

**The Geochemist's Workbench®**

Release 17

**GWB  
Essentials  
Guide**



**The Geochemist's Workbench®**

Release 17

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# **GWB Essentials Guide**

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The GWB software was originally developed by the students, staff, and faculty of the Hydrogeology Program in the Department of Geology at the University of Illinois Urbana-Champaign. The package is currently developed and maintained by Aqueous Solutions LLC.

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## **Origin of the programs**

The GWB package was originally developed at the Department of Geology of the University of Illinois at Urbana-Champaign over a period of more than twenty years, under the sponsorship of a consortium of companies and government laboratories. The members of the consortium, past and present, include:

- Amoco Production Company
- Arco Oil and Gas Company
- Chevron Petroleum Technology Corporation
- ConocoPhillips Company
- ExxonMobil Upstream Research Company
- Hewlett Packard, Incorporated
- Idaho National Engineering Lab
- Japan National Oil Corporation
- Lawrence Livermore National Laboratory
- Marathon Oil Company
- Mobil Research and Development Corporation
- Sandia National Laboratories
- SCKCEN (Belgian nuclear authority)
- Silicon Graphics Computer Systems
- Texaco, Incorporated
- Union Oil Company of California
- United States Geological Survey

The original GWB package was written by Craig Bethke with the assistance of Ming-Kuo Lee and Jeffrey Biesiadecki of the Hydrogeology Program in the Department of Geology, University of Illinois at Urbana-Champaign. The GWB is currently developed and supported by Aqueous Solutions LLC, located in Champaign, Illinois.

A number of programmers in the Hydrogeology Program, including Rick Hedin, Peter Berger, Tren Haselton, Ester Soriano, David Solt, and Lalita Kalita helped develop the user interface. Brian Healy and Walter Kreiling developed a library used by the programs to produce graphical images on various output devices, and David Solt, Tren Haselton, Changlin Huang, Ester Soriano, Xiang Zhao, and Kevin Gorczowski have updated and eventually replaced this library over the years. J.K. Bohlke, Eric Daniels, and MingKuo

Lee compiled the dataset of isotope fractionation factors; Daniel Saalfeld helped translate thermodynamic datasets to the GWB format; Amy Berger helped develop the surface complexation model; Qusheng Jin helped implement the redox kinetics and microbiological features; and Jungho Park created the GWBSymbol font and helped develop React's ability to use custom rate laws. Peter Berger, Rick Hedin, Phil Parker, Dan Saalfeld, and Sharon Yeakel developed the active graphics facilities and other features of

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release 7.0; Sharon Yeakel helped prepare documentation for the release. Phil Parker worked on developing the multithreaded versions of X1t and X2t for release 8.0, and Dan Saalfeld, Sharon Yeakel, and Jesse Luehrs developed program GSS and other features of the release. Dan Saalfeld, Sharon Yeakel, and Jesse Luehrs, with the assistance of Brian Farrell, developed release 9.0.

Dan Saalfeld, Sharon Yeakel, Brian Farrell, Bryan Plummer, Steven Canning and Craig Bethke developed release 10.0. Dan Saalfeld, Sharon Yeakel, Yusheng Hou, Oscar Garcia, Brian Farrell, Katelyn Zatwarnicki, Shelley Goel, Peter Berger and Craig Bethke developed the GWB 11 release. Brian Farrell, Yusheng Hou, Daniel Saalfeld, Melika Sharifironizi and Craig Bethke developed GWB12. Brian Farrell, Melika Sharifironizi, Jia Wang, Taha Anwar, Daniel Saalfeld, Yusheng Hou, and Craig Bethke developed subsequent versions of the software, which have been released continuously as a subscription service.

The software authors appreciate the assistance of more people than we can remember who over the years helped with software development and testing. These people include Theresa Beckman, Bill Bourcier, Pat Brady, Tenhung Chu, David Finkelstein, Ted Flynn, Annette Fugl, Oscar Garcia Cabrejo, Man Jae Kwon, Matt Kyrias, Kurt Larson, Meng Lei, Melinda Legg, Gordon Madise, Chuck Norris, Hernán Quinodoz, Derik Strattan, and Melinda Tidrick. We also thank the many students and users who have suggested improvements to the codes and documentation.

# Introduction

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The Geochemist's Workbench is a set of software tools for manipulating chemical reactions, calculating stability diagrams and the equilibrium states of natural waters, tracing reaction processes, modeling reactive transport, plotting the results of these calculations, and storing the related data. The Workbench, designed for personal computers running MS Windows, is distributed in four packages:

- **GWB Essentials** contains tools for balancing reactions, calculating activity diagrams, computing speciation in aqueous solutions, plotting the results of these calculations, and storing the related data.
- **GWB Standard** contains the tools included in GWB Essentials, as well as a program for modeling reaction processes.
- **GWB Professional** includes all the programs in the Standard release, plus programs for modeling reactive transport in one and two dimensions, and for plotting modeling results. The package also includes programs for constructing phase diagrams. Finally, the package includes the ChemPlugin self-linking software object.
- **GWB Advanced Professional** extends the package to include MPI versions of the reactive transport models for use on computing clusters, the ChemPlugin self-linking software object adapted for cluster computers, and other specialized codes.

The GWB Essentials release consists of seven programs:

- **GSS** stores analyte and sample data in a spreadsheet specially developed to work with the GWB set of software tools.
- **Rxn** automatically balances chemical reactions, calculates equilibrium constants and equations, and solves for the temperatures at which reactions are in equilibrium.
- **Act2** calculates and plots stability diagrams on activity and fugacity axes. It can also project the traces of reaction paths calculated using the **React** program.
- **Tact** calculates and plots temperature-activity and temperature-fugacity diagrams and projects the traces of reaction paths.
- **SpecE8** calculates species distributions in aqueous solutions, the saturation state of minerals and solid solutions, and the fugacity and partial pressure of

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gases. **SpecE8** can account for sorption of species onto mineral surfaces according to a variety of methods, including surface complexation and ion exchange. **SpecE8** can additionally figure the fractionation of stable isotopes.

- **Gtplot** graphs **SpecE8** results and **GSS** datasets, including on xy plots, ternary, Piper, Durov, and Stiff diagrams.
- **TEdit** displays, modifies, and creates the thermodynamic and surface reaction datasets used by the various GWB applications.

The GWB Standard release also includes the program:

- **React**, in addition to having the capabilities of **SpecE8**, traces reaction paths involving fluids, minerals, solid solutions, and gases. **React** can also predict the fractionation of stable isotopes during reaction processes. The simulation results can be rendered with **Gtplot**.

The GWB Professional release contains the additional programs:

- **Phase2** is an extension of **React** used to calculate phase diagrams.
- **P2plot** draws the phase diagrams calculated by **Phase2**.
- **X1t** simulates reactive transport in one-dimensional systems. The program has all of **React**'s geochemical modeling capabilities coupled with groundwater flow and transport.
- **X2t** simulates reactive transport in two-dimensional systems.
- **Xtplot** plots in map view and as xy plots the results of reactive transport simulations made using **X1t** and **X2t**.
- **ChemPlugin** is a self-linking software object for building reactive transport models in any configuration, and for repurposing flow models as reactive transport simulators.

GWB Advanced Professional adds:

- **cX1t** and **cX2t**, parallel processing versions of **X1t** and **X2t** for use on computing clusters.
- **ChemPlugin\_MPI**, a cluster computing version of **ChemPlugin**.
- Other specialized software; contact the developers for current information.

Each of the programs operates in a similar fashion, so once you learn to use one, you will find the others easy to work with.



## 1.1 GWB documentation

Depending on the package, the GWB comes with a set of User's Guides accessible as pdf files from the Help pulldown of any of the programs, and also available in printed form:

- **GWB Essentials Guide**—A guide to **GSS**, **Rxn**, **Act2**, **Tact**, **SpecE8**, **Gtplot**, and **TEdit** (this document).
- **Reaction Modeling Guide**—Information on reaction modeling using **React**, and using **Gtplot** to render simulation results, along with information on using **Phase2** and **P2plot** to construct phase diagrams.
- **Reactive Transport Modeling Guide**—A guide to reactive transport modeling with **X1t**, **X2t**, and **Xtplot**.
- **Command Reference**—A comprehensive guide to commands for the GWB programs.
- **Reference Manual**—A guide to the format of the thermodynamic datasets, the report command, the plug-in feature, graphics output, and so on.
- **ChemPlugin™ User's Guide**—A tutorial and reference for using the self-linking software object.

A considerable amount of information, including a large number of fully worked examples, is available in *Geochemical and Biogeochemical Reaction Modeling* by Craig M. Bethke, available from Cambridge University Press.

## 1.2 Online tutorials

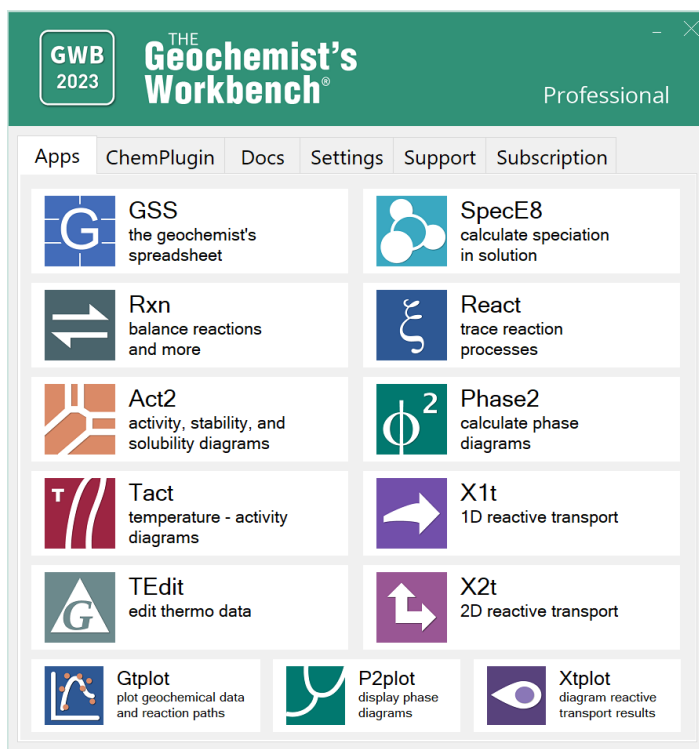
The GWB website—[www.gwb.com](http://www.gwb.com)—contains a variety of step-by-step tutorials showing how to use the GWB software package. The website also contains a large number of diagrams and movies showing the results of GWB calculations. By clicking the icons next to each case, you can download the input scripts used to configure the calculation, or start the appropriate GWB application, configured and ready to run.

The GWB YouTube channel—[www.youtube.com/user/GeochemistsWorkbench](http://www.youtube.com/user/GeochemistsWorkbench)—contains a number of instructional video clips that will quickly and efficiently help you become expert in using the software.

## 1.3 GWB dashboard

The GWB dashboard is the platform from which you run the GWB programs, access documentation, find online video tutorials, activate and configure the software, and upgrade your software installation.

Start the GWB dashboard from the **Start** button on your Windows desktop. Select **The Geochemist's Workbench 17** in the menu, which brings up the GWB dashboard. The dashboard looks like:

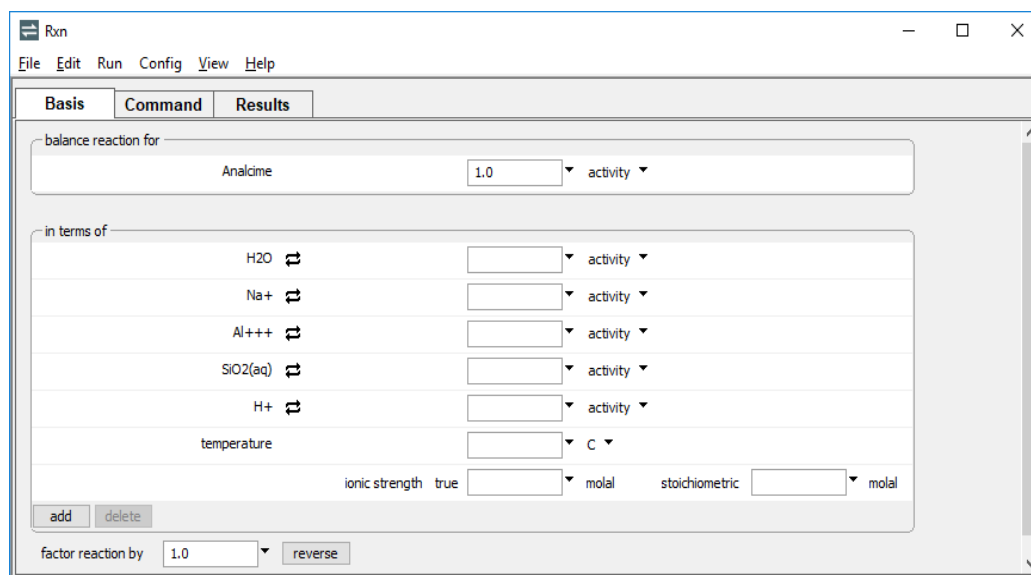


Take a moment to explore each of the tabs along the top of the window.

You can launch the various GWB programs from the **Apps** pane. On the **ChemPlugin** pane you can find information on and examples of applying the self-linking software object. The **Docs** pane takes you to options for printed documentation. You can configure the software on the **Settings** pane, and the **Support** pane provides tools to activate the software and obtain user support. The **Subscription** pane shows options for upgrading or renewing your software license. You can start the individual GWB programs in any of several ways: click on the program's icon in the **Apps** pane, open (e.g., double-click on) a GWB input file from Windows, or simply drag an input file into the GWB dashboard.

## 1.4 GWB modeling programs

When **Rxn**, **Act2**, **Tact**, **SpecE8**, **React**, **Phase2**, **X1t**, and **X2t** start, they appear as a window containing several panes and a menubar. **Rxn**'s window, for example, is shown here.



The window contains three panes:

- The **Basis** pane, where you can set the most important calculation constraints, as described below.
- The **Command** pane, where you can type **Rxn** commands.
- The **Results** pane, where you view calculation results.

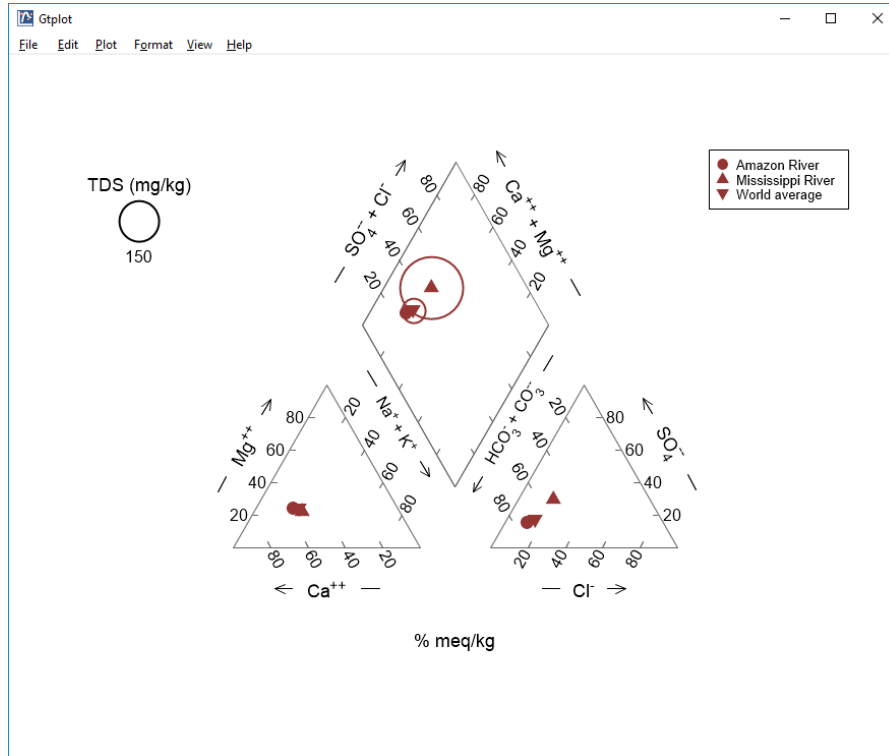
You can detach each pane by dragging the pane title to the desktop with the left mouse button. In this way you can arrange and size the panes individually. The window also contains a menubar, from which you can select a number of options and display a variety of dialog boxes.

When **Rxn**, **Act2**, **Tact**, **SpecE8**, **React**, **Phase2**, **X1t**, and **X2t** start, they assume the working directory from the previous run. The programs write output into this directory and look there for input files. You can change the working directory at any time by selecting **File** → **Working Directory** (**Ctrl+Shift+W**); the current setting is displayed on the window frame.

Once you have configured a calculation, you generate the calculation results by selecting **Run** → **Go** or, on the **Results** output pane, pressing the **Run** button (or in **Act2** and **Tact**, the **Update Plot** button). Once you have viewed the calculation results, you can move to another pane or select options from the menubar to modify the program's configuration.

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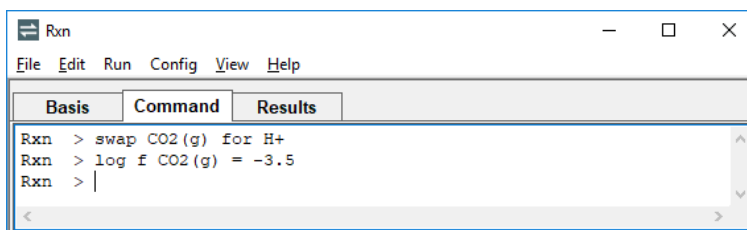
**Gtplot** contains a graphics area and a menubar, but there are no panes to select (as shown below). You configure this program using the mouse (or keyboard shortcuts) to select options from the menubar, or by left-clicking, right-clicking, or double-clicking on aspects of the plot displayed.



## 1.5 To GUI or not to GUI

Some people like to work interactively with a GUI (a GUI is a Graphic User Interface, or “goosey”), whereas others prefer to type commands from the keyboard. In **Rxn**, **Act2**, **Tact**, **SpecE8**, **React**, **Phase2**, **X1t**, and **X2t**, you can work either way, or switch freely from one to the other.

To enter commands, select the **Command** pane and type your input at the prompt, as shown here.



Alternatively, each GWB command has a GUI counterpart, which you invoke on a different pane, or by selecting an option or dialog from the program's menubar.

You can quickly find the GUI equivalents to each command by exploring the program, or by consulting the ***GWB Command Reference***. Example calculations in this Guide are most commonly shown as sequences of commands, because the commands can be listed concisely. You can work the examples following either the command listings or their GUI equivalents.

## 1.6 Saving and reading input files

You can save the current settings in **Rxn**, **Act2**, **Tact**, **SpecE8**, and **TEdit** for later use. To do so, select **File → Save As...** (**Ctrl+S**). Or typing

```
save My_file.ac2
```

within **Act2**, for example, writes the program's current configuration into a dataset "My\_file.ac2".

Saved datasets contain input commands that can be read later by the program. Select an input dataset using the **File → Open → Read script...** dialog, or by typing

```
read My_file.ac2
```

Alternatively, simply open the file. A list of the most recently opened files can be accessed with **File → Recent Files**. The number of files in the list can be set in **File → Preferences...**

The following filename extensions are defined under Windows for the GWB programs:

.gss	<b>GSS</b>	.sp8	<b>SpecE8</b>	.p2p	<b>P2plot</b>	.tdat	Thermo data
.rxn	<b>Rxn</b>	.gtp	<b>Gtplot</b>	.x1t	<b>X1t</b>	.sdat	Surface data
.ac2	<b>Act2</b>	.rea	<b>React</b>	.x2t	<b>X2t</b>		
.tac	<b>Tact</b>	.ph2	<b>Phase2</b>	.xtp	<b>Xtplot</b>		

Double-clicking on "My\_file.ac2", for example, launches **Act2** and executes the commands in the file.

When you exit **Rxn**, **Act2**, **Tact**, **SpecE8**, and **GSS**, they automatically save their current configurations to files such as "rxn\_resume.rxn" and "act2\_resume.ac2" in your profile directory (found by typing %appdata% in the File Explorer Address bar, e.g., "c:\Documents and Settings\jones\Application Data\GWB"). Upon reentering the programs, you can restore the previous configuration by choosing **File → Resume**, or typing

```
resume
```

from the command line. Set the **File → Resume On Startup** option if each time you start one of the programs you would like to resume your previous session automatically.

**Gtplot** automatically saves the previous plot configuration in a dataset named “gtplot\_conf.gtc” when you exit the program with the **File → Quit** option (**Ctrl+Q**). When you restart in the same working directory, or when you open a “.gtc” file, the program configuration is restored. You can reset the configuration by choosing **File → Reset configuration** (**Ctrl+R**) or use the **File → Save As...** option (**Ctrl+S**) to save different configuration files in the same directory (see [Using Gtplot](#)).

## 1.7 Drag and drop feature

The drag and drop feature is a convenient way to transfer data within or between GWB programs, or between GWB programs and any other application that supports it.


Drag an input file from your Desktop or File Explorer into the GWB dashboard or any GWB application, and the input will be automatically loaded. For example, you could drag a script file (.sp8) or thermo data file (.tdat) into **SpecE8**, or drag a configuration file (.gtc) into **Gtplot**.

**Left-click, drag onto a GWB app, and release:**

- Input scripts and files
- Thermo and surface reaction datasets
- Conductivity, isotope fractionation, and water standards data
- Plot configuration files
- Scatter data and reaction traces

You can drag chemical data directly from your spreadsheet or table into any GWB program. Drag data to the **Basis** pane of **SpecE8** or **React** to analyze an individual sample, to one of the panes in **X1t** or **X2t** to constrain the initial, inlet, or injection fluids, or into **GSS** to transfer your data.

In **GSS**, right-click on an individual cell or on the sample header (to select an entire sample) and drag. In **MS Excel**, **MS Word**, or **MS PowerPoint**, highlight the cell or column, left-click the frame surrounding it, and drag. Release the mouse button over the selected input pane in the GWB program.

If dragging into **GSS**, bring the pointer to a sample header to fill that sample (as shown below), or to the  button to add new samples.

	1	2	3	
Sample ID	S1	S2	S3	
pH	6.5	5.9	6.9	
Na <sup>+</sup> mmol/kg	1.8	20	6.3	
Ca <sup>++</sup> mmol/kg	4.3	38	15	
HCO <sub>3</sub> <sup>-</sup> mmol/kg	19	113	58	

#### Right-click and drag samples:

- from one **GSS** data sheet to another.
- from **GSS** into **Basis**, **Initial** panes.
- from **GSS** into **MS Excel**.

#### Left-click and drag:

- samples from **MS Excel** into **GSS**.
- samples from **MS Excel** into **Basis**, **Initial** panes.
- in **GSS** to rearrange samples or analytes.

Right-click and drag any pane title to transfer data within a **GWB** program, from one **GWB** program to another, or to another application.

In **React**, in order to “pick up” the results of a calculation and use these results as the starting point for a new calculation, right-click the **Results** pane title and drag it onto the **Basis** pane.

Calculation output can be copied from the **Results** pane to any other application in the same way. Dragging the **Results** pane will copy and paste the last step components in the fluid.

Right-click on a dialog title bar and drag to copy the settings of the dialog box from one **GWB** application to another. For example, if in **SpecE8** you have the **Alter Log Ks** dialog all set up and filled with the values you would like to use in **React**, right-click the **Alter Log Ks** dialog title bar and drag it into **React**. The destination dialog box does not need to be open at the time.

#### Right-click and drag panes and dialogs to transfer:

- data from one instance of **React**, for example, to another.
- data from one **GWB** program to another.
- in **React**, calculation results from the **Results** pane to the **Basis** pane.
- calculation results into **GSS**.
- **Basis**, **Initial** pane values into **GSS**.
- data into **MS Excel**, **MS Word**, or **MS PowerPoint**.
- text into **WordPad** to see what the drag/drop actual text is.

You can rearrange the order of the panes by left-clicking and dragging the pane titles. You may also detach each pane by left-clicking on the pane title and dragging it to the desktop. In this way, you can arrange and size the panes individually to view and work with several panes at the same time. For example, you can type commands in the Command pane and immediately see the effect on the Basis, Results, and Plot panes. Re-attach panes with their close buttons. **View → Reset Windows** resizes, re-attaches, and reorders all of the panes to the default configuration.

You can drag data tables, elements, any type of species, or virial coefficients from one thermo or surface dataset open in **TEdit** to another. Left-click an entry on the tree structure of the source dataset, drag it to the tree structure or current entry of the target dataset, and release. If the source and target datasets are open in the same **TEdit** window, you can switch to the target dataset by hovering over its tab while dragging.

**Left-click and drag panes:**

- to rearrange the order of the panes.
- to detach panes and arrange them on the desktop.

Re-attach panes with their close buttons or **View → Reset Windows (Alt+S)**.

The User's Guides provide many examples of how to configure the programs, how to use the various commands, and how to create input scripts. You can highlight any of these examples in the pdf files, left-click within the selected text, drag with the left mouse, and drop into a GWB program. The commands will be automatically executed in order. Open the **Run → History...** dialog box to review them, or type `history` in the Command pane. You might also create an input script by dropping the selected text into an application such as WordPad and saving the file as a plain text document with the appropriate extension (.sp8, .rea, etc.).

\*Note: If you are having trouble with Adobe Reader X drag and drop, go to **Edit → Preferences → Categories → General** and uncheck "Enable Protected Mode at startup".

**Left-click and drag from the pdf User's Guides:**

- command examples to the GWB programs or other applications.
- script examples to the GWB programs or other applications.

If you have a spreadsheet that contains the results of a large number of analyses, an alternative to drag and drop is to prepare a short script that performs the operations automatically, reading the analyses one at a time and adding the calculation results to the spreadsheet. For details of this process and a fully worked example, refer to the **Multiple Analyses** chapter of the *GWB Reference Manual*.



## 1.8 Helpful features

The command line interface for the Command pane in **Rxn**, **Act2**, **Tact**, **SpecE8**, **React**, **Phase2**, **X1t**, and **X2t** includes a number of helpful features:

- **Spelling completion.** When you type commands in the **Command** pane, the programs automatically complete the spelling of a mineral, chemical, or command name (given enough characters to identify the name uniquely)—just press the [tab] key. When the program cannot identify a unique name, it will cycle through the possible completions with subsequent [tab] key presses. You can also show all names beginning with a combination of characters by pressing **Ctrl+D**.
- **Command history.** The programs maintain a list of previously executed commands, which can be retrieved, modified, and re-executed. Type `history` or select **Run → History...** to view the history list.
- **Special characters.** A group of control characters is provided on the **Command** pane for purposes such as spelling completion and input correction.
- **Startup files.** Users can establish files in their profile directories containing commands for **Rxn**, **Act2**, **Tact**, **SpecE8**, **React**, **Phase2**, **X1t**, and **X2t** to execute at startup. These files should be named with the app name and `_startup` (e.g., `act2_startup.ac2`) and placed in your profile directory (found by typing `%appdata%` in the File Explorer Address bar, e.g., “C:\Documents and Settings\jones\Application Data\GWB”).
- **Calculator.** The interface will automatically evaluate any numerical expression typed in the **Command** pane. This feature facilitates, for example, conversion of numbers to logarithms, or vice versa.
- **Online documentation.** The GWB User’s Guides are available in pdf format online from any of the GWB programs. Select **Help** on the menubar to access them.

These features are described fully in the **User Interface** chapter of the *GWB Reference Manual*.

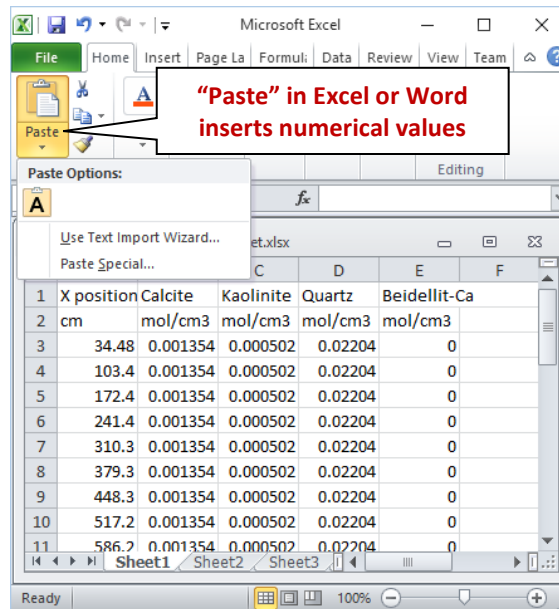
## 1.9 Exporting results

Programs **Act2**, **Tact**, **Gtplot**, **P2plot**, and **Xtplot** make it convenient to use the plots you create in articles, reports, presentations, and databases. You can copy the current plot to the clipboard and then paste it into a variety of applications, in a format meaningful to the application.

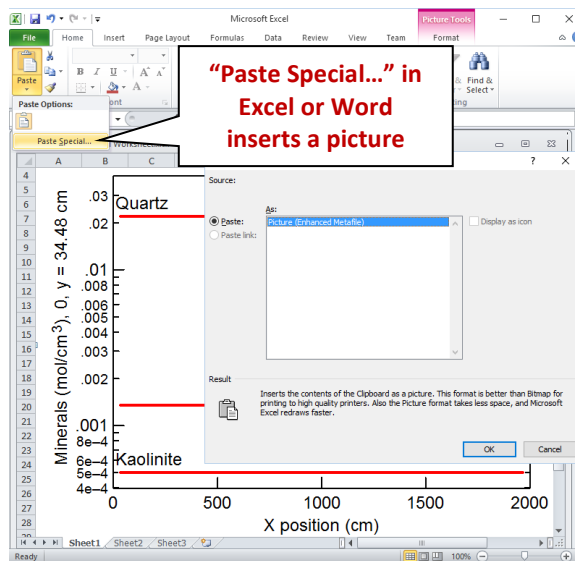
To copy a plot, use **Edit → Copy (Ctrl+C)**. If you paste the plot into MS PowerPoint, it will appear as an EMF (an MS Enhanced Metafile) graphic object. Pasting into Adobe Illustrator places a native AI graphic.

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If you paste a plot from **Gtplot**, **P2plot**, or **Xtplot** into MS Excel or a text editor such as Notepad or MS Word, the numerical values of the data points that make up the lines on the plot will appear in spreadsheet format (as shown below).



In MS Word or MS Excel, use **Paste Special...** to paste the plot as a picture instead.



You can control the format in which the plot is copied to the clipboard by selecting **Edit** → **Copy As**. You can choose to copy the plot as an AI object, an EMF object, or a bitmap, or

the data points in the plot as tab delimited or space delimited text. Use the tab delimited option to paste the data into a spreadsheet program like MS Excel. For examining the data in a text file created with an editor like Notepad or MS Word, the space delimited option writes a nicely aligned table.

When importing AI graphics to Adobe Illustrator, the program may prompt you to update the legacy text before you can edit the file. In this case, choose “Update”. You need to release the clipping mask before you attempt to edit individual elements of the plot. Use the “Ungroup” and “Group” functions when repositioning or modifying elements.

The programs can save plots to files in various formats by selecting **File → Save Image...** from the menubar. The **Graphics Output** section of the *GWB Reference Manual* summarizes the options available for saving and using graphical output.

## 1.10 Automatic plot updates

The software is designed so that whenever **SpecE8**, **React**, **Phase2**, **X1t**, or **X2t** completes a simulation, any instances of **Act2**, **Tact**, **Gtplot**, **P2plot**, or **Xtplot** that are displaying the results of that simulation will update their plots automatically. Similarly, whenever a **GSS** spreadsheet is updated, any app plotting that data directly or as scatter data will sync automatically, unless automatic updates have been disabled in **GSS**.

## 1.11 Further reading

This guide is intended as an introduction to using the programs in The Geochemist’s Workbench Essentials package, and as a reference for the software package. For information about geochemical modeling in general, including a number of examples of how the software can be applied, please refer to the text *Geochemical and Biogeochemical Reaction Modeling* by Craig M. Bethke, available from Cambridge University Press. The [Further Reading](#) chapter in this guide gives literature references to this text and a number of other sources that provide starting points for further reading.

## 1.12 User resources

The [GWB website](#) holds a set of [visual tutorials](#) that show how to use the GWB apps to solve a range of problems in geochemistry. Browse the [GWB YouTube channel](#) for a series of narrated video clips showing the GWB in action.

The GWB website also contains galleries of [diagrams](#) and [movies](#), along with the input files used to compute them. Finally, the [GWB Online Academy](#) is a self-guided course in geochemical and reactive transport modeling that takes you from beginner to expert.

Gwb\_users is an independent group of users who share comments and results and answer questions of general interest over the Internet. The group maintains an online forum that serves as a bulletin board for posting announcements, bug notices, and other current information about the software.

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To subscribe to the forum (there is no charge), unsubscribe, or post a message, select **GWB Users' Group** from the GWB dashboard or the Help pulldown in any of the GWB programs. Alternatively, you can visit the group's home page at [forum.gwb.com](http://forum.gwb.com).

# Configuring the Programs

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## 2.1 Configuring a calculation

Rxn, Act2, Tact, and SpecE8 all work in the same manner. Each program maintains a set of species, known as the basis, with which it writes reactions. Initially, the basis is the set of aqueous species that appears at the beginning of the thermodynamic database (see [Table 2.1](#)). This set is known as the “original basis.”

You can alter the basis to reflect the geochemical constraints that you wish to impose in your calculation by substituting (“swapping”) another aqueous species, mineral, solid solution end member, or gas for an entry in the original basis. To specify equilibrium with quartz, for example, you swap quartz for the basis species  $\text{SiO}_2(\text{aq})$ . Or, to set the  $\text{CO}_2$  fugacity of your geochemical system, you swap  $\text{CO}_2(\text{g})$  for either the  $\text{HCO}_3^-$  or  $\text{H}^+$  basis entries. Examples in **Chapters 4–7** illustrate the basis swapping technique.



To perform a calculation, follow these steps:

1. **Set the basis.** First, add or swap the aqueous species, minerals, solid solution end members, or gases you wish to use to constrain your calculation into the basis. The basis should contain any species at known activity, such as  $\text{H}^+$  if the pH is known, minerals or end members co-existing with the system, or gases at known fugacity or partial pressure. If you are calculating a stability diagram, the basis also includes the species to appear on the diagram axes.
2. **Constrain the basis.** Next, specify the temperature for the calculation and assign a value (“constraint”) for total concentration, mineral or end member mass, activity, fugacity, or partial pressure for each entry in the basis.
3. **Go.** Select **Run → Go** to initiate the calculation, which might be letting the program balance a reaction, calculate and display a diagram, or trace a reaction path.
4. **Revise.** When the calculation is completed, you can adjust the basis by adding new components or varying your constraints; then, recalculate the model. You can continue to revise and recalculate until you decide to quit.


Table 2.1 Basis species in the LLNL thermodynamic database, “thermo.tdat”			
H2O	Water	Li+	Lithium
Ag+	Silver	Mg++	Magnesium
Al+++	Aluminum	Mn++	Manganese
Am+++	Americium	NO3-	Nitrogen
As(OH)4-	Arsenic	Na+	Sodium
Au+	Gold	Ni++	Nickel
B(OH)3	Boron	Np++++	Neptunium
Ba++	Barium	O2(aq)	Oxygen
Br-	Bromine	Pb++	Lead
Ca++	Calcium	PuO2++	Plutonium
HCO3-	Carbon	Ra++	Radium
Cs+	Cesium	Rb+	Rubidium
Cl-	Chlorine	Ru+++	Ruthenium
Co++	Cobalt	SeO3- -	Selenium
Cr+++	Chromium	SiO2(aq)	Silicon
Cu+	Copper	Sr++	Strontium
Eu+++	Europium	SO4- -	Sulfur
F-	Fluorine	TcO4-	Technetium
H+	Hydrogen	Th++++	Thorium
HPO4- -	Phosphorus	Sn++++	Tin
Hg++	Mercury	U++++	Uranium
I-	Iodine	V+++	Vanadium
Fe++	Iron	Zn++	Zinc
K+	Potassium		

## 2.2 Setting and constraining the basis

You set the basis by adding the appropriate entries for the original basis list ([Table 2.1](#)) to the calculation. Then, if necessary, you swap another species, mineral, end member, or gas for the original basis entry. If you prefer to type your input, you use the `add` and `swap` commands.

To configure the basis with the GUI, move to the **Basis** pane. You will see a list of current basis entries. Click the  button (**Ctrl+N**) to add an entry to the basis. A menu of available entries appears. Navigate the menu with the mouse, the up and down arrow keys, or by typing the entry's first letter(s). To swap, click on the entry's  button, and select an aqueous species, mineral, end member, or gas to swap into the basis.

Once you have created a list of basis entries (e.g., as shown in [Table 2.1](#)), you can manipulate it in several ways. You constrain an entry by choosing a unit (e.g., the activity of a species or fugacity of a gas) and setting a value in the corresponding box.

You can change the order of the entries by simply dragging them. To delete a basis entry, or several, select the entire entry and press the Delete key or the  button. To configure another invocation of the program with these entries, right-click on the pane title, drag it, and release (see [Drag and drop](#)).

## 2.3 Thermodynamic datasets

The programs work from any of the thermodynamic databases installed with the software, as well as those sourced elsewhere. Each database contains the properties of aqueous species, minerals, solid solutions, and gases; equilibrium constants for reactions among species; and data required to calculate activity coefficients and fugacity coefficients. In many cases, the data span the temperature range 0°C–300°C, at one atm pressure below 100°C, and along the vapor pressure of water at higher temperatures, but the temperature range and pressure profile are set at the discretion of the database author.

You can view, edit, and even create your own thermo datasets in the **TEdit** graphical editor (see [Using TEdit](#)). You can alternatively alter datasets using a text editor such as Notepad, but **TEdit** shows the database structure at a glance and provides significant verification and troubleshooting capabilities. The **Thermo Datasets** chapter in the *GWB Reference Manual* gives details of the database format.

The default dataset, named “thermo.tdat”, supports activity coefficients calculated according to an extended form of the Debye-Hückel equation (the “Bdot” equation; see [Activity coefficients](#) under [Using SpecE8](#)). The database was compiled by Thomas Wolery, Joan Delany, Ken Jackson, James Johnson, and other members of the geochemical modeling group at Lawrence Livermore National Laboratories (LLNL). The dataset is based in large part on the SUPCRT data compilation (see references in the [Further Reading](#) section).

The GWB is distributed with a number of other thermodynamic databases. Dataset “thermo.com.V8.R6+.tdat” is the “combined” LLNL dataset, version 8, release 6, in which the redox coupling among organic species has been modified somewhat. You may prefer to use this dataset if you are working extensively with systems containing organic species.

Dataset “thermo\_cemdata.tdat” is the Cemdata18 thermodynamic database designed for modeling reactions in cements and concrete (see [Further Reading](#)), extended to include entries for phosphate and zeolite minerals from the Swiss Federal Laboratories for

Materials Science and Technology (Empa). The dataset uses a variation of the Debye-Hückel model, as implemented in the PhreeqC program, described below and in [Activity coefficients](#) under **Using SpecE8**. The dataset includes definitions for several Guggenheim and ideal binary solid solutions.

**SpecE8, React, Phase2, X1t, and X2t** can use virial methods to model the activities of electrolyte species in saline fluids. Such calculations require thermo datasets containing the virial coefficients. Dataset “thermo\_hmw.tdat”, included with the software release, includes coefficients for the Harvie-Møller-Weare activity model, a formalism of the Pitzer equations (see [Activity coefficients](#) under **Using SpecE8**). There is no provision in this dataset for calculations at temperatures other than 25°C.

Datasets “thermo\_ympr.R2.tdat” and “THEREDA\_2021\_GWB.tdat” are the Yucca Mountain Project and THEREDA Project’s compilations, respectively, each of which also follows the Harvie-Møller-Weare formalism. The datasets contain more chemical components than “thermo\_hmw.tdat”, and include provision for extrapolating the data for many of the components to temperatures other than 25°C. Before applying any Pitzer dataset at temperatures other than 25°C, you should study its documentation (see [Further Reading](#)) carefully.

Datasets “thermo\_frezchem.tdat” and “thermo\_coldchem.tdat” carry the H-M-W method to temperatures well below the freezing point of pure water. The former file is based on data from the FREZCHEM program, as set out by Toner and Sletten; the latter is taken from Toner and Catling (see [Further Reading](#)).

Datasets “thermo\_sit.tdat” and “thermo\_nea.tdat”, available from the ThermoChimie project and the Nuclear Energy Agency, respectively, include coefficients for the Specific Ion Interaction Theory (SIT) activity model (see [Activity coefficients](#) under **Using SpecE8**).

Several other datasets are provided with the GWB release for compatibility with other geochemical modeling software. Files “thermo\_minteq.tdat”, “thermo\_phreeqc.tdat”, “thermo\_phrqpitz.tdat”, and “thermo\_wateq4f.tdat” contain data from the MINTEQ, PHREEQC, PHRQPITZ, and WATEQ4F software packages, respectively, which can be downloaded from the Visual Minteq home page (MINTEQ) and the U.S. Geological Survey (PHREEQC, PHRQPITZ, and WATEQ4F). When the GWB programs load these datasets, they use the same method as the original program (MINTEQ, and so on) to calculate activity coefficients.

The programs can compute fugacity coefficients for gases using the methods of Tsionopoulos, Peng and Robinson, and Spycher and Reed (see [Further Reading](#)). Datasets distributed with recent releases contain factors needed to calculate fugacity coefficients for certain gases by these methods, as functions of temperature and pressure. The programs assign ideal behavior to gases lacking the factors required by the method in use.

Starting with **GWB 2022**, the programs can account for binary solid solutions. The apps can determine activity coefficients for the end members accounting for site-mixing, a Guggenheim model, or various other nonideal methods, or can assume ideal behavior.



Any number of solid solutions can be defined within a thermo dataset, by the user at run time, or both.

The programs at startup look for a dataset named “thermo.tdat” by default, but you can specify an alternative on the **File → Preferences...** dialog. If you set the default file to “mythermo.tdat”, for example, the programs will read the file “mythermo.tdat” as the default thermo dataset.

The programs, at startup, look for the thermodynamic dataset in your working directory and, failing to find it there, in the public “gtdata” directory (commonly, “\Program Files\GWB\Gtdata”). You may set an alternative default directory on the **File → Preferences...** dialog.

To load a different thermodynamic database into an open program, go to the **File → Open → Thermo Data...** dialog, use the `data` command within the **Command** pane, or simply drag the database into the application window.

## 2.4 Redox couples

The thermodynamic dataset contains a number of redox coupling reactions that link species of differing oxidation states. There are redox couples between  $\text{Fe}^{++}$  and  $\text{Fe}^{+++}$ ,  $\text{HS}^-$  and  $\text{SO}_4^{--}$ ,  $\text{CH}_4(\text{aq})$  and  $\text{HCO}_3^-$ , and so on. You can enable or disable coupling reactions interactively. In this way, you control the extent to which the programs honor redox equilibrium in their calculations.

Each of the redox coupling reactions is identified by a redox species, which is a basis species in an alternative oxidation state (Table 2.2). In the examples in the previous paragraph,  $\text{Fe}^{+++}$ ,  $\text{HS}^-$ , and  $\text{CH}_4(\text{aq})$  are the redox species; the corresponding basis species are  $\text{Fe}^{++}$ ,  $\text{SO}_4^{--}$ , and  $\text{HCO}_3^-$ . The programs, by default, honor each redox couple and hence assume redox equilibrium. You can disable any number of the couples, however, by selecting **Config → Redox Couples...**, or invoking the `decouple` command.

Once a redox couple has been disabled, the redox species in question becomes an entry in the basis list and can be constrained independently of the other basis entries. In an equilibrium calculation, for example, you need only constrain the basis entry  $\text{Fe}^{++}$  and the oxidation state to consider ferrous and ferric iron species. By disabling the redox couple between  $\text{Fe}^{+++}$  and  $\text{Fe}^{++}$ , however, ferric and ferrous iron are treated separately. You would need to further constrain  $\text{Fe}^{+++}$  to include ferric iron species in the calculation.

Redox reactions in a thermo dataset are set out in a flexible fashion. Many datasets balance redox reactions in terms of the species  $\text{O}_2(\text{aq})$ , but they can alternatively be written in terms of other species, such as  $\text{O}_2(\text{g})$ ,  $\text{H}_2(\text{aq})$ ,  $\text{H}_2(\text{g})$ , or as half-cells in terms of  $\text{e}^-$ .

**Table 2.2**    Oxidation states of redox and basis species (basis species in bold) in “thermo.tdat”

-4	-3	-2	-1	0	+1	+2
	AsH <sub>3</sub> (aq)					
					Au <sup>+</sup>	
CH <sub>4</sub> (aq)				CH <sub>3</sub> COO <sup>-</sup>		
			Cl <sup>-</sup>			
						Co <sup>++</sup>
						Cr <sup>++</sup>
					Cu <sup>+</sup>	Cu <sup>++</sup>
						Eu <sup>++</sup>
						Fe <sup>++</sup>
				H <sub>2</sub> (aq)	H <sup>+</sup>	
					Hg <sub>2</sub> <sup>++</sup>	Hg <sup>++</sup>
						Mn <sup>++</sup>
	NH <sub>4</sub> <sup>+</sup>			N <sub>2</sub> (aq)		
						Ru <sup>++</sup>
		HS <sup>-</sup>				
		Se <sup>--</sup>				
						Sn <sup>++</sup>

+3	+4	+5	+6	+7	+8
<b>Am<sup>+++</sup></b>	Am <sup>++++</sup>	AmO <sub>2</sub> <sup>+</sup>	AmO <sub>2</sub> <sup>++</sup>		
<b>As(OH)<sub>4</sub><sup>-</sup></b>		AsO <sub>4</sub> <sup>---</sup>			
Au <sup>+++</sup>					
	HCO <sub>3</sub> <sup>-</sup>				
				ClO <sub>4</sub> <sup>-</sup>	
Co <sup>+++</sup>					
<b>Cr<sup>+++</sup></b>		CrO <sub>4</sub> <sup>---</sup>	CrO <sub>4</sub> <sup>--</sup>		
<b>Eu<sup>+++</sup></b>					
Fe <sup>+++</sup>					
			MnO <sub>4</sub> <sup>--</sup>	MnO <sub>4</sub> <sup>-</sup>	
NO <sub>2</sub> <sup>-</sup>		NO <sub>3</sub> <sup>-</sup>			
Np <sup>+++</sup>	<b>Np<sup>++++</sup></b>	NpO <sub>2</sub> <sup>+</sup>	NpO <sub>2</sub> <sup>++</sup>		
Pu <sup>+++</sup>	Pu <sup>++++</sup>	PuO <sub>2</sub> <sup>+</sup>	<b>PuO<sub>2</sub><sup>++</sup></b>		
<b>Ru<sup>+++</sup></b>	Ru(OH) <sub>2</sub> <sup>++</sup>		RuO <sub>4</sub> <sup>--</sup>	RuO <sub>4</sub> <sup>-</sup>	RuO <sub>4</sub>
			SO <sub>4</sub> <sup>--</sup>		
	SeO <sub>3</sub> <sup>--</sup>		SeO <sub>4</sub> <sup>--</sup>		
	<b>Sn<sup>++++</sup></b>				
Tc <sup>+++</sup>	TcO <sup>++</sup>	TcO <sub>4</sub> <sup>---</sup>	TcO <sub>4</sub> <sup>--</sup>	<b>TcO<sub>4</sub><sup>-</sup></b>	
U <sup>+++</sup>	<b>U<sup>++++</sup></b>	UO <sub>2</sub> <sup>+</sup>	UO <sub>2</sub> <sup>++</sup>		
<b>V<sup>+++</sup></b>	VO <sup>++</sup>	VO <sub>4</sub> <sup>---</sup>			

## 2.5 Solid solutions

The GWB programs can account for binary solid solutions—minerals that vary in composition between two end members—taking the solutions to be either ideal or nonideal. The apps can further allow solid solutions to vary continuously or cast them as a sequence of discrete compositional tranches; **Act2** and **Tact**, however, employ only the discrete method.

In an ideal solution, the simplest case, the activity of a solution's end member is equal to its mole fraction  $x$ . The activity of a pure mineral, then, is unity. In a nonideal solution, an end member's activity is the product of its mole fraction  $x$  and activity coefficient  $\gamma$ .

One of several activity coefficient models can be invoked. In a Guggenheim model, for example, a Redlich-Kister-type expansion with up to three dimensionless Guggenheim parameters  $a_0$ ,  $a_1$ , and  $a_2$  describes the excess free energy of mixing between end members 0 and 1:

$$\Delta G_E = x_0 x_1 R T [a_0 + a_1(x_1 - x_0) + a_2(x_1 - x_0)^2] \quad (2.1)$$

Activity coefficients consistent with this expression are determined according to

$$\ln \gamma_0 = x_1^2 [a_0 - a_1(3x_0 - x_1) + a_2(x_0 - x_1)(5x_0 - x_1)] \quad (2.2)$$

$$\ln \gamma_1 = x_0^2 [a_0 + a_1(3x_1 - x_0) + a_2(x_1 - x_0)(5x_1 - x_0)] \quad (2.3)$$

End member 0 appears first in the solution's definition, followed by end member 1. When one end member contains only minor amounts of the other, the major component should be listed first. Otherwise, the end members can be specified in arbitrary order.

The activity coefficient expressions are asymmetric with respect to end member order whenever  $a_1$  is nonzero. The order in which end members are defined affects the sign of the Guggenheim parameter  $a_1$  (but not  $a_0$  or  $a_2$ ). Reversing end member order, then, negates  $a_1$ . In collecting Guggenheim coefficients from the literature, keep in mind that the convention set out in the equations above is inverted by some authors, requiring the sign of their  $a_1$  values to be reversed for use with the GWB.

Expressed differently, the GWB apps expect a positive value for  $a_1$  to shift the excess free energy curve towards  $x_1$ , the second end member. If a solid solution is not fully miscible, a positive value for  $a_1$  will further shift the miscibility gap in this direction. In drawing data from the literature, furthermore, take care to respect the stoichiometries assigned to end member minerals, as well as the minerals' assumed stabilities.

Any number of solid solutions can be defined within the thermodynamic database in use (see **Solid solutions** under **Thermo Datasets** in the *GWB Reference Manual*), configured by the user at run time, or both. A solid solution may be specified as ideal or nonideal and may be set as a continuous or discrete series. You define a solid solution at

run time using the **Config → Solid Solutions...** dialog or the `solid_solution` command. You can further change the properties of a solution set out in the thermo dataset using the same dialog, or with the `alter` command.

To define a calcite-rhodochrosite solid solution, for example, go to **Config → Solid Solutions...**, click **add** under “Define new solid solutions”, and expand the **+** button. Supply a name such as “Cal-Rds” in the first box, choose end-member minerals “Calcite” and “Rhodochrosite” using the pulldown menus, and supply a tag such as “Cal” or “Rds” for each. To set a Guggenheim activity model, for example, change “type” from “ideal” to “guggenheim” and enter appropriate values for coefficients “a0” (“3” here), “a1” (“0.0”), and “a2” (“0.0”).

Click **Apply** to create the solution. The command

```
solid_solution Cal-Rds Calcite tag Cal contains \
Rhodochrosite tag Rds guggenheim a0= 3
```

serves the same purpose.

**Rxn**, **SpecE8**, **React**, **Phase2**, **X1t**, and **X2t** by default take solid solutions as continuous series. An end member is named following the syntax `<solid_solution>::<end member tag>`. Thus, the calcite end member of the calcite-rhodochrosite solution set out above is “Cal-Rds::Cal”. End members are swapped into the basis much like minerals, but in pairs (see [Setting and constraining the basis](#) under **Configuring the Programs**).

As solid solutions are read in, configured, and altered, the apps use the Guggenheim parameters to check each continuous solid solution for a miscibility gap. They first search for spinodal points, which, if found, indicate a partially immiscible solution. They proceed to solve for the binodal points—compositions spanning the miscibility gap—and append the resulting two binodes to the list of minerals carried in the calculation. A solid

solution's spinodals and binodals are reported in the **Config → Show...** dialog, or when you issue the `explain` command followed by the solution name.

In discrete mode, the programs treat a solid solution as a series of fixed-composition minerals, or tranches. The programs generate tranches spanning the prescribed range in the mole fraction (from 0 to 1, by default) and spaced apart by the step specified ( $1/20^{\text{th}}$  of the range, unless set otherwise). The tranches are named by combining end member tags and mole fractions, e.g., “Cal(.95)-Rds(.05)”, “Cal(.9)-Rds(.1)”, and so on. For solid solutions containing a trace of one end member, you might set a smaller range (e.g. from 0 to 0.01) to more precisely model uptake of the minor end member.

The apps calculate an equilibrium constant for each tranche from the end members' equilibrium constants, mole fractions, and activity coefficients, according to

$$\log K = x_0(\log K_0 + \log \gamma_0 + \log x_0) + x_1(\log K_1 + \log \gamma_1 + \log x_1) \quad (2.4)$$

The tranches generated in this way are appended to the list of minerals taken from the thermo dataset. Each tranche is then treated in the calculations as if it were a simple mineral. Tranches can be directly swapped into the basis, suppressed, and so on. A tranche's stability can be altered only indirectly, however, by adjusting the log *K*s for the end member minerals.

When a discrete solid solution has a miscibility gap, tranches within the gap become unstable relative to those outside it and so will not appear in the calculation results. Where the miscibility gap is large enough that each end member incorporates only a minor amount of the other, you may prefer to define solid solutions at opposite ends of the compositional range, thereby eliminating many superfluous tranches. For example, the aragonite-strontianite solid solution has a miscibility gap at 25°C from  $\sim .0048 < X_{\text{Str}} \sim .8579$  (see Parkhurst and Appelo, 2013 in [Further Reading](#)). The solution might be configured with the commands

```
solid_soln Sr-Aragonite Aragonite tag Arg contains \
  Strontianite tag Str from 0 to .0048 discrete \
  guggenheim a0= 3.43 a1= -1.82

solid_soln Ca-Strontianite Strontianite tag Str contains \
  Aragonite tag Arg from 0 to .1421 discrete \
  guggenheim a0= 3.43 a1= 1.82
```

Steps were set for neither solution, so default to  $1/20^{\text{th}}$  of the ranges specified.

Other properties of end members and tranches reflect those of the simple minerals in question. Mole volumes are taken from the corresponding minerals, weighted in the case of tranches by end member mole fractions. In models that account for surface complexation (see [Sorption onto mineral surfaces](#)), site densities and specific surface

areas of end members are assumed to be equal to those of their corresponding minerals; again, the properties of tranches are weighted by end member content.

In models that account for isotope fractionation (see [Isotope fractionation datasets](#)), you use the name of the corresponding simple mineral to segregate an end member or set its fractionation factor and isotopic composition. Fractionation factors for tranches are determined by averaging, as before. Alternatively, you can set out the polynomial expansion for an individual tranche in the isotope fractionation dataset.

The following sections describe alternative solid solution activity models supported in the GWB programs. For more information on solid solutions, see [Further Reading](#).

