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**GMIN: A Computerized
Chemical Equilibrium Model
Using a Constrained Minimization
of the Gibbs Free Energy**

A. R. Felmy

April 1990

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GMIN: A COMPUTERIZED CHEMICAL
EQUILIBRIUM MODEL USING A
CONSTRAINED MINIMIZATION OF
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Richland, Washington 99352

SUMMARY

This document is a user's manual and technical reference for the computerized chemical equilibrium model GMIN. GMIN calculates the chemical composition of systems composed of pure solid phases, solid-solution phases, gas phases, adsorbed phases, and the aqueous phase. In the aqueous phase model, the excess solution free energy is modeled by using the equations developed by Pitzer and his coworkers, which are valid to high ionic strengths. The Davies equation can also be used. Activity coefficients for nonideal solid-solution phases are calculated using parameters of a polynomial expansion in mole fraction of the excess free energy of mixing. The free energy of adsorbed phase species is described by the triple-layer site-binding model.

The mathematical algorithm incorporated into GMIN is based upon a constrained minimization of the Gibbs free energy. This algorithm is numerically stable and reliably converges to a free energy minimum.

The data base for GMIN contains all standard chemical potentials and Pitzer ion-interaction parameters necessary to model the system Na-K-Ca-Mg-H-Cl-SO₄-CO₂-B(OH)₄-H₂O at 25°C.

Version 1 of GMIN is available for IBM[®](a)-compatible personal computers. To run GMIN requires 512K of RAM, a hard disk, and a math coprocessor. Version 1 is limited to applications at 25°C.

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INTRODUCTION

Over the past decade or so, several computerized chemical equilibrium models have been developed to support geochemical field and laboratory studies. The most notable of these include EQ3/EQ6 (Wolery 1979), PHREEQE (Parkhurst et al. 1980), and MINTEQ (Felmy et al. 1984). These models solve the chemical equilibrium problem using mathematical algorithms based upon the "mass-action approach" (Van Zeggeren and Storey 1970). In the mass-action approach, the reaction equilibrium condition, $\sum_i \mu_i = 0$, is always maintained and convergence to the final solution is achieved by relaxing the mass-balance constraints.

The mass-action approach for solving the chemical equilibrium problem has proven successful when applied to problems that are readily defined in terms of equilibrium constants. However, it can be somewhat cumbersome to apply to problems that are not readily formulated in terms of equilibrium constants. In addition, convergence to the final solution of the chemical equilibrium problem may in fact depend on the user's choice of starting estimates for the unknown activities or mole numbers.

Because of these limitations of the conventional mass-action-based models, researchers at the University of California, San Diego (led by John H. Weare), began exploring the development of alternate methods for the solution of the chemical equilibrium problem. These efforts revealed that alternate methods, in particular constrained minimization of the Gibbs free energy, were easier to adapt for solving a wider range of possible chemical equilibrium problems. In addition, when properly implemented, some of these methods were virtually certain to converge. These findings led researchers to develop an algorithm for solving the chemical equilibrium problem that is based on a constrained minimization of the Gibbs free energy. This algorithm is numerically stable, reliably converges to the solution of the chemical equilibrium problem, and can be easily adapted for treating a wide variety of problems. Harvie et al. (1987) and Greenberg et al. (1985) have given complete details of the mathematical algorithm. Their mathematical development forms the basis for GMIN.

This report begins by describing the specific free-energy models incorporated into GMIN. These free-energy models include the Pitzer equations and the Davies equation for the excess solution free energy. Free-energy models for solid-solution phases and adsorbed phase species are also described. The final section describes how to install and run GMIN on IBM and IBM-compatible personal computers, describes how to use the model, and presents a detailed description of the input file.

Appendix A presents a mathematical description of the free-energy minimization approach and details the advantages of this approach over the more conventional mass-action approach. Appendix B describes the thermodynamic data base, which includes Pitzer ion-interaction parameters for the system Na-K-Ca-Mg-H-Cl-SO₄-CO₂-B(OH)₄-H₂O. Appendix C gives the output from an example test case. Appendix D gives a detailed description of the equations required for including the triple-layer site-binding adsorption model in free-energy minimization approaches like GMIN.

THERMODYNAMIC MODELS FOR THE CHEMICAL POTENTIALS

One of the major advantages of using a free-energy minimization approach is its ability to solve a variety of chemical equilibrium problems. Widely different models for the free energy are easily accommodated, because the modeling approach requires specifying only the chemical potentials and the derivatives of the chemical potentials. The general equations defining the chemical potentials for species in different phases considered by GMIN are given in Table 1.

TABLE 1. General Equations for Different Phase Species

Aqueous Phase Species

$$\text{Solvent (H}_2\text{O)} \quad \mu_i/RT = \mu_i^0/RT - \frac{RTW}{1000} \left(\frac{\sum_{i=1}^{ns} m_i}{\sum_{i=1}^{ns} m_i} \right) \phi$$

$$\text{Solute Species} \quad \mu_i/RT = \mu_i^0/RT + \ln m_i + \ln \gamma_i$$

Pure Solid Phase Species

$$\mu_i/RT = \mu_i^0/RT$$

Solid-Solution Species

$$\mu_i/RT = \mu_i^0/RT + \ln x_i + \ln \gamma_i$$

Adsorbed Phase Species

$$\mu_i/RT = \mu_i^0/RT + \ln \underline{M}_i + Z_i F \psi$$

Gas Phase Species

$$\mu_i/RT = \mu_i^0/RT + \ln f_i$$

In all of the equations in Table 1,

- μ = chemical potential
- μ_i^0 = standard chemical potential
- ϕ = osmotic coefficient
- W = molecular weight of water (18.016)
- m_i = molality of species i
- $\bar{M}_i$ = moles of species i adsorbed per liter of solution
- γ_i = activity coefficient of species i
- ψ = electrostatic potential
- f_i = fugacity of species i

The explicit models used to define the functions γ , ϕ , f , and ψ are described in the remainder of this section.

ACTIVITY COEFFICIENTS FOR AQUEOUS SPECIES

GMIN contains two formulations for activity coefficients for aqueous species. The first model is based on work by Pitzer (1979) and coworkers. In this model, the activity coefficients are expressed in a virial-type expansion of the form

$$\ln \gamma_i = \ln \gamma_i^{\text{DH}} + \sum_j B_{ij}(I)m_j + \sum_j \sum_k C_{ijk} m_j m_k + \dots \quad (1)$$

where $\ln \gamma_i^{\text{DH}}$ is a modified Debye-Hückel activity coefficient, and thus a universal function of ionic strength. The variables $B_{ij}(I)$ and C_{ijk} are specific for each ion interaction. Pitzer (1973) has given explicit phenomenological expressions for the ionic-strength dependence of B . The form of B is different for like, unlike, and neutral ion interactions. The third virial coefficient, C , is taken to be independent of ionic strength. A detailed description of the exact form of Equation (1) has been given by Felmy and Weare (1986).

The necessary chemical potential derivatives with respect to mole numbers, Hessian matrix elements, have been described in complete detail by Felmy (1988, Section 2.10, Appendix A).

The second activity coefficient formulation was developed by Davies (1962). The formulation is based primarily on empirical observations of the mean activity coefficients of electrolytes, principally 1:1 electrolytes. Because the model is principally an empirical formulation, its effectiveness will vary with the type of ionic medium. For example, given that the formulations are based principally upon data for 1:1 electrolytes, the model will be accurate to higher ionic strengths for 1:1 electrolytes than for 2:1 electrolytes. In the case of multicomponent solutions, the Davies equation should not be applied to aqueous systems with ionic strengths greater than 0.05 m.

The activity coefficient formulation of Davies is

$$\ln \gamma_i = - A \ln(10) Z_i^2 \left(\frac{I^{0.5}}{1+I^{0.5}} - 0.3 I \right) \quad (2)$$

The Hessian matrix elements are correspondingly simple. In addition to the usual ideal term, we have

$$\left(\frac{\partial \ln \gamma_i}{\partial m_j} \right)_{\bar{m}} = - A \ln(10) \frac{Z_i^2 Z_j^2}{2} \left(\frac{1}{2 I^{0.5} (1+I^{0.5})^2} - 0.3 \right) \quad (3)$$

where $\bar{m}$ means all other molalities are held constant. Equation (3) completely defines the Hessian matrix. A completely defined Hessian matrix significantly improves GMIN's ability to converge. This ability to converge gives GMIN a significant advantage over mass-action models, such as MINTEQ, in which the activity coefficient derivatives are set to zero.

