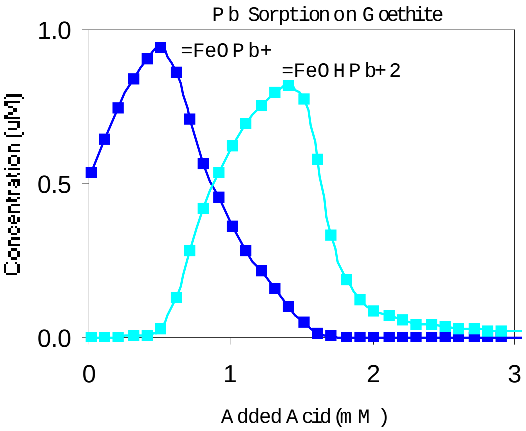
MINTEQA2
for
Windows



Equilibrium Speciation Model
version 1.50

Allison Geoscience Consultants, Inc.
and
HydroGeoLogic, Inc.

MINTEQA2 for Windows®

Equilibrium Speciation Model

Version 1.50 for
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Developed by

Allison Geoscience Consultants, Inc.
3920 Perry Lane
Flowery Branch, GA 30542
770-525-1191

and

HydroGeoLogic, Inc.
1155 Herndon Parkway
Suite 900
Herndon, VA 20170

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Getting Started

MINTEQA2 for Windows is an easy to use equilibrium speciation model for aqueous systems. It uses the same computational algorithms and thermodynamic databases as the DOS version distributed by the U.S. Environmental Protection Agency. (MINTEQA2 for Windows will be referred to simply as MINTEQA2 in this documentation; when reference to the U.S. EPA's DOS version is intended, it will be explicitly indicated.)

Installation and Overview

To install MINTEQA2, insert the CD in your CD drive. If autorun is enabled on your computer, the setup program will begin automatically. If setup does not begin automatically, click Run on the Windows Start menu, then type D:\setup (assumes D is the drive letter of your CD drive). After setup begins, follow the instructions on your screen.

To use MINTEQA2, you must specify the fundamental chemical composition and constraints for the system of interest. You do this by clicking buttons along the left side of the main screen. Buttons presented include:

General Parameters - Specify ionic strength, temperature, units of concentration, etc.

Total Concentrations - Specify total concentrations of Ca, Na, CO3, and other components

Equilibrium Constraints - Specify constraints such as equilibrium pH, pe, solid and gas phases

Sorption - Specify a sorption model and associated sorption reactions

DOM - Specify dissolved organic matter reactions

Precipitation - Specify solid phases permitted to precipitate

Excluded Species - Specify species to be excluded from the equilibrium calculations

The status of entries you have made is displayed in the screen area to the right of these buttons. Upon equilibration, this area displays the output information that describes the equilibrium speciation.

Buttons on the menu bar at the top of the main screen provide options for file manipulation, setting up sensitivity analysis runs, editing thermodynamic data, and equilibrating the system.

Upon selecting **Equilibrate** from the menu bar or clicking the **Equilibrate** button located on the left side of the main screen, MINTEQA2 computes the equilibrium speciation of the system you have posed. The output is first displayed in summary form, but more detailed output can be displayed by clicking the **Full Output** button. Graphs showing the concentration of any species versus a sensitivity parameters can be displayed by clicking the **View Graph** button.

Three example/tutorial problems with step-by-step instructions are provided in the online help document and in this guide (beginning on p. 33) under the heading Examples. The examples are organized in order of complexity (simplest first). Use of MINTEQA2 for Windows is intended to be intuitive, but in case it is not so for you, working through these three problems will quickly make you acquainted with the most important model options.

Technical Support

The online help document is designed to answer most questions about MINTEQA2 for Windows and how to use it. Technical support is available from Allison Geoscience Consultants, Inc. You may email us at minteq@allisongeoscience.com. Please include a description of the problem you are having and, if applicable, send the input file that generates the problem as an attachment. You may also call us at 770-535-1191. We are happy to expend reasonable efforts to be of service.

The user manual for the DOS version distributed by the U.S. EPA Center for Exposure Assessment Modeling also contains information that may be helpful. Visit (http://www.epa.gov/ceampubl/mmedia/minteq/index.htm) to obtain this document and a later user manual supplement. These documents provide information that may help you understand how the MINTEQA2 calculations are performed, but keep in mind that they were developed for the DOS version.

Using MINTEQA2: The Main Screen

The opening window is also the main window for MINTEQA2 for Windows. The method of using this model consists of specifying system variables and parameters, chemical total concentrations, and optional constraints or reactions and then equilibrating the system. The starting place for doing all of these things in the main screen. Buttons along the left side of the main screen allow you to specify the various types of input parameters.

A summary of all system and chemical parameters that have been entered or set is displayed in the **Project** window on the main screen. After all parameters are set as desired, you can equilibrate the system by simply clicking the **Equilibrate** button or by clicking **Equilibrate** from the menu bar. The calculations are performed and the result is stored in an output file. The output file is displayed in either summary or full form in the **Output** window on the main screen which allows you to scroll to examine the result. Special options allow you to specify that the model run is to be treated as a sensitivity run. These options are selected from the **Sensitivity Analysis** menu bar item. The output file from sensitivity runs will also be displayed in the **Output** window, but you may choose to view the result graphically. The **View Graph** button on the main screen presents the **Graph** window. From this window you can specify what is to be plotted and set plot parameters. You can toggle back and forth among the **Output** window, the **Graph** window, and the **Project** window by clicking the buttons on the main screen.

General Parameters

Use the **General Parameters** button on the MINTEQA2 main screen to select options for ionic strength, alkalinity, activity coefficients, temperature, and units of concentration.

Ionic Strength

The equilibrium ionic strength can be calculated by MINTEQA2 based on species concentrations, or you may specify the equilibrium ionic strength. You may indicate your choice on the **General Parameters** window. If MINTEQA2 is to calculate the ionic strength (I), it uses

$$I = 0.5 \sum_i z_i^2 [S_i]$$

where Z_i is the charge of species I and $[S_i]$ is its concentration.

You may wish to specify the equilibrium ionic strength as a sensitivity parameter to investigate its effect on speciation (see Sensitivity Analysis).

Alkalinity

MINTEQA2 can use the measured alkalinity of the water sample to determine the total inorganic carbon. If the total inorganic carbon of the sample is available as a separate measurement (usually expressed as total HCO_3^- or total CO_3^{2-}), then that measurement can be entered directly as the appropriate total concentration for the component CO_3^{2-}, and alkalinity should not be entered. However, sometimes total inorganic carbon is not specifically measured. In that case, alkalinity can be entered and MINTEQA2 will use it to provide an estimate of the total inorganic carbon in the system.

Alkalinity may be entered by the user with units of mg CO_3/L, mg $CaCO_3$/L, or meq/L. The equilibrium pH corresponding to the sample pH **must** be specified when alkalinity is specified. The estimation of total inorganic carbon from the specified alkalinity is based on the assumption that the alkalinity titration was continued to the CO_2 equivalence point.

A default alkalinity equation is used by MINTEQA2 that includes all relevant carbonate species and certain non-carbonate species. In the default equation presented below, only the most important carbonate species are listed for brevity.

$$ALK = [HCO_3^-] + 2[CO_3^{2-}] + 2[CaCO_3(aq)] + 2[NaCO_3^-]$$

$$- [H^+] + [OH^-] + [CaOH^+]$$

$$- [H_3PO_4] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [CaHPO_4]$$

$$+ [NH_3(aq)] + [HS^-] + 2[S^{2-}] + [H_2BO_3^-] + [H_3SiO_4^-]$$

If species in the alkalinity equation are not relevant to a particular problem because their components are not all present, they are simply dropped from the equation. For some problems, other species may need to be added to the alkalinity equation. This must be done manually by editing the file ALK.DBS. See the U.S. EPA MINTEQA2 version 3.0 user manual for instructions or contact Allison Geoscience Consultants for advice (see Technical Support).

Activity Coefficients

MINTEQA2 allows the user to choose from two available methods to estimate activity coefficients for ionic species: the Davies equation or the modified Debye-Hückel equation.

Because of non-ideal effects, the thermodynamic activity of a species in solution differs from its actual concentration. For any particular species *I*, the activity coefficient (is a proportionality factor relating the activity of the species $\{S_i\}$ to the concentration of the species $[S_i]$:

$$\{S_i\} = \gamma[S_i]$$

For most charged species within the ionic strength domain appropriate for MINTEQA2, the activity coefficient will be less than unity. The activity coefficient for a neutral species may be greater that unity. In an ideal solution (infinitely dilute), the activity coefficients will all be unity.

You can choose the method of calculating activity coefficients on the **Specify General Parameters** window.

Temperature

MINTEQA2 is suitable for speciation of aqueous systems in the temperature range of 0 to 100 degrees C. The log K values for reactions in the database are specified for a temperature of 25 C (the default temperature in MINTEQA2). If a different temperature is specified in a model run, the log K values are adjusted. For most species, the temperature adjustment is accomplished by use of the reaction enthalpy (from the thermodynamic database) and the van't Hoff equation. For a small number of species, the adjustment is determined from an empirical expression relating log K to temperature. These empirical relationships are stored in the file ANALYT.DBS.

The temperature is specified on the **Specify General Parameters** window.

Units of Concentration

The concentration units used to specify input data in MINTEQA2 are mol/L, mg/L, or meq/L. You can set the **Default Concentration Units** on the **Specify General Parameters** window. This sets the initial units presented to the user in data entry fields and the concentration units that will be written in the MINTEQA2 input file being created. For specific entries, you are often given the option of specifying concentration in units other than the default units setting.

In the output file, all concentrations are expressed in mol/L unless otherwise indicated.

Total Concentrations

The "total concentration" of a component upon input refers to the concentration assigned by the user for that component. The total concentration must be specified for the particular species that MINTEQA2 employs as the component species. For example, the user may wish to specify that calcium is a component and that its total concentration is 40 mg/L. This is done by clicking the **Total Concentrations** button on the main screen to display the **View or Change Total Concentrations** window. Click **Add or Delete Components** and a list of all MINTEQA2 components appears in the left panel from which you may select components as needed by highlighting each and clicking **Add**. To add calcium, highlight the component species Ca+2 and click **Add**. After all components are chosen, click **OK** and the **View or Change Total Concentrations** window displays all selected components with space to enter the concentration (and concentration units) of each. It must be understood that by entering 40 mg/L the user is NOT imposing a constraint that the equilibrium Ca+2 concentration be 40 mg/L. Ca+2 is simply the component species used in MINTEQA2 for calcium; the actual distribution of the 40 mg/L calcium among the many possible calcium-containing species at equilibrium, including the equilibrium concentration of Ca+2, is determined by MINTEQA2.

You may also introduce total concentrations by adding Initial Finite Solid Phases. The component totals for an initially present solid phase is treated as additional to any component total concentrations already specified. For example, if you pose a problem in which you specify a total component concentration of Ca of 0.001 M and you also specify 0.001 moles of calcite as an initially present finite solid, the total system concentration of Ca is 0.002 mol/L.

The total concentration of a component at equilibrium may exceed the "total concentration" entered (as component total or finite solid) if redox-sensitive components are present and the equilibrium has resulted in redox transformation (e.g., ferrous iron to ferric iron). Also, the total concentrations of components involved in equilibrium gas phases at fixed partial pressure or equilibrium solid phases change as these species dissolve into the system or leave the system via degassing or precipitation.

Finite Solid Phases

Upon input, initial solid phases present in finite, measurable amounts can be specified by clicking the **Initial Finite Solid Phases** button on the **View or Change Total Concentrations** window. The solid phase that is to be treated as initially present is selected by first selecting the class of solid phases to which it belongs (select from drop-down menu) and then choosing the specific solid phase desired. For example, to specify 100 mg/L of gibbsite, use the drop down menu to select "Hydroxides" as the class of solids (minerals), then highlight gibbsite in the list of available solids, then click **Add** . A follow-up screen will request the concentration of this solid phase.

