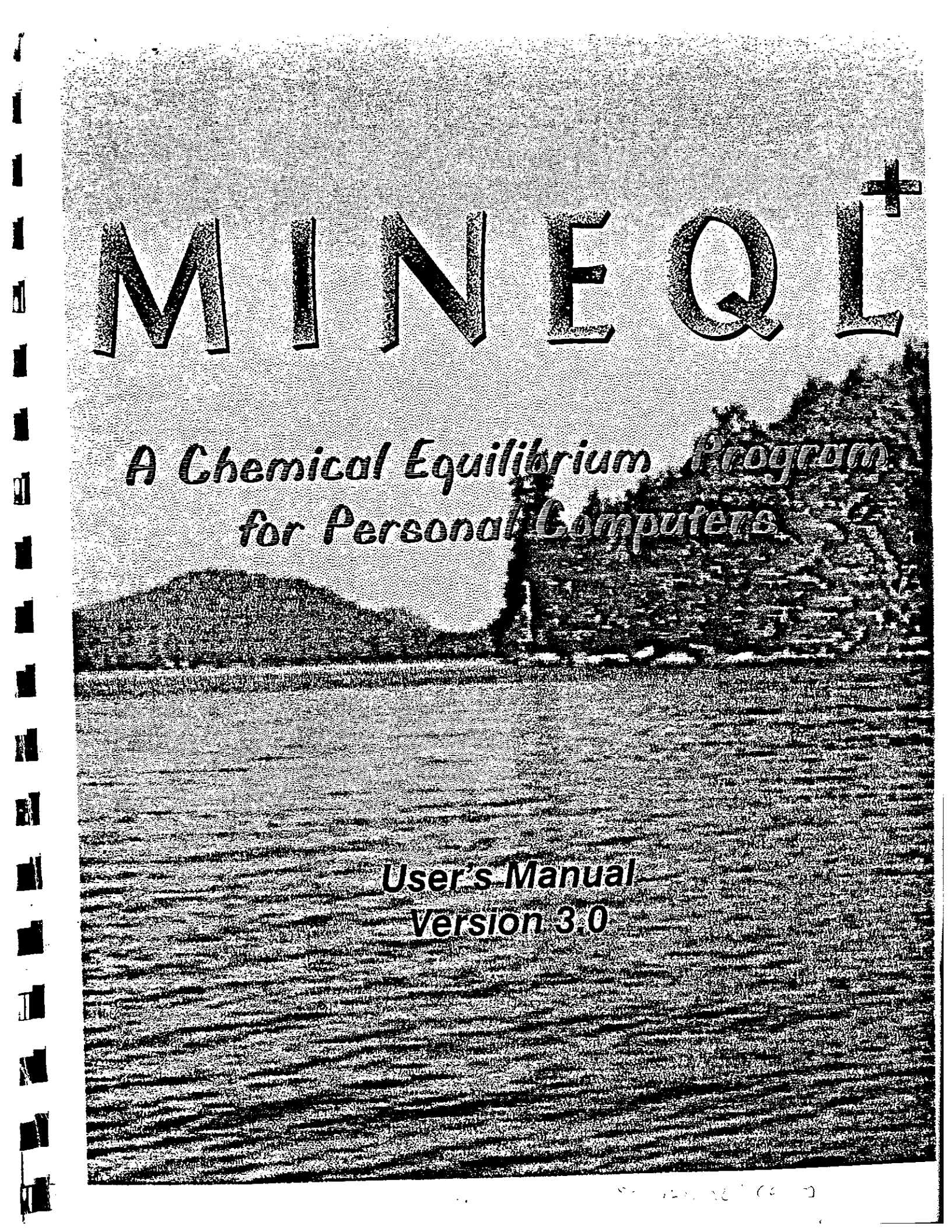
MINEQL+
A Chemical Equilibrium Program
for Personal Computers
User's Manual
Version 3.0

MINEQL$^+$: A Chemical Equilibrium Program for Personal Computers

User's Manual
Version 3.0

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Preface

This manual is intended as an introduction and tutorial to the MINEQL$^+$ software. Much of the theory that is related to solving chemical equilibrium problems can be found in other sources (e.g., Stumm and Morgan, 1981; Morel, 1983, Westall et al., 1976). The advantages and disadvantages of implementing a chemical equilibrium approach varies from system to system. Clearly, limitations in thermodynamic data and interferences from rate dependent reactions are the greatest restrictions. Nevertheless, the equilibrium approach provides a way of understanding potential chemical interactions. The presence of uncertainty in input data or in underlying system processes should not deter anyone from using equilibrium programs to explore hypotheses and unravel hidden mechanisms. Often, the interesting information comes from how a system differs from equilibrium, rather than the equilibrium answer itself.

MINEQL (Westall et al., 1976) and its precursor, REDEQL (Morel and Morgan, 1972), were developed to solve mass balance expressions using equilibrium constants. WATEQ3 (Ball et al., 1981) addressed the same problem through minimization of Gibbs Free Energy. The use of Gibbs Free Energy or equilibrium constants are both valid approaches, however WATEQ3 greatly advanced research in chemical speciation through providing a comprehensive and up-to-date thermodynamic database. Recently, efforts were made to combine the database of WATEQ3 and the numerical structure of MINEQL (MINTEQA1; Brown and Allison, 1987).

The growth of chemical equilibrium research is rooted within mainframe computing environments. Until recently, this has been by necessity. However, the introduction of personal computers (PC's) with more than 64 Kbytes of memory meant that chemical equilibrium calculations could be run on less expensive machines and with greater ease. Not surprisingly, all attempts to transfer these mainframe programs to PC's relied on software interface techniques that were more suited for mainframes.

In an age where database software, spreadsheets and word-processors are common, state-of-the-art software must provide a spacial and intuitive interface. This is important, not only in learning the software and its underlying concepts, but in providing quick and sensible methods for operating the software for "expert" users. MINEQL$^+$ is an interactive data management system for chemical equilibrium modeling, which uses the original MINEQL program as an underlying numerical engine (Schecher and McAvoy, 1992). The fundamental structure of MINEQL has not been altered except with regard to input/output protocol. The result is an integrated software package that has a solid theoretical foundation superimposed on advanced data management tools.

MINEQL$^+$ is the result of an collaborative, five-year project with Environmental Research Software, and the Procter & Gamble Co. to develop advanced software tools for water quality research. A summary of MINEQL$^+$ software attributes includes:

- A spatial user interface.
- On-line help screens.
- MINTEQA1 thermodynamic data with additional data from the original MINEQL database.
- Advanced relational database techniques for scanning thermodynamic data and managing output data.
- A relational spreadsheet editor for creating, altering, or deleting chemical species input.

- A Multi-Run Manager for processing field monitoring data, creating synthetic titrations or performing sensitivity analysis.
- A utility for creating and accessing a personal thermodynamic database.
- An object-oriented database tool for managing model output.
- On line DOS utilities.
- Extensive error checking.

In addition, the software allows options for temperature and ionic strength correction.

Version 3.0 of MINEQL$^+$ also supports:

- Graphical display of output data as X-Y plots or bar charts.
- Support for graphical output to video displays and printers.
- A wide variety of surface complexation models including the Triple Layer Model, the Generalized Two-Layer Model (plus a specific instance for FeOH solids), and the Constant Capacitance Model.
- An updated thermodynamic database for adsorption of anions and cations on to FeOH surfaces.
- An improved user interface for many file maintenance functions.

This manual includes four main sections: *Getting Started*, a *User's Guide*, a *Command Reference*, and a *Tutorial*. *Getting Started* introduces basic terminology and explains how to install the software. The *User's Guide* provides an overview of the software, its physical layout and philosophy. Its intent is to give the user a roadmap by which to navigate the software. The *Command Reference* is an alphabetical listing of the major menu options available in MINEQL$^+$ and is intended for more advanced users as a quick way to look up functions. Finally, the *Tutorial* is a compilation of specific chemical equilibrium problems that are presented as examples of how to model various systems. The examples range from simple (e.g., fixed pH) to advanced (e.g., redox or surface complexation) chemical equilibrium problems.

ACKNOWLEDGEMENTS

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MINEQL$^+$ would not have been possible without the prior existence of MINEQL to form its numerical foundation.

We would like to thank the following individuals for their assistance and advice throughout product development and testing:

Dr. John Westall, Oregon State University (Ver 2.0)
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Dr. David A. Dzombak, Carnegie Mellon University (Ver 3.0)
Dr. Janet G. Hering, University of California, Los Angeles (Ver 3.0)

GETTING STARTED

Running MINEQL$^+$

System Requirements

MINEQL$^+$ requires a minimum of 512 Kbytes of random access memory and a hardisk. The software will work on both monochrome and color monitors. The software does not require a math coprocessor chip, but it will work faster if one is present.

Installation

MINEQL$^+$ is distributed in a compressed format, so you must use the INSTALL program to run the program. To install MINEQL$^+$ type:

INSTALL

If you have trouble displaying the installation program on a monochrome screen type:

INSTALL -M

To start the program, from any directory, type: **MINEQL**

MINEQL$^+$ contains several files that are required for its proper operation. If you want to copy MINEQL$^+$ for a friend, please copy the original diskettes. This will ensure that all the files get copied.

Terminology

The mathematics and theory used in MINEQL can be found elsewhere (Westall et al., 1976), however using the software requires understanding certain terms:

1. **Components** - mathematically, these are the independent variables of the mass balance equations (for a linear system). They are a set of chemical entities that are used to create every **species** via a chemical reaction involving these entities. In addition, no other component can be used to represent a particular component other than itself. The selection of a component is somewhat arbitrary. For instance, in a H_2O-CO_3 system, the component for carbonate could be CO_3^{2-}, HCO_3^- or H_2CO_3. However, once the choice of a component has been made, this decision becomes a reference point for defining all thermodynamic constants and reactions. For MINEQL$^+$, the selection of a reference point for components is predefined through the thermodynamic database.

2. **Species** - chemical entities that are the result of reactions in which the reactants are **components.** There are two kinds of species: **soluble species** and **solids.**

3. **Soluble Species** - any species that can exist in the aqueous phase. A soluble species can be a soluble **component** or a complex (i.e., the product of chemical reactions involving components). They can include aquo species (e.g., Ca^{2+}, H^+, SO_4^{2-}), complexes (e.g., $CaCO_3$ (aq), AlF_2^+), chelates (e.g., FeCIT, Na_2EDTA), etc.. The concentration of all soluble species is variable and is a function of the species' thermodynamic data and the concentration of the components that compose the species.

4. **Solids** - any species that have a fixed activity. For regular solid phases (e.g., $CaCO_3$(s), $Al(OH)_3$(s)) the activity is equal to one. However, under this definition, gases with fixed partial pressures are also treated as solids. This definition can also be extended to concepts such as pH and pe. There are two kinds of solids: **dissolved** and **precipitated.**

5. **Dissolved Solids** - solids that have the potential to precipitate if their solubility constraints are exceeded. They do not contribute to the overall mass balance of a problem.

6. **Precipitated Solids** - solids that are present at a fixed activity. If solubility constraints are not met, (i.e., the system is undersaturated) the solid will be converted to a dissolved solid and removed from the calculation.

The above six definitions pertain to all chemical equilibrium calculations and correspond to MINEQL's use of six *Types* of species in its calculations.

Type-I Species: are soluble species that correspond to the system's components.

Type-II Species: are aqueous complexes (i.e., all soluble species excluding the system's components).

Type-III Species: are solids that have a fixed activity. For a regular solid (e.g., $CaCO_3$) this is equivalent to having an infinite reservoir of the solid present. Also, gases at a fixed partial pressure would fall under this Type as would any soluble species (e.g., pH) that must be present at a fixed concentration.

Type-IV Species: are precipitated solids that have the potential to be converted to dissolved solids if they become undersaturated.

Type-V Species: are dissolved solids that have the potential to precipitate if their solubility constraints are exceeded.

Type-VI Species: are species that are not considered in the calculation.

Change Drive

Function: Change the current working disk drive.

Found in: Main → Utilities

Remarks: **Change Drive** displays a list of drive letters based on DOS system information. Any of the drives can be selected for current use.

Possible Errors: Some drives may be displayed that are not physically available. If one of these drives is selected, the default drive will remain unchanged.

Change Direct

Function: Changes the current working directory.

Found in: Main → Utilities

Remarks: **Change Direct** displays a list of subdirectories within the current directory. By using this function it is possible to either move down into these subdirectories or move up closer to the root directory.

Possible Errors: If the current directory does not contain the thermodynamic data or other system information, then MINEQL$^+$ will search the PATH (in the DOS environment) to find them. If the MINEQL$^+$ directory is not listed within the PATH, several problems can arise including system lockup. *Also see: Getting Started.*

Complexes

Function: Allows editing of equilibrium problem.

Found in: Main → Data/Run

Remarks: **Complexes** opens the editor for Type II species (aqueous complexes). There are 2 modes within the editor: View and Edit. View mode is indicated by a large cursor. While in this mode, it is possible to insert or delete individual species (using the **Ins** or **Del** keys) or to move reaction data to another species Type (using the **F3** key). Edit mode (**F2** key) allows the alteration of individual data fields and has a smaller cursor. The editor addresses 3 main types of problem data: (1) stoichiometric coefficients, (2) thermodynamic data, and (3) total concentrations of components. Each of these data types can be accessed from the Edit mode (using the **F2** key again).

Any new species that you add to the problem set can be saved separately using **ThermSave.**

Possible Errors: If you insert a new species into the problem set using the editor, you must always supply at least one stoichiometric coefficient; otherwise the species is considered NULL. If you try to submit a NULL species to the numerical engine, the following error message will appear: *ID Not Found.*

You cannot enter the **Complexes** menu without first selecting components (*see Components*).

Components

Function: Allows selection of chemical components

Found in: Main → Data/Run

Remarks: **Components** displays a list of chemical components that can be selected for any problem set. There are 145 predefined components and 55 NULL components that can be defined by the user (using the **F5** key to activate the input form). A maximum of 25 components can be selected for any given run. Although not strictly required, the main database of thermodynamic data is generally scanned when the user is through selecting components. This will automatically place the user into the **Complexes** editor so the total concentrations can be entered. However, it is also possible to press **Esc** after component selection and create mass action data from scratch.

The number of columns allocated within the editor corresponds to the number of components selected within **Components.** It is possible to delete columns from the editor by eliminating components (from **Components**) and pressing **Esc.** The resulting problem set will be reduced by the number of species eliminated, but all total concentrations and altered data will remain intact.

Possible Errors: For all aqueous systems, H_2O and H^+ must be selected to remain compatible with the main database.

Configure

Function: Sets the graphics hardware options.

Found in: Main → Graphics

Remarks: **Configure** displays a tool that allows the alteration of video display type, printer type, and printer port. MINEQL$^+$ supports two general types of printers: HP Laser Jet and Epson Dot Matrix. Several printer manufacturers support these two protocols. In addition, the software will support output to all parallel ports. Currently, serial port output is not supported.

To change any of the default settings, move the cursor to the desired option and press **Return.** A pull-down menu will appear with available hardware options.

Manipulating a Data View

Once the data is displayed on the screen, it is possible to visually scan the data (Figure 2.18). To view data that is off of the screen, simply use the cursor keys:

- **left arrow:** moves the data view left one cell width;
- **right arrow:** moves the data view right one cell width;
- **up arrow:** moves data view up one row;
- **down arrow:** moves data view down one row;
- **page up:** skips up one page width;
- **page down:** skips down one page width;
- **home key:** top of data view;
- **end key:** bottom of data view.

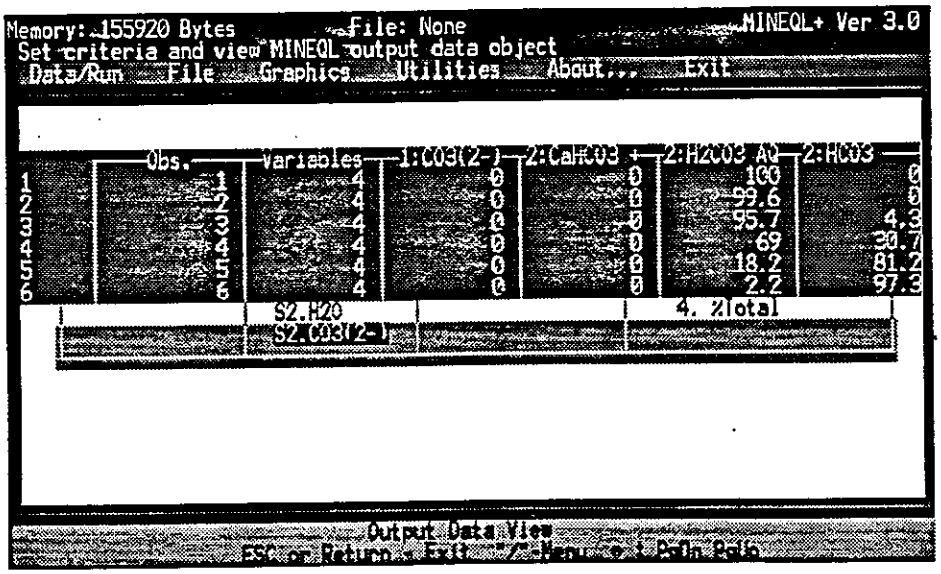


Figure 2.18.

Column Headers

A note about column headers: in the S2 view, the species names are preceded by a number and a colon. The number refers to the species Type as defined in MINEQL. So a header of 1:H(+) indicates a proton in Type I. However, for Types IV and V, a number is not given because a solid can move between these two Types in the course of a multiple-run calculation. In these cases, an "S" (for solid) is used rather than the species Type. There are several indicators that can be used to find out whether a solid is dissolved or precipitated. First, you could refer to the S1 view, which includes a column for species Type. Second, you could look at the Log file to see if any solids have precipitated.

The column headers in the multiple-run view also have some abbreviations. If you selected the total concentration of a component within the Multi-Run Manager, the column header will display T:*ccc* (where *ccc* is the component). Likewise, the log K and enthalpy of a species are displayed as L:*sss* and H:*sss* respectively.

Column Extract, Print & Save

A secondary menu can be activated while viewing the data by pressing the "/" key (Figure 2.19). From this menu, you will be able to extract individual columns, save the data in various file formats or print the data.

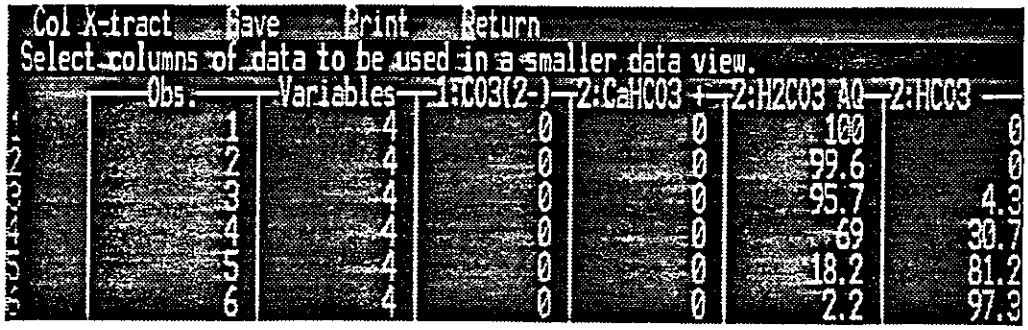


Figure 2.19.

If you select **Col X-tract** from the menu, a cursor will appear above the data view. Move this cursor left or right and click off those columns that you want to keep by hitting the **Return** key (Figure 2.20). The columns that you don't click off will not appear in the current view, but there won't be any permanent alterations to your data object.

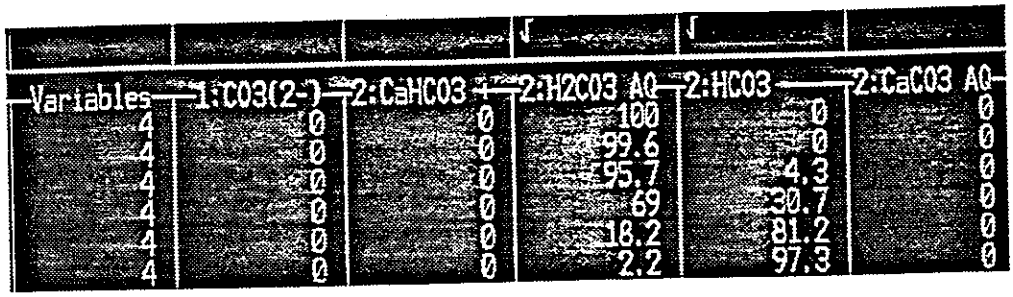


Figure 2.20.