ACTIVITY COEFFICIENTS FOR SOLID SOLUTIONS

GMIN has the capability for handling both multicomponent ideal solid solutions and binary non-ideal solid solutions. The activity coefficients for binary non-ideal solid solutions are expressed as

$$\ln \gamma_A = x_B^2 \left[A_0 + A_1(3x_A - x_B) \right] \quad (4)$$

and

$$\ln \gamma_B = x_A^2 \left[A_0 - A_1(3x_B - x_A) \right] \quad (5)$$

where the subscripts A and B represent the first and second components of the binary solid solution and A_0 and A_1 are constants. These expressions have been described by Plummer and Busenberg (1987) and are based upon a polynomial expansion in mole fraction of the excess free energy of mixing (Guggenheim 1967). These expressions should be treated solely as empirical. The first non-ideal term, A_0 , yields a symmetric free energy of mixing with respect to mole fraction; the second term, A_1 , yields an asymmetric free energy of mixing.

The Hessian elements are then

$$\left(\frac{\partial \ln \gamma_A}{\partial n_A} \right) = \frac{-2x_B^2}{n_T} A_0 + \frac{6x_B A_1}{n_T} \left[2x_A^2 - 3x_A + 1 \right] \quad (6)$$

where n_T is $n_A + n_B$. All other Hessian elements are calculated from either the Gibbs-Duhem relation or the appropriate Maxwell equation.

OSMOTIC COEFFICIENTS

When the Pitzer ion-interaction model is used to model the activity coefficients of aqueous species, the osmotic coefficient is completely defined by the derivative of the excess Gibbs energy with respect to the number of moles of water. The complete expression has been detailed by Felmy and Weare (1986). When the Davies equation is used to model the activity coefficients, the osmotic coefficient is set equal to 1, i.e., an ideal solvent is assumed.

FUGACITIES

GMIN treats gas phases in the same manner as pure solid phases, except that the standard chemical potential of the gas phase is modified to reflect the fugacity of the gas phase, i.e.,

$$\mu_i^0/RT = \mu_i^0(f=1)/RT + \ln f_i \quad (7)$$

In this manner, GMIN either includes gas phases at a fixed fugacity or effectively sets an upper limit on the fugacity of the gas phase species. In the latter case, if the calculated gas phase fugacity should exceed the fugacity specified by Equation (7), then GMIN will impose the fugacity constraint and effectively "precipitate" the gas phase.

ELECTROSTATIC POTENTIAL

In the case of adsorbed species, the electrostatic potential at the solid surface must be included in the chemical potential relation. This inclusion results in the definition of an electrochemical potential, $\bar{\mu}$. All other aspects of the free-energy minimization problem are the same. The relevant equations are detailed in Appendix D.

MODEL USE

GMIN is relatively easy to use. The only requirement is preparation of the input file gmin.dat. This section gives instructions for installation of GMIN on personal computers and a complete description of the gmin.dat file. Examples of various input files are also given. When preparing gmin.dat, refer to a copy of file comp.dat (Appendix B), which contains all of the species identification numbers.

MODEL INSTALLATION

GMIN is available for use on IBM®(a) and IBM-compatible personal computers. A hard disk, an 8087/80287 math coprocessor, and 512K of RAM are required. To install GMIN on your hard disk, first make a subdirectory GMIN:

```
c:> md GMIN
```

and then change to this subdirectory:

```
c:> cd GMIN
```

Now copy all of the files from the GMIN diskette to this subdirectory. Assuming your diskette is in drive a:, type

```
c:\GMIN> copy a:*.*
```

Begin by running the model test case stored in the model input file, gmin.dat. To run the test case, simply type

```
c:\GMIN> gmin > gmin.out
```

(a) IBM® is a trademark of International Business Machines Corporation, Boca Raton, Florida.

The model output will now be stored in file gmin.out and can be compared to the test case output found in Appendix B.

To run the model for a specific set of conditions, you must modify the model input file gmin.dat using a text editor. Instructions for preparing the gmin.dat file follow.

SECTION 1

The first section of the input file gmin.dat consists of the first three lines of the file.

Line 1 (format 1X,4I5) contains information on four GMIN options. Option 1, idebgl, is a print option for debugging the code. This value should be set to 0 unless specific information on QR factorization, Hessian calculations, or other information on the progress of the iteration sequence is desired. Option 2, isopt, is the activity coefficient option. A value of 0 implements the Pitzer ion interaction model. A value of 1 implements the Davies equation. Option 3, idopt, is an ideal option. If this value is set to 1, the free-energy model is assumed to be ideal and all activity coefficients are set equal to 1. This can be useful for constant ionic media calculations. Generally this parameter should be set to 0. Option 4, iphopt, is a print option. If set to 0, calculated species concentrations and mineral saturation indices are output only at the end of the calculations. A value of 1 for iphopt causes species information to be printed every time a new species or phase is added to the phase assemblage. This option is useful for obtaining mineral saturation indices at intermediate stages of the calculation.

Line 2 [format I3,5(1X,F12.4)] allows input of necessary adsorption information. The first input field, I3, is the adsorption option. A value of 0 prevents adsorption calculations, a value of 1 allows adsorption calculations. The next five fields are for the specific surface area (m^2/g), concentration of solid (g/L), volume of solution (L), inner-layer capacitance (F/m^2), and outer-layer capacitance (F/m^2).

The third line of input [format 2(F7.3,1X)] is for input of the pH and a fixed partial pressure of $\text{CO}_2(\text{g})$. If a pH value is entered, then species

101000 (a fictitious H^+ solid) must be included later, in the solid-phase input section, and must be assigned a mole number (usually 10 moles). To fix the partial pressure of $CO_2(g)$, include the logarithm of the partial pressure in the second input field and include species 100060 [$CO_2(g)$] in the solid-phase input section with an assigned mole number (usually 10 moles).

SECTION 2 (AQUEOUS AND ADSORBED SPECIES)

The second section of input, which begins on line 4, is for the designation of aqueous and adsorbed species (format I6,F15.3). The first format field is for the species identification (ID) number. The species ID numbers are in file comp.dat. The second field is for the starting number of moles (not the molality) of that species. If you wish to work in the molality scale, enter 55.508 for the mole number of water. Every species entered must be assigned a finite mole number. If only an elemental total composition is known and several species containing that element are entered in this section, assign one species the total moles and give all other species containing that element very small, but not zero, initial mole numbers. GMIN will then partition the total mass according to the chemical equilibrium constraints.

Two points must be made: 1) Species 101080 (water) must be the first species entered, and 2) GMIN will consider only the species you designate.

Terminate this section by entering a species ID number of 0 in the first format field.

SECTION 3 (SOLIDS, GASES, SOLID-SOLUTION COMPONENTS)

This section (format I6,F15.3) is similar to the aqueous species input section, with solid phases, gas phases, and components of solid solutions being input. If a phase is present in the system initially, enter the starting mole number. Again, GMIN will consider only the phases you designate, so you must enter all species that you wish to consider, even if they start with very small mole numbers.

For solid-solution components, include ID numbers and mole numbers for each end-member component in this section.

This section is terminated by a -1 in the first format field.

SECTION 4 (INFORMATION FOR SOLID SOLUTIONS)

Each solid-solution phase requires two lines of input. The first line [format I6,A12,I2,5(1X,I2)] contains an ID number for the solid solution (you can assign any value between 200000 and 299999), the solid solution name (you can enter any 12-character name), the number of end-member components, and then the species number (not the ID number) of each end-member component. The species number is the sequential number representing the order in which the species are entered in gmin.dat. Species 101080 (water) is always species number 1. Count all species including H₂O, aqueous species, adsorbed species, solid phases, and components of solid solutions.

This section is ended with a -1 in the first format field.

The user is cautioned that GMIN has not been made a particularly user-friendly code. GMIN will detect errors in species ID numbers and in counting the total number of allowed species. However, the code will not automatically detect all errors in preparing gmin.dat. Therefore care should be taken to avoid errors.

Table 2 presents the input file, gmin.dat, for the test case output presented in Appendix B. Table 3 presents an example of what the input file might be for a problem that includes a fixed pH, fixed P_{CO_2} , and addition of a non-ideal solid solution.

TABLE 2. The Input File gmin.dat for the Test Case. The first three lines are for choices of options, adsorption information, and fixed P_{CO_2} or pH. In later lines, the first column contains species ID numbers and the second column starting mole numbers.

```

      0      0      0      0
0
0
001080      55.5080000
011000      1.047201040
019000          0.02653
020000          .0001759
012000          .0001792
001000          .000000001
012080          .000000001
020051          .000000001
012051          .000000001
000170          .768440236
000160          .13500
000161          .000000001
000080          .000000001
000061          .000001001
000060          .000000001
000051          0.03600
000052          .000000001
000053          .000000001
000000
100060
120160
111160
120170
120060
119160
112170
111161
112080
111060
120061
111170
-1
-1

```

TABLE 3. Input Data File for a Case Including Solid Solutions, Fixed pH, and Fixed P_{CO_2} . pH and P_{CO_2} are fixed on line 3. Information on the solid solutions included follows the -1 on line 18.

```

0
0      8.0      -3.5
001080  55.5080000
011000  1.000000000
020000  .0010000000
012000  .0200000000
001000  .0000000001
000060  .0210000000
000061  .0000100000
000170  1.000000000
000000
120061  0.0000000000
112061  0.0000000000
101000  10.000000000
100060  10.000000000
-1
212201Ca-Mg-CO3 ss 2 9 10
      3.425      -0.000
-1

```


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APPENDIX A

THE FREE-ENERGY MINIMIZATION APPROACH

APPENDIX A

THE FREE-ENERGY MINIMIZATION APPROACH

This appendix gives only an outline of the free-energy minimization approach used in GMIN. The reader is referred to Van Zeggeren and Storey (1970) for a general introduction to free-energy minimization methods and to Harvie et al. (1987) and Greenberg et al. (1985) for more complete details of the algorithm. Advantages of the free-energy minimization approach over the conventional mass-action approach are outlined.