Initially present finite solids are subject to complete dissolution if equilibrium conditions dictate. If you want to specify an equilibrium solid phase , i.e., one that is required to be present at equilibrium, click **Equilibrium Constraints** on the main screen.

Equilibrium Constraints

Certain equilibrium constraints on the system can be imposed by the user . The user can specify the equilibrium pH, the equilibrium pe (Eh), the partial pressure of one or more equilibrium gas phases, or the existence of one or more equilibrium solid phases (minerals). Such constraints can be specified in various combinations. The user is cautioned that the imposition of any equilibrium constraint may significantly impact the resulting equilibrium composition of the system and that imposing such constraints implies knowledge about the equilibrium state of the system.

pH Options

MINTEQA2 allows the user to impose an equilibrium pH on the system. The alternative, of course, is to allow the model to calculate the equilibrium pH. The question of whether to specify the equilibrium pH or allow it to be calculated is an important one. The choice is made based on what you know about the system (and what you do not). In order for MINTEQA2 to calculate the equilibrium pH, you must know and enter the total concentration for the component for hydrogen (H^+). This quantity is referred to as the TOTH in various textbooks on aqueous chemistry.

Imposing an equilibrium pH does not require knowledge of the TOTH of the system. Instead, it implies that the user knows the equilibrium activity of H^+ (i.e., the pH).

pE or Eh Options

The pE is the negative logarithm of the electron activity. (The Eh is related to the pE by a proportionality constant for a particular temperature.) The user may elect to specify the equilibrium pE or it may be calculated. If the equilibrium pE is specified, the electron activity is constrained accordingly. If a redox couple is also specified as an equilibrium constraint, mass is shifted from one member of the redox couple to the other in such a way as to honor the Nernst equation at equilibrium. For example, if Fe^{2+} and Fe^{3+} are selected as components, the pe is specified and the redox couple

$$Fe^{3+} + e^- = Fe^{2+}$$

is specified as an equilibrium constraint, MINTEQA2 will calculate the amount or iron in each of the two oxidation states corresponding to the specified equilibrium pE.

If the equilibrium pe is not specified and a redox couple is imposed, it is implicit that the user has provided the model with measured total concentrations for the two members of the redox couple and that MINTEQA2 is expected to use the component activities in the Nernst equation to calculate the equilibrium pE. In this case, no redox transformation will take place.

Other species that impact the equilibrium pE are certain solid phases and equilibrium gases that include redox transformations in the reaction. Examples include pyrite and O2(g).

Equilibrium Solid Phases

Equilibrium solid phases are constrained to be present at equilibrium-- they are not subject to total dissolution and no input concentration is required. The particular solid phase desired can be selected from the list of solids for a particular class of solids. For example, to specify that dolomite is present at equilibrium, click the **Equilibrium Constraints** button on the main screen, then the **Add/Delete** button under Solid Phases. Use the drop down menu to select "Carbonates" as the class of solids (minerals), then highlight dolomite in the list of available solids, then click **Add** .

Note: See finite solid phase to see how to specify a measured amount of a solid phase as an input entry. Such finites solids are not imposed as equilibrium constraints.

Equilibrium Gas Phases

Equilibrium gas phases are constrained to exert a fixed partial pressure at equilibrium. The gases may dissolve into or be expelled from the system in accord with specified partial pressure and the solution composition. They are not subject to total dissolution. The user must specify the gas partial pressure, which may be given in bars (bar) or atmospheres (atm). The particular gas phase desired can be selected from the list of gases. For example, to specify that O2(g) is present at an equilibrium partial pressure of 0.2 atm, click **Equilibrium Constraints** on the main screen, then click the **Add/Delete** button under Gas Phases. Highlight O2(g) in the list of available gases, then click **Add** . Be sure to enter the equilibrium partial pressure of 0.2 atm on the follow-up screen.

Fixed Ratio Redox Couples

The ratio of the activities of two members of a redox couple may be imposed as an equilibrium constraint. This ratio is implicit in the standard reduction potential of the half redox reaction

$$\mathrm{Ox} + n\mathrm{e}^{-} = \mathrm{Red} \qquad \log K$$

where Ox represents the oxidized component, e^- represents the electron, n is the stoichiometry of the electron, and Red represents the reduced component. When such a redox couple is specified as an equilibrium constraint and the equilibrium pE (or Eh) is also specified, mass is shifted from one member of the redox couple to the other in such a way as to honor the Nernst equation at equilibrium. For example, if Fe^{2+} and Fe^{3+} are selected as components, the pE is specified and the redox couple

$Fe^{3+} + e^{-} = Fe^{2+}$

is specified as an equilibrium constraint, MINTEQA2 will calculate the amount or iron in each of the two oxidation states at equilibrium.

If the equilibrium pE is not specified and a redox couple is imposed, it is implicit that the user has provided the model with measured total concentrations for the two members of the redox couple and that MINTEQA2 is expected to use the component activities in the Nernst equation to calculate the equilibrium pE. In this case, no redox transformation will take place.

The particular redox couple desired can be selected from the list of available couples. For example, to specify the sulfur couple SO_4^{2-} to HS^-, click **Equilibrium Constraints** on the main screen, then click the **Add/Delete** button under Redox. Highlight the HS^-/SO_4^{2-} couple in the list of available couples, then click **Add**.

Sorption

Sorption reactions may be included in MINTEQA2 calculations. All sorption parameters are accessible by clicking the **Sorption** button on the main screen. There are seven sorption models available in MINTEQA2. The user may specify up to two sorbing surfaces (sorbents), and each sorbent may have up to two site types. (Generally only one sorbent is used; two are included for academic rather than practical reasons.)

For all sorption models, it is the user's responsibility to add sorption reactions, either by appending a file containing an already prepared database of reactions, by directly defining reactions within this application, or by a combination of these methods. Reactions organized and entered for a particular model run, whether included by reading from an existing file or by directly defining, or by both methods, may be saved in a sorption reaction file for subsequent use. Besides the sorption reactions themselves, one or more of the various sorption models may require that the user specify the sorbent material concentration, the sorbing site concentration, the specific surface area of the sorbent, and/or various electrostatic terms. The table below lists the available sorption models (somewhat in the order of increasing complexity) with the required input parameters.

Model	**Mass of Soil**	**Sorbent Conc.**	**Site Conc.**	**Specific Surface Area**	**Capacitance Terms**
Activity K_d	Yes	No	No	No	No
Activity Freundlich	No	No	No	No	No
Activity Langmuir	No	No	Yes	No	No
Ion Exchange	No	No	Yes	No	No

Model	**Mass of Soil**	**Sorbent Conc.**	**Site Conc.**	**Specific Surface Area**	**Capacitance Terms**
Diffuse-Layer	No	Yes	Yes	Yes	No
Constant Capacitance	No	Yes	Yes	Yes	one
Triple-Layer	No	Yes	Yes	Yes	two

Sorption Models

Seven sorption models are available in MINTEQA2 including common empirical models, an ion exchange model, and surface complexation models. The Langmuir model is essentially a surface complexation model without electrostatic terms. Other surface complexation models include the constant capacitance model, the diffuse layer model, and the triple layer model. Click the links below for more details about each model.

Activity K_d Model

The linear partitioning or Activity K_d model is the simplest of the sorption models included in MINTEQA2. It provides for linear partitioning of the sorbate ion between the sorbent and the solution. Like the Activity Freundlich model, it does not require the user to specify the concentration of sorption sites. The supply of sorption sites is assumed to be limitless and no mass balance is performed on the sites. For a solute metal subject to sorption, the infinite concentration of sites implies that the fraction of metal sorbed is unaffected by the supply of remaining unreacted sites. Thus, for a particular system, increasing the total metal concentration results in a proportionate increase in the amount sorbed. This effectively limits the application of the linear partitioning model to systems with low metal concentration relative to the concentration of sorbing sites.

The traditional isotherm expression for K_d is

$$C_s = K_d \; C_d$$

where C_s and C_d are the equilibrium sorbed and dissolved metal concentration, respectively, and K_d is the proportionality constant. In MINTEQA2, the linear partitioning model is implemented by including reactions formulated as follows:

$$M \quad + \quad X \quad = \quad MX \qquad\qquad K_d$$

where M is a metal solute ion, X is the neutral surface site, and K_d is the equilibrium constant for formation of the product according to the mole balance equation:

$$K_d = \frac{[MX]}{\{M\}\;\{X\}}$$

where quantities in square brackets represent concentration and those in braces represent activity. The correspondence between this expression and the form of the isotherm as shown above is apparent by observing that the activity of sites {X} is equal to one by definition because the supply is limitless. Thus,

$$[MX] = K_d \{M\}$$

The key difference between this expression and the traditional expression above is that this involves the activity of the *free* metal component in solution, whereas C_d above represents the *total* metal in solution as it is distributed among many species.

Charges are omitted from the above reaction for convenience, but charge balance is maintained by assigning charge to the product as implied by the neutral charge of the site X and the valency of the metal.

Note that MINTEQA2 assumes that the activity coefficients of all surface species are unity. It is for this reason that the mole balance equation above involves the concentration of product [MX] rather than its activity.

Soil Mass

This is the mass of soil with which one liter of solution is equilibrated. It is used in these calculations to "unnormalize" the Kd which is presumed to have units of L/kg. After multiplying by the mass of soil (kg/L), the dimensionless Kd simply represents the ratio of sorbed metal to dissolved metal for one liter of solution. This dimensionless Kd is then used in equilibrium calculations.

Activity Freundlich Model

The Activity Freundlich sorption model provides for sorption reactions that obey the Freundlich Isotherm. Like the Activity K_d model, it does not require the user to specify the concentration of sorption sites. The supply of sorption sites is assumed to be limitless and no mass balance is performed on the sites. For a solute metal subject to sorption, the infinite concentration of sites implies that the fraction of metal sorbed is unaffected by the supply of remaining unreacted sites. However, the Freundlich model is still able to account for the decrease in fraction of metal sorbed as the total metal concentration is increased. This effect is included by means of an exponent in the traditional isotherm expression

$$C_s = K_f \; C_d^{\alpha}$$

where C_s and C_d are the equilibrium sorbed and dissolved metal concentration, respectively, " is an exponent that represents the non-linearity in the isotherm, and K_f is the proportionality constant. The Freundlich isotherm is identical to the linear partitioning model if is made equal to one. In MINTEQA2, the Activity Freundlich model is implemented by including reactions formulated as follows:

$$M + X = MX \qquad K_f$$

where M is a metal solute ion, X is the neutral surface site, and K_f is the equilibrium constant for formation of product according to the mole balance equation:

$$K_f = \frac{[MX]}{\{M\}^{\alpha}[X]}$$

where quantities in square brackets represent concentration and those in braces represent activity. The correspondence between this expression and the traditional form of the isotherm as shown above is apparent by observing that the activity of sites {X} is equal to one by definition because the supply is limitless. Thus,

$$[MX] = K_f \{M\}^{\alpha}$$

The key difference between this expression and the one above is that this involves the activity of the *free* metal component in solution, whereas C_d above represents the *total* metal in solution as it is distributed among many species.

Charges are omitted from the above reaction for convenience, but charge balance is maintained by assigning charge to the product as implied by the neutral charge of the site X and the valency of the metal.

Note that MINTEQA2 assumes that the activity coefficients of all surface species are unity. It is for this reason that the mole balance equation above involves the concentration of product [MX] rather its activity.

