate the component whose activity has become zero.

Same comment as MV3.00-09.

MV3.00-11 02

A phase rule violation has occurred.

**REMEDY:** Too complex to explain here. See the User's Manual.

Phase rule violations are more likely when a FINITE solid with non-zero concentration is specified in the input file. This is because the solid specified may not be the most insoluble at equilibrium. If it is not, MINTEQA2 will dissolve it in favor of the more insoluble form. Should the replacing mineral precipitate before the initial one has dissolved, a phase rule violation may occur. The remedy is to either remove the FINITE solid from the input file or set its concentration to zero. In either case, the total dissolved concentrations of its constituent components must be supplemented as discussed in Chapter 4 (EDIT LEVEL II OPTION 7).

Also, phase rule violations are more likely when all oversaturated solids of the database are allowed to precipitate (see Chapter 4, EDIT LEVEL I OPTION 8). If this option is used and a phase rule violation occurs, execute the model a second time with no solids allowed. The saturation indices of database solids will be printed out and can be used as a guide for deciding which solids to specifically allow.

A general observation regarding this type of phase rule violation is illustrated by imagining a model run with several metal components. In such a run, imagine that after converging several times and precipitating a solid each time, a solid of metal "M" precipitates. Iterations continue and several more solids precipitate, none involving metal "M." Finally, a second solid of metal "M" precipitates and execution ends with a phase rule violation. It is usually the case that the correct remedy is to run the model again with that solid of metal "M" that precipitated first explicitly EXCLUDED. That this is the correct remedy can be verified by examining the listing of saturation indices in PART 6 of the output file. If no phase rule violation occurs and the index calculated for the EXCLUDED solid is less than zero, the problem has been correctly resolved. It may be that the first phase rule violation will be eliminated, but a new one involving a different solid (which has taken the place of the one you excluded and is now the first precipitate of metal "M") now occurs. Try applying the same procedure again, excluding the new offending solid as well as that which was formerly excluded. It may be necessary to repeat the procedure several times before the most insoluble solid is finally the first to precipitate.

MV3.00-12 04

The number of degrees of freedom is zero. This problem is over-constrained.

**REMEDY:** Specify additional components or reduce the number of fixed species. Remember that each solid that precipitates introduces an additional fixed constraint on the system.

There are too many fixed species for computations to continue. If, for example,  $\text{Ca}^+$ ,  $\text{CO}_3^{2-}$ , and  $\text{H}^+$  are the only components (other than  $\text{H}_2\text{O}$ ) and if the pH is fixed and a  $\text{CO}_2(\text{g})$  phase with fixed partial pressure is imposed, and if solids are allowed to precipitate, this error will occur when a solid containing calcium precipitates. In that case, there will be four components and four fixed species and no variables remaining in the problem. Add inert components to allow computations to continue or restrict certain solids from precipitation.

MV3.00-13 04

The number of iterations has reached the maximum allowed as specified in the input file.

**REMEDY:** Use PRODEFA2 to re-set this to a larger value or else make better initial activity guesses to produce convergence in fewer iterations.

Most well-formulated problems take fewer than 100 iterations unless there are many solid phases.



## REFERENCES

1. Ball, J.W., E.A. Jenne and M.W. Cantrell. 1981. WATEQ3: A Geochemical Model with Uranium Added. U.S. Geological Survey, Washington, DC, Open File Report 81-1183.
2. Benjamin, M.M. and J.O. Leckie. 1981. Multiple-Site Adsorption of Cd, Cu, Zn, and Pb on Amorphous Iron Oxyhydroxide. *J. Coll. Inter. Sci.* 79:209-221.
3. Davies, C.W. 1962. Ion Association. Butterworths Pub., Washington, DC. 190 pp.
4. Davis, J.A., R.O. James and J.O. Leckie. 1978. Surface Ionization and Complexation at the Oxide/Water Interface: I. Computation of Electrical Double Layer Properties in Simple Electrolytes. *J. Coll. Inter. Sci.* 63:480-499.
5. Davis, J.A. and J.O. Leckie. 1978. Surface Ionization and Complexation at the Oxide/Water Interface: II. Surface Properties of Amorphous Iron Oxyhydroxide and Adsorption of Metal Ions. *J. Coll. Inter. Sci.* 67:90-107.
6. Dzombak, D.A. 1986. Toward a Uniform Model for the Sorption of Inorganic Ions on Hydrous Oxides. Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge Massachusetts.
7. Felmy, A.R., S.M. Brown, Y. Onishi, S.B. Yabusaki and R.S. Argo. 1984. MEXAMS--The Metals Exposure Analysis Modeling System. U.S. Environmental Protection Agency, Athens, GA. EPA-600/3-84-031.
8. Felmy, A.R., D.C. Girvin, and E.A. Jenne. 1984. MINTEQ--A Computer Program for Calculating Aqueous Geochemical Equilibria. U.S. Environmental Protection Agency, Athens, GA. EPA-600/3-84-032.
9. Garrels, R.M. and C.L. Christ. 1965. Solutions, Minerals, and Equilibria. Freeman, Cooper and Company, San Francisco, CA.
10. Helgeson, H.C. 1969. Thermodynamics of Hydrothermal Systems at Elevated Temperatures and Pressures. *Amer. J. of Sci.* 267:729-804.
11. Ingle, S.E., M.D. Schuldt and D.W. Shults. 1978. A Users Guide for REDEQL.EPA. A Computer Program for Chemical Equilibria in Aqueous Systems. U.S. Environmental Protection Agency, Corvallis, OR. EPA600/3-78-024.

12. James, R.O. and G.A. Parks. 1982. Characterization of Aqueous Colloids by Their Electric Double-Layer and Intrinsic Surface Chemical Properties. *Surface Colloid Sci.* 12:119-216.
13. Loux, N.T., D.S. Brown, C.R. Chafin, J.D. Allison and S.M. Hassan, 1989. Chemical Speciation and Competitive Cationic Partitioning on Sandy Aquifer Material. *Journal of Chemical Speciation and Bioavailability.* 1: 111-125.
14. Morel, F.M.M. 1983. *Principles of Aquatic Chemistry.* John Wiley and Sons, New York, NY, 446 pp.
15. Parkhurst, D.L., D.C. Thortenson and L.N. Plummer, 1980. PHREEQE--A Computer Program for Geochemical Calculations. U.S. Geological Survey, Water Resources Investigations 80-96, 210 pp.
16. Pitzer, K.S. 1973. Thermodynamics of Electrolytes. I. Theoretical Basis and General Equations. *Jour. Phys. Chem.* 77:268-277.
17. Pitzer, K.S. and J.J. Kim. 1974. Thermodynamics of Electrolytes. IV. Activity and Osmotic Coefficients for Mixed Electrolytes. *J. Am. Chem. Soc.* 96:5701-5707.
18. Pitzer, K.S. and G. Mayorga. 1973. Thermodynamics of Electrolytes. II. Activity and Osmotic Coefficients for Strong Electrolytes with One or Both Ions Univalent. *Jour. of Phys. Chem.* 77:2300-2308.
19. Truesdell, A.H. and B.F. Jones. 1974. WATEQ, A Computer Program for Calculating Chemical Equilibria in Natural Waters. U.S. Geological Survey J. Res., Washington, DC, 2:233-248.
20. Van Zeggeren, F. and S.H. Storey. 1970. *The Computation of Chemical Equilibria.* Cambridge University Press, London, England.
21. Westall, J.C. 1986. MICROQL. A Chemical Equilibrium Program in BASIC. Report No. 86-02, Oregon State University, Corvallis, OR.
22. Westall, J.C. and H. Hohl. 1980. A Comparison of Electrostatic Models for the Oxide/Solution Interface. *Adv. Coll. Inter. Sci.* 12:265-294.
23. Westall, J.C., J.L. Zachary and F.M.M. Morel. 1976. MINEQL, A Computer Program for the Calculation of Chemical Equilibrium Composition of Aqueous Systems. Tech. Note 18, Dept. Civil Eng., Massachusetts Institute of Technology, Cambridge, MA.
24. Wolery, T.J. 1982. Computer Program for Geochemical Aqueous Speciation--Solubility Calculations. Lawrence Livermore Laboratory, Livermore, CA, 224 pp.