Press the **F6** key to perform the extraction. The new data view will appear on the screen (Figure 2.21).

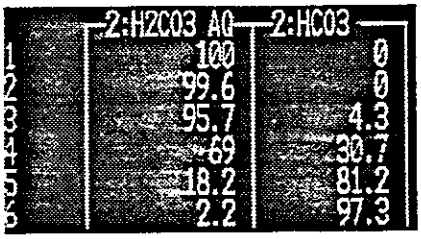


Figure 2.21.

Once you have a data view that is satisfactory, you will probably want to save it in a file. Again, press the "/" key to activate the data view menu. Move the cursor to the **Save** option and press **Return.** There are three data formats in which you can save the data: **Paradox, Lotus 1-2-3,** or **ASCII.** A pull-down menu appears with these options (Figure 2.22). Select one, and the screen will prompt you for a filename. Follow the instructions on the screen, and the data view will be saved with column headers in the current directory.

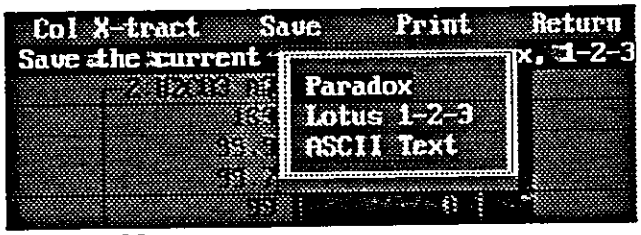


Figure 2.22.

The **Print** option is also in the data view menu. To print the data view, you need to have a printer hooked up to LPT1:. Also, for S2 views you may want to perform some column extraction before printing since the length of a row may be too long and cause the data to wrap.

Copying and Deleting Output Objects

Since there are several files associated with any given object, copying and deleting objects cannot be handled using the standard DOS commands. As a result, whenever you are planning to move or erase an output object ***always use the Output Manager or the Copy or Delete option in the Utilities menu.*** If you fail to do this, you may damage the data object and leave it unreadable.

To delete a data object, place the cursor in the Object window and press the **Del** key. The highlighted object and all of its members will be deleted. To copy an object, press the **F3** key. A menu of current drives will appear. Select one as the destination drive. The entire object will be copied.

File Options

The second choice in the Main menu relates to file operations: saving and retrieving problem sets, creating and reading a personalized thermodynamic database, browsing and printing text files (Figure 2.23). Saving and retrieving (**Save** and **Read**) allows you to save input files and retrieve them at a later date without having to scan the thermodynamic database again or reset the total concentrations for each component. The **Browse** and **Print** options are used to view ASCII files on screen or with a text printer.

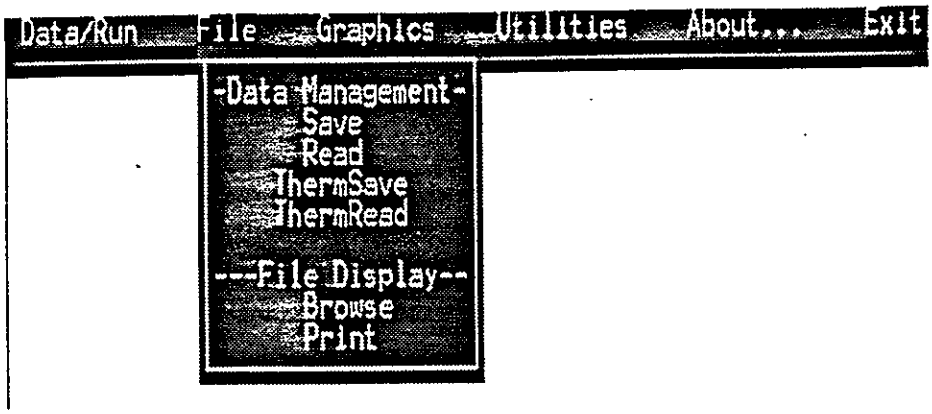


Figure 2.23.

The user interface for all **File** options except **ThermSave** and **ThermRead** provides you with a File Directory Box (Figure 2.24). The criterion at the top of the box will be used to select files in a directory. The default criterion for **Save** and **Read** is **.MIF*, which will display all files with an "MIF" extension located on the current directory. A criterion of **.xx* would display only files with extensions of *xx*. See the DOS manual for further clarification of file criterion. In general, the file criteria does not need to be altered. To read a file located on the current directory, move the cursor to the desired file and press **Return**. On the other hand, to write a new file to the directory, move the cursor to the field labeled "File" and type in the new name. In order to leave the File Directory Box without reading or writing a file, press the **Esc** key to return to the Main Menu.

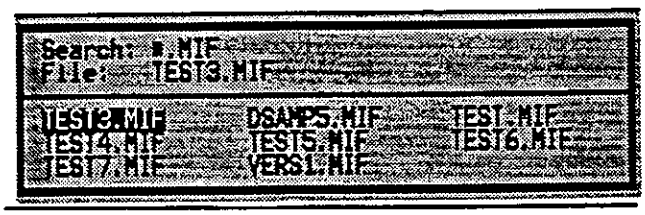


Figure 2.24.

Creating and Using a Personal Thermodynamic Database

During any given session, you may add or alter mass action data with the editor. In some cases, you may have data that you want to reuse. The **ThermSave** option allows you to create a repository of thermodynamic data that can be accessed later. This activates the Personal Database Manager (Figure 2.25). The utility automatically scans the current problem set to see if you have added or altered any data. If not, it returns to the Main menu. Otherwise, the utility displays each new species, one at a time, and asks you to either: (1) go on to the **Next** species, (2) **Add** the species to the personal database, or (3) return to the Main menu (**Continue**).

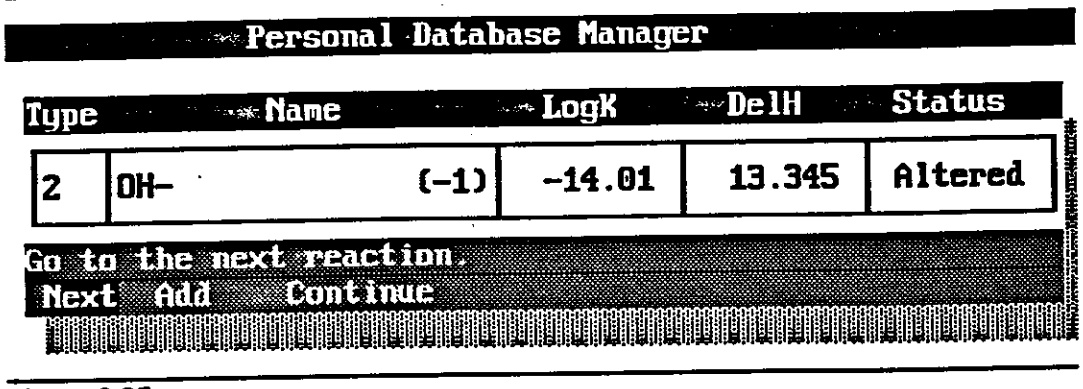


Figure 2.25.

This personal database must be read in explicitly (using **ThermRead**) in addition to the normal scanning of the main thermodynamic database. Basically, **ThermRead** is used to append data onto the current problem set after the main database has been scanned. In contrast, when a main database scan is performed (**F2** within the components menu), a new problem set is started. **ThermRead** *and* **ThermSave** *never have any affect on the main thermodynamic database.*

This feature, along with the ability to create your own components makes MINEQL$^+$ completely customizable. It is conceivable that you could create your own ligands or metal components, determine the mass action data for their interactions, and catalog the data within a personal database.

Graphics

The third choice in the Main menu (**Graphics**) relates to the display of output data as bar charts or X-Y plots (**Open**) and the configuration of graphical display devices (**Configure**; Figure 2.26).

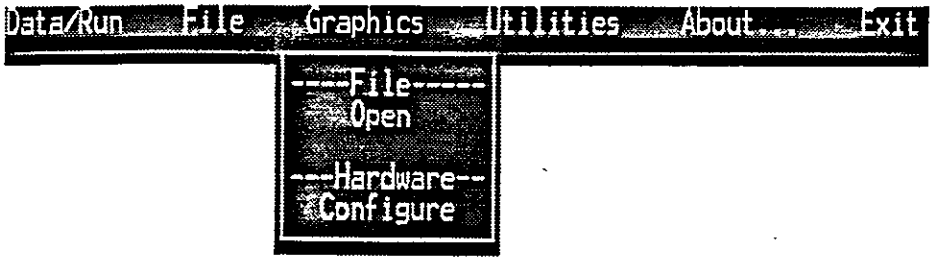


Figure 2.26

Generating Output Graphics

To open a data object for plotting, move the cursor to the **Open** option in the **Graphics** menu. You will be shown a tool called the MDO Selector which will allow you to choose the output file that you want to plot (Figure 2.27).

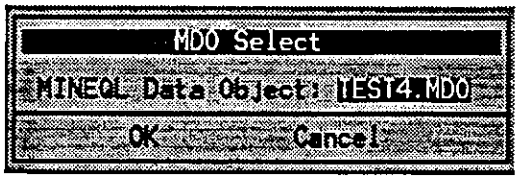


Figure 2.27

To choose a data object that is different than the default one, make sure that the cursor is located on the field labeled "MINEQL Data Object" and press **Return.** A pull-down menu will appear with any additional data objects that are located on your directory. If the data object is correct, move the cursor to the **OK** option and press **Return.** The Graphics Manager will appear (Figure 2.28).

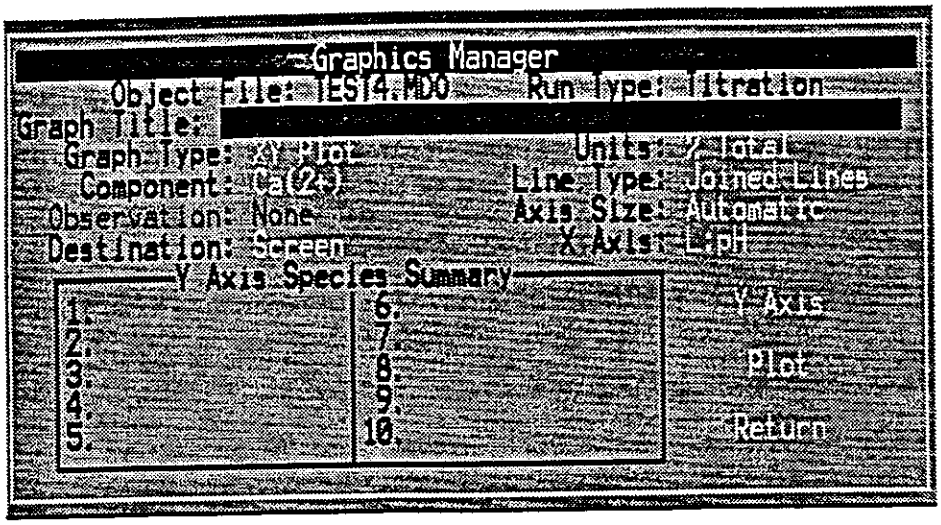


Figure 2.28

All graphical output is manipulated with the Graphics Manager which is a uniform user interface tool for controlling the data and attributes of a plot. The Graphics Manager will allow certain types of user interaction depending on the type of calculation that was performed when generating the output data. Table 2.2 outlines the type of graphs that are possible with each type of calculation.

Table 2.2 Plot Types used with Calculation

Calculation	Bar Chart	X-Y Plot
Single	YES	NO
Titration	YES	YES
2-Way	YES	YES (Contour)
Field Data	YES	YES

The top line of the Graphics Manager displays the name of the data object that will be plotted as well as the type of calculation that was performed to create the object. The rest of the Graphics Manager is composed of the following set of menu fields:

- **Graph Title** - An input field that allows you the option of displaying a short sentence on the top of all charts and plot.

- **Graph Type** - A toggle switch that indicates whether a graph is to be displayed as a bar chart or an X-Y plot. This toggle also activates/deactivates certain options within the Graphics Manager because some user interface features are not appropriate for both bar charts and X-Y plots.

- **Component** - A pull-down menu that contains the list of components used within the calculation. All charts and plots are for a single component and all its species.

Setting Display Options

All information about graphics display devices can be set by using the **Configure** option in the **Graphics** menu. This option will display a tool that will allow you to alter the type of video display, printer, the printer resolution and the printer port (Figure 2.31). To change any of the device information, move the cursor to the device item of interest and press **Return**. A pull-down menu with device options will appear on the screen. This information is automatically saved when you finish a MINEQL$^+$ session.

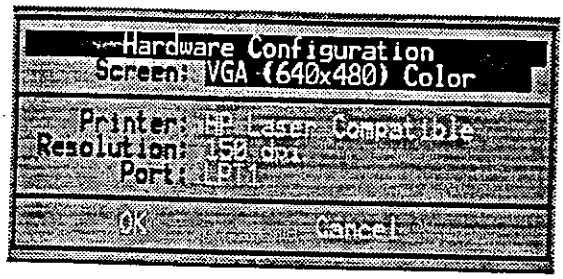


Figure 2.31.

Utilities

The **Utilities** choice in the Main menu is provided as a way to manage MINEQL Data Objects (MDO's). The utilities allow copying and deleting MDO's, changing the current directory or disk, viewing the disk contents, as well as exiting to a DOS shell (Figure 2.32).

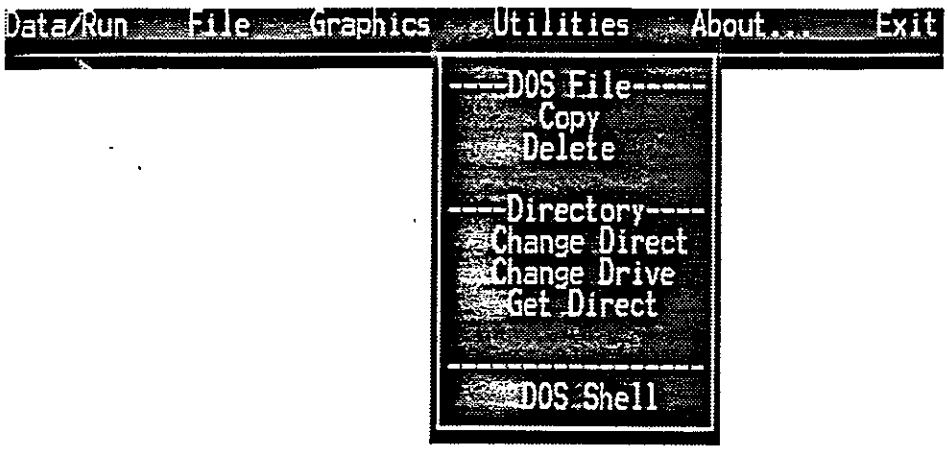


Figure 2.32.

Copy

After moving the cursor to **Copy** and pressing **Return**, a tool will appear that will allow data backup (Figure 2.33). Select the Data Object that you want to copy by moving the cursor to the field labeled **Source Object** and press **Return**. You will be presented with a list of all MDO files available on the current directory. Select the Object by pressing **Return**. Next, in the field labeled **Destination Path**, type in the pathname to where you want the Object copied. When you are finished, move the cursor to the **OK** option and press **Return**. The Data Object (and all support files) will be copied to the destination.

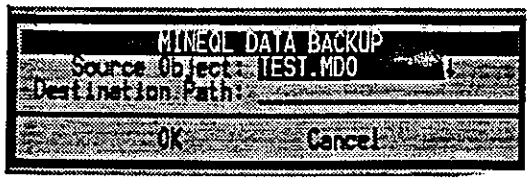


Figure 2.33.

Deleting Files

Deleting an MDO is similar to the procedure for copying Objects. Select **Delete** and press **Return.** A tool will appear that will allow the deletion of MINEQL Data Objects (Figure 2.34). Move the cursor to the option labeled **Data Object to Delete** and press **Return.** A menu will appear that will contain all available MDO files. Select the Data Object that you want to delete and press **Return.** To delete the Object, move the cursor to the **OK** option and press **Return.** The Object file and all its support files will be deleted from disk.

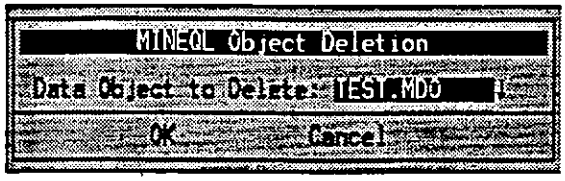


Figure 2.34.

Changing the Current Directory

The DOS directory is based on a tree-structure in which any directory can have subdirectories. The form and depth of these branches are defined by you when you use the **MD** (make directory) command. By changing the current directory, you are traveling throughout the directory tree. There are four types of directory information displayed in this option (Figure 2.35):

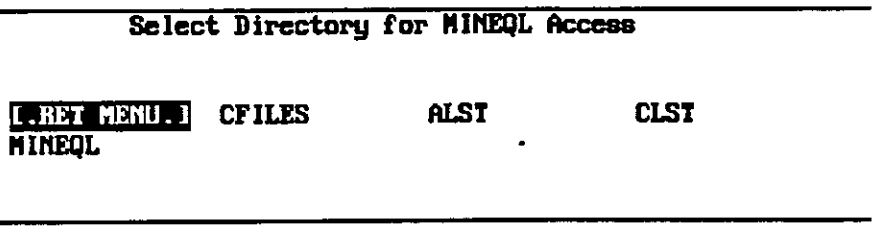


Figure 2.35.

- **The Current Working Directory:** indicated on a status line at the bottom of the menu.
- **The [.RET MENU.] Button:** allows you to return to the Main menu.
- **A List of Subdirectories:** if a directory contains any subdirectories, they will be displayed in the menu.
- **The [.PREV DIR.] Button:** allows you to go to the directory above the current one.

Using different directories for data management is beneficial when you have a wide range, or large number, of problem sets.

Changing the Current Drive

Using a different default drive is similar to changing the current directory. A menu will appear that contains the available drives along with the **[.RET MENU.]** option (Figure 2.36). To select a new drive, move the cursor to the choice on the menu that corresponds to the drive of interest and press **Return.** If you have less than five drives you will still see menu choices for five. This is because DOS sets the default number of drives to five, whether they are there or not. Selecting a drive that is not present will not have any effect on the current drive status.

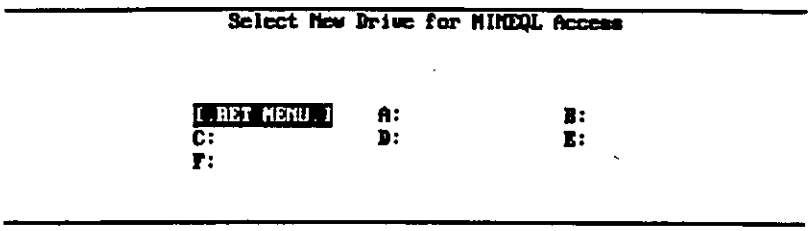


Figure 2.36.