Activity Langmuir Model

The Langmuir sorption model treats sorption reactions as completely analogous to other solution coordination reactions. It requires the user to specify the concentration of sorption sites, which is subject to the same mass balance constraints as other components whose total concentrations are specified. This is in contrast to the Activity K_d and Activity Freundlich models for which the site concentration is assumed to be limitless. For a solute metal subject to sorption, the finite concentration of sites results in a smaller fraction of sorbed metal at high total metal concentration as compared with low total metal concentration. The reduction in the fraction of metal that is sorbed at high metal concentration is due to the reduction in the number of remaining (unreacted) sites. The Langmuir model is implemented in MINTEQA2 by including reactions formulated as follows:

$$M + X = MX \qquad K_L$$

where M is a metal solute ion, X is the neutral surface site, and K_L is the equilibrium constant for formation of product according to the mole balance equation

$$K_L = \frac{[MX]}{\{M\}[X]}$$

Charges are omitted from the above reaction for convenience, but charge balance is maintained by assigning charge to the product as implied by the neutral charge of the site X and the valency of the metal. More complicated reactions can be included. For example, X may be envisioned as a hydroxyl group (XOH) subject to protonation or deprotonation. Also, competitive sorption of major ions and trace metals can be included by including the appropriate reactions.

Note that MINTEQA2 assumes that the activity coefficients of all surface species are unity. It is for this reason that the MX and X species in the mole balance equation above are written in terms of concentrations rather than activities. The electrostatic models in MINTEQA2 use the same basic formulation as the Langmuir model, but activity coefficients are treated as electrostatic interaction terms whose form is dependent on the particular model used (Constant Capacitance, Diffuse-Layer, or Triple-Layer).

Ion Exchange Model

Ion exchange sorption is the process by which an ion from solution is exchanged for one on the solid surface. Solution activities and intrinsic properties of ions determine their relative propensity to compete for surface sites. The ion exchange model in MINTEQA2 assumes that the site on the surface is initially occupied by an exchangeable ion that will be expelled into solution when exchange occurs. The ion exchange reaction and its corresponding mass action expression are given by:

$$SOHM_1 \quad + \quad M_2 \quad = \quad SOHM_2 \quad + \quad M_1$$

and

$$K_{ex} \quad = \quad \frac{[SOHM_2]\,\{M_1\}}{[SOHM_1]\,\{M_2\}}$$

where M_1 is the ion initially present on the exchange site SOH, M_2 is the replacing ion to be adsorbed, and $SOHM_1$ and $SOHM_2$ are surface sites occupied by the respective ions. Note that the site name is arbitrary: you can use "X" or any other convenient designation instead of SOH.

No attempt is made to calculate activity coefficients for the surface sites; activity coefficients are arbitrarily taken as unity. K_{ex} is sometimes called the selectivity coefficient; it can be written in terms of concentrations by replacing the activity of each solute species in the mass action equation with the product of the concentration and activity coefficient. If M_1 and M_2 are of equal charge, the activity coefficients cancel.

When specifying an ion exchange reaction, the user must specify the ion that initially occupies the site (the ion to be expelled to solution), the ion to be sorbed, the reactant stoichiometries, and the selectivity coefficient. Note that reaction stoichiometries may be related to the ion charge. For example, a single Ca^{2+} ion may replace two Na^{+} ions and thus occupy two sites. Selectivity coefficients can be derived from the literature for most common ions, such as Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, etc., but they are seldom available for trace metals

Diffuse-Layer Model

MINTEQA2 is capable of including sorption reactions that behave according to the MIT Two-Layer model (also called diffuse-layer model, DLM) developed by D. Dzombak (see Dzombak and Morel, 1990).

The DLM is accessible by clicking **Sorption** on the main screen, then selecting Diffuse Layer model. There are pre-defined databases of sorption reactions for hydrous ferric oxide (HFO) and goethite for the diffuse-layer model. The former corresponds to reactions for HFO given in Dzombak and Morel (1990); the latter corresponds to reactions for goethite given in Mathur (1995) .

Users may indicate that either of these databases is to be used or may supply their own reactions on the **Select Sorption Model and Define Surfaces** screen by clicking the **Edit Reactions** button pertaining to the site where the reaction occurs.

Constant Capacitance Model

MINTEQA2 is capable of including sorption reactions that behave according to the constant capacitance model (CCM) developed by Schindler, Stumm, and others (Schindler et al., 1976; Stumm et al., 1976, 1980).

The CCM is accessible by clicking **Sorption** on the main screen and selecting the constant capacitance model. The required input parameters for the CCM include the concentration of sorbent (sorbing surface), the capacitance (farads/m^2), the specific surface area of the sorbent (m^2/g), and the site concentration in moles of sites per liter. Up to two types of sites where reactions occur may be defined on each of two available surfaces. There is no pre-defined database of sorption reactions for the CCM; the user must supply reactions on the **Select Sorption Model and Define Surfaces** screen by clicking the **Edit Reactions** button pertaining to the site where the reaction occurs. For more information about the CCM, see the references cited above or a concise review of sorption models and their use in chemical equilibrium models in Goldberg (1995).

Sorption reactions entered for use in a particular model run may be saved for use in subsequent runs without tedious re-entry. This option is available in the course of defining sorption reactions.

Capacitance

The constant capacitance adsorption model employs a capacitance term in representing the electrostatic field associated with the sorbent surface. The capacitance C relates surface charge density to surface potential.

With its single plane of charge, the constant capacitance model requires a single capacitance density expressed in farads per square meter (farads/m^2). Experimentally determined capacitance densities often show great variability, even for a single mineral surface. But in practice, a single optimum value is commonly used for a particular mineral surface. Examples are C=1.8 farads/m^2 for goethite and C=1.06 farads/m^2 for aluminum oxide. See Goldberg (1992) for more information.

Triple-Layer Model

MINTEQA2 is capable of including sorption reactions that behave according to the triple-layer model (TLM) developed by Davis and coworkers (Davis et al., 1978, Davis and Leckie, 1978, 1980). A modified version of the TLM was developed by Hayes and Leckie (1986) in which sorption products for metals and ligands may be treated as inner-sphere complexes. MINTEQA2 includes this capability as well.

The TLM is accessible by clicking **Sorption** on the main screen and selecting the triple-layer model. The user must enter the concentration of sorbent (g/L), the inner-layer and outer-layer capacitances (farads/m^2), the specific surface area of the sorbent (m^2/g), and the site concentration in moles of sites per liter. Up to two types of sites where reactions occur may be defined. There is no pre-defined database of sorption reactions; the user must supply reactions on the **Select Sorption Model and Define Surfaces** screen by clicking the **Edit Reactions** button pertaining to the site where the reaction occurs. Each reaction is entered by indicating the site stoichiometry in the reaction and the stoichiometries of all other reactants. The reactants must be MINTEQA2 components. The electrostatic potential terms are entered automatically by MINTEQA2 in accordance with whether the reaction is to be treated as an inner-sphere complex or an outer-sphere complex. Note that the sorption or desorption of H^+ is always treated as an inner-sphere complex and the sorption of an electrolyte ion is always treated as an outer-sphere complex. Metals and ligands may be treated either way in accord with the user’s wishes (indicated separately for each reaction on the **Add or Edit Sorption Reaction** screen).

For more information about the triple-layer model, see the references cited above or a concise review of sorption models and their use in chemical equilibrium models by Goldberg (1995) .

Inner and Outer-Layer Capacitance

The triple-layer adsorption model employs two capacitance terms in representing the electrostatic field associated with the sorbent surface. The capacitance C relates surface charge density to surface potential.

Capacitance density is expressed in farads per square meter (farads/m^2). Experimentally determined capacitance densities often show great variability, even for a single mineral surface. But in practice, a single optimum value is commonly used for a particular mineral surface.

The triple-layer model assumes three planes of charge denoted o-, β -, and d-planes. Two capacitance densities are required to represent the relationships between surface charges and surface potentials. The "inner-layer" capacitance relates charge and potential between the o-plane and the β -plane. The "outer-layer" capacitance relates charge and potential between the β -plane and the d-plane. Although experimental studies show variation in capacitance densities with pH and ionic strength, the capacitance densities are usually treated as adjustable parameters in practical use with the triple-layer model. The value of the inner-layer capacitance density is adjusted to find the value that optimizes the fit of the experimental data and the outer-layer capacitance density is set at 0.2 farads/m^2 (Goldberg, 1995).

Sorbents

You may specify up to two sorbents (sorption surfaces) in a model run. These are generically identified as Surface 1 and Surface 2 on the **Select Sorption Model and Define Surfaces** screen. (As a practical matter, one surface only is used for most problems.) The parameters needed to define each surface depend on the sorption model used. Parameters that are needed for the selected model are automatically activated on the screen; parameters not relevant to that model are greyed out. Each sorption surface can have up to two sorption sites defined. Each site can have multiple reactions. Parameters that may be required include:

1. An arbitrary name for the sorbing surface or sorbent (e.g., sorbent1, FeOx, HFO, etc.)
2. The specific surface area of the sorbent (m^2/g)
3. The concentration of sorbent (g/L)
4. The site concentration in moles of sites per liter for one or two site types.

The site represents the surface entity which reacts with solutes thus defining a sorption reaction.

Only those parameters on the **Select Sorption Model and Define Surfaces** screen that are activated (not greyed out) are needed. (See Sorption for a table indicating which parameters are relevant to each model.)

Once a site is specified and its activated parameters are specified, click the **Edit Reactions** button to define or edit sorption reaction for that sorption site.

Sorbent Concentration

The sorbent concentration is needed for the constant capacitance, diffuse-layer and triple-layer sorption models. It is the concentration in g/L of the sorbing substance– the substance whose surface properties are responsible for the sorption phenomenon. For example, if the sorbent is hydrous ferric oxide (HFO), the sorbent concentration is the amount of HFO that one liter of equilibrating solution has access to. In a natural groundwater system, this generally will be much smaller than the corresponding amount of soil (or aquifer material) that contains the HFO (and the solution).

Sorbent Sites

MINTEQA2 can accommodate two types of sorption sites for each sorbent (sorption surface) defined. The distinction between the two sites is completely dependent upon the user's definition of site reactions-- there is no implicit distinction between the sites. For each site type, multiple reactions may be defined. In order for the site to be active, at least one reaction must be defined for it. If a site is defined but no reactions are defined for it, it will appear in the MINTEQA2 run but will remain unreacted.

Sorbent Site Concentration

The sorbent site concentration in moles of sites per liter of solution is required for the Langmuir, constant capacitance, diffuse-layer, triple-layer, and ion exchange models. In the scientific literature, the site concentration is sometimes given in number of sites per gram of sorbent or number of sites per square meter of sorbent. You can use the sorbent concentration (g/L) and/or the specific surface area (m^2/g) and Avogadro's number to convert the site concentration to the required mol/L.

Define Sorption Reactions

For each sorption site, the user must supply relevant sorption reactions. Reactions must always be defined in terms of MINTEQA2 components. Buttons on the **Define Sorption Reactions** window are provided for editing, adding, deleting, reading and writing individual reactions.

To Add a Reaction

To add a new sorption reaction, click the **Add New Reaction** button to display a form for entering your reaction. The form that appears depends upon the type of sorption model you have selected. For all models except the triple-layer model (TLM), a two-line fill-in-the-blank reaction form appears. A different form appears for entering TLM reactions; it requires you to assign your reactants to the o-plane or beta-plane.

To Edit a Reaction

To edit any reaction that has been added or read from a file, highlight it in the window of currently defined reactions and click **Edit this Reaction**. The reaction will be entered in the reaction form editor with the sorbent site and other reactants on the left side of the reaction and the reaction product (sorption species) and other products displayed on the right. You may eliminate or add reactants, adjust stoichiometries, or change the log K or enthalpy.