## APPENDIX A

### THE THERMODYNAMIC DATABASE USED BY MINTEQA2

The thermodynamic database used by MINTEQA2 contains over 1000 species. The best way to search the database for a species of interest is to use PRODEFA2 or an editor with a search/find utility. If the latter option is used, you must know how the species ID number or names are derived and expressed. Because FORTRAN does not support the use of super- or subscripts, the customary method of writing chemical formulas cannot be accommodated without modification. The following naming rules are used in MINTEQA2.

- 1) Stoichiometric coefficients are written with parentheses and brackets enclosing the elements in the formula to which the stoichiometry applies.
- 2) Species charge numbers will always be preceded with a sign (+/-). The one (1) in (+1) and (-1) may be omitted. If a species name ends with an unsigned number, that number represents stoichiometry.
- 3) Species names involving organics may be shortened by leaving out letters.

Examples:

H2O means  $H_2O$

CR(OH)2+ means  $Cr(OH)_2^+$

HG(OH)2 means  $Hg(OH)_2$

SO4-2 means  $SO_4^{2-}$

TARTRAT means Tartrate

The following is an explanation of MINTEQA2's thermodynamic database files. This information is useful for adding new reactions to any of the four database files: THERMO.DBS, TYPE6.DBS, REDOX.DBS or GASES.DBS. Before attempting to add to or modify these files, note the following.

- You should make a backup copy of the file you are going to modify before you start. Give the copy a name such as TYPE6.SAV. This is just in case things do not go as planned.

- When adding to or modifying the thermodynamic database, if the reaction is an AQUEOUS species, you need only edit THERMO.DBS. If the reaction is a SOLID (mineral), REDOX couple, or GAS, you must edit two files as explained below. The main file, THERMO.DBS, is divided into several sections delineated by blank lines and lines that contain a zero in column 7. The first section is for AQUEOUS species and is followed by three lines with zeroes separated by blank lines. After these separator lines, the next section is for SOLIDS and that section is followed with one blank line and one line with a zero. The next section is for REDOX couples and is followed immediately by the GAS section. The file is terminated with a blank line then a line with a zero. YOU MUST HONOR THE SECTIONAL DIVISIONS WHEN MAKING ADDITIONS--DO NOT DELETE OR CHANGE THE SEPARATOR LINES. The arrangement of these sections serves to signal MINTQA2 as to the nature of the species (AQUEOUS species, SOLID, etc.).

- To add a new AQUEOUS species, it need only be entered in THERMO.DBS. The other files remain unchanged.

- To add a new SOLID (MINERAL), it must be entered in THERMO.DBS and in TYPE6.DBS.

- To add a new REDOX couple, it must be entered in THERMO.DBS and in REDOX.DBS.

- After all desired changes are made to THERMO.DBS and TYPE6.DBS, new versions of the corresponding files that are actually used by MINTQA2 and PRODEFA2 must be created. This is easily accomplished by executing the program UNFRMT.EXE (included on the distribution media). Before executing UNFRMT, rename the current THERMO.UNF and TYPE6.UNF to something else for safe keeping. UNFRMT creates unformatted versions of THERMO and TYPE6 that can be read faster than their formatted counterparts. The unformatted files cannot be edited directly because they are unintelligible. The program FRMT.EXE does exactly the inverse of UNFRMT so that THERMO.DBS and TYPE6.DBS can be recreated from the unformatted files if desired.

- To add a new GAS, it must be entered in THERMO.DBS and in GASES.DBS.

- Constants for all entries are referenced to a temperature of 25 degrees C. AQUEOUS species constants are for ionic strength of zero, REDOX couple constants are for zero potential, and GAS constants are for a partial pressure of one atmosphere.

### The Component Database File

The component database file is shown below. The 3-digit ID number, MINTQA2 name, and real chemical name are shown for each component. Note that ID numbers 240 through 259 are reserved and should not be used for newly created components. Also, note the adsorption components are numbered 811 through 859.