Displaying a Detailed File Directory

A detailed file directory is similar to using the DOS **DIR** command in that it contains information about the file size and time of creation. To use this option, press the **Directory** choice in the **Utilities** menu. A file criteria box will appear. Once you press **Return**, the screen will display six types of information (Figure 2.37):

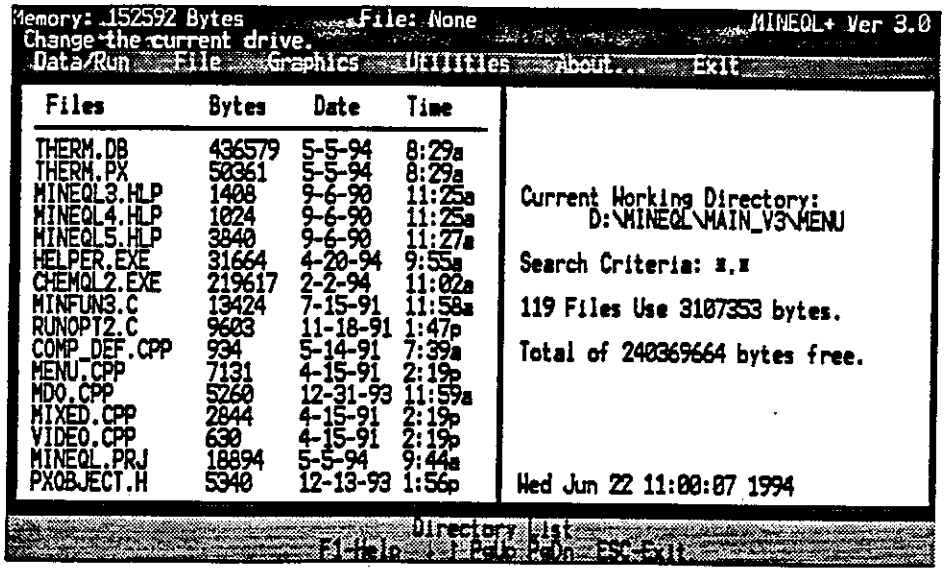


Figure 2.37.

- **File Directory:** a complete, DOS-like directory that can be scrolled up or down.
- **The Search Criterion:** the criterion that was specified in the criteria box.
- **The Number of Files:** the number of files that meets the specified search criterion.

- **The Number of Bytes:** the amount of space that these files occupy.
- **Free Space:** the amount of space that is remaining on the current drive.
- **Current Date and Time:** self explanatory.

Exiting to a DOS Shell

The **DOS Shell** option is provided so that you can exit MINEQL$^+$ temporarily. In order to return to MINEQL$^+$, type **EXIT** at the DOS prompt.

About...

This option is for informational use only. In it, you will find details about copyrights, how to become a registered user, technical references, and various legal notices.

COMMAND REFERENCE

2-Way

Function: Allows the creation of a 1 or 2 way sensitivity analysis.

Found in: Main → Data/Run → Multiple Runs

Remarks: The 2-Way analysis creates synthetic input data for multiple runs. Parameters that can be varied include temperature, surface area, the total concentration of any component, the log K or enthalpy of any species. Either 1 or 2 input parameters can be varied at a time. The number of actual runs that will be created will be the product of the number of points generated for each parameter. *Also see: Titration.*

Possible Errors: The starting and ending values must be valid for the parameter being varied.

About...

Function: Shows information on software.

Found in: Main

Remarks: None

Possible Errors: None

Browse

Function: Views text files on screen.

Found in: Main → File

Remarks: File browsing was incorporated into version 1.0 of MINEQL$^+$ as a means of viewing ASCII output files. Since output is no longer in this format, the browse function has limited use. However, there are still times when having direct access to text files (such as the header or log files) is convenient.

Possible Errors: Browse will only read in files that are smaller than the available memory.

An Overview of Chemical Equilibrium Problem Solving

The process of chemical equilibrium modeling can be broken down into several categories, not the least of which is the development of numerical code with traditional programming languages. Although development of numerical code in modeling is important, MINEQL$^+$ was designed for those modelers whose focus is centered on the accuracy and manipulation of data. In the context of chemical equilibrium modeling, data management is directed toward:

- The review, alteration, selection and management of thermodynamic constants;
- The input of total concentrations of chemical constituents as well as parameters like temperature and surface area;
- The processing of multiple-run calculations; and
- The manipulation and analysis of species distribution output.

This shift in emphasis from code to data should not be interpreted as an attempt to trivialize the code side of chemical equilibrium modeling - just the opposite is true. It is because chemical equilibrium research has developed such advanced code that MINEQL$^+$ can address the other side of the problem: the effective manipulation of model data.

In a sense, chemical equilibrium modeling is fairly simple. There are only three questions that must be answered in order to run any chemical equilibrium model: (1) What chemical entities (components) are present in the system? (2) How do they interact with each other (to form chemical species)? and (3) How much of each chemical is present (the total concentration of each component)? MINEQL$^+$ is designed to facilitate answering these questions and to help in generating multiple calculations that can be used in spreadsheet, database or statistical software.

A typical MINEQL$^+$ session is outlined as follows (Figure 1.1): (1) select chemical components from the component menu (question 1 from above), (2) scan the thermodynamic database (question 2), (3) input the total concentration of each component (question 3), (4) (optional) alter the set of thermodynamic constants and mass action expressions for the system, (5) (optional) set criteria for a multiple run, (6) start calculations, (7) (a) review output data and extract data subset for use in database or spreadsheet program or (b) view graphical representation of output data.

What MINEQL$^+$ Can Do:

Typical calculations with MINEQL$^+$ include:

- Calculation of the distribution of chemical species in an aqueous system;
- Determination of the theoretical pH values for a system;
- Simulation of surface adsorption behavior; and
- Modeling the precipitation of solid phases.

These calculations can be applied to:

- Modeling the transport of ions in porous media;
- Formulating mechanisms for toxicological interactions;
- Aiding laboratory quality assurance/quality control; and
- Developing new thermodynamic data;

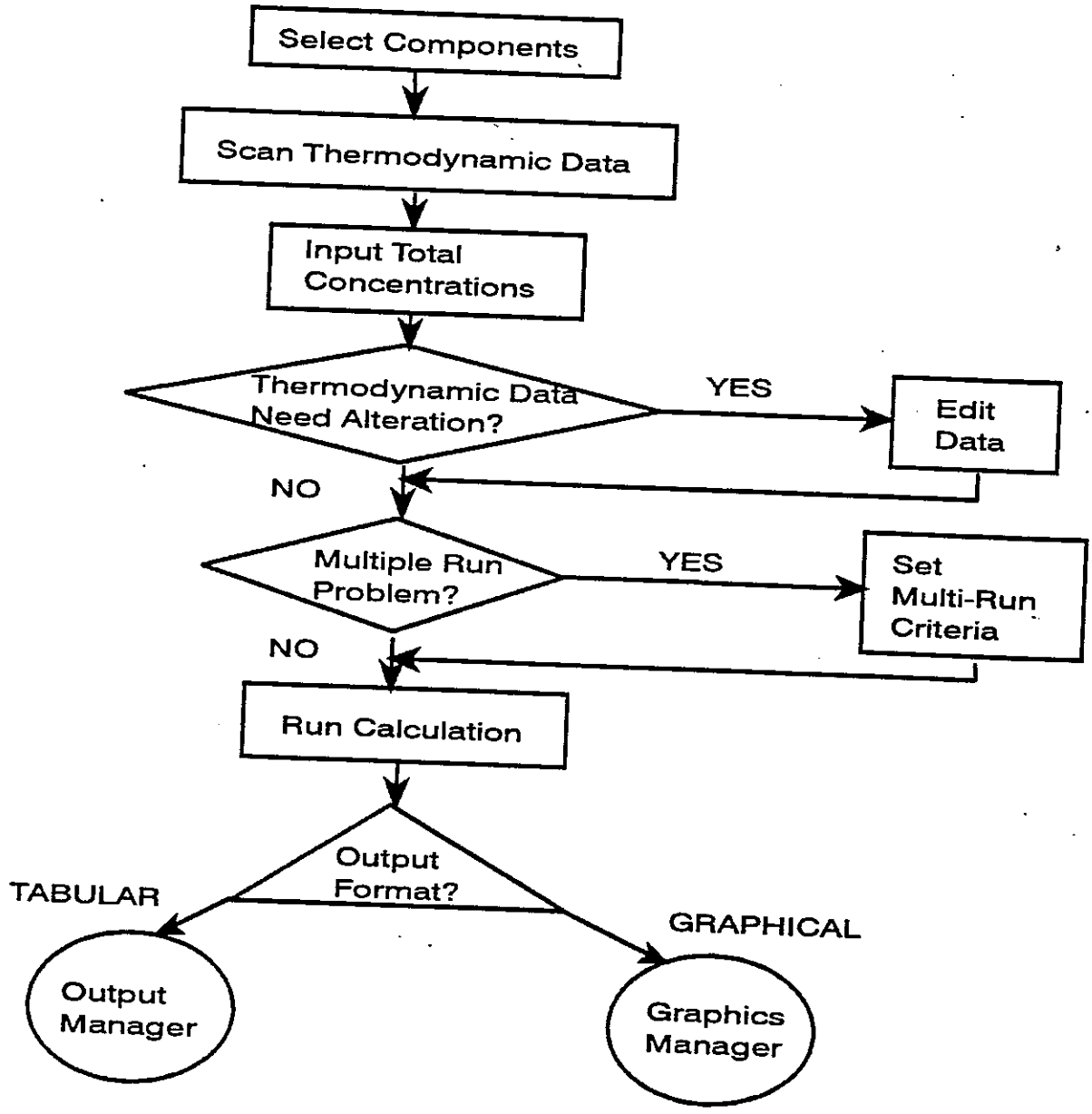


Figure 1.1

USER'S GUIDE

USER'S GUIDE

The Main Menu

Once the software is loaded and the copyright notice has been displayed, the Main menu will occupy the entire screen (Figure 2.1). There are a number of features of the interface that should be discussed at this point:

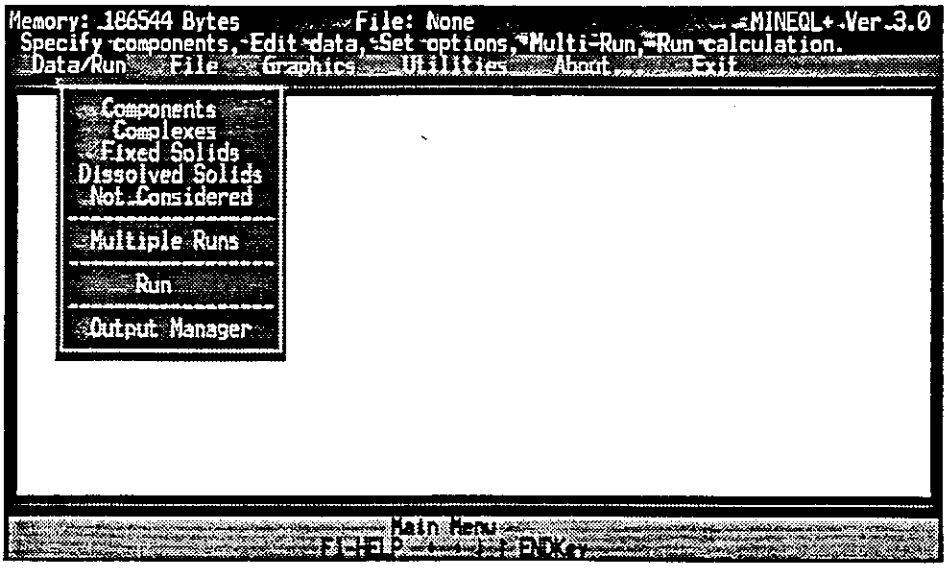


Figure 2.1

• **Pull-down Menus:** The menus in MINEQL$^+$ are controlled with the cursor keys and the cursor is indicated by a rectangle whose movement corresponds to the pressing of these keys. The menus are organized into two types: the horizontal (Main) menu and vertical sub-menus.

• **Status Lines:** There are two types of status lines on the screen. The first is located on the second line from the top and its content changes depending on the location of the cursor. This line functions as a "short" help line. The second status line is at the bottom of the screen and it indicates which keys are active on the keyboard as well as the current menu level.

• **Memory Status:** The memory status is located in the upper left corner of the screen. The number present is the amount of memory (in bytes) that is available for work. This number will change as you read in thermodynamic data and will vary depending on problem size. For MINEQL$^+$ to calculate a problem, the memory status number must be at least 180,000 bytes prior to scanning the thermodynamic database.

• **Tag Keys:** An option within the Main menu can also be accessed by typing its highlighted letter. For instance, the UTILITIES option can be selected by moving the cursor to **Utilities** and pressing **Return**, or by pressing the letter "**U**".

• **Help Screens:** Pressing the **F1** function key activates the context-sensitive help screens. The screens are summaries of this manual and provide reminders of basic concepts for running the software.

Within the Main menu are options called: **Data/Run, File, Graphics, Utilities, About...** and **Exit.** Each of these options are discussed in below.

Data/Run Options

The set of options under the class of **Data/Run** pertain to selecting components (which define the chemical equilibrium problem), editing the problem, setting multiple-run options, running a calculation, and accessing the Output Manager. The usual procedure for beginning a problem is to move the cursor to the **Components** option in the **Data/Run** menu and press **Return** (Figure 2.2).

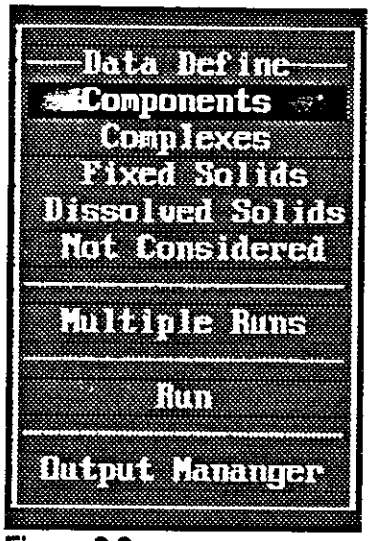


Figure 2.2

Selecting Components

Once the **Components** option has been selected, the screen will change to show an array of components that are used in the version 3.0 database (Figure 2.3). To select a particular component, move the cursor to the component's location and press **Return.** At this point, the component will be highlighted (with a different color on color systems or with asterisk on monochrome). Figure 2.3 shows an example screen with four components selected: H_2O, Ca^{2+}, H^+ and CO_3^{2-} (*H_2O must be always selected for aqueous systems*). There are 145 components to choose from (listed in alphabetical order), but since the screen can only fit 60 at a time, you will need to scroll through the list to view additional components. Scrolling of the component list can be accomplished with the cursor keys or with the **PgUp** or **PgDn** keys. In addition to the 145 components provided with MINEQL$^+$ there are an additional 55 "NULL" components that can be defined for your personalized use.

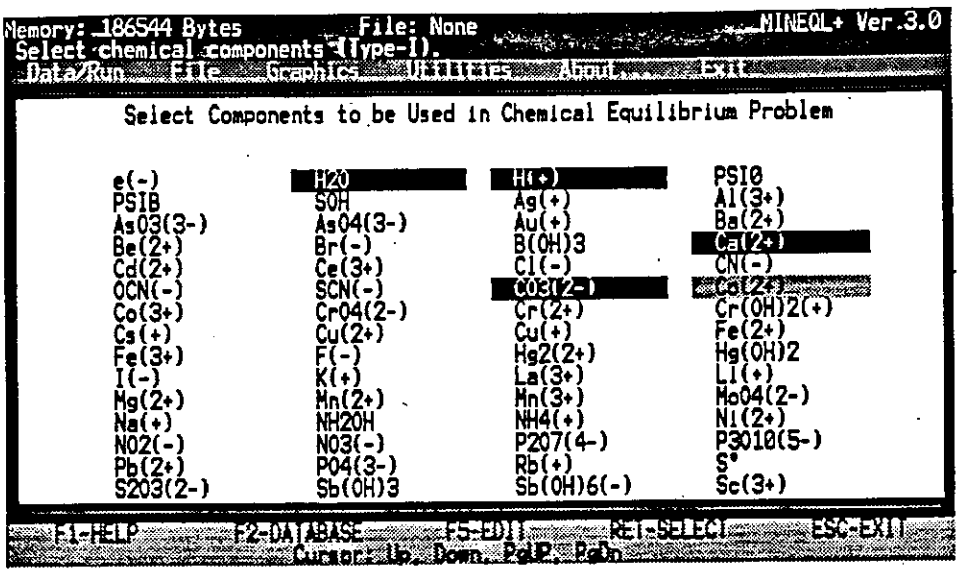


Figure 2.3

To define a NULL component, press the **F5** key. An input form will be displayed on the screen (Figure 2.4). Four pieces of information are needed here, the component's: (1) name, (2) ionic charge, (3) κ^0, (equivalent ionic conductance at infinite dilution) and (4) ionic radius. With the exception of the component's name, this data is used to calculate solution conductivity. Conductivity is computed as a side calculation when you turn on ionic strength corrections. If you are not planning on running ionic strength corrections, or you don't care about the solution conductivity, you don't have to supply this data. The estimated value for conductivity has no effect on the calculation of ionic strength.

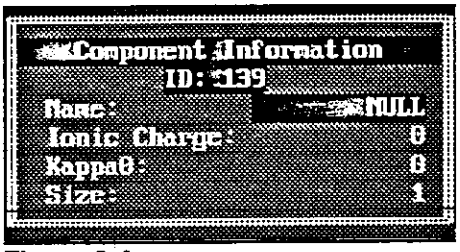


Figure 2.4

Once a set of components is selected (25 maximum), the thermodynamic database is scanned by pressing the **F2** key. Depending on the number of components you have selected, this step usually takes 0.5 - 12 seconds. As with all levels of the menuing system, the **Esc** key will allow you to reverse your steps and return to the previous menu level. In this case, pressing **Esc** would bring you back to the Main menu without scanning the database.

Editing a Problem

Four menu options are available for editing an equilibrium problem and correspond to the MINEQL Types defined in *Getting Started*.

MINEQL TYPE	MENU OPTION
II	Complexes
III	Fixed Solids
IV	**NA**
V	Dissolved Solids
VI	Not Considered

The format for the editor (Figure 2.5) is identical in all cases, only the Type of species is different. The editor is segmented into four distinct fields: species names (vertically on the left), a table of stoichiometric coefficients (in the middle of the screen), corresponding equilibrium constants (Log K) and enthalpy values (Delta H) (vertically on the right), and a set of total concentrations (mole/L) for each component (horizontally on the bottom). The field containing the names of each species cannot be accessed directly, but is altered through changing the values of the stoichiometric coefficients.

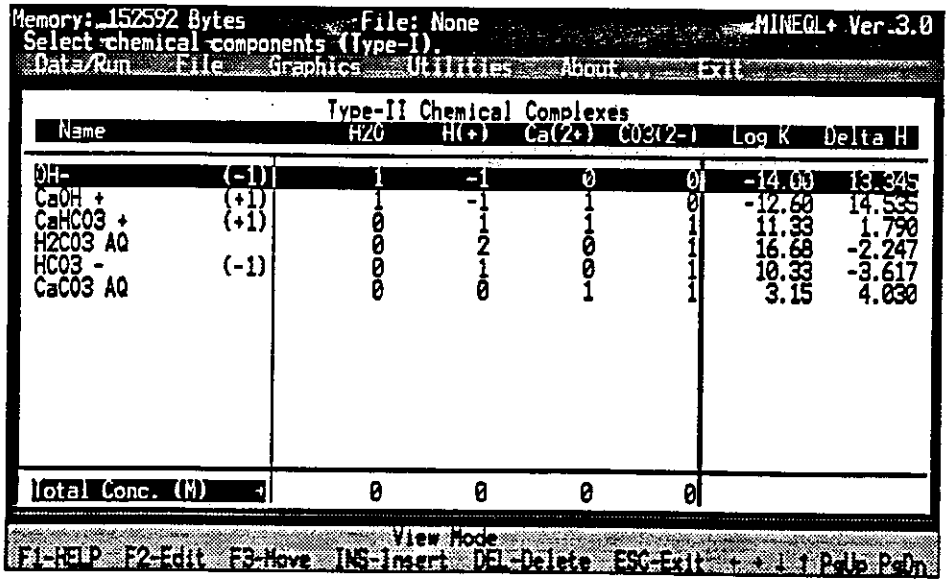


Figure 2.5

The editor uses a modified spreadsheet format for accessing the data. Often, a problem will contain more than four components. Because, the editor can only display 4 columns (components) and 13 rows (species) at one time, the cursor keys are used to scroll the screen left/right (to access additional components) or up/down

(to access different species).

The editor runs in two modes: View and Edit. View mode is indicated on the bottom status line and by a large cursor that spans the width of the screen. This mode is used to transverse the input data quickly without changing existing values. This mode is also used for deleting, inserting and moving species.

The **Del** key is used to delete a species at the current cursor location. The **Ins** key will insert a NULL species at the current location. A NULL species must be further edited to be included in the mass balance calculations since it does not contain any information about stoichiometry, Log K, etc. (see examples in Section 4). Moving a species from one Type to another is accomplished by pressing the **F3** key and selecting the destination Type for the species (Figure 2.6).