To Delete a Reaction

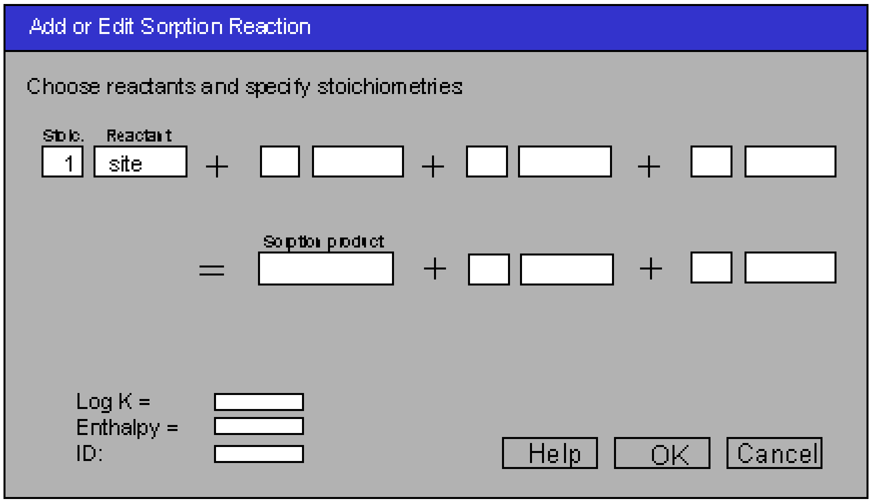
To delete any reaction that has been added or read from a file, highlight it in the window of currently defined reactions and click **Delete this Reaction** .

To Write or Read Reactions to/from a File

Click the **Write Reactions to File** button to write currently defined reactions to a file for safekeeping. Files containing reactions that have been saved may be read for use again by clicking the **Read Reactions from File** button.

Add Sorption Reaction (not Triple-Layer)

MINTEQA2 provides a form for entering sorption reactions. The form is accessed by clicking the **Add New Reaction** button on the **Define Sorption Reactions** window. This form is used to enter reactions for all sorption models except the triple-layer model (TLM)



Choose reactants and specify stoichiometries

Stoic.: 1
Reactant: site

Rules for Using the Reaction Form

There are some important rules to observe in using the reaction form:

1. Notice that the two-line reaction is written with the sorbent site on the left side of the reaction (left of the equals sign) and the primary sorption product (sorption species for which you must supply a name) on the right side. The sorbent site is entered with a stoichiometry of 1, but you may change it if desired; you may also supply a more chemically descriptive name (e.g., XOH if desired). The primary sorption product has an implicit unalterable stoichiometry of 1. Use the drop-down menu to indicate each component involved in the reaction on both the reactant and product sides. Up to five components not counting the sorbent site may be specified; enter the reaction stoichiometry of each. (Note: The primary sorption reaction product cannot be a MINTEQA2 component species. All other reactants and products involved in the reaction MUST be MINTEQA2 component species.)

2. If the reaction you wish to model is not written in terms of MINTEQA2 components, you must reformulate it so that it is. Do this before you enter any reactants on the reaction form. For example, if you wish to model

$XOH + Cr^{3+} = XO^{-}\_Cr^{3+} + H+ \quad \log K = 3.4$

you must reformulate it because Cr^{3+} is not the component used in MINTEQA2 for trivalent Cr. The appropriate component is $Cr(OH)_2^{+}$. The process of reformulating a reaction in other components is basically one of adding or subtracting other reactions. In most cases, the reaction that should be added or subtracted can be obtained from the MINTEQA2 thermodynamic database (THERMO.DBS). In the example above, the reaction

$Cr(OH)_2^{+} - 2H2O + 2H^{+} = Cr^{3+} \quad \log K = 9.5688$

obtained from THERMO.DBS should be added to the sorption reaction to give

$XOH + Cr(OH)_2^{+} - 2H2O + H^{+} = XO^{-}\_Cr^{3+} \quad \log K = 13.0$

This reaction is now ready for entry on the reaction form. Notice that as the reactions were added, so also were their log K values.

3. The form accommodates the unique features of each sorption model: when using the Freundlich model, a special field appears on the screen for entry of the Freundlich exponent; when using the Kd model, the Kd value you enter will be used with the soil mass entered to compute the log K for the reaction.

4. The mass action expression for sorption reactions composed for the constant capacitance model and diffuse-layer model contains an exponential term that represents the electrostatic potential term. The net charge of the sorption species is used automatically in MINTEQA2 to compute the coefficient (net change in charge) for the potential term. For example, the reaction

$XOH + Cd^{+2} = XOCd^{+} + H^{+}$

entered for the constant capacitance or diffuse-layer models will have the following mass action expression:

$$K = \frac{[XOCd^{+}]\{H^{+}\}}{[XOH]} \exp[F\psi_{o}/RT]$$

The coefficient for the potential term (psi) is +1 because the change in charge of the site due to the reaction is +1. The exponential term is absent for all other sorption models except the TLM; the more complicated potential terms for TLM reactions require a special form. (See link above.)

Examples showing the entries on the reaction form for several typical reactions are provided in the online help document in MINTEQA2 for Windows.

Add Triple-Layer Model Sorption Reaction

MINTEQA2 provides a form for entering TLM sorption reactions. The form is accessed by clicking the **Add New Reaction** button on the **Define Sorption Reactions** window. This form is used to enter reactions for the triple-layer model only.

The triple-layer model (TLM) allows for specific adsorption on two separate planes. In the original TLM (Davis et al., 1978, Davis and Leckie, 1978, 1980), protons and hydroxyl only are sorbed on the o-plane. Other specifically adsorbed ions including metals, ligands, and ions of the background electrolyte are assigned to the beta-plane. A modified version of the TLM was developed by Hayes and Leckie (1986) in which sorption products for metals and ligands may be assigned to the o-plane. Each plane is associated with an electrostatic potential term in the mathematical formulation of the model. The necessity of designating the plane (potential term) that a sorbed solute is to be associated with requires a more complicated form for entering TLM reactions. The reaction form provided in MINTEQA2 is intended to allow flexibility in designing reactions for either version of the TLM. In the TLM reaction form, you must indicate whether the reaction product is an inner-sphere complex (all sorption is assigned to the o-plane) or outer-sphere complex (protons and hydroxyl may react at o-plane but all other specific sorption is assigned to beta-plane). If you click inner-sphere complex, the (blue) beta-plane area on the form is deactivated (greyed-out).

In considering whether you wish to designate a reaction obtained from a book or journal article as inner- or outer-sphere, you should carefully observe the name of the sorption product you are modeling. Outer-sphere complexes are frequently indicated by splitting the o-plane and beta-plane portions with dashes or underscores. For example, beginning with the neutral site (XOH), the reaction

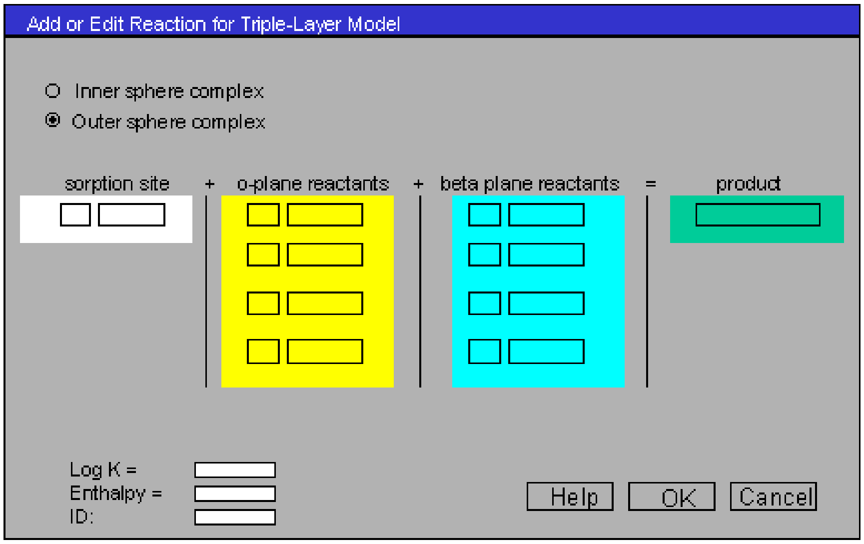
$XOH + Pb^{2+} = XO^{-}\_Pb^{2+} + H^{+}$

produces the primary sorption product $XO^{-}\_Pb^{2+}$. This complex is easily identified as outer-sphere by the format of its name. Notice that the product charge is shown separately for the two parts of this product: the o-plane portion is shown with a (-1) charge and the beta-plane portion is shown with a +2 charge. The overall charge of this product is +1.

A reaction that produces the inner-sphere complex $XOPb^{+}$

$$XOH + Pb^{2+} = XOPb^{+} + H^{+}$$

has the same stoichiometry as the outer-sphere reaction for all reactants, but all are assigned to the o-plane. The name of the primary product is not split and the charge shown at the end of the name is the charge of the overall product.



○ Inner sphere complex
● Outer sphere complex

Rules for Using the TLM Reaction Form

There are some important rules to observe in using the TLM reaction form:

1. Unlike other reaction forms in MINTEQA2, this form provides that only the primary sorption product be situated on the right hand side (RHS) of the reaction (right of the equals sign). This means that all other product entities must be moved to the left hand side (LHS). Moving a product from the RHS to the LHS (or vice-versa) is perfectly legitimate but must be accompanied by multiplying its stoichiometric coefficient by (-1). For example, the traditional reaction for producing OH^{-} can be written

$$H2O - H^{+} = OH^{-}$$

2. If the reaction you wish to model is not written in terms of MINTEQA2 components, you must reformulate it so that it is. Do this before you enter any reactants on the reaction form. For example, if you wish to model

$XOH + Cr^{3+} = XO^{-}\_Cr^{3+} + H+$ log K = 3.4

you must reformulate it because Cr^{3+} is not the component used in MINTEQA2 for trivalent Cr. The appropriate component is $Cr(OH)_2^{+}$. The process of reformulating a reaction in other components is basically one of adding or subtracting other reactions. In most cases, the reaction that should be added or subtracted can be obtained from the MINTEQA2 thermodynamic database (THERMO.DBS). In the example above, the reaction

$Cr(OH)_2^{+} - 2H2O + 2H^{+} = Cr^{3+}$ log K = 9.5688

obtained from THERMO.DBS should be added to the sorption reaction to give

$XOH + Cr(OH)_2^{+} - 2H2O + H^{+} = XO^{-}\_Cr^{3+}$ log K = 13.0

This reaction is now ready for entry on the reaction form. Notice that as the reactions were added, so also were their log K values.

3. As you begin to enter the reaction on the form, start by clicking the radio button to indicate whether you wish to model an inner-sphere or an outer-sphere complex. When inner-sphere complex is clicked, the beta-plane area of the form is deactivated.

4. The mass action expression for TLM sorption reactions contains an exponential term that represents the electrostatic potentials of each plane. The net charge on each plane is used automatically in MINTEQA2 to compute the coefficients for these potentials. For example, the reaction

$XOH + Cd^{2+} = XO^{+}\_Cd^{2+} + H^{+}$

has the mass action expression

$$K = \frac{[XO^{-}\_Cd^{2+}]\{H^{+}\}}{[XOH]\{Cd^{2+}\}} \exp\left[F(2\psi_{\beta} - \psi_{o})/RT\right]$$

The net charge on the o-plane is (-1) and the net charge on the beta-plane is +2. These are expressed as coefficients in the respective potential terms (subscripted psi) in the exponential term (highlighted). (Note that in this and in other mass action expressions displayed below the charge appears in its proper place as a superscript. Note also that square brackets [ ] are used to enclose sorption species to indicate concentration. Activity coefficients for these species are treated as equal to one. Other solutes appear in braces { } to indicate activity.)