001 E-1	e <sup>-</sup>	020 Ag+1	Ag <sup>+1</sup>
002 H2O	H <sub>2</sub> O	030 Al+3	Al <sup>+3</sup>

060 H3AsO3	H <sub>3</sub> AsO <sub>3</sub>	813 ADS1PSI0	Adsorbant 1, electrostatic surface layer
061 H3AsO4	H <sub>3</sub> AsO <sub>4</sub>	814 ADS1PSIB	Adsorbant 1, electrostatic β layer
090 H3BO3	H <sub>3</sub> BO <sub>3</sub>	815 ADS1PSID	Adsorbant 1, electrostatic d layer
100 Ba+2	Ba <sup>+2</sup>	821 ADS2TYP1	Adsorbant 2, type 1
130 Br-1 Br <sup>-1</sup>		822 ADS2TYP2	Adsorbant 2, type 2
140 CO3-2	CO <sub>3</sub> <sup>-2</sup>	823 ADS2PSI0	Adsorbant 2, electrostatic surface layer
143 CN-	CN <sup>-</sup>	824 ADS2PSIB	Adsorbant 2, electrostatic β layer
144 OCN-	OCN <sup>-</sup>	825 ADS2PSID	Adsorbant 2, electrostatic d layer
150 Ca+2	Ca <sup>+2</sup>	831 ADS3TYP1	Adsorbant 3, type 1
160 Cd+2	Cd <sup>+2</sup>	832 ADS3TYP2	Adsorbant 3, type 2
180 Cl-1 Cl <sup>-1</sup>		833 ADS3PSI0	Adsorbant 3, electrostatic surface layer
210 Cr+2	Cr <sup>+2</sup>	834 ADS3PSIB	Adsorbant 3, electrostatic β layer
211 Cr(OH)2+	Cr(OH) <sub>2</sub> <sup>+</sup>	835 ADS3PSID	Adsorbant 3, electrostatic d layer
212 CrO4-2	CrO <sub>4</sub> <sup>-2</sup>	841 ADS4TYP1	Adsorbant 4, type 1
230 Cu+1	Cu <sup>+1</sup>	842 ADS4TYP2	Adsorbant 4, type 2
231 Cu+2	Cu <sup>+2</sup>	843 ADS4PSI0	Adsorbant 4, electrostatic surface layer
240-259 RESERVED		844 ADS4PSIB	Adsorbant 4, electrostatic β layer
270 F-1 F <sup>-1</sup>		845 ADS4PSID	Adsorbant 4, electrostatic d layer
280 Fe+2	Fe <sup>+2</sup>	851 ADS5TYP1	Adsorbant 5, type 1
281 Fe+3	Fe <sup>+3</sup>	852 ADS5TYP2	Adsorbant 5, type 2
330 H+1	H <sup>+1</sup>	853 ADS5PSI0	Adsorbant 5, electrostatic surface layer
360 Hg2+2	Hg <sub>2</sub> <sup>+2</sup>	854 ADS5PSIB	Adsorbant 5, electrostatic β layer
361 Hg(OH)2	Hg(OH) <sub>2</sub>	855 ADS5PSID	Adsorbant 5, electrostatic d layer
380 I-1 I <sup>-1</sup>		870 TI+1	TI <sup>+1</sup>
410 K+1	K <sup>+1</sup>	871 TI(OH)3	TI(OH) <sub>3</sub>
440 Li+1 Li <sup>+1</sup>		891 U+4	U <sup>+4</sup>
460 Mg+2	Mg <sup>+2</sup>	890 U+3	U <sup>+3</sup>
470 Mn+2	Mn <sup>+2</sup>	892 UO2+1	UO <sub>2</sub> <sup>+1</sup>
471 Mn+3	Mn <sup>+3</sup>	893 UO2+2	UO <sub>2</sub> <sup>+2</sup>
490 NH4+1	NH <sub>4</sub> <sup>+1</sup>	900 V+2	V <sup>+2</sup>
491 NO2-1	NO <sub>2</sub> <sup>-1</sup>	901 V+3	V <sup>+3</sup>
492 NO3-1	NO <sub>3</sub> <sup>-1</sup>	902 VO+2	VO <sup>+2</sup>
500 Na+1	Na <sup>+1</sup>	903 VO2+1	VO <sub>2</sub> <sup>+1</sup>
540 Ni+2	Ni <sup>+2</sup>	950 Zn+2	Zn <sup>+2</sup>
580 PO4-3	PO <sub>4</sub> <sup>-3</sup>	955 Dietham	diethylamine
600 Pb+2	Pb <sup>+2</sup>	956 Nbutyam	n-butylamine
680 Rb+1	Rb <sup>+1</sup>	958 Metham	methylamine
730 HS-1	HS <sup>-1</sup>	959 Dimetham	dimethylamine
731 S S		960 Trbutph	tributylphosphate
732 SO4-2	SO <sub>4</sub> <sup>-2</sup>	961 Hexam	hexylamine
740 Sb(OH)3	Sb(OH) <sub>3</sub>	963 EN ethylenediamine	
741 Sb(OH)6-	Sb(OH) <sub>6</sub> <sup>-</sup>	964 Npropam	n-propylamine
760 HSe-1	HSe <sup>-1</sup>	965 Ipropam	iso-propylamine
761 HSeO3-1	HSeO <sub>3</sub> <sup>-1</sup>	966 Tmetham	tri-methylamine
762 SeO4-2	SeO <sub>4</sub> <sup>-2</sup>	967 Citrate	citrate
770 H4SiO4	H <sub>4</sub> SiO <sub>4</sub>	968 NTA-3	nitritriacetate <sup>-3</sup>
800 Sr+2	Sr <sup>+2</sup>	969 EDTA-4	EDTA <sup>-4</sup>
811 ADS1TYP1	Adsorbant 1, type 1	971 Prpanot	propanoate
812 ADS1TYP2	Adsorbant 1, type 2	972 Butanot	butyrate

973 Isobuty	iso-butyrate
980 2Metpyr	2-methyl pyridine
981 3Metpyr	3-methyl pyridine
982 4Metpyr	4-methyl pyridine
983 Formate	formate
984 Isvaler	iso-valerate
985 Valerat	valerate
990 Fulvate	fulvate
991 Humate	humate
992 Acetate	acetate
993 Tartrat	tartrate
994 Glycine	glycine
995 Salicyl	salicylate
996 Glutama	glutamate
997 Phthala	phthalate

### Format of Database Species Entries

Each reaction in THERMO.DBS, TYPE6.DBS, GASES.DBS, and REDOX.DBS is specified by a two or three line entry. The explanation of each line is as follows:

#### FIRST line

Column(s)	Meaning	Format
1 - 7	Species reaction product ID number. If you are adding a new reaction, you create this number.	I7

For AQUEOUS and GAS species, the 7-digit ID is formed from the 3-digit component ID # of the major cation suffixed by the 3-digit component ID # of the major anion suffixed by a single digit to ensure that the resulting 7-digit number is unique within the entire database.

For SOLID species, the 3-digit component ID # of the major cation is prefixed with a 2-digit code that represents the class to which the solid belongs. The 2-digit class codes are listed below. The resulting

5-digit number is suffixed with 2-digits to ensure that the final 7-digit number is unique within the entire database.

#### 2-Digit Codes for Classes of Solids

---

Code Class	Code Class
00 Elemental	51 Nitrate
10 Sulfide	52 Borate
11 Cyanide	60 Sulfate
12 Selenide	61 Selenite,Selenate
14 Antimonide	70 Phosphate
20 Oxide and Hydroxide	72 Arsenate
30 Multiple Oxide	73 Vanadate
40 Bromide	80 Orthosilicate
41 Chloride	82 Chain Silicate
42 Fluoride	84 Framework Silicate
43 Iodide	86 Sheet Silicate
50 Carbonate	

---

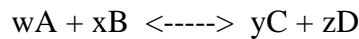
For REDOX couples, the 3-digit component ID # of one member of the redox pair is prefixed by the other and the resulting 6-digit number is suffixed by a single digit to ensure that the final 7-digit ID number is unique within the entire database.

- 8 blank
- 9 - 20 Species reaction product name. With only 12 A12 spaces, it may be necessary to abbreviate. Subscripts aren't possible but do use parentheses where appropriate. If the species is charged, always hang the charge on the end of the name prefixed with the appropriate algebraic sign. For SOLIDS, mineral names are preferred to chemical formula names.
- 21 - 30 Enthalpy change, i.e., delta H for the F10.4

reaction (kcal/mole). MINTEQA2 uses this value to adjust the equilibrium constant for temperatures other than 25 degrees C.

31 - 40 Log K. Common logarithm of the equilibrium constant for this reaction. F10.4

For AQUEOUS species, this is a thermodynamic stability or formation constant, i.e., for the reaction



$$K = \frac{\{C\}^y \{D\}^z}{\{A\}^w \{B\}^x}$$

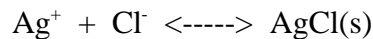
where braces { } denote activity.

For MINTEQA2, this reaction would be written



in the thermodynamic database where A, B, and C are MINTEQA2 components and D is an AQUEOUS species and is referred to here as the species reaction product.

For SOLIDS, K is the reciprocal (log K is the negative) of the solubility product. This is because MINTEQA2 treats precipitation reactions as if written with reactants on the left and precipitates on the right which is reversed compared with the solubility product rule. A representative MINTEQA2 precipitation reaction is



$$K = \frac{\{AgCl\}}{\{Ag^+\}\{Cl^-\}}$$



where brackets { } again denote activity. The activity of solid AgCl is 1.0 because it is a pure phase so that we may write

$$K = \frac{1}{\{Ag^+\}\{Cl^-\}}$$

Now, the solubility product rule applied to the silver chloride reaction gives

$$K_{sp} = \{Ag^+\}\{Cl^-\}$$

Therefore, the K needed in MINTEQA2 is related to the  $K_{sp}$

$$K = \frac{1}{K_{sp}}$$

$$\log K = -\log K_{sp} .$$

In summary, the log K value for a SOLID in the database is the negative of log  $K_{sp}$ .