### 2.5.1 Site-mixing model

In a site-mixing model, an end member's activity equals its mole fraction  $x$  raised to the power of the site number  $b$ . Activity coefficients are calculated according to

$$\ln \gamma_0 = (b - 1) \ln x_0 \quad (2.5)$$

$$\ln \gamma_1 = (b - 1) \ln x_1 \quad (2.6)$$

The site number reflects the stoichiometry of the exchange site in the end members. End members annite  $[\text{KFe}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2]$  and phlogopite  $[\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2]$ , for example, might form a solid solution biotite  $[\text{K}(\text{Fe,Mg})_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2]$  in which  $b$  equals 3. When  $b$  equals 1, the model is equivalent to an ideal solution.

In the **Solid Solutions...** dialog, configure a site-mixing solution by choosing “site\_mixing” for “type” and specifying the site number  $b$ . Or use commands like

```
solid_solution Biotite Annite tag Ann contains \
  Phlogopite tag Phl site_mixing b= 3
```

which serve the same purpose.

### 2.5.2 Guggenheim model (expanded)

As described above, you can set a Guggenheim model by defining parameters  $a_0$ ,  $a_1$ , and  $a_2$  directly. This is the simplest and most common method for configuring solutions of this type. Alternatively, you can allow activity coefficients to vary with temperature by setting Guggenheim parameters  $A_0$ – $A_2$  in J/mol units, such that  $A_0 = a_0 RT_K$ , and so on, where  $R$  is the gas constant and  $T_K$  is the temperature in Kelvins. In this case, you prescribe the J/mol parameters as a series of second-order temperature expansions

$$A_0 = p_1 + p_2 T_K + p_3 T_K^2 \quad (2.7)$$

$$A_1 = p_4 + p_5 T_K + p_6 T_K^2 \quad (2.8)$$

$$A_2 = p_7 + p_8 T_K + p_9 T_K^2 \quad (2.9)$$

using a set of coefficients  $p_1$ – $p_9$ . (The option is not available when performing polythermal simulations with **X1t**, **X2t**, or **Phase2**.)

To configure a solution in this manner, use the **Solid Solutions...** dialog to select a Guggenheim solution as before, but instead of entering values for  $a_0$ ,  $a_1$ , and  $a_2$  directly, click on the **+** button next to  $a_0$ , then enter coefficients  $p_1$ – $p_9$ . Borrowing from the Sr-Aragonite example from the previous section, we set expansions for  $A_0$  and  $A_1$  consistent with dimensionless Guggenheim coefficients  $a_0$  and  $a_1$  of 3.43 and  $-1.82$ , respectively, at 25°C, and equivalent to values of 2.66 and  $-1.16$  at 76°C

Or use commands like

```
solid_solution Sr-Aragonite Aragonite tag Arg contains \
  Strontianite tag Str guggenheim \
  p1= 13068.0 p2= -15.311 p3= 0.0 p4= -11201.0 p5= 22.435
```

which serve the same purpose. As is the case for  $a_1$ , the sign of  $p_4$ – $p_6$  are sensitive to end member order and convention.

### 2.5.3 Regular solution model

In the regular solution model, a single interaction coefficient  $W$  (J/mol) is used to calculate activity coefficients

$$RT \ln \gamma_0 = W x_1^2 \quad (2.10)$$

$$RT \ln \gamma_1 = W x_0^2 \quad (2.11)$$



The model is equivalent to the expanded Guggenheim model, truncated after the first interaction coefficient, but the coefficient  $W$

$$W = p_1 + p_2 T_K + p_3 P \quad (2.12)$$

has terms accounting for first-order temperature and pressure dependence, where  $P$  is the pressure in bar.

The GWB modeling programs, however, do not allow non-zero values for  $p_3$ . In taking data from the literature, you should not simply omit such a term, if it exists. Instead, the product  $p_3 P$  can be folded into the value of  $p_1$  for isobaric calculations. When thermo.tdat is loaded, for example, at any temperature between 0 and 100°C the  $p_1$  coefficient can be set equal to  $p_1 + p_3 \times 1.0134$ . The **TEdit** program, nonetheless, allows a value to be set for  $p_3$ , since the app can serve to edit thermodynamic databases for the **EQ3/6** package (see [Exporting EQ3/6 datasets](#) in the **Using TEdit** chapter of this guide).

Within the **Solid Solutions...** dialog, configure a regular solution by choosing “regular” for “type” and specifying values for  $p_1$  and  $p_2$ . Or use commands like

```
solid_solution Cal-Rds Calcite tag Cal contains \
Rhodochrosite tag Rds regular p1= 7436.73 p2= 0.0
```

which serve the same purpose. The example here is equivalent to a dimensionless Guggenheim coefficient  $a_0$  of 3 at 25°C, as configured in the opening section of this chapter, but decreases inversely with temperature.

### 2.5.4 Cubic Maclaurin model

In the cubic Maclaurin model, activity coefficients are calculated from interaction parameters  $W_0$  and  $W_1$  (J/mol) according to

$$R T \ln \gamma_0 = (2W_1 - W_0)x_1^2 + 2(W_0 - W_1)x_1^3 \quad (2.13)$$

$$R T \ln \gamma_1 = (2W_0 - W_1)x_1^2 + 2(W_1 - W_0)x_1^3 \quad (2.14)$$

The interaction parameters are determined as first-order expansions in temperature (K) and pressure (bar) using coefficients  $p_1$ – $p_6$

$$W_0 = p_1 + p_2 T_K + p_3 P \quad (2.15)$$

$$W_1 = p_4 + p_5 T_K + p_6 P \quad (2.16)$$

As with the regular solution, the GWB modeling programs do not currently support nonzero values for the pressure terms.

Within the **Solid Solutions...** dialog, configure a cubic Maclaurin model by choosing “cubic” for “type” and specifying values for  $p_1$ – $p_2$  and  $p_4$ – $p_5$ . Or use commands like

```
solid_soln Sr-Aragonite Aragonite tag Arg contains \
  Strontianite tag Str cubic \
  p1= 1867.0 p2= 7.124 p3= 0.0 p4= 24269.0 p5= -37.746
```

which serve the same purpose. Note, the activity coefficient expressions depend on the order in which end members are ordered. Reversing order, then, requires  $W_0$  and  $W_1$ , and thus  $p_1$ – $p_3$  and  $p_4$ – $p_6$ , to be switched. This configuration is equivalent to the expanded Guggenheim Sr-Aragonite example above.

### 2.5.5 Third-order Maclaurin model

In the third-order Maclaurin model, activity coefficients are calculated from interaction parameters  $W_1$ ,  $W_2$ , and  $W_3$  (J/mol) according to

$$RT \ln \gamma_0 = [-(W_2/2)x_1^2 - (W_3/3)x_1^3] \quad (2.17)$$

$$RT \ln \gamma_1 = [-(W_2 + W_3/2)x_0^2 + (W_3/3)x_0^3 + (W_1 + W_2/2 + W_3/6)] \quad (2.18)$$

where  $W_1$  is actually recalculated according to

$$W_1 = -W_2/2 - W_3/6 \quad (2.19)$$

The GWB modeling programs, however, do not currently support nonzero  $p_3$  values. The model, then, is currently equivalent to a regular solution, where  $W = -p_2/2$ .

Within the **Solid Solutions...** dialog, configure a third-order Maclaurin model by choosing “third\_order” for “type” and specifying values for  $p_1$ – $p_2$ . Or use commands like

```
solid_solution Cal-Rds Calcite tag Cal contains \
  Rhodochrosite tag Rds third_order p1= 7436.73 p2= -14873.5
```

which serve the same purpose. The activity model here is equivalent to the regular solution example above.

## 2.6 Sorption onto mineral surfaces

**Rxn**, **SpecE8**, **React**, **Phase2**, **X1t**, and **X2t** can account for the sorption of aqueous species onto mineral surfaces by a number of methods, including the two-layer surface complexation model (including the constant capacitance and constant potential models),

the triple-layer and CD-MUSIC models, ion exchange, distribution coefficients ( $K_d$ ), Freundlich isotherms, and Langmuir isotherms.

In each case, you supply a dataset of surface reactions. You can load into the GWB modeling programs more than one surface dataset and can mix datasets representing different methods in a single program run. **TEdit** provides a graphic interface for creating and modifying surface datasets or you can use a text editor. The **Surface Datasets** chapter in the *GWB Reference Manual* gives details of the database format for each method.

### 2.6.1 Two-layer surface complexation model

**Rxn**, **SpecE8**, **React**, **Phase2**, **X1t**, and **X2t** can account for surface complexation reactions by which species in solution sorb onto mineral surfaces. The programs employ the modified two-layer (or double-layer) model, as presented by Dzombak and Morel (see [Further Reading](#)). By this model, surface complexes form by reaction of aqueous species with sites on a mineral surface.

Dataset “FeOH.sdat” contains reactions for hydrous ferric hydroxide (HFO), which sorbs strongly and plays a significant role in many oxidizing environments. Alternative datasets can be prepared in a parallel format for other sorbing minerals. The programs can consider several types of surfaces at a time. Each surface, furthermore, may occur on more than one mineral (e.g., a sorbing silica surface might be distributed across several zeolite minerals) and can contain a number of sorbing sites.

The “FeOH.sdat” dataset considers two types of sites, labeled  $>(s)\text{FeOH}$  and  $>(w)\text{FeOH}$ . These sites represent, respectively, strong and weak sorbing positions on the surface. The dataset specifies that the sites occur on the surfaces of three minerals—hematite,  $\text{Fe}(\text{OH})_3$  precipitate, and goethite—and sets specific surface areas and site densities for each.

The remainder of the dataset contains reactions describing the protonation, deprotonation, and complexation of surface sites. The reactions, each with a specified  $\log K$  at 25°C, yield surface species such as  $>(w)\text{FeOH}_2^+$ ,  $>(w)\text{FeO}^-$ , and  $>(w)\text{FeOCa}^{++}$ .

A second dataset supplied with the GWB, “FeOH+.sdat”, is identical to dataset “FeOH.sdat”, except it contains reactions from the Dzombak and Morel compilation for which  $\log K$  values have been only estimated. A third dataset, “FeOH\_minteq.sdat”, contains the surface complexation data from Visual Minteq release 2.20 for HFO.

Datasets “Goethite.sdat” and “Gibbsite.sdat” are like the HFO compilation but represent sorption on goethite and gibbsite, respectively. As with the HFO datasets, additional versions “Goethite+.sdat” and “Gibbsite+.sdat” are expanded with estimated constants and “Goethite\_minteq.sdat” and “Gibbsite\_minteq.sdat” are expanded versions formatted for use with the Visual Minteq thermo dataset.

When using multiple surface datasets in a calculation, you should take care to avoid redundancy. To use one of the HFO datasets with a goethite dataset, for example, you should comment out goethite’s sorbing sites in the former.

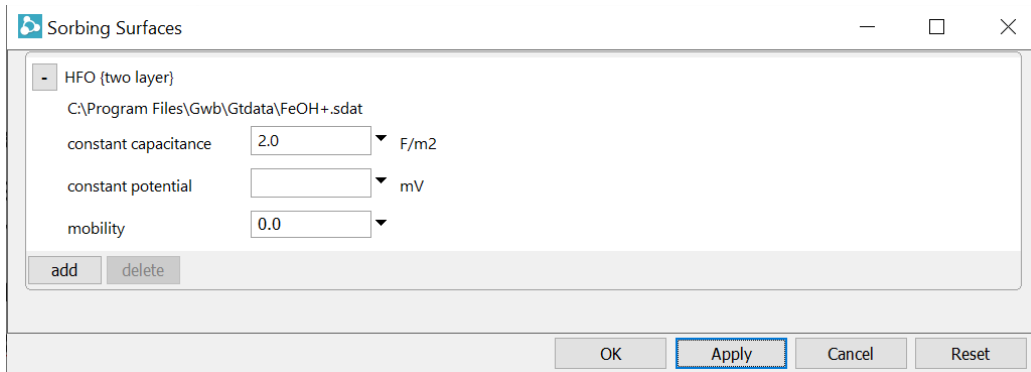
**2.6.1.1 Constant capacitance model**

The constant capacitance is a special case of the two-layer surface complexation model, described above. In the two-layer model, the program calculates surface potential ( $\psi$ , in volts) from the electrical charge density ( $\sigma$ , in C/m<sup>2</sup>) on the sorbing surface according to the well-known result of Gouy and Chapman. The capacitance  $C$  of the surface is the ratio

$$C = \sigma / \psi \quad (2.20)$$

where  $C$  has units of F/m<sup>2</sup>.

When treating systems of relatively high ionic strength or low surface charge, or both, the value of  $C$  may be taken as constant. This assumption simplifies the calculation since  $\psi$  can be calculated directly from  $\sigma$ . You set a constant capacitance model in **Rxn**, **SpecE8**, **React**, **Phase2**, **X1t**, or **X2t** by loading a surface complexation dataset in the **File → Open → Sorbing Surfaces...** (or **Config → Sorbing Surfaces...**) dialog, setting a value for capacitance in F/m<sup>2</sup>, then hitting **Apply**



or with the `surface_capacitance` command

```
surface_capacitance = 2
```

If you have loaded more than one dataset of surface reactions, you identify the surface in question with its “type”, as shown in the dataset header. For example, for dataset “FeOH.sdat”, you could enter

```
surface_capacitance HFO = 2
```

To revert to the default relationship between surface charge and potential, enter

```
surface_capacitance = ?
```

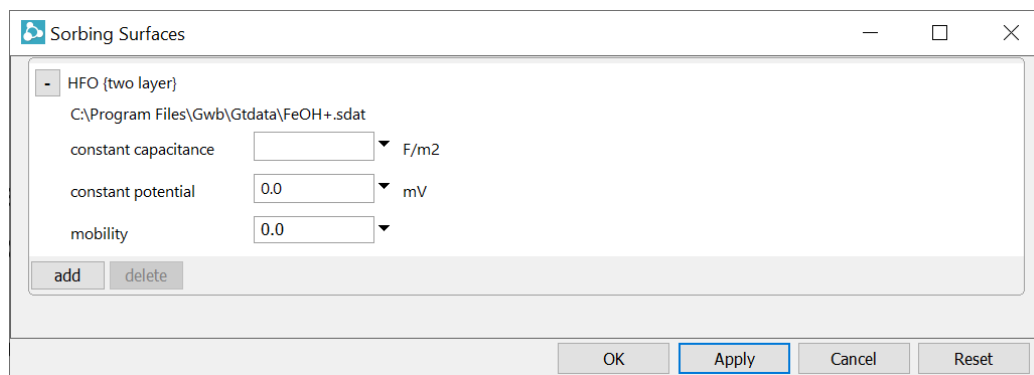
In this case, the program reverts to the standard two-layer model.

You may alternatively set a constant value for surface capacitance in the header of a surface complexation dataset. In this case, the value specified is carried unless the user modifies it with the `surface_capacitance` command.

### 2.6.1.2 Constant potential model

The constant potential model is a second special case of the two-layer surface complexation model. In the constant potential model, a single value of the surface potential is assigned, regardless of surface charge. Most commonly, the potential is set to 0, which is equivalent to ignoring electrostatic effects on ion sorption.

You set a constant potential model in **Rxn**, **SpecE8**, **React**, **Phase2**, **X1t**, or **X2t** in the **File → Open → Sorbing Surfaces...** (or **Config → Sorbing Surfaces...**) dialog



or using the `surface_potential` command

```
surface_potential = 0
surface_potential HFO = 0
surface_potential = ?
```

to set a value for electrical potential in mV. The command has the same format as the `surface_capacitance` command discussed above. You can also specify a constant value for potential in the header of a surface complexation dataset. Note that for a sorbing surface, you can set a constant capacitance or a constant potential model, but not both.

## 2.6.2 Triple-layer model

**SpecE8**, **React**, **Phase2**, **X1t**, and **X2t** can use the triple-layer method to model complexation of aqueous species with mineral surfaces, and **Rxn** can balance reactions involving triple-layer complexes. In the method, three planes – the 0,  $\beta$ , and  $d$  planes – make up a mineral’s complexing surface. The surface at the 0 plane can protonate by complexing with hydrogen ions from solution, or deprotonate by releasing them. Other ions in solution, including oxyions, hydroxyions, and so on, can form inner-sphere complexes on the 0 plane, as well as outer-sphere complexes at the  $\beta$  plane.

The  $d$  plane represents the inner bound of a diffuse layer of counter-ions, ions that are attracted to electrical charge on the 0 and  $\beta$  planes. Charge on the  $d$  plane, reflecting net electrical charge within the diffuse layer, counter-balances charge on the 0 and  $\beta$  planes. From a distance into the solution, then, the mineral surface appears electrically neutral. The region between the 0 and  $\beta$  planes has a specified capacitance  $C_1$ ; capacitance of the layer between the  $\beta$  and  $d$  planes is also known and denoted  $C_2$ .

Successfully solving a triple-layer complexation problem yields consistent values for (1) the concentrations of the various surface complexes considered in the calculation, (2) the charge densities  $\sigma_0$ ,  $\sigma_\beta$ , and  $\sigma_d$  on the three planes; and (3) the corresponding electrical potentials  $\psi_0$ ,  $\psi_\beta$ , and  $\psi_d$ .

To make use of the triple-layer method, you load a surface reaction or “.sdat” dataset identified in the header as containing data for the “three-layer” model type. A triple-layer dataset provides the charges  $z_0$  and  $z_\beta$  on the 0 and  $\beta$  planes, respectively, for each surface complex. In keeping with GWB convention, reactions in a surface dataset represent dissociation of the surface complex. A reaction’s log  $K$  value, then, is the negative of log  $K$  for the corresponding association reaction, as might be presented in the literature.

Three examples of triple-layer datasets are installed with the software. The datasets “Goethite\_Se.sdat”, “Goethite\_NaCl.sdat”, and “Goethite\_NaClO4.sdat” represent, respectively, the surface complexation of selenite, sodium chloride, and sodium perchlorate.

## 2.6.3 CD-MUSIC model


The programs can also use the CD-MUSIC method to model complexation on mineral surfaces. Like the triple-layer model, CD-MUSIC distributes mass across three layers. Unlike the simpler model, however, an ion’s charge in the CD-MUSIC model can be distributed among the 0,  $\beta$ , and  $d$  planes, so that charge at each plane in a surface complex may be fractional.

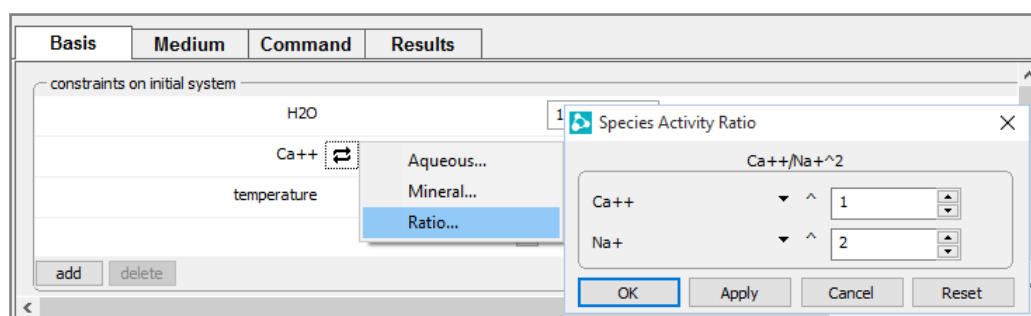
You invoke the CD-MUSIC method by loading a “.sdat” dataset identified in the header as the “cd-music” model type. As with the triple-layer model,  $C_1$  is the capacitance of the region between the 0 and  $\beta$  planes,  $C_2$  denotes capacitance between  $\beta$  and  $d$ , and each reaction in the dataset has an associated log  $K$ . The CD-MUSIC model, however, sets out for each reaction changes in electrical charge —  $\Delta z_0$ ,  $\Delta z_1$ , and  $\Delta z_2$  — at each of the planes

0,  $\beta$ , and  $d$ , respectively. Recall that since GWB datasets describe dissociation, a reaction's  $\log K$  as well as its  $\Delta z$  values are negated relative to the corresponding association reaction.

The GWB distribution contains two example CD-MUSIC datasets, “Goethite\_Cu.sdat” and “Goethite\_P.sdat”, as well as two larger datasets “Ferrihydrite\_cdmusic.sdat” and “Goethite\_cdmusic.sdat” derived from a compilation for the PhreeqC software (see [Further Reading](#)).

### 2.6.4 Ion exchange

The GWB programs can model ion exchange reactions on mineral surfaces in two ways. The first and simplest, although less general, method is to swap an activity ratio into the basis and prescribe its value. For example, from the **Basis** pane select the swap button  next to an exchanging ion like Ca++ and select **Ratio...** Set “Ca++” for the numerator and “Na+” squared in the denominator with an exponent of “2”.



Then type the desired value for the ratio into the entry box. Or, if for a ratio of 0.2,

```
swap Ca++/Na+^2 for Ca++
ratio Ca++/Na+^2 = 0.2
```

This method works in each of the GWB modeling programs (**Rxn**, **Act2**, **Tact**, **SpecE8**, **React**, **Phase2**, **X1t**, and **X2t**).

Using this simple method is equivalent to assuming that the reservoir of exchanging ions on the exchanging surface is sufficiently large that its composition can be taken as invariant. A second, more general method for modeling ion exchange is available in **Rxn**, **SpecE8**, **React**, **Phase2**, **X1t**, and **X2t**. This method accounts for the number of sites on the exchanging surface.

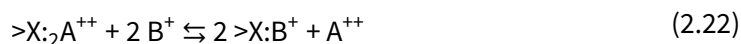
To invoke the second method, you prepare a small dataset of exchange reactions, using file “IonEx.sdat” as a template. (This file is distributed with the GWB and installed with the thermo datasets, generally in directory “\Program Files\GWB\Gtdata”.) The program **TEdit** provides a convenient way to create the new dataset (see the chapter

Using TEdit in this guide). You can prepare the dataset to honor the Gaines-Thomas, Vanselow, or Gapon convention.

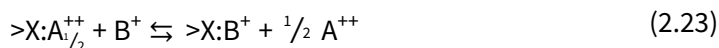
Each exchange reaction is of the form



where  $A^+$  and  $B^+$  are ionic species and  $>X:$  represents the exchanging site. For the Gaines-Thomas and Vanselow conventions, the exchange reaction involving a divalent ion takes the form



where  $A^{++}$  is the doubly charged ion. Such a reaction under the Gapon convention takes the form



A selectivity coefficient serves as the equilibrium constant for the mass action equation corresponding to each exchange reaction.

It is important to note that the GWB carries mass action equations for ion exchange reactions written in terms of the activities rather than the molalities of the aqueous species. In taking selectivity coefficients from the literature, therefore, you should be careful to check units and convert from total molality to free activity, as necessary.

### 2.6.5 Distribution coefficients ( $K_d$ )

You can account for ion sorption in **Rxn**, **SpecE8**, **React**, **Phase2**, **X1t**, and **X2t** according to the distribution coefficient ( $K_d$ ) approach. This approach does not carry a mass balance on the sorbing sites, so it is straightforward to implement and hence rather popular. The method's accuracy, however, can be poor, so the technique should be applied with caution.

According to the distribution coefficient approach, sorption reactions are written



where  $>M^{++}$  and  $M^{++}$  represent an ion in sorbed and free form. In the GWB, the distribution coefficient  $K_d$  represents the ratio of the sorbed mass, in moles per gram of solid phase, to the activity  $a_{M^{++}}$  of the free ion.



Note that in taking  $K_d$  values from the literature, you may need to convert the ion's total molality to free activity. It is also important to remember that, unlike other sorption models, the distribution coefficient approach carries the sorbed concentration in moles per mass solid, rather than liquid phase.

To set up a calculation, read one or more datasets containing distribution coefficients for sorption reactions using **File → Open → Sorbing Surfaces...** (or **Config → Sorbing Surfaces...**) or the `surface_data` command. Prepare the datasets using the file “Kd.sdat” as a template.

### 2.6.6 Freundlich isotherms

Freundlich isotherms are similar to the  $K_d$  approach, differing in that the sorbed mass  $SM_{>M^{++}}$  of an ion, in moles per gram of solid phase, is given from the ion's free activity, the Freundlich coefficient  $K_f$ , and an exponent  $n_f$  according to

$$SM_{>M^{++}} = K_f a_{M^{++}}^{n_f} \quad (2.25)$$

where  $0 < n_f < 1$ . For an exponent  $n_f$  of one, the method reduces to the  $K_d$  approach. To invoke Freundlich isotherms, prepare a dataset of surface reactions using the file “Freundlich.sdat” as a template.

### 2.6.7 Langmuir isotherms

In **Rxn**, **SpecE8**, **React**, **Phase2**, **X1t**, and **X2t**, you can also describe ion sorption in terms of Langmuir isotherms. In this method, ions are taken to sorb according to a reaction



where  $>L:A^+$  is the surface complex,  $>L:$  is a sorbing site, and  $A^+$  is the sorbing ion.

Each sorbing reaction has a corresponding equilibrium constant, commonly labeled  $K_{ads}$ . As with other reactions in the GWB, the equilibrium constants refer to mass action equations for dissociation reactions written in terms of species' free activity, rather than total molality. You may, therefore, need to correct data for this unit change when extracting data from the literature.

The Langmuir method is in many ways similar to the two-layer surface complexation model. It does not, however, consider electrostatic forces. You set the number of sorbing sites explicitly, instead of having the software calculate this number from the mass of a sorbing mineral.

To invoke a Langmuir model, prepare a reaction dataset containing the sorbing reactions and their equilibrium constants using the format of the file “Langmuir.sdat” as a template.

### 2.6.8 Polydentate sorption

The programs **Rxn**, **SpecE8**, **React**, **Phase2**, **X1t**, and **X2t** can account for polydentate sorption, in which an aqueous species complexes with more than one surface site, following various protocols. A polydentate reaction may be set in a Langmuir, double layer, triple layer, or CD-MUSIC dataset, but the surface sites in the reaction must be of the same type: a species cannot form a complex with dissimilar sites.

Given a polydentate sorption reaction in which a surface complex  $>S_nB$  is composed of a species B complexed with to  $n$  sites  $>S$



a mass action equation can be written according to any of the protocols shown in [Table 2.3](#). In the mass action expressions,  $[>S_nB]$  and  $[>S]$  are the molal concentrations of complexed and un-complexed sites, respectively, and the notation  $[>S]_{tot}$  represents the total site concentration, the sum of the concentrations of all sites, whether complexed or uncomplexed.

<b>Table 2.3 Polydentate sorption</b>	
<i>Protocol</i>	<i>Mass action equation</i>
stoichiometric	$K = \frac{[>S]^n [B]}{[>S_nB]}$
davis-leckie	$K = \frac{[>S][B]}{[>S_nB]}$
hiemstra-vanriemsdijk	$K = \frac{([>S] / [>S]_{tot})^n [B]}{[>S_nB] / [>S]_{tot}}$
appelo-postma	$K = \frac{([>S] / [>S]_{tot})^n [B]}{n[>S_nB] / [>S]_{tot}}$

The protocol is specified in the header section of a surface dataset, by appending the tag in the first column of [Table 2.3](#) to the “Model type:” line. For example,

```
Model type: two-layer hiemstra-vanriemsdijk
or
Model type: cd-music appelo-postma
```

The default protocol is `hiemstra-vanriemsdijk`. Since many datasets either do not contain polydentate reactions or invoke the default formalism, the final argument on this line is many times omitted when constructing a surface dataset.

## 2.7 Isotope fractionation datasets

**SpecE8**, **React**, **Phase2**, **X1t**, and **X2t** can compute the equilibrium fractionation of the stable isotopes of any element for which one mass is dominant. The programs in a single run are able to consider fractionation of any number of the isotopes, from any combination of elements. They can, as examples, compute the distribution of both  $^{13}\text{C}$  and  $^{18}\text{O}$ ,  $^{17}\text{O}$  as well as  $^{18}\text{O}$ , or all three isotopes together.

The GWB is distributed with a default database “`isotope.dat`” that contains coefficients for determining fractionation factors for the isotopes  $^2\text{H}$ ,  $^{13}\text{C}$ ,  $^{18}\text{O}$ , and  $^{34}\text{S}$ . Specifically, the dataset contains polynomial expansions as functions of temperature of the fractionation factors for aqueous species, minerals, and gases.

The factors describe fractionation of chemical species relative to a reference species for each isotope. The reference species are the solvent  $\text{H}_2\text{O}$  for  $^{18}\text{O}$  and  $^2\text{H}$ , dissolved  $\text{CO}_2$  for  $^{13}\text{C}$ , and aqueous  $\text{H}_2\text{S}$  for  $^{34}\text{S}$ . Note the dataset is incomplete, and that the program will assume a fractionation factor of 0 (zero) for any species not listed.

Since an isotope fractionation file is an ascii (character) file, you can alter it using a text editor such as Notepad. You may add fractionation data for additional aqueous species, minerals, and gases, as well as for surface complexes, using the same data format as for other species. Following the format in “`isotope.dat`”, further, you can add fractionation data for the isotopes of elements not listed, such as  $^{57}\text{Fe}$  and  $^{58}\text{Fe}$ .

You may also expand the dataset to include additional isotopes of the elements already present, such as  $^{17}\text{O}$ . In any event, an isotope in the dataset needs to be a minor isotope, one that comprises a small fraction of the mass of the element in question, that fractionates relative to a dominant isotope that makes up most of the element's mass.

To load an isotope database besides “`isotope.dat`” into the program, go to the **File** → **Open** → **Isotope Data...** dialog. You can equivalently use the `isotope_data` command on the **Command** pane, or simply drag the database into the application window. To specify a new default for the isotope dataset, go to the **File** → **Preferences...** dialog.

## 2.8 Electrical conductivity

Programs **SpecE8**, **React**, **Phase2**, **X1t**, and **X2t** calculate electrical conductivity using one of two approaches: the USGS method, the default, and the older APHA method. The USGS approach, proposed by McCleskey, Nordstrom, Ryan, and Ball (see [Further Reading](#)), can be applied to solutions with ionic strengths up to 1 mol/kg, and at temperatures in the range 5°C –95°C. You invoke the USGS method by loading file “`conductivity_USGS.dat`” from the **File** → **Open** → **Conductivity Data...** dialog, or by dragging the dataset into the

app's window. The dataset contains the coefficients of quadratic equations giving the ionic molal conductivities for various ions, as functions of ionic strength and temperature.

The APHA procedure is outlined in *Standard Methods for the Examination of Water and Wastewater*, Section “2510A” (see [Further Reading](#)), and the equivalent conductances for different ions and their derivatives with respect to temperature are included in the file “conductivity\_APHA.dat”. This approach is valid for temperatures between 20°C –30°C and ionic strengths up to 0.5 mol/kg.

Significantly, the GWB programs correctly do not assume complete ionization; they use free species concentrations rather than total concentrations in performing the calculations.

## 2.9 Environment variables

You can specify various default settings for the GWB programs by defining environment variables. In a command line environment, you might, for example, issue the command

```
set GWB_THERMODATA=my_thermo.tdat
```

which would define “my\_thermo.tdat” as the default thermodynamic dataset that loads whenever a GWB app starts. You set environmental variables globally from the Windows **Control Panel**, under **System → Advanced system settings**.

You can set the following environment variables:

GWB_GTDATA	The directory where the apps will look for thermo datasets, if not found in the working directory.
GWB_THERMODATA	The default thermodynamic dataset.
GWB_CONDUCTIVITYDATA	The dataset of coefficients for calculating electrical conductivity.
GWB_ISOTOPEDATA	The dataset of isotope fractionation factors.
GWB_SURFACEDATA	Dataset(s) of surface sorption reactions.

# Using GSS

---

**GSS**—The Geochemist's Spreadsheet—is a program developed to hold, manipulate, and graph the results of water chemistry analyses. **GSS** is a full-featured spreadsheet designed to work with the other software tools in the **GWB**.

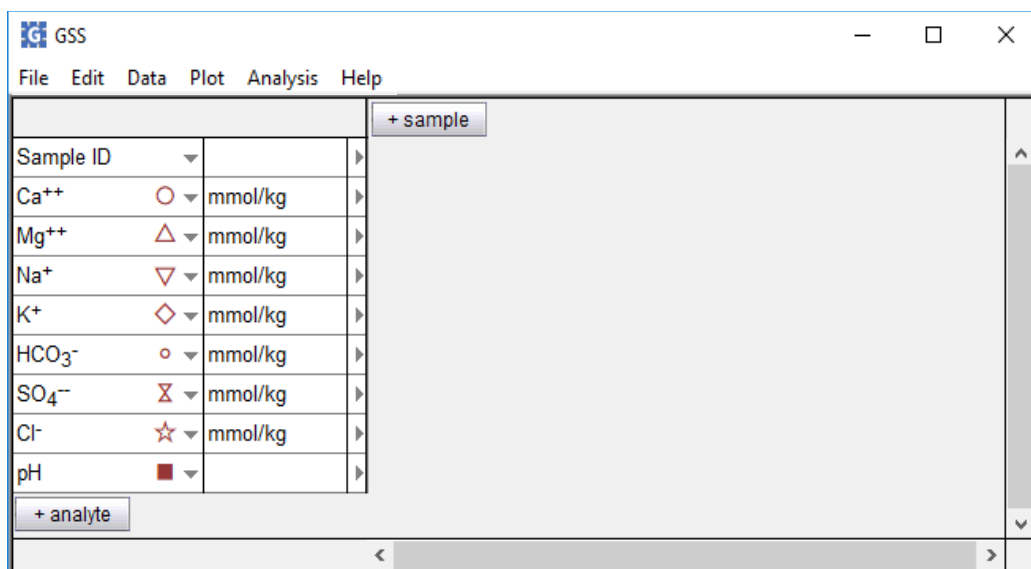
Enter or paste the analyses for all your samples, for each analyte measured, into a **GSS** data sheet. You can copy your data as a block and paste them in one step, thus creating a data sheet need take only a moment. Once ready, it can do a number of things that would be difficult with an ordinary spreadsheet. It can, for example,

- Convert units with a click of the mouse
- Use **Gtplot** to make cross plots and series or time series graphs
- Create your favorite plots: triangular, Piper, Durov, Schoeller, Stiff, and so on
- Overlay data on a redox-pH or activity diagram created with **Act2** or **Tact**, or on a variety of diagrams created in **Gtplot**, **P2plot**, or **Xtplot**
- Compare replicate analyses and check standards
- Check results against regulatory limits or remedial objectives
- Calculate speciation, mineral saturation, gas fugacity, and so on
- Evaluate equations you specify
- Mix samples in any proportion
- Launch **SpecE8** or **React** for any sample

The next section describes how to set up the data sheet, and later sections explain how to perform calculations and graph results. **GSS** is designed to be up and running quickly, so there's no reason to hesitate.

## 3.1 Your first data sheet

To create a data sheet, start **GSS** or select **File → New** if it is already running. You will see an empty data sheet containing some common analytes.

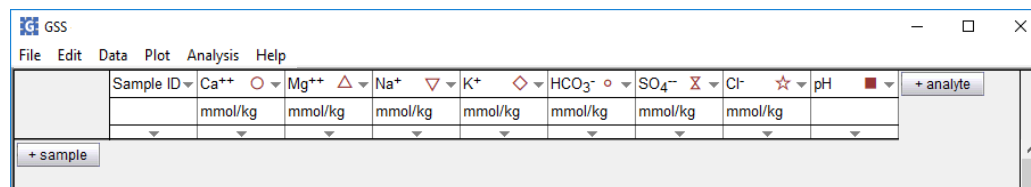


Begin by adding to the data sheet the analytes you need, and deleting those you don't.

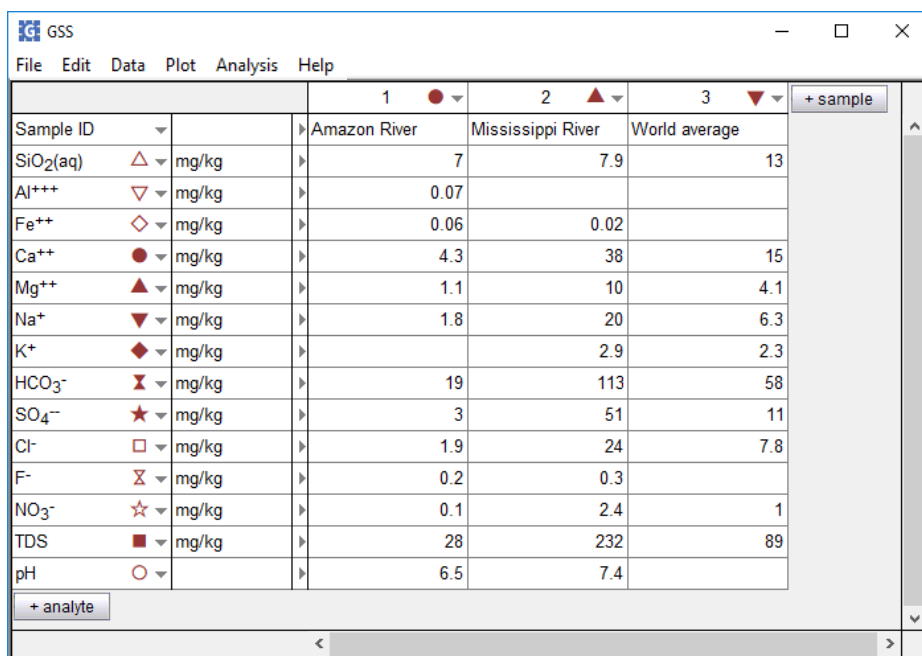
Add analytes by clicking on **+ analyte** and choosing from various **Chemical parameters**, **Physical parameters**, or any of the **Basis species** in the thermodynamic dataset. If you don't see what you need, choose **User analytes** and create your own. If you'd like to evaluate an equation using analytes in your spreadsheet, choose **User equations** and specify its form. You can add any number of the previously mentioned analytes in one step by selecting **Multiple Analytes....** To delete an analyte, select it and press the Delete key.

If the unit for an analyte doesn't match your data, right-click on it. To change units for more than one analyte, select a group of analytes by holding down the shift or control key, then right-clicking on the group. Using the "As" pulldown, you can set units as elemental equivalents: "mg/kg SO<sub>4</sub>-- as S" or "mg/l As(OH)<sub>4</sub>- as As". Similarly, you can set units as species equivalents, in terms of protonated or deprotonated forms of the basis or redox species: "mg/kg HPO<sub>4</sub>-- as PO<sub>4</sub>---", "mg/l NH<sub>4</sub><sup>+</sup> as NH<sub>3</sub>", and so on.

Now arrange the analytes to match your data. Simply drag an analyte, or a group of analytes, to the desired point in the list. To arrange the datasheet with the analytes in columns rather than rows, click **Edit → Transpose Data Sheet**. The data sheet might look like the following example.



You are ready to add your data. Click on **+ sample** in your data sheet to create a column (or row) of empty data cells. You can enter values into the cells individually, but it's easier to copy from a source such as an Excel spreadsheet. Copy a block of values for all of your analytes and samples, then paste it into GSS with **Edit → Paste**. A completed data sheet is shown below.



Sample ID	1	2	3	+ sample
Amazon River	Mississippi River	World average		
SiO <sub>2</sub> (aq)	7	7.9	13	
Al <sup>+++</sup>	0.07			
Fe <sup>++</sup>	0.06	0.02		
Ca <sup>++</sup>	4.3	38	15	
Mg <sup>++</sup>	1.1	10	4.1	
Na <sup>+</sup>	1.8	20	6.3	
K <sup>+</sup>		2.9	2.3	
HCO <sub>3</sub> <sup>-</sup>	19	113	58	
SO <sub>4</sub> <sup>-</sup>	3	51	11	
Cl <sup>-</sup>	1.9	24	7.8	
F <sup>-</sup>	0.2	0.3		
NO <sub>3</sub> <sup>-</sup>	0.1	2.4	1	
TDS	28	232	89	
pH	6.5	7.4		

## 3.2 Working with a data sheet

Once you have set up a data sheet containing your data, you can work with it in various ways. Example datasets are installed with the software, under “\Program Files\GWB\Script”. You can open one of these in GSS (**File → Open → GSS Spreadsheet...**) to experiment with the program.

### 3.2.1 Changing the view

You can change how the data is displayed on the current data sheet with the **Edit → Appearance...** dialog, and the default appearance for data sheets under **File → Preferences....** This allows you to set the font, point size, and number of significant digits shown in the data cells.

Zoom in and out with **Edit → Zoom → Zoom In (Ctrl++)** and **Zoom Out (Ctrl+-)**; **Zoom 100% (Ctrl+Shift+Z)** returns to the font size set in **File → Preferences....**

To change the width of the data cells, drag the dividing line between columns left or right. Dragging changes the width of all the data cells in the column at once.

If you have too much data to view, you can temporarily hide analytes or samples. Select the rows or columns you wish to hide, then under **Data → Hide and Show** choose **Hide Analytes** or **Hide Samples**; restore the display with **Show All Analytes** or **Show All Samples**.

### 3.2.2 Data cells

Each cell in a data sheet contains a numerical value, such as the concentration of a species, a character string, or a date or time. If you have no data for a cell, set a character string such as “n/d”, or just leave the cell empty.

Where an analysis falls below the detection limit, enter a value such as “<0.01”. **GSS** carries this value as it changes units, and will display it with a special “less than” symbol on plots.

You can enter dates in various formats: “Sep 21, 2016”, “9/21/16”, “September 21”, and so on. **GSS** displays the field in the local format set for your computer. Enter time as a value such as “2:20 PM”, “14:20”, or “2:20:30 PM”.

### 3.2.3 Changing units

To change units on the data sheet, select one or more analytes and right-click on the unit field, or choose **Data → Units**. Either way, from the **As** option you can set concentrations in elemental equivalents, such as “mg/kg SO<sub>4</sub><sup>--</sup> as S”, or in species equivalents, in terms of protonated or deprotonated forms of the basis or redox species, such as “mg/kg HS<sup>-</sup> as H<sub>2</sub>S”. When you change units, you can choose to convert the values in the corresponding data cells to the new unit or leave the numbers unchanged.

Some unit conversions require knowledge of the fluid’s dissolved solids content (the TDS) or density, or both. If you enter values for these analytes, **GSS** uses the entries directly. Otherwise, the program estimates values for each sample from the information provided. It is best in that case to enter the complete analysis for a sample before converting units, so **GSS** can estimate density and TDS as accurately as possible.

The program calculates TDS for each sample by adding the masses of the solutes, and figures density as that of an NaCl solution of the same TDS at the specified temperature, or 25°C if none is set. Converting from concentration units (mg/kg, mmolar, ...) to absolute mass (grams, mmoles, ...) requires an entry for solution mass. If a solution mass is not entered, the program calculates it from the concentrations given for the various solutes, assuming a solvent mass of 1 kg.

### 3.2.4 Error bars

Set an error bar for the entry in a data cell as a triplet of values separated by vertical bars. An entry 0.5|2.0|3.5, for example, appears in **GSS** plots as a data point at 2.0 overlying an error bar extending from 0.5 to 3.5. Entry 0.5|3.5 appears as an error bar alone with no specified data point.



### 3.2.5 Calculating analytes

You can add a number of calculated values to your data sheet, including

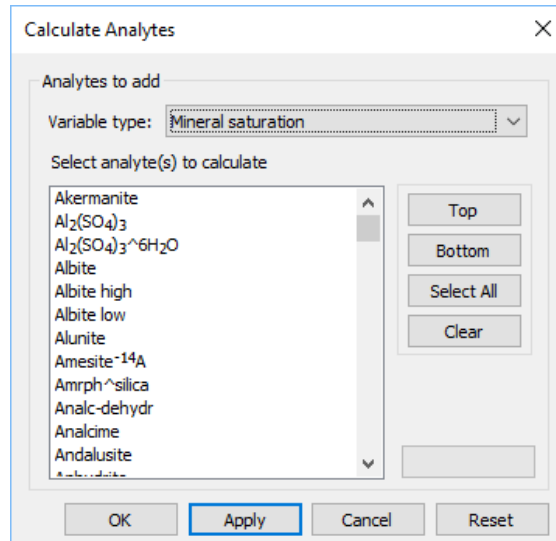
- Chemical parameters, such as TDS, electrical conductivity, and hardness
- Physical parameters, such as fluid density and viscosity
- Components in fluid
- Free concentration, activity, and activity coefficients of aqueous species
- Saturation indices of minerals, such as calcite, and solid solutions
- Fugacity and partial pressure of gases, such as CO<sub>2</sub>

**GSS** doesn't do the calculation itself; instead, it sends data from the data sheet to **SpecE8**, which does the calculations and returns the results to **GSS**. The **SpecE8** program is described in the [Using SpecE8](#) chapter.

Keep in mind that the order of the analytes in the data sheet is important. In its calculations, **SpecE8** will use the first constraint it finds for a particular basis component. For example, if both Eh and O2(aq) are present, **SpecE8** will use whichever is first in the data sheet. You can easily change the order of the analytes by dragging, or hide analytes you don't want used in the calculations.

If the data sheet has hidden analytes, "less than" (<0.001) values, or 0 values, you may choose to omit them when generating input for **SpecE8** in the **Analysis → Options...** dialog. You can also add additional commands to the **SpecE8** input there or in the **Analysis → Launch...** dialog. Header command lines will be inserted near the beginning, just after the thermo data is read. Trailer command lines will be added to the end of the input.

To add calculated analytes to your data sheet, click on **+ analyte** → **Calculate with SpecE8...** or **Analysis → Calculate with SpecE8...** The Calculate Analytes dialog box is shown below.

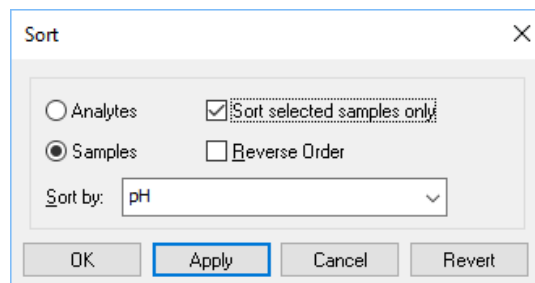


Choose a variable type, then select one or more analytes and click **OK** or **Apply**. The calculated data will appear as a new row (or column) of cells in your data sheet.

Your calculated analytes will not update automatically if the data in your spreadsheet changes. Trigger **SpecE8** to repeat a calculation by right-clicking on an analyte's name and selecting **Recalculate Analyte**.

### 3.2.6 Sorting

You can sort the analytes or samples in the data sheet numerically, or alphabetically for text entries, with the **Data → Sort...** dialog shown below.



You might sort analytes so the components with the highest concentrations appear at the top of the sheet, and the lowest at the bottom. Or you could sort samples so they are ordered with the most acidic pH values to the left and most alkaline to the right.

Classes of analytes are grouped together in the sorted results. Basis species, then, are grouped, not interspersed with chemical parameters or other analytes. Sort a subset of the data, instead of the entire data sheet, by selecting the data and checking the “Sort selected analytes/samples only” box. You can sequentially undo your sorts with the **Revert** button.

### 3.2.7 Notes

You can save relevant information—the site’s location, who conducted the sampling, what laboratory analyzed the samples, and so on—along with your data sheet. To do so, select **Data → Notes....** Information you type into the text box is saved with your **GSS** document.

### 3.2.8 Comments

You can embed comments within individual data cells. Right-click on a cell and select “Add Comment”, then type into the yellow box that opens. Click outside the box to embed the comment. View a comment by moving your mouse over the right side of a yellow-shaded cell or by right-clicking on the cell and selecting “Comment”. With the comment box open, you can edit or delete the comment. Delete all comments by going to **Data → Delete all Comments**.

### 3.2.9 Undo and redo

You can reverse one or more recently performed actions in **GSS** by choosing **Edit → Undo (Ctrl+Z)**. You set the number of levels of undo allowed in the **File → Preferences...** dialog. To cancel the effects of an undo, select **Edit → Redo (Ctrl+Y)**.

### 3.2.10 Saving and exporting data

Choosing **File → Save** saves your data sheet as a “.gss” file. Files of this type are in a special format that contains not only the entries in the data cells, but the settings for the program options, the display, the name of the thermo dataset, and so on.

You can export the entries in a **GSS** data sheet to other programs in several ways. The easiest way is to use **GWB**’s drag and drop feature (see [Drag and drop](#)). In **GSS**, select a Sample ID with the right mouse button, drag to the other program, and release. Alternatively, you can select the data cells of interest, copy them to the clipboard (**Edit → Copy**), and paste them in an application such as MS Excel, Notepad, or MS Word.

You can also save the data sheet as a tab-delimited or comma-delimited file (“.txt” or “.csv”) that other applications can read. Select **File → Save As...** and choose the file type and file name. You can specify on this dialog the data orientation and whether to export hidden analytes or samples.


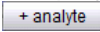
### 3.2.11 Resuming your session

You can continue working on the data sheet from the last time you had **GSS** open by choosing **File → Resume → Resume**. To have **GSS** do this automatically each time you open the program, set **File → Resume → Resume On Startup**.

## 3.3 Analytes

Analytes are the measurements or sample properties that **GSS** can store, use, and display. Analytes in **GSS** fall into six categories:

- Chemical parameters
- Physical parameters
- Basis species
- User analytes
- User equations
- Calculated values

Add analytes individually by clicking on  and choosing an option from the first five categories, or add multiple analytes in one step by selecting **Multiple Analytes....** For values requiring a speciation calculation, click  → **Calculate with SpecE8....**

### 3.3.1 Chemical parameters

A number of commonly used analytes are predefined within **GSS**. The chemical parameters include temperature, pH, Eh, TDS, and so on.

### 3.3.2 Physical parameters

The physical parameters include fluid density, length, width, X position, and Y position.


### 3.3.3 Basis species

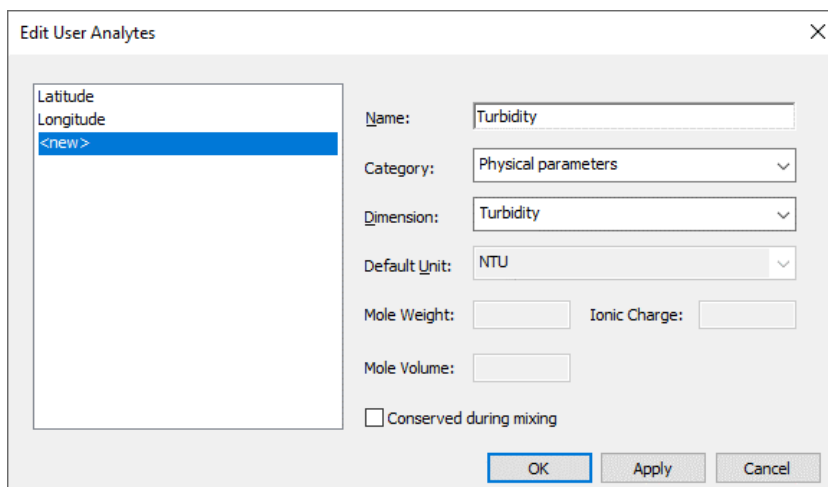
Each of the primary basis species and redox species in the thermodynamic dataset loaded with your session is available as an analyte. The primary basis species might include components such as  $\text{Na}^+$ ,  $\text{Ca}^{++}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{--}$ , and  $\text{Fe}^{++}$ , whereas  $\text{Fe}^{+++}$ ,  $\text{HS}^-$ , and so on might appear in the thermo dataset as redox species.

A number of thermo datasets are installed with the **GWB** software, and others are available on the **GWB.com** website. When you create a new data sheet, **GSS** opens the thermo dataset listed in **File → Preferences....**, looking for it in the directory shown. You can edit the entries in the thermo dataset or create your own dataset, as described in the **Thermo Datasets** chapter of the ***GWB Reference Manual***.

To change datasets, use **File → Open → Thermo Data....**, or **File → Recent Files**. **File → File Properties → Thermo Data...** shows information about the thermo dataset currently in use.


### 3.3.4 User analytes


If you can't find the analyte you need, you can quickly define your own. You might, for example, set latitude or longitude as a text field, specify a numerical value for turbidity, and so on. To create an analyte, click  → **User analytes** → **Edit...** to launch the **Edit User Analytes** dialog



Enter a name, choose the category in which the analyte will plot, then select its dimension and default unit (see the **Units Recognized** chapter in the *GWB Reference Manual* for a list of dimensions and units). Click **Apply** to finish. The analyte will be added to the spreadsheet, where you can assign a value for each sample.

The left side of the dialog lists user analytes in the order they appear in the spreadsheet. You can click on an analyte in the list to see its properties, or click <new> to add more. By right-clicking, you can create, copy, or delete analytes.

**GSS** keeps a list of your user analytes—those you define and any encountered in data sheets you open—in your computer's registry, so they are available from one run to the next. These are accessible from  → **User analytes** → **Recent**. From the **Recent** submenu, select an analyte to add it to the sheet, or **Clear All** to clear the list.

To bring in an analyte from another .gss file, if not in your registry, use  → **User analytes** → **Import....**

### 3.3.5 User equations

User equations are similar to user analytes, except you specify a simple equation for **GSS** to evaluate, rather than specifying values individually. You might use **GSS** to calculate ion ratios, simple geothermometers, water quality metrics, and so on.

To create an equation, click + analyte → **User equations** → **Edit...**

In addition to the information required of user analytes, supply the equation to be evaluated, which can consist of four basic types of input:

- Analytes in the spreadsheet, such as the  $\text{Ca}^{++}$  concentration in meq/l
- Constants of geochemical interest, such as the molar gas constant
- Functions, such as SQRT(), EXP(), LN(), or LOG()
- Mathematical operators, such as +, -, \*, /, ^

Analytes in an equation can be any of the supplied chemical or physical parameters or basis species, as well as user analytes, other user equations, or calculated values. Analyte names and their units to use in the calculation, which can differ from their current units in the spreadsheet, should be enclosed within  $\{ \}$ , as in the examples below:

```

 $\{ \text{Ca}^{++}, \text{ meq/l} \}$ 
 $\{ \text{HCO}_3^-, \text{ mg/kg as C} \}$ 
 $\{ \text{SiO}_2(\text{aq}), \text{ log mg/kg} \}$ 

```

Examples of constants include:

```

R (J/mol/K)
e

```

**Table 3.1** describes the functions recognized by **GSS**. Examples of functions accepting one argument or multiple arguments separated by commas, respectively, include:

```
LN({Ionic strength, molal})
SUM({Na+, mmolal}, {K+, mmolal}, {Ca++, mmolal})
```

Group terms using parentheses:

```
{Na+, mol/l} / ({Na+, mol/l} + {Ca++, mol/l})
```

You can type the equation directly or use the pulldowns beneath the equation box to insert recognized options. The first pulldown lists the input types and the second lists options for that type. The third, where applicable, lists units, “as” options, and log settings. Click **Insert** to add the input to the equation, then continue with more input until your equation is complete. Be sure the default unit you set corresponds to the equation as specified. An example equation to calculate the sodium adsorption ratio from the Na<sup>+</sup>, Ca<sup>++</sup>, and Mg<sup>++</sup> concentrations in your spreadsheet is shown below:


```
{Na+, meq/l} / SQRT(.5* ({Ca++, meq/l} + {Mg++, meq/l}))
```

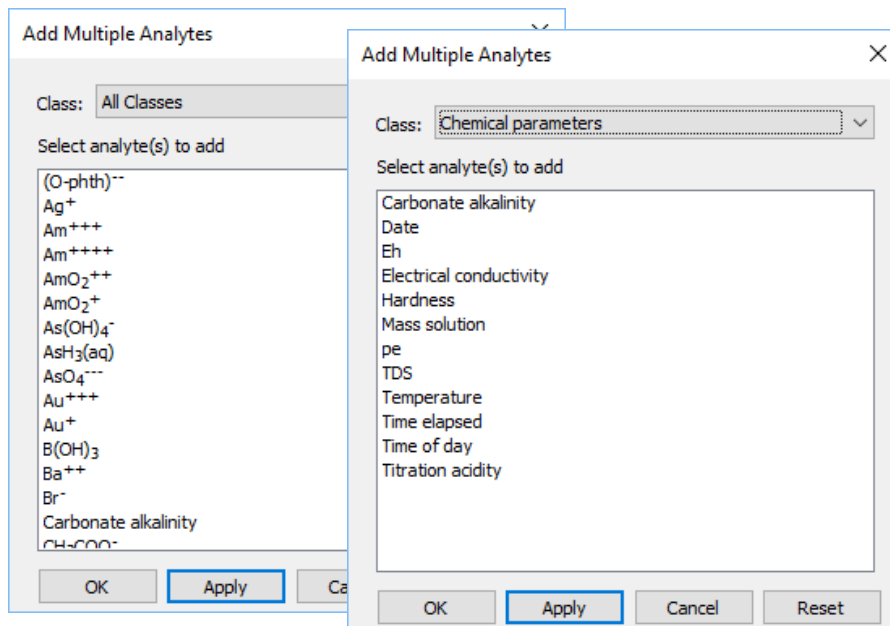
As with calculated analytes, user equations will not update automatically if the data in your spreadsheet changes. Trigger **GSS** to recalculate a user equation by right-clicking on the analyte’s name and selecting **Recalculate Analyte**.