Both free-energy minimization approaches and mass-action approaches deal with the same basic mathematical constraints and therefore must obtain the same final solution. However, the two approaches deal with the problem entirely differently. In the mass-action approach, chemical equilibrium constraints are always maintained and mass-balance constraints are relaxed. In the free-energy minimization approach, mass-balance constraints are always maintained and chemical equilibrium constraints are relaxed. In the mass-action approach, convergence is determined by checking that the mass-balance constraints are satisfied. In the free-energy minimization approach, convergence is determined by checking the reaction equilibrium condition, i.e., by checking that $\sum \nu_i \mu_i = 0$, where ν_i is the stoichiometric coefficient of reacting species i .

DEFINING THE PROBLEM

The free-energy minimization problem in GMIN is formulated as

$$\text{minimize } G = \sum_{j=1}^{ns} \mu_j n_j \quad (\text{A.1})$$

subject to the mass- and charge-balance constraints

$$\sum_{j=1}^{ns} a_{ji} n_j = b_i, \quad i=1, m_c \quad (A.1a)$$

$$\sum_{j=1}^{nas} z_j n_j = 0 \quad (A.1b)$$

$$n_j \geq 0, \quad \text{for all species } j \quad (A.1c)$$

where G = the Gibbs free energy

ns = total number of chemical species

nas = number of aqueous species

μ_j = chemical potential of species j

n_j = mole number of species j

b_i = total number of moles of element i

m_c = number of linearly independent mass-balance constraints

a_{ji} = number of moles of component i in species j

z_j = charge on species j

At this point, it is also convenient to define a species-constraint matrix D . Species constraints are added to prevent species from reacting. The number of species constraints is designated by $nspcon$. The D matrix is therefore an $(nspcon \times ns)$ matrix, the value of whose elements are either one (when species are constrained) or zero.

In GMIN the first step in solving Equation (A.1) is to augment the mass-balance coefficient matrix a defined in Equation (A.1a) with the z vector defined in Equation (A.1b), forming the system of constraint equations

$$\sum_{j=1}^{ns} A_{ji} = b_i, \quad i=0, \text{irank} \quad (\text{A.2})$$

where $A_{j0} = z_j$

$$b_0 = 0$$

irank = number of linearly independent mass- and charge-balance constraints

The variable irank is determined by a QR factorization (analogous to a Gram-Schmidt factorization; Strang 1980) of the augmented coefficient matrix A defined in Equation (A.2). In this factorization, the orthonormal (ns x ns) Q matrix can be partitioned into two submatrices, $Q_1(\text{irank}, ns)$ and $Q_3(nq3, ns)$, where nq3 is the number of independent reaction directions (i.e., ns - irank). Where species constraints are also present (i.e., the D matrix is nonzero), the A matrix is augmented with the species-constraint matrix D. The QR factorization of the augmented (A|D) matrix yields a Q matrix, which can be partitioned into three submatrices, $Q_1(\text{irank}, ns)$, $Q_2(nspcon, ns)$, and $Q_3(nq3, ns)$, where nq3 is now equal to (ns - irank - nspcon). Use of the QR factorization allows the model to determine optimum reaction directions during the calculations. This means that, as species are added or deleted from consideration, new stable reaction directions are automatically determined by the model. There is no need to designate basis species (which would impose reaction directions). Not designating basis species prevents the generation of poor reaction directions that can occur with mass-action models when the unknown activities of basis species become extremely small. The use of QR factorization is one of the key reasons for the success of GMIN because it allows reaction directions to be automatically redetermined. The actual QR factorization is done using routines obtained from the LINPACK statistical package (Dongarra et al. 1979).

A complete description of the properties of the Q_1 , Q_2 , and Q_3 matrices has been given by Harvie et al. (1987). In GMIN, the Q_1 matrix is not used, the Q_2 matrix is used for calculating the phase multipliers or saturation indices, and the Q_3 matrix contains the permissible reaction directions, i.e., the directions that do not violate mass-balance, charge-balance, or

species constraints. A simple example of the elements of the Q_3 matrix is given in Table A.1 for a problem involving only $H_2O(aq)$, H^+ , and OH^- . In this problem, there is only one possible reaction direction so that Q_3 matrix is reduced to a vector. The elements of the Q_3 matrix are all less than 1 because the Q matrix as a whole is orthonormal. The reaction equilibrium condition is given by the matrix equation $Q_3^T \vec{\mu} = 0$ (i.e., $0.5774 \mu_{H^+} + 0.5774 \mu_{OH^-} - 0.5774 \mu_{H_2O} = 0$). This equation is used to check for convergence in GMIN.

THE MINIMIZATION ALGORITHM

To solve the chemical equilibrium problem, we begin by defining the step direction vector $\vec{p}$ using the equation

$$n_j^{(k+1)} = n_j^{(k)} + \alpha \vec{p}_j^{(k)} \quad j=1,ns \quad (A.3)$$

where $n_j^{(k+1)}$ = mole number of species j at the $k+1$ iteration

$n_j^{(k)}$ = mole number of species j at iteration k

α = underrelaxation parameter ($0 \leq \alpha \leq 1$)

TABLE A.1. Elements of the Q_3 Matrix for the Pure H_2O Problem

<u>Species</u>	<u>Q3 Elements</u>
H_2O	-0.5774
H^+	0.5774
OH^-	0.5774

Newton's method is then used to solve for the step direction vector $\vec{p}$. To use Newton's method, we begin with the second-order approximation to the free energy given by

$$G = G^{(k)} + \sum_{j=1}^{ns} \mu_j^{(k)} p_j^{(k)} + \frac{1}{2} \sum_{j=1}^{ns} \sum_{i=1}^{ns} p_j^{(k)} H_{ji}^{(k)} p_i^{(k)} \quad (A.4)$$

where the Hessian matrix H is defined by

$$H_{ij}^{(k)} = \frac{\partial^2 G}{\partial n_i^{(k)} \partial n_j^{(k)}} \quad (A.5)$$

GMIN contains a completely defined Hessian. A completely defined Hessian can significantly enhance the model's ability to converge over that of mass-action models in which the Hessian, or jacobian in mass-action models, is assumed to be ideal.

Differentiating Equation (A.4) with respect to the elements of $\vec{p}$ yields the first-order approximation to the chemical potentials

$$\vec{\mu}^{(k+1)}(\text{first order}) = \mu^{(k)} + H^{(k)} \vec{p}^{(k)} \quad (A.6)$$

Operating on Equation (A.6) with Q_3^T then yields

$$Q_3^T H^{(k)} \vec{p}^{(k)} + Q_3^T \mu^{(k)} = 0 \quad (A.7)$$

To solve Equation (A.7) we expand the columns of Q_3

$$\vec{p}^{(k)} = Q_3 \vec{\delta}^{(k)} \quad (A.8)$$

and substituting Equation (A.8) into Equation (A.7) yields the matrix equation

$$Q_3^T H(k) Q_3 \delta_3(k) = -Q_3^T \mu(k) \quad (A.9)$$

The projected Hessian, $Q_3^T H Q_3$, is a square matrix, and the vector $-Q_3^T \mu$ is referred to as the projected gradient. Equation (A.9) is then solved for the unknown vector δ_3 , and the step direction vector $\vec{p}$ is calculated from Equation (A.8).

The calculation of δ_3 in GMIN involves a Cholesky factorization of the positive definite Projected-Hessian matrix (Dongarra et al. 1979). The procedure of Gill and Murray (1974) ensures that the projected Hessian is positive definite. This is an important step in GMIN. If the projected Hessian were not positive definite, the free energy would be nonconvex. A nonconvex free energy makes the chemical equilibrium problem unsolvable because, under such conditions, the free energy has a maximum rather than a minimum. The inability to detect and, if possible, correct a nonconvex free energy can be a major reason for nonconvergence in mass-action chemical equilibrium models.

SPECIES AT LOW CONCENTRATION (AND PHASE REMOVAL)

In the solution of the chemical equilibrium problem, an initial phase assemblage is specified and initial estimates of the species mole numbers are provided. In the process of solving for a local minimum, the mole numbers of some species may decrease to very low values. In such cases, the projected Hessian may become poorly conditioned. When this happens, a special step is taken, whereby the mass of the low-concentration species is set to a pre-determined lower limit. This is done by rearranging Equation (A.3),

$$\alpha = (sp_{ll} - n_j)/p_j \quad (A.10)$$

where sp_{ll} is the species lower limit, set to 5×10^{-14} in GMIN. The calculated value of α is then used in the Newton step, Equation (A.3), instead

of the default value of 1.0. The species is then prevented from further reaction by augmenting the D matrix with a species constraint. The new (A|D) matrix is then refactored and new reaction directions are determined.