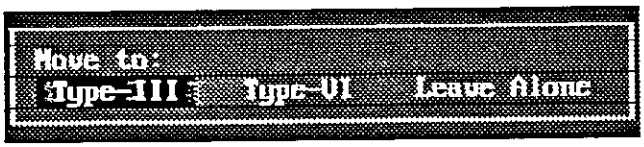


Figure 2.6

Edit mode is indicated on the bottom status line and by a smaller cursor. This mode is used to access individual entry cells (e.g., a single coefficient, a thermodynamic constant, or a total concentration). To enter edit mode, press the **F2** key. The cursor will be ready to travel within the table of stoichiometric coefficients. Pressing the **F2** key a second time will put the cursor in the list of thermodynamic data. Pressing **F2** a third time will place the cursor in the field where the total concentrations are found. Finally, pressing **F2** again will bring the cursor back to the table of coefficients. To exit Edit mode and return to View mode, press the **Esc** key.

While in Edit mode, any of the individual cells in the three fields (coefficients, constants and totals) can be changed. If you change the value of a stoichiometric coefficient, the name of the species will automatically be changed. For instance, $CaCO_3$ has a 1 in the Ca(2+) column and a 1 in the CO3(2-) column. If the coefficient in the Ca(2+) column is changed to 2, the resulting species name is changed to $Ca_2CO_3^{2+}$. Also note that the appropriate ionic charge is automatically calculated for any given species.

To edit an input value, press any alphanumeric key or **Ctrl-Return.** The cursor will change to a smaller size (one character wide). Type in the new value for the cell and press **Return.** If you put in a value that is inappropriate for the cell, MINEQL$^+$ will display an error message and require you to try again.

Generally, the coefficients and thermodynamic data do not have to be altered to run a problem. However, the total concentrations for all components are not known at start-up. Therefore, *all total concentrations must be initialized by the user.*

To exit the editor, press the **Esc** key while in View mode.

Setting Multiple-Run Options

Although you are not required to perform several runs at a time, the real power of MINEQL$^+$ will become more evident if you do. The ability to apply chemical equilibrium calculations to a network of field monitoring data or simulate the titration of an aqueous solution helps to broaden the overall applicability of chemical equilibrium calculations.

To perform a multiple-run calculation, you will need to set up a problem in the same manner as you would a single-run calculation: select components, scan the thermodynamic database, input the total concentrations of chemical components. This information establishes the initial conditions for the multiple-run. Next, you will need to select the type of multiple-run for the calculation (Figure 2.7) by moving the cursor to the **Multiple Runs** option, and pressing **Return** twice.

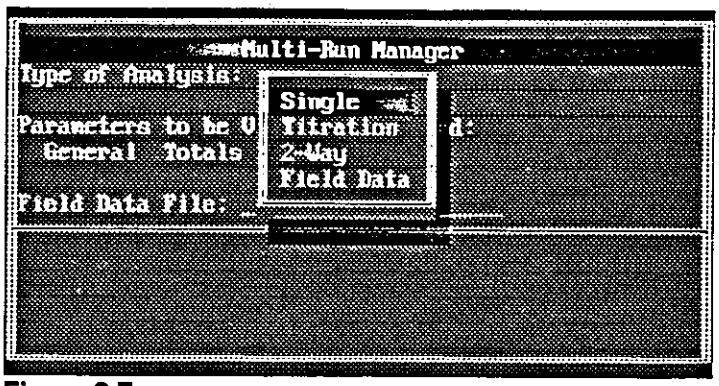


Figure 2.7

Multiple-Run Analysis

The Multi-Run Manager contains four types of multiple-run calculations: **Single, Titration, 2-Way** and **Field Data.** The default option is **Single,** in which case no multiple-run options are in effect. The **Titration** option generates synthetic input data in a manner that is analogous to an actual titration (Figure 2.8). Up to three multiple-run parameters (discussed below) can be varied at one time and MINEQL$^+$ adds them to the solution simultaneously. For example, titrating a system with $NaHCO_3$ would require that three components be selected as multiple-run parameters (**Na(+), H(+)** and **CO3(2-)**). The calculation would proceed so that the multiple-run parameters are incremented together (as a dependent system). The **2-Way** option (2-way sensitivity analysis) also generates synthetic input data but, unlike **Titration,** multiple-run parameters can be varied independently from each other and a maximum of two parameters can be selected at once (Figure 2.8). A typical example of a **2-Way** calculation would be a calcite system in which you want to know the concentration of Ca^{2+} as a function of pH and P_{CO2}. One multiple-run parameter, say P_{CO2}, is held constant while the other is varied. This process would be repeated at various increments of P_{CO2}. The size of the resulting output data set would contain *nxm* runs; where *n* and *m* are the number of increments attributed to each multiple-run parameter. Finally, **Field Data** analysis is any multiple-run calculation where you supply an external data set for processing. An example of this would be environmental field monitoring data where several samples are taken over time.

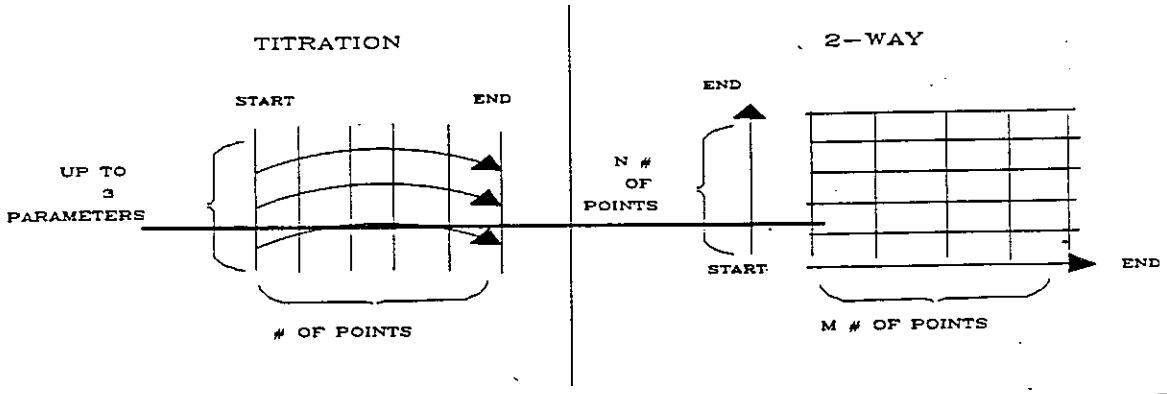


Figure 2.8

Selecting Multiple-Run Parameters

In the Multi-Run Manager, different multiple-run parameters types can be selected and a corresponding pull-down menu will appear. The pull-down menus list parameters to be varied, and depend on what components and species are present in your system (Figure 2.9).

Table 2.1 The Multiple-Run Parameter Types

- **General:** temperature and surface area;
- **Total:** the total concentration of individual components;
- **LogK:** the equilibrium constants for each species;
- **DelH:** the enthalpy values for each species.

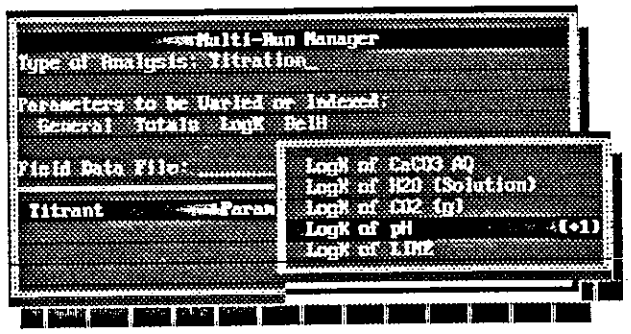


Figure 2.9.

The basic process is one in which you move the cursor to the parameter that you want to vary, and select it by pressing **Return.** When running a **Titration** or **2-Way** analysis, additional information will be asked for: (1) *Starting Value*, (2) *Ending Value*, and (3) *Number of Points* (Figure 2.10). It is important to understand that the values used in starting and ending a titration refer to *cumulative* values. For example, if you want to simulate a titration of a 1 liter distilled water system with 1.0N HCl, and if you add it in 1 μl increments, then the HCl is being added in increments of 1×10^{-6} moles. Given that this titration will have 10 points, the starting value of H(+) and Cl(-) would be 1×10^{-6} and the ending value 1×10^{-5} (i.e., 1×10^{-6} multiplied by the number of points). ***See the Tutorial for further examples of setting these values.***

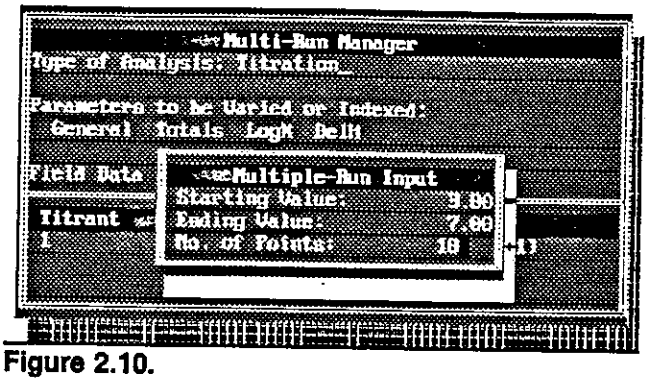


Figure 2.10.

For a titration, the *Number of Points* is only asked for once, while in 2-Way analysis, you need to input this information for each component or parameter to be varied.

For **Field Data** calculations, the process of selecting a multiple-run parameter is almost the same as the one described above. However, since you must provide the multiple-run data from an external data file, MINEQL$^+$ will not ask for information related to the starting and ending values. Only two pieces of information are required to run **Field Data** analysis: (1) the column order of your data file, and (2) the name of the file. The file must be an ASCII text file and must be organized such that each column is a separate parameter (see Table 2.1) and each row a separate run or observation. There can be no more than 25 columns in the file and the maximum number of rows should be below 4000 if you plan on generating output compatible with Lotus 1-2-3 file format. Otherwise, the file can maintain a free format. To tell MINEQL$^+$ which columns are associated with which parameters, you must select the multiple-run parameters in the order that they appear in the data file (Figure 2.11). To review the order of multiple-run parameters, press the **F6** key and scroll the bottom window of the Multi-Run Manager.

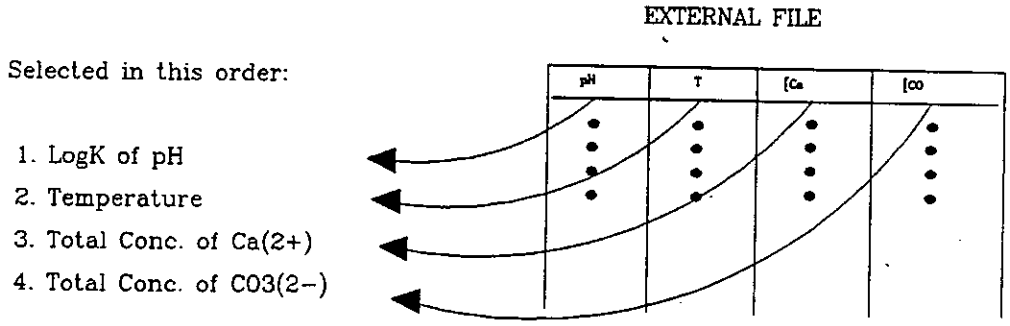


Figure 2.11.

Running a Calculation

Select the **Data/Run** choice on the Main menu, followed by **Run**. The screen will change to the Run-Time Manager (Figure 2.12). There are several parameters that can be modified before running a calculation.

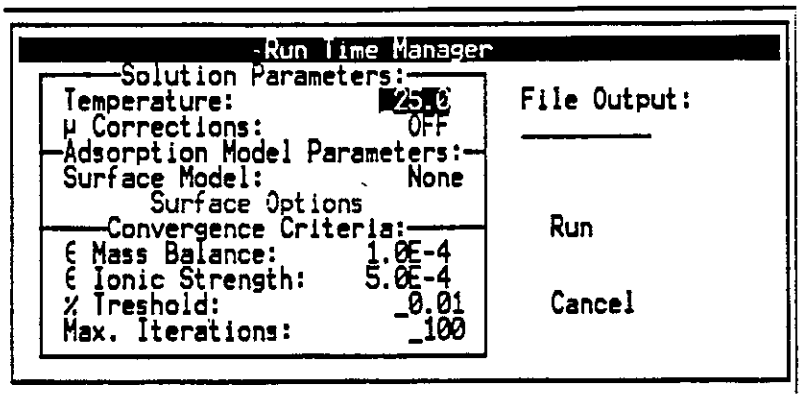


Figure 2.12.

Solution Parameters

- **Temperature:** aqueous solution temperature in degrees C.
- μ **Corrections:** a toggle indicating whether ionic strength corrections should be made during the calculation.

Adsorption Model Parameters

- **Surface Model:** a pull-down menu indicating which electrostatic surface model (Triple Layer, Two Layer FeOH, General Two Layer, Constant Capacitance), if any, is to be applied to the equilibrium problem.
- **Surface Options:** opens the Surface Complexation Manager, a generic input form for setting the input parameters for electrostatic surface complexation problems (*see the Tutorial for examples*).

Convergence Criteria

- **Mass Balance** ϵ: a small number ($<10^{-3}$) that specifies the degree of accuracy in mass balance calculations. The smaller the number, the higher the accuracy, but calculations will take longer to converge.
- **Ionic Strength** ϵ: specifies how accurate the estimates for ionic strength need to be. For some systems, the presence of solids can create an oscillatory response when ionic strength corrections are assumed. One way to help guarantee convergence is by increasing this criterion.
- **Threshold:** this number represents the smallest percent total to report in the output. Values smaller than this number are considered to be zero.

• **Max. Iterations:** a number that tells the program to stop calculating when this many iterations have been performed, even if a solution has not been found.

File Output

Give the name of a file in which you want all output to be stored. To perform and save successive runs, this name must be changed between each run, or else the old output will be replaced with new output.

Run

When selecting the **Run** option, the numerical engine is engaged and a window appears that indicates that calculations are in progress (Figure 2.13). The output data will be in an object oriented data format that you can access with the **Output Manager.** To save successive runs, the filename must be changed between each run. If not, a prompt will appear asking you whether or not to replace the old data object with the new one (Figure 2.14). If you do not want to replace the old data, MINEQL$^+$ will return to the Main menu.

Figure 2.13.

Figure 2.14.

Return

Return to the Main menu (same as pressing the **Esc** key).

With the exception of *File Output*, all of the run-time options have default settings:

Temperature: 25
μ **Corrections:** OFF
Surface Model: NONE
Mass Balance ϵ: 10-4
Ionic Strength ϵ: 5x10-4
Threshold: 0.01
Max. Iterations: 100

Although it is not necessary to alter these values to run a calculation, you may want to do so for specific applications.

Accessing the Output Manager

The Output Manager provides a method of examining output data from various view points. The output data is in the form of a data object. Data objects are essentially sets of data files that can be managed and manipulated in a logical manner. The data files that comprise an object are referred to as data members. In MINEQL$^+$, every data object can have 5 basic types of data members: header, log, multiple-run structure, 1st data structure view (S1), and 2nd data structure view (S2) (Figure 2.15).

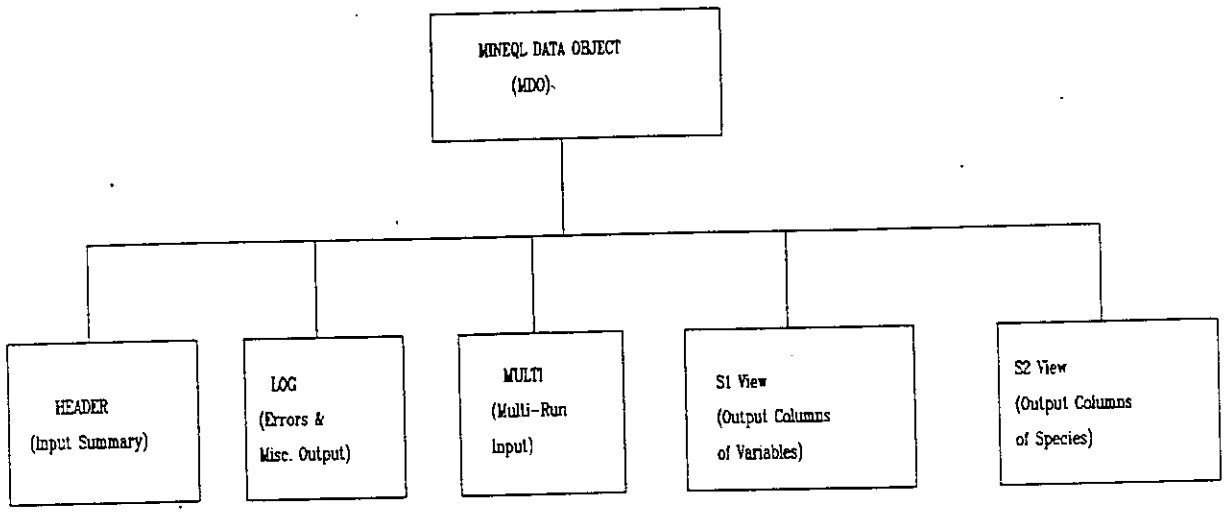


Figure 2.15.

• **The header** provides a summary of the input conditions as well as a reminder of the stoichiometry used in mass action expressions.

• **The log** contains miscellaneous output (e.g., total charge in solution) as well as any error messages. If the calculation required more iterations than was allowed in the runtime options, the last iteration's output is dumped to the log.

• **The multiple-run structure** contains a reiteration of the data used in a Titration, 2-Way or Field Data analysis. If a single run is performed, this member will not be present. In general, the multiple-run structure contains the independent variables for an analysis, whereas the dependent variables can be found in the S1 or S2 structures.

• **The S1 and S2 data view** is actually several data files, one for each component in the system (e.g, S1.H(+), S1.CO3(2-), S1.Ca(2+), etc.). What distinguishes the S1 structure is its column headers: output data is organized in columns of variables (i.e., concentration, logC, logK and %total). Like S1, the S2 data view is also comprised of several component files (e.g., S2.H(+), S2.CO3(2-), etc.); however, S2 organizes the data within columns of chemical species (e.g., HCO3(-), H2CO3, etc.). An alternative way of visualizing the output structure is as a 3-D data space (Figure 2.16). The dimensions of this space are

variables, species and observations. So for a single run, the space would only have 2 dimensions. Within the 3-D space is every possible way the data can be viewed. Looking from the variables by species side, you can page through observations. Alternatively, you could view the data from the variables by observation side and page through species. The last combination would be to view it from species by observations and page through variables.

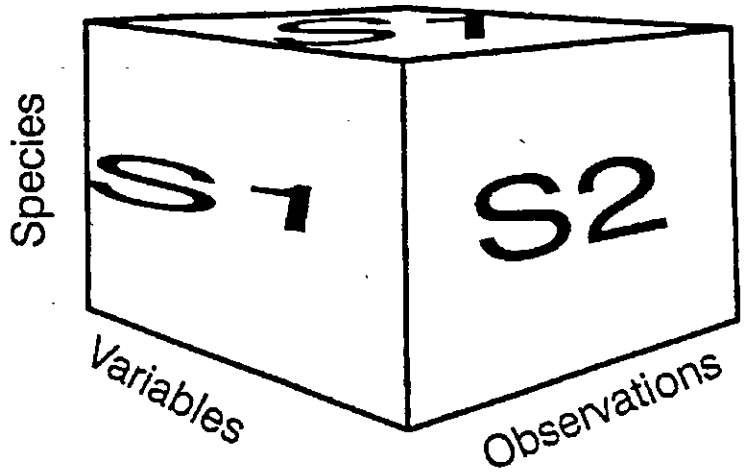


Figure 2.16.