**Table 3.1** Functions recognized as input to user equations

<i>Function</i>	<i>Arguments</i>	<i>Description</i>
ABS(), EXP(), LN(), LOG(), SQRT(), SGN()	1	Absolute value, exponentiation, natural and common logarithms, square root, and sign functions
SIN(), COS(), TAN(), ASIN(), ACOS(), ATAN(), SINH(), COSH(), TANH()	1	Trigonometric functions (taking values in radians), their inverses, and hyperbolic trig functions
MOD()	2	Modulus operation
MIN(), MAX	any number	Minimum or maximum of values
SUM(), AVERAGE(), STDEV()	any number	Sum, average, or standard deviation of a set of values

### 3.3.6 Adding Multiple Analytes

The fastest way to add more than one analyte is with the **Add Multiple Analytes** dialog. Click  **analyte** → **Multiple Analytes...** or **Data** → **Add Analytes...** to open it. Initially, “All classes” is selected, but you can filter the category of analytes shown using the “Class” pulldown. Hold **Ctrl** or **Shift** while selecting to include multiple analytes, or use **Ctrl+A** to select all, then click **OK** or **Apply**.



With the User analytes or User equations classes selected, you can right-click on an analyte to access more options. Choose to create a new analyte, edit an existing analyte, bring in an analyte from another .gss file, or clear the analyte from the registry.

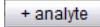
After adding your analytes, you can reorder them, change units, and transpose the data sheet to match your data source, then copy and paste a block of values into selected cells.

### 3.3.7 Calculated values

As described in the previous section, **GSS** can use **SpecE8** to calculate

- Chemical parameters, such as TDS, electrical conductivity, and hardness
- Physical parameters, such as fluid density and viscosity
- Components in fluid (e.g. the H<sup>+</sup> component, when pH is set)
- Species' concentration, activity, and activity coefficients
- Mineral and solid solution saturation indices
- Gas fugacity and partial pressure




as described in the [Using SpecE8](#) chapter of this guide. Select  → **Calculate with SpecE8...** or **Analysis → Calculate with SpecE8...** to add calculated analytes to the data sheet.

You can control the details of how **SpecE8** figures calculated values by going to the **Analysis → Options...** dialog. Here, you tell **SpecE8** what to do if it encounters 0 or “less than” values. You can also set commands (see **SpecE8 Commands** in the *GWB Command Reference*) for **SpecE8** to execute either before or after defining the chemical system, as it runs for each sample. You might, for example, enter a command such as

```
balance on SO4--
```

to cause the program to force an ionic charge balance.

### 3.3.8 Analyte properties

You can see the properties of each analyte in the data sheet by choosing **Data → Analyte Properties** and selecting a class. The “Description” and “Source” fields can be set directly from the properties sheet; other fields are set in the thermo data, or from the **Edit User Analytes** or **Edit User equations** dialogs. To return to the data sheet, use the  button on the right.

## 3.4 Regulations, replicates, standards, and mixing

**GSS** can flag analyses violating regulatory limits or remedial objectives, compare replicate analyses, check analytical standards, and mix water samples.

### 3.4.1 Flagging regulatory violations

**GSS** can flag entries that fall outside the regulatory limits or remedial objectives for an analyte. To flag violations, select the **Analysis → Check Regulatory Limits** option. Entries below an analyte’s minimum level or above its maximum appear on your data sheet emboldened in red.

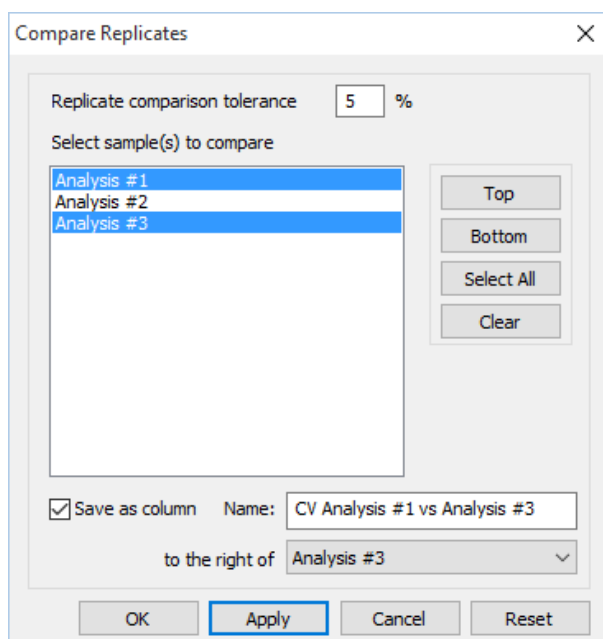
**GSS** reads the regulatory limits from a text file that looks like

# Analyte	Min	Max	Unit	Notes
# -----				
Al+++	--	0.05	"mg/kg as Al"	NSDWR
AsO4---	--	0.01	"mg/kg as As"	MCL
AsH3(aq)	--	0.01	"mg/kg as As"	MCL
pH	6.5	8.5	pH	NSDWR
...				

You specify the file to read on the **File → Preferences...** dialog. By default, the program reads a dataset “WaterQualityRegs.dat” installed with the software in “\Program Files\GWB”. You can use this file, based loosely on the US EPA’s drinking water standards, but most commonly you prepare a dataset to meet your own needs.

### 3.4.2 Replicate analyses

GSS can compare replicate analyses, analyses made of splits of the same sample, to verify the results agree to within an error tolerance. Select two or more samples on your data sheet, then choose **Analysis → Compare Replicates...** The dialog that appears below shows the error tolerance and the samples to be compared.



When you click **OK** or **Apply**, a column appears to the right (or bottom) of the data sheet showing the coefficient of variance among the samples for each analyte, along with a ✓ or ✗, depending on whether or not the variance is within the tolerance indicated. Small coefficients of variance indicate good agreement among the replicates.

To incorporate the variances into the data sheet, check the “Save as column” option. You can change the error tolerance, which defaults to  $\pm 5\%$ , by right-clicking on one of the errors. Close the replicate display by clicking on ✕.

### 3.4.3 Checking standards

GSS can check analyses of standards, samples of well-known composition, for accuracy. Enter the standard’s known composition in a data sheet, along with its analysis or analyses. Select the standard and at least one analysis, then choose **Analysis → Compare**

**To Standard...**, which opens the dialog shown below, which shows the error tolerance to be allowed, the standard itself, and the analyses to compare to the standard.

When you click **OK** or **Apply**, a column appears to the right (or bottom) of the data sheet showing the average deviation, along with a or , depending on whether or not the deviation is within the tolerance indicated.

To incorporate the deviation results into the data sheet, check the “Save as column” option in the dialog box shown above. You can change the error tolerance by right-clicking on the error. Close the error display by clicking on .

### 3.4.4 Mixing samples

GSS can show the results of mixing two or more water samples in any proportion using the values of the total components calculated using **SpecE8**. Choose **Analysis → Mix Samples...** to open the Smart Mix wizard, then select the samples to mix and click **Next >**.

You can control the details of how **SpecE8** performs its calculations by going to the **Analysis → Options...** dialog. Here, you tell **SpecE8** what to do if it encounters 0 or “less than” values.

The wizard will list the Sample ID and the extent of the samples you’ve chosen to mix. GSS will mix samples volumetrically by default, but you can choose instead to mix

samples gravimetrically by selecting “mass” from the “Mix by” pulldown. When the “equal proportions” option is checked, each sample will be assigned a value of 1 liter (or 1 kilogram of solution, if mixing by mass). By unchecking this option you can set values for samples individually. If you are mixing by mass and your spreadsheet includes values for the chemical parameter “Mass solution”, **GSS** will use those values. Otherwise, select a sample, set a value in the box, and click the **Apply** button, then repeat for the remaining samples. The **Reset mixing** button returns all settings to their defaults. Click **Next >** to move on to the next step.

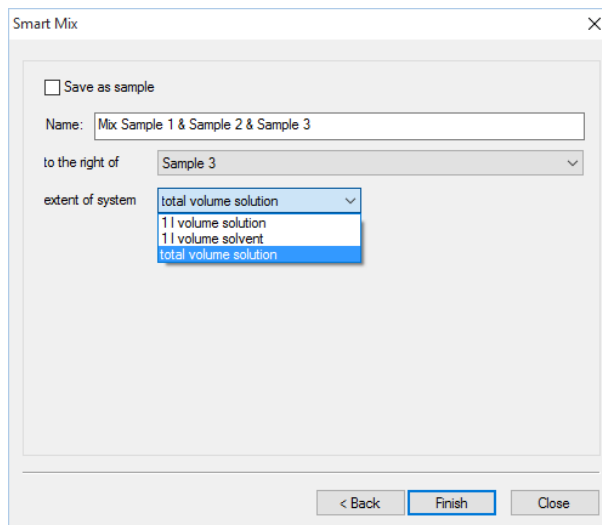
Sample	Value
Sample 1	1.000
Sample 2	1.000
Sample 3	1.000

Mix by: volume  
☒ equal proportions  
 1.0  
 Apply  
 Reset mixing  
 < Back   Next >   Close

**GSS** will test each sample for convergence and report success or failure before beginning the mixing calculations. You can click **More info...** to see the **SpecE8** input and calculation results for failed samples. Check the “show successful samples” box to show input and results for all samples. If a sample fails to converge, the **Next >** button to move on to the next step will be disabled. You can click **< Back** to remove the unsuccessful sample from the mix, or click **Close** to check the values in the spreadsheet before restarting the Smart Mix wizard.

You can choose how **GSS** reports the extent of the mixed sample. If samples were mixed volumetrically, you can report the mixture’s total solution volume or scale the results to 1 liter of solution or solvent water. If samples were mixed by mass, you can report the total mass of the mixed fluid or scale the sample to 1 kilogram of solution or solvent water. Complete the mixing by clicking **Calculate**.

The composition of the mixture will appear to the right (or bottom) of the data sheet, showing the results for each analyte in the spreadsheet. Unlike **GWB** releases 9.0 and earlier, **GWB14** will automatically calculate the values of certain parameters that are not conserved during mixing, such as pH. Close the mixture display by clicking on ✕.



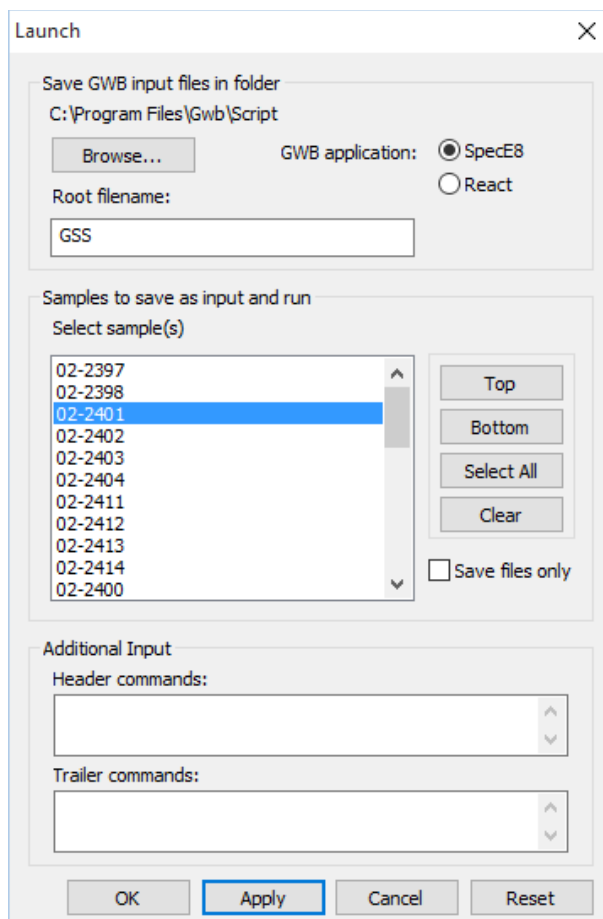
To work with the mixture as if it were a sample, select the “Save as sample” option in the dialog box shown above. The result of the mixing calculation is placed in the data sheet as a new sample to the right of the selected column (or below the selected row).

### 3.5 Launching SpecE8 and React

You can use the chemical analyses in a **GSS** data sheet to set up and run **SpecE8** or **React** calculations. These programs are described in the [Using SpecE8](#) chapter in this guide and the **Using React** chapter in the *GWB Reaction Modeling Guide*.

Select one or more samples on the data sheet, then choose **Analysis → Launch....** If a sample has “less than” (<0.001) values, 0 values, or hidden analytes, you can choose to omit them when generating the input by going to the **Analysis → Options...** dialog.

You can add additional commands to the **SpecE8** or **React** input script created by **GSS**. Header command lines will be inserted near the beginning, just after the thermo data is read. Trailer command lines will be added at the end of the script.



When you hit **Apply** or **OK**, **GSS** writes into the specified directory an input file for each sample you have selected. The input files are named (Root filename) + (Sample ID) + “.sp8” or “.rea”.

Unless you have selected “Save files only”, an instance of **SpecE8** or **React** will be launched configured with the values in the first sample. If you have selected more than one sample, the program will do a batch run, writing the results to an output and plot file for each sample.

### 3.6 Graphing data

**GSS** can call on **Gtplot** to diagram the data in your data sheet in a variety of ways. The [Using Gtplot](#) chapter describes in detail the **Gtplot** program and the types of plots it creates.

### 3.6.1 Series and time series plots

To graph the entries in your data sheet as a series, sample by sample, select the analyte or analytes to plot and click on **Plot → XY Plot → Series Plot...** In the **Gtplot** window that opens, the samples are arranged along the x axis in the order they appear in your data sheet. To change which analytes are shown, or the axis units or data range, double-click on the y-axis label.

To associate markers or their colors or sizes with samples in the data sheet, rather than analytes, go to **Format → GSS Data...** To control whether the markers are connected by line segments, right-click on a marker and select or deselect “Connect Scatter Points”.

To change the marker representing an analyte or sample, click in **GSS** on the marker next to the analyte or sample name. Choose a symbol and its color and size. **GSS** will automatically sync the changes with **Gtplot** unless the **Plot → Auto Updates** option is unchecked, in which case you can click on **Plot → Update Plot(s)** when you are ready to update **Gtplot**.

To create a plot versus time, make sure “Date”, “Time”, or “Time elapsed” appears as an analyte in the data sheet, then choose **Plot → XY Plot → Time Series Plot →**, then choose from **Time elapsed...**, **Time and date...**, or **Time of day...**, if available. **GSS** will determine elapsed time for each sample from its date and time, if not specified directly.


### 3.6.2 Cross plots

To plot one analyte, or several, against another, select the analytes to appear in the diagram, then choose **Plot → XY Plot → Cross Plot...** To change which analytes appear on the x or y axis, or the units or data range for either, double-click in **Gtplot** on the axis label. Control the markers and which samples appear in the plot as you would with a series plot.

### 3.6.3 Ternary, Piper, and Durov diagrams

To create a ternary (triangular) diagram, select in the data sheet three analytes to appear on the diagram axes, then choose **Plot → Ternary Diagram...** Change the analytes appearing on the diagram axes or the axis units by double-clicking on the axis label.

To plot a Piper or Durov diagram, select **Plot → Piper Diagram...** or **Durov Diagram...** Control the markers and which samples appear in the plot as you would with a series plot.

In order to see TDS represented as circles on Piper, ternary, and Durov diagrams, add TDS as an analyte in the data sheet and enter a value for each sample. Alternatively, you may select  **analyte** → **Calculate with SpecE8...** to add calculated TDS to the data sheet, as described in the [Calculating analytes](#) section of this chapter. If you do not supply a measured value or use **SpecE8** to calculate it, **GSS** will estimate TDS as described in the [Changing units](#) section of this chapter.

### 3.6.4 Other diagrams

Create a Schoeller, Stiff, or radial diagram by clicking on **Plot → Schoeller Diagram...**, **Stiff Diagram...**, or **Radial Plot...** To plot a bar or pie chart representing ion balance, choose **Plot → Ion Balance → Bar Chart...** or **Pie Chart...** Choose samples from the **Samples** pane of the appropriate dialog (**Schoeller Diagram...**, and so on), which can be accessed in **Gtplot** under the **Plot** pulldown.

### 3.6.5 Scatter data

You can overlay the data entries in a **GSS** data sheet on any plot produced by the **GWB** applications, including activity diagrams made by **Act2** and **Tact** and plots of the results of reaction and reactive transport models from **Gtplot**, **P2plot**, and **Xtplot**.

To plot “scatter data,” first save your data sheet as a **.gss** file. In **Act2**, **Tact**, **Gtplot**, **P2plot**, or **Xtplot**, read the **.gss** file by selecting **File → Open → Scatter Data...** Data points representing each sample will appear on the plot if the **.gss** file contains analytes corresponding to the plot axes.

For details on plotting scatter data from **.gss** files, see the [Using Act2](#), [Using Tact](#), and [Using Gtplot](#) chapters in this guide, the [Using Gtplot](#) and [Using P2plot](#) chapters in the *GWB Reaction Modeling Guide*, and the [Using Xtplot](#) chapter in the *GWB Reactive Transport Modeling Guide*.

Table 3.2	Keyboard shortcuts in GSS
Ctrl+A	Select all cells in the data sheet
Ctrl+C	Copy
Ctrl+Shift+C	Open a new conductivity file
Ctrl+D	Select all data cells in the data sheet
Ctrl+F	Find
F1	Open <i>GWB Essentials Guide</i>
F3	Find next instance
Shift+F3	Find previous instance
Ctrl+L	Check regulatory limits toggle
Ctrl+N	Create new data sheet
Ctrl+Shift+N	Open Notes... dialog
Ctrl+O	Open an existing <b>.gss</b> file



Ctrl+P	Print
Ctrl+Q	Quit the program
Ctrl+Shift+R	Restore the last data sheet configuration
Ctrl+S	Save the current spreadsheet to a file
Ctrl+T	Open a new thermo dataset
Ctrl+U	Update graphs in Gtplot
Ctrl+V	Paste
Ctrl+W	Open a new water quality regulatory standards file
Ctrl+X	Cut
Ctrl+Y	Redo
Ctrl+Z	Undo
Ctrl++	Zoom in
Ctrl+-	Zoom out
Ctrl+Shift+Z	Zoom 100%—to font size in Preferences...



# Using Rxn

**Rxn** is a program that, among other things, automatically balances chemical reactions among minerals, dissolved species, and gases. The program is easy to use, and quite useful. To show the balanced reaction by which analcime dissolves to form aqueous species, for example, start the program and move to the **Basis** pane. Clicking on the entry (initially, it is “???”) under “balance reaction for”, select “Analcime” from the list of “Minerals”.

The **Rxn** window looks like this:

The screenshot shows the Rxn software window with the following components:

- Menu Bar:** File, Edit, Run, Config, View, Help
- Tabs:** Basis (selected), Command, Results
- Balance Reaction For:** A dropdown menu showing "Analcime" with a value of "1.0" and a unit dropdown set to "activity".
- In Terms Of:** A list of species with their respective coefficients and units:
  - H<sub>2</sub>O: coefficient box, unit dropdown set to "activity"
  - Na<sup>+</sup>: coefficient box, unit dropdown set to "activity"
  - Al<sup>+++</sup>: coefficient box, unit dropdown set to "activity"
  - SiO<sub>2</sub>(aq): coefficient box, unit dropdown set to "activity"
  - H<sup>+</sup>: coefficient box, unit dropdown set to "activity"
  - temperature: coefficient box, unit dropdown set to "C"
- Additional Parameters:** "ionic strength" set to "true", "molal" set to a coefficient box, and "stoichiometric" set to a coefficient box.
- Buttons:** "add" and "delete" buttons.
- Factor Reaction By:** A dropdown menu showing "1.0" and a "reverse" button.

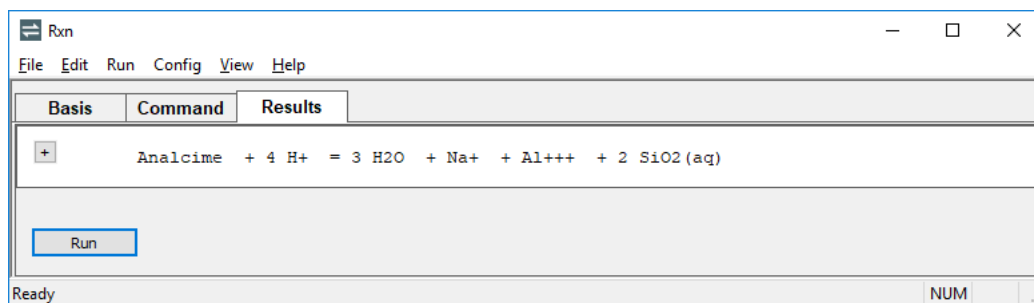
To see the balanced reaction, select **Run → Go**,



press the **Run** button on the **Results** pane, or type

```
react Analcime
go
```

The program gives the result



The species  $\text{H}^+$ ,  $\text{Na}^+$ , etc. are members of the original basis set carried in the thermodynamic database (see [Table 2.1](#)).

You can change the basis to generate reactions in alternative forms. To see the reaction balanced in terms of quartz and albite in place of  $\text{SiO}_2(\text{aq})$  and  $\text{Al}^{+++}$ , use the  $\rightleftharpoons$  button to swap “Quartz” for “ $\text{SiO}_2(\text{aq})$ ”, and “Albite” for “ $\text{Al}^{+++}$ ”.

Or type

```
swap Quartz for SiO2(aq)
swap Albite for Al+++
go
```

The program gives the result

**Rxn** will calculate a reaction's equilibrium constant at a temperature of interest whenever the temperature is given. To find the equilibrium constant for the above reaction at 250°C, set temperature on the **Basis** pane,

The screenshot shows the 'Rxn' window with the 'Basis' tab selected. The reaction is defined as 'Analtime = H2O + Na+ + Albite + Quartz + H+'. The temperature is set to 250.0 C, highlighted with a red circle. The ionic strength is set to 'true', the units are 'molal', and the stoichiometric coefficient is 1.0. The 'factor reaction by' is also set to 1.0.

which gives the result  $\log K = 0.3039$ . To unset the temperature, choose “reset” on the temperature pulldown menu, or type  $T = ?$ .

The program can calculate additional information, including a polynomial fit that gives  $\log K$  as a function of temperature (typically from 0°C to 300°C), the equilibrium equation for the reaction under various conditions, or the temperature at which a reaction is in equilibrium. To calculate additional information, put the program in “long” format by clicking on the **+** button on the **Results** pane, or by typing the command `long`. Return to the original “short” format by clicking on the **-** button, or typing `short`.

For example, unsetting temperature and setting long mode generates the response:

The screenshot shows the 'Results' tab in 'long' mode. The reaction is 'Analtime + Quartz = H2O + Albite'. The results include a table of  $\log K$  values for temperatures from 0°C to 300°C, a polynomial fit equation, and the equilibrium equation.

Temperature (C)	$\log K$
0	0.1982
25	0.1834
60	0.1794
100	0.1909
150	0.2202
200	0.2591
250	0.3039
300	0.3553

Polynomial fit:  
 $\log K = .1981 - .0008043 T + 9.709e-6 T^2 - 2.719e-8 T^3 + 3.198e-11 T^4$

Equilibrium equation:  
 $\log K = \log a[H_2O]$

You can see that at equilibrium the water activity equals the reaction's equilibrium constant. The water activity is likely to be 1 or less, but the equilibrium constant is greater than 1 over the temperature range. The minerals albite, quartz, and analcime are unlikely, then, to be in equilibrium between 0°C and 300°C.

If you set the water activity to unity on the **Basis** pane, or type

```
(cont'd)
a H2O = 1
go
```

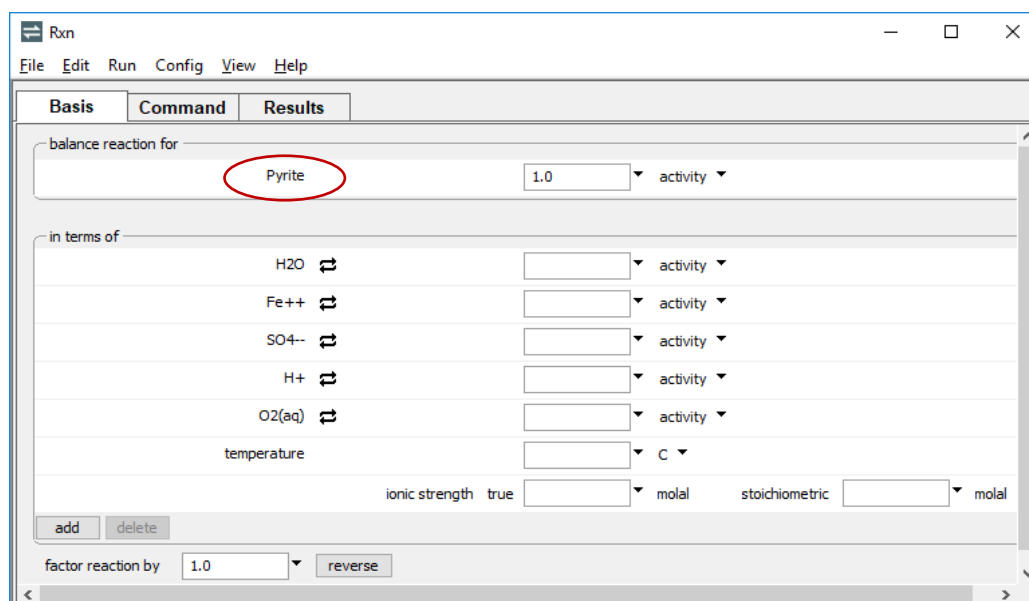
the program reports in the **Results** pane that analcime in the presence of quartz should react to form albite:

```
Equilibrium equation:
log K = 0
Reaction is not in equilibrium between 0 and 300 C
Products favored over this temperature range
```

## 4.1 Balancing reactions

Using basis swaps, you can balance any primary reaction. As an example of how Rxn balances reactions by basis swapping, consider the dissolution reaction of pyrite. Start on the **Basis** pane and under “balance reaction for”, select “??? → Mineral... → Pyrite.

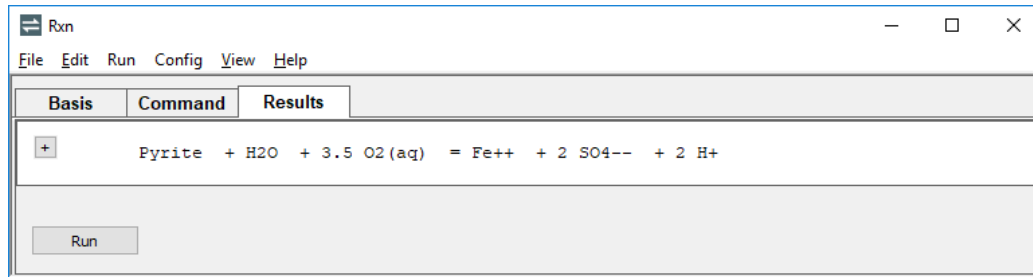
The pane should look like this



Alternatively, type

```
react Pyrite
go
```

Move to the **Results** pane and click **Run** to see the reaction



written in terms of the species in the original basis.

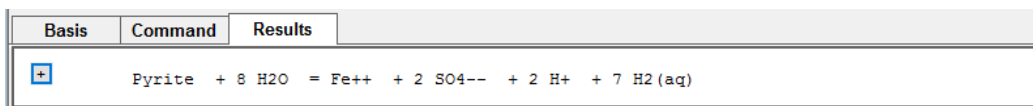
Alternatively, you could write the reaction producing hydrogen instead of consuming dissolved oxygen. Move back to the **Basis** pane, click on the  $\rightleftharpoons$  button next to O2(aq), and select **Aqueous... → H2(aq)**

H2(aq)  $\rightleftharpoons$  O2(aq)  activity ▼

or type

```
(cont'd)
swap H2(aq) for O2(aq)
go
```

which gives the result



Swapping dissolved H2S for the SO4-- ion (and unswapping the H2(aq))


H2S(aq)  $\rightleftharpoons$  SO4--  activity ▼



or

```
(cont'd)
unswap H2(aq)
swap H2S(aq) for SO4--
go
```

gives the reaction written in terms of reduced sulfur


Basis	Command	Results
	Pyrite + H2O + 2 H+ = Fe++ + 2 H2S(aq) + .5 O2(aq)	

Finally, replacing oxygen in the basis with H2S(aq)

H2S(aq)

O2(aq)
▼ activity ▼


gives a dissolution reaction written in terms of SO4-- and H2S

Basis	Command	Results
	Pyrite + H2O + 1.5 H+ = Fe++ + .25 SO4-- + 1.75 H2S(aq)	

that involves neither oxygen nor hydrogen.

## 4.2 Calculating equilibrium equations

To calculate the equilibrium equation corresponding to a reaction, constrain species activities and gas fugacities as needed and set **Rxn** in long format.

To calculate the line between hematite ( $\text{Fe}_2\text{O}_3$ ) and  $\text{Fe}^{++}$  in Eh-pH coordinates at 25°C, assuming an iron activity of  $10^{-8}$ , for example, start **Rxn** and move to the **Basis** pane. Under “balance reaction for”, select “???” → **Mineral...** → **Hematite**. Change the unit for  $\text{H}^+$  from “activity” to “pH”. Set the  $\text{H}_2\text{O}$  activity to “1”. Change the unit for  $\text{Fe}^{++}$  to “log activity” and set the value to “-8”. Click on the  button next to  $\text{O}_2(\text{aq})$  and select **Aqueous...** → **e-**, then change the unit from “activity” to “Eh”. Finally, set the temperature to “25°C”.

The pane should look like this

Rxn

File Edit Run Config View Help

**Basis** Command Results

balance reaction for

Hematite 1.0 activity

in terms of

H+		pH
H2O	1.0	activity
Fe++	-8.0	log activity
e- ↔ O2(aq)		Eh
temperature	25.0	C

ionic strength true molal stoichiometric molal

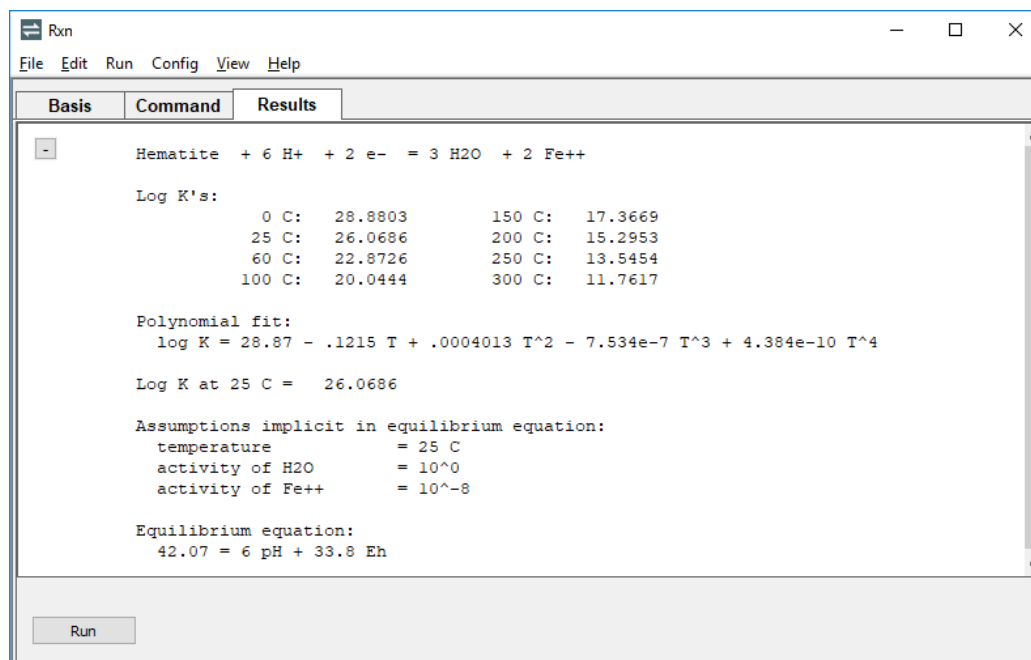
add delete

factor reaction by 1.0 reverse

Or, type the commands

```
T = 25
react Hematite
swap e- for O2(aq)
log activity Fe++ = -8
activity H2O = 1
pH = ?
Eh = ?
long
go
```

The result, shown on the **Results** pane, is



The equation can be simplified by setting “factor reaction by” in the **Basis** pane to “1/6”,


factor reaction by

or

factor = 1/6

which gives the equilibrium equation

7.011 = pH + 5.634 x Eh

As a second exercise, we calculate at 200°C the equilibrium ratio of K<sup>+</sup> to H<sup>+</sup> activities for the reaction of muscovite to potassium feldspar (microcline) in the presence of quartz. Reset the configuration (select **File** → **Reset Configuration**) and move to the **Basis** pane. Under “balance reaction for”, select “???” → **Mineral...** → **Maximum Microcline**. Click on the  button next to K<sup>+</sup> and select **Ratio....** Set “K<sup>+</sup>” for the numerator, and “H<sup>+</sup>” in the denominator. Swap “Muscovite” for “Al+++” and “Quartz” for “SiO2(aq)”. Finally, set the temperature to “200°C”.

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The pane should look like this

Rxn

File Edit Run Config View Help

**Basis** Command Results

balance reaction for

Maximum Microcline 1.0 activity

in terms of

H2O	↔		activity
K+/H+	↔	K+	ratio
Muscovite	↔	Al+++	activity
Quartz	↔	SiO2(aq)	activity
H+	↔		activity
temperature		200.0	C

ionic strength true molal stoichiometric molal

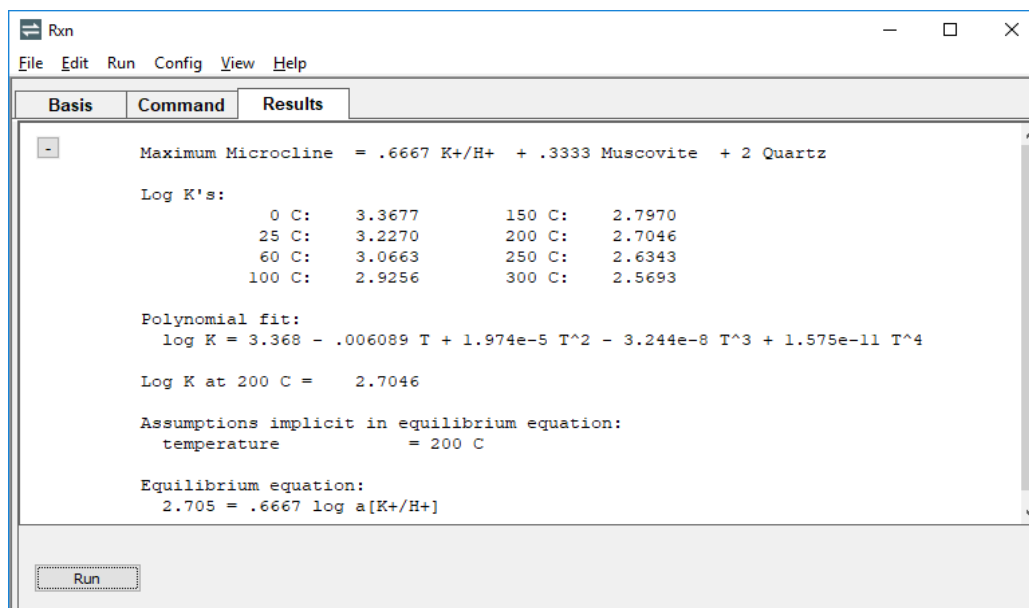
add delete

factor reaction by 1.0 reverse

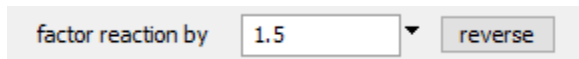
Alternatively, type the commands

```
T = 200 C
react "Maximum Microcline"
swap Muscovite for Al+++
swap Quartz for SiO2(aq)
swap K+/H+ for K+
long
go
```

Run the calculation and on the **Results** pane click  for long format results.



Setting “factor reaction by” in the **Basis** pane to “3/2”



will simplify the result, giving the equilibrium activity ratio directly

```
1.5 Maximum Microcline = K+/H+ + .5 Muscovite + 3 Quartz
Equilibrium equation:
4.057 = log a[K+/H+]
```

at this temperature.

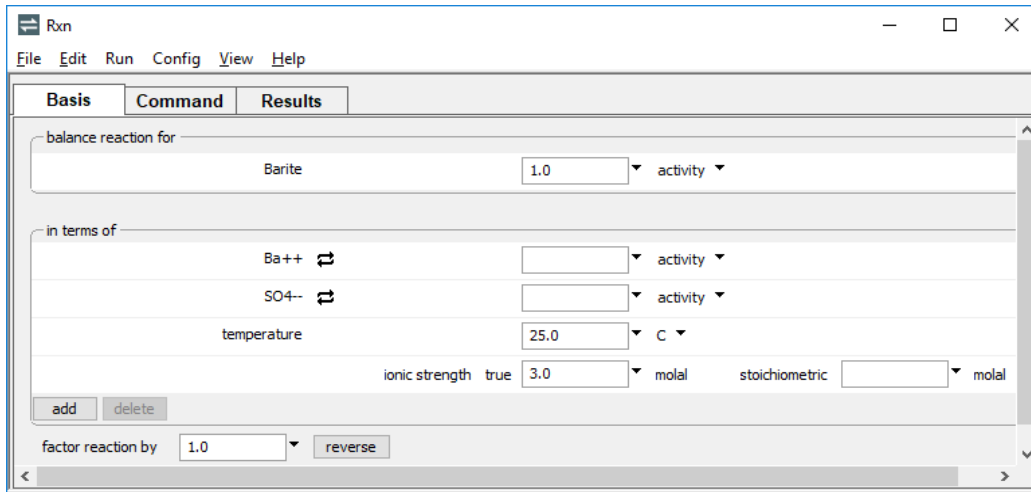
### 4.3 Determining activity coefficients

You can use **Rxn** to calculate activity coefficients from a version of Debye-Hückel theory, according to the dataset in use (see [Activity coefficients](#) under **Using SpecE8**). To do so, specify temperature and set solution ionic strength in molal units on the **Basis** pane, or use the `ionic_strength` (or `I`) command. To have **Rxn** calculate the activity of water, set the solution’s stoichiometric ionic strength on the **Basis** pane, or with the `stoich_IS` (or `SI`) command.

Note, **Rxn** uses the Davies equation in place of virial methods. Additionally, **Rxn** will use the setting for stoichiometric ionic strength, if any, as a proxy for the sum of species

concentrations when calculating water activity by the Wolery (1992b) and Garrels and Christ (1965) methods (see **Thermo Datasets** in the *GWB Reference Manual*).

To calculate activity coefficients, start **Rxn** and move to the **Basis** pane. Under “balance reaction for”, select “??? → Mineral... → Barite”. Set the temperature to “25°C”. Finally, set the ionic strength to “3 molal”. The pane should look like this

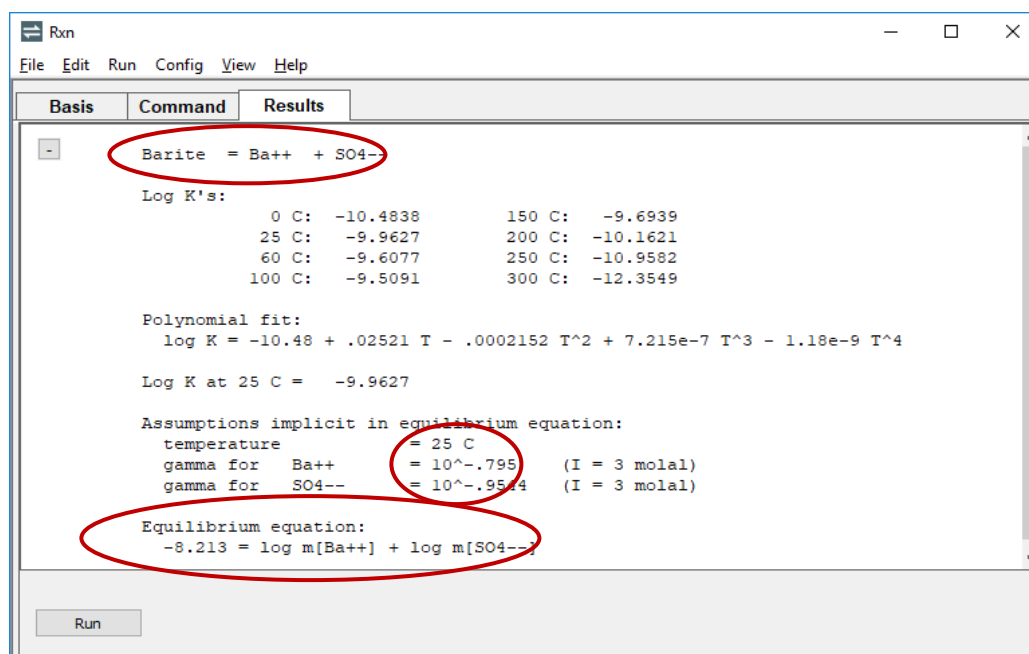


Alternatively, type the commands

```
react Barite
T = 25 C
I = 3
long
go
```

Running the calculation causes the program to balance the reaction and report activity coefficients (“gammas”) for species  $\text{Ba}^{++}$  and  $\text{SO}_4^-$  in a solution of 3 molal ionic strength at 25°C. The corresponding values, expressed directly instead of in exponential form, are 0.16 and 0.11.

On the **Results** pane, the program gives the equilibrium equation for the reaction.



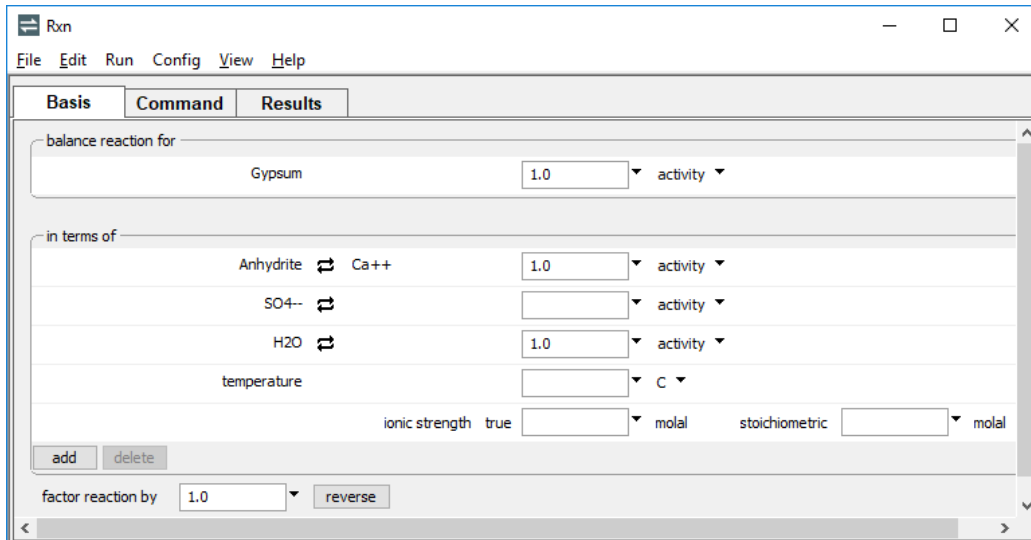
Here, Rxn has used the calculated values for activity coefficients to simplify the equation, replacing activities with species molalities.

## 4.4 Calculating equilibrium temperatures

Rxn can calculate the temperature (or temperatures) at which a reaction is in equilibrium if the activity of each species and fugacity of each gas in the reaction is known. To calculate the temperature at which gypsum converts to anhydrite, swap the two minerals into the basis and set the water activity.

Start Rxn and move to the **Basis** pane. Under “balance reaction for”, select “???” → **Mineral...** → **Gypsum**. Swap “Anhydrite” in for the “Ca++” and set the water activity to “1”.

The pane should look like this



At unit water activity, the long format result is

```
Gypsum = Anhydrite + 2 H2O
```

```
Reaction is in equilibrium at 43.7° C
```

```
Products favored above this temperature
```

To calculate the temperature at lower water activity (which might be appropriate for a brine), set the activity of water to “0.7”. The program gives the result

```
Reaction is in equilibrium at 11.8° C
```

```
Products favored above this temperature
```

Rxn’s ability to calculate equilibrium temperatures can be useful for sorting among a mineral’s polymorphs to determine which is stable. For example, selecting **Config** → **Show...** and then selecting “Albite”, or typing

```
polymorphs Albite
```

produces a list of minerals in the database that have the same chemical formula as albite, which are “Albite high” and “Albite low”.



### The steps

```
react Albite
swap "Albite high" for Al+++
long
go
```

generate the information that high albite is the unstable form from 0°C to 300°C.

## 4.5 Free energy change

When you set a temperature and constrain a reaction sufficiently that either the reactants or reaction products are favored thermodynamically, **Rxn** will report the corresponding free energy change of reaction.

Set **Rxn** to balance the reaction for the dismutation of acetate ion at 25°C, assuming bicarbonate is present at mmol/kg, and acetate and methane at  $\mu\text{mol/kg}$  levels.

Start **Rxn** and move to the **Basis** pane. Under “balance reaction for”, select “???” → **Aqueous...** → **CH<sub>3</sub>COO<sup>-</sup>** and set its log activity to “-6”. Swap “CH<sub>4</sub>(aq)” for the “O<sub>2</sub>(aq)” and set its log activity to “-6”. Set the log activity of HCO<sub>3</sub><sup>-</sup> to “-3” and the water activity to “1”. Finally, set the temperature to “25°C”.

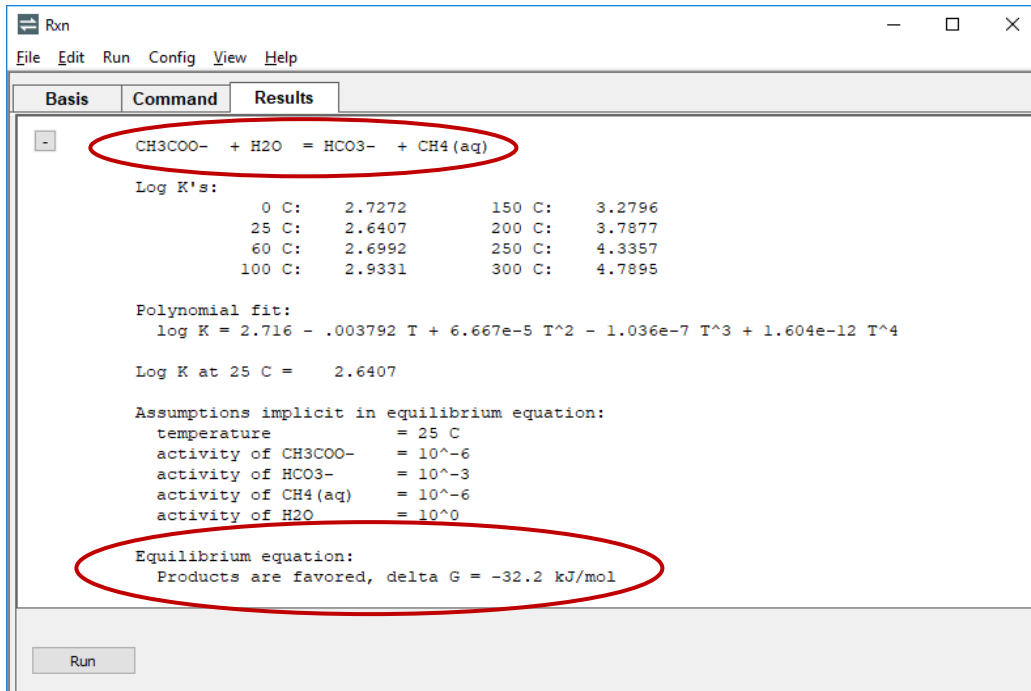
The pane should look like this

The screenshot shows the **Rxn** software window with the **Basis** tab selected. The configuration is as follows:

- balance reaction for:** CH<sub>3</sub>COO<sup>-</sup> (log activity: -6.0)
- in terms of:**
  - HCO<sub>3</sub><sup>-</sup> (log activity: -3.0)
  - H<sup>+</sup> (activity: 1.0)
  - CH<sub>4</sub>(aq) ↔ O<sub>2</sub>(aq) (log activity: -6.0)
  - H<sub>2</sub>O (activity: 1.0)
  - temperature: 25.0 °C
  - ionic strength: true
  - molal: true
  - stoichiometric: true
- factor reaction by:** 1.0 (with a **reverse** button)

Buttons for **add** and **delete** are located below the list of species.

On the **Results** pane, the program reports the acetoclastis reaction



along with the result that the reaction has a modest thermodynamic drive to proceed forward.

## 4.6 Solid solutions

Rxn can balance reactions involving end members of continuous, and tranches of discrete solid solutions (see **Configuring the programs**). You can work with solid solutions defined in the thermo dataset, or create new solutions with the **Config → Solid Solutions...** dialog or the `solid_solution` command.

To configure a calcite-rhodochrosite solid solution, for example, select **Config → Solid Solutions...**, click **add** under “Define new solid solutions”, and expand the entry with the “+” button. Supply a name like “Cal-Rds”, choose end-member minerals “Calcite” and “Rhodochrosite”, and add tags such as “Cal” and “Rds”, respectively. Change the “type” from “ideal” to “Guggenheim”, set “a0” to “-3.2” and click **Apply**

Alternatively, the command

```
solid_solution Cal-Rds Calcite tag Cal contains \
Rhodochrosite tag Rds guggenheim a0 = -3.2
```

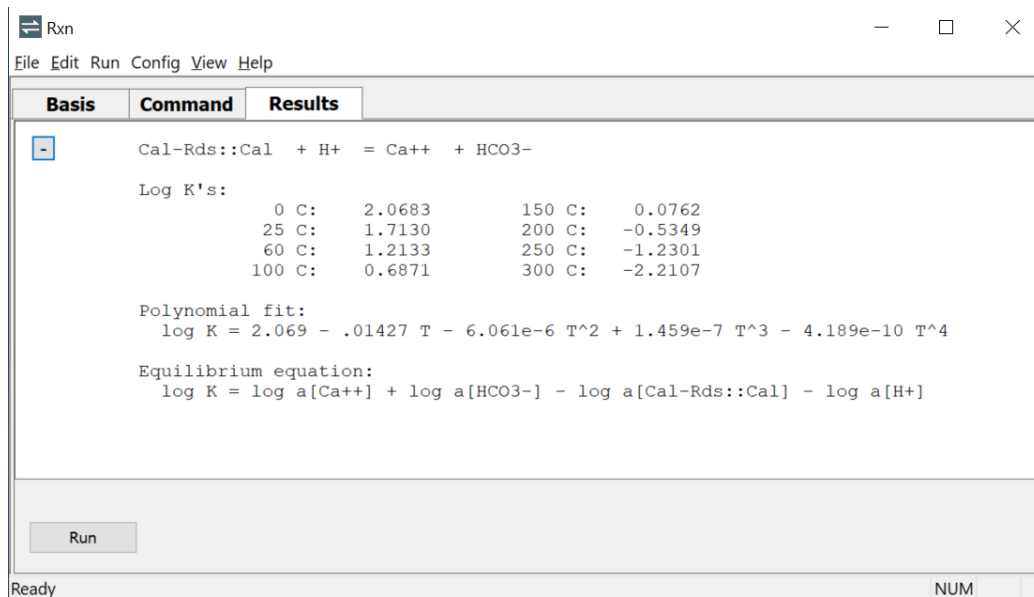
serves the same purpose.

To figure the equilibrium equation for the dissolution reaction of the calcite end member, move to the **Basis** pane and under “balance reaction for”, click “???” → **End member...** → **Cal-Rds::Cal**. Alternatively, use the command

```
react Cal-Rds::Cal
```

where “Cal-Rds” is the name of the solid solution and “Cal” is the end member’s tag.

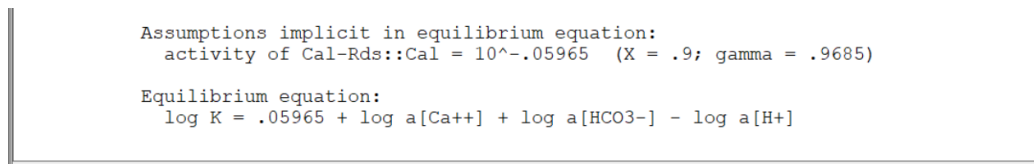
On the **Results** pane, click **Run** and expand the results by clicking the “+” button. The dissolution reaction and log  $K$  values are the same as for the pure mineral calcite. The equilibrium equation, however, carries the activity of the calcite end member



Return to the **Basis** pane and set the “mole fraction” of “Cal-Rds::Cal” to a value “0.9”, or use the command

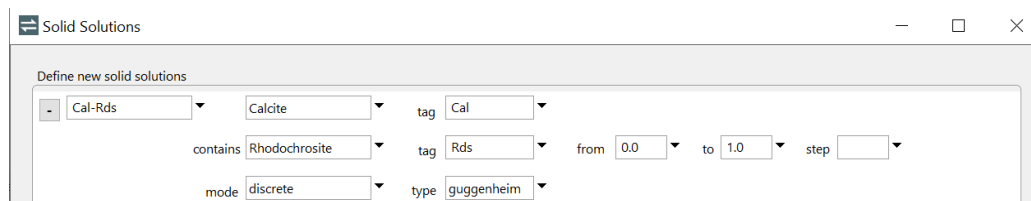
```
xss Cal-Rds::Cal = 0.9
```

Rerun the calculation and note how **Rxn** reports the end member’s activity coefficient and carries its activity in the equilibrium equation



Note if the solid solution activity model in use is temperature-dependent, you must additionally set the temperature to evaluate the activity coefficient expression.

To consider the dissolution of a discrete-composition solid solution, as a second example, return to the **Solid Solutions...** dialog, change the “mode” pulldown to “discrete”



and click **Apply**. Note the “from” and “to” entries, as well as the “step”, which is 1/20<sup>th</sup> of the range by default. **Rxn** will use these values to generate a series of fixed-composition minerals, Cal(.95)-Rds(.05), Cal(.9)-Rds(.1), and so on.