This procedure ensures that reaction directions are always optimum. It is equivalent to an automatic transformation of basis in mass-action models. The procedure also automatically removes phases from the phase assemblage while determining a local minimum, rather than retaining the solid phases in the calculations until convergence is reached (Felmy et al. 1984) and then removing those phases that show a negative mass and solving again for a new minimum.

PHASE ADDITION

Once a local minimum is reached, the addition of other phases, such as pure solid phases, gas phases, or solid-solution phases can lower the free energy of the system. This fact leads to the calculation of phase multipliers (Harvie et al. 1987; Greenberg et al. 1985). The phase multiplier is defined by

$$\omega_j = \mu_j - \mu_j(\text{soln}) \quad (\text{A.11})$$

where ω_j is the phase multiplier for species j and $\mu_j(\text{soln})$ is the calculated chemical potential of the species in the aqueous solution phase. As one example, $\mu_j(\text{soln})$ for the species halite would be equal to $\mu_{\text{Na}^+} + \mu_{\text{Cl}^-}$. From this definition, we can see that if the phase multiplier is negative [i.e., $\mu_j(\text{soln}) > \mu_j$], addition of the species will lower the free energy. Phase multipliers are calculated by the matrix equation

$$Q_2^T D \vec{\omega} = Q_2^T \vec{\mu} \quad (\text{A.12})$$

[see Harvie et al. (1987) for details]. The $\vec{\omega}$ vector is then calculated from Equation (A.12).

Once the phase multipliers are determined, the species with the lowest phase multiplier is brought into the phase assemblage by removing a species constraint from the D matrix and updating the Q matrix, using the procedure given by Harvie et al. (1987, appendix).

The phase multiplier is directly related to the saturation index (defined as the logarithm of the ratio of ion activity product over the reaction equilibrium constant) commonly used in mass-action models by the relation

$$(SI)_j = -\omega_j / \ln(10) \quad (A.13)$$

where $(SI)_j$ is the saturation index for species or phase j.

SOLID SOLUTION ADDITION

Addition of a solid-solution phase is more complicated than addition of a pure phase because what must be determined is not just which solid-solution phase should be brought into the phase assemblage but also what initial mole fraction each species in the solid-solution phase should have. To determine which solid-solution phase to bring in and what the starting mole fractions should be requires solving a sub-minimization problem. This problem involves minimizing the sum of the differences between the chemical potentials for each of the components of the aqueous and solid-solution phases. The minimization problem is described as

$$\begin{aligned} \lambda^S &= \text{minimum} \sum_{j=1}^{nssc} X_j [\mu_j(X) - \mu_j(\text{soln})] \\ \text{subject to} \quad &\sum_{j=1}^{nssc} X_j = 1 \end{aligned} \quad (A.14)$$

where λ_s = phase multiplier for the solid-solution phase as a whole

nssc = number of components of the solid solution

X_j = mole fraction of component j in the solid solution

The solution of the minimization problem posed by Equation (A.14) is completely analogous to the solution of Equation (A.3), except that 1) the unknown mole fractions replace the mole numbers, 2) the phase multipliers for each component of the solid solution replace the chemical potentials, and 3) convergence is checked by ensuring that the minimum in the free-energy difference between the aqueous phase and the solid-solution phase will occur when the phase multipliers for each component of the solid solution phase are equal (Harvie et al. 1987). The phase multipliers for each component of the solid solution are calculated according to Equation (A.11).

The solid-solution phase with the lowest phase multiplier is then brought into the phase assemblage. In this phase-addition step, all components of the solid-solution phase are added. The mole numbers for the components of the solid-solution phase are then treated in the same way as the mole numbers of any other species, except that the chemical potential for components of solid solutions is given by the equation

$$\mu_j = \mu_j^0 + RT \ln X_j + RT \ln \gamma_j \quad (\text{A.15})$$

and the mole fractions are continually recalculated as the mole numbers for the components of the solid solution change.

APPENDIX B

THERMODYNAMIC DATA BASE

APPENDIX B

THERMODYNAMIC DATA BASE

The thermodynamic data base in GMIN is based upon the thermodynamic model of Felmy and Weare (1986) for the complex Na-K-Ca-Mg-H-Cl-SO₄-CO₂-B(OH)₃-H₂O system at 25°C. All of the standard chemical potentials and Pitzer ion-interaction parameters were taken from Felmy and Weare (1986) and Harvie et al. (1984).

Data for a few adsorbed species defined by Zachara et al. (1987) are included as examples of the triple-layer model formulations.

GMIN uses five thermodynamic data files: comp.dat, binaryp.dat, ternaryp.dat, lambda.dat, and ads.dat.

The file comp.dat (Table B.1) contains the species ID numbers, species names, species charge, standard chemical potentials (all divided by RT), the elemental atomic number, and the number of moles of each element in the species. The elemental stoichiometries are based upon atomic number, i.e., hydrogen is 1, oxygen is 8, etc. The file format is [I6,A12,1X,I2,F15.3,1X,10(I2,F4.1)]. The file must end with a -1.

The file binaryp.dat (Table B.2) contains the ID number of each species in each binary interaction considered (e.g., NaCl, KCl) and the Pitzer ion-interaction parameters β^0 , β^1 , β^2 , and C^ϕ for binary systems. The file format is (I6,1X,I6,4F7.3). The file must end with a zero ID number.

The file ternaryp.dat (Table B.3) contains the Pitzer ion-interaction parameters for the common ion ternary systems, Θ and ψ . The first two columns include the cation-cation or anion-anion ID numbers associated with the ion-interaction parameter, Θ , in column three. Subsequent columns include the anion or cation ID number and the triple ion-interaction parameter, ψ , associated with that triple ion interaction. For example, the first ψ in row 1, column 2, has a value of -0.0018 and is indexed for the Na⁺

(ID 011000), K^+ (ID 019000), Cl^- (ID 000170) interaction. The file format is [I6,1X,I6,F7.3,1X,20(I6,1X,F7.3,1X)]. The file must end with a zero ID number.

The file lambda.dat (Table B.4) contains the Pitzer ion-interaction parameters for the neutral species, λ and δ . The first column of this file contains the ID number for the neutral species, and the second column contains the ID number for the cation or anion involved in the neutral-cation or neutral-anion interaction parameterized by the Pitzer λ parameter included in the third column. Subsequent columns are for higher-order neutral interactions. For example, the value of δ in row 1, column 5, represents the $B(OH)_3$ (ID 000050), Na^+ (ID 011000), SO_4^{2-} (ID 000160) ion interaction. The file format is [I6,1X,I6,F7.3,1X,20(I6,1X,F7.3,1X)]. The file must end with a zero ID number.

The file ads.dat (Table B.5) contains information on the charge contribution of each adsorbed species in the zero and b adsorption planes. The file format is (I6,1X,2F10.4). The ID numbers for adsorbed species must be greater than 300000 and are defined in the file comp.dat. This file must end with a -1.

TABLE B.1. File comp.dat. This file contains information defining all species to be considered by GMIN.