The Output Manager makes the process of viewing the data from different perspectives very easy. The interface for the manager is setup in a hierarchical manner. There are four windows within the manager: Object, Members, Row Type and Display Criteria (Figure 2.17a). The Object window displays all MINEQL$^+$ data objects on the current directory. As you move the cursor from one object to another, the Members window changes to display the data members within the current object. If you press **Return** or the **right cursor** key, the current object is selected and you can move the cursor to select a data member for display. If you select **Header**, **Log** or **Multi** the information will be displayed immediately, but further criteria are needed to display S1 or S2 structures. For S1 structures, the Row Type window will display selections for **Observations** or **Species** (Figure 2.17b). Simply put: S1 makes columns of variables, do you want rows of observations or species? On the other hand, S2 structures only need to display rows of observations (to avoid redundancy with S1), so the Row Type window allows only one option in S2 (Figure 2.17c). Finally, display criteria must be selected. In S1 (columns of variables), if you select a row type of **Observations**, then you have to choose which species to view (Figure 2.17d). Similarly, if you choose a row type of **Species**, you will need to pick which observation or run to view (Figure 2.17e). For S2 (species as columns), since you have to choose a row type of **Observations**, you need to select which variable to display (Figure 2.17f).

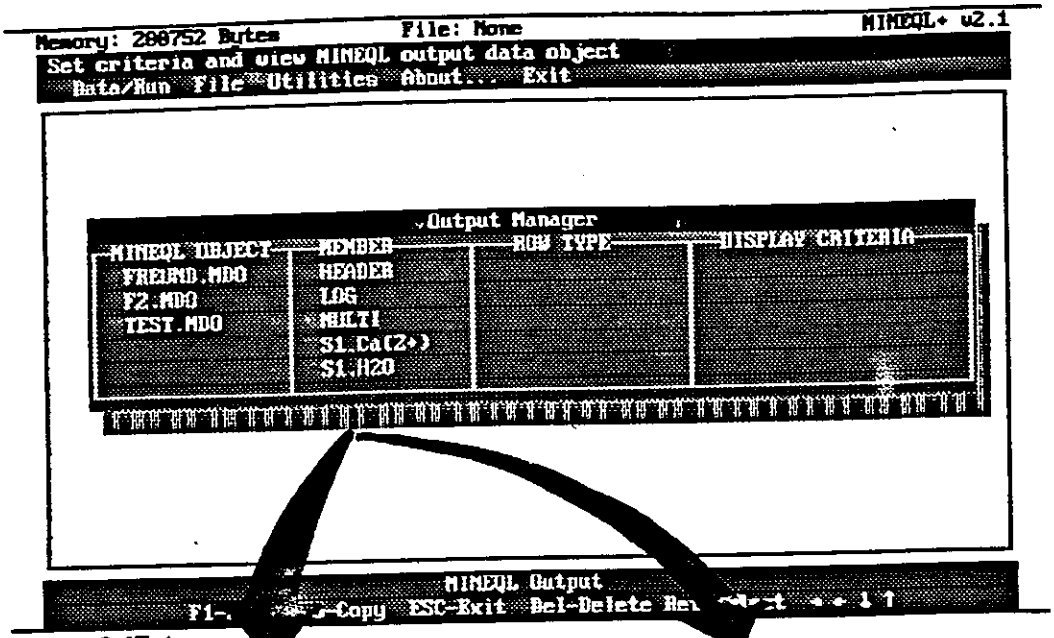
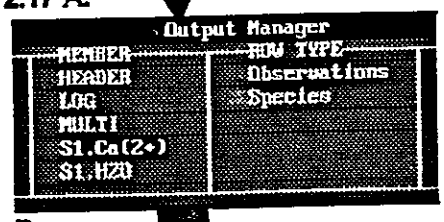
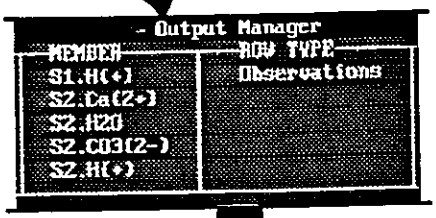


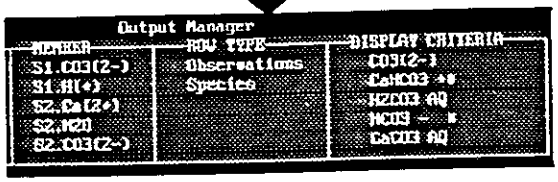
Figure 2.17 A.



B.

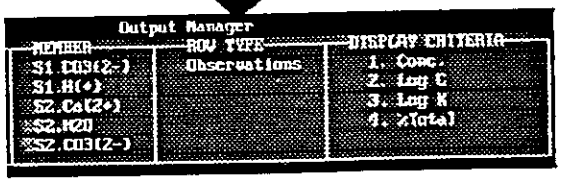


C.

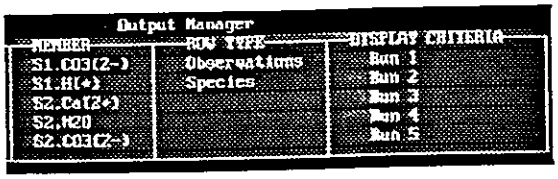


D.

OR



F.



E.

Possible Errors: No errors are possible at this stage, but if you set the hardware configuration incorrectly, unpredictable results may happen when you try to view or print a graph.

Copy

Function: Copies a MINEQL Data Object (MDO) to another disk location.

Found in: Main → Utilities

Remarks: **Copy** displays a list of the MDO's on the current directory. One of these objects may be selected and copied to a specified destination. All files that are associated with the MDO are copied.

Possible Errors: Destination pathname must be valid.

Data/Run

Function: General class of functions for defining and running problems.

Found in: Main

Remarks: Includes **Components, Complexes, Fixed Solids, Dissolved Solids, Species Not Considered, Multiple Runs, Run, and Output Manager.**

Possible Errors: None

Delete

Function: Deletes a MINEQL Data Object (MDO) from the current directory.

Found in: Main → Utilities

Remarks: **Delete** displays a list of the MDO's on the current directory. One of these objects may be selected and deleted from the disk. All files that are associated with the MDO are deleted.

Possible Errors: Possible accidental deletion of MDO, otherwise this function is straight forward.

Dissolved Solids

Function: Allows editing of equilibrium problem.

Found In: Main → Data/Run

Remarks: **Dissolved Solids** opens the editor for Type V species (solids that may precipitate if solubility constraints are exceeded). *Also see: Complexes.*

DOS Shell

Function: Temporarily exits to a DOS shell.

Found In: Main → Utilities

Remarks: Type **EXIT** while in the DOS shell to return to MINEQL$^+$.

Possible Errors: None.

Exit

Function: Terminates the current session.

Found In: Main

Remarks: No warning message is given.

Possible Errors: None

Field Data

Function: Allows the processing of external multiple-run data.

Found In: Main → Data/Run → Multiple Runs

Remarks: **Field Data** allows user-defined data, such as environmental field monitoring data, to be processed in a multiple-run. The initial conditions for the problem are defined like a single run calculation, and the parameters to be varied are found within an external file. Parameters that can be varied include temperature, surface area, the total concentration of any component, the log K or enthalpy of any species. Up to 25 parameters can be varied at one time. The external file must be in a row-column format, with each column a separate parameter and each row a separate observation or run. The width and format of each column does not need to be specified. Columns are distinguished from one another by providing a space between them. The order that

parameters are selected within the Multi-Run Manager must be the same as the column order within the external file.

Possible Errors: Information pertaining to the external file must be accurate.

File

Function: General class of file related functions.

Found In: Main

Remarks: Functions include **Save, Read, ThermSave, ThermRead, Browse, and Print.**

Possible Errors: None

Fixed Solids

Function: Allows editing of equilibrium problem.

Found In: Main → Data/Run

Remarks: **Fixed Solids** opens the editor for Type III species (fixed solids). *Also see: Complexes.*

Get Direct

Function: Displays file directory.

Found In: Main → Utilities

Remarks: **Get Direct** displays a directory similar to the DOS file directory. Before displaying the directory, the function asks for a file criterion. The file list can be scrolled up and down, and additional directory information (e.g., current path, space available on disk, number of files meeting a criterion, etc.) is also displayed.

Possible Errors: If there are no files that meet a given criterion, MINEQL$^+$ will return to the main menu.

Graphics

Function: General class of graphics display tools.

Found in: Main

Remarks: These include **Open** and **Configure**

Possible Errors: None

Multiple Runs

Function: Opens the Multi-Run Manager.

Found in: Main → Data/Run

Remarks: The Multi-Run Manager is a utility to perform sequential runs either by internal generation of synthetic input data or by reading in an external data set. *Also see: Titration, 2-Way and Field Data.*

Possible Errors: No errors possible at this stage, but each type of multiple-run has its own error conditions. See the sub-functions mentioned above for more information about these errors.

Not Considered

Function: Allows editing of equilibrium problem.

Found in: Main → Data/Run

Remarks: **Not Considered** opens the editor for Type VI species (species not considered). *Also see: Complexes.*

Open

Function: Selects and controls the display of graphical output.

Found in: Main → Graphics

Remarks: **Open** initially displays a tool that allows you to select an MDO to graph. Once the data is chosen, the Graphics Manager is displayed. There are two types of plots that are possible with MINEQL+: X-Y Plots and Bar Charts. Bar Charts relate to distribution of chemical species in a single run and X-Y Plots show the distribution of

species over multiple runs.

In MINEQL+, multiple-runs are generated by **Titration**, **2-Way** analysis, or **Field Data**. The independent variables used in any of these calculation types are stored in the output member called "MULTI". These variables are relegated to the X-axis. All other output data can be displayed on the Y-axis.

Depending on the type of analysis used to produce the output, X-Y Plots are treated differently. For **Titration** and **Field Data** output, up to 10 species can be plotted on the Y-axis at a time. For output from **2-Way** analysis, only one species can be selected for the Y-Axis, but it is plotted multiple times. Remember that **2-Way** analysis performs calculations on all the combinations of two independent variables. For example, pH and P_{CO2} could be the two independent variables in a **2-Way** calculation. The X-Y Plot for this system could plot the log of CO_2 versus pH at each level of P_{CO2}. X-Y Plots for **2-Way** output use the first independent variable that you select for the X-axis. In the example above, if you selected pH from the Multi Run Manager first, then pH is on the X-axis.

Chemical species can be displayed on the Y-axis as concentration, Log C, Log K, or % total. Output can be directed to a printer or the video screen. The maximum and minimum of the axes can be set manually or be calculated automatically. Manual settings for the axes allow you to zoom in on areas of interest.

Possible Errors: Hardware configuration must be correct.

Output Manager

Function: Opens the Output Manager.

Found in: Main → Data/Run

Remarks: The Output Manager is a tool used to create and save specific output data views. Output is organized into sets of files called objects. The files that compose each object are called members. The Output Manger displays each object on the current directory and its associated members. In a hierarchical manner, objects are selected from the display, followed by particular members, and finally particular views of the members.

There are 5 types of data members: a Header, a Log, a multiple-run file, and two output views (S1 and S2). The Header stores a summary of the basic input information, including the stoichiometric coefficients. The Log file holds all error messages and miscellaneous output (e.g., total charge in solution). The multiple-run file is a reiteration of the multiple-run input data and is not present for single runs.

The other members are classified based on chemical component and view bias (S1 and S2 views). An S1 view displays the output in columns of variables (concentration, log C, LogK, and %Total), while an S2 view shows columns of chemical species. An S1 view can have rows of species or rows of observations, but an S2 view can only have

rows of observations. In this manner, a 3-dimensional data set (variables by species by observations) can be extracted and managed.

Once a view has been created on screen, the view can be further reduced by performing column extraction. This is accomplished by pressing the "/" key while in view mode and selecting **Col. X-tract** from the sub-menu. The columns to be kept in the new view are checked-off with the **Return** key. Extract the columns by pressing **F6**.

The final view can be saved in several file formats (Paradox, Lotus 1-2-3, or ASCII text) or printed.

To delete an object, use the **Del** key while in the Object window. Similarly, to copy an object, press the **F3** key. Also, you can use the **Copy** or **Delete** option from the **Utilities** menu to perform the same functions.

Possible Errors: None

Print

Function: Prints text files to a line printer.

Found in: Main → File

Remarks: **Print** will display a tool to show the available file directory. Any one of the listed files can be printed by selecting it from the directory list. You can set a search criterion from within this tool to reduce the number of listed files.

Possible Errors: **Print** assumes that the line printer is located on the port specified in the **Graphics/Configure** options. If not, an error is displayed and no action will be taken.

Print will only print text files and does not make provisions for rows that are wider than the carriage width. Depending on the printer configuration, long lines will either be wrapped or truncated.

Output should be printed using the **Print** option found within the Output Manger. Graphics can be printed under the Graphics Manager by setting the destination to **Printer** and selecting the **Plot** option.

Read

Function: Retrieves a problem set.

Found in: Main → File

Remarks: A problem set contains all the information needed to run a calculation: a component list, a list of mass action expressions and the total concentrations of each component. A complete problem set can be saved to disk (using **Save**) and subsequently read back (using **Read**).

Possible Errors: **Read** will only work with files that have been written to disk using **Save**. If a different file is encountered, an error message will appear and the problem set will be cleared (i.e., no components or species will be present).

Run

Function: Set run options and start a calculation.

Found in: Main → Data/Run

Remarks: **Run** displays the current run options in a table format. Options pertain to the temperature, ionic strength corrections, convergence criteria, the presence of an adsorbing surface, the type of adsorption model (if any) and the name of the output data object. The default values are displayed on screen and often do not need to be altered to run a calculation. *See the Tutorial for specific examples.* To start a calculation, select the **Run** option within the table.

If the name of the output object is the same as one already present on disk, a message will appear asking whether the new object should be replaced. If you answer "No," MINEQL$^+$ will return to the main menu.

Possible Errors: A problem set must be defined before **Run** will function.

Several run-time errors are possible, however in all cases these errors will be displayed on the screen. The most common errors are: (1) presence of a NULL species (no component ID found), (2) Gibb's Phase Rule Violation (too many solids or fixed species trying to control the concentration of a component), (3) invalid thermodynamic data (may cause math overflow or underflow, this shouldn't be a problem when using the main database). In other cases, a calculation may run successfully but contain errors due to poor conceptualization. Calculations where pH is determined numerically must result in a low total charge of solution.

Save

Function: Saves a problem set.

Found in: Main → File

Remarks: A problem set contains all the information needed to run a calculation: a component list, a list of mass action expressions and the total concentrations of each component. A complete problem set can be saved to disk (using **Save**) and subsequently read back (using **Read**).

Possible Errors: **Save** will only work if a problem set is currently active; it will not save a NULL set.

Single

Function: Designates a single-run calculation.

Found in: Main → Data/Run → Multiple Runs

Remarks: **Single** (the default setting) specifies that the output object will contain only one run. Any information pertaining to multiple runs that may have been specified in previous runs will be ignored under **Single.**

Possible Errors: None

ThermRead

Function: Reads in a personal thermodynamic database.

Found in: Main → File

Remarks: **ThermRead** scans the database of personal thermodynamic data and uses only those mass action expressions that apply to the current problem set. If no personal data exists or no problem set is present, then **ThermRead** returns to the main menu. *Also see: ThermSave.*

Possible Errors: None

ThermSave

Function: Saves mass action expressions in a personal thermodynamic database.

Found In: Main → File

Remarks: **ThermSave** scans the problem set for mass action expressions that have been altered or inserted. Such new species can be added to the personal thermodynamic database for future use. The Personal Database Manager allows the user to see each new species in sequence and determine whether the species should be added to the database (**Add**) or skipped (**Next**). The data is appended to the existing personal database, so that repetitive alterations to a particular species will result in only the last alteration being active. *Also see: ThermRead.*

Possible Errors: None

Titration

Function: Allows the creation of a synthetic titration.

Found In: Main → Data/Run → Multiple Runs

Remarks: **Titration** creates synthetic input data for multiple runs. Parameters that can be varied include temperature, surface area, the total concentration of any component, the log K or enthalpy of any species. Either 1, 2 or 3 input parameters can be used as a titrating parameter at one time. The parameters are varied simultaneously, so the number of final runs is the same as the number of points specified in the Multi-Run Manager. *Also see: 2-Way.*

Possible Errors: The starting and ending values must be valid for the parameter being varied.

Utilities

Function: General class of DOS related functions.

Found In: Main

Remarks: These include **Copy, Rename, Delete, Change Direct, Change Drive, Get Direct, DOS Shell.**

Possible Errors: None

TUTORIAL

Introduction

This Tutorial is a collection of examples that can be used to help get started with MINEQL$^+$. The systems are intentionally simple for ease of illustration and are not intended to be discussions of underlying theory. The examples are organized as follows:

Example 1: The Basics
- **1A:** Fixed pH, $CaCO_3$ System
  - how to fix pH
  - how to fix P_{CO2}
  - how to display a Bar Chart of species distribution
- **1B:** pH Titration of a $CaCO_3$ System
  - Example 1A as a pH titration
  - Using the Output Manager
    - determination of species distribution
    - calculation of alkalinity
    - use of saturation indexes
    - use of charge discrepancy
  - Displaying an X-Y Plot of species distribution
- **1C:** MINEQL Calculation of pH

Example 2: Surface Adsorption Modeling
- **2A:** Langmuir Adsorption
- **2B:** Freundlich Adsorption
- **2C:** Triple-Layer Adsorption
- **2D:** Two-Layer Adsorption[1]
- **2E:** Constant Capacitance Adsorption[1]
- **2F:** Two-Layer Adsorption, Hydrous Ferric Oxide[1]

Example 3: Oxidation-Reduction Systems
- **3A:** Fixed pe Calculations
- **3B:** Control of pe with Dissolved O_2
- **3C:** Control of pe with Fixed Ion Ratios

For the rest of this tutorial, a shorthand notation will be used to indicate how an output view was extracted. For instance, a S1 view of H(+), with rows of observations and a display criterion of CaOH would be written S1.H(+)/OBS/CaOH.

1. The indicated examples were contributed by Dr. David Dzombak, Department of Civil and Environmental Engineering, Carnegie Mellon University, Pittsburgh, PA.

Example 1. The Basics

Example 1A: Fixed pH, $CaCO_3$ System

The System: 10^{-3} M of $CaCO_3$ is dissolved in water and allowed to equilibrate with the atmosphere (P_{CO2} = $10^{-3.5}$ atm). An unknown amount of a strong acid is then added to the system until a pH of 4.5 is measured.

The Goal: What is the chemical distribution of all species in solution, the alkalinity, the amount of strong acid added to the system, and did any solids precipitate?

The Method: Step 1. Define the components of the system. As a rule of thumb, almost all of the components in the thermodynamic database are listed as unassociated species. In this case, the components would be Ca^{2+}, H^+, H_2O and CO_3^{2-} (Figure 4.1). Remember, always include H^+ and H_2O in the set of components if H_2O is the solvent. For more information about selecting components, see the *User's Guide.*

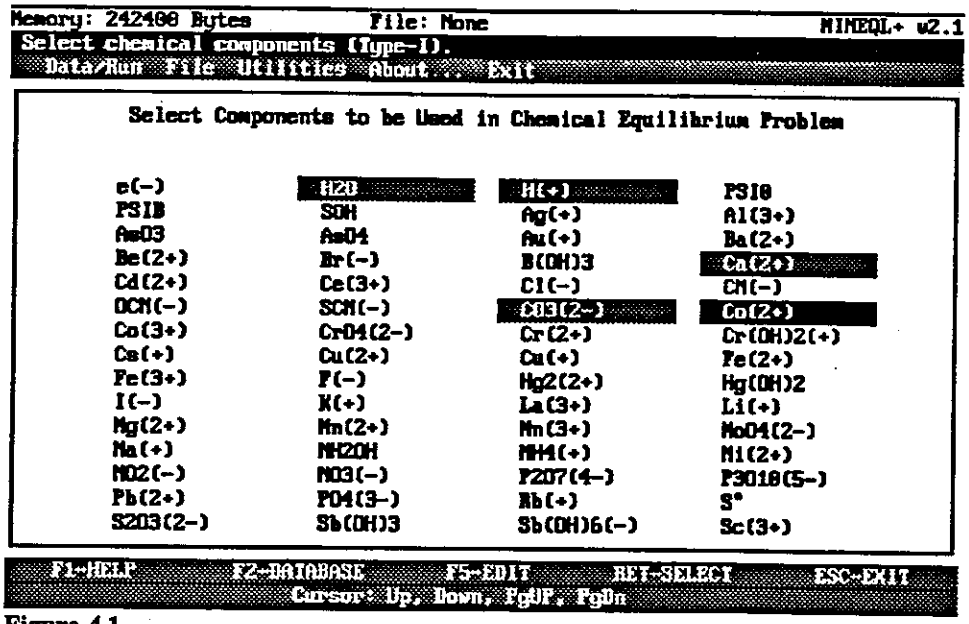


Figure 4.1.