The continuous solid solution end member was removed from the reaction’s left side. Replace it with a tranche of the solid solution: Click “???” → **Mineral...** → Cal(.9)-Rds(.1) and recalculate the reaction. Alternatively, use the commands

```
(cont'd)
solid_solution Cal-Rds discrete
react Cal(.9)-Rds(.1)
go
```

The tranche dissolves in the resulting reaction to form 0.9 Ca<sup>++</sup> and 0.1 Mn<sup>++</sup>. The log *K* reported was determined as a function of the end member log *K*s, mole fractions, and activity coefficients, as described in [Solid solutions](#) under **Configuring the Programs**.

## 4.7 Sorption reactions

**Rxn** manipulates the reactions by which ions sorb to a mineral in the same way it handles other types of reactions. Access a dataset of surface reactions by dragging it into the **Rxn** window; selecting **File** → **Open** → **Sorbing Surfaces...** (or **Config** → **Sorbing Surfaces...**), clicking on **add**, and selecting a surface dataset; or with the `surface_data` (or `surf_data`) command. Once entered, you can view the surface sites and complexes by selecting **Config** → **Show...**, or typing `show surfaces`.

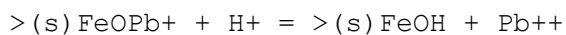
### 4.7.1 Surface complexation

To work with a surface complexation reaction, read a dataset of complexation reactions, such as “FeOH.sdat” supplied with the GWB.

To try the feature, load this dataset by dragging it into the **Rxn** window, or by using one of the methods described above, and move to the **Basis** pane. Under “balance reaction for” select “???” → **Surface species...** → **>(s)FeOPb+**. Set the units for “H<sup>+</sup>” to “pH”.

The pane should look like this

On the **Results** pane, Rxn will report the reaction



and its corresponding equilibrium equation

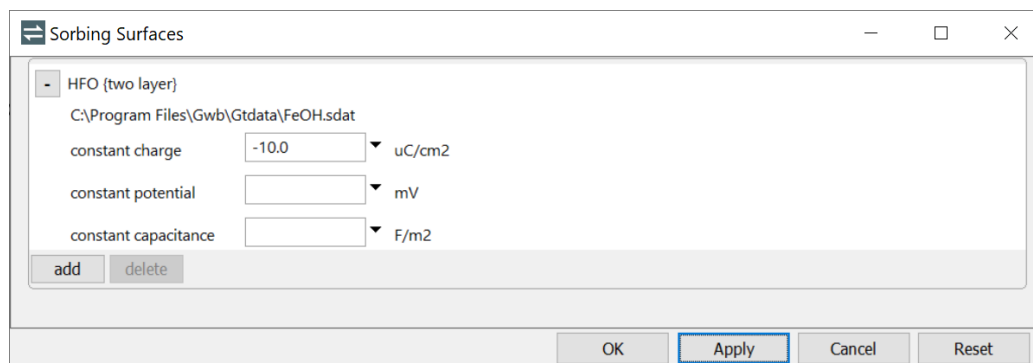
$$\log K + (\text{PSI}[\text{HFO}] F) / (2.303 R TK) = \log m[>(s) \text{FeOH}] + \log a[\text{Pb}^{++}] - \log m[>(s) \text{FeOPb}] + \text{pH}$$

The second term in the equation is the logarithm of the Boltzman factor, which accounts for electrostatic forces between the surface and solution. Here,  $F$  is the Faraday constant,  $PSI$  is mean surface potential,  $R$  is the gas constant, and  $TK$  is absolute temperature;  $m$  represents molal concentration.

For two-layer reactions, **Rxn** will evaluate the Boltzman factor numerically if you specify temperature and ionic strength (on the **Basis** pane), and the charge density on the sorbing surface. Provide the latter value in units of  $\mu\text{C}/\text{cm}^2$  on the **Sorbing Surfaces...** dialog (**Config** → **Sorbing Surfaces...**) next to “constant charge” and hit **Apply**, or with the `surface_charge` (or `surf_charge`) command.

Continuing on the **Basis** pane, set temperature to “25°C” and the ionic strength to “0.1”

On **Sorbing Surfaces...**, set the constant charge to “-10.0  $\mu\text{C}/\text{cm}^2$ ”, then hit **Apply**



Selecting **Run → Go** gives the simplified equation

$$-5.707 = \log m[>(s)\text{FeOH}] + \log m[\text{Pb}^{++}] - \log m[>(s)\text{FeOPb}^{+}] + \text{pH}$$

corresponding to 25°C, an ionic strength of 0.1 molal, and a surface charge density of -10  $\mu\text{C}/\text{cm}^2$ .

The constant capacitance and constant potential models are variants of the surface complexation model. Set these on the **Sorbing Surfaces...** dialog (**Config → Sorbing Surfaces...**), or using the `surface_capacitance` and `surface_potential` commands, as described in the [Configuring the Programs](#) chapter.

When working with triple-layer and CD-MUSIC reactions, the equilibrium equation involves a distinct surface charge and the corresponding surface potential for each of three layers. Determining a consistent set of charge densities and potentials requires a full solution to the surface speciation problem. As such, **Rxn** does not provide for simplifying the Boltzman factor for reactions from triple-layer or CD-MUSIC datasets.

### 4.7.2 Ion exchange

As described in the [Configuring the Programs](#) chapter, you can model ion exchange in two ways. The first method is to swap an activity ratio into the basis. This method is equivalent to assuming that there exists a sufficiently large reservoir of exchanging ions that the composition of the exchanging surface remains invariant.

For a more general treatment, prepare a small dataset of exchange reactions using the file “IonEx.sdat” as a template. Load a dataset of exchange reactions by selecting **File → Open → Sorbing Surfaces...**, or with the `surface_data` (or `read`) command. The exchange reactions in this dataset are now available to your **Rxn** session.

You can load one or more exchange datasets (containing one or more exchange reactions) at a time, and in a single run combine ion exchange datasets with other types of surface reaction datasets.

### 4.7.3 Distribution coefficients ( $K_d$ )

To use distribution coefficients ( $K_d$ ) to model sorption, prepare one or more datasets containing the sorption reactions and corresponding distribution coefficients using the file “Kd.sdat” as a template (see the [Configuring the Programs](#) chapter). As with any sorption model, read the dataset(s) by selecting **File → Open → Sorbing Surfaces...**, or using the `surface_data` command. Once the dataset(s) has been read, the sorption reactions they contain are available to your **Rxn** session.

In the distribution coefficient model, the concentration of a sorbed ion is carried in units of moles per gram solid. If you wish to constrain the sorbed concentration of an ion in **Rxn**, do so in units of mol/g using the `sorbed_mass` (rather than the `molality`) command.

### 4.7.4 Freundlich isotherms

The use of Freundlich isotherms is broadly similar in implementation to the  $K_d$  approach, as described in the previous section, except the dataset of surface reactions follows the format of “Freundlich.sdat”, rather than “Kd.sdat”.

### 4.7.5 Langmuir isotherms

To model sorption according to Langmuir isotherms, prepare a dataset containing the sorption reactions in the format of dataset “Langmuir.sdat”.

Enter the dataset into an **Rxn** run by selecting **File → Open → Sorbing Surfaces...**, or with the `surface_data` (or `read`) command. You can enter one or more Langmuir datasets, and mix Langmuir datasets with datasets for other sorption methods.

## 4.8 Rxn command line

You can start **Rxn** by clicking the icon on the GWB dashboard, opening a “.rxn” file, or entering the command `rxn.exe` from the Windows “Command Prompt.”

When you start **Rxn** from the command line (as opposed to clicking on the icon), you can specify a number of arguments. For example, the command

```
rxn -i my_script -d my_thermo.tdat
```

causes **Rxn** to read input commands from a file “my\_script”, and to use “my\_thermo.tdat” as the thermodynamic database.



The following options are available from the command line:

<code>-cd</code>	Change the working directory to the directory containing the input script specified with the <code>-i</code> option.
<code>-nocd</code>	Do not change the working directory.
<code>&lt;input_script&gt;</code> <code>-i &lt;input_script&gt;</code>	Set a file from which to read input commands.
<code>-gtd &lt;gtdata_dir&gt;</code>	Set directory to search for thermodynamic datasets.
<code>-d &lt;thermo_data&gt;</code>	Set the thermodynamic dataset.
<code>-s &lt;surface_data&gt;</code>	Set a dataset of surface sorption reactions.
<code>-append</code>	Keep previous results of the “block” command on the clipboard.
<code>-main species</code>	Set the species to appear on the left side of the reaction.
<code>-short   -long</code>	Set the output to be written in concise or detailed format.



# Using Act2

**Act2** is a program that calculates and plots activity-activity diagrams. This class of diagrams shows the stability of minerals and the predominance of aqueous species in chemical systems. A species activity, gas fugacity, activity or fugacity ratio, pH, Eh, or pe may serve as an axis variable.

To diagram the effects of pH and the activity of dissolved oxygen on the speciation of uranium in water, for example, start the program and select “U++++” under “diagram species”. To do so, click on the current setting, initially “???”, to show the choice of basis entries available to diagram (remember that pressing U moves down the list to “U++++”). To the right, change the units by selecting “log activity”, then enter “-10” for the species’ log activity.

In the box below, select “H+” for the x-axis species, and “O2(aq)” for the y axis. Then set “pH” as the unit for the x axis and adjust the y-axis range. The **Basis** pane should look like this:

The screenshot shows the Act2 software window with the 'Basis' tab selected. The configuration is as follows:

- diagram species:** U++++, log activity, -10.0
- on axes:**
  - H+ (x-axis):** pH, from 0.0 to 14.0, increment 2.0
  - O2(aq) (y-axis):** log activity, from -90.0 to 0.0, increment 10.0
- in the presence of:**
  - H2O:** activity, 1.0, solvent
  - temperature:** 25.0, C
  - pressure:** bars

Buttons for 'add' and 'delete' are located at the bottom left of the configuration area.

Alternatively, enter the commands

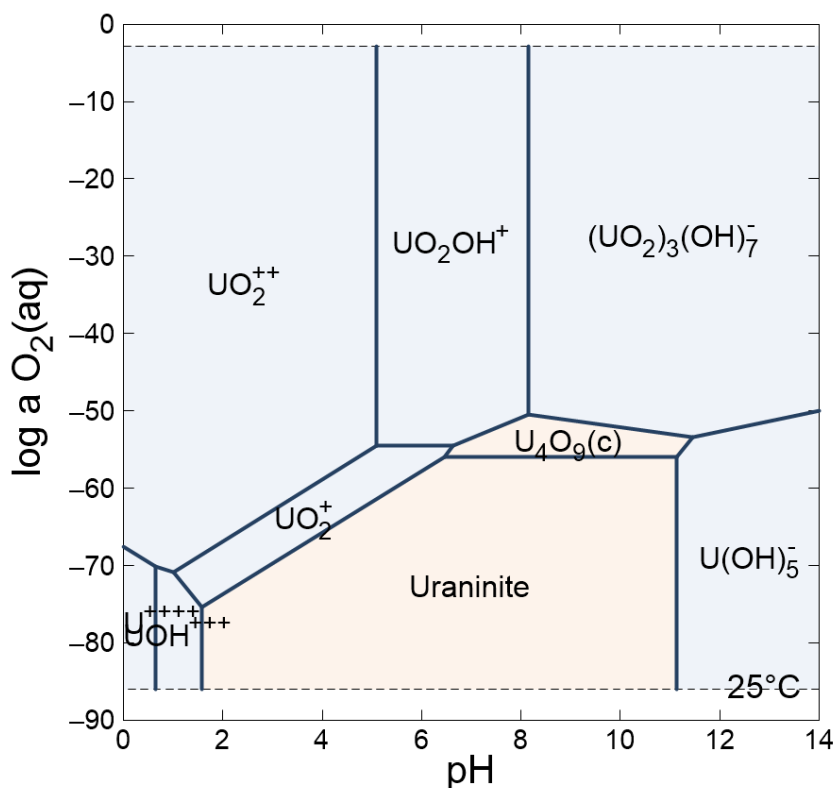
```

diagram U++++ on O2(aq) vs pH
log a U++++ = -10
x from 0 to 14; y from -90 to 0
go

```

Here we have set a uranium activity of  $10^{-10}$  and, by default, a temperature of 25°C. Specify axis ranges in terms of the logarithms of activity or fugacity values, and linearly in terms of pH, pe, and Eh. Move to the **Plot** pane to display the result.

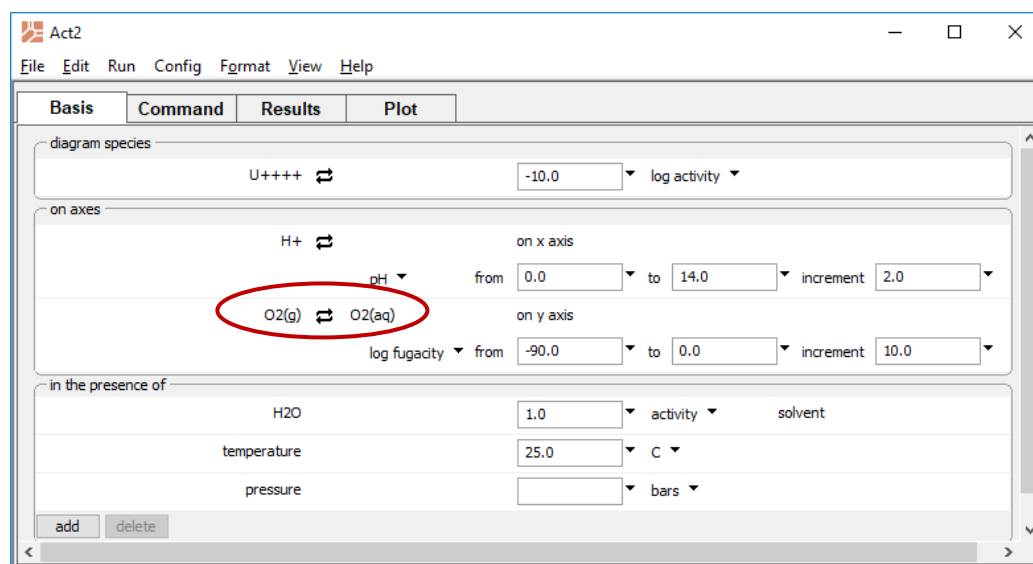
The program produces a file “Act2\_output.txt” describing the calculation (select **File → View → Act2\_output.txt** to inspect this dataset) and displays the diagram on the **Plot** pane. The figure below shows the resulting plot, a redox-pH diagram for uranium plotted against the activity of dissolved oxygen. Dashed lines show stability limits for water at 1 atm pressure. (Note that many of the figures in the User’s Guide have been simplified slightly or relabeled to allow for reduction and printing.)



You can click on any boundary on the plot, including the water limits, to see the reaction it represents in a tooltip.

You can return to the **Basis** or **Command** pane to alter the program configuration and produce further diagrams. To plot the fugacity of oxygen gas along the vertical axis on the diagram we just calculated, move to the **Basis** pane and swap the gas species into the basis by clicking on the  $\rightleftharpoons$  next to the y-axis entry and selecting **Gas...  $\rightarrow$  O<sub>2</sub>(g)**.

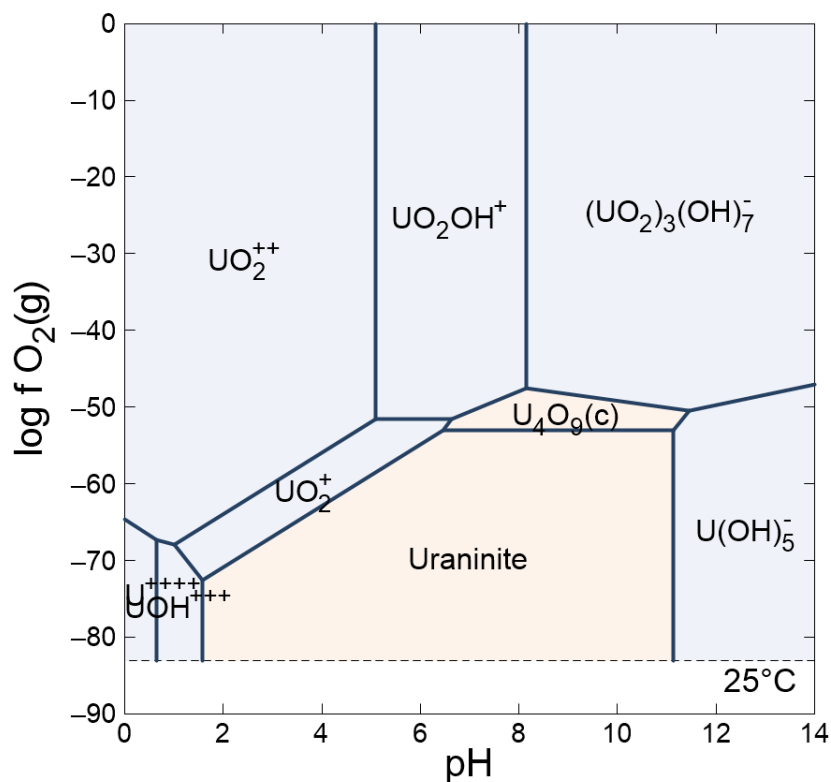
The pane should look like this



Alternatively, enter the commands

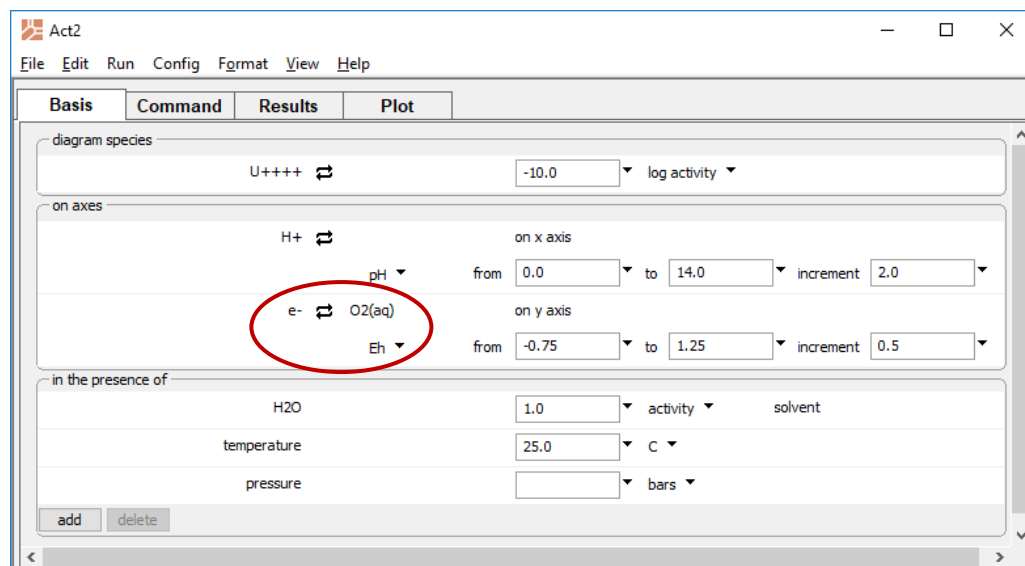
```
(cont'd)
swap O2(g) for O2(aq)
y from -90 to 0
go
```

Move to the **Plot** pane to view the diagram. The figure below shows the results, a redox-pH diagram for uranium plotted against the fugacity of oxygen gas.



Swapping the electron into the basis allows you to plot oxidation state in terms of Eh. On the **Basis** pane, swap **Aqueous...** → **e-** for O<sub>2</sub>(aq), and set units of “Eh”.

The pane should look like this

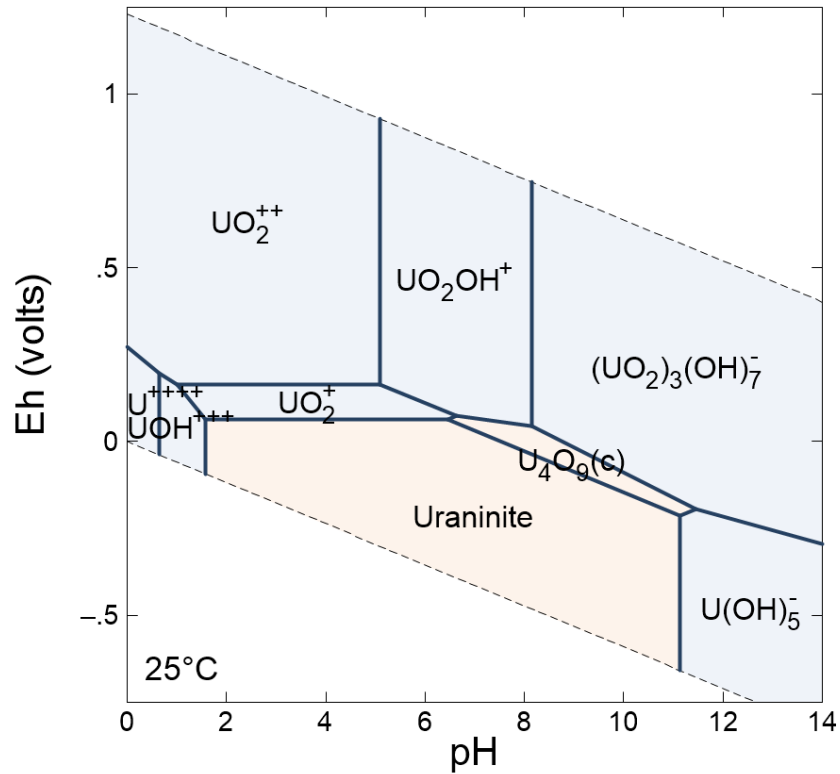



Equivalent commands are


```
(cont'd)
swap e- for O2(aq)
diagram on Eh
y from -.75 to 1.25
go
```

Move to the **Plot** pane to view the diagram.

The figure below shows the results for the redox-pH diagram plotted against Eh.



The oxidation state can be also represented in terms of the log activity ratio of a redox pair such as ferrous and ferric iron. On the **Basis** pane, click on  next to the y-axis entry and select **Ratio....** Set “Fe+++” with a power of “1” as the numerator species, and “Fe++” with the same power in the denominator:

 Species Activity Ratio
✕

Fe+++ / Fe++

Fe+++
▼ ^

1

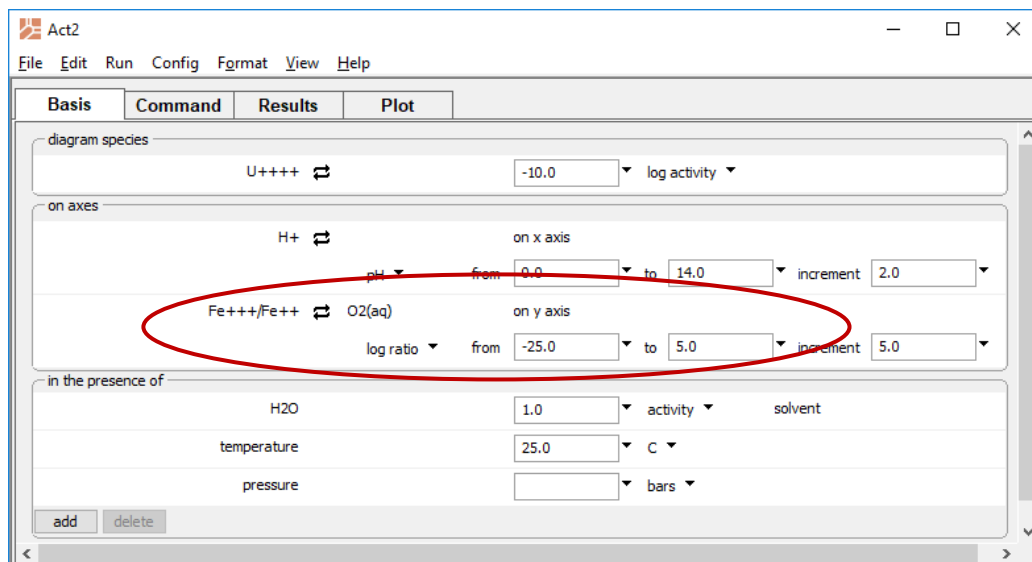
Fe++
▼ ^

1

OK
Apply
Cancel
Reset



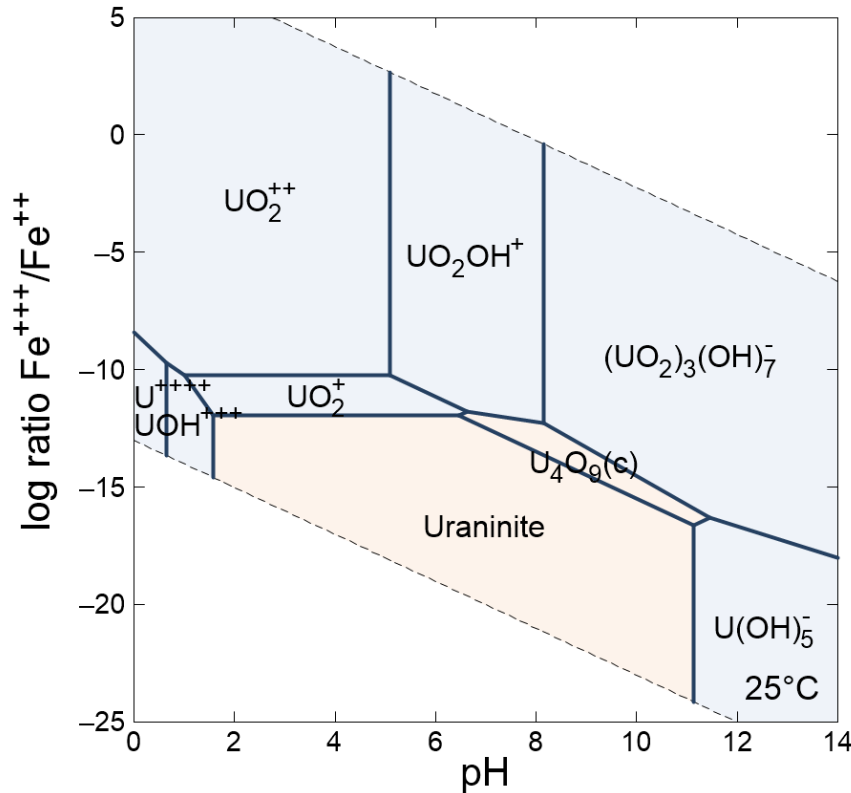
To the right of this entry in the **Basis** pane, set the axis to range from “-25” to “5”. The pane should look like this



Alternate commands are

```
(cont'd)
swap Fe+++ / Fe++ for O2(aq)
y from -25 to 5
go
```

Move to the **Plot** pane to view the diagram. The figure below shows the results for the redox-pH diagram plotted against the activity ratio of  $\text{Fe}^{+++}$  to  $\text{Fe}^{++}$ .



In calculating a diagram, **Act2** balances each reaction possible among the aqueous species and minerals in the system and lists them along with their equilibrium equations in the “Act2\_output.txt” dataset.

## 5.1 Diagram calculation

The most familiar class of activity-activity diagram is the redox-pH, but **Act2** can calculate diagrams on any activity or fugacity axis, as well as diagrams that account for the presence of minerals, complexing species, and gas buffers.

To evaluate the effect at 60°C of chloride complexing on copper at a  $\text{CO}_2$  fugacity of 1, for example, you could set the  $\text{Cl}^-$  activity and  $\text{CO}_2$  fugacity in your input.

Under “diagram species”, click on “???” and select “Cu+”. Change “activity” to “log activity” and set the value to “-6”.

In the box below, select “H+” for the x-axis species, and “O2(aq)” for the y axis. Then select “pH” as the unit for the x axis and set the y-axis range from “-80” to “0”.

Under “in the presence of”, click **add** and select “HCO<sub>3</sub><sup>-</sup>”, then click on the  $\rightleftharpoons$  button next to it and select **Gas... → CO<sub>2</sub>(g)**. Set the fugacity to “1”. Next, click **add** and select “Cl<sup>-</sup>”, then set its value to “.1”. Finally, set temperature to “60°C”.

The **Basis** pane should look like this:

The screenshot shows the Act2 software window with the 'Basis' tab selected. The configuration is as follows:

- diagram species:** Cu+ with a log activity of -6.0.
- on axes:**
  - on x axis:** H+ vs pH, ranging from 0.0 to 14.0 with an increment of 2.0.
  - on y axis:** O<sub>2</sub>(aq) vs log activity, ranging from -80.0 to 0.0 with an increment of 10.0.
- in the presence of:**
  - H<sub>2</sub>O: activity 1.0, solvent.
  - CO<sub>2</sub>(g)  $\rightleftharpoons$  HCO<sub>3</sub><sup>-</sup>: fugacity 1.0.
  - Cl<sup>-</sup>: activity 0.1.
  - temperature: 60.0 °C.
  - pressure: (empty field) bars.

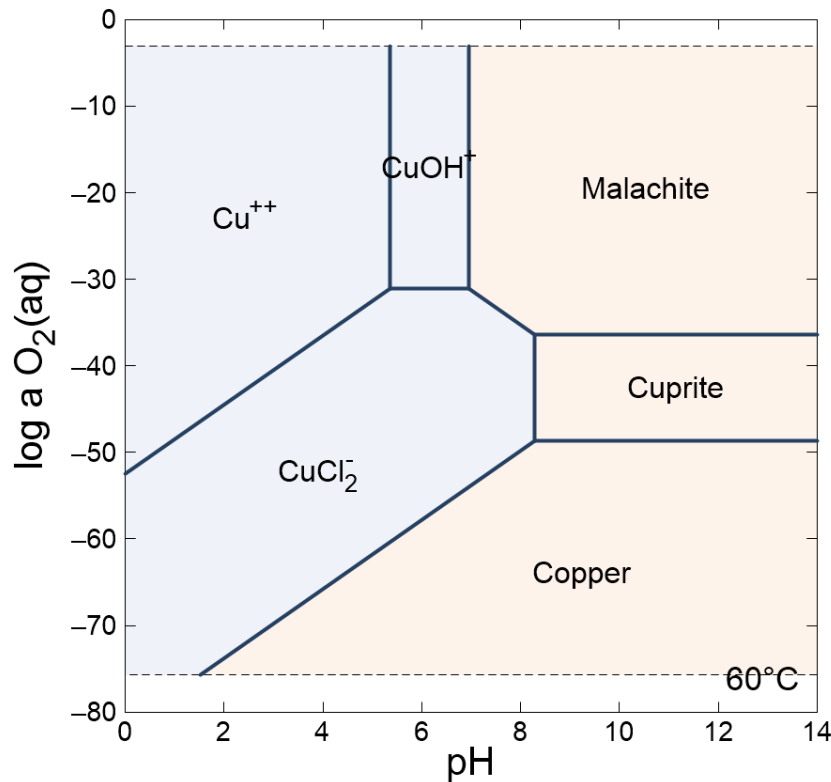
Buttons for 'add' and 'delete' are at the bottom left of the pane.

Or, use the commands

```
T = 60
diagram Cu+ on O2(aq) vs pH
x from 0 to 14
y from -80 to 0
swap CO2(g) for HCO3-
log a Cu+ = -6
a Cl- = 0.1
f CO2(g) = 1
go
```

Move to the **Plot** pane to view the diagram.

The figure below shows the activity-activity diagram drawn at 60°C for the copper-CO<sub>2</sub>-chlorine system at  $f_{\text{CO}_2} = 1$  versus oxygen activity and pH at  $a_{\text{Cl}^-} = .1$ :



Note the implausibility of maintaining in nature this CO<sub>2</sub> fugacity under alkaline conditions.

The effect might be shown better by drawing the diagram at a pH of 6 using the activity of Cl<sup>-</sup> as an axis. Return to the **Basis** pane and click on "H+", then select "Cl-" to take its place as the x-axis species. Set the log activity to range from "-3" to ".5". Finally, note that "H+" has been automatically shifted to the "in the presence of" section with "pH" units. Set the value to "6".

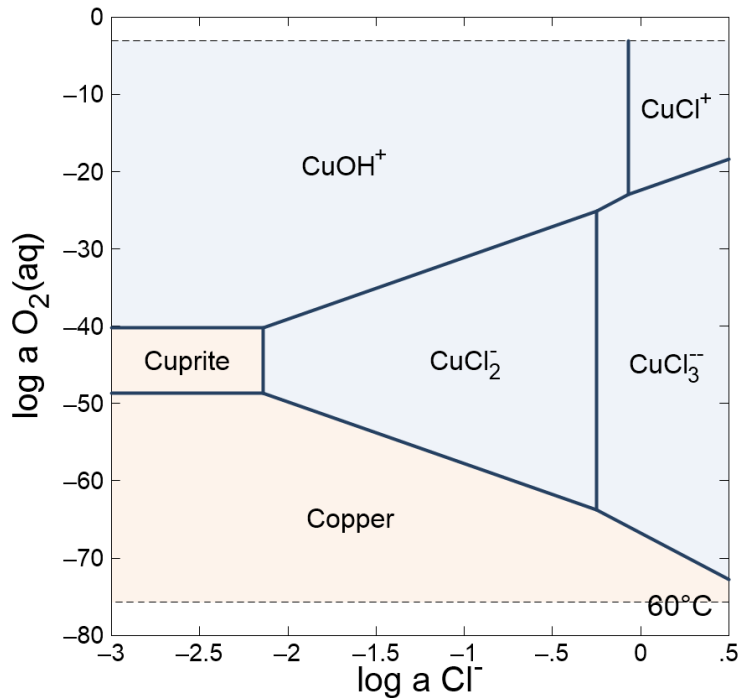
The pane should look like this

The screenshot shows the Act2 software interface with the 'Basis' pane selected. The interface includes a menu bar (File, Edit, Run, Config, Format, View, Help) and four tabs: Basis, Command, Results, and Plot. The 'Basis' pane is divided into several sections:

- diagram species:** A table with one entry: Cu+ with a log activity of -6.0.
- on axes:**
  - on x axis:** Cl- with log activity from -3.0 to 0.5, increment 0.5.
  - on y axis:** O2(aq) with log activity from -80.0 to 0.0, increment 10.0.
- in the presence of:**
  - H2O: activity 1.0, solvent.
  - H+: pH 6.0.
  - CO2(g) and HCO3-: fugacity 1.0.
  - temperature: 60.0 °C.
  - pressure: (empty field) bars.

At the bottom of the 'in the presence of' section are 'add' and 'delete' buttons.

Move to the **Plot** pane to view the diagram. The figure below shows the activity-activity diagram drawn at 60°C for the copper-CO<sub>2</sub>-chlorine system at  $f_{\text{CO}_2} = 1$  versus oxygen activity and  $a_{\text{Cl}^-}$  at pH = 6.



A number of simple aluminosilicate minerals can be formed from kaolinite by exchanging cations for protons and adding or removing silica. The diagram defined by the following steps shows the stability of potassic and calcic aluminosilicates in the presence of quartz.

Reset the configuration (select **File** → **Reset Configuration**) and move to the **Basis** pane. Under “diagram species”, set “Al+++” and then **Mineral... → Kaolinite**.

On the x axis, select “Ca++” and then **Ratio....** Set “Ca++” for the numerator and “H+” squared in the denominator with an exponent of “2”. Set the range from “12” to “20”. On the y axis, select “K+” and then **Ratio....** Set “K+” for the numerator and “H+” in the denominator. Set the range from “2” to “10”.

Under “in the presence of”, click  and select “SiO2(aq)”, then **Mineral... → Quartz**. The **Basis** pane should look like this

The screenshot shows the Act2 software window with the 'Basis' tab selected. The interface includes a menu bar (File, Edit, Run, Config, Format, View, Help) and a tabbed interface with 'Basis', 'Command', 'Results', and 'Plot' tabs. The 'Basis' tab contains several configuration sections:

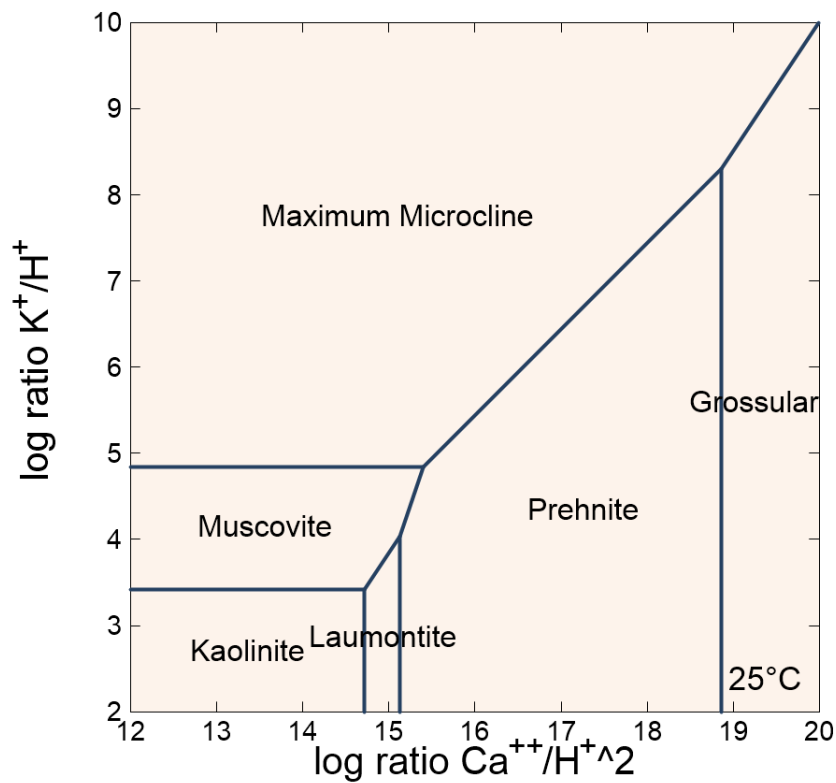
- diagram species:** A table with one entry: Kaolinite ↔ Al+++ with an activity of 1.0.
- on axes:**
  - X-axis: Ca++/H+^2 ↔ Ca++ with a log ratio from 12.0 to 20.0 and an increment of 1.0.
  - Y-axis: K+/H+ ↔ K+ with a log ratio from 2.0 to 10.0 and an increment of 1.0.
- in the presence of:**
  - H2O with an activity of 1.0, labeled as 'solvent'.
  - Quartz ↔ SiO2(aq) with an activity of 1.0.
  - temperature: 25.0 °C.
  - pressure: (empty field) bars.


At the bottom of the 'Basis' tab are 'add' and 'delete' buttons.

Or configure the diagram by the commands

```
swap Kaolinite for Al+++
swap Quartz for SiO2(aq)
swap K+/H+ for K+
swap Ca++/H+^2 for Ca++
diagram Kaolinite on K+/H+ vs Ca++/H+^2
x 12 20; y 2 10
go
```

Move to the **Plot** pane to view the diagram. The figure below shows the stability diagram for aluminosilicate minerals at 25°C plotted versus  $a_{K^+}/a_{H^+}$  and  $a_{Ca^{++}}/a_{H^+}^2$  in the presence of quartz.



To show the effect of varying the silica activity, replace the x axis with  $a_{SiO_2(aq)}$ . Return to the **Basis** pane and next to “Quartz” click  **Unswap**. Next, click on “ $Ca^{++}/H^{+^2}$ ” on the x axis and select “ $SiO_2(aq)$ ” to take its place. Set the x axis to range from “-5” to “-2”. Next, set the y axis to range from “-5” to “10”. Finally, move to the “in the presence of” section and select “ $Ca^{++}/H^{+^2}$ ”, then press **delete**. The pane should look like this



The screenshot shows the Act2 software window with the 'Basis' tab selected. The interface includes a menu bar (File, Edit, Run, Config, Format, View, Help) and four tabs: Basis, Command, Results, and Plot. The 'Basis' tab contains the following configuration sections:

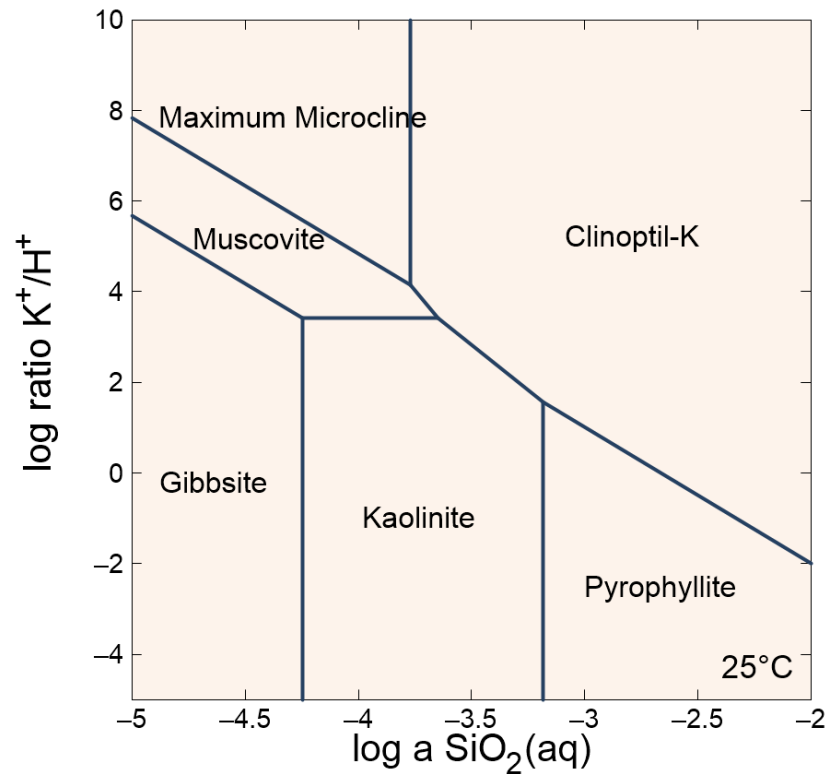
- diagram species:** A table with columns for species, reaction, and activity. It lists 'Kaolinite' with reaction 'Al+++', an activity of '1.0', and a dropdown set to 'activity'.
- on axes:**
  - on x axis:** Species 'SiO2(aq)' with reaction 'log activity', ranging from '-5.0' to '-2.0' with an 'increment' of '0.5'.
  - on y axis:** Species 'K+/H+' with reaction 'K+', ranging from '-5.0' to '10.0' with an 'increment' of '2.0'.
- in the presence of:**
  - 'H2O' with activity '1.0', dropdown 'activity', and label 'solvent'.
  - 'temperature' set to '25.0' with a dropdown 'C'.
  - 'pressure' with an empty field and a dropdown 'bars'.

At the bottom of the 'Basis' tab are 'add' and 'delete' buttons.

Or use the commands

```
(cont'd)
unswap Quartz
diagram vs SiO2(aq)
remove Ca++/H+^2
x -5 -2; y -5 10
go
```

Move to the **Plot** pane to view the diagram. The figure below shows the stability diagram for aluminosilicate minerals at 25°C plotted versus  $a_{K^+}/a_{H^+}$  and  $a_{SiO_2(aq)}$  in the presence of quartz.



## 5.2 Solubility diagrams

Solubility diagrams are similar to the diagrams calculated to this point, except that the activity of the main species, instead of being set to a constant value, appears as an axis variable.

To calculate the solubility of  $U^{++++}$  versus pH, for example, move to the **Basis** pane and under “diagram species”, select “ $U^{++++}$ ”. Leave the activity blank. Under “on axes”, set “ $H^+$ ” and units of “pH” for x. For the y axis, select “ $U^{++++}$ ” and set a range from “-16” to “-6”.

The **Basis** pane should look like this

The screenshot shows the Act2 software window with the 'Basis' tab selected. The configuration is as follows:

- Diagram species:** U++++ (activity, on y axis)
- on axes:**
  - on x axis:** H+ (pH, from 0.0 to 14.0, increment 2.0)
  - on y axis:** U++++ (log activity, from -16.0 to -6.0, increment 1.0)
- in the presence of:**
  - H2O (1.0 activity, solvent)
  - temperature (25.0 C)
  - pressure (bars)

Buttons for 'add' and 'delete' are located at the bottom left of the configuration area.

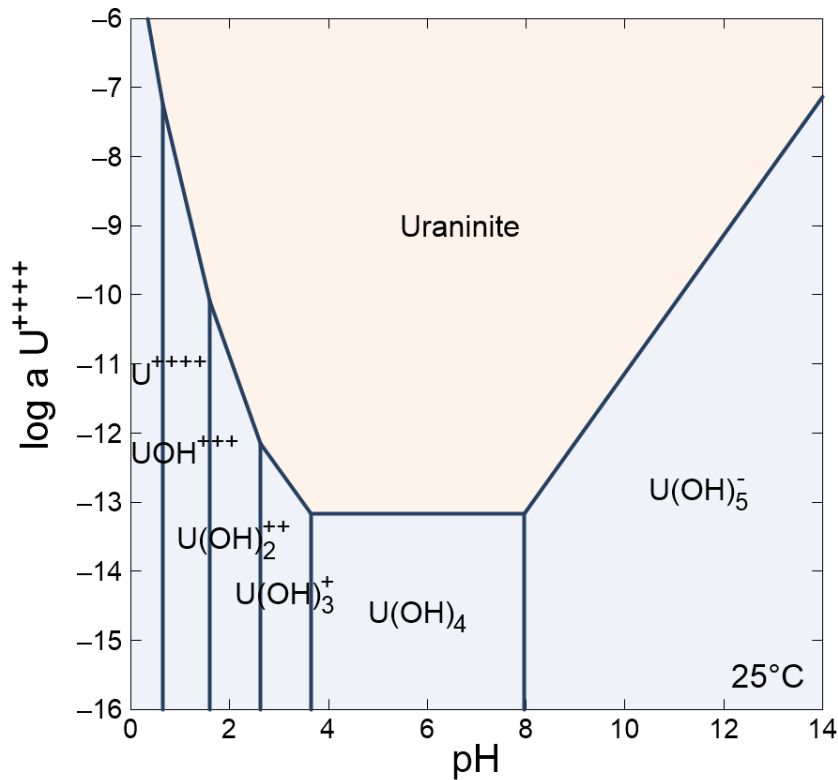
An alternate method would be

```

diagram U++++ on U++++ vs pH
x from 0 to 14
y from -16 to -6
go

```

Move to the **Plot** pane to view your diagram. The figure below shows the solubility diagram for uraninite versus pH at 25°C:



You can similarly take steps to draw a diagram showing the solubility of  $\text{Al}^{+++}$  as a function of pH at 60°C in the presence of quartz. Reset the configuration (select **File** → **Reset Configuration**) and move to the **Basis** pane. Under “diagram species”, select “ $\text{Al}^{+++}$ ”. Leave the activity blank. Under “on axes”, set “H+” and units of “pH” for x. Set the range from “3” to “8”. For the y axis, select “ $\text{Al}^{+++}$ ” and set a range from “-8” to “-5”.

Under “in the presence of”, click  and select “ $\text{SiO}_2(\text{aq})$ ”, then **Mineral...** → **Quartz**. Set temperature to “60°C”. The pane should look like this

Act2

File Edit Run Config Format View Help

**Basis** Command Results Plot

diagram species

Al+++  $\rightleftharpoons$  activity on y axis

on axes

H+  $\rightleftharpoons$  on x axis  
pH from 3.0 to 8.0 increment 0.5

Al+++  $\rightleftharpoons$  on y axis  
log activity from -8.0 to -5.0 increment 0.5

in the presence of

H2O 1.0 activity solvent

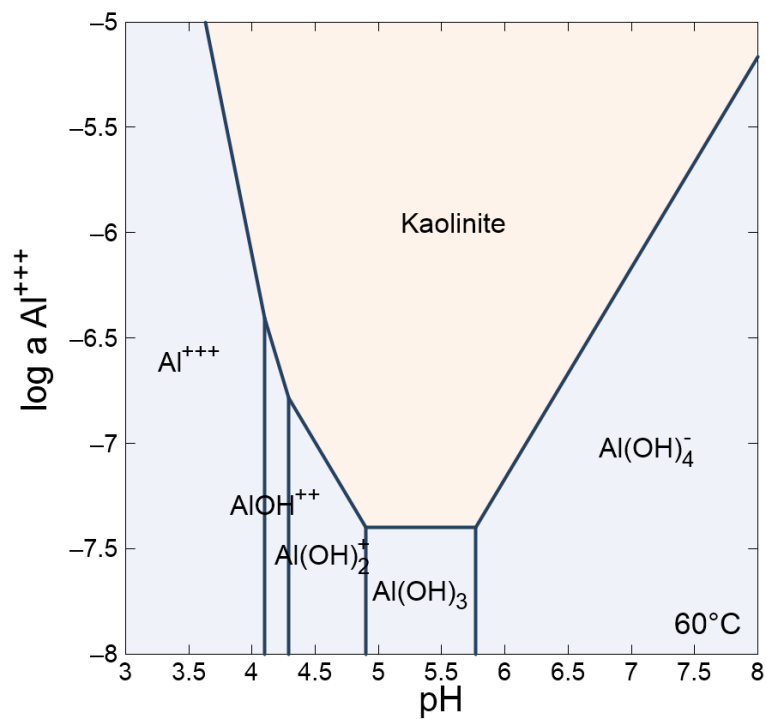
Quartz  $\rightleftharpoons$  SiO2(aq) 1.0 activity

temperature 60.0 C

pressure bars

add delete


Move to the **Plot** pane to view the diagram, which is shown below.




### 5.3 Mosaic diagrams

Calculating diagrams that include complexing ions is complicated in some cases by the speciation of the ions over the diagram axes. For example, while the bicarbonate ion  $\text{HCO}_3^-$  is important at moderate pH values, it reacts under acidic conditions to form  $\text{CO}_2(\text{aq})$ , and under alkaline conditions to form  $\text{CO}_3^{2-}$ . Similarly, the sulfate ion  $\text{SO}_4^{2-}$  occurs in acidic waters as  $\text{HSO}_4^-$  and under reducing conditions as  $\text{H}_2\text{S}(\text{aq})$ ,  $\text{HS}^-$ , and  $\text{S}^{2-}$ ;  $\text{NO}_3^-$  is found in the reduced forms  $\text{HNO}_2$ ,  $\text{NO}_2^-$ ,  $\text{N}_2$ ,  $\text{NH}_4^+$ , and  $\text{NH}_3$ ; and  $\text{HPO}_4^{2-}$  reacts depending on pH to form  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{PO}_4^-$ , and  $\text{PO}_4^{3-}$ .

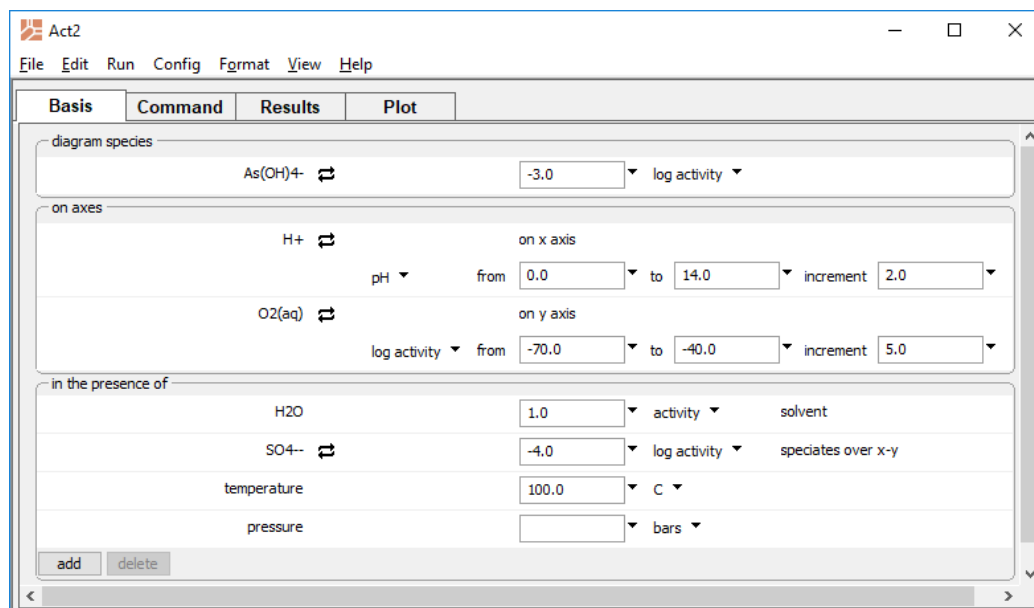
In such cases, **Act2** can calculate mosaic diagrams in which the overall calculation is divided into subdiagrams, in which a single form of a complexing species predominates in each. Assembled, the subdiagrams form the complete diagram. The program allows any number of complexing ions to speciate. Each ion may speciate by reaction with the species on both of the axes, or the x axis or y axis alone.

Set a mosaic diagram by adding a species to the diagram using the  button on the **Basis** pane in the “in the presence of” section. Then, under the corresponding units pulldown, select to speciate that species over x, y, or both x and y. Alternatively, you can use the `speciate` command.

The following example, using the chemistry of the arsenic-sulfur system, shows the importance of the mosaic diagram. Move to the **Basis** pane and, under “diagram species”, select “ $\text{As}(\text{OH})_4^-$ ”. Set the log activity to “-3”. Under “on axes”, set “H+” and units of “pH” for x. For the y axis, select “ $\text{O}_2(\text{aq})$ ” and set a range from “-70” to “-40”.

Under “in the presence of”, click  and select “ $\text{SO}_4^{2-}$ ”. Set log activity to “-4”, then click the pulldown next to log activity and select “speciates over x-y”. Set temperature to “100°C”.

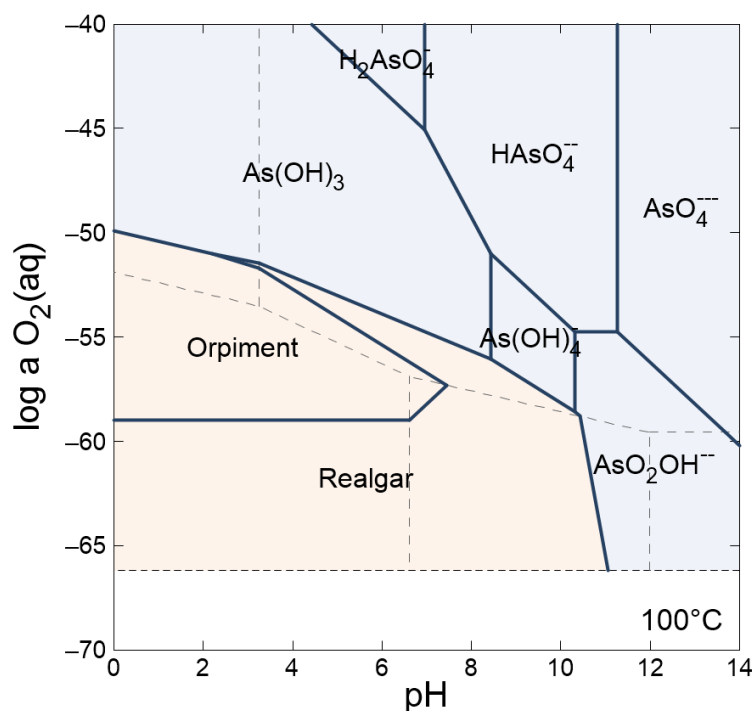
The pane should look like this



Or use the commands

```
T = 100 C
diagram As(OH)4- on O2(aq) vs pH
x from 0 to 14
y from -70 to -40
log a As(OH)4- = -3
log a SO4-- = -4
speciate SO4--
go
```

Move to the **Plot** pane to view the diagram. The figure below shows a diagram predicting the importance of the sulfide minerals orpiment ( $\text{As}_2\text{S}_3$ ) and realgar ( $\text{AsS}$ ) under reducing conditions.