ID #	name	z	μ°/RT	composition
001080	H2O	0	-95.6635	1 2.0 8 1.0
011000	Na+	1	-105.651	11 1.0
019000	K+	1	-113.957	19 1.0
020000	Ca++	2	-223.300	20 1.0
012000	Mg++	2	-183.468	12 1.0
001000	H+	1	-000.000	1 1.0
012080	MgOH+	1	-251.940	12 1.0 8 1.0 1 1.0
000170	Cl-	-1	-52.9550	17 1.0
000160	SO4--	-2	-300.386	8 4.016 1.0
000161	HSO4-	-1	-304.942	16 1.0 8 4.0 1 1.0
000080	OH-	-1	-63.435	1 1.0 8 1.0
000060	CO3--	-2	-212.944	8 3.0 6 1.0
000061	HCO3-	-1	-236.751	1 1.0 8 3.0 6 1.0
000062	CO2(aq)	0	-155.680	6 1.0 8 2.0
020060	CaCO3(aq)	0	-443.500	6 1.020 1.0 8 3.0
012060	MgCO3(aq)	0	-403.155	12 1.0 6 1.0 8 3.0
000050	B(OH)3	0	-390.810	5 1.0 8 3.0 1 3.0
000051	B(OH)4-	-1	-465.200	1 4.0 8 4.0 5 1.0
000052	B3O3(OH)4-	-1	-963.770	1 4.0 8 7.0 5 3.0
000053	B4O5(OH)4--	-2	-1239.100	1 4.0 8 9.0 5 4.0
020051	CaB(OH)4+	1	-692.300	20 1.0 5 1.0 1 4.0 8 4.0
012051	MgB(OH)4+	1	-651.890	12 1.0 5 1.0 1 4.0 8 4.0
100060	CO2(GAS)		-159.092	6 1. 8 2.
120160	ANHYDRITE		-533.730	20 1. 16 1. 8 4.
111160	APHTHALITE		-1057.05	19 3. 16 2. 11 1. 8 8.
120170	ANTARCTICITE		-893.650	20 1. 17 2. 8 6. 1 12.
120060	ARAGONITE		-455.170	6 1. 8 3. 20 1.
119160	ARCANITE		-532.390	19 2. 16 1. 8 4.
112170	BISCHOFITE		-853.100	17 2. 12 1. 8 6. 1 12.
111161	BLOEDITE		-1383.600	16 2. 12 1. 11 2. 8 12. 1 8.
112080	BRUCITE		-335.4	12 1. 1 2. 8 2.
111060	BURKEITE		-1449.4	11 6. 6 1. 16 2. 8 11.
120061	CALCITE		-455.600	6 1. 8 3. 20 1.
120171	CACL2.4H2O		-698.7	20 1. 17 2. 8 4. 1 8.
120172	CA-OXY-A		-2658.45	20 4. 17 2. 8 19. 1 32.
120173	CA-OXY-B		-778.41	20 2. 17 2. 8 3. 1 4.
119170	CARNALLITE		-1020.300	19 1. 17 3. 12 1. 8 6. 1 12.
112060	DOLOMITE		-871.990	20 1. 12 1. 6 2. 8 6.
112160	EPSOMITE		-1157.830	16 1. 12 1. 8 11. 1 14.
120062	GAYLUSSITE		-1360.50	11 2. 20 1. 6 2. 8 11. 1 10.
111162	GLAUBERITE		-1047.450	20 1. 16 2. 11 2. 8 8.
120161	GYPNUM		-725.560	20 1. 16 1. 8 6. 1 4.
111170	HALITE		-154.990	17 1. 11 1.
112161	HEXAHYDRITE		-1061.600	16 1. 12 1. 8 10. 1 12.
119171	KAINITE		-938.200	19 1. 17 1. 16 1. 12 1. 8 7. 1 6.
119060	KALICINITE		-350.060	19 1. 1 1. 8 3. 6 1.

TABLE B.1. (contd)

ID #	name	z	μ°/RT	composition
112162	KIESERITE		-579.800	16 1. 12 1. 8 5. 1 2.
111163	LABILE SALT		-1751.450	20 1. 16 3. 11 4. 8 14. 1 4.
112163	LEONHARDTIT		-868.550	16 1. 12 1. 8 8. 1 8.
119161	LEONITE		-1403.970	19 2. 16 2. 12 1. 8 12. 1 8.
112061	MAGNESITE		-414.45	12 1. 6 1. 8 3.
112171	MG-OXY		-1029.5	12 2. 17 1. 8 7. 1 11.
119167	MERCALLITE		-417.57	19 1. 1 1. 16 1. 8 4.
111164	MIRABILITE		-1471.150	16 1. 11 2. 8 14. 1 20.
119162	MISENITE		-3039.24	19 8. 1 6. 16 7. 8 28.
111061	NAHCOLITE		-343.330	11 1. 6 1. 8 3. 1 1.
111062	NATRON		-1382.780	11 2. 6 1. 8 13. 1 20.
112062	NESQUEHONIT		-695.300	12 1. 6 1. 1 6. 8 6.
112164	PENTAHYDRIT		-965.130	16 1. 12 1. 8 9. 1 10.
119163	PICROMERITE		-1596.1	19 2. 16 2. 12 1. 8 14. 1 12.
111063	PIRSSONITE		-1073.10	11 2. 20 1. 6 2. 8 8. 1 4.
119164	POLYHALITE		-2282.500	20 2. 19 2. 16 4. 12 1. 8 18. 1 4.
120080	PORTLANDITE		-362.12	20 1. 8 2. 1 2.
119061	K-CARB-3/2		-577.370	19 2. 6 1. 8 4.5 1 3.
119062K	SESQUICARB		-2555.400	19 8. 1 10. 6 6. 8 21.
119063	K-NA-CARB-6		-1006.8	19 1. 11 1. 6 1. 8 9. 1 12.
119064	K-TRONA		-971.740	19 2. 11 1. 1 5. 6 2. 8 8.
119165	K3H(SO4)2		-950.8	19 3. 1 1. 16 2. 8 8.
111165	NA3H(SO4)2		-919.6	11 3. 1 1. 16 2. 8 8.
111064	NA-CARB-7		-1094.950	11 2. 6 1. 8 10. 1 14.
119172	SYLVITE		-164.840	19 1. 17 1.
119166	SYNGENITE		-1164.8	20 1. 19 2. 16 2. 8 9. 1 2.
112172	TACHYHYDRIT		-2015.900	20 1. 17 6. 12 2. 8 12. 1 24.
111166	THENARDITE		-512.350	16 1. 11 2. 8 4.
111065	THERMONATRI		-518.8	11 2. 6 1. 8 4. 1 2.
111066	TRONA		-960.380	11 3. 6 2. 8 8. 1 5.
111050	Borax		-2224.16	11 2. 5 4. 8 17. 1 20.
111051	Pentaborate		-1854.80	11 1. 5 5. 8 13. 1 10.
111052	Metaborate		-761.420	11 1. 5 1. 8 6. 1 8.
111053	Teepelite		-725.770	11 2. 5 1. 8 4. 1 4. 17 1.
100500	Boric acid		-390.880	5 1. 8 3. 1 3.
112063	Northupite		-989.600	11 3. 17 1. 12 1. 6 2. 8 6.
101000	H(solid)	1	-4.60517	1 1.0
356000	FeOH	0	0.00	97 1.0 1 1.0
356001	FeOH2+	1	-12.4340	97 1.0 1 2.0
356002	FeO-	-1	23.7166	97 1.0
420560	FeO-CA++	1	-208.794	97 1.020 1.0
456160	FeOH2+-SO4	-1	-327.096	97 1.016 1.0 1 2.0 8 4.0
456161	FeOH2+HSO4	0	-340.221	97 1.016 1.0 1 3.0 8 4.0

-1

TABLE B.2. File binaryp.dat. This file contains the Pitzer ion-interaction parameters for binary systems.

ID cation	ID anion	β^0	β^1	β^2	$C\phi$
011000	000170	.0765	.2664	.000	.00127
011000	000160	.01958	1.113	.000	.00497
011000	000161	.0454	.398	.000	.0000
011000	000080	.0864	.253	.000	.0044
011000	000061	.0277	.0411	.000	.0000
011000	000060	.0399	1.389	.000	.00440
011000	000051	-.0427	.089	.000	.0114
011000	000052	-.056	-.910	.000	.0000
011000	000053	-.110	-.40	.000	.0000
019000	000170	.04835	.2122	.000-	.00084
019000	000160	.04995	.7793	.000	.0000
019000	000161	-.0003	.1735	.000	.000
019000	000080	.1298	.320	.000	.0041
019000	000061	.0296	-.013	.000-	.00800
019000	000060	.1488	1.43	.000-	.00150
019000	000051	.0350	.14	.000	.0000
019000	000052	-.130	.00	.000	.0000
019000	000053	-.022	.00	.000	.0000
020000	000170	.3159	1.614	.000-	.00034
020000	000160	.20	3.1973	-54.24	.000
020000	000161	.2145	2.530	.000	.000
020000	000080	-.1747	-.2303	-5.72	.000
020000	000061	.400	2.9770	.000	.000
012000	000170	.35235	1.6815	.000	.00519
012000	000160	.2210	3.343	-37.23	.025
012000	000161	.4746	1.729	.000	.000
012000	000061	.329	.6072	.000	.00
012080	000170	-0.1	1.658	.000	.00
001000	000170	.1775	.2945	.000	.0008
001000	000160	.0298	.0000	.000	.0438
001000	000161	.2065	.5556	.000	.000
012051	000170	.1600	.0000	.000	.000
020051	000170	.1200	.0000	.000	.000
000000					

TABLE B.3. File ternaryp.dat. This file contains the Pitzer ion-interaction parameters for common ion ternary systems.