Step 2. Scan the thermodynamic database. Press the **F2** key to scan the database and a screen will appear with the Type II species list from the editor.

Step 3. Input the total concentrations of each component. Assuming that the set of reactions and their corresponding equilibrium constants are satisfactory, press the **F2** key twice to bring the cursor to the *Totals* field. In the Ca(2+) and CO3(2-) columns, type in "1E-3". The H(+) and H_2O columns can remain 0 because they are fixed by default (Figure 4.2).

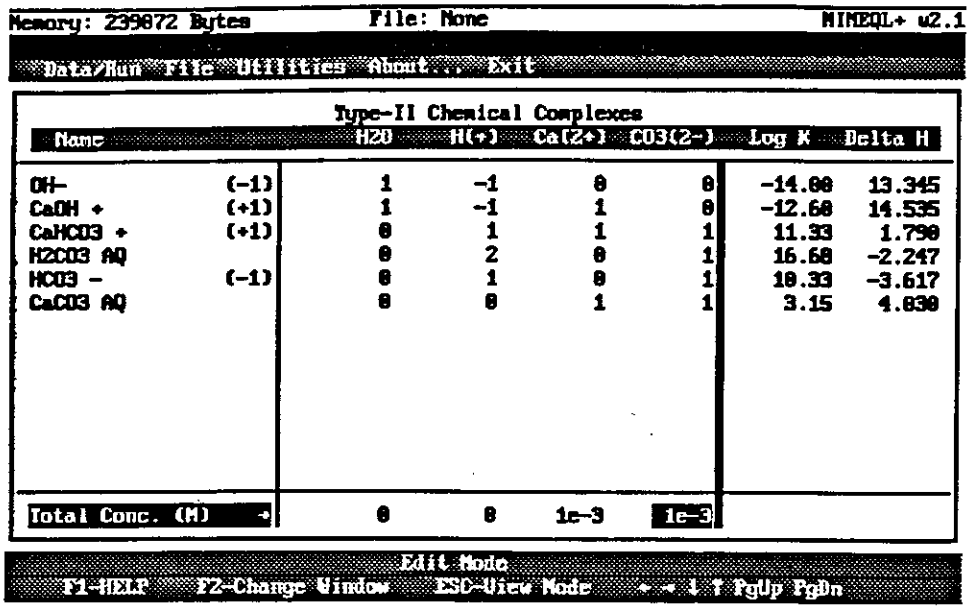


Figure 4.2.

Step 4. Define the Fixed Solids. From the information about the system, it is known that the pH is 4.5 and that the solution is open to atmospheric CO_2. Solution pH is fixed by default at a value of 7.00. This value can be changed by going into the editor for fixed solids and pressing **F2** twice to move the cursor to the field of thermodynamic data (Figure 4.3). Type in the pH of the aqueous solution in the equilibrium constant column (in this case 4.5).

You may notice that there are other species included under Fixed Solids. H_2O is always present with a fixed activity of 1 (Log K = 0) because it is the solvent for aqueous systems. In this Example, dissolved CO_2 is also present, but with a default Log K value that is inappropriate for our system.

To set the PCO_2 of the system, use the following formula for calculating the formation constant β:

$$\beta = -\text{Log}(K_H \times K_1 \times K_2 \times P_{CO2}) = \text{Log } K_{CO2} \qquad (4.1)$$

where:

K_H = Henry's Law Constant ($\sim 10^{-1.5}$),
K_1 = First dissociation constant for carbonic acid ($10^{-6.35}$),
K_2 = Second dissociation constant for carbonic acid ($10^{-10.33}$),
P_{CO2} = Partial pressure of CO_2 in atmospheres ($10^{-3.5}$ for this example).

Note that a value of 18.16 is given by default for the Log K_{CO2}. This value corresponds to a system where the P_{CO2} is 1 atmosphere. Thus, to fix the P_{CO2} with the atmosphere (i.e., $P_{CO2} = 10^{-3.5}$), add 3.5 to the default value of Log K_{CO2}; this value would be 21.66. While in Edit mode for thermodynamic data, move the cursor to the equilibrium constant for the dissolved CO_2 species and enter in 21.66. The final screen should look like Figure 4.3. Press the **Esc** key twice to return to the main menu.

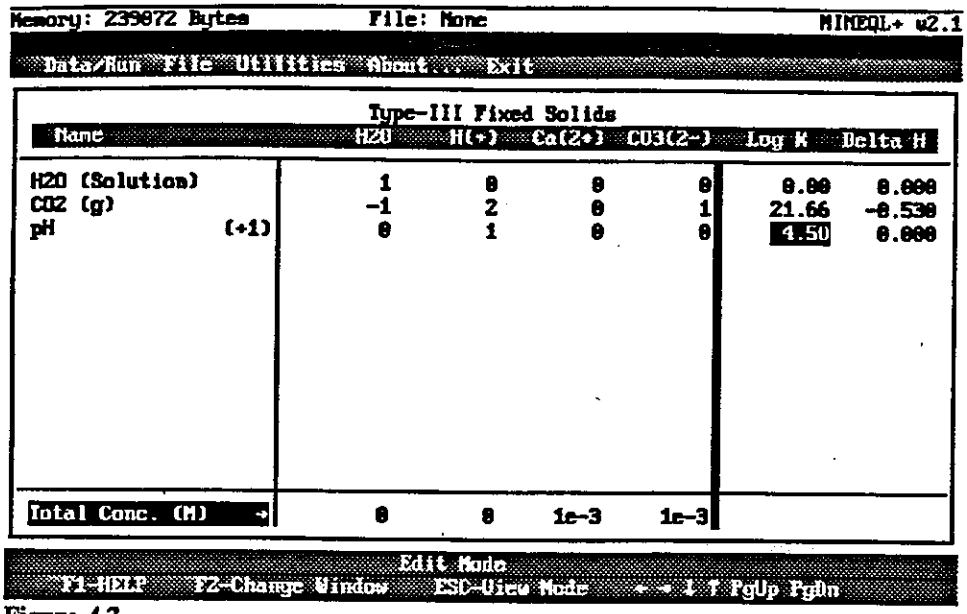


Figure 4.3.

Step 5. Set the Dissolved Solids. For this example, we will prevent any solids from precipitating by moving all Dissolved Solids to Type VI species (Not Considered). This will have the effect of removing the solids from the calculation but will allow us to monitor whether any solubility constraints were exceeded. Move the cursor to **Dissolved Solids** and press **Return.** Press the **F3** key (Move). A tool will appear that will allow you to move the current species to another type. Move the cursor to "Type VI" and press **Return.** Continue this process for all the remaining Dissolved Solids.

Step 6. Run the Problem. Move the cursor to the **Run** option and press **Return.** Type in the name of the output object where you want your output to be stored. MINEQL$^+$ will automatically append an "MDO" extension to your output object. When completed, press the **Esc** key. Move the cursor to the next **Run** option and press **Return.** The screen will display a banner (Figure 4.4) indicating that calculations are in progress. When the run is finished, the main menu will reappear.

Figure 4.4.

The Output: Move the cursor to the **Output Manger** option and press **Return.** The output object is composed of several members:

- **The Header:** Move the cursor to the output object you just created and press **Return.** Select **HEADER** from the Members window. The header will be displayed on screen (Figure 4.5). The header contains a summary of the input data and provides a way to see how species names and mass action expressions correspond. The total concentration of each component is listed at the top of the header under the column "T". To determine the composition of a complex, use the following examples:

CA(2+)	1.0	CO3(2-)	1.0			is $CaCO_3$;
H(+)	2.0	H2O	2.0	CO3(2-)	1.0	is H_2CO_3.

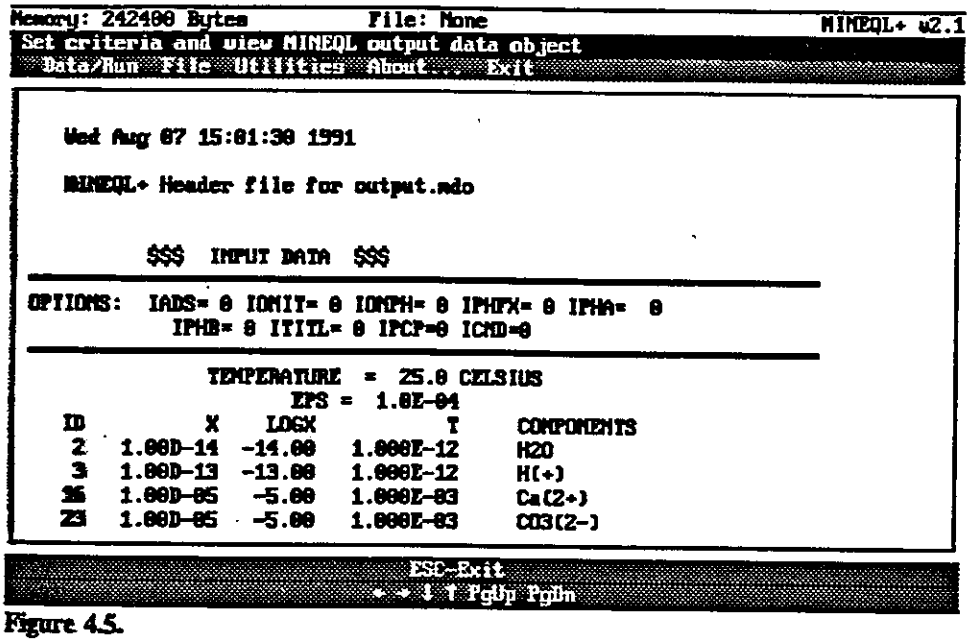


Figure 4.5.

- **The Log:** Press **Esc** from the Header file and select **LOG** from the Members window. The log will be displayed (Figure 4.6). The Log file will include the number of iterations, temperature, total charge in solution and any error messages. Since there are no errors, press the **Esc** key and return to the Members window.

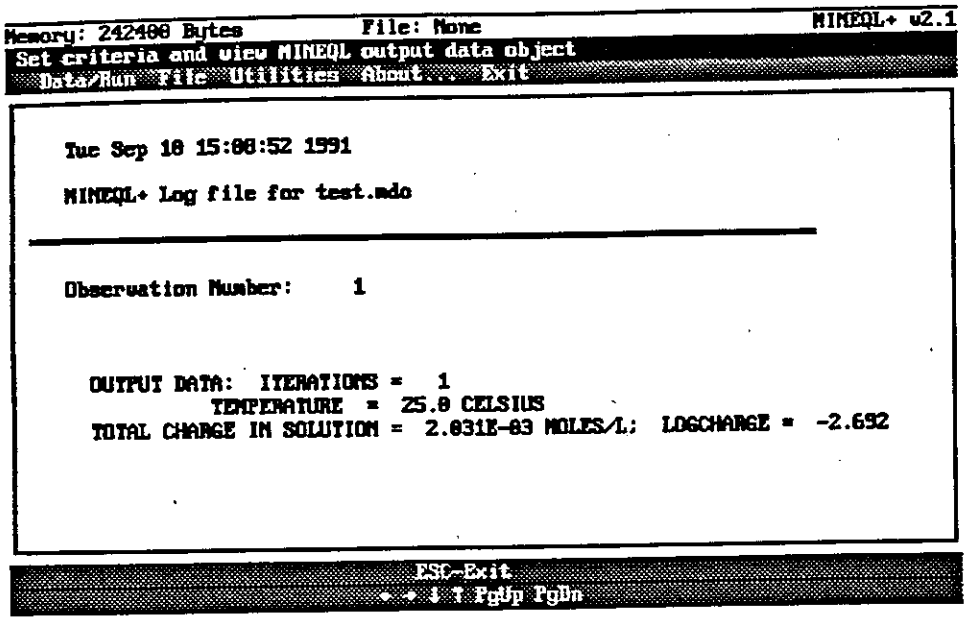


Figure 4.6.

- **The S1 and S2 view:** The overall structure of these data views are discussed in the *User's Guide*. The S1 view will be used for the current example. Later, the problem will be expanded to a multiple-run problem, and the S2 view will also be used. You should note that the S1 views are organized by chemical component, so some species may be present in 2 or more members. For example, H_2CO_3 can be found in both S1.H(+) and S1.CO3(2-).

To complete this example, information requested at the beginning of the problem needs to be extracted.

1. **The alkalinity of the system.**

$$Alk = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \qquad (4.2)$$

The concentrations of each of these species can be found in the **S1.H(+)/SPEC/RUN1** and **S1.CO3(2-)/SPEC/RUN1** views. The total alkalinity for this problem is:

$[HCO_3^-]$	$+1.48X10^{-7}$
$2[CO_3^{2-}]$	$+2(2.19X10^{-13})$
$[OH^-]$	$+3.18X10^{-10}$
$-[H^+]$	$-3.16X10^{-5}$
Alk	$-3.14X10^{-5}$ eq/L

This calculation can be facilitated by using the S2 view for H(+) and CO3(2-) and performing column extraction. The resulting views would need to be saved and manipulated within a spreadsheet package. The use of S2 views in the multiple-run part of this tutorial will be expanded on in Example 1B.

2. **The amount of strong acid added to the system.** For fixed pH calculations, the final answer does not have to be electrically neutral. However, in reality, the aqueous solution must always observe electroneutrality. As a result, the part of the Log file that displays the total charge in solution (the degree to which the answer deviates from electroneutrality in equivalents/L) is also the amount of equivalents of strong acid that were added to the system (as long as you kept the concentration of H^+ = 0). In this example, the amount of strong acid added to the system is $2.031X10^{-3}$ M.

Also note that by setting the initial H^+ concentration to zero, any addition or subtraction of protons will show up in the "concentration" of the fixed pH (**S1.(H+)/Spec/Run1**). In this case, C = $-2.031X10^{-3}$ for the pH "species". The negative of this number is the amount of equivalents of strong acid that were added to the system.

3. **Precipitation of Solids.** The Header shows only calcium solids for this problem (Figure 4.5), so you can look under **S1.Ca(2+)/SPEC/RUN1** for a listing of calcium species. The list shows only Type V (Dissolved Solids), meaning that none of the Ca solids in this problem precipitated. The degree of undersaturation can be found by using the Solids Saturation index (SI):

$$SI = Log\frac{Q}{K_s} \qquad (4.3)$$

where:

Q = the ion activity product, and
K_s = the solubility constant for the solid.

An SI value of 0 indicates equilibrium, a negative value shows system undersaturation and a positive value shows oversaturation. The SI values can be found by looking at the Log C column of the **S1.Ca(2+)/SPEC/RUN1** view. In this case, the SI values are:

$CaCO_3$ solids	
Calcite	-7.18
Aragonite	-7.3
$Ca(OH)_2$ solids	
Lime	-26.8
Portlandite	-16.7

This indicates that these solids are highly undersaturated.

4. **The distribution of chemical species.** By looking at the member **S1.Ca(2+)/SPEC/RUN1**, the %Total column contains the relative distribution of calcium in the system: 100% of Ca is present as Ca^{2+}. Similarly, **S1.CO3(2-)/SPEC/RUN1** shows 98.6% and 1.4% of the total CO_3 is present as H_2CO_3 and HCO_3^-, respectively.

Graphical Format

As an alternative approach to using the Output Manager, we could view the distribution of chemical species graphically. In the Main Menu, move the cursor to the **Graphics** menu and then move the cursor down and select the **Open** option. A tool will appear that will allow you to pick an MDO for display. If the data object that is listed in the tools is not one created for this example, press **Return** and a pull-down menu will appear with any additional objects. Move the cursor to the correct data object and press **Return.** Once the correct MDO has been selected, move the cursor to the **OK** option and press **Return.** The Graphics Manager will appear (Figure 4.7).

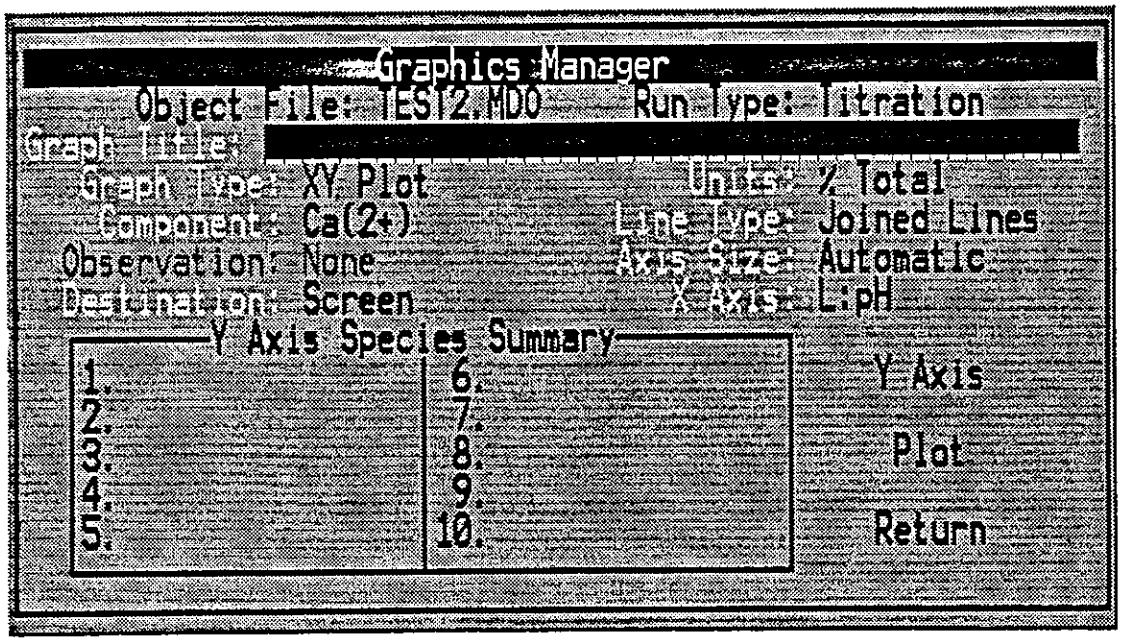


Figure 4.7.

Since this problem is a single run, only bar charts will be available for display. To view the distribution of CO_3 species, move the cursor to the field labeled "Component" and press **Return.** A pull-down menu will appear with all appropriate components for this calculation. Move the cursor to the **CO3(2-)** option and press **Return.** Move the cursor to the **Plot** option and press **Return.** The distribution of CO_3 species will be displayed on the screen (Figure 4.8).

Using the same methods described for CO_3, plot the distribution of the Ca species. The plot should look like Figure 4.9.