Interior broken lines show mosaic boundaries for sulfur speciation. Subdiagrams in the mosaic, from upper left to lower right, are for the species  $\text{HSO}_4^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{H}_2\text{S(aq)}$ ,  $\text{HS}^-$ , and  $\text{S}^{2-}$ . The basal broken line (black) is the stability limit for water under reducing conditions at 1 atm pressure. You can hover with your mouse over any field in the diagram to see the species assemblage there as a tooltip, and over any line to see the reaction it represents.

Note that if we had not made a mosaic diagram but had instead assumed that  $\text{SO}_4^{2-}$  or  $\text{HS}^-$  predominates over the entire diagram, the result would be significantly in error.

To test the first variation, click the pulldown next to log activity and select “speciates over x-y” once again to disable the option. The pane should look like

SO4--
↔


-4.0

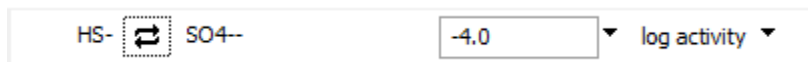
▼
log activity
▼

You could also type

*(cont'd)*  
 unspeciate SO4--  
 go



To test the second case, click the  button next to “SO4--” and choose **Aqueous... → HS-**, as shown below,




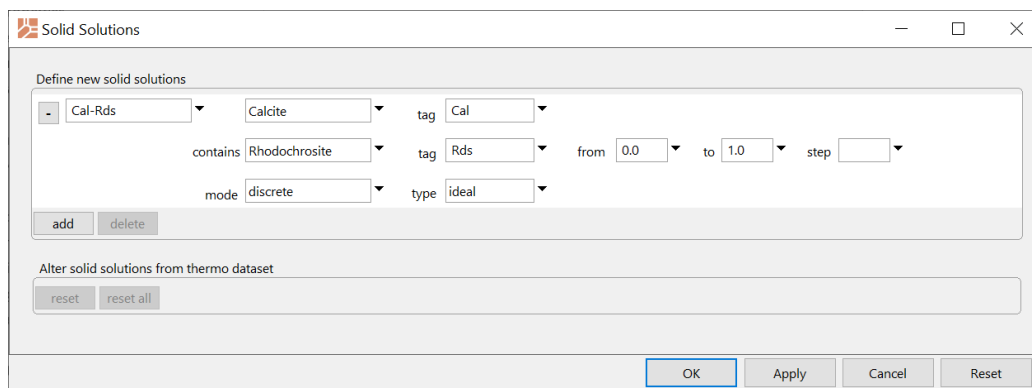
or type

```
(cont'd)
swap HS- for SO4--
go
```


## 5.4 Solid solution diagrams

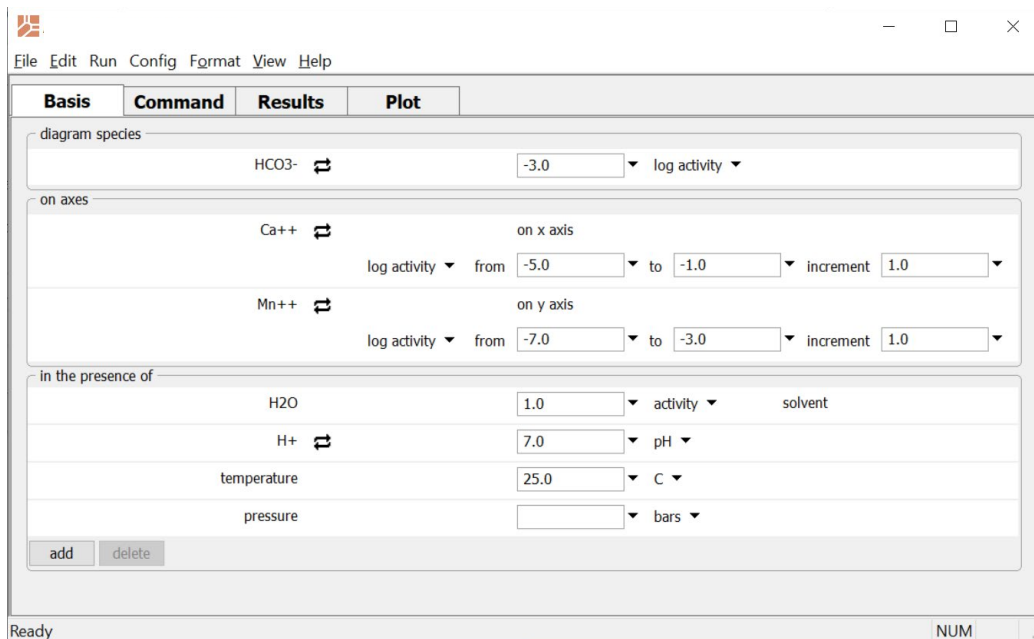
**Act2** can create diagrams accounting for solid solutions in discrete mode (see [Solid solutions](#) under **Configuring the Programs**), in which the solution is represented by a series of tranches spanning the solution’s range in composition.

As an example, we diagram an ideal solution of calcite,  $\text{CaCO}_3$ , and rhodochrosite,  $\text{MnCO}_3$ . Go to **Config → Solid Solutions...**, click  under “Define new solid solutions”, and expand the selection with the “+” button. Supply a name “Cal-Rds” in the first box, choose end-member minerals “Calcite” and “Rhodochrosite”, and set tags “Cal” and “Rds”, respectively. Click **Apply**



Since no step was set, the tranches are spaced by  $1/20^{\text{th}}$  of the compositional range. As such, the app will construct tranches Cal(.95)-Rds(.05), Cal(.9)-Rds(.1), and so on.

On the **Basis** pane, under diagram species, click on “???” and select “ $\text{HCO}_3^-$ ”. Set “log activity” to “-3”. Under “on axes”, set “ $\text{Ca}^{++}$ ” along  $x$  with a range from “-5” to “-1”. Along the  $y$  axis, select “ $\text{Mn}^{++}$ ” and set a range from “-7” to “-3”. Under “in the presence of”, click  and select “ $\text{H}^+$ ”. Set “pH” for the entry to “7”. The pane should look like



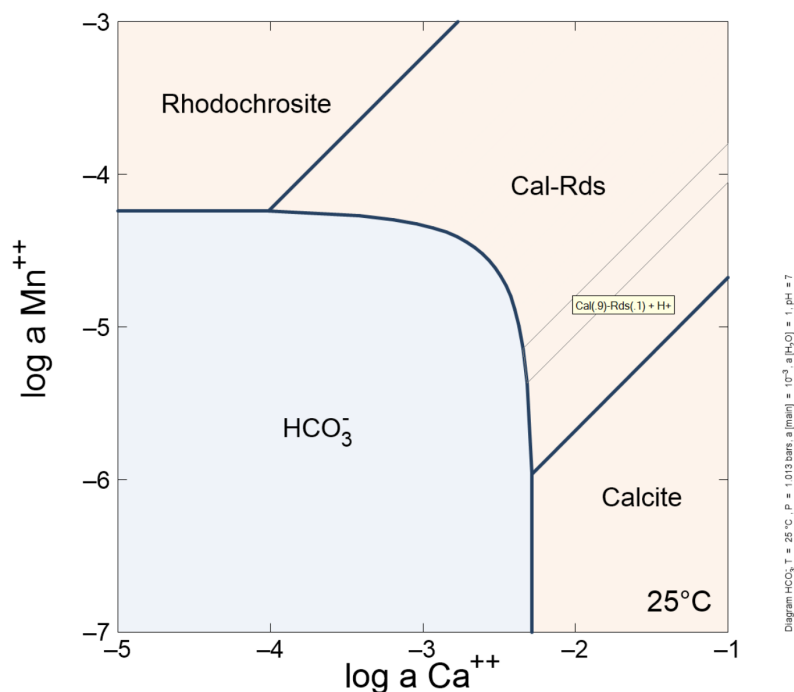
Alternatively, use the commands

```
solid_solution Cal-Rds Calcite tag Cal contains \
Rhodochrosite tag Rds

diagram HCO3- on Mn++ vs Ca++
x from -5 to -1 increment 1
y from -7 to -3 increment 1
log a HCO3- = -3
pH = 7
go
```

to configure the calculation.

Move to the **Plot** pane to view the diagram, which shows the stability of the solid solution as a function of the activity of the substituting ions. You can click within the solid solution field “Cal-Rds” to outline the stability of any tranche. Hovering your cursor over the tranches reveals its composition in a tooltip, as shown below



The tranches are grouped into a stability field and labeled with the solid solution's name. The end members are plotted separately but should not be interpreted as distinct phases. The boundary between an end member and the closest tranche is simply a reflection of the discretization ("step") used for the calculation. The line separating "Cal-Rds" from "HCO3-" appears to be curved but is in fact composed of a series of short straight segments, one per tranche.

The solid solution has a larger stability field than its pure end-member minerals combined, which we can see by suppressing it on the **Suppress...** dialog or by typing

```
(cont'd)
suppress Cal-Rds
go
```

Reenabling the solid solution, we can compare a non-ideal version by changing the "type" pulldown on the **Solid Solutions...** dialog to "Guggenheim" and setting a hypothetical value of "2.2" for the "a0" coefficient, or by typing

```
(cont'd)
unsuppress Cal-Rds
solid_solution Cal-Rds Guggenheim a0 = 2.2 a1 = 0
go
```

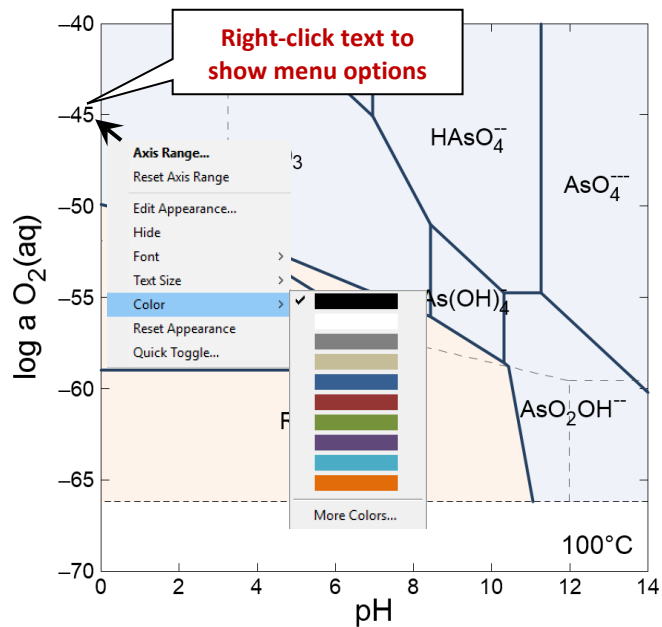
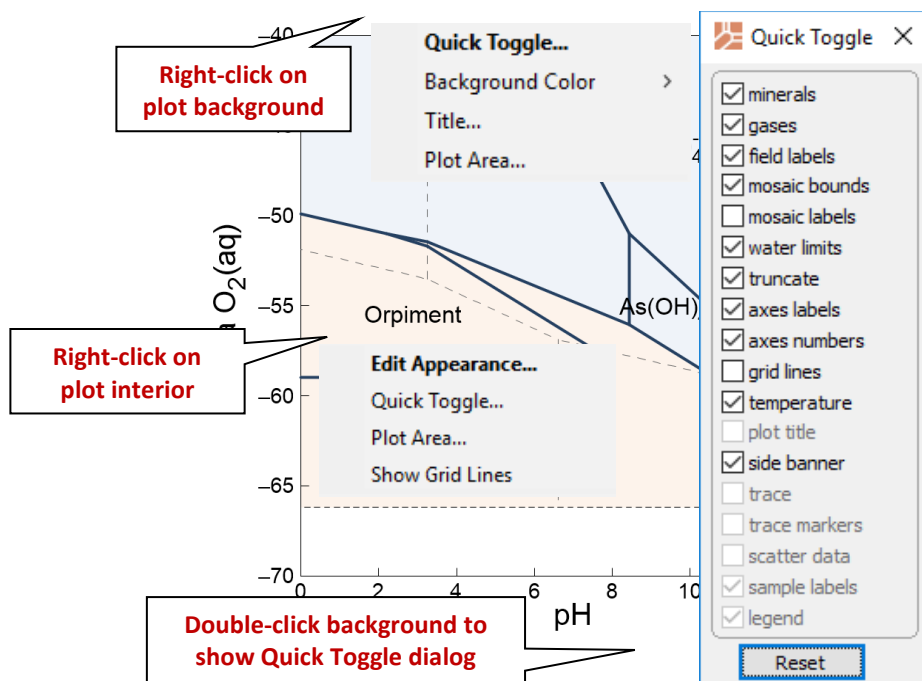
In this case, a miscibility gap can be ascertained by a sharp change in curvature of the “Cal-Rds” and “HCO<sub>3</sub>-” boundary, and by the exclusion of one or more adjacent tranches within the Cal-Rds stability field.

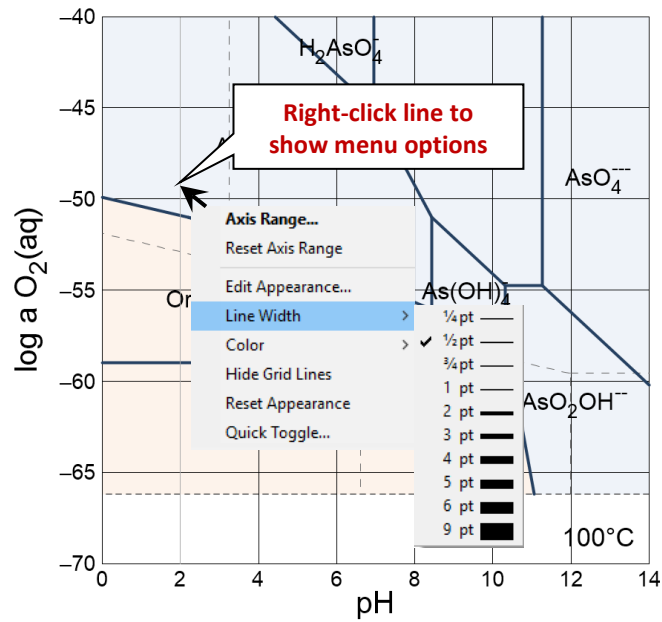
Upon close inspection, compositions between Cal(.25)-Rds(.75) and Cal(.75)-Rds(.25) are not stable. The miscibility gap is symmetrical about a mole fraction of 0.5, reflecting the zero-value assumed for the “a<sub>1</sub>” Guggenheim coefficient. A positive “a<sub>1</sub>” value would shift the miscibility gap towards rhodochrosite, the second end member.

In the preceding example, the discrete solid solution was described adequately by discretizing the entire possible range. When a solid solution contains trace amounts of an end member, you may prefer to limit the range using the “from” and “to” fields. When a solid solution has a very large miscibility gap, you might benefit from specifying two solid solution entries, as described in [Solid solutions](#) under **Configuring the Programs**.

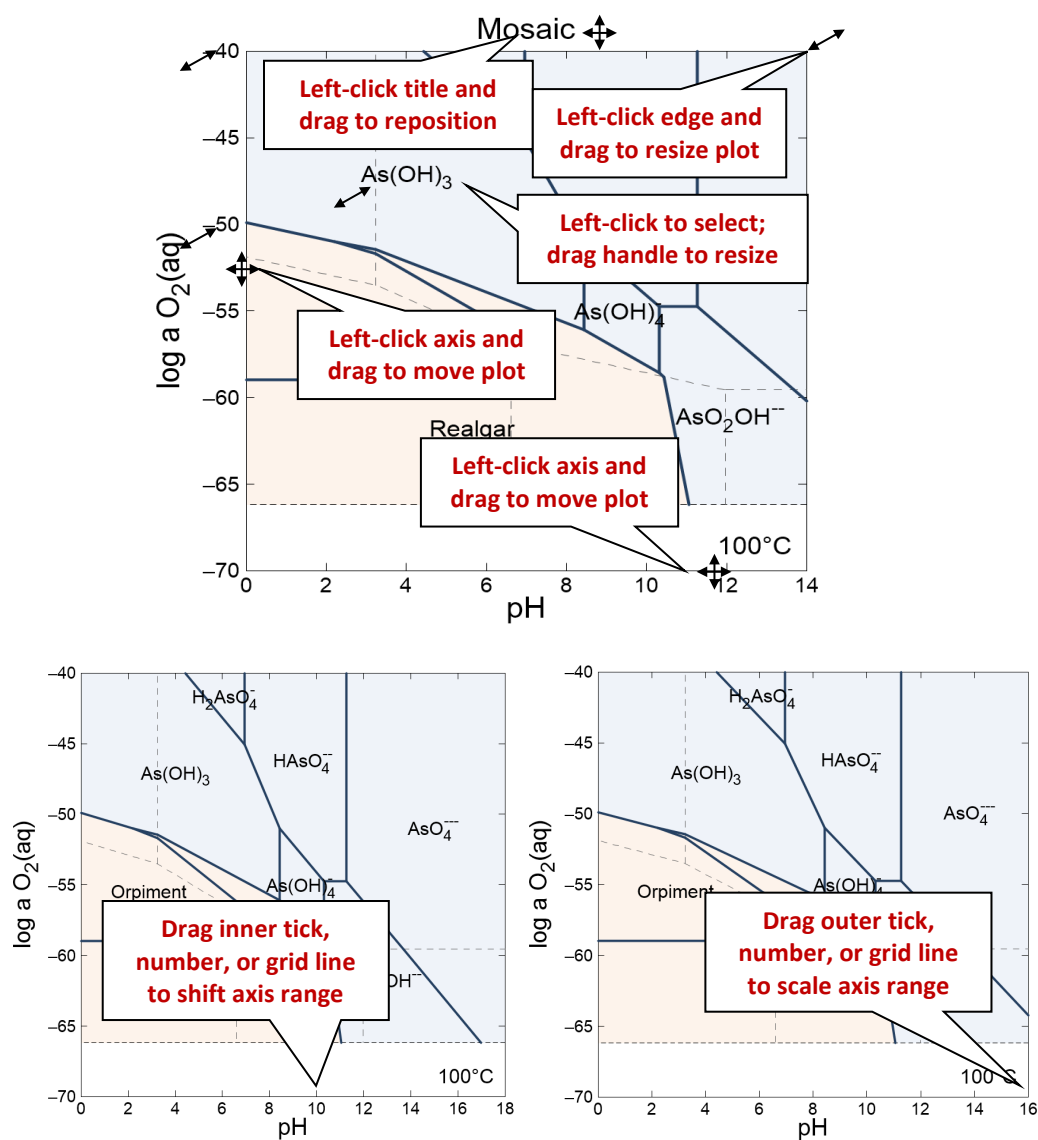
## 5.5 Editing plot appearance

In **Act2** you can interactively modify many aspects of the diagram. A **right-click** on an aspect or area of the plot displays a menu showing the options available. You may choose to reset an axis range or an aspect’s appearance to its default state. A **double-click** on an aspect brings up a dialog box related to the first item on the pulldown menu, which in most cases is the aspect’s appearance dialog. The dialogs can also be accessed through the **Format** menu. To change the font for individual aspects, choose **Font** from that aspect’s menu. A double-click on the background area will bring up the **Quick Toggle...** dialog, which lets you select the graphical elements to be shown.





A **left-click** on an aspect causes it to be “selected”. An aspect has been selected when its color changes, as in the case of lines, or when it is surrounded by manipulation handles, in the case of text or markers. Change the size of text, markers, and the plot itself by dragging the sizing cursors. Adjust the placement of the plot by clicking within the plot or on either axis and dragging it. The plot title can be moved in the same way.

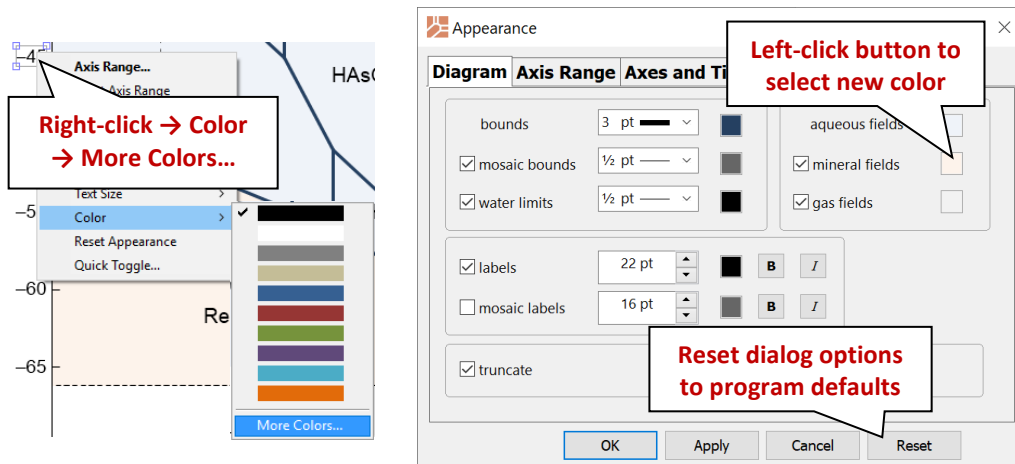


You can change the range on an axis by **clicking and dragging** a tick mark, number, or grid line. Dragging a tick within an axis shifts all of the values along the axis, effectively changing the minimum and maximum values at the ends of the axis, but keeping the spacing the same. Dragging the tick at an end of an axis changes the minimum or maximum value. To reset the axis range to span the range of the data being plotted, choose **Reset Axis Range** from the aspect menu.

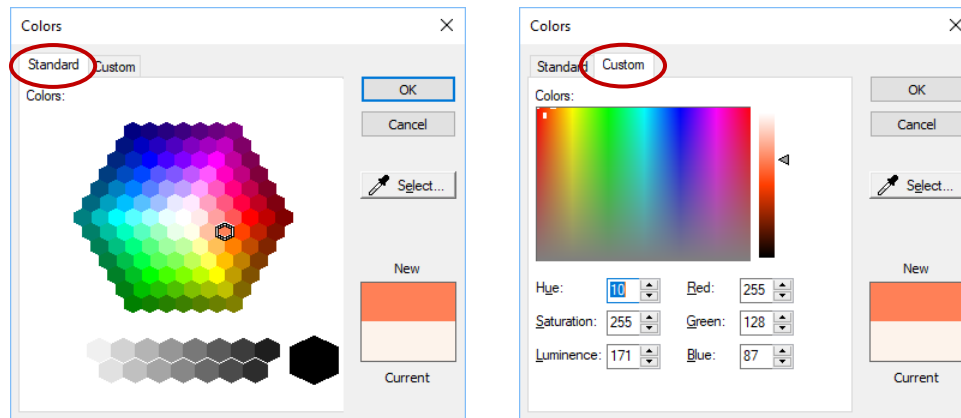
You can set all of the graphical attributes in the aspect appearance dialogs available through the **Format** menu. When you make changes to values or selections in an aspect appearance dialog, the changes don't take effect on the plot immediately. You can set up

your choices for as many of the aspects as you like, or use the **Reset** button to reset the dialog to its default values. Use the **Apply** or **OK** button to apply the changes to the plot. Use the **Cancel** button if you decide that you don't want the changes applied.

Selecting **Color** → **More Colors...** from any aspect menu or clicking on any color button in an aspect appearance dialog allows you to set the color of the relevant aspect.



The **Colors** dialog presents a hexagonal palette of colors on the **Standard** tab. To create custom colors, move to the **Custom** tab.



In either tab, the current color of the aspect is displayed, as is any new selection you make. You can click **Select...** to turn your cursor into a dropper that picks the color from any window on your monitor. Once you make a selection, click **OK** to set the color, or **Cancel** to discard the selection and close the dialog.



## 5.6 Reaction traces

**Act2** can overlay onto a diagram the trace of a reaction path calculated with the **React** program. To project the trace of a reaction, first use **React**, as described in **Using React** in the *GWB Reaction Modeling Guide*, to calculate the reaction path. **React** produces an output dataset “React\_plot.gtp”, which **Act2** can read.

Within **Act2**, select **File** → **Open** → **Reaction Trace...** to select a “.gtp” file produced by a previous **React** run. After making the selection, the **Trace...** dialog (which is accessible from the **Format** pulldown menu) can be used to add additional “.gtp” files or remove them from the diagram. The dialog shows the status of each selected trace. A “.gtp” file will be skipped if, for example, it is incompatible with the axis variables or the temperature range of the diagram.

Use the **Trace...** dialog to change the default line width and color of a trace, as well as the symbol, color, and size (in points) of the markers on the trace. Unique settings for the markers at the start or end of the reaction path can be used to indicate the direction of reaction progress. Use the checkbox next to each aspect to show or hide it on the diagram.

After you hit **Apply** or **OK**, the program will read the data points and project them onto the diagram. Clear a trace file by selecting it and hitting the **delete** button, or remove all files by clicking **Reset**.

When multiple “.gtp” files are loaded, check the box labeled “set trace data appearance individually” to independently control the appearance of the trace and markers for each dataset.

## 5.7 Scatter data

You can overlay the data points in a **GSS** data sheet (a .gss file) as “scatter data” on your **Act2** diagram. First, check that the .gss file contains the axis variables on your diagram (pH, Eh, pe, species activity, or gas fugacity) or the activities of the original basis entries in the thermo dataset, so **Act2** can figure these values. **Act2** can figure an activity ratio from the activity of individual species in your .gss file.

Remember that **Act2** diagrams are plotted in terms of species’ activities and fugacities, not chemical concentrations. You can quickly add activities and fugacities to your .gss files as “calculated analytes,” as described in the [Calculating analytes](#) section of the **Using GSS** chapter in this guide. Alternatively, you can add user analytes for species’ activities, fugacities, or activity ratios when these values are known. See the [User analytes](#) section of the **Using GSS** chapter in this guide for more information. For an activity ratio such as  $a_{\text{Ca}^{++}}/a_{\text{H}^{+}}^2$ , choose the user-defined analyte category “Species activities”, and write the analyte’s name as Ca<sup>++</sup>/H<sup>+</sup><sup>2</sup> to match its appearance on the activity diagram.

Even if your data sheet contains O<sub>2</sub>(aq) concentration in mg/kg, for example, it would have to also include the *activity* of O<sub>2</sub>(aq) in order for the data to appear on a log a O<sub>2</sub>-pH

diagram. Add O<sub>2</sub>(aq) activity to your data sheet as a calculated analyte, separate from the dissolved oxygen measurements.

An example of a .gss dataset containing **Act2** scatter data is

			1 ●	2 ▲	3 ▼	+ sample
Al <sup>+++</sup>	▲ mg/kg	▶	0.07			
Fe <sup>++</sup>	▼ mg/kg	▶	0.06	0.02		
Ca <sup>++</sup>	● mg/kg	▶	17.96	45.04	14.99	
Mg <sup>++</sup>	▲ mg/kg	▶	1.1	10	4.1	
Na <sup>+</sup>	▼ mg/kg	▶	1.8	20	6.3	
K <sup>+</sup>	◆ mg/kg	▶		2.9	2.3	
HCO <sub>3</sub> <sup>-</sup>	✱ mg/kg	▶	19	113	58	
SO <sub>4</sub> <sup>2-</sup>	◆ mg/kg	▶	3	51	11	
Cl <sup>-</sup>	☆ mg/kg	▶	1.9	24	7.8	
F <sup>-</sup>	⊕ mg/kg	▶	0.2	0.3		
NO <sub>3</sub> <sup>-</sup>	◆ mg/kg	▶	0.1	2.4	1	
TDS	◆ mg/kg	▶	28	232	89	
pH	■	▶	6.5	7.4		
Ca <sup>++</sup>	○ log activity	▶	-3.418	-3.113	-3.524	
K <sup>+</sup>	▽ log activity	▶		-4.166	-4.253	
SiO <sub>2</sub> (aq)	◇ log activity	▶	-3.934	-3.882	-3.665	

+ analyte

Click on **File → Open → Scatter Data...** to read a .gss file into **Act2**. After making the selection, the **Scatter Dialog...** dialog (which is accessible from the **Format** menu) can be used to add additional “.gss” files or remove them from the diagram. The dialog shows the status of each selected dataset. A “.gss” file will be skipped if, for example, it is incompatible with the axis variables or the temperature range of the diagram.

After you hit **Apply** or **OK**, the program will read the data points and project them onto the diagram. Clear a scatter dataset by selecting it and hitting the **delete** button or remove all datasets by clicking **Reset**.

The marker representing each sample in the scatter data is set in the .gss file. In **GSS**, right-click on a sample to change the marker used and its color and size. When you modify a .gss file, the changes will sync with **Act2** automatically. To add error bars to the scatter points, enter triplets (0.5|2.0|3.5) in the data cells (see **Error bars** in **Using GSS**).

You can label each data point with the sample’s “Sample ID”, as set in the .gss file, and display a legend showing the symbols used. In **Act2**, choose **Format → GSS Data...** and under “Labels” select the checkbox for “Sample” to show sample labels, and the “Legend” box to display the legend. Use the **Format → Quick Toggle...** dialog to quickly toggle on and off display of the scatter data, data labels, and legend.

In **GWB** releases 7.0 and earlier, the program took scatter data from a specially formatted text file, rather than a .gss data sheet. Legacy scatter files are still supported and described in the **Scatter Data** chapter in the **GWB Reference Manual**.

## 5.8 Act2 command line

You can start **Act2** by clicking the icon under the “Start” menu, opening a “.ac2” file, or entering the command `act2.exe` in the Windows “Command Prompt.”

When you start **Act2** from the command line (as opposed to clicking on the icon), you can specify a number of arguments. For example, the command

```
act2 -i my_script -d my_thermo.tdat
```

causes **Act2** to read input commands from a file “my\_script”, and to use “my\_thermo.tdat” as the thermodynamic database.

The following options are available from the command line:

<code>-cd</code>	Change the working directory to the directory containing the input script specified with the <code>-i</code> option.
<code>-nocd</code>	Do not change the working directory.
<code>&lt;input_script&gt;</code> <code>-i &lt;input_script&gt;</code>	Set a file from which to read input commands.
<code>-gtd &lt;gtdata_dir&gt;</code>	Set directory to search for thermodynamic datasets.
<code>-d &lt;thermo_data&gt;</code>	Set the thermodynamic dataset.



# Using Tact

**Tact** is a program that calculates and plots temperature-activity and temperature-fugacity diagrams. Diagrams of this type show the effect of temperature on the stability of minerals and the predominance of aqueous species in chemical systems. **Tact** is very similar to **Act2**, except that the vertical axis represents temperature instead of an activity or fugacity.

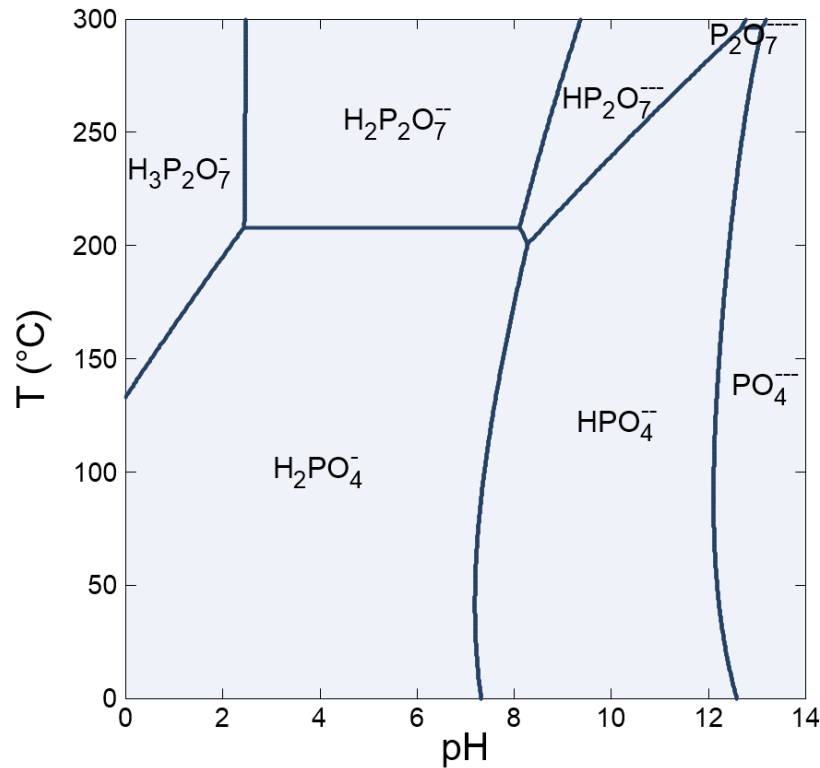
To diagram, for example, the thermal stability of phosphate species versus pH, you follow the same steps you would use in **Act2**, except that you need not specify a variable for the y axis. Under “diagram species” on the **Basis** pane, click on “???” (or any species already there), select “HPO4--”, and then set the species’ log activity to “-3”. Under “on axes”, click on “???” , choose “H+” and set units to “pH”. The **Basis** pane should look like this:

The screenshot shows the Tact software window with the 'Basis' pane selected. The 'diagram species' section has 'HPO4--' selected with a log activity of -3.0. The 'on axes' section has 'H+' selected for the x-axis (pH) ranging from 0.0 to 14.0 with an increment of 2.0, and 'temperature' selected for the y-axis (C) ranging from 0.0 to 300.0 with an increment of 50.0. The 'in the presence of' section has 'H2O' selected with an activity of 1.0, and 'pressure' is set to bars. There are 'add' and 'delete' buttons at the bottom.

Alternatively, enter the commands

```
diagram HPO4-- vs pH
a HPO4-- = 10^-3
x from 0 to 14
go
```

on the **Command** pane. Now move to the **Plot** pane to display the resulting diagram, which shows the predominance of phosphate species versus temperature and pH.



The program also produces text output in dataset “Tact\_output.txt” (click on **File** → **View** → **Tact\_output.txt**).

## 6.1 Diagram calculation

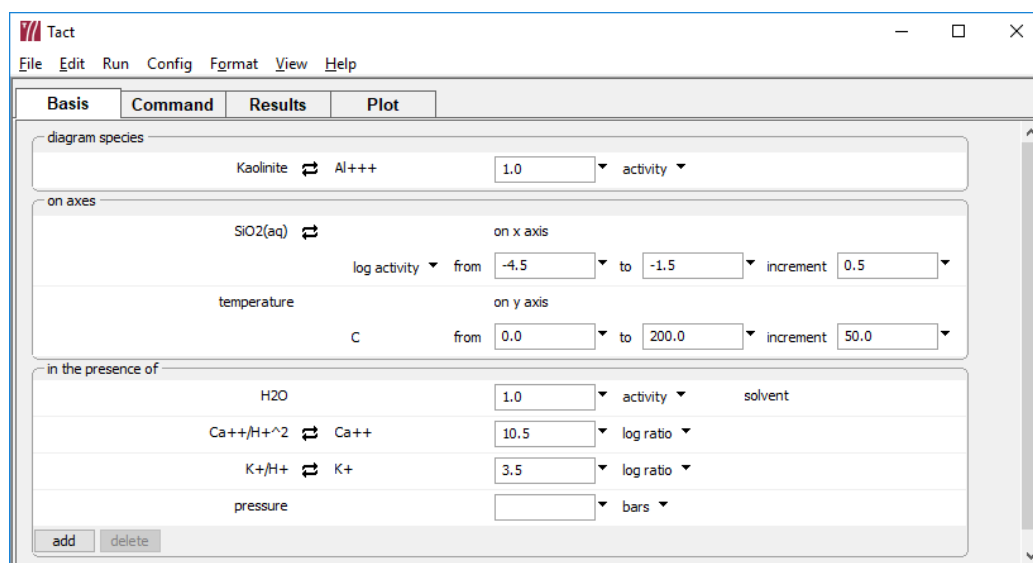
**Tact**, like **Act2**, can assume any activity or fugacity variable on the x axis and can account for the presence of minerals, complexing species, and gas buffers. You might, for example, calculate the stabilities of aluminosilicate minerals versus  $\text{SiO}_2(\text{aq})$  activity in a system of known ratios  $a_{\text{Ca}^{++}}/a_{\text{H}^+}^2$  and  $a_{\text{K}^+}/a_{\text{H}^+}$ .

To start, move to the **Basis** pane. Under “diagram species”, set “Al+++” and then **Mineral...** → **Kaolinite**.

On the x axis, select “ $\text{SiO}_2(\text{aq})$ ” and then set the range from “-4.5” to “-1.5”. Set the y-axis range from “0” to “200”.

Under “in the presence of”, click  and select “Ca++”, then click on **Ratio...** Set “Ca++” for the numerator and “H+” squared in the denominator with an exponent of “2”. Change the unit to “log ratio” and set the value to “10.5”.

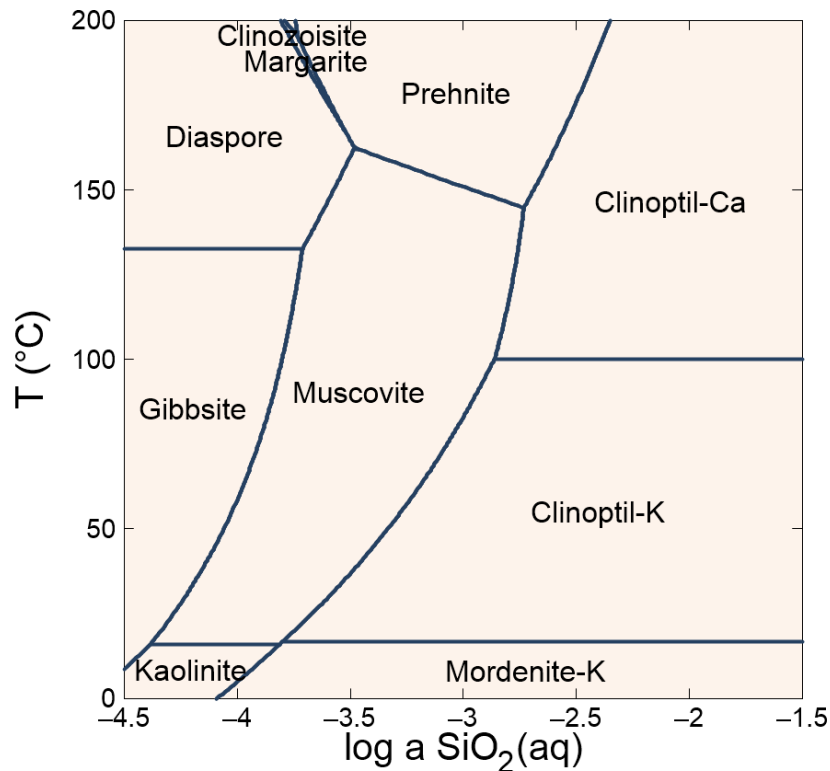
Next, click **add** and select “K+”, then click on **Ratio....** Set “K+” for the numerator and “H+” in the denominator. Change the unit to “log ratio” and set the value to “3.5”.  
The **Basis** pane should look like this



Alternative steps are

```
swap Kaolinite for Al+++
swap Ca++/H+^2 for Ca++
swap K+/H+ for K+
diagram Kaolinite vs SiO2(aq)
log ratio Ca++/H+^2 = 10.5
log ratio K+/H+ = 3.5
x from -4.5 to -1.5 incr 1/2
y from 0 to 200
go
```

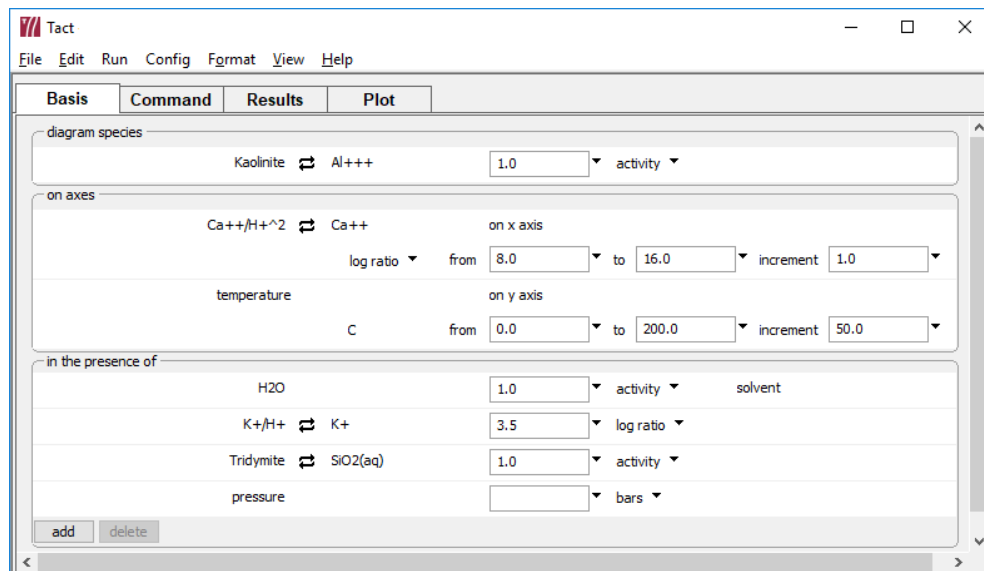
Move to the **Plot** pane to view the diagram of the stability of aluminosilicate minerals versus  $a_{\text{SiO}_2(\text{aq})}$ , assuming  $a_{\text{K}^+}/a_{\text{H}^+} = 10^{3.5}$  and  $a_{\text{Ca}^{++}}/a_{\text{H}^+}^2 = 10^{10.5}$ .



To diagram the same system with the  $\text{SiO}_2(\text{aq})$  activity fixed by equilibrium with tridymite, and the  $a_{\text{Ca}^{++}}/a_{\text{H}^+}^2$  ratio as the axis variable, return to the **Basis** pane. Move to the “in the presence of” section and select “Ca<sup>++</sup>/H<sup>+</sup>^2”, then press **delete**. Under “on axes”, click on “SiO<sub>2</sub>(aq)” and select “Ca<sup>++</sup>” from the pulldown to take its place, then click **Ratio**. Set “Ca<sup>++</sup>” for the numerator and “H<sup>+</sup> squared in the denominator with an exponent of “2”. Set the x axis to range from “8” to “16”.



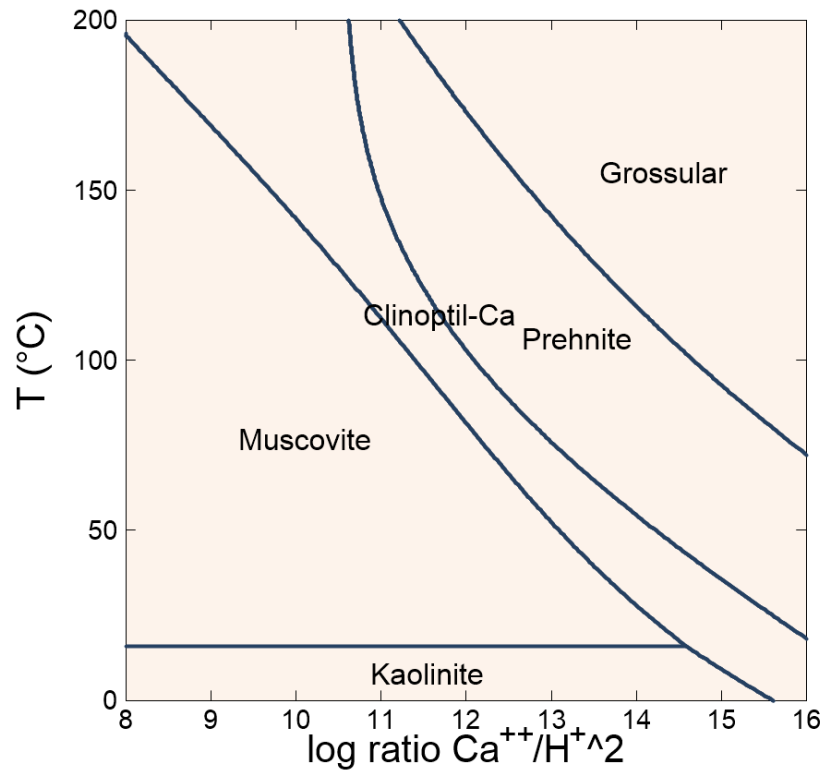
Now that “SiO<sub>2</sub>(aq)” has been automatically transferred to the “in the presence of” section, select **↔ Mineral → Tridymite**. The pane should look like this



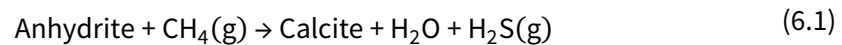
Or type the commands

```
(cont'd)
diagram vs Ca++/H+^2
swap Tridymite for SiO2(aq)
x from 8 to 16
```

Move to the **Plot** pane to view the diagram. The resulting diagram is shown here.



As a second exercise, diagram the equilibrium point of the souring reaction of natural gas



in terms of the fugacity ratio of methane to  $\text{H}_2\text{S}$ . Reset the configuration (select **File → Reset Configuration**) and move to the **Basis** pane. Under “diagram species”, set “ $\text{Ca}^{++}$ ” and then **Mineral... → Calcite**.

On the x axis, select “ $\text{SO}_4^{--}$ ” and then **Ratio....** Set “ $\text{H}_2\text{S}(\text{g})$ ” for the numerator and “ $\text{CH}_4(\text{g})$ ” in the denominator. Set the range from “-15” to “10”.

The **Basis** pane should look like this

The screenshot shows the Tact software window with the 'Basis' tab selected. The configuration is as follows:

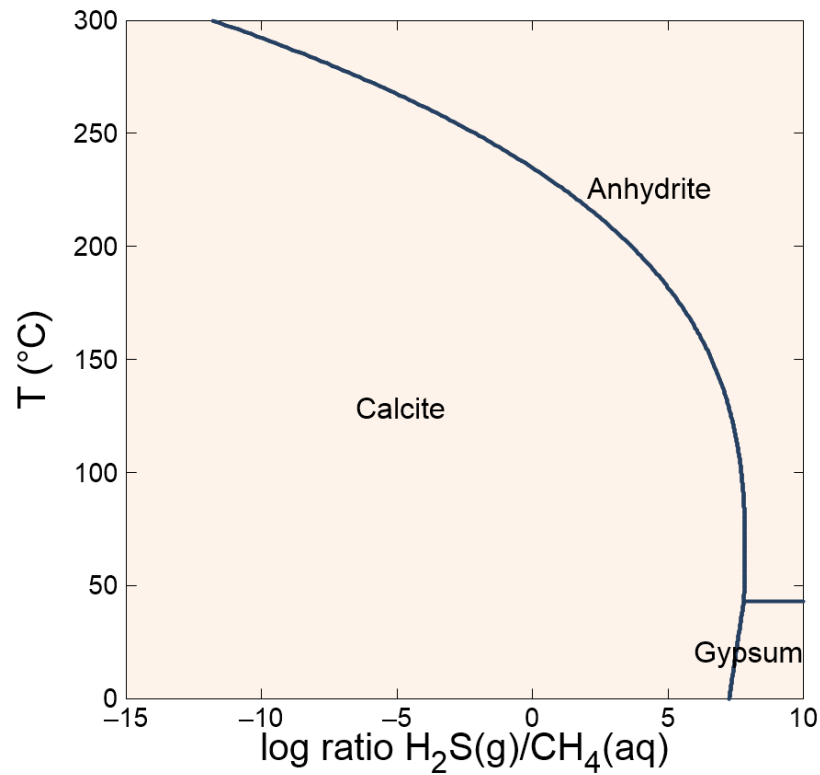
- Diagram species:** Calcite ↔ Ca++ with an activity of 1.0.
- On axes:**
  - X-axis:** H2S(g)/CH4(aq) ↔ SO4-- with a log ratio from -15.0 to 10.0 and an increment of 5.0.
  - Y-axis:** temperature in °C from 0.0 to 300.0 with an increment of 50.0.
- In the presence of:**
  - H2O with an activity of 1.0, labeled as solvent.
  - pressure (field is empty), labeled as bars.

Buttons for 'add' and 'delete' are located at the bottom left of the configuration area.

Or use the commands

```
swap Calcite for Ca++
swap H2S(g)/CH4(g) for SO4--
diagram Calcite vs H2S(g)/CH4(g)
x from -15 to 10
go
```

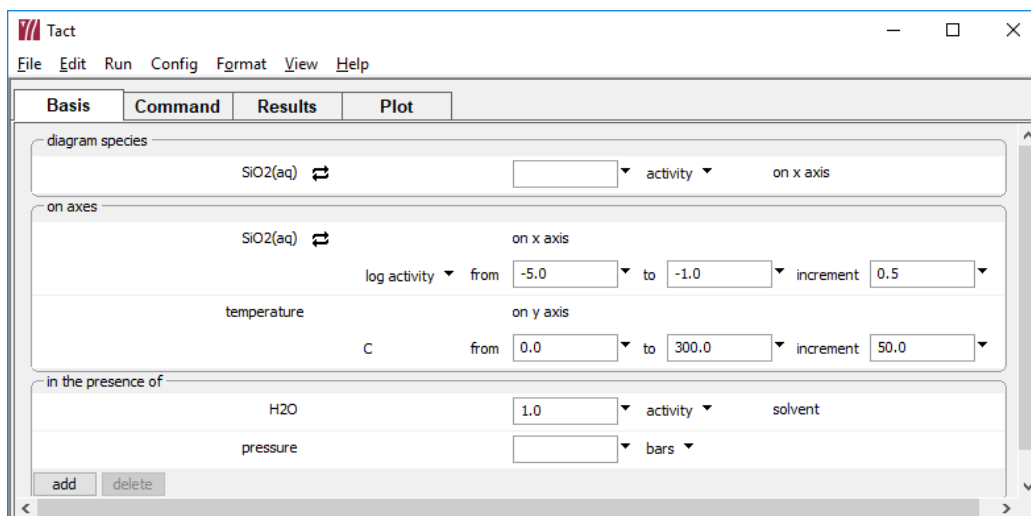
Move to the **Plot** pane to view the diagram, which shows the equilibrium point of the methane souring reaction, calculated as a function of temperature.



## 6.2 Solubility diagrams

To construct a solubility diagram, specify the main species as the x-axis variable. To plot the solubility of quartz (in terms of  $\text{SiO}_2$  activity), for example, set “ $\text{SiO}_2(\text{aq})$ ” under “diagram species”, and then again under “on axes” as the x-axis variable. Set the log activity to range from “-5” to “-1”.

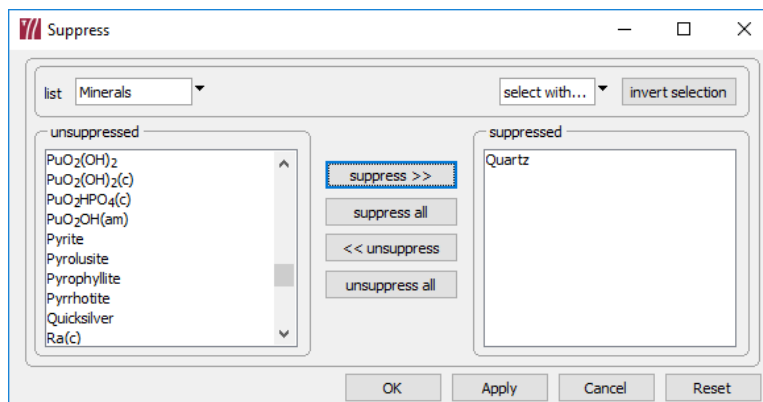
The pane should look like



Alternatively, use the commands

```
diagram SiO2(aq) vs SiO2(aq)
x from -5 to -1
go
```

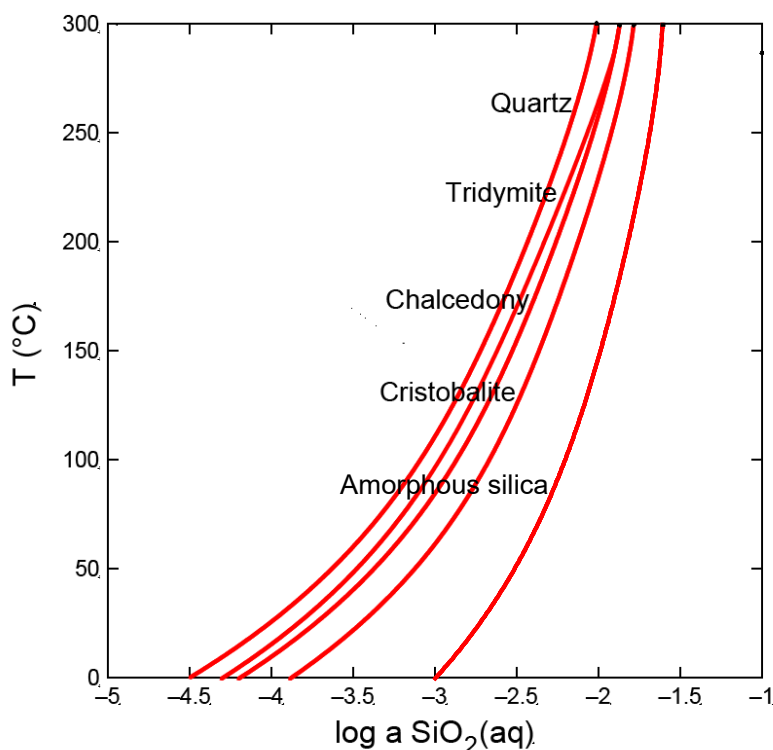
Move to the **Plot** pane to view the diagram. If you suppress quartz using the **Config → Suppress...** dialog



or by typing

```
(cont'd)
suppress Quartz
go
```

the resulting diagram shows the solubility of the next most stable polymorph, tridymite (and a small field for chalcedony at high temperature). Continuing this cycle produces plots of the solubilities of each of the silica polymorphs. The figure below shows a composite of five **Tact** diagrams.

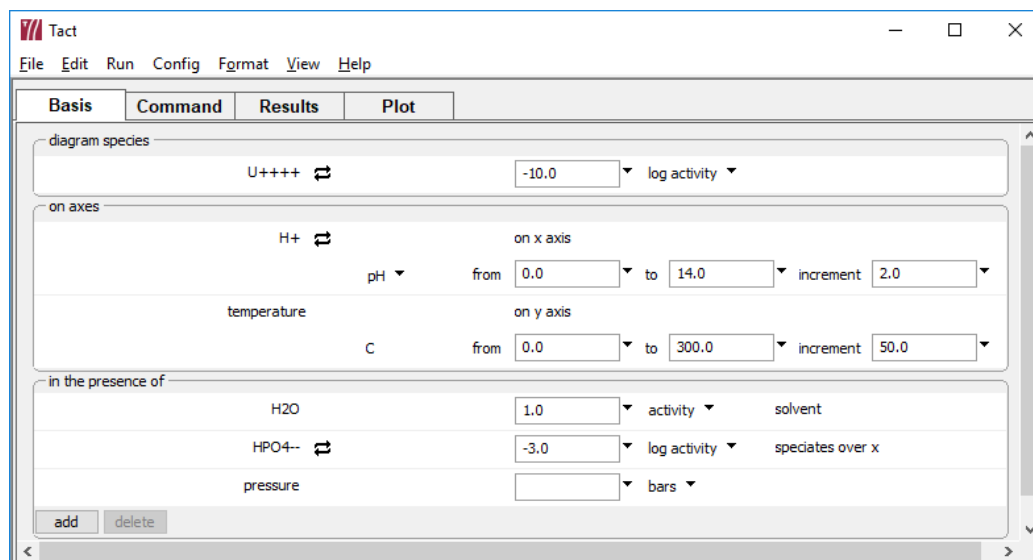


## 6.3 Mosaic diagrams

**Tact**, like **Act2**, can consider complexing ions that speciate over the diagram axes. To calculate the stable forms of uranium versus pH in the presence of dissolved phosphate, for example, **Tact** must first consider the speciation of the phosphate ion, which has already been calculated (see the example in [section 6.1](#)).