For REDOX couples, the value entered for log K is computed from the Nernst equation

$$E = E^\circ - 2.303 RT/nF \log Q$$

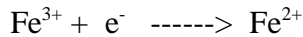
where E is the potential,  $E^\circ$  is the standard reduction potential at 25 degrees C, R is the molar gas constant, T is the absolute temperature, F is the Faraday constant, n is the number of electrons in the half-reaction, and Q is that function of concentrations (activities) of products and reactants that occurs in the equilibrium constant which is sought. For potentials measured in volts at 25 degrees C

$$E = E^\circ - (1/n) (0.05916) \log Q .$$

Just as log K's for AQUEOUS species are referenced to an ionic strength of zero, the log K's for REDOX couples are referenced to a potential of zero. So, with rearrangement and taking  $E = 0$ , the above equation becomes

$$\log Q = 16.903 nE^{\circ}$$

For the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  couple (species ID # 2812800),

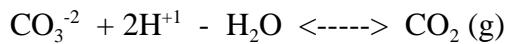


for which the standard reduction potential is 0.771 and  $n = 1$ , the above expression gives

$$\log Q = 13.032.$$

This is the value entered for log K in that reaction.

For GASES, the log K entered is  $\log K_p$  where the partial pressure of the gas is in atmospheres. The values currently in the database files are for a partial pressure of one atmosphere. If you want to compute equilibria at pressures other than one atm, you will need to adjust the  $\log K_p$  accordingly. PRODEFA2 makes this adjustment for you by asking for the desired partial pressure, obtaining the constant for one atm from the database, and entering the corrected log K in your input file. An example of a gas reaction and the partial pressure adjustment is species 3301403



The  $\log K_p$  at one atm is 18.16. The log of the partial pressure of  $\text{CO}_2 (\text{g})$  in the atmosphere is about -3.5. Therefore, the corrected  $\log K_p$  is

$$\begin{aligned} \log K_p &= \log K_p - \log 10^{-3.5} \\ &= 18.16 - (-3.5) \\ &= 21.66 \end{aligned}$$

MINTEQA2 requires that the partial pressures of all gases be fixed for a given problem.

- 41 - 48    Maximum reported log K. This entry is made    F8.3  
 only for SOLID species and is not actually  
 used in MINTEQA2's equilibria calculations.  
 It is intended to provide a means of judging  
 the reliability of the log K given in columns  
 31 - 40.
- 49 - 56    Minimum reported log K. This entry is made    F8.3  
 for SOLID species only and is not actually  
 used in MINTEQA2's equilibria calculations.  
 It is intended to provide a means of judging  
 the reliability of the log K given in columns  
 31 - 40.
- 57 - 61    Charge of species reaction product.            F5.2
- 62 - 66    Debye-Hückel a parameter for species reaction    F5.2  
 product.
- 67 - 71    Debye-Hückel b parameter for species reaction    F5.2  
 product.
- 72 - 80    Gram formula weight of species reaction        F9.4  
 product. No entry for REDOX couples.

-----

SECOND line

Column(s)	Meaning	Format
1 - 5	Carbonate alkalinity factor. This entry is made only for AQUEOUS species that have carbonate (ID # 140) as a component. In cases where the user has chosen to specify the inorganic carbon as alkalinity (this is an option when executing MINTEQA2), the carbonate alkalinity factor is used to determine total dissolved inorganic carbon concentration from a measure of alkalinity.	F5.2

To compute the carbonate alkalinity factor for a new species, use the formula:

$$\text{alkalinity factor} = 2 \times \text{STOIC}(\text{CO}_3^{2-}) - \text{STOIC}(\text{H}^+)$$

where STOIC(x) is the stoichiometry of component x in the reaction.

- 6 blank
- 7 Number of components (as reactants or products) in this reaction. Maximum = 9. I1
- 8 - 10 blank
- 11 - 17 Stoichiometry of the first component. F7.3  
Negative if the component is a reaction product, that is, if it occurs in the left-hand side of the chemical equation with a negative coefficient.
- 18 blank
- 19 - 21 ID number of the first component.
- 22 - ? Additional stoichiometry/component ID # pairs with separating spaces so that the total number of pairs is equal to the number of components as specified in column 7. These are entered in the same manner as the first pair in columns 8 - 21. That is, 3 blank columns followed by seven columns for the stoichiometry in F7.3 format, one blank column and finally, three columns for the component ID # in I3 format. The remainder of the second line will hold 4 additional pairs through column 77. If the total number of components is greater than 5, continue on a third line with the 3 columns 78 - 80 of the second line counted as the 3 blank columns for the sixth pair. Use columns 1 - 7 of the third line for the stoichiometry of the sixth pair. Column 8 should be blank and columns 9 - 10 should contain the component ID #.

Continue with the 3X,F7.3,1X,I3 format for up to three additional pairs on the third line.

### Examples of Entries in the Thermodynamic Database Files

The following are excerpts from the thermodynamic database files. Each excerpt is followed by an explanation of all entries. The explanation is presented with the component names just as they appear in MINTEQA2.

#### AQUEOUS Species

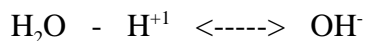
```
3300020 OH-      13.345 -13.998      -1. 3.5 0.0 17.0074
  2  1.000 2  -1.000 330
1501401 CaCO3 AQ  4.0300  3.1500      0. 0.0 0.0 100.0890
2.00 2  1.000 150  1.000 140
2113300 CR+3    -20.1400  9.62      3.00 0.00 0.00 51.9960
0.00 3  1.000 211  2.000 330  -2.000 2
```

#### EXPLANATION:

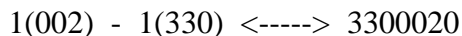
First reaction --

Species ID number: 3300020      Minimum Log K: not used  
Species name:      OH<sup>-</sup>      Species charge: -1  
Delta H:      13.345 kcal/mol      Debye-Hückel a: 3.5  
Log K:      -13.998      Debye-Hückel b: 0 or unknown  
Maximum Log K:      not used      Gram Formula Wt.: 17.0074

Alkalinity factor: none      Number of components: 2  
Chemical Equation (from stoichiometry/components):



or, in terms of (stoichiometry)component ID #'s:

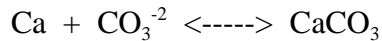


Second reaction --

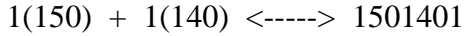
Species ID number: 1501401      Minimum Log K: not used  
Species name:      CaCO<sub>3</sub> (aq)      Species charge: 0  
Delta H:      4.03 kcal/mol      Debye-Hückel a: 0 or unknown  
Log K:      3.15      Debye-Hückel b: 0 or unknown  
Maximum Log K:      not used      Gram Formula Wt.: 100.089

Alkalinity factor: 2.0      Number of components: 2

Chemical Equation (from stoichiometry/components):



or, in terms of (stoichiometry)component ID #'s:

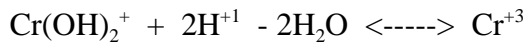


Third reaction --

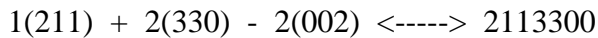
Species ID number: 2113300      Minimum Log K: not used  
Species name: Cr+3      Species charge: +3  
Delta H: -20.140 kcal/mol      Debye-Hückel a: 0 or unknown  
Log K: 9.62      Debye-Hückel b: 0 or unknown  
Maximum Log K: not used      Gram Formula Wt.: 51.996

Alkalinity factor: none      Number of components: 3

Chemical Equation (from stoichiometry/components):



or, in terms of (stoichiometry)component ID #'s:



### SOLID (Mineral) species

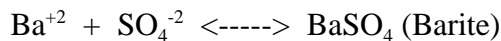
6010000 BARITE      -6.280    9.976    .000    9.773      233.4016  
2    1.000 100    1.000 732

### EXPLANATION:

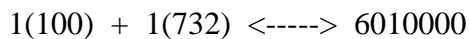
Species ID number: 6010000      Minimum Log K: 9.773  
Species name: Barite      Species charge: 0  
Delta H: -6.280 kcal/mol      Debye-Hückel a: unknown  
Log K: 9.976      Debye-Hückel b: unknown  
Maximum Log K: unknown      Gram Formula Wt.: 233.4016

Alkalinity factor: none      Number of components: 2

Chemical Equation (from stoichiometry/components):



or, in terms of (stoichiometry)component ID #'s:



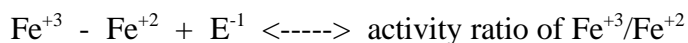
## REDOX Couple

2812800 FE+3/FE+2 -10.0 13.032  
3 1.000 281 -1.000 280 1.000 1

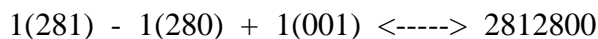
### EXPLANATION:

Species ID number: 2812800      Minimum Log K: not used  
Species name: Fe+3/Fe+2      Species charge: not used  
Delta H: -10.0 kcal/mol      Debye-Hückel a: not used  
Log K: 13.032      Debye-Hückel b: not used  
Maximum Log K: not used      Gram Formula Wt.: not used

Alkalinity factor: none      Number of components: 3  
Chemical Equation (from stoichiometry/components):



or, in terms of (stoichiometry)component ID #'s:



## GAS species

3301403 CO2(GAS) -0.53 18.16      41.0100  
3 1.000 140 2.000 330 -1.000 2

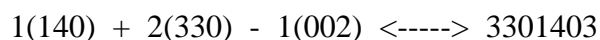
### EXPLANATION:

Species ID number: 3301403      Minimum Log K: not used  
Species name: CO2 (g)      Species charge: 0  
Delta H: -0.53      Debye-Hückel a: unknown  
Log K: 18.16      Debye-Hückel b: unknown  
Maximum Log K: not used      Gram Formula Wt.: 41.010

Alkalinity factor: none      Number of components: 3  
Chemical Equation (from stoichiometry/components):



or, in terms of (stoichiometry)component ID #'s:



## APPENDIX B

### NEWTON-RAPHSON APPROXIMATION METHOD

The Newton-Raphson approximation method is an iterative technique for finding a value  $x$  such that  $y(x) = 0$ . When only one variable is involved, successive (improved) values of  $x$  ( $x_n, x_{n+1}, x_{n+2}, \dots$ ) are obtained from the difference quotient.

$$\frac{y(x_{n+1}) - y(x_n)}{x_{n+1} - x_n} = -z_n \tag{B1.01}$$

where the derivative evaluated at  $x_n$  is denoted by  $z_n$ .

In each successive step, the function  $y(x_{n+1})$  is set to zero (because this is the solution sought) and Equation B1.01 is solved for  $x_{n+1}$  in terms of the previously known values of  $x_n, y(x_n)$  and  $z_n$ . When  $y(x_{n+1})$  in Equation B1.01 is set to zero

$$z_n \Delta x = y(x_n) \tag{B1.02}$$

where  $\Delta x = x_n - x_{n+1}$ .

The new value of  $x$  is then found from:

$$x_{n+1} = x_n - \Delta x \tag{B1.03}$$

Similar reasoning applies to problems in more than one variable except that the analog to Equation B1.02 becomes the matrix equation

$$\mathbf{Z}_n \Delta \mathbf{X} = \mathbf{Y}_n \tag{B1.04}$$

where  $\mathbf{Z}_n$  is the Jacobian of  $\mathbf{Y}$  with respect to  $\mathbf{X}$  evaluated at  $\mathbf{X}_n$ . A solution for  $\Delta \mathbf{X}$  is found from Gaussian elimination and back substitution and  $\mathbf{X}_{n+1}$  is calculated from:

$$\mathbf{X}_{n+1} = \mathbf{X}_n - \Delta \mathbf{X} \tag{B1.05}$$



## APPENDIX C

### MINTEQA2 MODEL DISTRIBUTION

#### Introduction

Refer to the READ.ME, README.1ST, and/or README.TOO file(s) for the latest supplemental information, changes, and/or additions to the MINTEQA2 model or documentation. Copies of these files are included on each distribution diskette set or can be down loaded from the Center for Exposure Assessment Modeling (CEAM) electronic bulletin board system (BBS). Each can be installed on a hard disk using the appropriate installation program. They are ASCII (non-binary) text files that can be displayed on the monitor screen by using the DOS TYPE command (e.g., TYPE READ.ME) or printed using the DOS PRINT command (e.g., PRINT READ.ME).

#### Distribution

The MINTEQA2 model system and all support files and programs (e.g. PRODEFA2) are available on diskette from CEAM, located at the U.S. EPA Athens Environmental Research Laboratory, Athens, Georgia, at no charge. The CEAM has an exchange diskette policy. Diskettes must be received before sending a copy of the model system (refer to *Obtaining a Copy of the MINTEQA2 Model System*).

Included in a distribution diskette set are

- o installation DOS batch command and documentation support files for the latest release of the model package
- o data base files and support programs and documentation
- o test and help files in the form of PRODEFA2 dialogue (\*.HLP) and MINTEQA2 input (\*.INP) and output (\*.LST) files
- o executable task image files for the MINTEQA2 model and the PRODEFA2 program; also the FRMT and UNFRMT data base support programs
- o FORTRAN source code files for IBM PC and compatible microcomputer systems
- o batch command files to compile, link, and run selected task image files

A FORTRAN compiler and link editor are NOT required to execute any portion of the model. If the user wishes to modify the model, it will be up to the user to supply and/or obtain

- o an appropriate text editor that saves files in ASCII (non-binary) text format
- o FORTRAN development tools to recompile and link edit any portion of the model

CEAM cannot support, maintain, and/or be responsible for modifications that change the function and/or operational characteristics of the executable task image, MAKE, or DOS command files supplied with the model package.

The microcomputer release of the MINTEQA2 model system is a full implementation of the VAX/VMS version. The microcomputer implementation of this model performs the same function as the U.S. EPA mainframe/minicomputer version.

### Obtaining a Copy of the MINTEQA2 Model System

NOTE: k=1,024; m=1,048,576; b=1 byte

#### Diskette

To obtain a copy of the MINTEQA2 model system on diskette, send

- o the appropriate number of double-sided, double-density (DS/DD 360kb) 5.25 inch, or double-sided, high-density (DS/HD 1.44mb) 3.5 inch error-free diskettes

NOTE: To obtain the correct number of diskettes, contact CEAM at 706/546-3549.