Note: to place titles on top of a graph, type in the title information in the field labeled **Graph Title.**

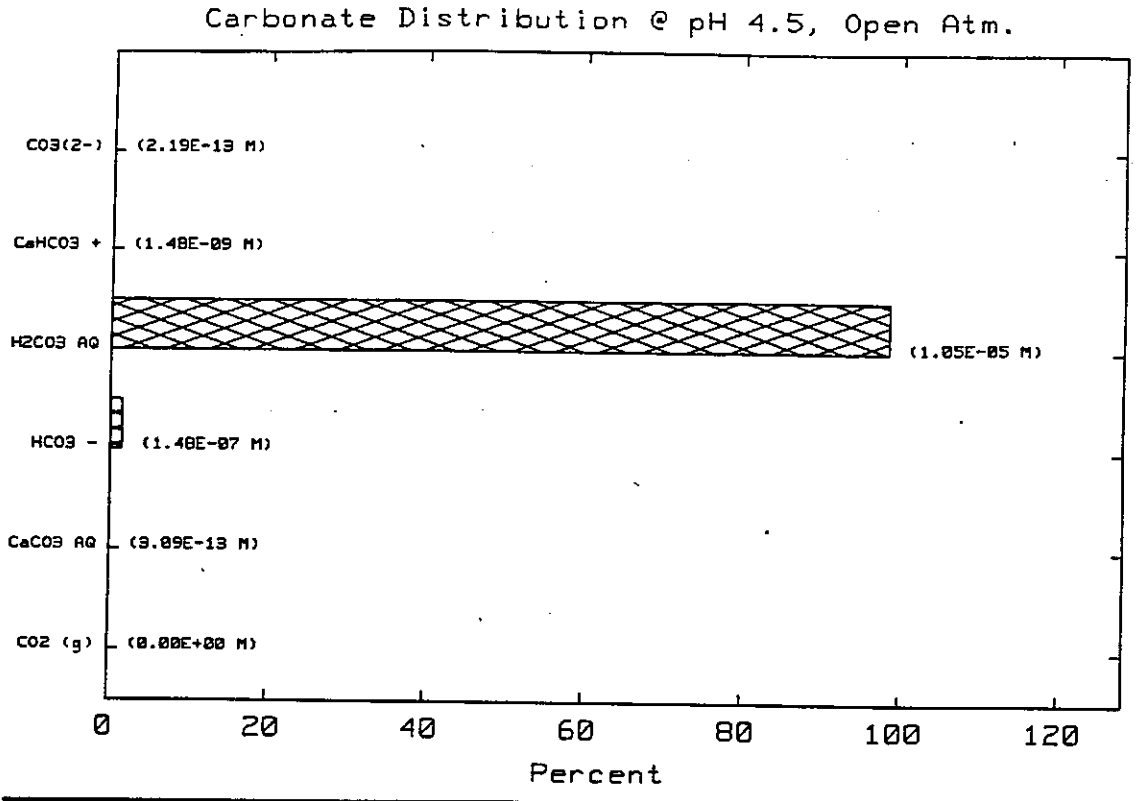


Figure 4.8.

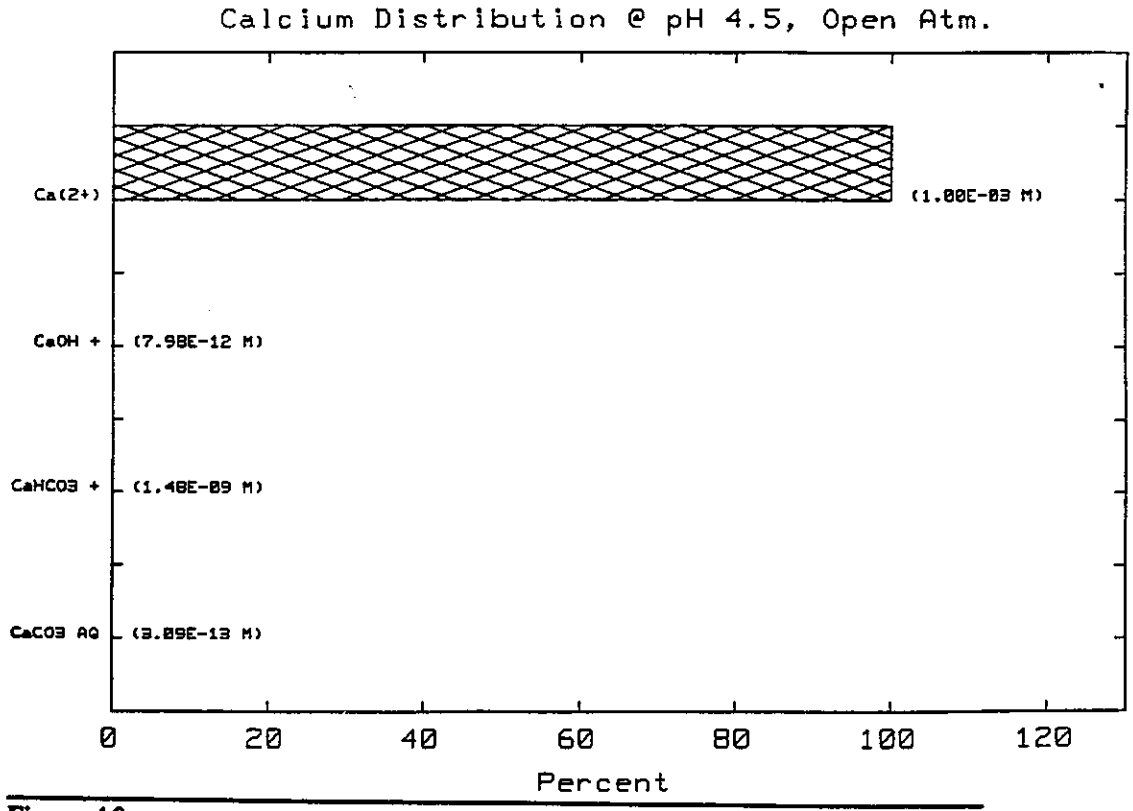


Figure 4.9.

Example 1B. pH Titration of a $CaCO_3$ System

Example 1A demonstrated how to setup a single run problem and extract information from the resulting model output. Often, in environmental systems, you are interested in performing several runs in order to simulate a titration, perform a sensitivity analysis or process field data. In this example, you will re-work Example 1A and allow a range of pH to govern the system.

The System: 10^{-3} M of $CaCO_3$ is dissolved in water and allowed to equilibrate with the atmosphere (P_{CO2} = $10^{-3.5}$ atm). An unknown amount of a strong acid is added to the system and the pH varies from 3.0 to 9.0.

The Goal: What is the chemical distribution of all species in solution, the alkalinity, the amount of strong acid added to the system, and will any solids precipitate at each pH value?

The Method: Step 1. If you don't already have Example 1A as an active problem set, perform steps 1 through 5 of Example 1A. Don't worry about what value is present for pH at this point. The pH values will be controlled by the Multi-Run Manager.

Step 2. Select **Multiple Runs** from the Data/Run menu. The calculation type is set to **Single** by default. Press **Return** and select **Titration** as the new calculation type (Figure 4.10). At this point, other menu options will be available. Notice that there are 4 types of parameters with which you can titrate: **General, Totals, LogK,** and **DelH.**

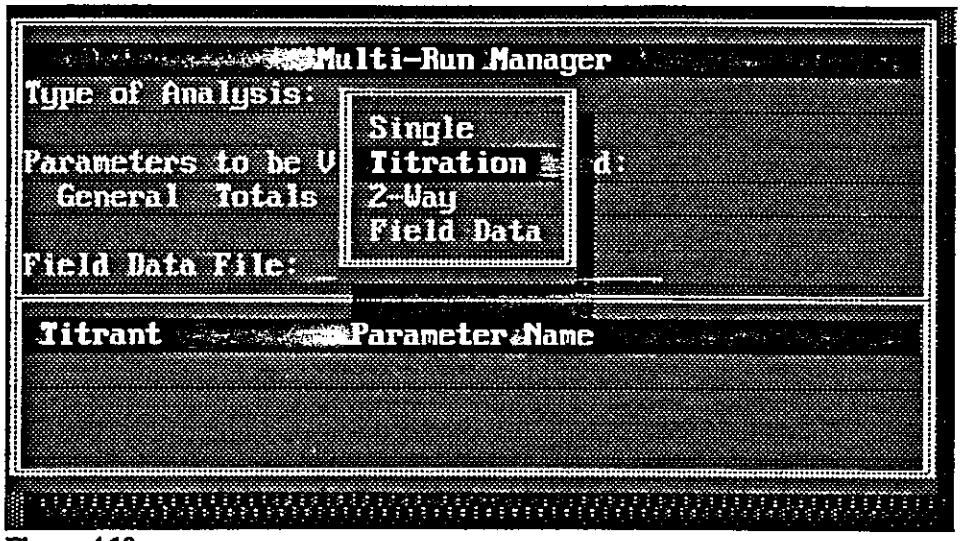


Figure 4.10.

In the single-run problem, pH was present as a Type III (Fixed Solid) and you controlled its value through editing the value of its LogK. Similarly, for a multiple-run problem, pH is found under the class of parameters labeled **LogK.** Move the cursor to **LogK** and press **Return.** A menu will appear with all the species for the current problem set. The Log K values for any of the species can be selected at this point. Move the cursor down to the pH "species" and press **Return** (Figure 4.11).

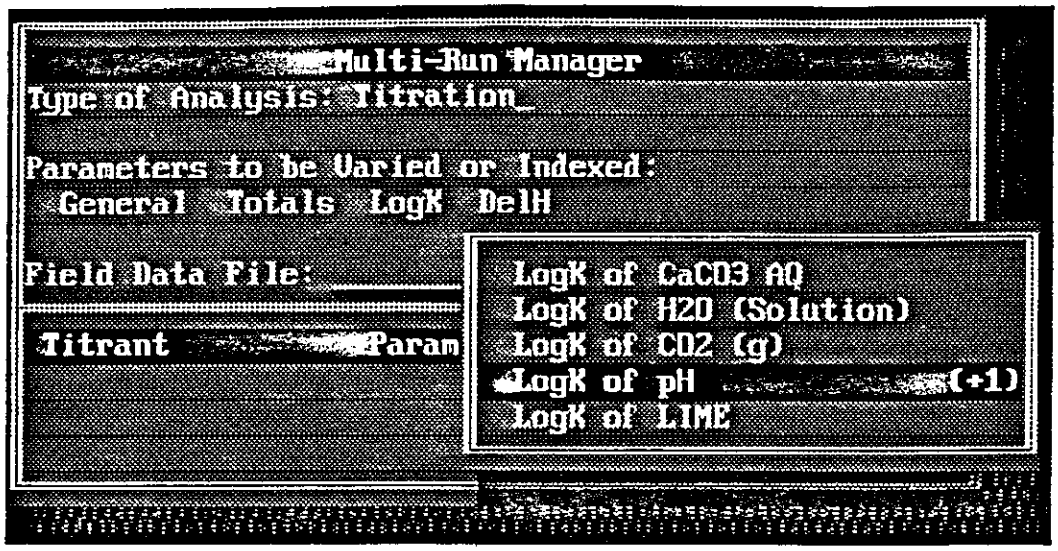


Figure 4.11.

A new entry form will appear that asks for the starting point, ending point, and the number of points to be generated for the problem. The starting pH will be 3.0 and the ending value will be 9.0. The number of points can be any number greater than 1. You will get better resolution of the titration curve if you use more points, but it will take longer to run. For this problem, use 14 points (Figure 4.12). Press **Esc** when finished, and then press **Esc** 2 more times to return to the main menu.

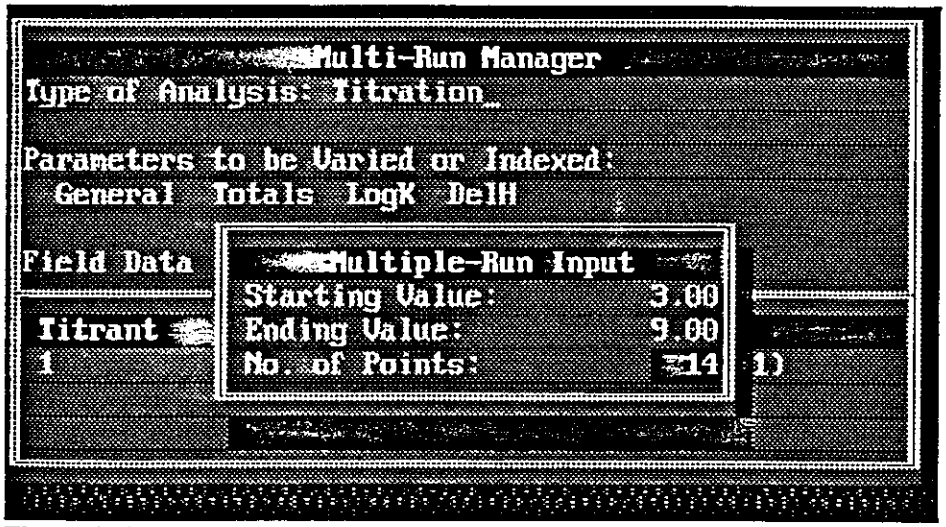


Figure 4.12.

Step 3. Continue with step 6 from Example 1A and run the problem.

The Output:

Tabular Format

Open the Output Manager and select the output object that you just created. In the Members window, select the **Multi** file. Press the "/" key and select the **Save** option. Save the Multi file in a format that can be used later in your spreadsheet or database software. All of the views that you will create can be combined using third-party software for graphical or statistical analysis. The Multi file contains the independent variables for an analysis; in this case, pH.

1. **The distribution of Ca and CO_3.** Move the cursor down to the first S2 view. You will be focusing on S2 views for all of this problem. For information on S1 views, see the Example 1A or the *User's Guide*. Select the **S2.Ca(2+)/OBS/%Total** view. Notice that many of the columns have zeros. It would be useful to extract only those columns that have non-zero values. Press the "/" key and select **Col. X-tract** from the menu. Move the cursor to the Ca(2+) and Calcite columns and select them by pressing **Return**. Press the **F6** key to perform the extraction. The new view should look like Figure 4.13.

	1:Ca(2+)	5:CALCITE
1	100	
2	100	
3	100	
4	100	
5	100	
6	100	
7	100	
8	100	
9	100	
10	99.9	
11	99.8	
12	99	
13	12.8	86.5
14	1.5	97.9

Figure 4.13.

Save the view and repeat this process for the **S2.CO3(2-)/OBS/%Total** view. The resulting extracts can now be combined in a spreadsheet or database for further analysis.

Graphical Format

As an alternative to the tabular form of data, MINEQL$^+$ will allow you to create X-Y plots using the Graphics Manager. Select the data object for this example for use under the Graphics Manager (**Graphics/Open**). Notice that the status line at the top of the window indicates that this calculation was a Titration. Any of the multiple-run calculations (**Titration, 2-Way, Field Data**) will allow the creation of X-Y plots. Of course, you can always produce a bar chart for an individual run, but X-Y plots allow you to view changes over a series of runs.

For the remainder of the examples, we will try to use the Graphics Manager whenever possible. The exceptions will be cases where composite variables (i.e., chemical measures that are not calculated by MINEQL and are derived from other output variables; for instance, alkalinity) are being plotted.

A quick way to navigate the Graphics Manager is as follows:

1. Select the component that you want plotted (e.g., CO_3^{2-}, Ca^{2+}, H^+).
2. Move the cursor to **Y Axis** and select up to 10 chemical species to display on the Y axis. If you make a mistake, re-select the species and it will be removed from the list of species to be plotted.
3. Make sure that the units for the Y axis are correct. You have a choice between concentration, Log C, Log K, and % Total.
4. Make sure that the correct X axis variable is active. If you choose more than 1 titrating element in your calculation (not so in this example) or if you performed a **Field Data** calculation, then you will have several independent variables. Any one of these could be placed on the X axis.
5. Select the line type to use in drawing the plot (optional). Plots can be drawn with spline fits, moving means (good for field data), connected points, no points, or no lines. Experiment to see which one suits your needs.
6. Plot the data.

Other options include: (1) redirecting the output to a graphics printer, (2) adjusting the size of the axis, and (3) adding a title to the graph.

To continue with this problem, **Open** the current problem under the Graphics Manager. Make sure the following settings are in place:

Graph Type:	XY Plot
Component:	Ca(2+)
Destination:	Screen
Units:	% Total
Line Type:	Spline Fit
Axis Size:	Automatic
X Axis:	L:pH

Select Ca(2+), CaHCO3(-), CaCO3 AQ for display on the Y axis. The results are shown in Figure 4.14. Similarly, plot the distribution for CO_3^{2-} by changing the active component to CO3(2-) and placing H2CO3, HCO3(-), CO3(2-) and CaCO3 on the Y axis. The resulting graph is shown in Figure 4.15.

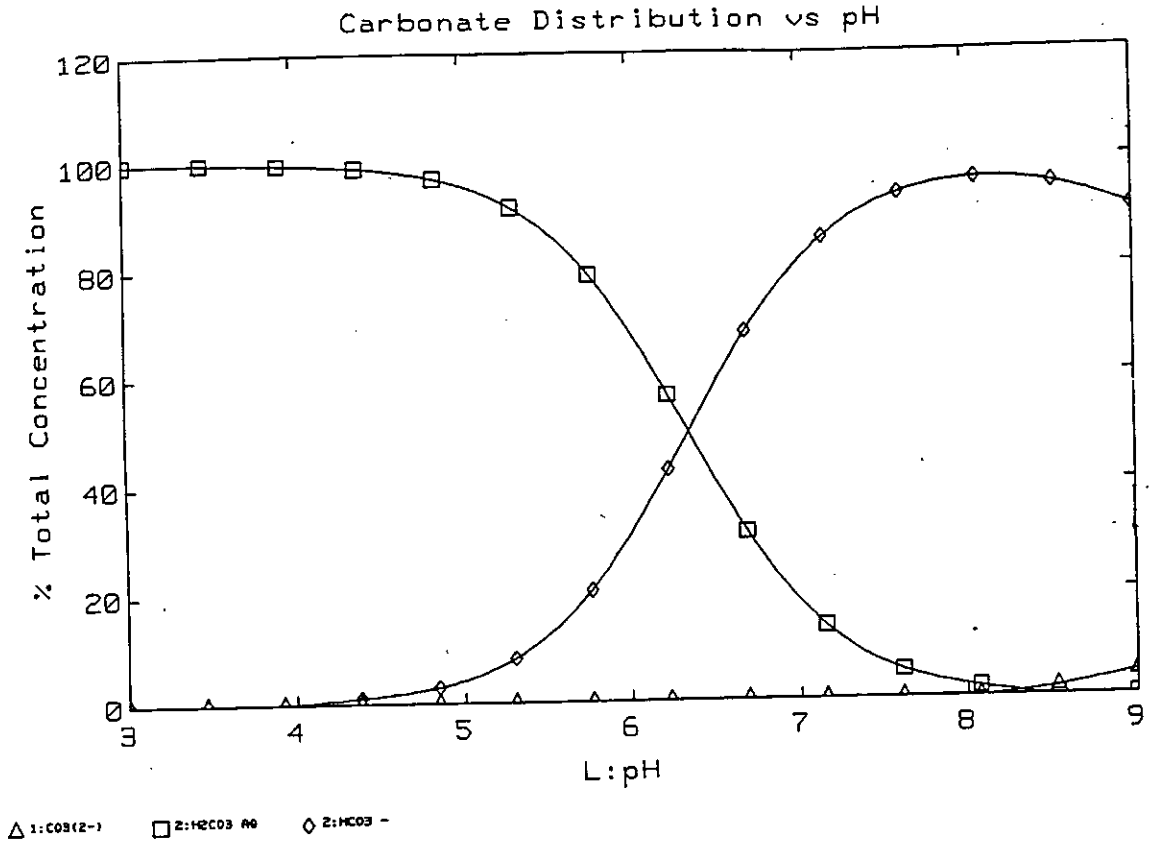


Figure 4.14.

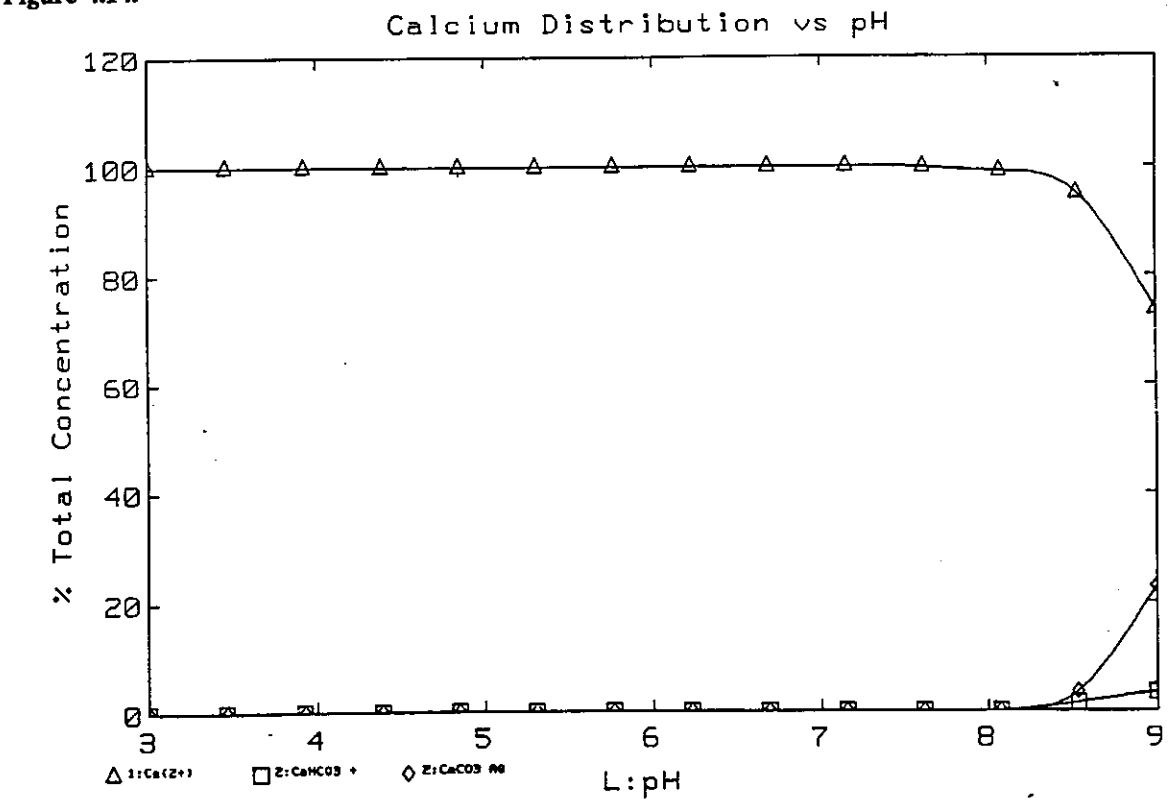


Figure 4.15.