ID #	ID #	θ	ID #	ψ	ID #	ψ	ID #	ψ	ID #	ψ
011000	019000	-.012	000170	-.0018	000160	-.010	000061	-.0030	000060	.00300
011000	020000	.070	000170	-.007	000160	-.055				
011000	012000	.070	000170	-.012	000160	-.015				
011000	001000	.036	000170	-.004	000161	-.0129				
019000	020000	.032	000170	-.025						
019000	012000	.000	000170	-.022	000160	-.048				
019000	001000	.005	000170	-.011	000160	.197	000161	-.0265		
020000	012000	.007	000170	-.012	000160	.024				
020000	001000	.092	000170	-.015						
012000	012080	.000	000170	.028						
012000	001000	.10	000170	-.011	000161	-.0178				
000170	000160	.02	011000	.0014	020000	-.018	012000	-.0040		
000170	000161	-.006	011000	-.006	001000	.0130				
000170	000080	-.05	011000	-.006	019000	-.006	020000	-.0250		
000170	000061	.0300	011000	-.0150	012000	-.096				
000170	000060	-.0200	011000	.0085	019000	.00400				
000160	000161	.00	011000	-.00940	019000	-.0677	012000	-.0425		
000160	000080	-.013	011000	-.009	019000	-.050				
000160	000061	.01	011000	-.00500	012000	-.161				
000160	000060	.02	011000	-.005	019000	-.00900				
000080	000060	.100	011000	-.0170	019000	-.0100				
000061	000060	-.0400	011000	.00200	019000	.0120				
000051	000170	-.065	011000	-.0073						
000051	000160	-.012								
000052	000170	.12	011000	-.024						
000052	000160	.10								
000052	000061	-.10								
000053	000170	.074	011000	.026						
000053	000160	.12								
000053	000061	-.087								
000000										

TABLE B.4. File lambda.dat. This file contains ion-interaction parameters for neutral species.

ID neutral	ID c/a	λ	ID c/a	δ
000050	011000	-.097	000160	.046
000050	001000	.000	000170	-.0102
000050	019000	-.14		
000050	000170	.091		
000050	000160	.018		
000050	000052	-.20		
000062	011000	.100		
000062	019000	.0510		
000062	020000	.183		
000062	012000	.183		
000062	000170	-.0050		
000062	000160	.097		
000000				

TABLE B.5. File ads.dat. This file contains information necessary for the GMIN adsorption model.

ID number	charge zero plane	charge b plane
356000	0.00	0.00
356001	1.00	0.00
356002	-1.00	0.00
420560	-1.00	2.00
456160	1.00	-2.00
456161	1.00	-1.00
-1		

APPENDIX C

TEST CASE

APPENDIX C

TEST CASE

This appendix contains the output for the GMIN test case. (The input data for this test case are in the input file gmin.dat, shown in Table 2.) The GMIN output file can be divided into two sections. The first section gives a complete listing of all of the data considered by the model, beginning with a listing of the starting species, in terms of their ID numbers, names, starting number of moles, charge, and standard chemical potential divided by RT (μ_0^0/RT). This listing is followed by information on the charge- and mass-balance constraint equations considered by the model. Next comes a complete listing of the Pitzer ion-interaction parameters for single- and mixed-electrolyte systems. This listing of parameters concludes the first section.

The second section begins with some brief run-time information on the calculations actually being performed, starting with the output statement "Factoring constraint matrix". Next, the results of the model calculations are presented. The species ID number, name, calculated number of moles, molality (for aqueous species), natural logarithm of the species activity, and chemical potential are listed. Finally, solid phases and their calculated saturation indices are listed.

TABLE C.1. Output for Sample Test Case. The first section lists the input data considered in the calculations. The last section presents the results of the model calculations.

AQUEOUS SPECIES

ID	NAME	MOLES	Z	u0rt
1080	H2O	55.508000000000	0.	-95.664
11000	Na+	1.047201040000	1.	-105.651
19000	K+	.026530000000	1.	-113.957
20000	Ca++	.000175900000	2.	-223.300
12000	Mg++	.000179200000	2.	-183.468
1000	H+	.000000001000	1.	.000
12080	MgOH+	.000000001000	1.	-251.940
20051	CaB(OH)4+	.000000001000	1.	-692.300
12051	MgB(OH)4+	.000000001000	1.	-651.890
170	Cl-	.768440236000	-1.	-52.955
160	SO4--	.135000000000	-2.	-300.386
161	HSO4-	.000000001000	-1.	-304.942
80	OH-	.000000001000	-1.	-63.435
61	HCO3-	.000001001000	-1.	-236.751
60	CO3--	.000000001000	-2.	-212.944
51	B(OH)4-	.036000000000	-1.	-465.200
52	B3O3(OH)4-	.000000001000	-1.	-963.770
53	B4O5(OH)4--	.000000001000	-2.	-1239.100

SOLID PHASES

ID	NAME	MOLES	Z	u0rt
100060	CO2(GAS)	.000000000000	0.	-159.092
120160	ANHYDRITE	.000000000000	0.	-533.730
111160	APHTHALITE	.000000000000	0.	-1057.050
120170	ANTARCTICITE	.000000000000	0.	-893.650
120060	ARAGONITE	.000000000000	0.	-455.170
119160	ARCANITE	.000000000000	0.	-532.390
112170	BISCHOFITE	.000000000000	0.	-853.100
111161	BLOEDITE	.000000000000	0.	-1383.600
112080	BRUCITE	.000000000000	0.	-335.400
111060	BURKEITE	.000000000000	0.	-1449.400
120061	CALCITE	.000000000000	0.	-455.600
111170	HALITE	.000000000000	0.	-154.990

CONSTRAINT EQUATIONS

	0	1	8	11	19	20	12	5	17	16	6
H2O	.0	2.0	1.0	.0	.0	.0	.0	.0	.0	.0	.0
Na+	1.0	.0	.0	1.0	.0	.0	.0	.0	.0	.0	.0
K+	1.0	.0	.0	.0	1.0	.0	.0	.0	.0	.0	.0
Ca++	2.0	.0	.0	.0	.0	1.0	.0	.0	.0	.0	.0
Mg++	2.0	.0	.0	.0	.0	.0	1.0	.0	.0	.0	.0
H+	1.0	1.0	.0	.0	.0	.0	.0	.0	.0	.0	.0
MgOH+	1.0	1.0	1.0	.0	.0	.0	1.0	.0	.0	.0	.0
CaB(OH)4+	1.0	4.0	4.0	.0	.0	1.0	.0	1.0	.0	.0	.0

TABLE C.1. (contd)

MgB(OH)4+	1.0	4.0	4.0	.0	.0	.0	1.0	1.0	.0	.0	.0
Cl-	-1.0	.0	.0	.0	.0	.0	.0	.0	1.0	.0	.0
SO4--	-2.0	.0	4.0	.0	.0	.0	.0	.0	.0	1.0	.0
HSO4-	-1.0	1.0	4.0	.0	.0	.0	.0	.0	.0	1.0	.0
OH-	-1.0	1.0	1.0	.0	.0	.0	.0	.0	.0	.0	.0
HCO3-	-1.0	1.0	3.0	.0	.0	.0	.0	.0	.0	.0	1.0
CO3--	-2.0	.0	3.0	.0	.0	.0	.0	.0	.0	.0	1.0
B(OH)4-	-1.0	4.0	4.0	.0	.0	.0	.0	1.0	.0	.0	.0
B3O3(OH)4-	-1.0	4.0	7.0	.0	.0	.0	.0	3.0	.0	.0	.0
B4O5(OH)4--	-2.0	4.0	9.0	.0	.0	.0	.0	4.0	.0	.0	.0
CO2(GAS)	.0	.0	2.0	.0	.0	.0	.0	.0	.0	.0	1.0
ANHYDRITE	.0	.0	4.0	.0	.0	1.0	.0	.0	.0	1.0	.0
APHTHALITE	.0	.0	8.0	1.0	3.0	.0	.0	.0	.0	2.0	.0
ANTARCTICITE	.0	12.0	6.0	.0	.0	1.0	.0	.0	2.0	.0	.0
ARAGONITE	.0	.0	3.0	.0	.0	1.0	.0	.0	.0	.0	1.0
ARCANITE	.0	.0	4.0	.0	2.0	.0	.0	.0	.0	1.0	.0
BISCHOFITE	.0	12.0	6.0	.0	.0	.0	1.0	.0	2.0	.0	.0
BLOEDITE	.0	8.0	12.0	2.0	.0	.0	1.0	.0	.0	2.0	.0
BRUCITE	.0	2.0	2.0	.0	.0	.0	1.0	.0	.0	.0	.0
BURKEITE	.0	.0	11.0	6.0	.0	.0	.0	.0	.0	2.0	1.0
CALCITE	.0	.0	3.0	.0	.0	1.0	.0	.0	.0	.0	1.0
HALITE	.0	.0	.0	1.0	.0	.0	.0	.0	1.0	.0	.0

non-ideal electrolyte parameters

single electrolyte parameters

Na+	Cl-	.07650	.26640	.00000	.00127
Na+	SO4--	.01958	1.11300	.00000	.00497
Na+	HSO4-	.04540	.39800	.00000	.00000
Na+	OH-	.08640	.25300	.00000	.00440
Na+	HCO3-	.02770	.04110	.00000	.00000
Na+	CO3--	.03990	1.38900	.00000	.00440
Na+	B(OH)4-	-.04270	.08900	.00000	.01140
Na+	B3O3(OH)4-	-.05600	-.91000	.00000	.00000
Na+	B4O5(OH)4--	-.11000	-.40000	.00000	.00000
K+	Cl-	.04835	.21220	.00000	-.00084
K+	SO4--	.04995	.77930	.00000	.00000
K+	HSO4-	-.00030	.17350	.00000	.00000
K+	OH-	.12980	.32000	.00000	.00410
K+	HCO3-	.02960	-.01300	.00000	-.00800
K+	CO3--	.14880	1.43000	.00000	-.00150
K+	B(OH)4-	.03500	.14000	.00000	.00000
K+	B3O3(OH)4-	-.13000	.00000	.00000	.00000
K+	B4O5(OH)4--	-.02200	.00000	.00000	.00000
Ca++	Cl-	.31590	1.61400	.00000	-.00034
Ca++	SO4--	.20000	3.19730	-54.24000	.00000
Ca++	HSO4-	.21450	2.53000	.00000	.00000
Ca++	OH-	-.17470	-.23030	-5.72000	.00000
Ca++	HCO3-	.40000	2.97700	.00000	.00000