Under “diagram species”, set “U++++” and change the unit from “activity” to “log activity”. Set the value to “-10”.

On the x axis, select “H+” and set units to “pH”. Under “in the presence of”, click  and select “HPO4-”. Set log activity to “-3”, then click on the pulldown next to log activity and select “speciates over x”. The **Basis** pane should look like this



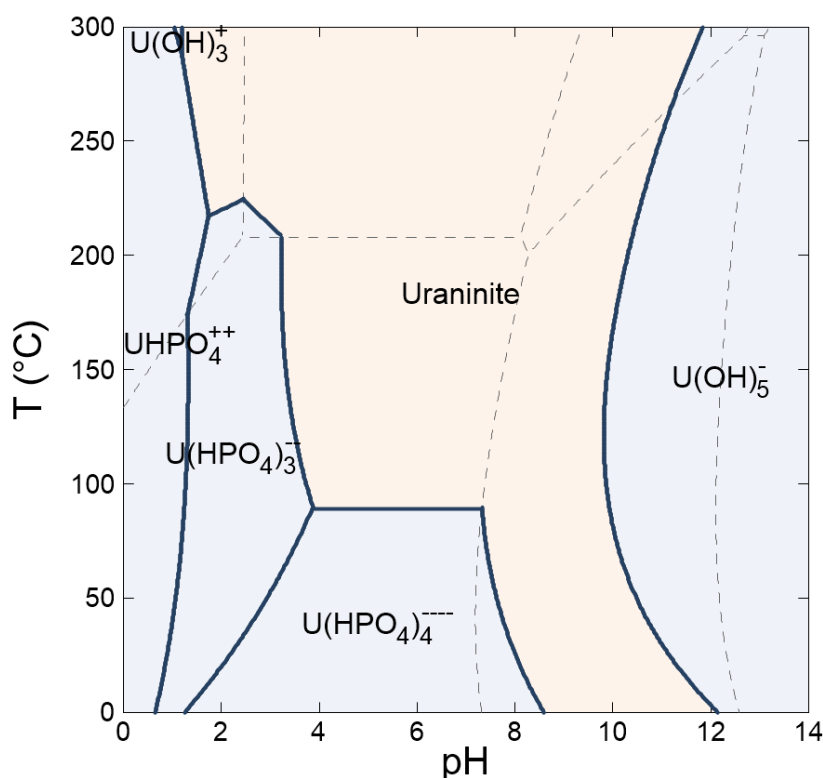
The commands are

```

diagram U++++ vs pH
x from 0 to 14
log a U++++ = -10
log a HPO4-- = -3
speciate HPO4--
go

```

Move to the **Plot** pane to view the mosaic diagram of the uranium-phosphate system versus temperature and pH.



Subdiagrams in mosaic, from upper left to lower right, are for  $\text{H}_3\text{P}_2\text{O}_7^-$ ,  $\text{H}_2\text{P}_2\text{O}_7^{--}$ ,  $\text{HP}_2\text{O}_7^{---}$ ,  $\text{P}_2\text{O}_7^{---}$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{--}$ , and  $\text{PO}_4^{---}$ . You can hover with your mouse over any field in the diagram to display the species assemblage there as a tooltip, and over any line to see the reaction it represents.

## 6.4 Solid solution diagrams

**Tact**, like **Act2**, can draw diagrams accounting for solid solutions in discrete mode. The details of constructing such plots are given in the [Using Act2](#) section of this guide.

## 6.4 Editing plot appearance

**Tact**, like **Act2**, allows you to interactively modify many aspects of the diagram. The details of using active items, aspect menus, and dialogs to edit the plot appearance are given in the [Using Act2](#) section of this guide.



## 6.5 Reaction traces and scatter plots

**Tact**, like **Act2**, can project reaction traces and scatter data onto a diagram. These features are especially useful for displaying polythermal reaction paths or datasets. The details of constructing such plots are given in the [Using Act2](#) section of this guide.

## 6.6 Tact command line

You can start **Tact** by clicking the icon under the “Start” menu, opening a “.tac” file, or entering the command `tact.exe` from the Windows “Command Prompt.”

When you start **Tact** from the command line (as opposed to clicking on the icon), you can specify a number of arguments. For example, the command

```
tact -i my_script -d my_thermo.tdat
```

causes **Tact** to read input commands from a file “my\_script”, and to use “my\_thermo.tdat” as the thermodynamic database.

The following options are available from the command line:

<code>-cd</code>	Change the working directory to the directory containing the input script specified with the <code>-i</code> option.
<code>-nocd</code>	Do not change the working directory.
<code>&lt;input_script&gt;</code> <code>-i &lt;input_script&gt;</code>	Set a file from which to read input commands.
<code>-gtd &lt;gtdata_dir&gt;</code>	Set directory to search for thermodynamic datasets.
<code>-d &lt;thermo_data&gt;</code>	Set the thermodynamic dataset.



# Using SpecE8


**SpecE8** is a flexible program that models the equilibrium states of geochemical systems that contain an aqueous fluid. The program calculates the equilibrium distribution of aqueous species in a fluid, the fluid's saturation state with respect to minerals, the sorption of aqueous species onto various types of surfaces, and the fugacity and partial pressure of gases dissolved in the fluid.

## 7.1 Example calculation

The input file “Freshwater.sp8” equilibrates a hypothetical water sample at 25°C. Double-click the file, which can be found in the “Scripts” subfolder of the GWB installation directory, to launch **SpecE8**, then move to the **Basis** pane to see the compositional constraints on the hypothetical water.

The screenshot shows the SpecE8 software window with the 'Basis' tab selected. The 'constraints on initial system' section lists various chemical species and their initial conditions. The species are listed in a table with columns for the species name, a unit/condition dropdown, and a unit/condition dropdown. The species are: H2O, Na+, K+, Ca++, Mg++, Al+++ (all with a double-headed arrow icon), SiO2(aq), Cl-, SO4--, HCO3-, and H+. The temperature is set to 25.0 C. The H2O entry is labeled 'solvent'. At the bottom, there are 'add' and 'delete' buttons, and a '+ advanced' button.

Species	Value	Unit/Condition
H2O	1.0	free kg
Na+	5.0	mg/kg
K+	1.0	mg/kg
Ca++	15.0	mg/kg
Mg++	3.0	mg/kg
Al+++	1.0	ug/kg
SiO2(aq)	3.0	mg/kg
Cl-	15.0	mg/kg
SO4--	35.0	mg/kg
HCO3-	50.0	mg/kg
H+	5.0	pH
temperature	25.0	C

If you were starting from scratch, you would click  and select each of the components Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>++</sup>, and so on to add them to the basis, then set appropriate constraints and units. You can select from a variety of chemical units using the pulldown for each basis entry.

Alternatively, typing the following commands

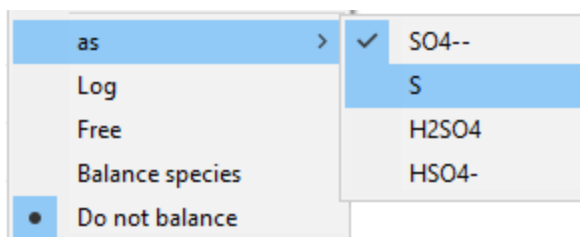
```
Na+ = 5 mg/kg
K+ = 1 mg/kg
Ca++ = 15 mg/kg
Mg++ = 3 mg/kg
Al+++ = 1 ug/kg
SiO2(aq) = 3 mg/kg
Cl- = 15 mg/kg
SO4-- = 35 mg/kg
HCO3- = 50 mg/kg
pH = 5
```

configures the same system.

You do not need to type the unit if it is the same as the unit on the previous line, although we will carry units throughout this manual for clarity. The following input is equivalent to that above

```
Na+ = 5 mg/kg
K+ = 1
Ca++ = 15
Mg++ = 3
Al+++ = 1 ug/kg
SiO2(aq) = 3 mg/kg
Cl- = 15
SO4-- = 35
HCO3- = 50
pH = 5
```

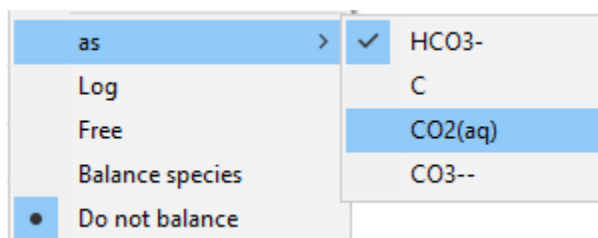
You can further set concentrations in elemental equivalents:  $\text{SO}_4^{--}$  as S,  $\text{HCO}_3^-$  as C,  $\text{As}(\text{OH})_4^-$  as As, and so on. For example, click on the unit pulldown for  $\text{SO}_4^{--}$  and select **as  $\rightarrow$  S**



rather than **as  $\rightarrow$   $\text{SO}_4^{--}$**  to constrain the mass of sulfur, rather than that of the sulfate oxyanion. Set the mass to “12 mg/kg as S”.

$\text{SO}_4^{--}$   $\rightleftharpoons$   mg/kg as S

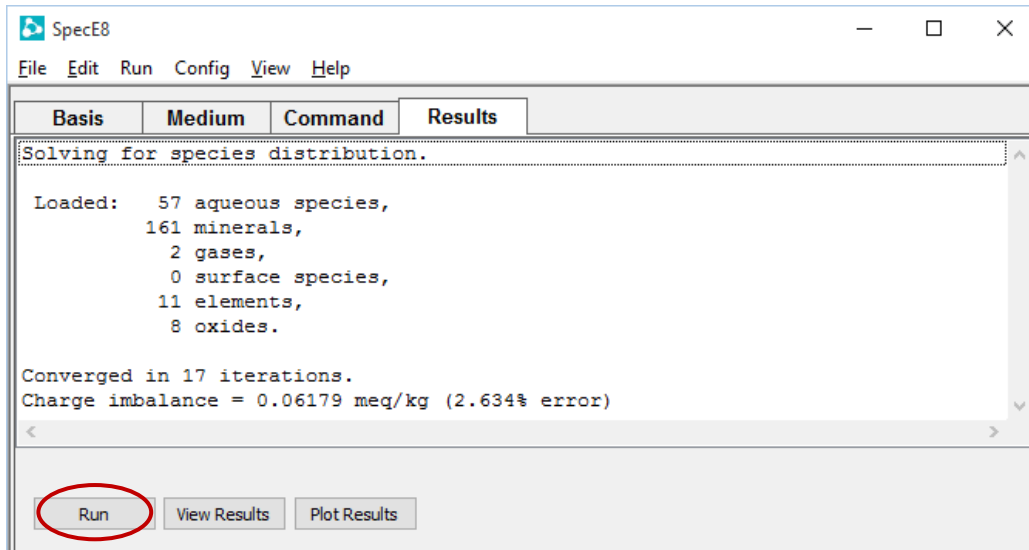
Similarly, you can set concentrations in terms of protonated or deprotonated forms of the basis entries:  $\text{HPO}_4^{--}$  as  $\text{PO}_4^{--}$ ,  $\text{NH}_4^+$  as  $\text{NH}_3$ , and so on. Click on the unit pulldown for  $\text{HCO}_3^-$  and select **as  $\rightarrow$   $\text{CO}_2(\text{aq})$**



rather than **as  $\rightarrow$   $\text{HCO}_3^-$** . Set the mass to “36 mg/kg as  $\text{CO}_2(\text{aq})$ ”.

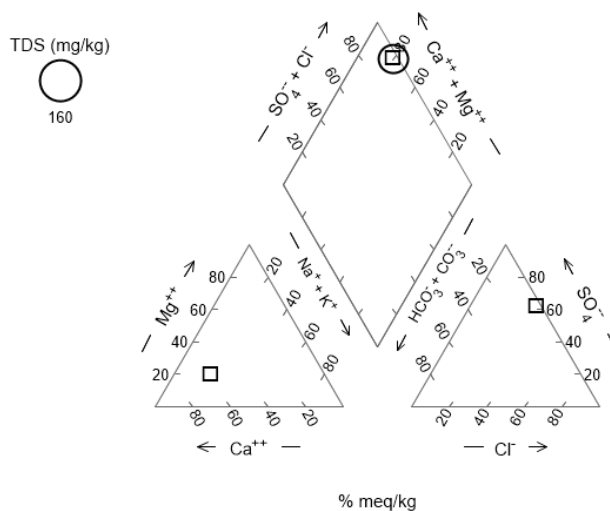
$\text{HCO}_3^-$   $\rightleftharpoons$   mg/kg as  $\text{CO}_2(\text{aq})$

Press the **Run** button on the **Results** pane



to calculate the equilibrium species distribution in the fluid. You can alternatively select **Run → Go** from the menubar or type `go` in the **Command** pane.

**SpecE8** produces as output a dataset "SpecE8\_output.txt" (click on **View Results** on the **Results** pane, or **File → View → SpecE8\_output.txt** from the menubar) that shows calculation results in tabular form, and a dataset "SpecE8\_plot.gtp" (click on **Plot Results** on the **Results** pane) that passes more complete information to the graphics program **Gtplot**. The plot below shows results from the calculation displayed on a Piper diagram. Use the **Plot** menu to control the type and configuration of the plot produced (see the section [Using Gtplot](#) in this guide).



## 7.2 Equilibrium models

When **SpecE8** calculates a model of a system's equilibrium state, it uses the input constraints you provide to predict the distribution of dissolved species in solution, the fluid's saturation state with respect to various minerals, the amount of species sorbed onto any sorbing surfaces you specify, and the fugacity and partial pressure of gases dissolved in the fluid.

For example, to calculate the equilibrium state of seawater in contact with the atmosphere, you could assume that the seawater's oxidation state is controlled by the partial pressure of oxygen in the atmosphere and that pH is set by atmospheric carbon dioxide.

To get started, double-click the “Seawater.sp8” input file to launch **SpecE8**, then move to the **Basis** pane.

Species	Value	Unit	Notes
H2O	1.0	free kg	solvent
O2(g) ↔ O2(aq)	0.2	fugacity	
CO2(g) ↔ H+	-3.5	log fugacity	
Na+	10760.0	mg/kg	
Mg++	1290.0	mg/kg	
Ca++	411.0	mg/kg	
K+	399.0	mg/kg	
Cl-	19350.0	mg/kg	
SO4--	2710.0	mg/kg	
HCO3-	142.0	mg/kg	
SiO2(aq)	6.0	mg/kg	
temperature	25.0	C	

add delete + advanced

To set the atmospheric buffer, O2 and CO2 have been swapped into the basis. If we had not done so already, you would click the ↔ button next to the basis entry for “O2(aq)” and select **Gas... → O2(g)**, then swap “CO2(g)” for “H+” and set appropriate fugacities for each.

The commands below prescribe the same model.

```

swap O2(g) for O2(aq)
swap CO2(g) for H+

Na+ = 10760 mg/kg
K+ = 399 mg/kg
Ca++ = 411 mg/kg
Mg++ = 1290 mg/kg
SiO2(aq) = 6 mg/kg
Cl- = 19350 mg/kg
SO4-- = 2710 mg/kg
HCO3- = 142 mg/kg

f O2(g) = 0.2
log f CO2(g) = -3.5
go

```

By default, the model calculation assumes that the system contains 1 kg of solvent water.

Execute the model by pressing the **Run** button on the **Results** pane, selecting **Run → Go** from the menubar, or typing `go` in the **Command** pane.


When **SpecE8** runs, it reports the imbalance in electrical charge in the system, as specified by the input constraints you provide. Alternatively, you can have the program adjust the concentration of one component as necessary to achieve an exact ionic charge balance, and report the amount of adjustment. To do so, select “Balance on” under the unit pulldown menu for the desired basis entry. You could, for example, have the program adjust the  $\text{Cl}^-$  concentration. The analytical concentration entered above for  $\text{Cl}^-$  is a starting point for iterating to a solution in this case, not a true constraint on the system’s composition.

When you run the preceding calculation, the “SpecE8\_output.txt” dataset contains the calculation results for seawater, including the concentration of a number of aqueous species, the saturation state of various minerals, fugacity and partial pressure of gases, and the system’s bulk composition. You can compare the results to the input commands. The  $\text{O}_2$  and  $\text{CO}_2$  fugacities agree exactly.

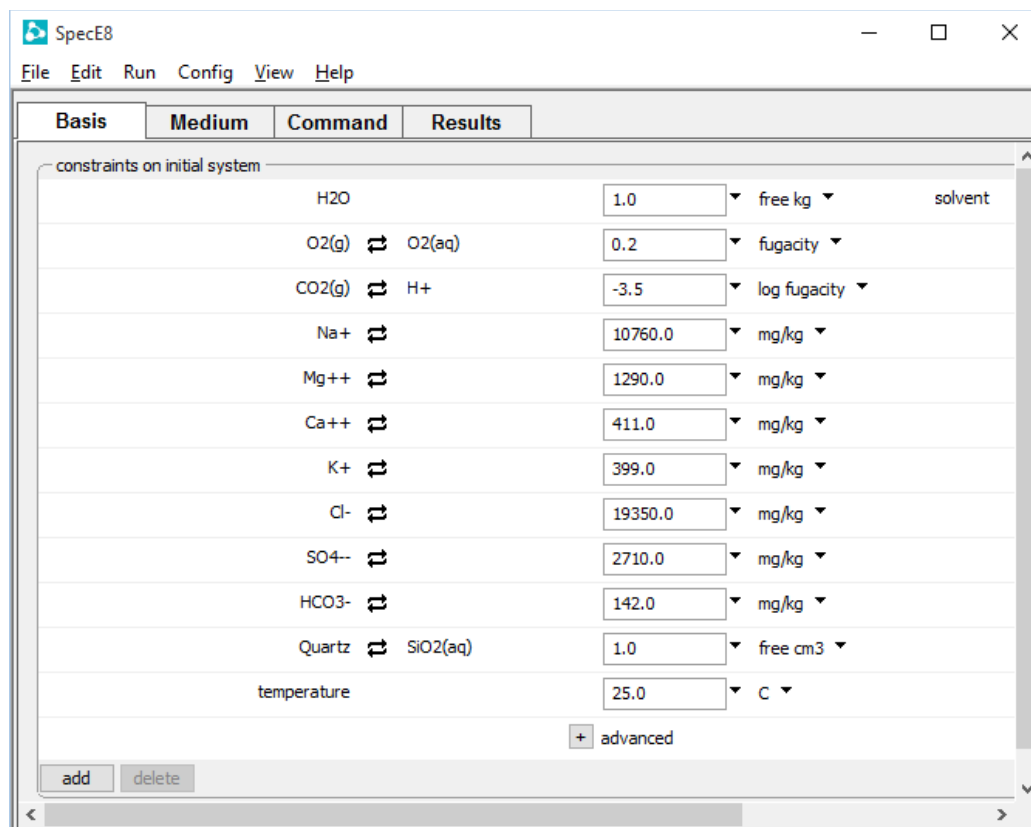
The concentrations of free species such as  $\text{Na}^+$ , however, do not agree with the input constraints. This apparent discrepancy occurs because the input sets the total amounts of all species containing  $\text{Na}^+$ , not just the  $\text{Na}^+$  ion. The fluid’s bulk composition, toward the bottom of the block, reflects the input.

To calculate a model in which the presence of a mineral buffers the fluid composition, swap the mineral into the basis and specify the mineral’s mass. Continuing in our



example, click the  button next to the basis entry for “SiO2(aq)” and select **Mineral... → Quartz**, then set “1” free cm<sup>3</sup> in the system.

The **Basis** pane should look like this



constraints on initial system			
H2O		1.0	free kg solvent
O2(g)	↔ O2(aq)	0.2	fugacity
CO2(g)	↔ H+	-3.5	log fugacity
Na+		10760.0	mg/kg
Mg++		1290.0	mg/kg
Ca++		411.0	mg/kg
K+		399.0	mg/kg
Cl-		19350.0	mg/kg
SO4--		2710.0	mg/kg
HCO3-		142.0	mg/kg
Quartz	↔ SiO2(aq)	1.0	free cm3
temperature		25.0	C

add delete + advanced

If you are working from the **Command** pane, continue by typing

```
(cont'd)
swap Quartz for SiO2(aq)
1 free cm3 Quartz
go
```

In this example, the system contains 1 kg solvent, various solutes, and 1 cm<sup>3</sup> of the mineral quartz. The amount of free quartz in the system does not affect the fluid composition, as long as some small amount of the mineral is present.

It is important to understand the difference between bulk and free constraints on the system's composition. In the previous example, the input constrains components Na<sup>+</sup>, Mg<sup>++</sup>, and the others to a bulk number of mg/kg. The value for Na<sup>+</sup> includes the sodium present in each of the dissolved species: Na<sup>+</sup>, NaSO<sub>4</sub><sup>-</sup>, NaCl, NaHCO<sub>3</sub>, etc. Only by

specifying units of free mg/kg would you constrain the  $\text{Na}^+$  ion alone. In contrast, pH is a free constraint, since it applies only to the free hydrogen ion,  $\text{H}^+$ . Settings for the  $\text{O}_2$  and  $\text{CO}_2$  fugacities similarly serve as free constraints.

The bulk amount of quartz in the system, by the same reasoning, includes the mineral quartz plus the silica dissolved in solution as species such as  $\text{SiO}_2(\text{aq})$ . The commands in the example specify 1  $\text{cm}^3$  of free quartz (i.e., the silica present as the mineral quartz itself). Mineral buffers generally should be set as free constraints instead of bulk values.

When setting the concentration or activity of species, the mass of minerals, or the fugacity or partial pressure of gases in the **Basis** pane, it is important to avoid 0 (zero) values, as these will prevent the GWB programs from solving for the distribution of mass. Where the concentration of a particular component is negligible, set a small positive value. Log values, such as log activity, pH, pe, or Eh, however, can be set to 0.

**SpecE8** recognizes a number of units for constraining a system's composition besides those introduced so far. Most of these can be applied either as bulk constraints or as free constraints by preceding the unit name with the word *free*. [Table 7.1](#) lists the units recognized by the program.

Table 7.1		Units for specifying the composition of the initial system		
By mass or volume (free or bulk):				
mol	mmol	umol	nmol	
kg	g	mg	ug	ng
eq	meq	ueq	neq	
cm3	m3	km3	l	
By concentration (free or bulk):				
mol/kg	mmol/kg	umol/kg	nmol/kg	
molal	mmolal	umolal	nmolal	
mol/l	mmol/l	umol/l	nmol/l	
g/kg	mg/kg	ug/kg	ng/kg	
wt%	wt fraction			
g/l	mg/l	ug/l	ng/l	
eq/kg <sup>1</sup>	meq/kg <sup>1</sup>	ueq/kg <sup>1</sup>	neq/kg <sup>1</sup>	
eq/l	meq/l	ueq/l	neq/l	

By carbonate alkalinity (applied to bicarbonate component):			
eq_acid	meq_acid	ueq_acid	neq_acid
eq_acid /kg	meq_acid /kg	ueq_acid /kg	neq_acid /kg
eq_acid /l	meq_acid /l	ueq_acid /l	neq_acid /l
g/kg_as_CaCO3	mg/kg_as_CaCO3	ug/kg_as_CaCO3	ng/kg_as_CaCO3
wt%_as_CaCO3			
g/l_as_CaCO3	mg/l_as_CaCO3	ug/l_as_CaCO3	ng/l_as_CaCO3
mol/kg_as_CaCO3	mmol/kg_as_CaCO3	umol/kg_as_CaCO3	nmol/kg_as_CaCO3
mol/l_as_CaCO3	mmol/l_as_CaCO3	umol/l_as_CaCO3	nmol/l_as_CaCO3
By activity or redox state (free constraints):			
activity	fugacity	ratio	
pH	V	pe	
Relative to system bulk volume:			
volume%	vol. frac.	(any unit)/cm3	(any unit)/m3
By ionic charge balance (a bulk constraint):			
balance			

<sup>1</sup>Expressed per kg solvent.

## 7.3 Redox disequilibrium

Redox reactions in natural waters, especially at low temperatures, cannot always be assumed to approach thermodynamic equilibrium. For this reason, you may want to calculate a model in which redox reactions are in a state of disequilibrium. You control the extent to which **SpecE8** honors redox equilibrium when calculating a chemical model by interactively enabling and disabling redox coupling reactions (see [Redox couples](#) in the **Configuring the Programs** chapter of this guide).

The coupling reactions, when enabled, prescribe redox equilibrium between species of differing oxidation states. You use the **Config → Redox couples...** dialog (or the `decouple` and `couple` commands) to control coupling between a redox species and a basis species. [Table 2.2](#) shows the relationships among redox and basis species.

As an example, double-click the “Redox.sp8” input file to launch **SpecE8**, then move to the **Basis** pane.

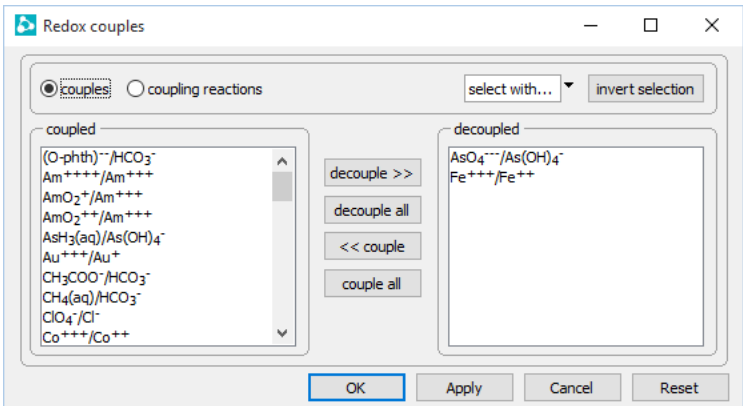
The screenshot shows the SpecE8 software window with the 'Basis' tab selected. The 'constraints on initial system' section lists various chemical species and their initial conditions. The species are listed in two columns, with their corresponding values and units in the third column. The units are indicated by dropdown menus. At the bottom, there are 'add' and 'delete' buttons, and a '+ advanced' button.

Species	Value	Unit
H2O	1.0	free kg
H+	6.0	pH
e- ↔ O2(aq)	0.4	V
Ca++	0.4	mg/kg
Mg++	0.6	mg/kg
Na+	0.1	mg/kg
K+	0.2	mg/kg
Fe++	0.7	mg/kg
HCO3-	0.6	mg/kg
SO4--	3.0	mg/kg
Cl-	1.4	mg/kg
Hematite ↔ Fe+++	1.0	free cm3
AsO4---	0.1	mg/kg
As(OH)4-	0.8	mg/kg
temperature	25.0	C

Buttons: add, delete, + advanced

The input configures a model of a fluid of a certain pH, Eh, and major ion composition, as shown above.

Open the **Config → Redox couples...** dialog



and note the decoupled redox pairs. Disabling the redox couples between ferric and ferrous iron and between trivalent and pentavalent arsenic [i.e., basis species  $\text{AsO}_4^{3-}$  and  $\text{As(OH)}_4^-$ ] causes the program to consider that oxidized and reduced iron and arsenic species exist in quantities not related to the value entered for Eh. Other redox couples, such as between  $\text{HS}^-$  and  $\text{SO}_4^{2-}$ , remain enabled and will reflect the specified Eh.

By nature, you need more information to constrain a model of a fluid in redox disequilibrium than you do for an equilibrium model. As you can see on the **Basis** pane in the example above, separate constraints are required for the oxidized and reduced forms of iron and arsenic. Analytical values constrain the fluid’s total  $\text{Fe}^{++}$ ,  $\text{AsO}_4^{3-}$ , and  $\text{As(OH)}_4^-$  content, and the amount of ferric iron in the fluid is controlled by equilibrium with hematite.

In the calculation results (in “SpecE8\_output.txt”), **SpecE8** honors mass balance and mass action among ferric species and among ferrous species, but ferric species do not exist in equilibrium with ferrous species. Similarly, the program honors equilibrium among oxidized and reduced arsenic species, but not between oxidation states.

Whenever there are two or more independent redox couples in a run, **SpecE8** reports in “SpecE8\_output.txt” the theoretical oxidation state of each couple. In this example, the couples and corresponding Nernst Eh and pe values are:

	Eh (volts)	pe
$\text{e}^- + \frac{1}{4} \text{O}_2(\text{aq}) + \text{H}^+ \rightleftharpoons \frac{1}{2} \text{H}_2\text{O}$	0.400	6.762
$2 \text{e}^- + 4 \text{H}^+ + \text{AsO}_4^{3-} \rightleftharpoons \text{As(OH)}_4^-$	0.081	1.362
$\text{e}^- + \text{Fe}^{+++} \rightleftharpoons \text{Fe}^{++}$	-0.002	-0.035

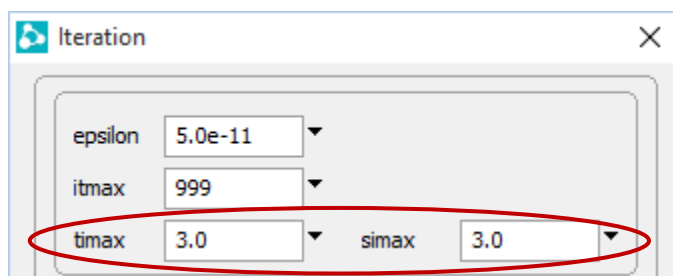
The first line reflects the Eh specified as an input constraint. The second and third lines show the oxidation states calculated from the activities of arsenic and iron species. The differences in oxidation state reflect the extent of redox disequilibrium in the solution.

## 7.4 Activity coefficients

**SpecE8** can employ two broad methods to calculate activity coefficients for the aqueous species—variations of the Debye-Hückel equation and virial methods—depending on the thermodynamic dataset in use. The methods are also known as “ion association” and “ion interaction” approaches, respectively.

Most commonly, the program uses the “B-dot” equation, an extended form of the Debye-Hückel equation described by Helgeson (see [Further Reading](#)). This method, which assigns a coefficient to each species in solution, is a general formulation that can be applied to a range of natural waters, including dilute fluids and dominantly Na-Cl solutions with ionic strengths of up to about 3 molal. This method is not especially accurate, however, at ionic strengths greater than about one-half molal.

In this method, species’ activity coefficients are calculated by using the solution’s ionic strength, and the water activity is calculated from the stoichiometric ionic strength. Because coefficients for the method have been correlated to ionic strengths of 3 molal, **SpecE8** limits the ionic strength values it uses in calculating activities. For species activities, it uses the value of the actual ionic strength or the value of variable “timax”, whichever is lowest. It normally calculates the water activity using the lower value of the stoichiometric ionic strength or variable “simax”. Variables “timax” and “simax” are initially set to “3” molal, but you can change them (see [Settable variables](#) in this section) on the **Config → Iteration...** dialog.



**SpecE8** can also emulate the activity coefficient calculations used in the MINTEQ, PHREEQC, and WATEQ4F software packages. These packages use Debye-Hückel based methods, such as the Truesdell-Jones and Davies equations, that are similar but not identical to the B-dot method described above. Consult the MINTEQ, PHREEQC, and WATEQ4F documentation for information about the ranges in temperature and ionic strength over which these calculations can be reliably applied.

Special options for calculating the activity of water and the activity coefficients of neutrally charged aqueous species in the various Debye-Hückel methods are described in the **Thermo Datasets** chapter of the *GWB Reference Manual*.

Virial methods provide an alternative technique for determining activity coefficients that can be applied to concentrated waters. The techniques employ expressions similar to the Debye-Hückel equation, but with extra terms that represent interaction among the solution components. The virial coefficients that appear in the extra terms have been determined empirically by statistical regression of a body of experimental data.

**SpecE8** makes use of a virial technique known as the Harvie-Møller-Weare (or H-M-W) method, a formalism of the “Pitzer equations” (see a reference by these authors in [Further Reading](#)). The H-M-W method may be used at very high ionic strength, but extra care should be taken because of the empirical nature of the virial techniques. Virial methods can give misleading results for fluids that differ in composition from those in the experiments used to regress the coefficients.

Projecting the methods to elevated (or lowered) temperatures also requires caution because the model coefficients were derived largely from the results of experiments conducted at 25°C. In addition, the methods treat solutes in bulk without attempting to predict their distribution among the various aqueous species. Virial methods, nonetheless, commonly predict saturation states for concentrated solutions that are considerably more accurate than those calculated by the Debye-Hückel method.

The H-M-W method requires its own databases, six of which—“thermo\_hmw.tdat”, “thermo\_phrqpitz.tdat”, “thermo\_ypf.R2.tdat”, “THEREDA\_2021\_GWB.tdat”, “thermo\_frezchem.tdat”, and “thermo\_coldchem.tdat”—are included in the software release. Database “thermo\_hmw.tdat” contains data from the Harvie-Møller-Weare compilation. This compilation contains data at only 25°C and should not be employed at any other temperature.

The “thermo\_phrqpitz.tdat” dataset contains an expanded version of the H-M-W database, as implemented in the PHRQPITZ geochemical model (see [Further Reading](#)). This dataset includes more components than the H-M-W version and provides some capability for temperature extrapolation. The data for temperature extrapolation, however, is not complete; it is important to read the PHRQPITZ documentation carefully before working at temperatures other than 25°C. [Table 7.2](#) lists the basis species available in “thermo\_hmw.tdat” and “thermo\_phrqpitz.tdat”.

Datasets “thermo\_ypf.R2.tdat” and “THEREDA\_2021\_GWB.tdat” are the Yucca Mountain Project and THEREDA Project’s compilations, each of which invokes the H-M-W activity model. The former dataset is based on the data0.ypf.R2 data file from EQ3/6. The two datasets contain more chemical components than “thermo\_hmw.tdat”, and include provision for extrapolating the data for many of the components to temperatures other than 25°C. Before applying any Pitzer dataset at temperatures other than 25°C, you should study its documentation (see [Further Reading](#)) carefully.

The “thermo\_frezchem.tdat” dataset is based on data from the FREZCHEM program, as set out by Toner and Sletten in the PhreeqC data file frezchem.dat (see [Further Reading](#)). The dataset contains a component set similar to “thermo\_hmw.tdat”, and can be applied at 25°C, but is designed to be carried down to temperatures well below the freezing point of pure water. The “thermo\_coldchem.tdat” dataset is another H-M-W parameterization for very low temperature applications, from Toner and Catling (see [Further Reading](#)). It is based on the PhreeqC data file ColdChem.dat. The dataset is for the Na-K-Ca-Mg-Cl-SO<sub>4</sub> system, and may be valid down to 200 K or below. As always, you should study details of their temperature dependence (see [Further Reading](#)) carefully.

**SpecE8** can also use the Specific Ion Interaction Theory (SIT) activity model, a virial technique significantly simpler in form than the Pitzer equations (see a reference for the method by Grenthe *et. al.* in [Further Reading](#)). Common implementations of the SIT method carry more ion pairs and complexes than many Pitzer compilations. The method is accurate to higher ionic strengths than the Debye-Hückel equations, but not to the salinities achievable using the Pitzer equations.

The “thermo\_sit.tdat” dataset is the ThermoChimie project’s database (version 10a) invoking the SIT method, and “thermo\_nea.tdat”, from the Nuclear Energy Agency (version 1.0), uses the same method. See reference by Giffaut *et. al.* in [Further Reading](#) for the ThermoChimie database, and by Lemire *et. al.*, along with earlier volumes in the series, for the NEA Thermochemical Database.

**Table 7.2 Basis species in the H-M-W and PHRQPITZ databases**

Harvie-Møller-Weare		
H <sub>2</sub> O	H <sup>+</sup>	Mg <sup>++</sup>
Ca <sup>++</sup>	HCO <sub>3</sub> <sup>-</sup>	Na <sup>+</sup>
Cl <sup>-</sup>	K <sup>+</sup>	SO <sub>4</sub> <sup>-</sup>
PHRQPITZ		
H <sub>2</sub> O	Fe <sup>++</sup>	Mn <sup>++</sup>
B(OH) <sub>3</sub>	H <sup>+</sup>	Na <sup>+</sup>
Ba <sup>++</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-</sup>
Br <sup>-</sup>	K <sup>+</sup>	Sr <sup>++</sup>
Ca <sup>++</sup>	Li <sup>+</sup>	
Cl <sup>-</sup>	Mg <sup>++</sup>	

To use the H-M-W method, go to **File → Open → Thermo Data...** and select database “thermo\_hmw.tdat”, or enter the command



```
read thermo_hmw.tdat
```

Similarly, selecting “thermo\_phrqpitz.tdat” invokes the PHRQPITZ database.

To use the SIT method, select “thermo\_sit.tdat” or type

```
read thermo_sit.tdat
```

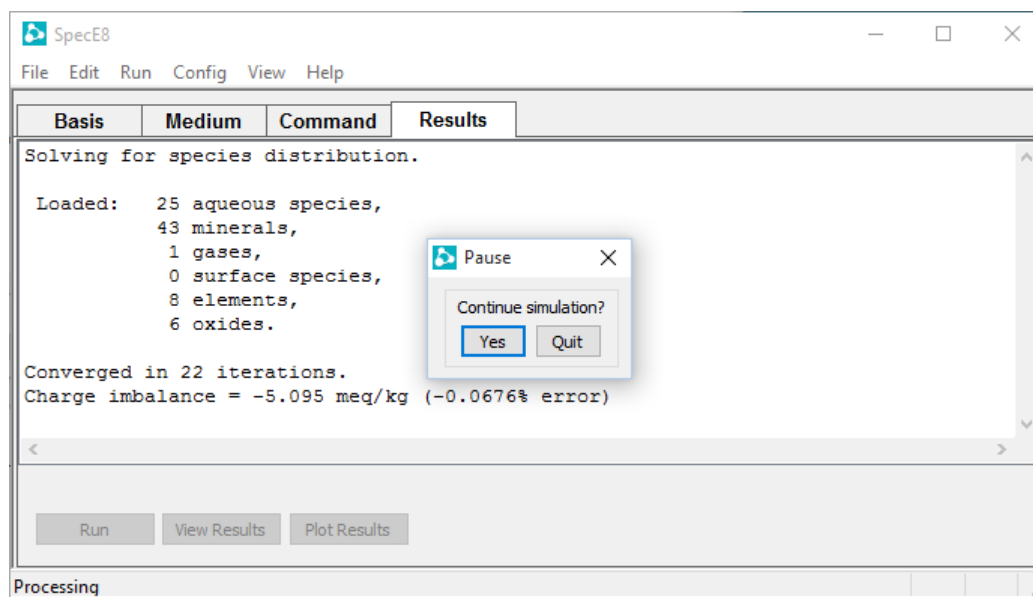
to load the ThermoChimie database, or use “thermo\_nea.tdat” for the NEA database.

The dataset “thermo.tdat”, which you can invoke with the command

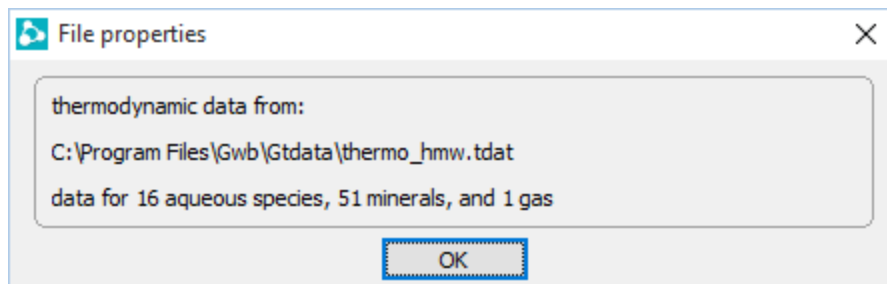
```
read thermo.tdat
```

returns the program to the default method for calculating activity coefficients.

In the following example, we use the Debye-Hückel B-dot and H-M-W methods to calculate the saturation index of halite in a groundwater sampled from an evaporite bed. Double-click the “HMW.sp8” input file to launch **SpecE8**. The program moves to the **Results** pane automatically, as shown below.



The example is set up to perform multiple calculations automatically, so take a look at the results from the first calculation (“SpecE8\_output.txt” and “SpecE8\_plot.gtp”) before continuing the simulation. These results show the log  $Q/K$  of halite for the B-dot extended Debye-Hückel method. To compare with the Harvie-Møller-Weare method, hit **Yes** to continue the simulation. The program will load “thermo\_hmw.tdat”



and repeat the calculation. With your original results still open, double-click on the new results files to compare the calculations side-by-side.

The calculations give the results

	log $Q/K$
Debye-Hückel B-dot	-0.94
Harvie-Møller-Weare	0.02

## 7.5 Gas partial pressure

**SpecE8** calculates the fugacity coefficients  $\varphi_i$  that relate the fugacity  $f_i$  of a gas  $i$  to its partial pressure  $P_i$ , where  $f_i = \varphi_i P_i$ , according to one of three models: Tsonopoulos, Peng-Robinson, and Spycher-Reed. Details of the three models are given in references listed under [Gas partial pressure](#).

The program by default uses the pressure model identified in the header section of the thermo dataset in use. Most of the databases distributed with the software set the default model to Tsonopoulos, although the PhreeqC, Wateq, and Cemdata18 databases set Peng-Robinson. You can, nonetheless, set an alternative pressure model on the **Config** → **Options...** dialog, or with the `press_model` command.

## 7.6 Solid solutions

**SpecE8** can incorporate into its calculations any number of binary solid solutions, each in either continuous or discrete mode (see [Solid solutions](#) in the **Configuring the Programs** chapter of this guide). To model equilibrium with a continuous solid solution, you swap its end members into the basis and constrain the mass of each. **SpecE8** will determine the equilibrium fluid composition, reflecting the basis constraints you set.

A solid solution has a saturation state, whether present in the basis or not. For each continuous solid solution, **SpecE8** will determine the composition at which the solution is most saturated, along with the saturation index at that composition.

Suppose we wish to determine the composition of a fluid in equilibrium with a plagioclase solid solution. We could define a solution “Plag” composed of end members albite (tag “Ab”) and anorthite (“An”). We would then swap **Plag::Ab** for “Na<sup>+</sup>” and

**Plag::An** for “Ca++”, and constrain the free mass of each end member. Equivalent commands might be

```
solid_solution Plag Albite tag Ab contains Anorthite tag An
swap Plag::Ab for Na+
swap Plag::An for Ca++
3 free mmol/kg Plag::Ab
7 free mmol/kg Plag::An
```

If you were to swap only one of a solid solution’s end members into the basis, **SpecE8** would treat it as a pure mineral. The amount of each end member, furthermore, is required, since **SpecE8** figures mole fractions from free masses of the end members, and the end member activities follow from the mole fractions.

**SpecE8** reports the calculation results to a plot file “SpecE8\_plot.gtp”, where it is available for diagramming with **Gtplot**. Output there includes end member masses, saturation states of the solid solutions considered (as well as any binodal points they may contain), and the resulting fluid composition. Calculation results are available as well in the text-format dataset “SpecE8\_output.txt”. The text file includes additional information about solid solutions, including total masses and the mole fractions, activity coefficients, and end member activities.

In a discrete model, **SpecE8** calculates saturation indices of each tranche considered in the solid solution. The end members’ activity coefficients are folded into the tranches’ log *Ks*, so the model treats tranches as if they were pure minerals. You can constrain a run by swapping a tranche in place of a single basis entry. For example,

```
(cont'd)
solid_solution Plag discrete
swap Ab(.3)-An(.7) for Na+
10 free mmol/kg Ab(.3)-An(.7)
Ca++ = 1 mg/kg
```

To approximate the continuous model previously considered, in which equilibrium with the solution constrains two basis entries, set a fine “step” before swapping two adjacent tranches into the basis

*(cont'd)*

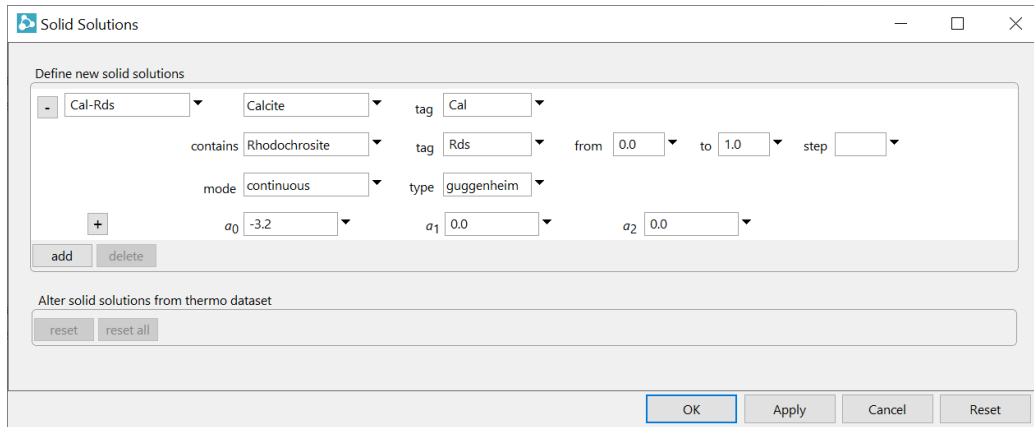
```

solid_solution Plag step .01
swap Ab(.3)-An(.7) for Na+
swap An(.31)-An(.69) for Ca++
5 free mmol/kg Ab(.3)-An(.7)
5 free mmol/kg Ab(.31)-An(.69)

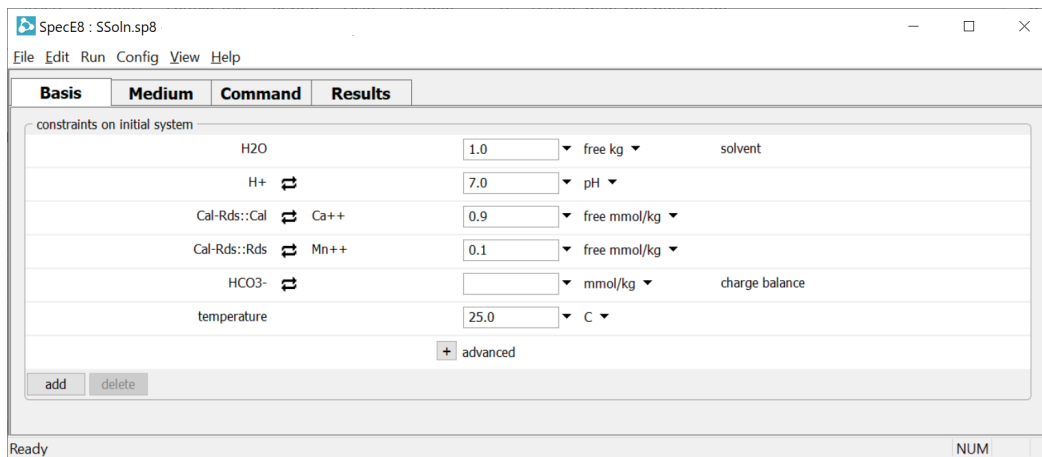
```

and rerunning the calculation.

To complete a fully worked example (“SSoln.sp8”), we model a fluid in equilibrium with a solid solution of calcite and rhodochrosite, using a continuous implementation. First, configure the solution on the **Config → Solid Solutions...** dialog



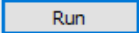
The single Guggenheim coefficient sets up a regular solution of the carbonate minerals.  
On the **Basis** pane



swap the two end members into the system and constrain the mass of each. As shown, **SpecE8** is set to find the equilibrium fluid composition when the mole fraction  $X_{\text{Calcite}}$  of calcite in the solid solution is 0.9. To work this problem from the **Command** pane instead, enter the commands

```
solid_solution Cal-Rds Calcite tag Cal contains \
  Rhodochrosite tag Rds Guggenheim a0= -3.2

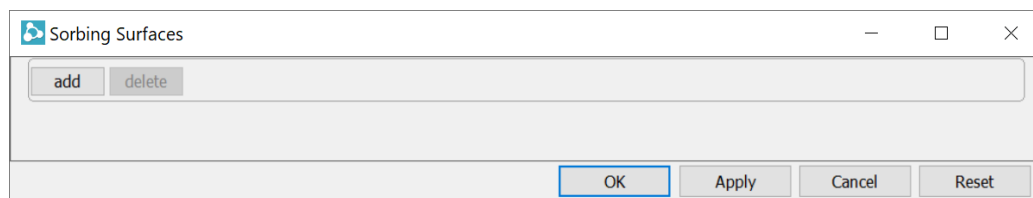
swap Cal-Rds::Cal for Ca++
swap Cal-Rds::Rds for Mn++
Cal-Rds::Cal = .9 free mmol/kg
Cal-Rds::Rds = .1 free mmol/kg
pH = 7
balance on HCO3-
```

In either case, move to the **Results** pane, click  and choose **View → Results** to examine the calculation results.


Since the solid solution's end members were set in equilibrium with the fluid, the solution's saturation index is zero. The minerals corresponding to the end members, in contrast, are undersaturated in the fluid, reflecting the greater stability of the solid solution relative to its pure components. The calculation predicts a log activity ratio for  $\text{Ca}^{++}/\text{Mn}^{++}$  of ~4. As an exercise, how would this value change if the solution were ideal? If it were replaced in the basis by the pure end member minerals?

## 7.7 Sorption onto mineral surfaces


**SpecE8** can model the sorption of species from solution onto mineral surfaces according to a number of methods (see [Sorption onto mineral surfaces](#) in the **Configuring the Programs** chapter of this guide). To consider sorption in your **SpecE8** calculation, drag a surface reaction dataset into the **SpecE8** window, or use the **File → Open → Sorbing Surfaces...** (or **Config → Sorbing Surfaces...**) dialog



(or the `surface_data` command) to point to a dataset for the surface of interest. Notably, you may load any number of surface datasets, describing reaction at any number of surfaces, in a single run and they will be considered simultaneously in your calculations.

To disable consideration of a surface complexation dataset, highlight the dataset on the **Sorbing Surfaces...** dialog and press the  button, or type the command

```
surface_data remove <dataset>
```

To disable all loaded datasets, select all of the datasets on the **Sorbing Surfaces...** dialog and press the  button, or type the command

```
surface_data off
```

### 7.7.1 Surface complexation

**SpecE8** can account for surface complexation according to any of the methods supported by the GWB, including the two-layer, triple-layer, and CD-MUSIC models. To invoke surface complexation, simply load the dataset or datasets of interest.

Dataset “FeOH.sdat”, for example, describes sorption onto the surface of hydrous ferric hydroxide according to the two-layer surface complexation model. Adding this dataset, as described above, causes the program to consider surface complexation whenever a hydrous ferric hydroxide mineral such as  $\text{Fe}(\text{OH})_3$  precipitate, goethite, or hematite appears in the system.

To trace an example, double-click on the “Surface.sp8” input file to launch **SpecE8**, then move to the **Basis** pane.

The SpecE8 window is shown with the 'Basis' tab selected. The 'constraints on initial system' section contains the following data:

Species	Value	Unit	Notes
H <sub>2</sub> O	1.0	free kg	solvent
Hematite ↔ Fe <sup>+++</sup>	1.0	free g	
H <sup>+</sup>	5.3	pH	
Ca <sup>++</sup>	2.4	mg/kg	
Mg <sup>++</sup>	3.5	mg/kg	
Ba <sup>++</sup>	0.04	mg/kg	
Na <sup>+</sup>	0.4	mg/kg	
Zn <sup>++</sup>	1.2	mg/kg	
SO <sub>4</sub> <sup>--</sup>	15.0	mg/kg	
Cl <sup>-</sup>	8.0	mg/kg	
temperature	25.0	C	

Buttons at the bottom: add, delete, + advanced

This input sets up a model of a dilute fluid coexisting with a ferric hydroxide surface. The program calculates the sorbing surface area from the amount of mineral present (1 g) and the specific surface area given in “FeOH.sdat” (600 m<sup>2</sup>/g).

The compositional constraints apply to species in the fluid, excluding those sorbed onto the surface, unless you specify otherwise by checking “sorbate” on the **Config → Options...** dialog

The Options dialog box contains the following settings:

- options**
  - ☐ Kd ☒ sorbate
  - gas pressure model: default
- density**
  - method: Batzle-Wang
  - use NaCl fluid of same: ☒ TDS ☐ chlorinity
- log K span**
  - ☐ extrapolate
  - ☐ span min: [ ] C max: [ ] C

Buttons at the bottom: OK, Apply, Cancel, Reset

or with the `sorbate` command (see **SpecE8 Commands** in the *GWB Command Reference*). In the example above, the fluid contains 2.4 mg/kg  $\text{Ca}^{++}$ , 15 mg/kg  $\text{SO}_4^{--}$ , etc.; the mineral surface will be in equilibrium with the fluid and hence contain sites with additional amounts of calcium, sulfate, and so on.

**SpecE8** writes the calculated sorbing surface area, surface charge density, mean surface potential, mole numbers of the surface species, and the sorbed fractions of each component into the text-format dataset “SpecE8\_output.txt”, as well as “SpecE8\_plot.gtp”, where it is available for plotting with **Gtplot**. In this example,  $\text{Ca}^{++}$  and  $\text{Ba}^{++}$  are sorbed only weakly, whereas  $\text{Zn}^{++}$  and  $\text{SO}_4^{--}$  sorb rather strongly.

Several datasets (“FeOH.sdat”, “FeOH+.sdat”, and “FeOH\_minteq.sdat”) describing surface complexation on hydrous ferric oxide are included in the software release, along with datasets for goethite and gibbsite, but you can prepare additional datasets for other surface types. You can also invoke more than one dataset in a single **SpecE8** calculation. For example, if you have prepared a dataset “SiOH.sdat” to describe sorption onto silica, adding both “FeOH.sdat” and “SiOH.sdat” with the **File → Open → Sorbing Surfaces...** dialog or the commands


```
surface_data FeOH.sdat
surface_data SiOH.sdat
```

causes **SpecE8** to account for sorption onto both ferric and silica surfaces.

The constant capacitance and constant potential models are variants of the surface complexation model. You set these models from the **Config → Sorbing Surfaces...** dialog, or using the `surface_capacitance` and `surface_potential` commands (see [Constant capacitance model](#) and [Constant potential model](#) in the **Configuring the Programs** chapter of this guide).

### 7.7.2 Ion exchange

As described in the **Configuring the Programs** chapter of this guide (see the [Ion exchange](#) section), you can model ion exchange in two ways. The first method is to swap an activity ratio into the basis. This method is equivalent to assuming that there exists a sufficiently large reservoir of exchanging ions that the composition of the exchanging surface remains invariant.