Examples showing the entries on the reaction form for several typical reactions are provided in the online help document in MINTEQA2 for Windows.

Databases of Sorption Reactions

MINTEQA2 for Windows includes databases of sorption reactions for hydrous ferric oxide and for goethite. Both of these are applicable only to the diffuse-layer model (MIT Two-Layer model) described in Dzombak and Morel (1990) . You may indicate your desire to use either of these databases by clicking **Read Reactions from File** on the **Define Sorption Reactions** screen. Both database files (HFO_DLM.SRP and GTH_DLM.SRP) are located in the subdirectory \Sorption Databases in the MINTEQA2 for Windows installation directory. (Note: The user specifies the name of the installation directory during installation. The default is C:\Program Files\MINTEQA2 for Windows.) The two databases are:

HFO_DLM.SRP This database contains sorption reactions for hydrous ferric oxide (HFO) as given in Dzombak and Morel (1990) . The database includes reactions for both site types suggested by Dzombak and Morel. Where necessary, reactions have been reformulated in terms of MINTEQA2 components. The equilibrium constants for some reactions are based on linear free energy relationships given in the Dzombak and Morel text. We have exercised reasonable care in transcribing the reactions and reformulating the reactions in terms of MINTEQA2 components (when necessary), but it is the user's responsibility to check that the reactions faithfully represent those given in Dzombak and Morel. When using this database, you should use the site densities recommended by Dzombak and Morel to calculate the site concentrations (0.005 moles sites per mole Fe for the low density, strong-binding site (their Type 1 site for cations only); 0.2 mole of sites per mole Fe for the high density, weak-binding site (their Type 2 site for protons, cations, and anions); also use the specific surface area recommended by Dzombak and Morel (600 m^2/g HFO). (Note: Dzombak and Morel assume HFO stoichiometry of Fe2O3.H2O; 89 g HFO/mol Fe.)

GTH_DLM.SRP This database contains sorption reactions for goethite as given in Mathur (1995) . The database includes reactions for one site type as suggested by Mathur. Where necessary, reactions have been reformulated in terms of MINTEQA2 components. The equilibrium constants for some reactions are based on linear free energy relationships given in the Mathur thesis. We have exercised reasonable care in transcribing the reactions and reformulating the reactions in terms of MINTEQA2 components (when necessary), but it is the user's responsibility to check that the reactions faithfully represent those given in Mathur's thesis. When using this database, you should use the site density recommended by Mathur to calculate the site concentration (0.018 moles sites per mole Fe); also use the specific surface area recommended by Mathur (60 m^2/g goethite). (Note: Mathur assumed goethite stoichiometry of FeOOH; 89g goethite/mol Fe.)

Dissolved Organic Matter (DOM)

MINTEQA2 includes a specialized sub-model for calculations involving dissolved organic matter. This sub-model, called the Gaussian distribution model, is based on the assumption that natural organic matter is a complex mixture of various functional groups that comprise a population of binding sites and that the probability of occurrence of a binding site is normally distributed with respect to its log K value for metal or proton binding (Dobbs et al., 1989). Each reaction involving DOM is supplied with a mean log K and standard deviation in log K. This is in contrast to all other reactants in MINTEQA2 which are implicitly treated as pure substances whose reactions involve only a single-valued equilibrium constant. A database of DOM reactions with mean log K values proposed by Susetyo et al. (1991) for the metals Al, Ba, Be, Ca, Cd, Cr(III), Cu, Fe(III), Mg, Pb, Ni, and Zn and for protons is included with the model. Please consult the listed references for further information about the Gaussian DOM model.

Required input parameters: DOC concentration in mg/L and site density in umol sites/mg C. Both are entered on the **Specify Dissolved Organic Matter Parameters** screen.

DOC Concentration

The DOC concentration is required for the Gaussian DOM model. DOM usually consists of about 50 to 60 percent DOC, so if you have a DOM value in mg/L, enter about 55 percent of that value as the DOC concentration (mg/L). (DOC is actually the measured quantity.)

DOM Site Density

The DOM site density is required for the Gaussian DOM model. It represents the density of DOM binding sites per mg of organic carbon in the DOM sample and is specified in micro-moles of sites per mg DOC (umol sites/mg C). The authors of the database of Gaussian reactions have recommended a site density of 1.0e-06 to 2.4E-06 mol/mg C (moles of sites per mg DOC).

Excluded Species

Any species that you wish to exclude from the speciation calculations may be specified as an excluded species. Assignment of a species to the excluded list is accomplished by clicking **Excluded Species** on the main screen, then selecting the species.

Unless they are specifically included, all gas species and solid (mineral) species are excluded by default. Likewise, all species that represent fixed-ratio redox couples are excluded by default. The option to assign other species to the excluded list allows the user to exercise geochemical judgment. For example, choosing to allow precipitation of all possible solids (whose solubility products are exceeded) may result in the precipitation of a mineral that the user feels would be unlikely to form for kinetic or other reasons. To remedy that, the doubtful solid species may be specifically excluded.

Certain species that are also components (the electron and components used to represent electrostatic potentials in sorption models) are automatically assigned to the excluded list without user intervention.

Specify Excluded Solid Phases

To edit the list of excluded solid phases, click the **Excluded Species** button on the main screen, then click the **Add/Delete** button for Excluded Solid Phases. On the **Specify Excluded Solid Phases** window, choose the class (hydroxide, carbonate, etc.) of the solid phase to be excluded, highlight the desired species in the Available Solid Phases list, and click **Add** to add the species to the excluded list**.** To remove a species from the excluded list, highlight it in the Selected Solid Phases list and click **Remove** .

Specify Excluded Aqueous Species

To edit the list of excluded solution species, click the **Excluded Species** button on the main screen, then click the **Add/Delete** button for Excluded Solution Species. On the **Specify Excluded Solution Species** window, choose the class (hydroxide, carbonate, etc.) of the solution species to be excluded, highlight the desired species in the Available Solution Species list, and click **Add** to add the species to the excluded list**.** To remove a species from the excluded list, highlight it in the Selected Solution Species list and click **Remove**.

Precipitation

Options regarding precipitation of mineral phases are selected by clicking **Precipitation** on the main screen. You may choose to allow precipitation only for certain solid phases that you specify or you may choose to allow any solid phase whose solubility product is reached to precipitate. In the former case, you can choose the specific solids allowed to precipitate by clicking **Add/Delete** and adding (or removing) solid phases to the **Selected Solid Phases** list. To select a solid to add to the list, choose the mineral class to which it belongs (hydroxide, carbonate, etc.) from the drop-down menu, then highlight the specific solid phase in the list. Use the **Add** button to add the highlighted solid to the Selected Solid Phases list. You can remove a solid phase from the Selected Solid Phases list by highlighting it and clicking **Remove**.

If a large number of solid phases are to be considered as candidates for precipitation, it may be easier to simply specify that all solid phases are to be considered for precipitation. If you choose this option, you may also specify a short list of solid phases that are to be excluded from the possibility of precipitation by clicking the Excluded Species button on the main screen.

Solid phases that are to be imposed as a strict condition of equilibrium must be specified by clicking the Equilibrium Constraints button on the main screen.

Solid phases may also be used as a means of introducing component mass into the system. Initially present solid phases (finite solids) are introduced via the Total Concentrations window. Note that any initially present solid specified by the user is automatically registered as an allowed solid.

Edit Thermodynamic Data

The option to change the log K or enthalpy of reaction for any species is provided by selecting the **Edit Thermodynamic Data** menu bar item. After identifying the species to which the desired change applies, you may specify new log K or enthalpy values that will override the default values from the thermodynamic database. The new values do not permanently replace values in MINTEQA2's database or change them in the database file. They simply replace the database values for the current model run. Thermodynamic data for allowed solid species, aqueous species, equilibrium solid species, and finite solid species may be overridden.

NOTE: There are 23 species in the MINTEQA2 thermodynamic database whose log K values cannot be altered in the manner described above. These species are those listed in the database file ANALYT.DBS (found in the MINTEQA2 for Windows installation directory); their names are listed in the online help document under the **Edit Thermodynamic Data** topic. The species in ANALYT.DBS are provided with analytical functions of log K with temperature and the current implementation of these functions in MINTEQA2 does not allow the user to specify an alternative log K. Please contact us for technical support if you must supply an alternative log K for one of these species.

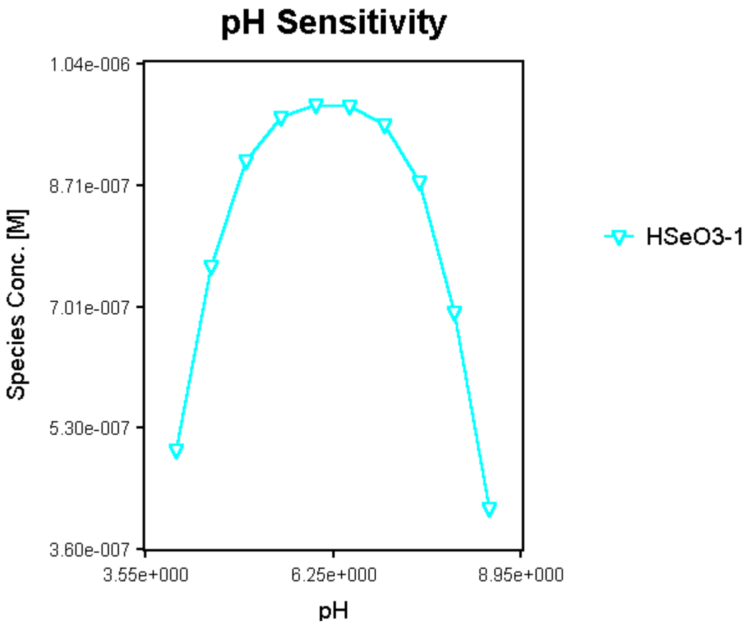
Model Output

The output file from the last execution of MINTEQA2 is displayed automatically upon completion of equilibration (i.e., after clicking the **Equilibrate** button). If the user has elected to display the current project by clicking the **View Project** button (shows MINTEQA2 input data) or graphs by clicking the **View Graph** button, the current output can be re-displayed by clicking the **View Output** button on the main screen. The output is shown in a window that permits display or printing only; the displayed file cannot be edited or changed. The output is initially displayed in summary form that gives just the essentials; a **Print** button is provided to print the summary output. You can display the full MINTEQA2 output by clicking the **Full Output** button in the output area. The full output display also presents a **Print** button. Output files are automatically saved in a file having the same name as the input file except with the file extension ".out".

Graphing

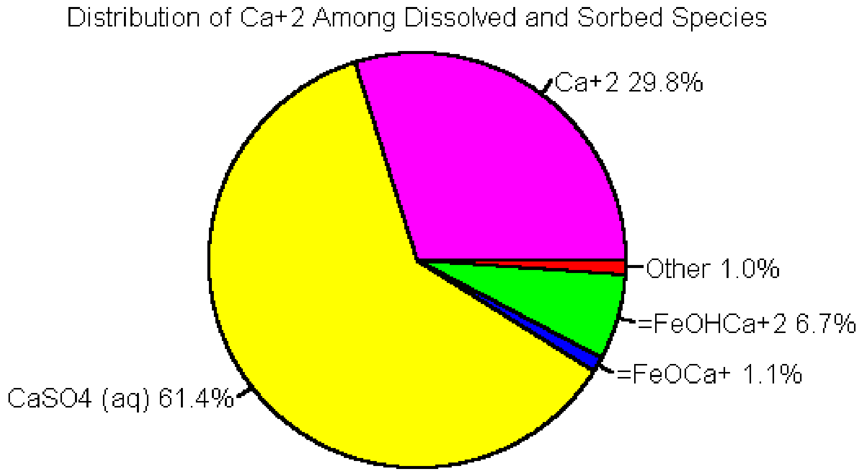
Certain results for runs involving a single equilibration point and for multiple equilibration points in a sensitivity analysis can be view graphically. For any equilibration point (single run or individual point in a sensitivity analysis), you can display a pie chart showing the distribution of any component among its most dominant solution species. For a sensitivity analysis, you can graph the concentration of any species versus the sensitivity parameter. Other types of plots are also available.