- o a cover letter, with a complete return address, requesting the MINTEQA2 model system to:

Model Distribution Coordinator  
Center for Exposure Assessment Modeling  
Environmental Research Laboratory  
U.S. Environmental Protection Agency  
960 College Station Road  
Athens, GA 30605-2720

Program and/or user documentation, or instructions on how to order documentation, will accompany each response.

#### Electronic Bulletin Board System (BBS)

To download a copy of the MINTEQA2 model system, or to check the status of the latest release of this model or any other CEAM software product, call the CEAM BBS 24 hours a day, 7 days a week. To access the BBS, a computer with a modem and communication software is needed. The phone number for the BBS is 706/546-3402. Communication parameters for the BBS are

- o 300/1200/2400/9600 baud rate
- o 8 data bits
- o no parity
- o 1 stop bit

### Technical support

For questions and/or information concerning

- o installation and/or testing of the MINTEQA2 model system and/or support programs or files, call 706/546-3590 for assistance
- o MINTEQA2 model and/or program content, application, and/or theory, call 706/546-3130 for assistance
- o use of the CEAM electronic bulletin board system (BBS), contact the BBS system operator (SYSOP) at 706/546-3590
- o CEAM software and distribution Quality Assurance and Control, call 706/546-3125
- o other environmental software and documentation distributed through CEAM, contact the Model Distribution Coordinator at 706/546-3549
- o other support available through CEAM, contact Mr. Dermont Bouchard, CEAM Manager by mail at the following address

Center for Exposure Assessment Modeling (CEAM)  
 Environmental Research Laboratory  
 U.S. Environmental Protection Agency  
 960 College Station Road  
 Athens, Georgia 30605-2720

- o by telephone at 706/546-3130
- o by fax at 706/546-2018
- o through the CEAM BBS message menu and commands. The CEAM BBS communication parameters and telephone number are listed above.

To help technical staff provide better assistance, write down a response to the following topics before calling or writing. If calling, be at the computer, with the computer on, and in the proper sub-directory (e.g., \MINTEQA2) when the call is placed.

- o program information:
  - describe the problem, including the exact wording of any error and/or warning message(s)
  - list the exact steps, command(s), and/or keyboard key sequence that will reproduce the problem machine information:

- o machine information:
  - list computer brand and model
  - list available RAM (as reported by DOS CHKDSK command)
  - list extended memory present and free (XMS)
  - list name and version of extended memory (XMS) manager (i.e., HIMEM, VDISK, RAMDRIVE, etc.)
  - list available hard disk space (as reported by DOS CHKDSK command)
  - list the brand and version of DOS (as reported by DOS VER command)
  - list the name of any memory resident (TSR) program(s) installed
  - printer brand and model
  - monitor brand and model

NOTE: If contacting CEAM by mail, fax, or BBS, include responses to the above information in your correspondence.

### Disclaimers

Mention of trade names or use of commercial products does not constitute endorsement or recommendation for use by the United States Environmental Protection Agency.

Execution of the MINTEQA2 model system, and modifications to the DOS system configuration files (i.e., \CONFIG.SYS and \AUTOEXEC.BAT) must be used and/or made at the user's own risk. Neither the U.S. EPA nor the program authors can assume responsibility for model and/or program modification, content, output, interpretation, or usage.

CEAM software products are built using FORTRAN-77, assembler, and operating system interface command languages. The code structure and logic of these products is designed for single-user, single-tasking, non-LAN environment and operating platform for microcomputer installations (i.e., single user on dedicated system).

A user will be on their own if he/she attempts to install a CEAM product on a multi-user, multi-tasking, and/or LAN based system (i.e., Windows, DESQview, any LAN). CEAM cannot provide installation, operation, and/or general user support under any combination of these configurations. Instructions and conditions for proper installation and testing are provided with the product in a READ.ME file. While multiuser/multitasking/LAN installations could work, none of the CEAM products have been thoroughly tested under all possible conditions. CEAM can provide scientific and/or application support for selected products if the user proves that a given product is installed and working correctly.

## APPENDIX D

### EXAMPLE MINTEQA2 FILES

The following example files are included on the distribution diskettes as TEST4.INP and TEST4.LST. The corresponding PRODEFA2 dialogue file, TEST4.HLP, is too lengthy to include here; it can also be found on the distribution diskettes.

#### TEST4.INP

TEST4 - Triple Layer Adsorption model with two adsorbing surfaces.

25.00 MOLAL 0.000  
0 0 1 0 0 0 0 0 1 1 1 0 0

3 2 6  
8.174E+00 129.00 1.200 0.200 81  
4.087E+00 600.00 1.400 0.400 82

330	1.000E-07	-7.00	/H+1
410	1.000E-01	-1.00	/K+1
492	1.000E-01	-1.00	/NO3-1
813	0.000E-01	0.00	/ADS1PSIo
814	0.000E-01	0.00	/ADS1PSIb
815	0.000E-01	0.00	/ADS1PSId
811	1.320E-04	-3.88	/ADS1TYP1
823	0.000E-01	0.00	/ADS2PSIo
824	0.000E-01	0.00	/ADS2PSIb
825	0.000E-01	0.00	/ADS2PSId
821	1.370E-04	-3.86	/ADS2TYP1

3	1		
330	7.0000	0.0000	/H+1
6	6		
813	0.0000	0.0000	/ADS1PSIo
814	0.0000	0.0000	/ADS1PSIb
815	0.0000	0.0000	/ADS1PSId
823	0.0000	0.0000	/ADS2PSIo
824	0.0000	0.0000	/ADS2PSIb
825	0.0000	0.0000	/ADS2PSId

2	8												
8113300	=ISO-	0.0000	-9.3100	0.000	0.000	0.00	0.00	0.00	0.0000				
0.00	3	1.000	811	-1.000	330	-1.000	813	0.000	0	0.000	0	0.000	0
0.000	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0
0	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000
8113301	=ISOH2+	0.0000	7.3300	0.000	0.000	0.00	0.00	0.00	0.0000				
0.00	3	1.000	811	1.000	330	1.000	813	0.000	0	0.000	0	0.000	0
0.000	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0
0	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000
8114920	=ISOH2NO3	0.0000	8.3300	0.000	0.000	0.00	0.00	0.00	0.0000				
0.00	5	1.000	811	1.000	492	1.000	330	1.000	813	-1.000	814	0.000	0
0.000	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0
0	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000
8114100	=ISO	0.0000	-8.3100	0.000	0.000	0.00	0.00	0.00	0.0000				
0.00	5	1.000	811	1.000	410	-1.000	330	-1.000	813	1.000	814	0.000	0
0.000	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0
0	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0	0.000
8213300	=ISO-	0.0000	-6.5200	0.000	0.000	0.00	0.00	0.00	0.0000				

```

0.00 3 1.000 821 -1.000 330 -1.000 823 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8213301 =2SOH2+ 0.0000 7.0100 0.000 0.000 0.00 0.00 0.00 0.000
0.00 3 1.000 821 1.000 330 1.000 823 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8214920 =2SOH2NO3 0.0000 5.3500 0.000 0.000 0.00 0.00 0.00 0.0000
0.00 5 1.000 821 1.000 492 1.000 330 1.000 823 -1.000 824 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8214100 =2SOK 0.0000 -5.3100 0.000 0.000 0.00 0.00 0.00 0.0000
0.00 5 1.000 821 1.000 410 -1.000 330 -1.000 823 1.000 824 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0 0.000 0

```

## TEST4.LST

---

PART 1 of OUTPUT FILE

---

PC MINTEQA2 v3.00 DATE OF CALCULATIONS: 2-AUG-90 TIME: 10:18:59

TEST4 - Triple Layer Adsorption model with two adsorbing surfaces.