TABLE C.1 (contd)

Ca++	CO3--	.00000	.00000	.00000	.00000
Ca++	B(OH)4-	.00000	.00000	.00000	.00000
Ca++	B3O3(OH)4-	.00000	.00000	.00000	.00000
Ca++	B4O5(OH)4--	.00000	.00000	.00000	.00000
Mg++	Cl-	.35235	1.68150	.00000	.00519
Mg++	SO4--	.22100	3.34300	-37.23000	.02500
Mg++	HSO4-	.47460	1.72900	.00000	.00000
Mg++	OH-	.00000	.00000	.00000	.00000
Mg++	HCO3-	.32900	.60720	.00000	.00000
Mg++	CO3--	.00000	.00000	.00000	.00000
Mg++	B(OH)4-	.00000	.00000	.00000	.00000
Mg++	B3O3(OH)4-	.00000	.00000	.00000	.00000
Mg++	B4O5(OH)4--	.00000	.00000	.00000	.00000
H+	Cl-	.17750	.29450	.00000	.00080
H+	SO4--	.02980	.00000	.00000	.04380
H+	HSO4-	.20650	.55560	.00000	.00000
H+	OH-	.00000	.00000	.00000	.00000
H+	HCO3-	.00000	.00000	.00000	.00000
H+	CO3--	.00000	.00000	.00000	.00000
H+	B(OH)4-	.00000	.00000	.00000	.00000
H+	B3O3(OH)4-	.00000	.00000	.00000	.00000
H+	B4O5(OH)4--	.00000	.00000	.00000	.00000
MgOH+	Cl-	-.10000	1.65800	.00000	.00000
MgOH+	SO4--	.00000	.00000	.00000	.00000
MgOH+	HSO4-	.00000	.00000	.00000	.00000
MgOH+	OH-	.00000	.00000	.00000	.00000
MgOH+	HCO3-	.00000	.00000	.00000	.00000
MgOH+	CO3--	.00000	.00000	.00000	.00000
MgOH+	B(OH)4-	.00000	.00000	.00000	.00000
MgOH+	B3O3(OH)4-	.00000	.00000	.00000	.00000
MgOH+	B4O5(OH)4--	.00000	.00000	.00000	.00000
CaB(OH)4+	Cl-	.12000	.00000	.00000	.00000
CaB(OH)4+	SO4--	.00000	.00000	.00000	.00000
CaB(OH)4+	HSO4-	.00000	.00000	.00000	.00000
CaB(OH)4+	OH-	.00000	.00000	.00000	.00000
CaB(OH)4+	HCO3-	.00000	.00000	.00000	.00000
CaB(OH)4+	CO3--	.00000	.00000	.00000	.00000
CaB(OH)4+	B(OH)4-	.00000	.00000	.00000	.00000
CaB(OH)4+	B3O3(OH)4-	.00000	.00000	.00000	.00000
CaB(OH)4+	B4O5(OH)4--	.00000	.00000	.00000	.00000
MgB(OH)4+	Cl-	.16000	.00000	.00000	.00000
MgB(OH)4+	SO4--	.00000	.00000	.00000	.00000
MgB(OH)4+	HSO4-	.00000	.00000	.00000	.00000
MgB(OH)4+	OH-	.00000	.00000	.00000	.00000
MgB(OH)4+	HCO3-	.00000	.00000	.00000	.00000
MgB(OH)4+	CO3--	.00000	.00000	.00000	.00000
MgB(OH)4+	B(OH)4-	.00000	.00000	.00000	.00000
MgB(OH)4+	B3O3(OH)4-	.00000	.00000	.00000	.00000
MgB(OH)4+	B4O5(OH)4--	.00000	.00000	.00000	.00000

TABLE C.1 (contd)

ternary electrolyte parameters										
			Cl-	SO4--	HSO4-	OH-	HCO3-	CO3-	B(OH)4-	B3O3(OH)4-
Na+	K+	-.01200	-.00180	-.01000	.00000	.00000	-.00300	.00300	.00000	.00000
Na+	Ca++	.07000	-.00700	-.05500	.00000	.00000	.00000	.00000	.00000	.00000
Na+	Mg++	.07000	-.01200	-.01500	.00000	.00000	.00000	.00000	.00000	.00000
Na+	H+	.03600	-.00400	.00000	-.01290	.00000	.00000	.00000	.00000	.00000
Na+	MgOH+	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
Na+	CaB(OH)4+	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
Na+	MgB(OH)4+	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
K+	Ca++	.03200	-.02500	.00000	.00000	.00000	.00000	.00000	.00000	.00000
K+	Mg++	.00000	-.02200	-.04800	.00000	.00000	.00000	.00000	.00000	.00000
K+	H+	.00500	-.01100	.19700	-.02650	.00000	.00000	.00000	.00000	.00000
K+	MgOH+	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
K+	CaB(OH)4+	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
K+	MgB(OH)4+	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
Ca++	Mg++	.00700	-.01200	.02400	.00000	.00000	.00000	.00000	.00000	.00000
Ca++	H+	.09200	-.01500	.00000	.00000	.00000	.00000	.00000	.00000	.00000
Ca++	MgOH+	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
Ca++	CaB(OH)4+	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
Ca++	MgB(OH)4+	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
Mg++	H+	.10000	-.01100	.00000	-.01780	.00000	.00000	.00000	.00000	.00000
Mg++	MgOH+	.00000	.02800	.00000	.00000	.00000	.00000	.00000	.00000	.00000
Mg++	CaB(OH)4+	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
Mg++	MgB(OH)4+	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
H+	MgOH+	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
H+	CaB(OH)4+	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
H+	MgB(OH)4+	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
MgOH+	CaB(OH)4+	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
MgOH+	MgB(OH)4+	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
CaB(OH)4+	MgB(OH)4+	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
B4O5(OH)4--										
Na+	K+	-.01200	.00000							
Na+	Ca++	.07000	.00000							
Na+	Mg++	.07000	.00000							
Na+	H+	.03600	.00000							
Na+	MgOH+	.00000	.00000							
Na+	CaB(OH)4+	.00000	.00000							
Na+	MgB(OH)4+	.00000	.00000							
K+	Ca++	.03200	.00000							
K+	Mg++	.00000	.00000							
K+	H+	.00500	.00000							
K+	MgOH+	.00000	.00000							
K+	CaB(OH)4+	.00000	.00000							
K+	MgB(OH)4+	.00000	.00000							
Ca++	Mg++	.00700	.00000							
Ca++	H+	.09200	.00000							
Ca++	MgOH+	.00000	.00000							
Ca++	CaB(OH)4+	.00000	.00000							
Ca++	MgB(OH)4+	.00000	.00000							

TABLE C.1 (contd)