To produce a plot of equilibrated results, click the **View Graph** button on the main screen. The **New Graph** window is displayed where you can select the type of plot and the data to be plotted. Note that some types of data are presented as X-Y plots and others as pie charts (see example plots below). Upon display of any plot, options are presented to allow you to customize the display. You may return to specify a different graph type by clicking the **New Graph** button.



Pie Charts

Pie charts are used to display the distribution of a component among its most dominant dissolved and/or sorbed species. When a pie chart is displayed, click the **Pie Chart** button to display the **Set Pie Chart Properties** window. The font used in pie chart labels and the horizontal position of the chart can be customized. Note that the horizontal position setting also affects the size of the chart.



Graph Legend

When any X-Y graph is displayed, click the **Graph Legend** button to display the **Set Legend** window. The content and position of the legend can be customized. Options provided include turning the legend on or off, changing its font, its text, and its horizontal and vertical position.

Graph Axis Properties

When any X-Y graph is displayed, click the **X-Axis** or **Y-Axis** button to display the **Define X-Axis** or **Define Y-Axis** window. The axis title, scale minimum and maximum, scale notation format, number of tick marks, and title and label fonts can be customized. The width and height of the graph can be modified. Also, the X or Y axis data can be transformed to a log scale.

Graph Titles

When any X-Y graph or pie chart is displayed, click the **Title** button to display the **Set Graph Title** window. Title and sub-title content and font can be modified.

Saving a Graph

When any X-Y graph or pie chart is displayed, click the **Save** button to display the **Save Graph to Clipboard or File** window. The image of a graph or pie chart can be saved to the clipboard (for subsequent pasting in a document) or to a file. Images can be saved in a variety of graphics formats.

This window also allows you to save the data points used in drawing an X-Y chart in an ASCII text file, a useful option if you want to use the data in a more sophisticated plotting program or in a spreadsheet. When data points are saved, eleven header lines describing the data are written to the file, followed by the data points with each line accounting for an X-Y pair and with the X-data in the first column.

Sensitivity Analysis

MINTEQA2 can perform a sensitivity analysis on any one of several parameters: total concentration of a particular species, ionic strength, pH, temperature, or the log K of a solution or solid species. A sensitivity analysis consists of a series of up to 48 independent model runs, each with a different value of the sensitivity parameter. The user can evaluate the results by examining the MINTEQA2 output file or by examining plots of dependent variables of interest versus the sensitivity parameter (see Graphing below).

To perform a sensitivity analysis, click **Sensitivity Analysis** on the menu bar. The following options are provided:

>Sensitivity to Concentration of a Species. This option (referred to as a concentration sweep) allows you to investigate the response of the system to various total concentrations of a particular sweep species.

>Sensitivity to Other Parameters. This option allows you to investigate the response of the system to changes in pH, pE, ionic strength, temperature, or the log K of any species.

>Clear All Sensitivity Parameters. This option clears all currently defined sensitivity settings.

When an input project file for a sensitivity run is saved, all sensitivity parameters are saved as well.

Sensitivity to Total Concentration of a Species

MINTEQA2 can perform a sensitivity analysis using either a MINTEQA2 species or a user defined species (defined in terms of MINTEQA2 components). Up to 48 total concentrations may be used. (A sensitivity analysis in which the total concentration of one species is varied is hereafter referred to as a "sweep.") The user can evaluate the results by looking at each of the resulting MINTEQA2 output file sections, or by using the graphical routines to plot values of dependent variables of interest against the systematically varied total concentration of the sweep species.

The sensitivity option is accessed from the **Sensitivity Analysis** item on the menu bar. After clicking the Sensitivity **Analysis** menu button, click **Sensitivity to Concentration of a Species (Concentration Sweep) > Select Sweep Species from MINTEQA2 Database** to choose an existing MINTEQA2 species as the species to be varied. To vary the total concentration of a species that is not in the MINTEQA2 database (e.g., NaCl), click **Sensitivity to Concentration of a Species (Concentration Sweep) > Define Sweep Species Manually.** This option will guide you in specifying the species you want by specifying its formula in terms of MINTEQA2 components. (The user-defined species must be charge neutral.)

Note that the sensitivity option in which the total concentration of a species is varied is similar to a titration, but there are differences. Experimental titrations are usually specified in terms of added volumes of a solution containing the titrant species at a known concentration. The initial system concentration of the species added is known (although it may be zero) and one can determine its new concentration in the system with each addition as the titrant volume is added. The concentration of other constituents in the system are diluted with each added volume of the titrant. In the MINTEQA2 sensitivity analysis Concentration Sweep, there is no dilution effect; each sweep point is identical to the preceding one except that *the total concentration of the sweep species only* is changed.

This option could also be used to model the addition of small quantities of a solid phase to a solution.

Specifying a Sweep Species

The user has the option to select the sweep species from the MINTEQA2 database or, if the desired species is not in the MINTEQA2 database, to define it in terms of MINTEQA2 components. After clicking **Sensitivity Analysis** on the menu bar and choosing **Sensitivity to Concentration of a Species (Concentration Sweep)**, you choose which of these options you prefer by choosing **Select Sweep Species from MINTEQA2 Database** or **Define Sweep Species Manually** .

If you choose to select the sweep species from the database, the **Select Sweep Species from MINTEQA2 Database** screen appears. Begin by indicating whether the database species is a solid, aqueous (non-component), or component species. If it is a solid or aqueous species, select the class (e.g., carbonate, hydroxide) to which it belongs, then select the species from the list that appears below (double-click the desired species). If the desired species is a component, indicate that and the list below will show all available components. Note that any component species may be selected as a sweep species regardless of species charge, but if selecting any other (non-component) aqueous species, it must be neutral.

If the species you desire to use as a sweep species is not in the MINTEQA2 database, you may define it by specifying it in terms of MINTEQA2 components. As an example, HCl is not in the MINTEQA2 database because is dissociates completely in solution. You can still use HCl as the sweep species by indicating its representation in terms of MINTEQA2 components on the **Define Sweep Species** screen. A two-line fill-in-the-blank reaction form appears on this screen. Notice that this reaction form is written with blanks fields to indicate reactants on the left side of the reaction (left of the equals sign) and the reaction product (sweep species for which you must supply a name) on the right side. The reaction product has an implicit, unalterable stoichiometry of 1. Use the drop-down menu to indicate each component involved in the reaction on both the reactant and product sides. Up to six components may be specified; enter the reaction stoichiometry of each. (Note: The primary reaction product (in this case, the sweep species) cannot be a MINTEQA2 component species. All other reactants and products involved in the reaction MUST be MINTEQA2 component species.)

Example:

The concentration of NaOH in a closed solution is 100 uM (0.0001 mol/L) and the equilibrium pH is 9.99. You want to know what the equilibrium pH would be if the NaOH concentration were 200 uM, 300 uM, 500 uM, and 1000 uM. The sweep species will be NaOH and because this species completely dissociates in aqueous solution, it is not present in the MINTEQA2 database. But of course, its components are present, so use the **Sensitivity to Concentration of a Species (Concentration Sweep) > Define Sweep Species Manually** option. The **Define Sweep Species** screen presents a fill-in-the-blank reaction form where you may specify the sweep species name on the product (right) side of the equals sign. You must also enter MINTEQA2 components as other products (if any) to the right of the equals sign and reactants to the left. Drop-down boxes allow you to choose the desired components by name. You must also specify the stoichiometry of each reactant or product.

The reaction you should enter for this example is:

$\underline{1}\ \underline{\text{Na+}} + \underline{1}\ \underline{\text{H2O}} = \underline{\text{NaOH}} + \underline{1}\ \underline{\text{H+}}$

(Entries in boxes on reaction form are underlined). Note that you do not specify the stoichiometry of the primary product (NaOH in this case); its stoichiometry is understood to be 1. Note also that the reaction must be such as to produce a neutral (charge balanced) sweep species. After writing the reaction, click **Next** to have opportunity to specify the set of sweep species concentrations.

Setting Total Concentration (Sweep) Points

A concentration sweep may contain up to 48 values of the total concentration for the sweep species. These values can be entered by specifying a starting value and an increment of change between successive values, or by entering all of the values explicitly.

Example:

The system of interest is composed of distilled water with 0.0003 mol/L $CaCO_3$ and 0.0002 mol/L $CaCl_2$. Thus, the initial total concentrations of components in the system are:

0.0005 mol/L of Ca

0.0003 mol/L CO_3

0.0004 mol/L Cl

Suppose you wish to model four other $CaCO_3$ concentrations (0.0004, 0.0005, 0.0006, and 0.0007 mol/L) in the system to observe the effect on calcite saturation index and pH. After clicking **Sensitivity Analysis** on the menu bar and selecting **Concentration Sweep** and **Select Sweep Species from MINTEQA2 Database**, choose calcite as the sweep species and click **Next**. On the **Specify Method of Sweep Point Entry** window, indicate that you will specify a starting concentration and increment and that there are to be 4 sweep points; make sure the units are set to mol/L. After clicking **Next**, the **Specify Sweep Concentration Start-Inc** window appears. In deciding what to enter, note that the concentrations specified for the sweep species *will be added to the initial component totals* for those components that comprise the sweep species. The system already has 0.0003 mol/L $CaCO_3$. Set the starting concentration for the sweep at 0.0001 mol/L and the increment at 0.0001 mol/L. The total $CaCO_3$ in the system for the four successive equilibrations will be 0.0004, 0.0005, 0.0006, and 0.0007 mol/L. Note that the final component totals for the first sweep point will be:

0.0006 mol/L of Ca

0.0004 mol/L CO_3

0.0004 mol/L Cl

Component totals for Ca and CO_3 for the other three sweep points will likewise be the sum of the initial totals for these components and the additional amount for each sweep point.

If desired, you may enter the 4 sweep concentrations explicitly rather than with starting value and increment. But as before, the values you specify *are added to the initially present totals* for the relevant components. To enter the values explicitly, indicate that choice on the **Specify Method of Sweep Entry Point** screen and click **Next**. On the **Specify Sweep Concentrations Explicitly** screen, enter the desired value for each point. For this example, the four sweep concentrations entered should be 0.0001, 0.0002, 0.0003, and 0.0004 mol/L. These values will be added to the 0.0003 $CaCO_3$ initially present.

Setting Sensitivity Values

A sensitivity analysis may contain up to 48 values of the sensitivity parameter (ionic strength, pH, pE, temperature, and the log K of an aqueous species, an equilibrium solid species, a finite solid species, or an allowed solid species). The values may be entered by specifying a starting value and an increment of change between successive values, or by entering all of the values explicitly.

Example:

Suppose you wish to model a system at four values of pH (4.5, 5.0, 5.5, 6.0). After clicking **Sensitivity Analysis** on the menu bar and selecting **Sensitivity to Other Parameters**, choose pH as the sensitivity parameter on the **Define Sensitivity Parameter** screen. On this same screen, indicate that you will specify a starting concentration and increment and that there are to be 4 sensitivity points. After clicking **Next**, the **Specify Starting Value and Increment** window appears. Set the starting pH at 4.5 and the increment at 0.5. Note that if you had previously entered an equilibrium pH on the **Equilibrium Constraints** window, that value will be overridden with the starting value entered here.