-----  
Temperature (Celsius): 25.00  
Units of concentration: MOLAL  
Ionic strength to be computed.  
If specified, total carbonate concentration represents total inorganic carbon.  
Do not automatically terminate if charge imbalance exceeds 30%  
Precipitation is allowed only for those solids specified as ALLOWED  
in the input file (if any).  
The maximum number of iterations is: 40  
The method used to compute activity coefficients is: Davies equation  
Intermediate output file  
Adsorption model: Triple Layer  
Number of adsorbing surfaces: 2  
-----

```

8.174E+00 129.00 1.200 0.200 81
4.087E+00 600.00 1.400 0.400 82
330 1.000E-07 -7.00
410 1.000E-01 -1.00
492 1.000E-01 -1.00
813 0.000E-01 0.00
814 0.000E-01 0.00
815 0.000E-01 0.00
811 1.320E-04 -3.88
823 0.000E-01 0.00
824 0.000E-01 0.00
825 0.000E-01 0.00
821 1.370E-04 -3.86

```

H2O has been inserted as a COMPONENT

```

3 1
330 7.0000 0.0000
6 6
813 0.0000 0.0000
814 0.0000 0.0000
815 0.0000 0.0000
823 0.0000 0.0000
824 0.0000 0.0000
825 0.0000 0.0000
2 8
8113300 =1SO- 0.0000 -9.3100 0.000 0.000 0.00 0.00 0.00 0.0000
0.00 3 1.000 811 -1.000 330 -1.000 813 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0 0.000 0

```

```

0.000 0 0.000 0 0.000 0
8113301=1SOH2+ 0.0000 7.3300 0.000 0.000 0.00 0.00 0.00 0.0000
0.00 3 1.000 811 1.000 330 1.000 813 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0 0.000 0

0.000 0 0.000 0 0.000 0
8114920=1SOH2NO3 0.0000 8.3300 0.000 0.000 0.00 0.00 0.00 0.0000
0.00 5 1.000 811 1.000 492 1.000 330 1.000 813 -1.000 814 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0 0.000 0

0.000 0 0.000 0 0.000 0
8114100=1SOK 0.0000 -8.3100 0.000 0.000 0.00 0.00 0.00 0.0000
0.00 5 1.000 811 1.000 410 -1.000 330 -1.000 813 1.000 814 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0 0.000 0

0.000 0 0.000 0 0.000 0
8213300=2SO- 0.0000 -6.5200 0.000 0.000 0.00 0.00 0.00 0.0000
0.00 3 1.000 821 -1.000 330 -1.000 823 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0 0.000 0

0.000 0 0.000 0 0.000 0
8213301=2SOH2+ 0.0000 7.0100 0.000 0.000 0.00 0.00 0.00 0.0000
0.00 3 1.000 821 1.000 330 1.000 823 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0 0.000 0

0.000 0 0.000 0 0.000 0
8214920=2SOH2NO3 0.0000 5.3500 0.000 0.000 0.00 0.00 0.00 0.0000
0.00 5 1.000 821 1.000 492 1.000 330 1.000 823 -1.000 824 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0 0.000 0

0.000 0 0.000 0 0.000 0
8214100=2SOK 0.0000 -5.3100 0.000 0.000 0.00 0.00 0.00 0.0000
0.00 5 1.000 821 1.000 410 -1.000 330 -1.000 823 1.000 824 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0 0.000 0

0.000 0 0.000 0 0.000 0

```

INPUT DATA BEFORE TYPE MODIFICATIONS

ID	NAME	ACTIVITY GUESS	LOG GUESS	ANAL TOTAL
330	H+1	1.000E-07	-7.000	1.000E-07
410	K+1	1.000E-01	-1.000	1.000E-01
492	NO3-1	1.000E-01	-1.000	1.000E-01
813	ADS1PSIo	1.000E+00	0.000	0.000E-01
814	ADS1PSIb	1.000E+00	0.000	0.000E-01
815	ADS1PSId	1.000E+00	0.000	0.000E-01
811	ADS1TYP1	1.318E-04	-3.880	1.320E-04
823	ADS2PSIo	1.000E+00	0.000	0.000E-01
824	ADS2PSIb	1.000E+00	0.000	0.000E-01
825	ADS2PSId	1.000E+00	0.000	0.000E-01
821	ADS2TYP1	1.380E-04	-3.860	1.370E-04
2	H2O	1.000E+00	0.000	0.000E-01

CHARGE BALANCE: UNSPECIATED

SUM OF CATIONS= 1.000E-01 SUM OF ANIONS = 1.000E-01

PERCENT DIFFERENCE = 5.000E-05 (ANIONS - CATIONS)/(ANIONS + CATIONS)

PARAMETERS OF THE COMPONENT MOST OUT OF BALANCE:

ITER	NAME	TOTAL MOL	DIFF FXN	LOG ACTVTY
0	ADS1TYP1	1.320E-04	5.648E-04	-3.88000
1	ADS2PSIo	-5.374E-05	-7.267E-05	0.02994
2	ADS1PSId	0.000E-01	-5.748E-04	-0.99717
3	ADS1PSId	-9.265E-06	-2.861E-04	-0.58694
4	ADS1PSId	-2.080E-05	-1.093E-04	-0.27410
5	ADS1PSId	-2.963E-05	-2.211E-05	-0.11052
6	ADS1PSId	-3.271E-05	-1.056E-06	-0.07223

ID	NAME	ANAL MOL	CALC MOL	ACTIVITY	LOG ACTVTY	GAMMA	NEW LOGK	DIFF FXN
821	ADS2TYP1	1.370E-04	1.670E-05	1.670E-05	-4.77721	1.000000	0.0000	-2.711E-20
410	K+1	1.000E-01	9.994E-02	7.750E-02	-1.11071	0.775441	0.1105	-1.037E-10
492	NO3-1	1.000E-01	9.995E-02	7.750E-02	-1.11069	0.775441	0.1105	-8.512E-11
813	ADS1PSIo	8.752E-05	3.650E-01	3.650E-01	-0.43771	1.000000	0.0000	8.754E-11
814	ADS1PSIb	-5.462E-05	4.733E-01	4.733E-01	-0.32489	1.000000	0.0000	3.957E-10
815	ADS1PSId	-3.290E-05	8.504E-01	8.504E-01	-0.07040	1.000000	0.0000	-2.370E-09
811	ADS1TYP1	1.320E-04	4.290E-05	4.290E-05	-4.36750	1.000000	0.0000	1.712E-11
823	ADS2PSIo	-7.826E-05	1.228E+00	1.228E+00	0.08911	1.000000	0.0000	0.000E-01
824	ADS2PSIb	5.817E-05	1.127E+00	1.127E+00	0.05193	1.000000	0.0000	1.355E-20
825	ADS2PSId	2.010E-05	1.044E+00	1.044E+00	0.01851	1.000000	0.0000	-1.317E-13
2	H2O	0.000E-01	-1.291E-07	9.966E-01	-0.00148	1.000000	0.0015	0.000E-01
330	H+1	1.000E-07	1.290E-07	1.000E-07	-7.00000	0.775441	0.1105	0.000E-01