Once you have swapped the activity ratio into the basis, constrain its value. For example, in the **Basis** pane, select  → **Ratio...** and set the ratio  $a_{\text{Ca}^{++}}/a_{\text{Na}^+}^2$  to “0.2”, or follow the steps

```
swap Ca++/Na+^2 for Ca++
ratio Ca++/Na+^2 = 0.2
```

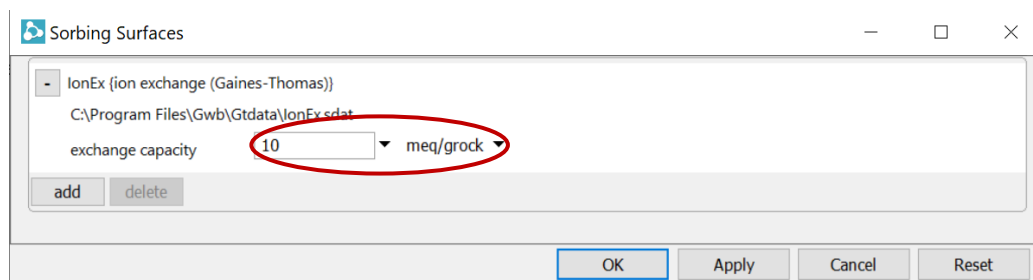


For a more general treatment of ion exchange, prepare a small dataset of the exchange reactions to be considered, using file “IonEx.sdat” as a template. Load the dataset of exchange reactions with the **File → Open → Sorbing Surfaces...** dialog, or the `surface_data` (or `read`) command

```
surface_data MyIonEx.sdat
```

You can load one or more exchange datasets (containing one or more exchange reactions) at a time, and in a single run combine ion exchange datasets with other types of surface reaction datasets.

**SpecE8**, in its calculations, maintains a mass balance on the exchanging sites and reports the composition of the exchanging surface. You must, therefore, specify the exchange capacity in the modeled system. On the **Sorbing Surfaces...** dialog, enter the value and hit **Apply**

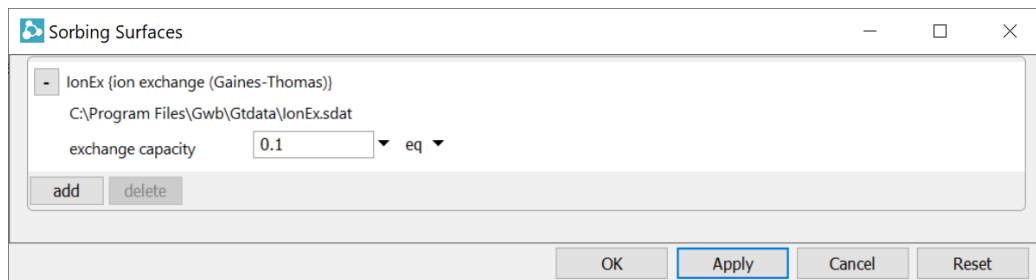


or use the `exchange_capacity` command

```
exchange_capacity = 10 meq/g
```

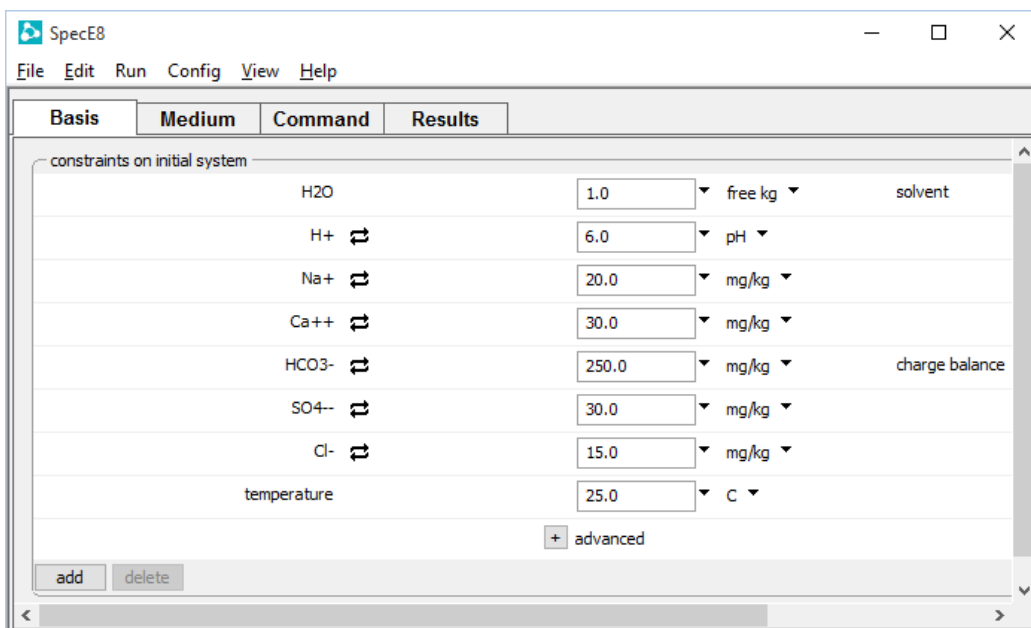
You can set the exchange capacity (i.e., the CEC or AEC) in terms of either the total number of charge equivalents in the system (eq, meq, and so on), or the number of equivalents per gram of mineral (eq/g, ...). In the latter case, the program determines the total mineral mass in the system, including equilibrium and kinetic minerals and end members, and unreactive or inert minerals in the system, to calculate the total exchange capacity. You set inert volume with the `inert` command, or on the **Medium** pane; inert minerals are taken to have a density 2.65 g/cm<sup>3</sup>.

As an example of a **SpecE8** calculation accounting for an ion exchange reaction, double-click on the “IonEx.sp8” input file to launch **SpecE8**. Go to the **Config → Sorbing Surfaces...** dialog



to confirm that you've loaded IonEx.sdat, a surface dataset of ion exchange reactions, and to see the value assumed for the surface's exchange capacity.

Move to the **Basis** pane



to see the composition of the fluid. In this example, the amount of Na<sup>+</sup> and Ca<sup>++</sup> in solution controls the composition of the exchanging surface.

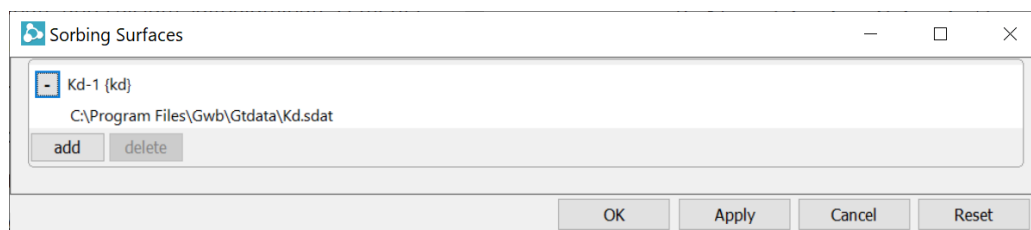
### 7.7.3 Distribution coefficients ( $K_d$ )

To set up a calculation considering sorption described by  $K_d$ , read one or more datasets containing distribution coefficients for sorption reactions from the **File** → **Open** → **Sorbing Surfaces...** dialog, or using the `surface_data` command (see [Distribution coefficients \( \$K\_d\$ \)](#) in the **Configuring the Programs** chapter of this guide). You prepare the datasets using “Kd.sdat” as a template file.

Unlike the other sorption methods, this approach carries the sorbed concentration in moles per mass solid, rather than liquid phase. It is important in configuring a **SpecE8**

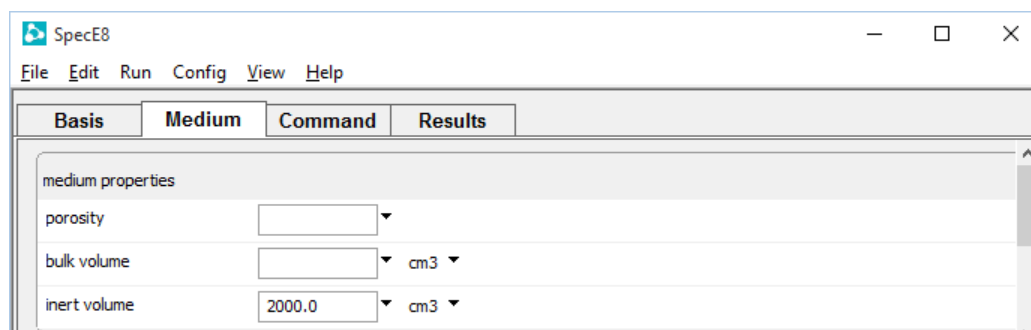
calculation, therefore, to specify carefully the mass of minerals in the system. Minerals include equilibrium and kinetic minerals and end members, as well as the unreactive or inert volume. You specify inert volume (in  $\text{cm}^3$ ) with the `inert` command, or on the **Medium** pane (the program converts this value to mass, assuming a density of  $2.65 \text{ g/cm}^3$ ).

As an example of using the distribution coefficient method to model ion sorption in **SpecE8**, double-click on the “KD.sp8” input file. When **SpecE8** opens, go to the **Config** → **Sorbing Surfaces...** dialog

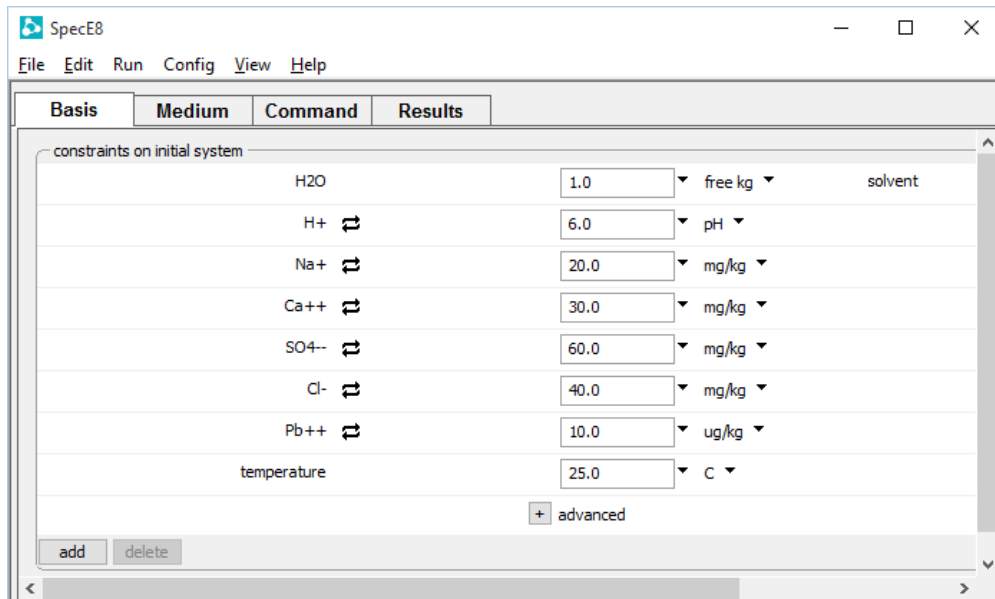


to confirm that you’ve loaded the Kd.sdat sorption dataset.

Move to the **Medium** pane



to see the volume of minerals in the system. The **Basis** pane

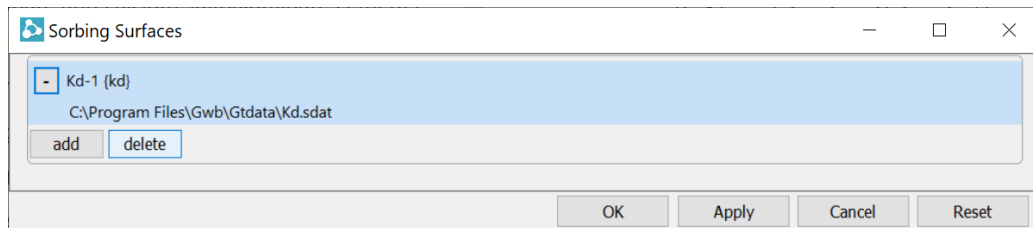


describes the fluid. In this case, the program models a system including a fluid containing 10  $\mu\text{g/kg}$  Pb<sup>++</sup> in contact with minerals onto which a considerably greater mass of the ion is predicted to be sorbed.

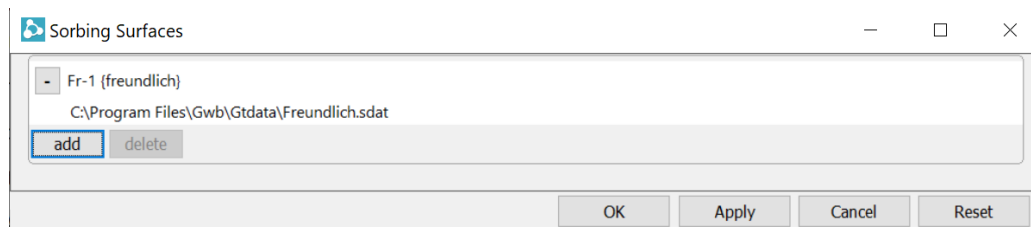
### 7.7.4 Freundlich isotherms

To describe sorption in terms of Freundlich isotherms (see [Freundlich isotherms](#) in the **Configuring the Programs** chapter of this guide), prepare a dataset of sorption reactions following the format of file "Freundlich.sdat". The procedure is otherwise parallel to the  $K_d$  approach, as described in the previous section.

Continuing the example above, use **Config → Sorbing Surfaces...** to select the "Kd.sdat" file and click the **delete** button, then hit **Apply**



then click **add** and select "Freundlich.sdat" from the Gtdata folder within the GWB installation directory



or use the steps

```
surface_data remove Kd.sdat
surface_data Freundlich.sdat
go
```

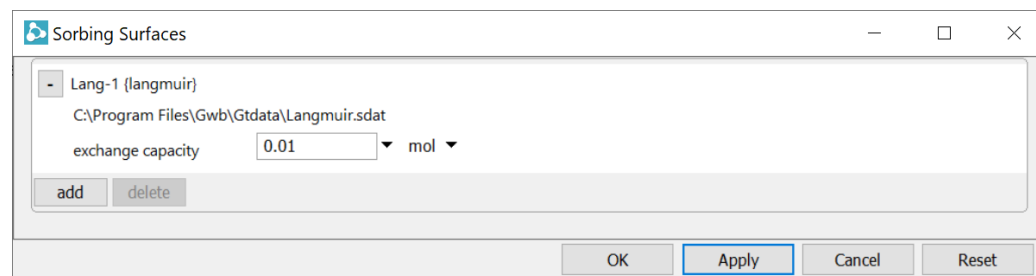
to implement the Freundlich model in place of the  $K_d$  approach. Alternatively, double-click on the “Freundlich.sp8” input file to load the example directly.

### 7.7.5 Langmuir isotherms

To model sorption according to Langmuir isotherms, prepare a reaction dataset containing the sorbing reactions and their equilibrium constants, as described under [Langmuir isotherms](#) in the **Configuring the Programs** chapter of this guide. Prepare the dataset in the format of file “Langmuir.sdat”.

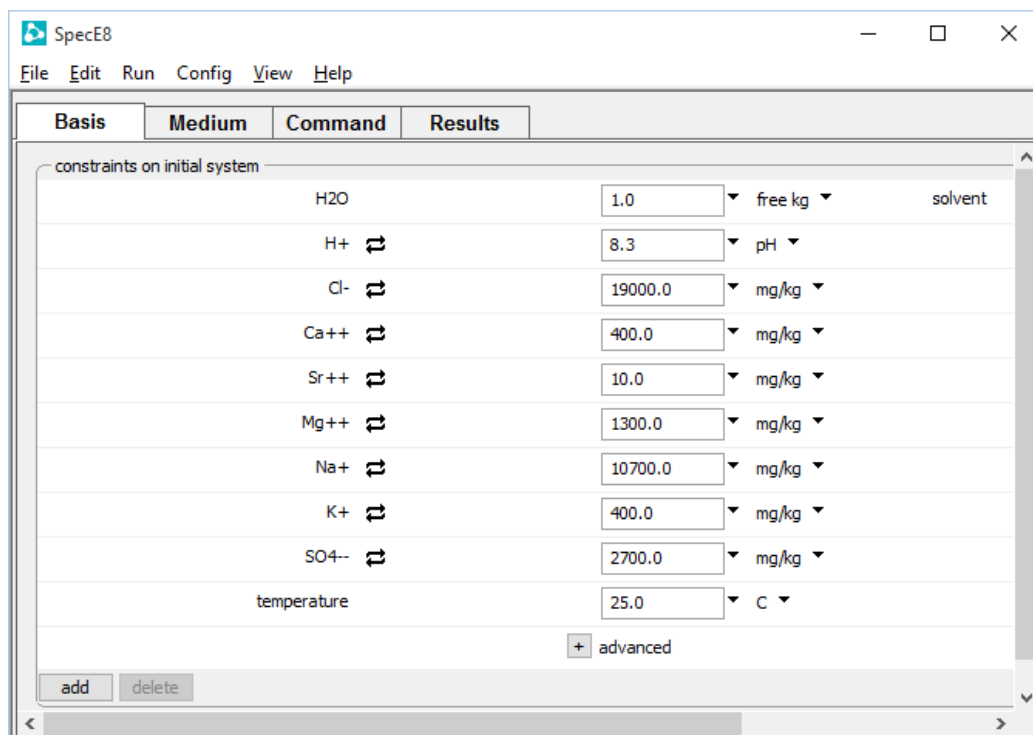
Enter the dataset into a **SpecE8** run, as above. You can enter one or more Langmuir datasets, and mix Langmuir datasets with datasets for other sorption methods. As with the ion exchange method, specify the total number of sorbing sites in either absolute terms (mol, mmol, ...) or per gram of dry sediment (mol/g, mmol/g, ...). Enter the sorption capacity on the **Sorbing Surfaces...** dialog, or with the `exchange_capacity` command.

As an example, double-click on the “Langmuir.sp8” input file. When **SpecE8** opens, go to the **Config → Sorbing Surfaces...** dialog



to confirm that you’ve loaded Langmuir.sdat, an example surface dataset, and to see the value assumed for the surface’s exchange capacity.

Move to the **Basis** pane



to see the composition of the fluid.

**SpecE8** accounts for the sorption of  $\text{Ca}^{++}$  and  $\text{Sr}^{++}$  according to the Langmuir isotherms in the example dataset “Langmuir.sdat”.

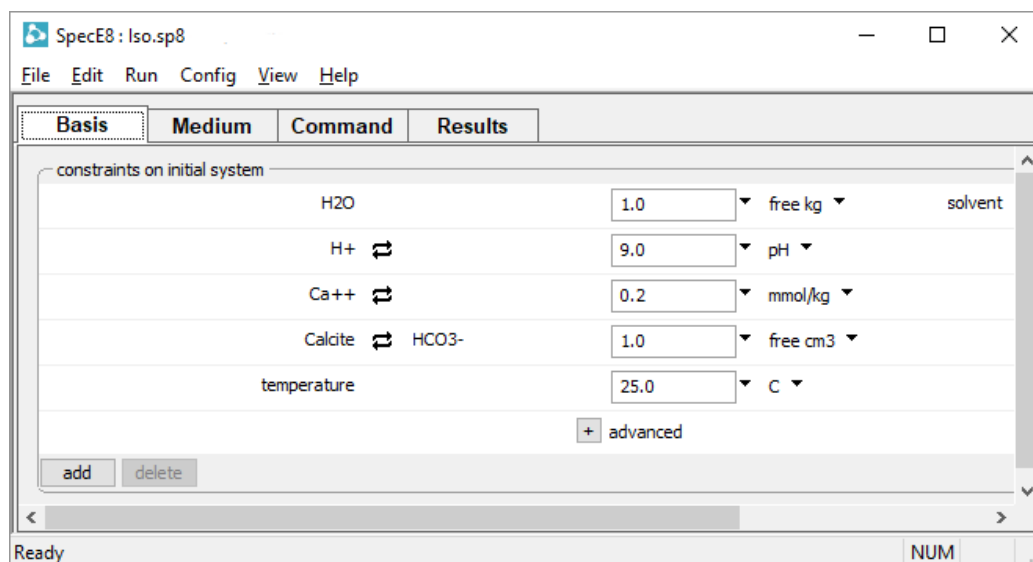
## 7.8 Fractionation of stable isotopes

**SpecE8** can figure the equilibrium fractionation of stable isotopes among solvent, aqueous and surface species, minerals, end members, and gases. To define an isotopic system, set the bulk isotopic composition of the fluid, either from the **Config → Isotopes...** dialog or the **Command** pane. The **Isotopes...** dialog lists the isotope systems included in the isotope fractionation file loaded into the program (see [Isotope fractionation datasets](#) in the **Configuring the Programs** chapter of this guide). The “isotope.dat” file, distributed with the software, contains coefficients for calculating fractionation factors of stable isotopes  $^2\text{H}$ ,  $^{13}\text{C}$ ,  $^{18}\text{O}$ , and  $^{34}\text{S}$  as functions of temperature.

To configure a **SpecE8** run, specify compositions relative to any isotopic standard, including SMOW, PDB, or CDT. The program predicts isotopic compositions for species, minerals, end members, and gases relative to the same standard, and writes the results to the dataset “SpecE8\_isotope.txt”, as well as to “SpecE8\_plot.gtp”, where it is available for plotting by **Gtplot**.

The program begins by calculating the compositions of solvent and dissolved species to honor the fluid's bulk composition, as specified, assuming isotopic equilibrium among species. The program then sets minerals and end members in the system and any buffered gases to isotopic compositions in equilibrium with the fluid.

As an example (file "Iso.sp8"), we calculate the isotopic composition of calcite ( $\text{CaCO}_3$ ) and  $\text{CO}_2(\text{g})$  in equilibrium with a Ca- $\text{HCO}_3$  water for which  $\delta^{13}\text{C} = 0\text{‰}$  and  $\delta^{18}\text{O} = -6\text{‰}$ . Begin by setting the water composition on the **Basis** pane



or enter the commands

```
pH      = 9
Ca++    = .2 mmol/kg
swap Calcite for HCO3-
Calcite = 1 free cm3
```

Next, move to the **Config → Isotopes...** dialog

to set the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  for the fluid, or issue the commands

```
carbon-13 = 0
oxygen-18 = -6
```

Move to the **Results** pane, click **Run**, then choose **View → Results → Isotopic** to display results of the calculation.

In output, we see the  $\delta^{13}\text{C}$  of calcite in isotopic equilibrium with the fluid is 2.8‰, and  $\delta^{18}\text{O}$  is 22.6‰. For  $\text{CO}_2(\text{g})$ ,  $\delta^{13}\text{C}$  is -7.6‰ and  $\delta^{18}\text{O}$  is 34.5‰. Owing to hydration effects, the carbon isotopic composition of the dissolved carbonate and bicarbonate species is higher than  $\text{CO}_2(\text{aq})$ . In terms of  $^{18}\text{O}$ , in contrast, dissolved carbon dioxide is heavier than the bulk fluid.

## 7.9 Settable variables

**SpecE8** allows you to alter the values of certain variables carried in the calculation. [Table 7.3](#) lists these variables and their units and default values. To change a variable, type the new value in the **Config → Iteration...** dialog box, on the **Basis** pane (click **+** to expand the “advanced” section), on the **Medium** pane, or enter as a command the variable name followed by the new value.



**Table 7.3**      **Settable variables, their units and default values**

<i>Pane or Dialog</i>	<i>Variable</i>	<i>Default</i>	<i>Unit</i>	<i>Description</i>
<b>Basis</b>	density	<i>not set</i>	g/cm <sup>3</sup>	Density of initial fluid.
	TDS	<i>not set</i>	mg/kg	Total dissolved solids, initial fluid.
<b>Medium</b>	inert	0	cm <sup>3</sup>	Volume of inert minerals in system.
<b>Iteration</b>	epsilon	5 x 10 <sup>-11</sup>	–	Convergence criterion.
	itmax	999	–	Allowed number of iterations.
	pitz_dgamma	0.1	–	For virial activity coeffs., maximum fractional change per iteration.
	pitz_precon	10	–	For virial activity coeffs., maximum number of pre-conditioning steps.
	pitz_relax	0.5	–	For virial activity coeffs., relaxation factor during iteration.
	simax	3	Molal	Maximum stoichiometric ionic strength used to calculate water activity (Debye-Hückel model).
	timax	3	Molal	Maximum true ionic strength used to calculate activity coefficients (Debye-Hückel model).

Examples:

```
itmax = 1000
epsilon = 10^-9
```

The value given must be in the units carried internally by the program, as listed in [Table 7.3](#).

To restore a variable to its default value, enter a blank field in the dialog box, or on the **Command** pane type its name without a value or followed by a `?`:

```
itmax  
itmax = ?
```

Current values of the variables can be viewed at any time by looking at the dialog box, the **Basis** or **Medium** pane, or using the command `show variables`.

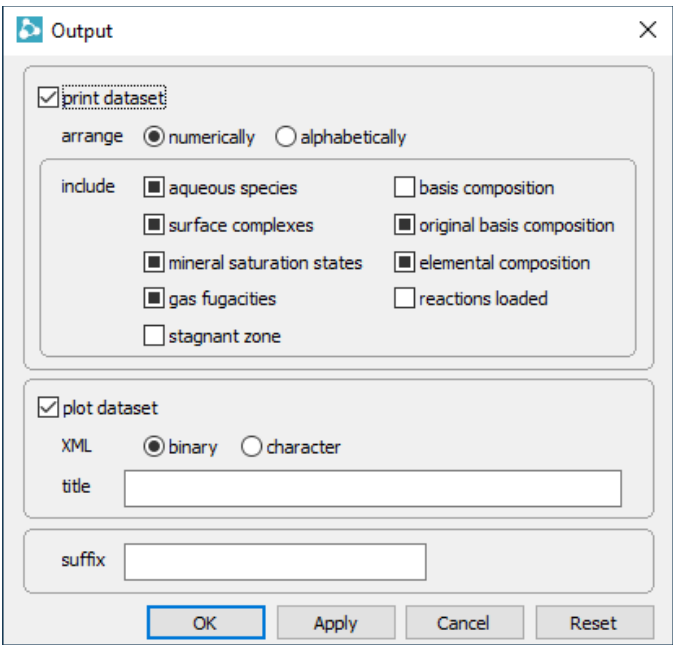
## 7.10 Controlling the printout

**SpecE8** lets you control the amount of detail presented in the calculation results written to “SpecE8\_output.txt”. The dataset is known commonly as the “printout”, although it need never be printed. The printout can contain information about (1) the concentration and activity of dissolved species, (2) the saturation indices of various minerals, (3) gas fugacity and partial pressure, (4) surface complexes, and (5) the system’s bulk composition in terms of elements of either the current or original basis. The printout can also contain a list of the chemical reactions considered in the calculation, and their initial log *K*s, as well as initial values of virial coefficients.

You can specify that any of these lists be excluded from the printout, or included in a short or long format. To vary the printout, the user can set each aspect in [Table 7.4](#) to “none”, “short”, or “long” on the **Config → Output...** dialog, or in a command. For example:

```
print species = long  
print basis = short  
print saturations = none
```

The current print settings can be viewed at any time by looking at the three-way check boxes on the **Config → Output...** dialog. A blank check box ☐ indicates exclusion from the printout, a check ☒ indicates inclusion in short format, and shading ☒ indicates inclusion in long format.



Alternatively, type

```
show printout
```

Table 7.4 Print options and default settings in SpecE8		
	Default	Description
print dataset	on	to “SpecE8_output.txt”
print alphabetically	off	Arrange entries in dataset alphabetically
species	long	Aqueous species
surfaces	long	Surface complexes
saturation	long	S./ of minerals and solid solutions
gases	long	Gas fugacity and partial pressure
basis	none	Composition, current basis
orig_basis	long	Composition, original basis
elements	long	Elemental composition
reactions	none	Reactions and log <i>K</i> s, and virial coefficients
stagnant	none	Composition of stagnant zone

## 7.11 SpecE8 command line

You can start **SpecE8** by clicking the icon under the “Start” menu, opening a “.sp8” file, or entering the command `spece8.exe` from the Windows “Command Prompt.” When you start **SpecE8** from the command line (as opposed to clicking on the icon), you can specify a number of arguments. For example, the command

```
spece8.exe -i my_script -d my_thermo.tdat
```

causes **SpecE8** to read input commands from a file “my\_script”, and to use “my\_thermo.tdat” as the thermodynamic database.

The following options are available from the command line:

<code>-cd</code>	Change the working directory to the directory containing the input script specified with the <code>-i</code> option.
<code>-nocd</code>	Do not change the working directory.
<code>&lt;input_script&gt;</code> <code>-i &lt;input_script&gt;</code>	Set a file from which to read input commands.
<code>-gtd &lt;gtdata_dir&gt;</code>	Set directory to search for thermodynamic datasets.
<code>-cond &lt;cond_data&gt;</code>	Set the dataset for calculating electrical conductivity.
<code>-d &lt;thermo_data&gt;</code>	Set the thermodynamic dataset.
<code>-iso &lt;isotope_data&gt;</code>	Set the file of isotope fractionation factors to be used.
<code>-s &lt;surface_data&gt;</code>	Set a dataset of surface sorption reactions.

# Using Gtplot

---

**Gtplot** is an interactive, mouse-driven program that produces various types of diagrams showing the results of modeling aqueous speciation with **SpecE8** or the data stored in a **GSS** spreadsheet.

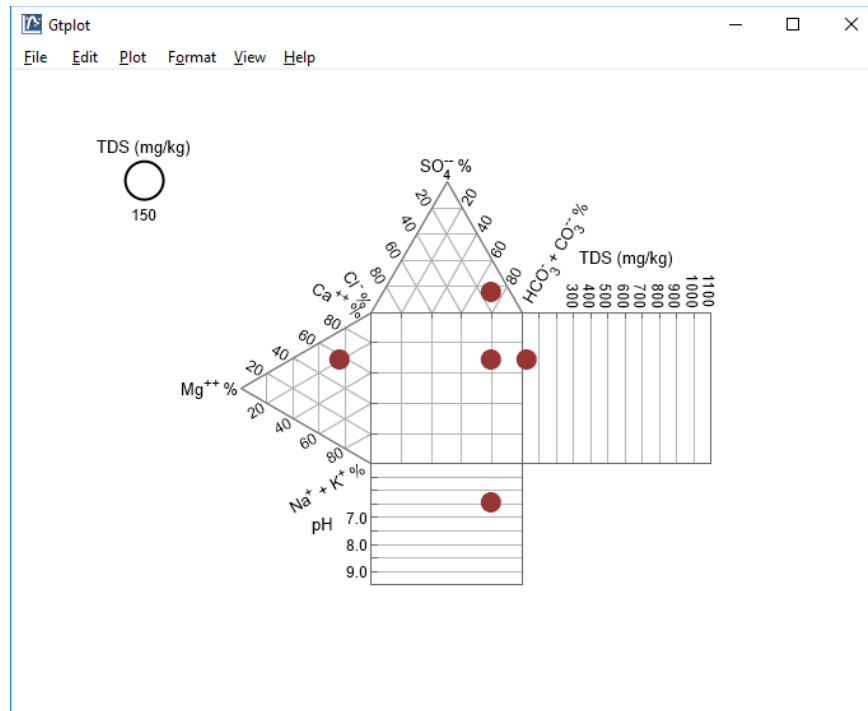
After running **SpecE8**, start **Gtplot** by clicking on **Plot Results** on the **Results** pane, or selecting **Run → Gtplot** from **SpecE8**'s menubar. The program will read the calculation results from the “.gtp” file **SpecE8** produced and render them on any of a number of types of geochemical diagrams. You can leave **Gtplot** active when you run further **SpecE8** calculations. Each time **SpecE8** completes a run, it signals **Gtplot**, which updates its display to reflect the new results.

After preparing a **GSS** spreadsheet (“.gss” file, see the [Using GSS](#) chapter of this guide), start **Gtplot** by selecting the analytes you want to plot and making a choice from the **Plot** menu. The program will load the data values and render them initially on the chosen type of diagram. You can select which samples to plot within the **Samples** pane of the dialog for that plot.

You can also start **Gtplot** by opening any “.gtp” file, clicking on the **Gtplot** icon under the “Start” menu, or by typing `gtplot -i <filename>` from the Windows command prompt.

You can take input from a different dataset by choosing **File → Open → Data File....** from the menubar and opening a “.gtp” or “.gss” file.

**Gtplot** opens a window on your computer screen, loads the input data, and renders the data as a two-dimensional plot. The window has three parts: a graphics area, a menubar with pulldown menus, and a frame showing the name of the input dataset and its activity model.

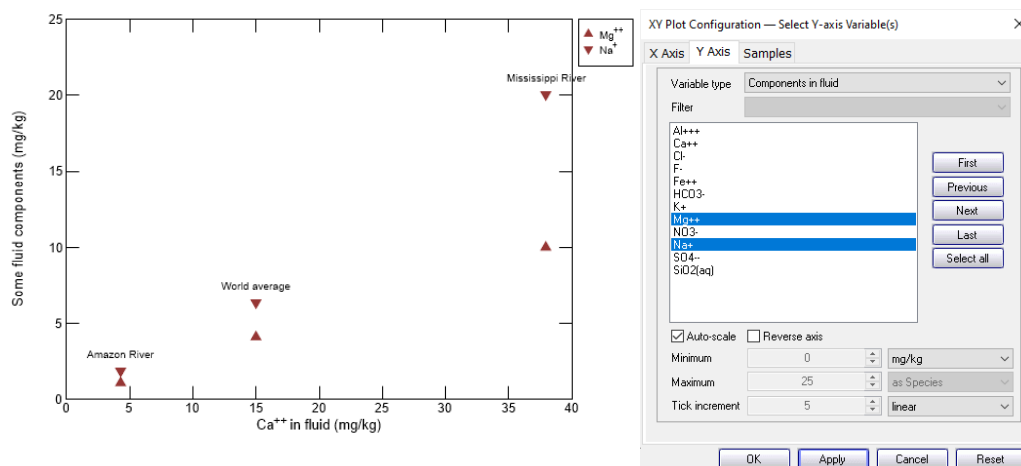


**Gtplot** works using information about the fluid modeled, including its bulk composition (i.e., its composition in terms of  $\text{Na}^+$ ,  $\text{Ca}^{++}$ , and so on), pH, TDS, and carbonate speciation. Plots labeled “ $\text{HCO}_3 + \text{CO}_3$ ” show the sum of the concentrations in solution, in terms of electrical equivalents per kg fluid, of the free  $\text{HCO}_3^-$  and  $\text{CO}_3^{--}$  species. The program calculates this sum from the fluid’s carbonate alkalinity, as determined by the **SpecE8** program. Hence, the value shown for the variable depends not only on carbonate concentration, but the fluid’s pH. In contrast, plots labeled “ $\text{HCO}_3$ ” represent the bulk carbonate concentration of the fluid, taking no account of the speciation of carbonate to the  $\text{CO}_3^{--}$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_2(\text{aq})$  species.

When **Gtplot** starts for the first time in a given directory, it assumes a default configuration. Upon finishing, the program saves for its next run a dataset containing the current configuration of your plots. You can select options from the **File** menu to specify an alternative configuration (see [Loading and saving plot configuration](#)) or reset the entire program configuration.

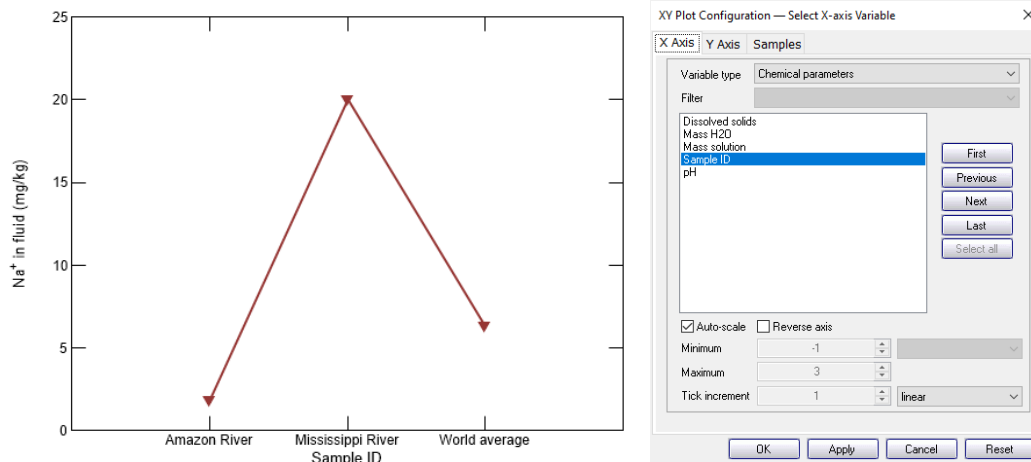
## 8.1 Plot types

Use the **Plot** menu to control the type and configuration of the plot produced.

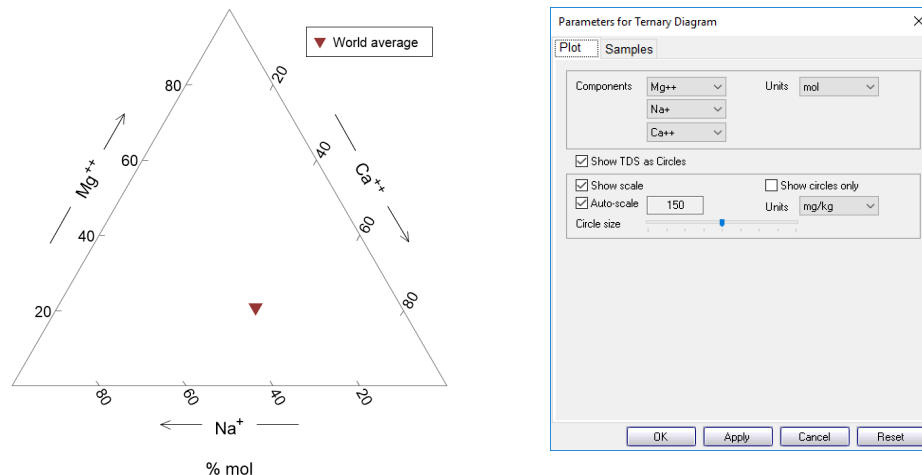


An **XY Plot** shows a plot of fluid composition, with one variable on the x axis and one or more variables on the y axis. Use the following to specify the way the variables are plotted:

- **Variable type** to control the type of variables to appear along the plot's axes.
- **Filter** to list, for species or mineral saturation plots, the set of just those that contain a given basis species.
- **Auto-scale** to set the data range for the axis to span the data to be plotted.
- **Minimum, Maximum, and Tick Factor** to set the data range for the axis.
- **Reverse axis** to reverse the sense of the axis.
- **Units** to select alternative units, if any, for the axis.
- **As** to plot values as elemental equivalents, or as protonated or deprotonated species equivalents.
- **Type** to set the axis to a linear, log, or delta scale. A delta scale shows change in a variable's value from the initial point in the reaction path.
- **First, Previous, Next, Last, and Select all** to cycle through the variable choices.



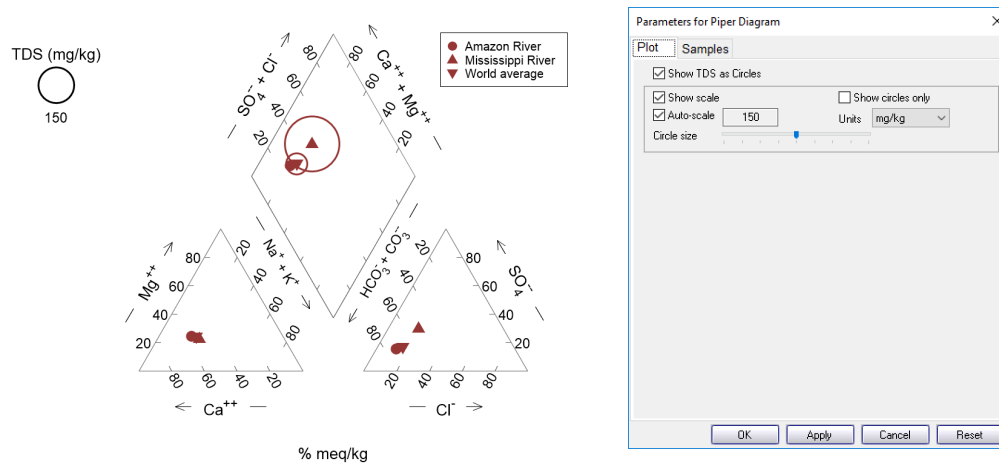
A **Series Plot** is a special type of xy plot that shows **GSS** data sample by sample, with one or more variables opposite the Sample ID. Other notable examples include the **Time and date** plot, in which **Gtplot** combines the “Date” and “Time” variables from **GSS** into a single variable, and **Time of day**, in which data from one or more days are plotted on a single 24-hour span.



A **Ternary Diagram** shows the fluid composition on a tri-linear plot. On the **Plot** pane, use the following to specify the way the diagram is plotted:

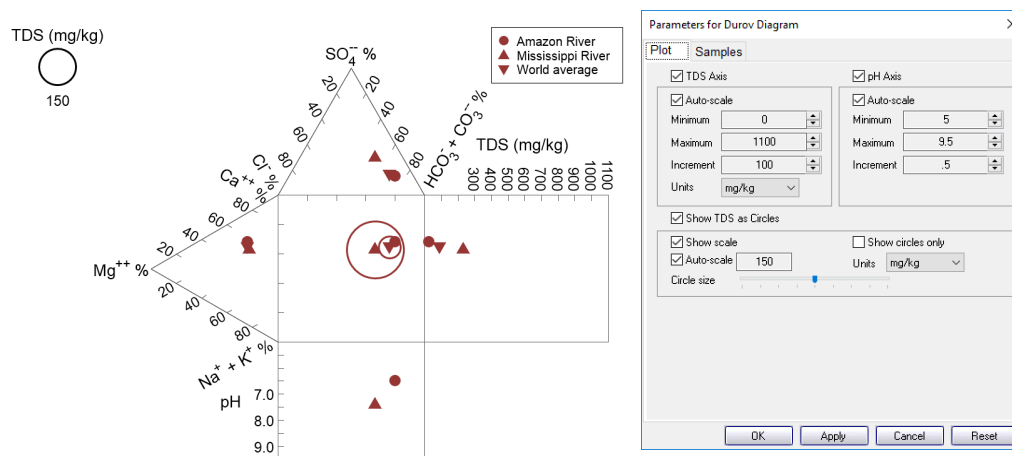
- **Components** to control the three components plotted on the diagram.
- **Units** to select alternative units for the axes, which are plotted as fractions.
- **Show TDS as circles** to control how circles representing a sample’s dissolved solids content should be displayed.





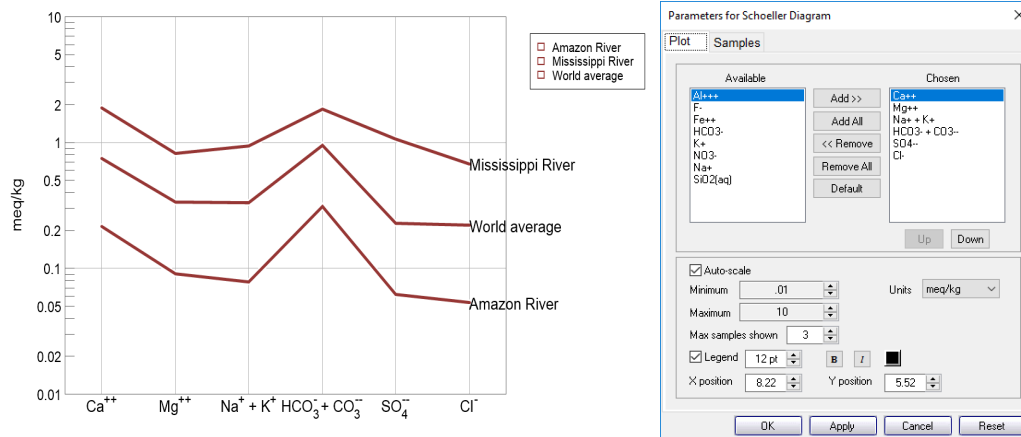
A **Piper Diagram** shows the fluid's major ion composition. Use:

- **Show TDS as circles** to control how circles representing a sample's dissolved solids content should be displayed.



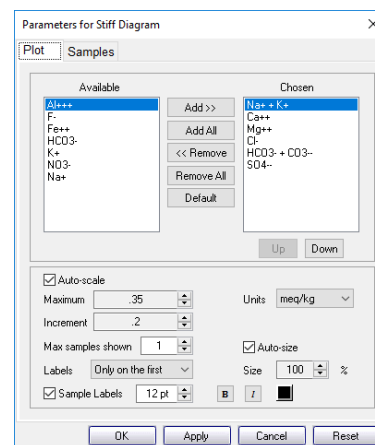
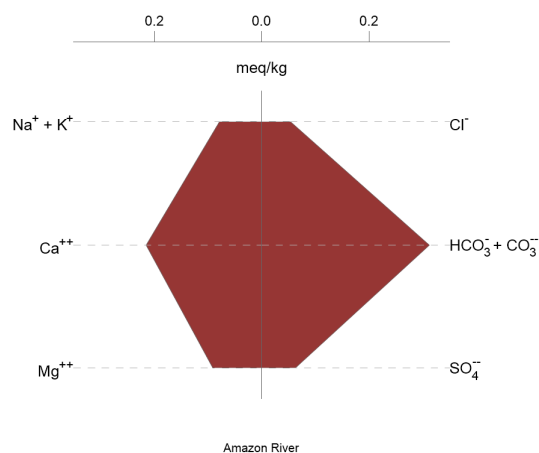
A **Durov Diagram** represents the fluid's major ion composition, TDS, and pH. Use:

- **TDS Axis** to set the Auto-scale; Minimum, Maximum, and Increment; and Units for the TDS axis.
- **pH Axis** to set the Auto-scale and Minimum, Maximum, and Increment for the pH axis.
- **Show TDS as circles** to control how circles representing a sample's dissolved solids content should be displayed.



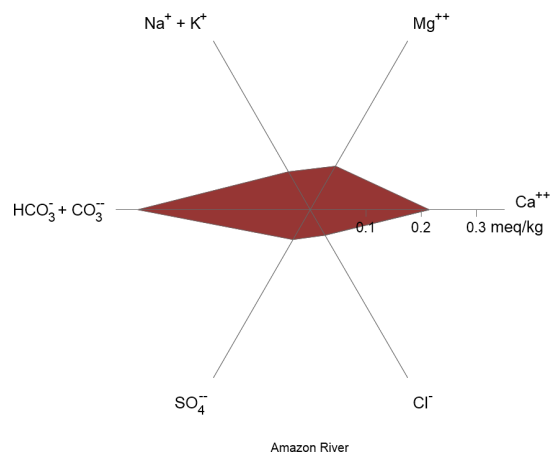
A **Schoeller Diagram** shows the pattern of component concentration on a logarithmic scale. Use:

- **Add, Add All, Remove, Remove All, and Default** to choose the components to include in the diagram.
- **Up, Down** to arrange the order of chosen components along the horizontal axis.
- **Auto-scale, Minimum, and Maximum** to set the data range for the vertical axis.
- **Units** to select alternative units for the vertical axis.
- **Max samples shown** to set the number of samples to display together when the “Block” and “Next Block” buttons on the **Samples** pane are clicked.



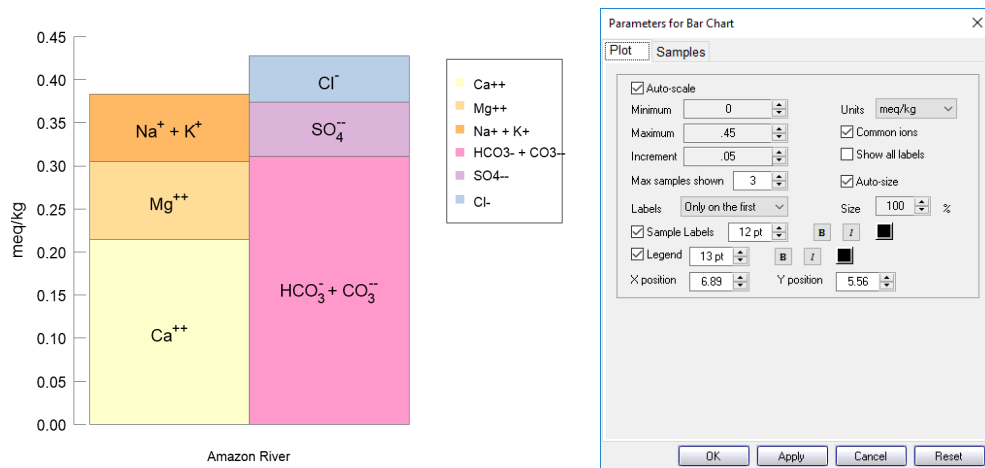
A **Stiff Diagram** represents the fluid's major ion composition as a polygonal shape. Use:

- **Add, Add All, Remove, Remove All, and Default** to choose the components to include in the diagram.
- **Up, Down** to arrange the order of chosen components, with cations plotting on the left and anions on the right.
- **Auto-scale, Maximum, and Increment** to set the data range for the diagram.
- **Max samples shown** to set the number of samples to display together when the “Block” and “Next Block” buttons on the **Samples** pane are clicked.
- **Labels** to control whether the axes and plot labels appear on all samples, only the first sample, or no samples.
- **Units** to select alternative electrical equivalent units.
- **Auto-size** and **Size** to optimize sizing and spacing of multi-sample plots.



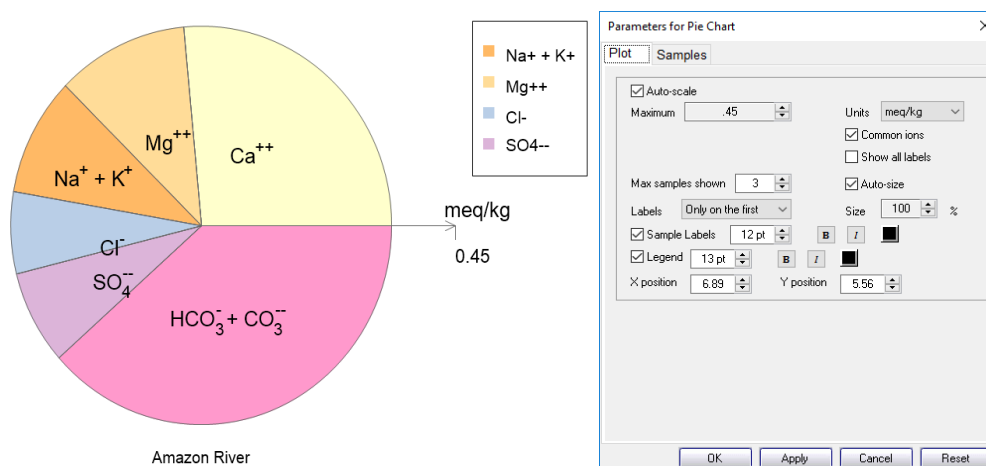
A **Radial Plot** shows the fluid's composition in a manner similar to a Stiff diagram, but in radial coordinates. Unlike Stiff diagrams, Radial plots can display uncharged components. Use:

- **Add, Add All, Remove, Remove All, and Default** to choose the components to include in the diagram.
- **Up, Down** to arrange the order of chosen components.
- **Auto-scale** and **Maximum** to set the data range for the diagram.
- **Max samples shown** to set the number of samples to display together when the “Block” and “Next Block” buttons on the **Samples** pane are clicked.
- **Labels** to control whether the axes and plot labels appear on all samples, only the first sample, or no samples.
- **Units** to select alternative units.
- **Auto-size** and **Size** to optimize sizing and spacing of multi-sample plots.



A **Bar Chart** represents the fluid's cation–anion balance graphically. Use:

- **Auto-scale**, **Minimum**, **Maximum**, and **Increment** to set the data range for the diagram.
- **Max samples shown** to set the number of samples to display together when the “Block” and “Next Block” buttons on the **Samples** pane are clicked.
- **Labels** to control whether the axes and plot labels appear on all samples, only the first sample, or no samples.
- **Units** to select alternative units for the axis.
- **Common ions** to control whether a default set of major ions or all ions in the sample are plotted.
- **Show all labels** to control whether all ions are labeled for a given sample, or only those that are abundant enough that the label would fit naturally.
- **Auto-size** and **Size** to optimize sizing and spacing of multi-sample plots.



A **Pie Chart** is an alternative method for showing cation–anion balance, with the radial direction representing the fluid’s total electrical equivalent content. Use:

- **Auto-scale** and **Maximum** to set the data range for the radial axis.
- **Max samples shown** to set the number of samples to display together when the “Block” and “Next Block” buttons on the **Samples** pane are clicked.
- **Labels** to control whether the axes and plot labels appear on all samples, only the first sample, or no samples.
- **Units** to select alternative units for the radial axis.
- **Common ions** to control whether a default set of major ions or all ions in the sample are plotted.
- **Show all labels** to control whether all ions are labeled for a given sample, or only those that are abundant enough that the label would fit naturally.
- **Auto-size** and **Size** to optimize sizing and spacing of multi-sample plots.

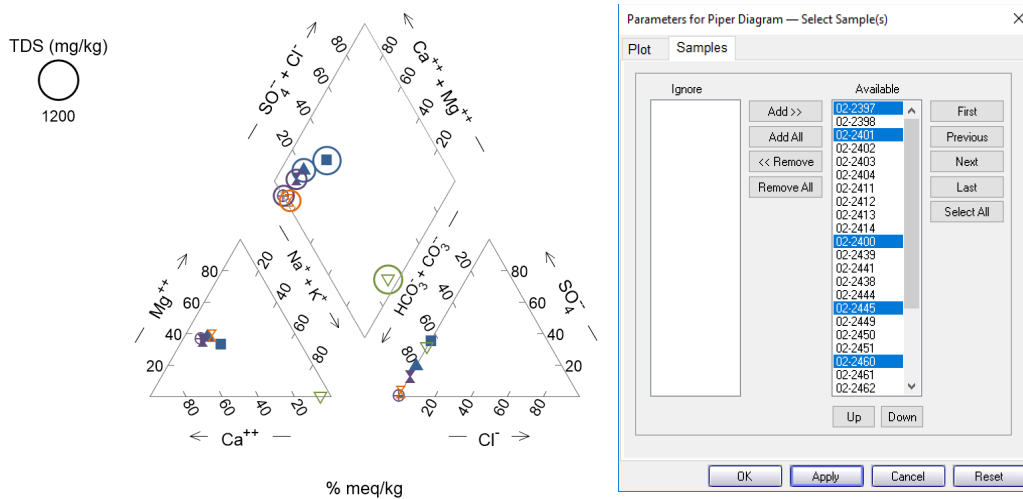
### 8.1.1 Sample selection

**Gtplot** can display data for multiple samples (when plotting **GSS** data) or calculation steps (when plotting results of **SpecE8** and **React** models) in all of its plots. For the **XY Plot**, **Ternary Diagram**, **Piper Diagram**, **Durov Diagram**, and **Schoeller Diagram**, all selected samples (or steps) are displayed on a single set of axes or in a single diagram. The other plots (**Stiff Diagram**, **Radial Plot**, **Bar Chart**, and **Pie Chart**) are more suitably displayed side-by-side.