2. **Precipitation of Solids.** A simple way to check whether there is a potential for solids to precipitate is to plot the values for saturation index (SI) versus pH. With the current problem residing in the Graphics Manager, make sure the following settings are in place:

Graph Type:	XY Plot
Component:	Ca(2+)
Destination:	Screen
Units:	Log C
Line Type:	Joined Lines
Axis Size:	Automatic
X Axis:	L:pH

Select lime, portlandite, aragonite, and calcite (all Type VI species) for display on the Y axis. Plot the graph. The results are shown in Figure 4.16.

Recall that in Example 1A, that values for SI are negative when solids are under saturated, positive when over saturated and zero when in equilibrium. The values for lime and portlandite are both negative for all pH levels, indicating that these solids would not form in this system. Aragonite and calcite are negative for all pH values less than 8.3, meaning that when pH is greater than this value, aragonite or calcite could form.

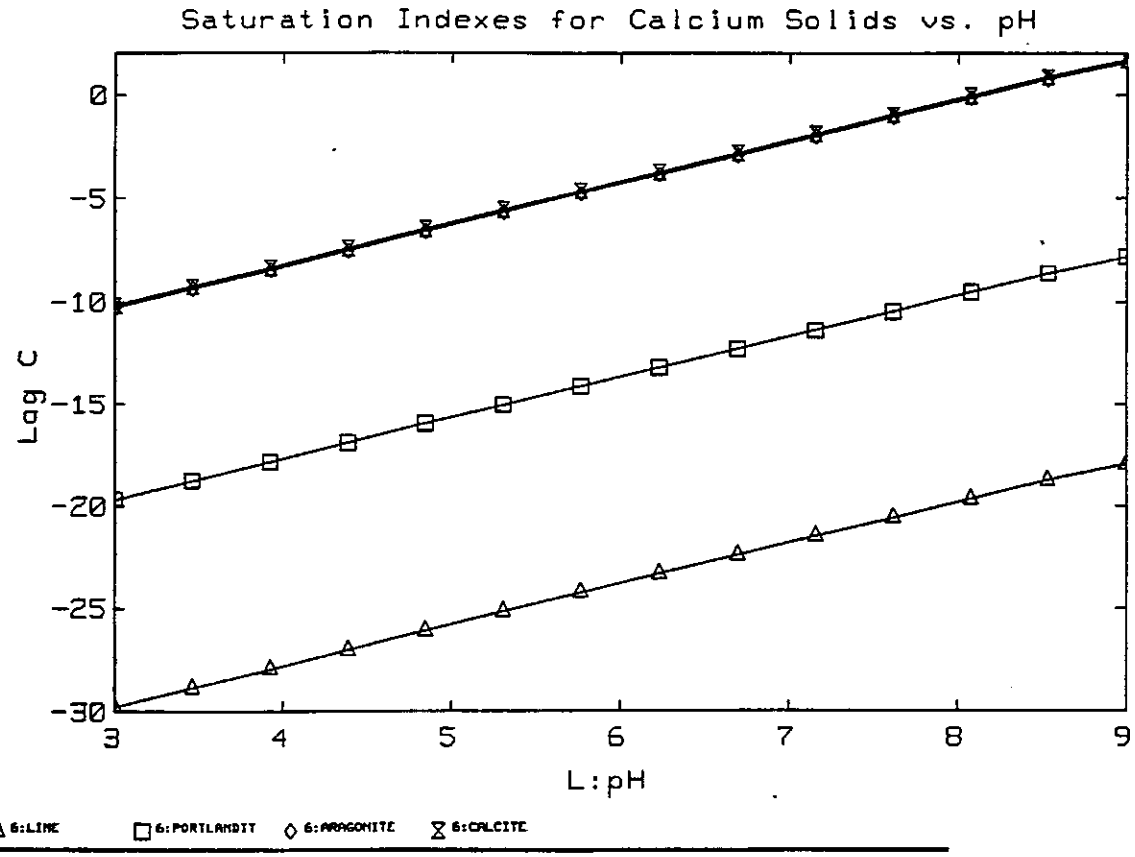


Figure 4.16.

3. **The amount of strong acid or base added to the system.** While the Graphics Manager is still open, change the active component to H(+) and the Units to Conc (M). For the Y axis, select 3:pH. This corresponds to the **S2.H(+)/OBS/Conc** view for pH and is equal to the amount of strong base added or subtracted (strong acid added) to the system. Plot the graph. The plot should look like Figure 4.17.

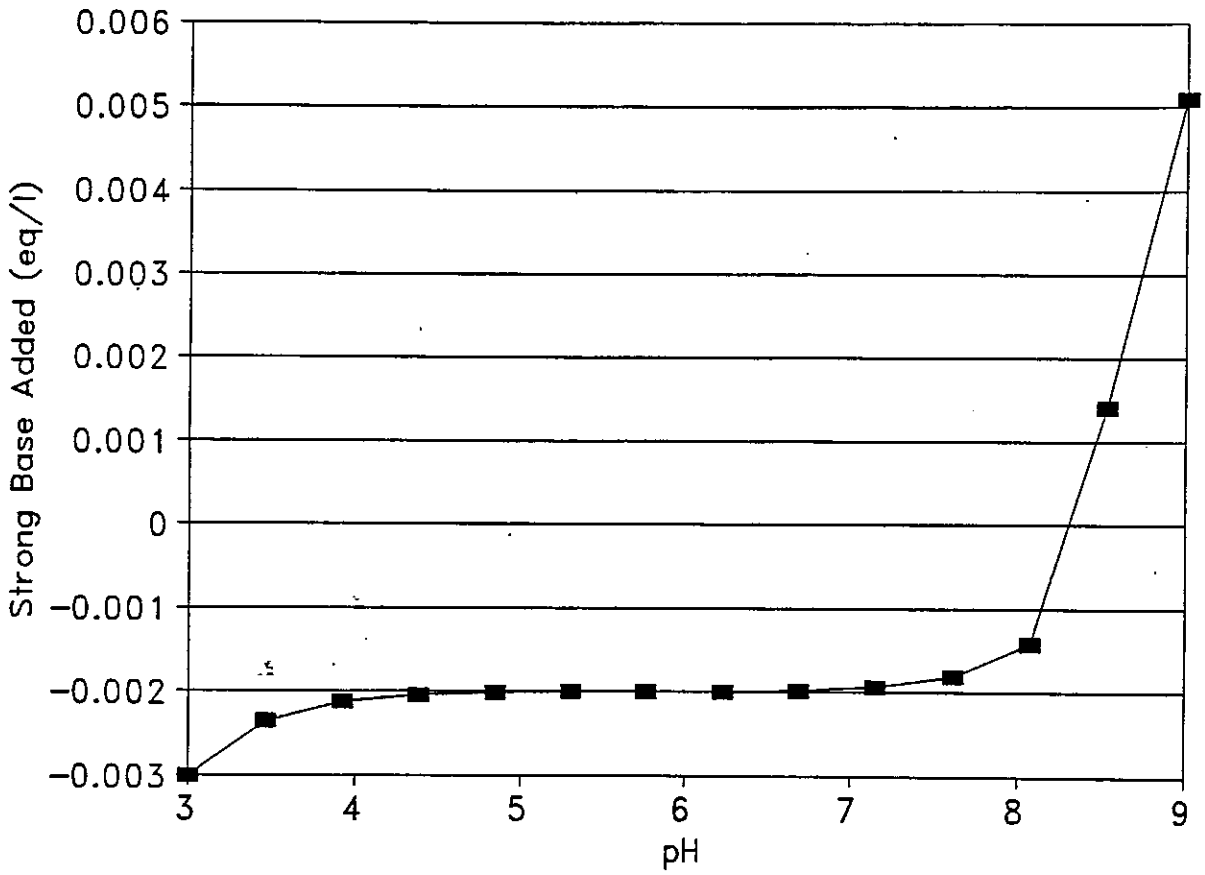


Figure 4.17.

4. **The alkalinity of the system.** Alkalinity is a composite variable since it is calculated from species contained in MINEQL$^+$ output. The Graphics Manager cannot plot a composite variable, so we must use the Output Manager in this case. Open the **S2.CO3(2+)/OBS/Conc** view and extract/save the HCO3(-) and CO3(2-) columns. Next, open the **S2.H(+)/OBS/Conc** view and extract/save the H(+) and OH(-) columns. Combine these two, along with the Multi file, into a spreadsheet. Calculate a new column within the spreadsheet that contains Equation 4.2. The resulting plot of alkalinity vs. pH should look like Figure 4.18.

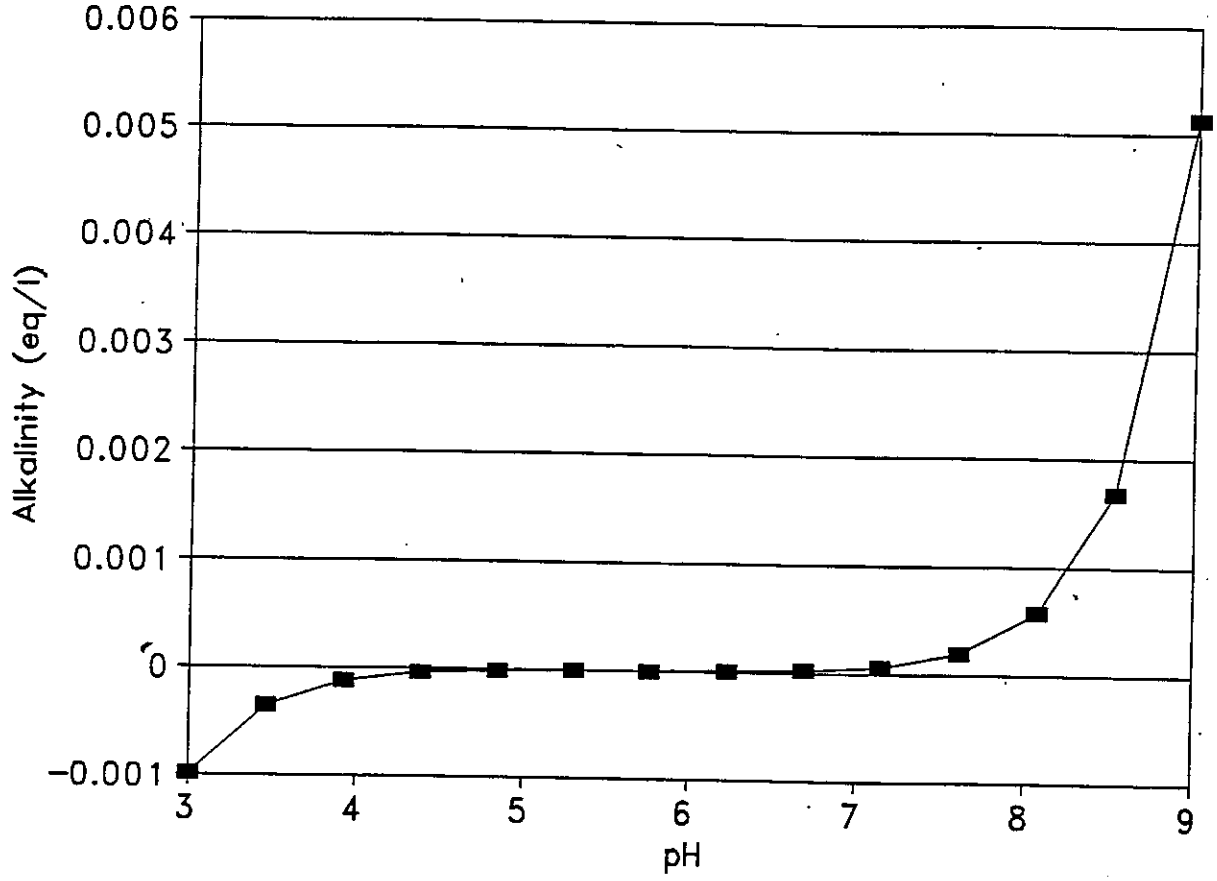


Figure 4.18.

Example 1C. MINEQL Calculation of pH

The System: This problem will be one in which 4.1×10^{-5} M Ca, 3.1×10^{-5} M Al and 1.3×10^{-4} M SO_4^{2-} were measured in a natural system.

The Goal: Calculate the theoretical pH of the system and compare it to the measured pH of 3.69 ± 0.05.

The Method: Step 1. To calculate pH, it is best to assume that electroneutrality is operative in the system. However, MINEQL does not perform a charge balance calculation and relies solely on the mass balance of H^+ to calculate pH. Therefore, the total $[H^+]$ ($[H^+]_T$) must be set at a proper level to achieve electroneutrality.

To start, $[H^+]_T$ is equal to all the proton binding species (weighted by the number of H^+ in each species) minus all the hydroxide binding species (weighted by the number of OH^- in each species). If you are looking at an experimental system, for instance the addition of $NaHCO_3$ to distilled water, you can determine $[H^+]_T$ simply by keeping an account of all the H-binding and OH-binding compounds that were added. For a natural system, however, it is not so simple because you do not know the form in which the components were initially added. Therefore, you have to solve the problem from a different direction. By assuming electroneutrality, the concentration of total proton in the system can be determined by:

$$-[H^+]_T = \sum_{i=1}^{n} z_i [M_i]_T + \sum_{j=1}^{m} z_j [L_j]_T \qquad (4.4)$$

where:

n = the number of cations in the system,
m = the number of anions in the system,
z_i = the charge on the cation,
z_j = the charge on the anion,
$[M_i]_T$ = the total concentration of cation i and,
$[L_j]_T$ = the total concentration of anion j.

For our system, $[H^+]_T = -2[Ca]_T + 2[SO_4]_T - 3[Al]_T$ or

$$\begin{aligned} &-2(4.1\text{X}10^{-5}) \\ &2(1.3\text{X}10^{-4}) \\ &\underline{-3(3.1\text{X}10^{-5})} \\ [H^+]_T &= 8.5\text{X}10^{-5} \end{aligned}$$

Step 2. Once you know $[H^+]_T$, running this problem is straight forward:

- select the components (H2O, H(+), Ca(2+), Al(3+), SO4(2-)),
- type in the total concentrations of each component (with the value for $[H^+]_T$ in the H(+) column),
- remove the pH "species" as a fixed solid (either by pressing the **Del** key and deleting the species or by pressing **F3** and moving it to Type VI)
- type in an output filename,
- run the numerical program.

Details of each step presented in Example 1A.

The Output: Use the **S1.H(+)/SPEC/RUN1** view to see the output (Figure 4.19).

	Name		Type	Conc	LogC	LogK
1	H(+)		1	0.000125	-3.9	0
2	OH-	(-1)	2	8.05e-11	-10.1	-14
3	Al(OH)2(+)	(+1)	2	7.4e-8	-7.13	-10.1
4	Al(OH)3 AQ		2	7.46e-10	-9.13	-16
5	Al(OH)4(-)	(-1)	2	5.98e-13	-12.2	-23
6	AlOH(+2)	(+2)	2	1.19e-6	-5.92	-4.99
7	CaOH +	(+1)	2	8.09e-14	-13.1	-12.6
8	HSO4 -	(-1)	2	1.52e-6	-5.82	1.99
9	DIASPORE		4	1.33e-5	-4.88	-6.87
10	Al2O3		5	5.83e-10	-9.23	-23
11	BOEHMITE		5	0.0197	-1.71	-8.58
12	ALOH3(A)		5	0.000311	-3.51	-10.4
13	GIBBSITE (C)		5	0.0127	-1.9	-8.77
14	AL4(OH)10SO4		5	1.21e-7	-6.92	-22.7

Figure 4.19.

The pH can be found in the LogC column for H(+), Type I. The pH of this system is calculated to be 3.9. This value is outside of the acceptable range of pH measured for the system. To double check this result, look at the total charge of solution in the Log file. It reads 3.320×10^{-10}, a value that is extremely small given that the average concentration of components in solution is of the order of 10^{-5}. As a result, the pH calculated here can be accepted with confidence since the system is essentially electrically neutral. Because the measured and calculated pH values do not match, you can assume that another component (maybe organic anion) is present in the natural system.

Example 2. Surface Adsorption Modeling

Example 2A. Langmuir Adsorption

The System: 5.98 mg of activated carbon is suspended in a liter of pure distilled water. In an incremental fashion, an organic ligand of known molecular weight is added to the system. The system is allowed to equilibrate before the next incremental addition. The following data was collected:

Ligand Added (mol/l)	Bulk Ligand Conc. @ Equil. (mol/l)
10^{-6}	4.57×10^{-7}
0.000106	6.28E-05
0.000211	0.000148
0.000316	0.000244
0.000422	0.000345
0.000527	0.00045
0.000632	0.000567
0.000737	0.000655
0.000842	0.000759
0.000947	0.000878

The Goal: Simulate the adsorption behavior using MINEQL$^+$ and a Langmuir adsorption model.

The Method: Step 1. **Before Using MINEQL$^+$:** The Langmuir adsorption model assumes that ligands adsorb onto a surface until the ligand concentration is high enough for monolayer coverage to be achieved. Not all surface systems behave in this manner, so you will have to check whether a Langmuir model applies in this case.

The adsorption reaction for this system is:

$$L+X=LX \tag{4.5}$$

and yields a mass action expression of:

$$[L][X]K=[LX] \tag{4.6}$$

The total number of surface sites is:

$$X_T=[X]+[LX] \tag{4.7}$$

By combining Equations 4.6 and 4.7, the isotherm for the system is:

$$[LX] = X_T \frac{K[L]}{1 + K[L]} \tag{4.8}$$

Through rearrangement, Equation 4.8 can be described as a linear equation:

$$\frac{[L]}{[LX]} = \frac{1}{K} \cdot \frac{1}{X_T} + \frac{[L]}{X_T} \tag{4.9}$$

with a Y-axis of [L]/[LX], an X-axis of [L], a slope of $1/X_T$ and an intercept of $(1/KX_T)$.

For our data set, you can assume that $[LX] \approx [L]_{added} - [L]_{equil}$ and that $[L] = [L]_{equil}$. This gives us the following derived data:

[LX] (mol/l)	[L]/[LX]
5.43×10^{-7}	0.843292
4.34×10^{-5}	1.44642
6.37×10^{-5}	2.316096
7.24×10^{-5}	3.371015
7.71×10^{-5}	4.466465
7.69×10^{-5}	5.849374
6.54×10^{-5}	8.662829
8.16×10^{-5}	8.029284
8.35×10^{-5}	9.084766
6.98×10^{-5}	12.56705

A plot of [L]/[LX] vs. [L] (Figure 4.20) has an R^2 of 0.97. This indicates that the Langmuir model will be an appropriate choice to simulate this adsorption behavior. In addition, the linear regression showed a slope of 12,573.07 and an intercept of 0.499128. From Equation 4.9, $X_T = 7.95 \times 10^{-5}$ mol/L and Log K = 4.40.