Type I - COMPONENTS AS SPECIES IN SOLUTION

ID	NAME	CALC MOL	ACTIVITY	LOG ACTVTY	GAMMA	NEW LOGK	DH
330	H+1	1.290E-07	0.0000001	-7.00000	0.775441	0.110	0.000
410	K+1	9.994E-02	0.0774988	-1.11071	0.775441	0.110	0.000
492	NO3-1	9.995E-02	0.0775015	-1.11069	0.775441	0.110	0.000
811	ADS1TYP1	4.290E-05	0.0000429	-4.36750	1.000000	0.000	0.000
821	ADS2TYP1	1.670E-05	0.0000167	-4.77721	1.000000	0.000	0.000

Type II - OTHER SPECIES IN SOLUTION OR ADSORBED

ID	NAME	CALC MOL	ACTIVITY	LOG ACTVTY	GAMMA	NEW LOGK	DH
8214100	=2SOK	5.820E-05	0.0000582	-4.23510	1.000000	-5.310	0.000
3300020	OH-	1.291E-07	0.0000001	-6.99948	0.775441	-13.888	13.345
8113300	=ISO-	5.757E-07	0.0000006	-6.23979	1.000000	-9.310	0.000
8113301	=ISOH2+	3.348E-05	0.0000335	-4.47520	1.000000	7.330	0.000
8114920	=ISOH2NO3	5.483E-05	0.0000548	-4.26100	1.000000	8.330	0.000
8114100	=ISOK	2.112E-07	0.0000002	-6.67538	1.000000	-8.310	0.000
8213300	=2SO-	4.108E-05	0.0000411	-4.38633	1.000000	-6.520	0.000
8213301	=2SOH2+	2.098E-05	0.0000210	-4.67810	1.000000	7.010	0.000
8214920	=2SOH2NO3	3.157E-08	0.0000000	-7.50072	1.000000	5.350	0.000

Type III - SPECIES OF FIXED ACTIVITY THAT DEFINE EQUILIBRIUM CONDITIONS

ID	NAME	CALC MOL	LOG MOL	NEW LOGK	DH
2	H2O	-1.291E-07	-6.889	0.001	0.000
330	H+1	-9.157E-06	-5.038	7.000	0.000

Type VI - EXCLUDED SPECIES (not included in mole balance)

ID	NAME	CALC MOL	LOG MOL	NEW LOGK	DH
823	ADS2PSIo	1.228E+00	0.089	0.000	0.000
815	ADS1PSId	8.504E-01	-0.070	0.000	0.000
814	ADS1PSIb	4.733E-01	-0.325	0.000	0.000
813	ADS1PSIo	3.650E-01	-0.438	0.000	0.000
825	ADS2PSId	1.044E+00	0.019	0.000	0.000
824	ADS2PSIb	1.127E+00	0.052	0.000	0.000



## PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG TYPE I and TYPE II (dissolved and adsorbed) species

ADS2TYP1	12.2	PERCENT BOUND IN SPECIES # 821	ADS2TYP1
42.5		PERCENT BOUND IN SPECIES #8214100	=2SOK
30.0		PERCENT BOUND IN SPECIES #8213300	=2SO-
15.3		PERCENT BOUND IN SPECIES #8213301	=2SOH2+
K+1	99.9	PERCENT BOUND IN SPECIES # 410	K+1
NO3-1	99.9	PERCENT BOUND IN SPECIES # 492	NO3-1
ADS1PSIo	38.3	PERCENT BOUND IN SPECIES #8113301	=1SOH2+
62.6		PERCENT BOUND IN SPECIES #8114920	=1SOH2NO3
ADS1PSIb	100.4	PERCENT BOUND IN SPECIES #8114920	=1SOH2NO3
ADS1PSId			
ADS1TYP1	32.5	PERCENT BOUND IN SPECIES # 811	ADS1TYP1
25.4		PERCENT BOUND IN SPECIES #8113301	=1SOH2+
41.5		PERCENT BOUND IN SPECIES #8114920	=1SOH2NO3
ADS2PSIo	74.4	PERCENT BOUND IN SPECIES #8214100	=2SOK
52.5		PERCENT BOUND IN SPECIES #8213300	=2SO-
ADS2PSIb	100.1	PERCENT BOUND IN SPECIES #8214100	=2SOK
ADS2PSId			
H2O	100.0	PERCENT BOUND IN SPECIES #3300020	OH-
H+1	1.4	PERCENT BOUND IN SPECIES # 330	H+1
361.7		PERCENT BOUND IN SPECIES #8113301	=1SOH2+
592.3		PERCENT BOUND IN SPECIES #8114920	=1SOH2NO3
226.7		PERCENT BOUND IN SPECIES #8213301	=2SOH2+

---

PART 5 of OUTPUT FILE

---

PC MINTEQA2 v3.00 DATE OF CALCULATIONS: 2-AUG-90 TIME: 10:19:16

----- EQUILIBRATED MASS DISTRIBUTION -----

IDX	NAME	DISSOLVED		SORBED		PRECIPITATED	
		MOL/KG	PERCENT	MOL/KG	PERCENT	MOL/KG	PERCENT
410	K+1	9.994E-02	99.9	5.841E-05	0.1	0.000E-01	0.0
492	NO3-1	9.995E-02	99.9	5.486E-05	0.1	0.000E-01	0.0
2	H2O	1.291E-07	100.0	0.000E-01	0.0	0.000E-01	0.0
330	H+1	-1.548E-10	0.0	9.257E-06	100.0	0.000E-01	0.0

CHARGE BALANCE: SPECIATED

SUM OF CATIONS = 9.994E-02 SUM OF ANIONS 9.995E-02

PERCENT DIFFERENCE = 1.776E-03 (ANIONS - CATIONS)/(ANIONS + CATIONS)

EQUILIBRIUM IONIC STRENGTH (m) = 9.994E-02

EQUILIBRIUM pH = 7.000

\*\*\*\*\* TRIPLE LAYER ADSORPTION MODEL \*\*\*\*\*

\*\*\*\* Parameters For Adsorbent Number 1 \*\*\*\*

Electrostatic Variables: psi0 = 0.025893 sig0 = 0.008009  
psib = 0.019219 sigb = -0.004998  
psid = 0.004165 sigd = -0.003011

Adsorbent Concentration (g/l): 8.174  
Specific Surface Area (sq. meters/g): 129.00

\*\*\*\* Parameters For Adsorbent Number 2 \*\*\*\*

Electrostatic Variables: psi0 = -0.005272 sig0 = -0.003079  
psib = -0.003072 sigb = 0.002289  
psid = -0.001095 sigd = 0.000791

Adsorbent Concentration (g/l): 4.087  
Specific Surface Area (sq. meters/g): 600.00

DATE ID NUMBER: 900802  
TIME ID NUMBER: 10191682

Saturation indices and stoichiometry of all minerals

ID #	NAME	Sat. Index	Stoichiometry (in parentheses) of each component
------	------	------------	--