Mg++	H+	.10000	.00000								
Mg++	MgOH+	.00000	.00000								
Mg++	CaB(OH)4+	.00000	.00000								
Mg++	MgB(OH)4+	.00000	.00000								
H+	MgOH+	.00000	.00000								
H+	CaB(OH)4+	.00000	.00000								
H+	MgB(OH)4+	.00000	.00000								
MgOH+	CaB(OH)4+	.00000	.00000								
MgOH+	MgB(OH)4+	.00000	.00000								
CaB(OH)4+	MgB(OH)4+	.00000	.00000								
			Na+	K+	Ca++	Mg++	H+	MgOH+	CaB(OH)4+	MgB(OH)4+	
Cl-	SO4--	.02000	.00140	.00000	-.01800	-.00400	.00000	.00000	.00000	.00000	
Cl-	HSO4-	-.00600	-.00600	.00000	.00000	.00000	.01300	.00000	.00000	.00000	
Cl-	OH-	-.05000	-.00600	-.00600	-.02500	.00000	.00000	.00000	.00000	.00000	
Cl-	HCO3-	.03000	-.01500	.00000	.00000	-.09600	.00000	.00000	.00000	.00000	
Cl-	CO3--	-.02000	.00850	.00400	.00000	.00000	.00000	.00000	.00000	.00000	
Cl-	B(OH)4-	-.06500	-.00730	.00000	.00000	.00000	.00000	.00000	.00000	.00000	
Cl-	B3O3(OH)4-	.12000	-.02400	.00000	.00000	.00000	.00000	.00000	.00000	.00000	
Cl-	B4O5(OH)4--	.07400	.02600	.00000	.00000	.00000	.00000	.00000	.00000	.00000	
SO4--	HSO4-	.00000	-.00940	-.06770	.00000	-.04250	.00000	.00000	.00000	.00000	
SO4--	OH-	-.01300	-.00900	-.05000	.00000	.00000	.00000	.00000	.00000	.00000	
SO4--	HCO3-	.01000	-.00500	.00000	.00000	-.16100	.00000	.00000	.00000	.00000	
SO4--	CO3--	.02000	-.00500	-.00900	.00000	.00000	.00000	.00000	.00000	.00000	
SO4--	B(OH)4-	-.01200	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	
SO4--	B3O3(OH)4-	.10000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	
SO4--	B4O5(OH)4--	.12000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	
HSO4-	OH-	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	
HSO4-	HCO3-	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	
HSO4-	CO3--	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	
HSO4-	B(OH)4-	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	
HSO4-	B3O3(OH)4-	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	
HSO4-	B4O5(OH)4--	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	
OH-	HCO3-	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	
OH-	CO3--	.10000	-.01700	-.01000	.00000	.00000	.00000	.00000	.00000	.00000	
OH-	B(OH)4-	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	
OH-	B3O3(OH)4-	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	
OH-	B4O5(OH)4--	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	
HCO3-	CO3--	-.04000	.00200	.01200	.00000	.00000	.00000	.00000	.00000	.00000	
HCO3-	B(OH)4-	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	
HCO3-	B3O3(OH)4-	-.10000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	
HCO3-	B4O5(OH)4--	-.08700	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	
CO3--	B(OH)4-	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	
CO3--	B3O3(OH)4-	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	
CO3--	B4O5(OH)4--	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	
B(OH)4-	B3O3(OH)4-	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	
B(OH)4-	B4O5(OH)4--	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	
B3O3(OH)4-	B4O5(OH)4--	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	

** Factoring constraint matrix **

** Working on solution **

** Constraint matrix refactored **

TABLE C.1 (contd)

OUTPUT DATA ITERATION = 11

ID	NAME	MOLES	MOLALITY	ln a	u
1080	H2O	5.5508E+01	5.5508E+01	-3.1808E-02	-9.5695E+01
11000	Na+	1.0472E+00	1.0472E+00	-4.2009E-01	-1.0607E+02
19000	K+	2.6530E-02	2.6530E-02	-4.2004E+00	-1.1816E+02
20000	Ca++	1.5060E-04	1.5060E-04	-1.0702E+01	-2.3400E+02
12000	Mg++	1.6192E-04	1.6192E-04	-1.0465E+01	-1.9393E+02
1000	H+	1.9516E-10	1.9516E-10	-2.2656E+01	-2.2656E+01
12080	MgOH+	3.8097E-07	3.8097E-07	-1.5033E+01	-2.6697E+02
20051	CaB(OH)4+	2.5305E-05	2.5305E-05	-1.1178E+01	-7.0348E+02
12051	MgB(OH)4+	1.6905E-05	1.6905E-05	-1.1520E+01	-6.6341E+02
170	Cl-	7.6844E-01	7.6844E-01	-7.6005E-01	-5.3715E+01
160	SO4--	1.3500E-01	1.3500E-01	-4.6174E+00	-3.0500E+02
161	HSO4-	2.2651E-10	2.2651E-10	-2.2717E+01	-3.2766E+02
80	OH-	1.1826E-04	1.1826E-04	-9.6045E+00	-7.3039E+01
61	HCO3-	3.5319E-07	3.5319E-07	-1.5551E+01	-2.5230E+02
60	CO3--	6.4881E-07	6.4882E-07	-1.6703E+01	-2.2965E+02
51	B(OH)4-	3.5755E-02	3.5755E-02	-4.2769E+00	-4.6948E+02
52	B3O3(OH)4-	3.5653E-05	3.5653E-05	-1.1496E+01	-9.7527E+02
53	B4O5(OH)4--	2.3995E-05	2.3996E-05	-1.4252E+01	-1.2534E+03

NAME	Log SI
CO2(GAS)	-8.760
ANHYDRITE	-2.291
APHTHITALITE	-5.863
ANTARCTICITE	-9.534
ARAGONITE	-3.682
ARCANITE	-3.877
BISCHOFITE	-9.744
BLOEDITE	-6.629
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Stop - Program terminated.

APPENDIX D

EQUATIONS FOR THE TRIPLE-LAYER SITE-BINDING MODEL

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EQUATIONS FOR THE TRIPLE-LAYER SITE-BINDING MODEL

The electrostatic potentials are calculated in GMIN by using the triple-layer site-binding model (Davis et al. 1978). In this model, each adsorbed species is influenced by electrostatic potentials at the surface, or zero plane, and at an outer or b plane. These potentials are also related to a diffuse-layer potential of counter ions. Felmy et al. (1984) and Westall (1979) give complete model formulations for implementation of the triple-layer model in mass-action models. This appendix presents a brief description of the same formulations, reworked for the free-energy minimization approach used in GMIN.

In the triple-layer model, the electrochemical potential for an adsorbed species is given by the following:

$$\bar{\mu}_i = \mu_i^0/RT + \ln M_i + Z_i^0 F \psi^0 + Z_i^b F \psi^b \quad (D.1)$$

where $\bar{\mu}_i$ = electrochemical potential of adsorbed species i
 Z_i^0 = charge on species i in the zero plane
 Z_i^b = charge on species i in the b plane
 ψ^0 = electrostatic potential in the zero plane
 ψ^b = electrostatic potential in the b plane

The molarity scale is used in Equation (D.1) because the equilibrium constants for the triple-layer adsorption reactions are usually calculated on this scale. This requires the model user to supply the volume of solution associated with the species mole numbers specified, usually one liter.

To calculate the two electrostatic potential terms in Equation (D.1), we begin by defining the electrostatic potential in the b plane in terms of the potential in the diffuse layer, using the constant capacitance equation for the outer adsorption plane:

$$\psi^b = \psi^d - \sigma^d/C_2 \quad (D.2)$$

where ψ^d = electrostatic potential in the diffuse plane

σ^d = electrostatic charge at the diffuse layer boundary

C_2 = outer-layer capacitance

The diffuse-layer charge is calculated from the charge-balance equation

$$\sigma^d = -(\sigma^0 + \sigma^b) \quad (D.3)$$

where σ^0 is the electrostatic charge in the zero plane and σ^b is the electrostatic charge in the b plane. These values are calculated from the number of moles of adsorbed species in each plane by the equations

$$\sigma^0 = B \left(\sum_{i=1}^{ns} Z_i^0 n_i \right)$$

and

$$\sigma^b = B \left(\sum_{i=1}^{ns} Z_i^b n_i \right)$$

where $B = F/S_A C_S V_S$

F = Faraday's constant

S_A = specific surface area (m^2/g)

C_S = concentration of solid (g/L)

V_S = volume of solution (L)

The other unknown in Equation (D.2), ψ^d , is calculated from the Guoy-Chapman equation,

$$\psi^d = \frac{2RT}{F} \cdot \sinh^{-1} \left[\frac{-\sigma^d}{(B2 \cdot I^{0.5})} \right] \quad (D.4)$$

where $B2$ is a constant, equal to 0.1174 at 25°C. These equations completely define the electrostatic potential at the b plane. The electrostatic potential at the surface plane is then calculated from the inner-layer constant capacitance equation by the equation

$$\psi^0 = \psi^b + \sigma^0 / C_1 \quad (D.5)$$

where C_1 is the inner-layer capacitance. This set of equations completely defines the electrochemical potentials for adsorbed species.

The Hessian matrix must also be modified to include the derivatives of the electrostatic potentials. The result is

$$\begin{aligned} \left(\frac{\partial \psi^b}{\partial n_j} \right)_{\bar{n}} &= \frac{2RT}{F} \left[\frac{1}{\left(\frac{-\sigma^d}{B2 \cdot I^{0.5}} \right)^2 + 1} \right] \left[\frac{B(z_j^0 + z_j^b)}{B2 \cdot I^{0.5}} + \frac{\sigma^d (z_j)^2}{4 \cdot B2 \cdot I^{1.5} \cdot V_S} \right] \\ &+ \frac{B}{C_2} (z_j^0 + z_j^b) \end{aligned} \quad (D.6)$$

and

$$\left(\frac{\partial \psi^0}{\partial n_j} \right)_{\bar{n}} = \left(\frac{\partial \psi^b}{\partial n_j} \right)_{\bar{n}} + \frac{B z_j^0}{C_1} \quad (D.7)$$

Of special interest in Equation (D.6) is the fact that the electrostatic potentials for adsorbed species also affect the Hessian elements for non-adsorbed species (through the ionic-strength derivatives). Such terms are neglected in models like MINTEQ, where derivatives of the ionic strength with respect to the component activities are neglected. However, inclusion of such terms can significantly improve model convergence when large masses of solutes are adsorbed.

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