If desired, you may enter the 4 pH values explicitly rather than with starting value and increment. This is handy if you want to see the speciation at specific values that are not separated by a constant increment. To enter the values explicitly, indicate that choice on the **Define Sensitivity Parameter** window and click **Next**. On the **Specify Values Explicitly** screen, enter the desired value for each point. For this example, the four pH values entered should be 4.5, 5.0. 5.5, and 6.0.

Examples

The examples listed below are in order of increasing complexity. Detailed instructions are provided for example problems that demonstrate

1. Entry of a water analysis for speciation at a specific pH;

2. A sensitivity analyses with temperature as the sensitivity parameter and plotting results;

3. Use of the diffuse-layer adsorption model with the goethite database, sensitivity analysis exploring Zn adsorption versus total Zn concentration, and plotting results.

By following the instructions for these problems, you will become familiar with many of the options available in MINTEQA2 for Windows.

Example 1. Simple Water Analysis Speciation

Example 2. Sensitivity Analysis and Plotting

Example 3. Adsorption, Sensitivity Analysis, and Plotting

1. Simple Water Analysis Speciation

The following step-by-step example/tutorial illustrates how to enter the components necessary to represent a simple water analysis and to specify the equilibrium pH.

Water analysis data (from Deutsch (1997) , Table 4-4, p. 83):

Chemical Constituent	Measured Value (mg/L)
Ca	163
Mg	89
Na	197
Cl	315
SO4	460
HCO3	353
pH	6.9

These data represent major ion composition in groundwater from a claystone aquifer.
Basic questions that might be asked include are the data reasonably charge balanced and does the chemistry depict supersaturation with respect to common minerals. MINTEQA2 does not specifically impose electroneutrality in solving the equilibrium problem. Thus, it is possible to

pose a system that is not charge balanced. The importance of maintaining charge balance in the model is dependent on the intended use of the results and on the cause of the imbalance. Charge imbalance means that the concentration of one or more constituents was overstated or understated, or that one or more constituents were left out altogether. The impact of this error depends on the answers to two questions: Is the constituent whose concentration is misstated (or omitted) reactive with other constituents in the system, or is it chemically inert? If it is reactive, then the model's equilibrium calculations could be seriously affected. If the constituent whose concentration is misstated is inert, then the second question is important: Is the misstated concentration of the inert ion severe enough to seriously impact the ionic strength estimated by the model? This question is important because activity coefficients of all species in the model are dependent on the solution ionic strength. If the modeler feels that all reactive constituents are accounted for with sufficient accuracy in the concentrations, and that the misstated concentration pertains to a relatively inert constituent, then the modeler may impose a reasonable estimate of ionic strength as an equilibrium condition (see **General Parameters > Ionic Strength**).

Before entering the water analysis data, click the **General Parameters** button and explore the options. You should decide whether you wish to impose an equilibrium ionic strength or compute it based on the water analysis chemistry. (The latter is suggested in this case.) Also, the default concentration units should be set at mg/L since that is how your data are presented. You may also set other parameters on the **Specify General Parameters** screen (project title, type of equation for activity coefficients, system temperature, alkalinity). For this example, leave these settings as they are.

To enter this water analysis in MINTEQA2, click the **Total Concentrations** button on the main screen. The **View or Change Total Concentrations** screen will be displayed. You may add components to your project by clicking the **Add or Delete Components** button. Upon doing so, the **Select Components** screen appears. This screen is divided into two panes. All available MINTEQA2 components are displayed in the left pane. The right pane shows currently selected components for your project. To add components to your project, highlight each desired component and click the **Add** button. The added component will appear in the right pane. You may add desired components one at a time or, by holding down the Ctrl key on your keyboard, you may highlight and add multiple components at once. Note: To remove a component, highlight it in the list of selected components (right pane) and click **Remove** .

Notice that MINTEQA2 uses real species as components. For example, the species Ca+2 is the component for calcium. Do not be confused by the use of real species: when specifying the entry for Ca from the above water analysis, you must choose Ca+2 as the component because it is the calcium species that the authors of MINTEQA2 have chosen to serve as the component for calcium. Entering the water analysis value of 163 mg/L as the total concentration for Ca+2 does not mean that the equilibrium Ca+2 concentration will be 163 mg/L. On the contrary, it is the purpose of MINTEQA2 to determine how much calcium is in each species at equilibrium (e.g., Ca+2, CaOH+, CaCO3(aq), etc.). It was necessary for the authors to choose a calcium species to serve as component and Ca+2 was a convenient choice.

Entry of all chemicals except HCO3 from the water analysis above is straightforward. You will notice that HCO3 is not listed among the available MINTEQA2 components. This is because the authors of the model chose CO3-2 as the component to represent carbonate. Thus, you must add the component CO3-2 to your project.

After adding all six of the necessary components to your project (H+ was present already by default), experiment with removing components from your project before leaving this screen. To remove a component, highlight it in the right pane and click remove. Practice by adding K+ to your project, then remove it. After becoming familar with how this screen works, click OK to return to the **View or Change Total Concentrations** screen.

You may now enter the concentrations of each of the added components. The units of concentration shown will be mg/L if you changed the default setting to mg/L on the **Specify General Parameters** window. If you did not, you can change the units individually for each component using the drop-down menu as each component concentration is entered. The pH of the sample is a measured value and the modeling that we are performing is merely to compute the speciation of the sample. Thus, we should impose the measured pH as an equilibrium value. A separate screen is provided for specifying user imposed equilibrium constraints. For now, you should realize that there is no need to enter a concentration for the component H+ in this project because the equilibrium pH will be specified. Enter the measured concentration from the water analysis for all other components. The measured value for HCO3- must be adjusted to reflect the choice of CO3-2 as the component for carbonate. The measured concentration of HCO3 (353 mg/L) should be multiplied by 60/61 (the ratio of the molar mass of CO3 to that of HCO3). The result, 347 mg/L, should be entered for the total concentration of CO3-2. The other portion of the HCO3- measurement, 6 mg/L (353 - 347 mg/L), is due to H+. If this project were not being modeled at fixed (user-specified) pH, the H+ component would have a viable total concentraion like all other components. In that case, the 6 mg/L from the bicarbonate should be added to whatever total already pertained to the H+ component. Because the equilibrium pH is specified, we may ignore the 6 mg/L H+. Click OK to return to the main screen.

Back at the main screen, click the **Equilibrium Constraints** button to display the screen that allows you to imposed various equilibrium constraints. The only constraint relevant to this project is the measured equilibrium pH. Click to indicate that you wish to specify the equilibrium pH and enter the water analysis value (6.9). Before leaving this screen, notice that you may also specify equilibrium solid phases, the partial prerssure of one or more gases, the equilibrium pE (Eh), and relationships between certain redox species. None of these pertain to this project; click OK to return to the main screen.

Notice that the parameters and components that you have entered are displayed in the Project Summary area on the main screen. This area is too small to display all parameter values and settings; you must click the button pertaining to the item of interest to see all settings for that item.

To equilibrate this water analysis and see how the measured chemical constituents are distributed among various species at equilibrium, click **Equilibrate** on the menu bar or click the **Equilibrate** button. When Equilibrate is clicked, you are prompted for a filename in which to save the current project. A filename extension is not necessary; an extension of .mtq will be assigned automatically. All settings in the current project will be saved in this file. You may open this file later to reproduce these results or to edit the project parameters. Note that after the project is equilibrated, an output file with the equilibrated results will be saved with the same filename as the input file except with the extension .out.

The output information for the equilibrated system is displayed in summary form in the output area. You may examine the full "traditional" MINTEQA2 output file by clicking the **Full Output** button. Either type of output may be printed by clicking the **Print** button. The summary output displays the equilibrium pH, ionic strength (mol/L), and charge imbalance in the sample. The concentrations of all relevant species found in the MINTEQA2 database are displayed as well. There is also a listing of the distribution of each component among its dominant species: for Ca, 80.8 percent is in Ca+2, 17.2 percent is in CaSO4(aq), etc. You can display the distribution of a component among its important species in the form of a pie chart for visual inspection. Click **View Graph** and select **Component Distribution Among Species** as the graph type. In the panes that will appear below, select the component whose distribution you want to see, then click OK.

After graphing, click **View Output File** on the left side of the main screen to return to the summary output file. The summary output also includes a listing showing the distribution of each component among phases. This display is of no interest in this example because there is only one phase: the solution. This display will be of interest for projects in which solid phases precipitate or where sorption is allowed. Like the distribution of components among species, the distribution among phases can be displayed as a pie chart.

The full output includes all information shown in the summary but with greater detail. It begins with a recap of input data and also includes saturation indices of all solid phases.

For the speciation of this water analysis, notice that the ionic strength is about 0.031 mol/L and the charge imbalance is only 2 percent, both reasonable values for this sample. Also, notice that the carbonate is mostly bound up in HCO3- and H2CO3, as expected at pH 6.9. There is very little CO3-2 at equilibrium even though that is the species we used to introduce carbonate. (Note: There is a small concentration of CO3-2, but it represents only a small fraction of the total carbonate in the system and so does not appear in the listing headed Component Distribution Among Species. Only those species comprising at least 1 percent of the total for a component are listed there.)

Referring to the full output, go to the bottom of the displayed data and see the listing of saturation indices for solid phases. Note that this water sample is close to saturation with calcite and gypsum.

NOTE: An example project input file for this problem is included in the \Examples subdirectory of the MINTEQA2 for Windows installation directory. (The user specifies the name of the installation directory during installation. The default is C:\Program Files\MINTEQA2 for Windows.) The project file for this example is Example _1.MTQ. The file you create in this example should be very similar to this example project file.

2. Sensitivity Analysis for Temperature with Plotting

The following step-by-step example/tutorial illustrates the use of the sensitivity analysis feature and plotting options. MINTEQA2 for Windows provides several choices for the sensitivity analysis parameter. In this example, the sensitivity parameter is temperature. The equilibrium constant (log K) for each reaction in the MINTEQA2 thermodynamic database corresponds to a temperature of 25 C. When a system temperature other than 25 C is specified, the enthalpy of reaction (also in the database) is used in the van't Hoff relation to adjust the log K value. (More accurate analytical functions for log K variation with temperature are present for some species.)

Problem: Perform an analysis of the effect of system temperature on speciation over a temperature range of 10 to 30 degrees C.

1. Click **File>Open** and open the file EXAMPLE_2.MTQ in the \Examples subdirectory of the MINTEQA2 for Windows installation directory. (Note: The user specifies the name of the installation directory during installation. The default is C:\Program Files\MINTEQA2 for Windows.) The file EXAMPLE_2.MTQ represents a simple CaCO3 system. Initially, it is not setup as a sensitivity run. After opening the file, note parameter settings displayed in the Project Summary area of the main screen. Use the **Total Concentration** button to view component concentrations. The next step is to add parameters for the sensitivity analysis.

2. Click **Sensitivity Analysis** on the menu bar, then click **Sensitivity to Other Parameters**. On the **Define Sensitivity Parameter** window, select Temperature as the sensitivity parameter and set the number of values to 21. Then indicate Specify Starting Value and Increment and click **Next**. On the **Specify Starting Value and Increment** window, enter 10 as the starting value, which corresponds to a starting temperature of 10 degrees C, set the increment to 1 degree C, and click OK. When this project is run, MINTEQA2 will run 21 independent cases, each with all parameters the same except for temperature, which will range from 10 to 30 deg C.

Run this case by clicking the **Equilibrate** menu bar item (or by clicking the **Equilibrate** button on the main screen). As usual, you are prompted to save the project file before the equilibration is performed. You may save it in the original filename (thus overwriting the original file), or you may specify a new filename and the original EXAMPLE_2.MTQ will remain unchanged. Upon completion of the equilibration, examine the summary and full output files and you will see that the output is divided into 21 sections, each one presenting the speciation for a particular temperature.

3. Plot the results by clicking on the **View Graph** button on the main screen. On the **New Graph** window, select Species Concentrations as the type of item to graph, then highlight Ca+2 and HCO3- in the left pane. Click **Add** to move these two species to the list of items selected for graphing (right pane). Click **OK** to see the graph. Experiment with the array of buttons on the left side of the window to change the graph scale, size, titles, and legend. Try saving the graph file or image and printing the graph. You can also experiment with other graph options on the **New Graph** window. Note that some graph options present results for a single equilibration

point in the analysis. Try plotting the Component Distribution Among Species for the carbonate component (CO3-2) at the first sensitivity point (10 degrees). You should see a pie chart with three dominant species (CO3-2, HCO3- and CaCO3(aq). Now do the same plot at the highest temperature (30 degrees) and note the change in the distribution of the carbonate species.

For another interesting plotting exercise using this same project, cancel the sensitivity analysis over temperature and define a new one with pH as the sensitivity parameter. You will be prompted to specify the pH as an equilibrium constraint. Specify a pH of 4, then design the sensitivity analysis so that the problem is equilibrated at pH 4, 4.5, 5, 5.5, etc. up to pH 11. Equilibrate and plot the resulting concentrations of H+, OH, CO3-2, HCO3-, and H2CO3(aq) versus pH.

3. Adsorption with Sensitivity Analysis and Plotting

The following step-by-step example/tutorial illustrates the use of the diffuse-layer adsorption model, sensitivity analysis with sweep over total concentration of a species, and plotting options. In this example, the goethite database of sorption reactions is used with the diffuse-layer model to estimate the sorbed fraction of Zn. The total concentration of Zn is varied using the sensitivity analysis (concentration sweep) option. The sorbed Zn concentration is plotted versus the dissolved Zn to generate an isotherm.

1. Click **File>Open** and open the file EXAMPLE_3.MTQ in the \Examples subdirectory of the MINTEQA2 for Windows installation directory. (Note: The user specifies the name of the installation directory during installation. The default is C:\Program Files\MINTEQA2 for Windows.) The file EXAMPLE_3.MTQ represents a simple groundwater chemistry. Notice that the equilibrium pH is specified as 8.2 and components for Ca, K, CO3, Cl, Mg, and SO4 have already been entered. You can examine the total concentrations entered for these components by clicking the **Total Concentrations** button on the main screen. Initially, this project is not setup to include a trace metal or sorption or a sensitivity analysis, so we must add these.

2. Click **Total Concentrations**, then click **Add or Delete Components** and add Zn to the project at a concentration of 0.001 mg/L. Click OK to return to the main screen.

3. Click **Sorption** to display options for sorption models. Select the diffuse-layer model. You must also designate a sorbing surface (sorbent) and give pertinent information. Only one surface will be defined in this exercise. In the area designated for surface 1, enter Goethite as the name. In this exercise we will read a database of sorption reactions for goethite and the diffuse-layer model as given by Mathur (1995) . Mathur's reactions assume a surface area of 60 m^2/g, so enter this for Surface Area. Assume a goethite concentration of 1.5 g/L (enter in the Concentration field to the right of the Surface Area field). Mathur recognized one type of binding site in his goethite database: check the box for Site 1-1. (NOTE: There is a built-in correspondence between the site names and the Assigned ID. The ID for Site 1-1 is 811; the ID of Site 1-2 is 812. The choice of which site you should use is arbitrary unless you are using a

database of sorption reactions that has already been prepared, as we are going to do here. In that case, you MUST know in advance what site ID was used in writing the reactions in the database. In the database of goethite reactions, site 811 was used. Thus, use Site 1-1 (which corresponds to 811).)

Mathur (1995) recommended a site density of 0.018 mol sites per mol Fe. Given that we have 1.5 g/L of goethite (FeOOH; molar mass 89 g), the number of moles of FeOOH is:

moles FeOOH = 1.5 g FeOOH/L X 1 mole FeOOH/89 g

= 1.685E-02

The number of moles of Fe is equivalent to the number of moles of FeOOH. Thus, the molar site concentration is:

Site conc (mol/L) = 1.685E-02 moles Fe X 0.018 moles sites/mole Fe

= 3.034E-04 mol/L

Enter 3.034E-04 for the Site 1-1 concentration.

After entering the site concentration, click **Edit Reactions** to add (or edit) sorption reactions for this site. On the **Define Sorption Reactions** screen, several options are available, among them **Read Reactions from File**. Click this option and open the file **GTH_dlm.srp** found in the subdirectory \Sorption Databases in the MINTEQA2 for Windows installation directory. (Note: The user specifies the name of the installation directory during installation. The default is C:\Program Files\MINTEQA2 for Windows.) This file contains 48 reactions pertinent to adsorption of major ions and trace metals onto goethite. The reactions are from Mathur (1995) ; where necessary, they have been reformulated in terms of MINTEQA2 components. Notice that when the file is read, you are informed that only those reactions written for the site you working with (811 in this example) will be read. Also, you are informed of the total number of reactions in the database file and of how many were entered in your project. Note that only those reactions that are pertinent to your project (their components are present in your project) are read. This means that if, after reading the file, you later add more components to the project, you should come back to read the sorption database file again so that any reactions for the added components can be retrieved. For this example, 12 goethite sorption reactions are retrieved from the database file. The names of the sorption reaction products and the log K's of the reactions are displayed. Notice that there are multiple reactions for some metals: there are two for Zn. According to Mathur's database, all reactions occur at the same site; different reactions for the same metal are distinct from one another by having different log K values or different stoichiometries of one or more components.

You may delete any of the displayed reactions by highlighting and clicking the **Delete This Reaction** button. You may also edit any reaction by highlighting it and clicking **Edit This Reaction**. Just to see how it works, highlight the reaction for =FeOZn+ and click Edit **This Reaction**. Observe that this reaction involves three components: Site 1-1 and Zn+2 on the reactant side of the reaction (left of the equals sign) and H+1 on the product side. Of course, the reaction product (=FeOZn+) is also displayed on the product side. The stoichiometry of each component is displayed in the small box before each component name. You may change the component stoichiometries (change to zero to eliminate the component from the reaction). You may also add a new component to the reaction by selecting it in an empty reactant or product field using the drop-down menu, then entering its stoichiometry. You may also change the reaction log K or enthalpy. (For the sake of our example, don't make any change in the =FeOZn+ reaction that you don't put back as it was originally; click Cancel if you have made changes and they will be discarded.) NOTE: All electrostatic terms needed for the diffuse-layer, constant capacitance, and triple-layer models are added automatically by MINTEQA2 and are invisible to the user.

Back at the **Define Sorption Reactions** screen, note that you can also add new reactions by clicking the **Add New Reaction** button. Doing so will display the same screen as the **Edit This Reaction** button except without any data filled in. We will not add a reaction in this example. Click OK to return to the **Select Sorption Model and Define Surfaces** screen, then OK again to return to the main screen.

4. Click **Equilibrate** on the main screen or on the menu bar to save this project and execute MINTEQA2. (You should save the project under a new name if you want to preserve the original EXAMPLE_3.MTQ file unchanged.) The output information for the equilibrated system is displayed in summary form in the output area. You may examine the full "traditional" MINTEQA2 output file by clicking the **Full Output** button. In Part 5 of the full output, notice that 98% of the Zn is sorbed and 2% is in solution at equilibrium. (This information is also present in the Summary Output.) In general the sorption of trace metals is concentration dependent. To observe this concentration dependency, we will solve the same problem at various total Zn concentrations. This is most easily done using the sensitivity analysis concentration sweep option. Before indicating the concentrations to use in the concentration sweep, click **Total Concentrations** on the main screen and reset the total Zn concentration to zero. Otherwise, the concentration of Zn that we are about to specify in our concentration sweep will be added to the 0.001 mg/L already present.

5. Click **Sensitivity Analysis** on the menu bar, then click **Sensitivity to Concentration of a Species (Concentration Sweep)**. From this point, two options are available: (1) you may select the sweep species (the species whose concentration is to be varied) from among MINTEQA2 components or species or (2) you may make up (define) your own sweep species by choosing a combination of MINTEQA2 components. In this example, we wish to view the speciation at different total zinc concentrations. We could do so by choosing the first option and selecting the component for Zn (Zn+2) as the sweep species. Doing so would involve introducing various concentrations of the Zn+2 cation without corresponding additions of anion, so the system will exhibit an increasing degree of charge imbalance with increasing Zn concentration. Although this is probably not a particularly important issue except at very high Zn concentration, we can maintain charge balance by entering a neutral sweep species. However, we do not want to introduce any reactive component besides Zn. The species Zn(NO3)2(aq) would be a good choice-- it will almost completely dissociate and nitrate is not reactive. We can select Zn(NO3)2 (aq) from the **Select Sweep Species from MINTEQA2 Database** screen. Click Aqueous

Species and then select the species class (Nitrates). A list of all aqueous nitrate species appears--select Zn(NO3)2 (aq) by double-clicking and it should appear in the Selected Sweep Species field. Click **Next** and the **Specify Method of Sweep Point Entry** screen appears allowing you to specify up to 48 individual concentrations; you may specify each one explicitly or by giving a starting concentration and increment. For this example, specify 36 concentrations (sweep points)and indicate that you will give a starting value and increment. Upon clicking **Next** , the **Specify Sweep Concentration Start - Inc** window appears; enter 2 (mg/L) as the starting value and set the increment to 2 (mg/L); click OK. When this project is run, MINTEQA2 will run 36 independent cases, each with all parameters the same except for the total Zn and NO3 concentrations which will be set in accordance with the specifications for starting value and increment: 2 to 72 mg/L of Zn(NO3)2.

Run this case by clicking the **Equilibrate** menu bar item (or by clicking **Equilibrate** on the MINTEQA2 main screen). As usual, you are prompted to save the project file before the equilibration is performed. You may save it in the original filename (thus overwriting the original file), or you may specify a new filename and the original EXAMPLE_3.MTQ will remain unchanged. Upon completion of the equilibration, examine the summary and full output files and you will see that the output is divided into 36 sections, each one presenting the speciation for a particular concentration of Zn(NO3)2(aq).

To plot the results, click on the **View Graph** button on the main screen. On the **New Graph** window, select Species Concentrations as the graph type, then highlight the two sorbed species of Zn in the left pane: =FeOZn+ and = FeOHZn+2. Click **Add** to move these two species to the list of items selected for graphing (right pane). Click **OK** to see the graph. Experiment with the array of buttons on the left side of the window to change the graph scale, size, titles, and legend. Try saving the graph file or image and printing the graph.

You can also experiment with other graph options on the **New Graph** window. For example, change the graph type to Components: Percent Sorbed and select Zn (Zn+2) as the component to plot. Click OK to view the percent Zn sorbed versus total Zn(NO3)2(aq). Note that some graph options present results for a single equilibration point in the analysis (e.g., a pie chart of how the component Zn component is distributed among aqueous and sorbed species for a particular sweep point). Others plot result over the range of the sensitivity parameter. Try this: On the **New Graph** window select the graph type Component Distribution Among Species and select sweep point 1 (2 mg/L). In the panes below, select Zn as the component to plot. Upon clicking OK, you should see a pie chart showing the dominant Zn species (sorbed and dissolved) at this concentration of the sweep species Zn(NO3)2(aq). Note that more than 75 percent of Zn is bound as the sorption species = FeOZn+. Repeat this graph for sweep point 36 (72 mg/L Zn(NO3)2(aq)). Notice that other species have increased drastically at the expense of the = FeOZn+ species, but it is still greater than 50 percent.

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