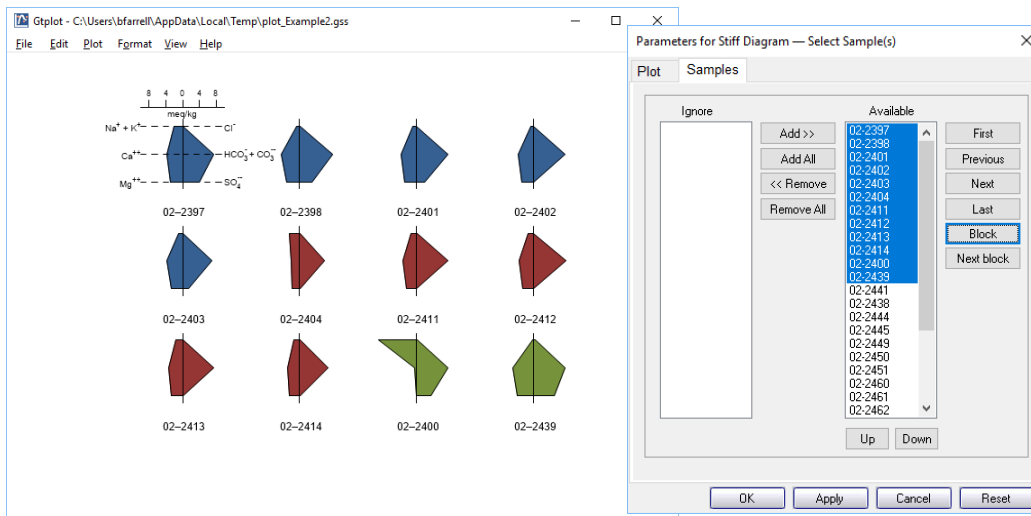
Use the **Samples** (or **Steps**) pane of the appropriate **Plot Configuration** dialog to select samples for plotting. For the **XY Plot**, **Ternary Diagram**, **Piper Diagram**, and **Durov Diagram**, use the following to specify the way samples are plotted:

- **Add**, **Add All**, **Remove**, and **Remove All** to make samples available or unavailable for plotting.

- **Up, Down** to rearrange the order of samples in the Available list.
- **First, Previous, Next, Last, and Select all** to cycle through the available samples. Only selected samples in the Available list will plot.



The **Samples** pane for the **Schoeller Diagram**, **Radial Diagram**, **Stiff Diagram**, **Bar chart**, and **Pie chart** is similar to that described above. Instead of a “Select all” button, however, the “Block” button plots a subset of samples together. Use “Next block” to plot the next subset of samples. You control the number of samples displayed in the “block” by setting “Max samples shown” on the **Plot** pane, as described above.

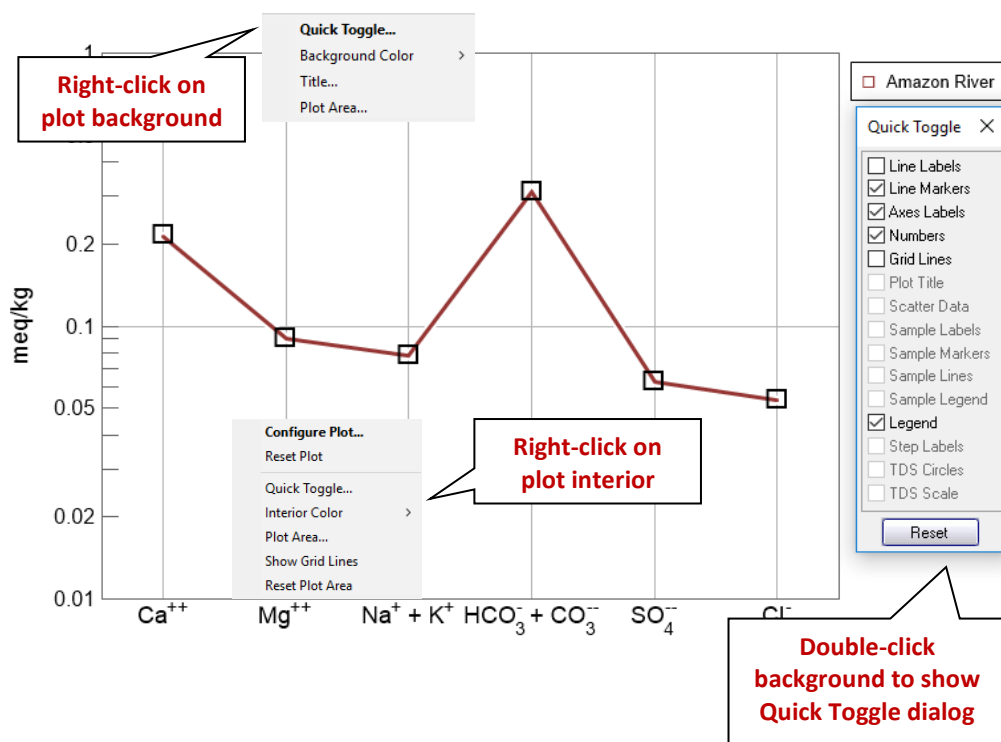


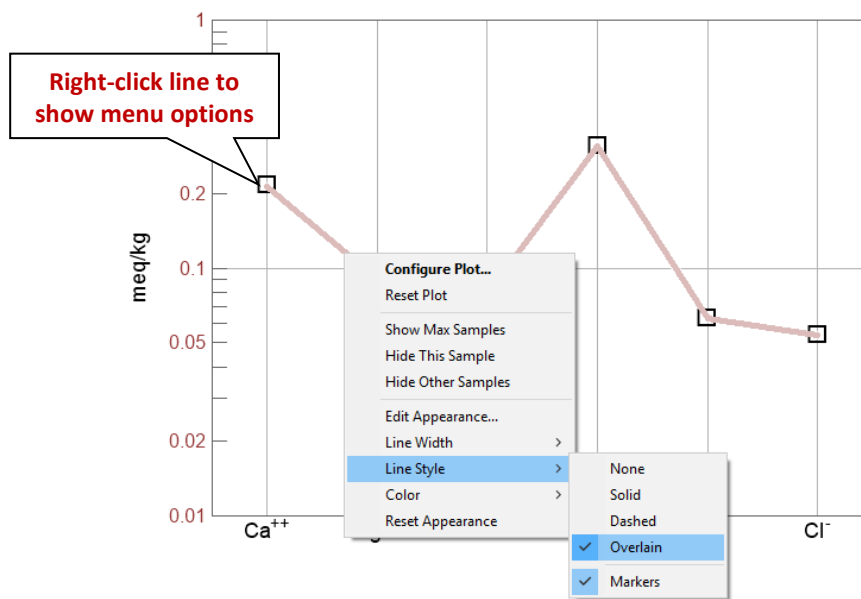
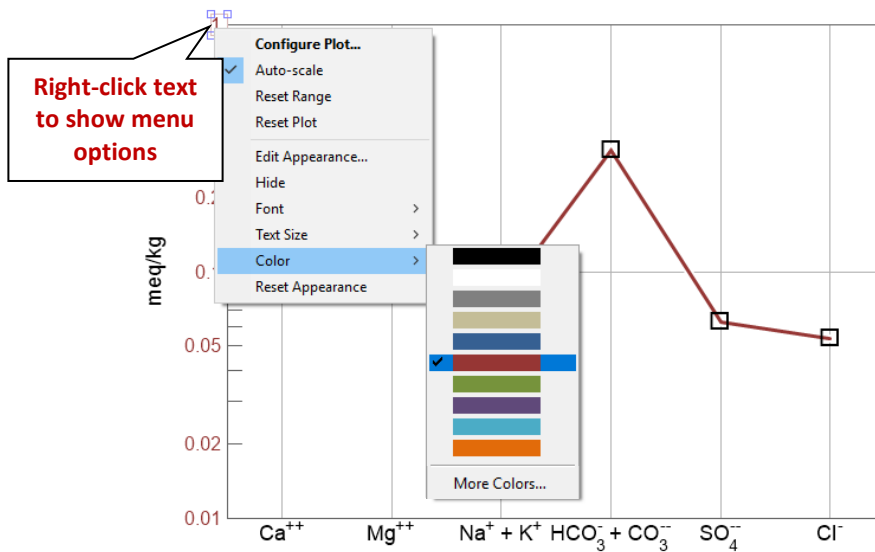
## 8.2 Editing plot appearance

In **Gtplot**, you can interactively modify many aspects of the diagram. A **right-click** on an aspect or area of the plot displays a menu showing the options available. You may choose to reset an axis range or an aspect's appearance to its default state. Using the **Font** tab within the **Format → Appearance...** dialog you can change the font for the entire plot.

To change the font for individual aspects, choose **Font** from that aspect's menu. A **double-click** on an aspect brings up a dialog box related to the first item on the pulldown menu, which in most cases is the plot configuration dialog. These dialogs can also be accessed through the **Plot** menu.

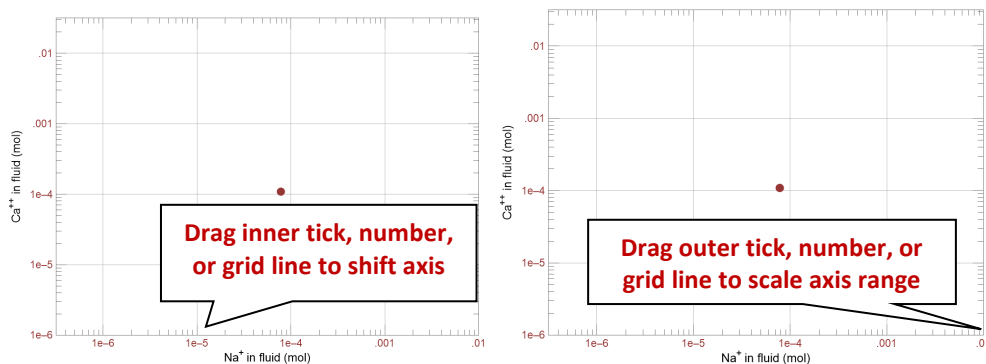
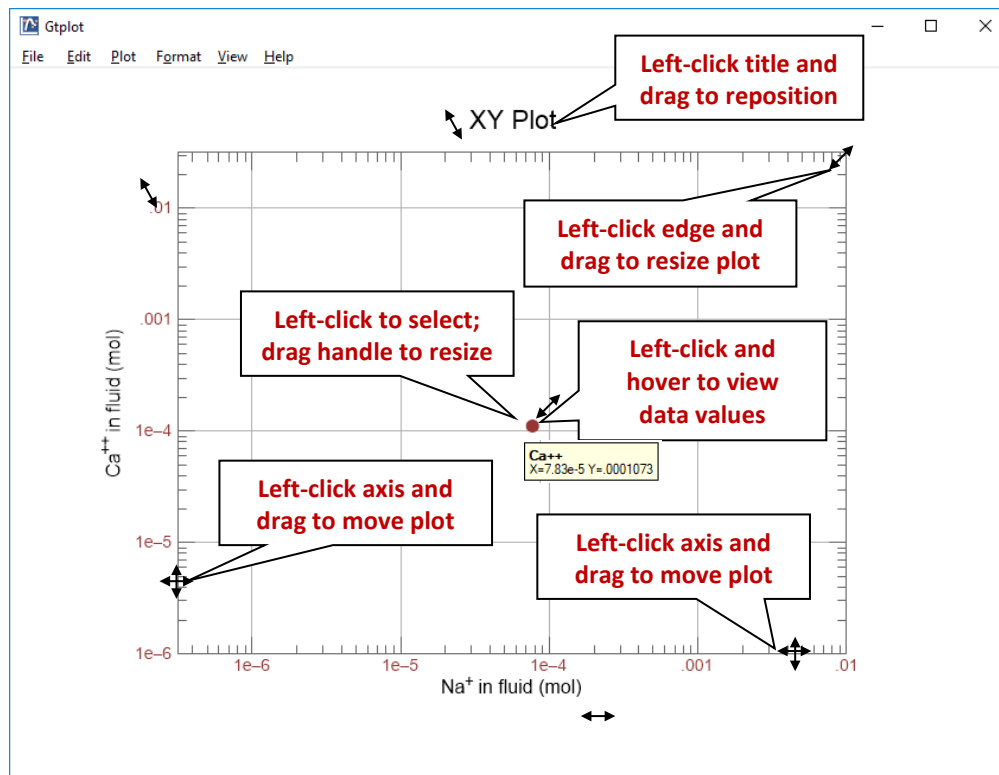
The aspect appearance dialogs can be accessed through the **Format** menu. A **double-click** on the background area will bring up the **Quick Toggle...** dialog, which lets you select the graphical elements to be shown.





A **left-click** on an aspect causes it to be “selected”. An aspect has been selected when its color changes, as in the case of lines, or when it is surrounded by manipulation handles, in the case of text or markers. Change the size of text, markers, and, in the case of the XY Plot, the plot itself by dragging the sizing cursors. Adjust the placement of the plot by clicking within the plot or on either axis and dragging it. The plot title can be moved in the same way.





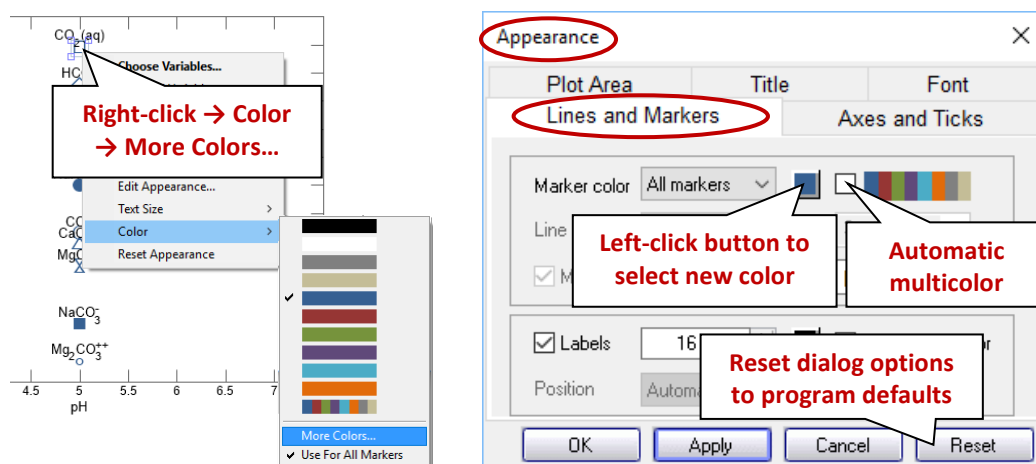
When you read new input data and update the plot with the **Auto-scale** option set, **Gtplot** automatically adjusts the axis ranges to the new data. Otherwise, **Gtplot** maintains the axis ranges you have set for the previous plot. This option lets you quickly adapt the axis ranges to new data.

You can change the range on an axis by **clicking and dragging** a tick mark, number, or grid line. Dragging a tick within an axis shifts all of the values along the axis, effectively

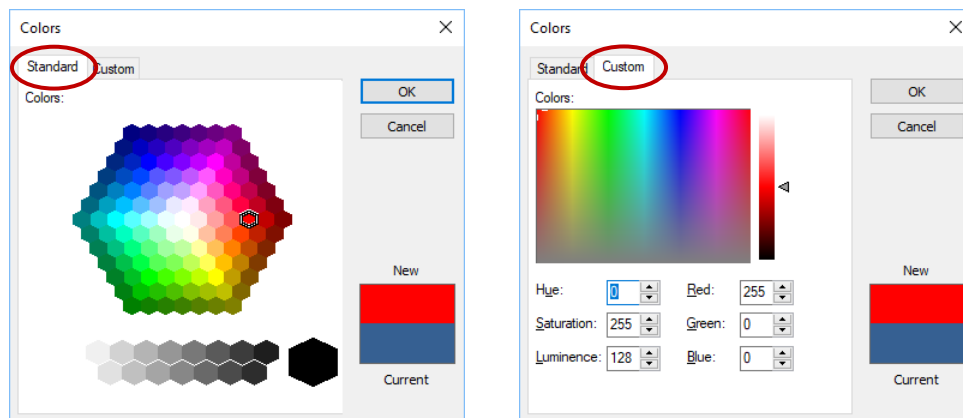
changing the minimum and maximum values at the ends of the axis, but keeping the spacing the same. Dragging the tick at the end of an axis changes the minimum or maximum value. Any tick in a Stiff diagram, radial plot, or pie chart behaves like an end tick because the minimum is always zero and cannot be changed. To reset the axis range to span the range of the data being plotted, choose **Auto-scale** or **Reset Range** from the aspect menu, or **Format** → **Reset Axis Range**.

You can set all of the graphical attributes in the aspect appearance dialogs available through the **Format** menu. When you make changes to values or selections in an aspect appearance dialog, the changes don't take effect on the plot immediately. You may set up your choices for as many of the aspects as you like, or use the **Reset** button to reset the dialog to its default values. Use the **Apply** or **OK** button to apply the changes to the plot. Use the **Cancel** button if you decide that you don't want the changes applied.

Selecting **Color** → **More Colors...** from any aspect menu or clicking on any color button in an aspect appearance dialog allows you to set the color of the relevant aspect.



The **Colors** dialog presents a hexagonal palette of colors on the **Standard** tab. To create custom colors, move to the **Custom** tab.



In either tab, the current color of the aspect is displayed, as is any new selection you make. Once you make a selection, click **OK** to set the color, or **Cancel** to discard the selection and close the dialog.

### 8.3 Scatter data

**Gtplot** can plot the data in a **GSS** data sheet (a .gss file) as “scatter data” in its own diagram, or overlay on a diagram of the results of a **SpecE8** or **React** calculation. You can plot chemical parameters in your data sheet, like pH and TDS, or the measured composition (mg/kg Na<sup>+</sup>, ...) of the samples in the sheet. Or you can plot “calculated analytes” such as species activity, gas fugacity, and mineral saturation state.

Your .gss file might look like

GSS		1	2	3	+ sample
File	Edit	Data	Plot	Analysis	Help
Sample ID		S1	S2	S3	
pH		6.5	5.9	6.9	
Na <sup>+</sup>	mmol/kg	1.8	20	6.3	
Ca <sup>++</sup>	mmol/kg	4.3	38	15	
HCO <sub>3</sub> <sup>-</sup>	mmol/kg	19	113	58	
+ analyte					

To read the file into **Gtplot**, select **File** → **Open** → **Scatter Data...** If some of the data points lie outside the plot's axis range, press **Ctrl+Z**. Clear scatter data from a diagram on the **Open** → **Scatter Data...** dialog, with the **OFF** button.

The marker representing each sample in the scatter data is set in the .gss file. In **GSS**, right-click on a sample to change the marker used and its color and size. When you modify

a .gss file, the changes will sync with open plots automatically, unless you've paused automatic plot updates (**Plot** → uncheck **Auto Updates**), in which case you can click **Plot** → **Update Plot(s)** when you are ready to sync the changes.

On xy plots, you can associate the marker for a data point with the analyte ( $\text{Na}^+$ ,  $\text{Ca}^{++}$ , ...), rather than the sample (Well #1, Well #2, ...). On the **Format** → **GSS Data...** dialog, you can assign the marker, its color, and its size according to the settings in the .gss file for the analytes, or for the samples.

You can label each scatter data point with the sample's "Sample ID", as set in the .gss file, and display a legend showing the symbols used. In **Gtplot**, choose **Format** → **GSS Data...**, and under "Labels" select the checkbox for "Sample" to show sample labels, and the "Legend" box to display the legend. If the "Color from sample" box is checked, the color for each sample label matches that of the sample's marker. Use the **Format** → **Quick Toggle...** dialog to quickly toggle on and off display of the scatter data, data labels, and legend.

If an analysis falls below detection limit, enter in your **GSS** data sheet the detection limit preceded by a "<", for example "< 0.01". **Gtplot** will add a downward arrow to the symbol for this entry, signifying it represents the upper limit to concentration. To add error bars to the scatter points, enter triplets (0.5|2.0|3.5) in the data cells in your .gss file (see **Error bars in Using GSS**).

In plots showing the variable " $\text{HCO}_3 + \text{CO}_3$ ", you should enter a value in the scatter dataset for the chemical parameter "Carbonate alkalinity" so **Gtplot** can render the variable correctly. If you do not enter a value for alkalinity, the program will render the variable in terms of the reported  $\text{HCO}_3$  concentration, if available, in which case the diagram produced will not account for the speciation of carbonate.

Certain unit conversions, such as changing mg/l to mmolar, or mg/kg of solute to mg, require knowledge of the fluid's density and TDS, and the mass of solution in the system. **Gtplot** first looks for entries "Density", "TDS", and "Mass solution" in the .gss file. If it does not find them, it estimates density and TDS, and assumes a solution mass of 1 kg.

In order to see TDS represented as circles on Piper, ternary, and Durov diagrams, you should enter a value for dissolved solids for each sample or use the **Calculate with SpecE8...** option to determine a value consistent with **SpecE8**'s speciation. Lacking either of these options, **Gtplot** will use a value estimated from the bulk composition in **GSS**.

To coordinate the plotting of scatter data versus time on a reaction path, include values for "Time elapsed", "Time", and/or "Date".

In **GWB** releases 7.0 and earlier, the program took scatter data from a specially formatted text file, rather than a .gss data sheet. Legacy scatter files are still supported and described in the **Scatter Data** chapter in the ***GWB Reference Manual***.

## 8.4 Loading and saving plot configuration

Upon exiting, **Gtplot** writes into the user's working directory a file, "gtplot\_conf.gtc", containing the configuration of the current plots. When the program starts again in the same directory, it reads the file and assumes the same configurations.

Choosing **File → Reset Configuration** or the `reset` option from the command line (see [Gtplot command line](#)) returns the configuration for each plot type to its default state. This option is useful, for example, when you begin to examine results of a **SpecE8** simulation unrelated to the previous run.

You can save plot settings to an alternative configuration file by selecting **File → Save As...** Later, double-click on the ".gtc" file to reopen the plot you saved. You may also read the file into **Gtplot** by selecting **File → Open → Configuration...**, or simply dragging it into an instance of **Gtplot**.

Exiting the program by choosing **File → Abort (No Save)** causes an immediate exit from the program; the plot configuration is lost.

## 8.5 Exporting the plot

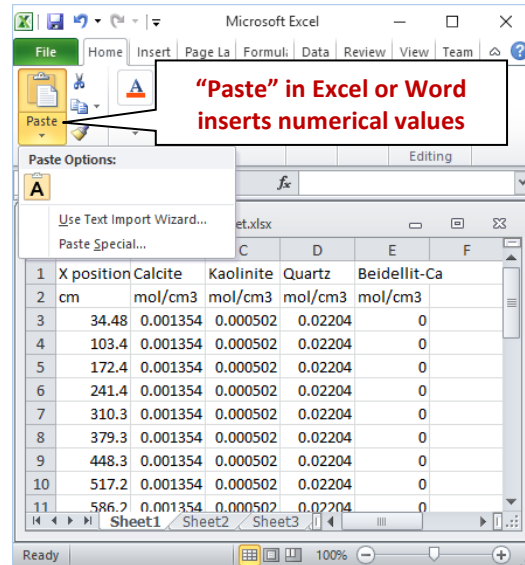
**Gtplot** makes it convenient to use the plots you create in articles, reports, presentations, and databases. You can copy the current plot to the clipboard and then paste it into a variety of applications, in a format meaningful to the application.

To copy a plot, use **Edit → Copy (Ctrl+C)**. If you paste the plot into MS PowerPoint, it will appear as an EMF (an MS Enhanced Metafile) graphic object. Pasting into Adobe Illustrator places a native AI graphic.

If you paste the plot into MS Excel or a text editor such as Notepad or MS Word, the numerical values of the data points that make up the lines on the plot will appear in spreadsheet format.

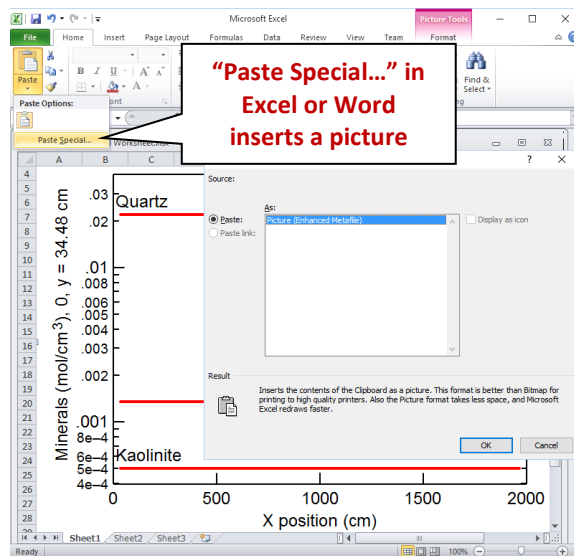
You can control the format in which the plot is copied to the clipboard by selecting **Edit → Copy As**. You can choose to copy the plot as an AI object, an EMF object, or a bitmap, or to copy the data points in the plot as tab-delimited or space-delimited text.

Use the tab-delimited option to paste the data into a spreadsheet program like MS Excel



For examining the data in a text file created with an editor like Notepad or MS Word, the space-delimited option writes a nicely aligned table.

In MS Word or MS Excel, use **Paste Special...**



to paste the plot as a picture instead.

Use **File → Save Image...** to copy the plot, in your choice of formats (selected under **Save as type:**), from the graphics area to a file in the specified directory. The **Enhanced Metafile** option, for example, saves the plot image in a format that can be read by most art and illustration programs (see **Graphics Output** in the *GWB Reference Manual*). The other file formats available are: **PNG, JPEG, TIFF, Bitmap, Adobe Illustrator, PDF, Scalable Vector Graphics, Compressed SVG, Encapsulated PostScript, Color PostScript, and B/W PostScript.**

When saving a PNG, JPEG, TIFF, or bitmap file, you may specify the quality of the saved image by choosing its resolution: High, Medium, Low, or Custom. Use **Custom...** to set the pixel width and height of the image, and to choose whether to preserve the aspect ratio of the plot.

Use the **Spreadsheet File (Tab delimited)** or **Text File (Space delimited)** option to save the numerical coordinates of the data points on the plot into a table. The spreadsheet table may be read directly into many popular spreadsheet programs.

Certain graphics types support font embedding. PDF files should always display and print properly, regardless of fonts installed on the system. PostScript files should also, if you have used the option to embed fonts.

If you may want to edit the PostScript file, however, you should deselect the option to embed fonts, because programs such as Adobe Illustrator may restrict your ability to edit a document using embedded fonts. To edit these files, be sure that all of the required fonts are installed on your computer (see **Font for data markers** in the *GWB Reference Manual*).

When importing AI graphics to Adobe Illustrator, the program may prompt you to update the legacy text before you can edit the file. In this case, choose “Update”. You need to release the clipping mask before you attempt to edit individual elements of the plot. Use the “Ungroup” and “Group” functions when repositioning or modifying elements.

## 8.6 Gtplot command line

To run **Gtplot**, click on the **Gtplot** icon on the GWB dashboard, or open a “.gtp” or “.gtc” file. The program can also be initiated from the Windows command prompt by typing `gtplot.exe`. Starting the program in this way allows you to make use of the command line arguments described below.

**Gtplot** accepts a number of arguments from the command line. For example, the command

```
gtplot -i SpecE8_plot1.gtp -c Config1.gtc
```

causes **Gtplot** to read as input the file “SpecE8\_plot1.gtp”, and to use the plot configuration stored in “Config1.gtc”.

The following options are available from the command line:

<code>&lt;input_data&gt;</code>	Set the “SpecE8_plot.gtp” dataset, produced by a SpecE8 run, which contains the data to be plotted. The program, by default, looks for file SpecE8_plot.gtp in the user’s working directory.
<code>-i &lt;input_data&gt;</code>	
<code>-c &lt;config_file&gt;</code>	Set the configuration file to be read at startup. By default, the program reads the file <code>gtplot_conf.gtc</code> if it exists in the working directory.
<code>-scat &lt;scatter file&gt;</code>	Take scatter data from the named dataset. By default, Gtplot does not plot scatter data.
<code>-graph &lt;plot_type&gt;</code>	Set the type of plot displayed at startup. By default, it is set from the configuration file. Choose from: xyplot, ternary, piper, durov, schoeller, stiff, radial, bar, pie, series, and time.
<code>-reset</code>	Set the default configuration at startup; do not read <code>gtplot_conf.gtc</code> .



<b>Table 8.1</b>	<b>Keyboard shortcuts in Gtplot</b>
Ctrl+Shift+A	Copy plot to the clipboard as an Adobe Illustrator file
Ctrl+Shift+B	Copy plot to the clipboard as a bitmap
Ctrl+C	Copy plot to the clipboard
Ctrl+Shift+E	Copy plot to the clipboard as an Enhanced Metafile
Ctrl+F	Refresh display
Ctrl+Shift+G	Get scatter data
Ctrl+L	Load a configuration file
Ctrl+M	Save the graphic image to a file
Ctrl+O	Open an input (“React_plot.gtp”) file
Ctrl+P	Print the plot
Ctrl+Q	Quit Gtplot, save configuration
Ctrl+Shift+Q	Abort Gtplot, do not save configuration
Ctrl+R	Reset the plot configuration
Ctrl+S	Save the current configuration to a file
Ctrl+Shift+S	Copy plot to the clipboard as a Spreadsheet (tab delimited)
Ctrl+Shift+T	Copy plot to the clipboard as Text (space delimited)
Ctrl+U	Update the plot from the current input file
Ctrl+X	Reset data range on the x axis
Ctrl+Y	Reset data range on the y axis
Ctrl+Z	Reset data ranges on the x and y axes
F1	Open GWB Essentials Guide



# Using TEdit

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**TEdit** is a graphical editor that lets you create and modify the thermodynamic and surface reaction datasets used by the GWB programs. You can alternatively use a simple text editor such as **Notepad** to modify the datasets. If you prefer to use a text editor, details of the datasets' formats are given in the **Thermo Datasets** and **Surface Datasets** chapters in the *GWB Reference Manual*.

With **TEdit** you can view and modify the entries in a dataset, as well as add or delete them. Specifically, you can alter

- Header lines, data tables, and dataset information
- Elements and species in the dataset, and their properties
- Reactions among the species, and their log  $K$  temperature expansions
- Binary solid solutions of end-member minerals, and their properties
- Virial coefficients for species pairs or triplets, and their temperature expansions

You can also:

- Copy entries from one dataset to another
- Filter entries by composition and search on text strings
- Swap to recast reactions and recalculate log  $K$ s
- Reduce arbitrarily written reactions to the set of basis and redox species
- Exchange the positions of basis, redox, and aqueous species
- Adjust the coupling of redox reactions
- Troubleshoot common errors
- Import datasets from the PhreeqC and EQ3/6 programs, and export to EQ3/6

## 9.1 Getting started with TEdit

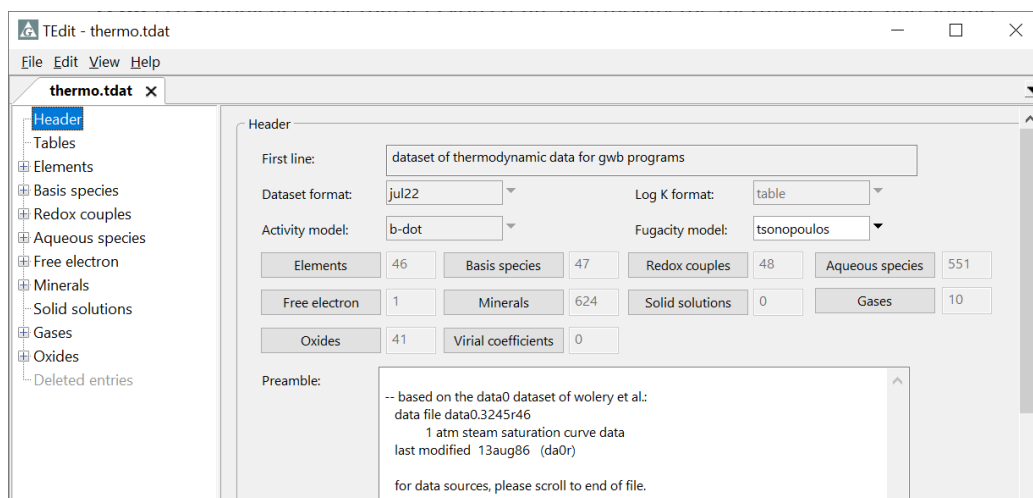
### 9.1.1 Opening datasets

To open **TEdit**, click its icon on the **Apps** pane of the GWB Dashboard. Then, go to **File → Open...** and browse to open any “.tdat” or “.sdat” file (for thermo and surface datasets, respectively), or a “.dat” file, for very old GWB reaction datasets. You can alternatively drag a file from your Desktop or File Explorer into **TEdit**. Either way, you can open several datasets in a single **TEdit** window. You can also double-click any “.tdat” or “.sdat” file to

open it in **TEdit**. To open a dataset currently loaded in any **GWB** program, go to **File** → **View** and select the desired file.

### 9.1.2 Navigating datasets

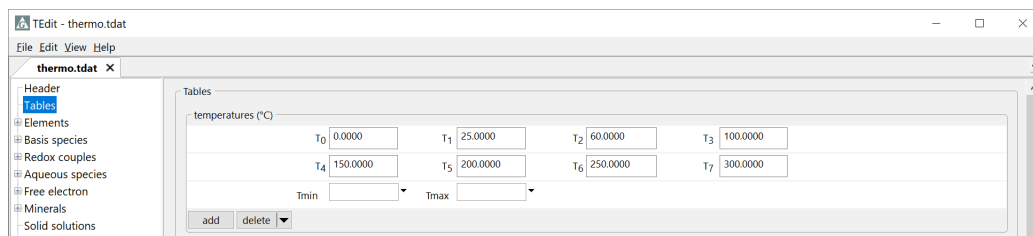
A thermo dataset in **TEdit** might look like this





On the left side of the window is a tree structure with sections labeled “Header”, “Tables”, “Elements”, “Basis species”, “Redox couples”, “Aqueous species”, “Free electron”, “Minerals”, “Solid solutions”, “Gases”, “Oxides”, and, in some cases, “Virial coefficients”. For detailed descriptions of each section, see the **Thermo Datasets** chapter in the ***GWB Reference Manual***.

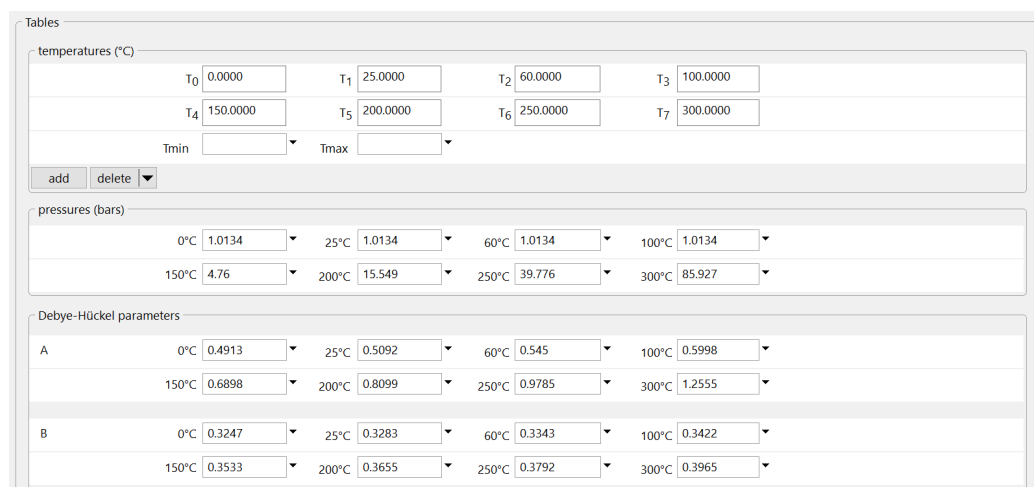
Click “Header” on the tree to view the dataset format, activity model, default fugacity model, log *K* temperature expansion format, and bibliographic information. The pane also shows the number of elements, basis species, and so on in the dataset. Click on one of the buttons to navigate to the corresponding section of the dataset.

The next section, “Tables”, contains tables showing how various coefficients used by the programs vary with temperature (see **Temperature expansions** under **Thermo Datasets** in the ***GWB Reference Manual***). The principal temperatures of the dataset are set in the top of this section



Additional temperatures can be appended or inserted as needed using , and values can be removed using . Note that deleting a principal temperature will also delete values of header variables and log  $K$ 's set at that temperature, when supplied as  $T$ -tables. You can optionally superimpose lower and upper temperature bounds on the database, if for some reason the limiting values differ from the first and last principal temperatures, by setting values for “Tmin” and “Tmax”.

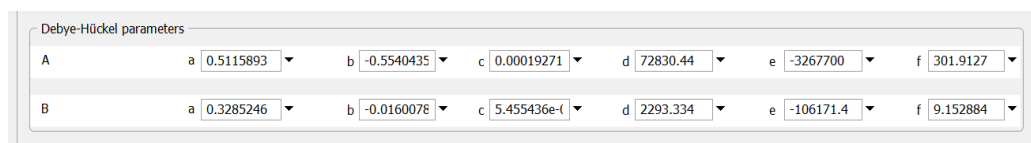
The temperature expansions may be given as either a  $T$ -table, with values corresponding to the principal temperatures




The 'Tables' dialog box contains three sections:

- temperatures (°C):** A table with 8 columns (T0 to T7) and 2 rows. Values range from 0.0000 to 300.0000. Below the table are 'Tmin' and 'Tmax' dropdowns and 'add'/'delete' buttons.
- pressures (bars):** A table with 8 columns (0°C to 300°C) and 2 rows. Values range from 1.0134 to 85.927.
- Debye-Hückel parameters:** Two sections, A and B, each with a table of 8 columns (0°C to 300°C) and 2 rows. Section A values range from 0.4913 to 1.2555. Section B values range from 0.3247 to 0.3965.

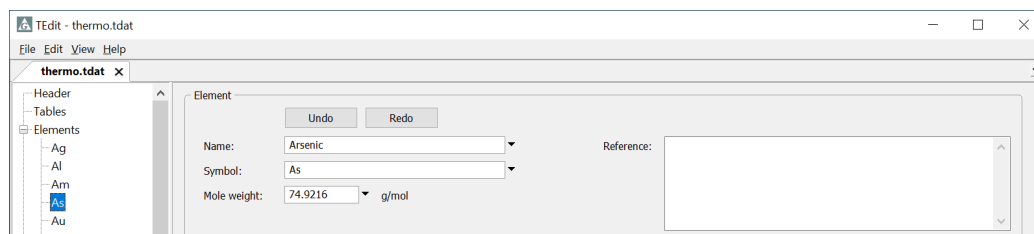
or as a set of six polynomial coefficients  $a-f$  spanning the range of those temperatures



The 'Debye-Hückel parameters' dialog box shows two rows, A and B, each with six columns (a to f) of polynomial coefficients. Values are provided for each coefficient, such as 0.5115893 for Aa and -0.5540435 for Ab.

Each subsequent section contains a list of entries. Use the  button to view its contents or expand the entire tree by going to **View → Expand All**.

Under “Elements” is a list of chemical elements from which species in the dataset can be created. Each element’s entry contains a name, symbol, and molecular weight



The TEdit main window shows a tree view on the left with 'Header', 'Tables', and 'Elements' expanded. The 'Elements' list includes Ag, Al, Am, As (highlighted), and Au. The right panel shows the details for the selected element, Arsenic (As), with a molecular weight of 74.9216 g/mol and a reference field.

The “Basis species” are listed in the next section. Each entry contains a name, charge, ion size parameter in angstroms (plus a second *b* term for activity coefficients in the phreeqc, minteq, wateq4f, and davies activity models), mole weight, and optionally, a chemical formula, in the labeled text boxes, as well as its elemental composition

The screenshot shows the TEdit - thermo.tdat window. On the left is a tree view with categories: Header, Tables, Elements, Basis species, and Redox couples. Under Basis species, several entries are listed, with As(OH)4- selected. The main panel displays the details for this species:

- Name:** As(OH)4-
- Charge:** -1
- Ion size:** 4 Å
- Mole weight:** 142.9508 g/mol
- Formula:** (empty)
- Status:** No errors found
- Elements in species:**

Element	Count
As	1
H	4
O	4

The “Redox couples” are similar to Basis species, except that redox couples are constructed from species in the dataset, rather than from elements. The species form a balanced reaction for which equilibrium constants are supplied as *T*-tables of log *K* values

The screenshot shows the TEdit - thermo.tdat window with the Redox couples section selected in the tree view. The main panel displays the details for the H2(aq) redox couple:

- Name:** H2(aq)
- Charge:** 0
- Ion size:** -0.5 Å
- Mole weight:** 2.0158 g/mol
- Formula:** (empty)
- Status:** No errors found
- Species in reaction:**

Species	Stoichiometric Coefficient
H2O	1
O2(aq)	-0.5
- Reaction:**  $\text{H}_2(\text{aq}) + .5 \text{O}_2(\text{aq}) = \text{H}_2\text{O}$
- Log Ks:**

Temperature (°C)	Log K
0°C	50.4955
25°C	46.1129
60°C	40.9736
100°C	36.2002
150°C	31.4328
200°C	27.5804
250°C	24.2906
300°C	21.4524

or as a polynomial temperature expansion, with an optional temperature range of validity

The screenshot shows the TEdit - thermo.tdat window with the Redox couples section selected. The main panel displays the details for the H2(aq) redox couple, showing the reaction and the polynomial temperature expansion for the log K values:

- Reaction:**  $\text{H}_2(\text{aq}) + .5 \text{O}_2(\text{aq}) = \text{H}_2\text{O}$
- Log Ks:**

Parameter	Value
a	46.096622
b	0
c	0
d	10963.44
e	0
f	-11.55477
- Temperature Range:**

Tmin (K)	Tmax (K)
298.15	298.15

In the absence of settings for “Tmin (K)” and “Tmax (K)”, the stability is assumed to span the range of the principal temperatures.

Entries in the following sections, for “Aqueous species”, “Free electron”, “Minerals”, “Gases”, and “Oxide” components, are added in a similar manner to redox couples, with a few differences. The name, charge, ion size parameter, and mole weight of the free electron cannot be modified, although you can modify its reaction and log  $K$  temperature expansion, as you would for any other species. Minerals have fields for entering the mineral’s molar volume, type, and formula. Gases have fields for the factors needed to calculate fugacity coefficients. Minerals, gases, and oxide components do not have fields for charge or ion size parameter. The oxide components do not have thermodynamic stabilities, so there is no place to enter log  $K$  values.

The “Solid solutions” are composed of end-member minerals defined in the preceding section. Entries include the activity coefficient model and parameters for evaluating that model, as needed, along with the end members and composition range of the solution.

Datasets that utilize virial equations (the H-M-W and SIT activity models) include coefficients describing the energetic interactions among basis, redox, and aqueous species. In “thermo\_hmw.tdat”, for example, the entry for  $\text{Ca}^{++}$  lists interaction terms with anions, cations, neutral species, and triplets of species. TEdit displays the interaction terms for various pair-wise and triplet combinations of species under “Virial coefficients”, as well as a summary view under the entry for all involved species.

The screenshot shows the TEdit window for thermo\_hmw.tdat. The left sidebar lists various species categories, with 'Basis species' expanded and 'Ca++' selected. The main window displays the details for the 'Ca++' basis species, including its name, charge (2), ion size (6), mole weight (40.08), and formula. Below this, the 'Elements in species' section shows 'Ca' with a count of 1. The 'Virial coefficients' section is divided into two tables: 'cation-anion pairs' and 'cation-cation pairs'.

cation-anion pairs		$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$c^b$	$\alpha^{(1)}$	$\alpha^{(2)}$
Ca++	Cl-	0.3159	1.6140	0.0000	-0.0003	2.0000	0.0000
Ca++	HCO3-	0.4000	2.9770	0.0000	0.0000	2.0000	0.0000
Ca++	HSO4-	0.2145	2.5300	0.0000	0.0000	2.0000	0.0000
Ca++	OH-	-0.1747	-0.2303	-5.7200	0.0000	2.0000	12.0000
Ca++	SO4--	0.2000	3.1973	-54.2400	0.0000	1.4000	12.0000

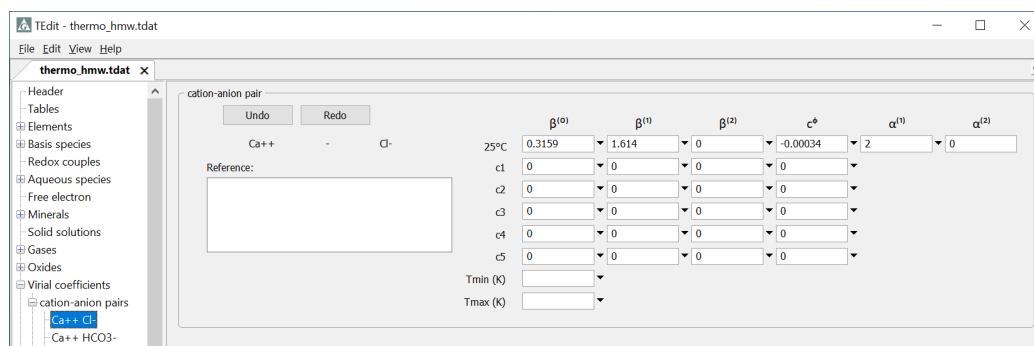
  

cation-cation pairs		$\theta$
Ca++	H+	0.0920
Ca++	K+	0.0320
Ca++	Mg++	0.0070

For example,  $\text{Ca}^{++}$  and  $\text{Cl}^-$  basis species both display a summary of the  $\text{Ca}^{++} - \text{Cl}^-$  cation-anion pair interaction terms, as well as all the triplets involving both species. If,

while on the entry for  $\text{Ca}^{++}$ , you double-click the row with the  $\text{Ca}^{++} - \text{Cl}^-$  pair, the  $\text{Ca}^{++} - \text{Cl}^-$  pair's entry on the tree will open, where you can view more information and edit the entry. After doing so, the summaries in the  $\text{Ca}^{++}$  and  $\text{Cl}^-$  basis entries will update.

In the entry for a pair or triplet, each coefficient is listed at 25°C (the value in the first row). You can enter up to five additional coefficients ( $b$ -fin the new polynomial, or  $c_1$ - $c_5$  for the legacy expansion) to account for temperature effects, as well as a range of validity. For more information, see **Virial Coefficients** under the **Thermo Datasets** chapter in the *GWB Reference Manual*.



Surface datasets are organized much like thermo datasets and can be navigated in TEdit using a similar tree structure. For detailed information about their contents, see the **Surface Datasets** chapter in the *GWB Reference Manual*.

### 9.1.3 Creating new datasets

To create a new thermo dataset, go to **File → New → Thermo Data....** In the dialog that opens, select an activity model, temperature expansions for header variables and log  $K$ s, and, for virial datasets, the virial coefficient format, then click **OK**. TEdit can format GWB datasets that invoke variations of the Debye-Hückel equations or the virial techniques (see **Thermodynamic datasets** under **Configuring the programs**, and **Activity coefficients** under **Using SpecE8**). Note the format labeled “b-dot” was previously labeled “debye-huckel”. Additionally, the format labeled “Pitzer” is outdated and not recognized by TEdit; support for the Pitzer equations has been superseded by the “h-m-w” format. TEdit can format the temperature expansions for header variables and log  $K$ s as a table of values at the principal temperatures or as coefficients in a polynomial. Virial coefficients can be formatted using the same polynomial, or a similar legacy format. For details of the temperature expansions, see the **Thermo Datasets** chapter in the *GWB Reference Manual*.

In the “Header” section, choose a default fugacity model; options include Tsonopoulos, Peng-Robinson, and Spycher-Reed.



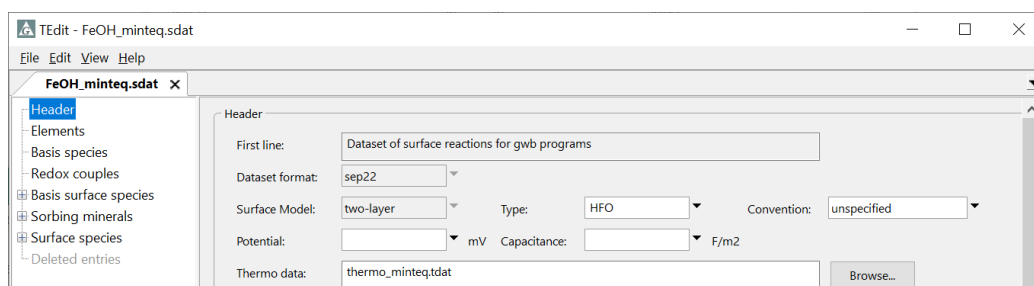
**TEdit** creates new datasets with a commonly used eight-temperature  $T$ -table spanning 0–300°C, but you can extend or limit the range, or add intermediate values, in the “Tables” section. Supply the temperature expansions for the required header variables.

Finally, add desired elements, species, reactions, and so on, as described later in [Adding and deleting entries](#).

In the same manner, to create a surface dataset, go to **File → New → Sorbing Surfaces...** In the dialog that opens, choose one of the surface models (see [Sorption onto mineral surfaces](#) under **Configuring the Programs**) and a convention, if required, then click **OK**. If you create a two-layer, three-layer, CD-MUSIC, or Langmuir dataset, you need to pick a convention for polydentate reactions (see [Polydentate sorption](#)). Similarly, an ion exchange dataset requires an activity convention.

You should set a unique “type” in the Header section for each surface to be considered at a given time. The “type” is a label that identifies the dataset within the GWB modeling programs when more than one surface dataset has been loaded.

Finally, identify a thermo dataset from which the species are drawn to make up surface reactions. The header lines in surface dataset “FeOH\_minteq.sdat”, for example, link it to the thermo dataset “thermo\_minteq.tdat”. **TEdit**, then, will look to “thermo\_minteq.tdat” to find aqueous species to be used in balancing chemical reactions within “FeOH\_minteq.sdat”.

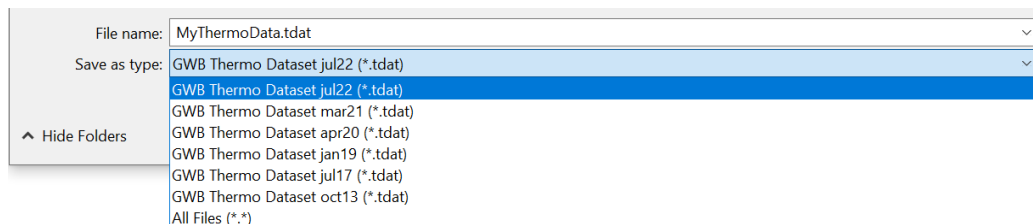


### 9.1.4 Saving and dataset formats

Click **File → Save** to save your dataset. Use **File → Save As...** to save the file with a new name or location. **TEdit** will save thermo datasets as “.tdat” files and surface datasets as “.sdat” files. If you try to save a dataset with errors, **TEdit** will open the **Troubleshoot...** dialog to list the errors it finds (see [Troubleshooting](#) in this section).

In the current release, thermo datasets are distributed in the “jul22” format, and surface datasets in the “sep22” format. **TEdit** can read and write datasets in these formats, which are preferred for current installations of the software, or in various legacy formats (see **Legacy formats** in the **Thermo Datasets** and **Surface Datasets** chapters of the ***GWb Reference Manual***) for use with earlier releases of the software package. To enable new features in a dataset created for an earlier release, update it by choosing the

most recent format in the **Save As...** dialog. To save a dataset for use with an earlier release, choose a legacy format and **TEdit** will downgrade the dataset as necessary.



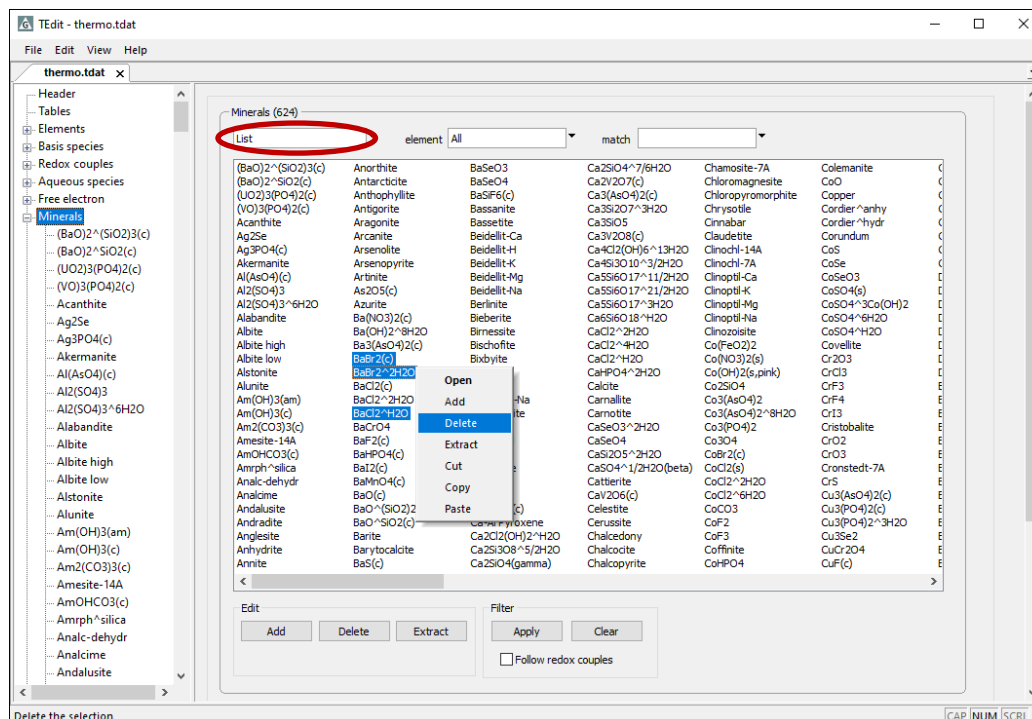
The earlier “jan19” format was the first to allow polynomial temperature expansions for log  $K$ s and header variables in thermo datasets. Although not recommended, you can convert such a dataset to use the older  $T$ -table expansion. On the Header section, change the “log  $K$  format” pulldown from “polynomial” to “table” before saving. Note, the transformation can only be performed once. **TEdit** does not convert  $T$ -tables to polynomial expansions.

The polynomial temperature expansions for virial coefficients can be set out in the legacy format, the new format used for header variables and log  $K$ s, or a combination of the two formats. To set the dataset to use only one format, select the appropriate entry on the “virial coefficient format” pulldown on the “Header” section before saving.

## 9.2 Working with datasets

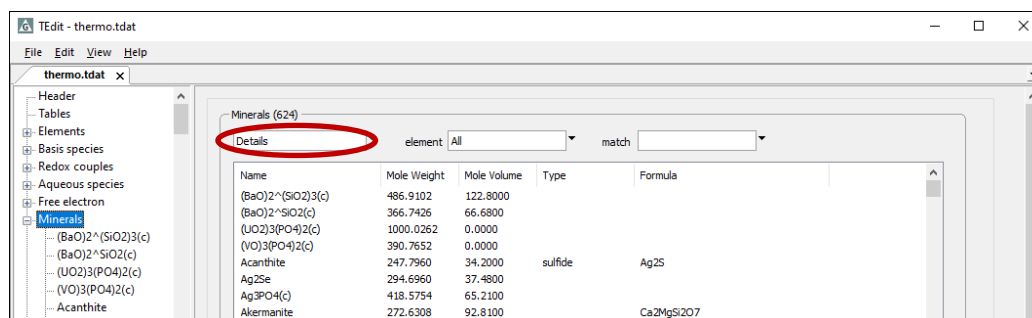
### 9.2.1 Summaries, filtering, and searching

When you click on any section (except “Header” and “Tables”) on TEdit’s tree structure, the program displays a pane summarizing its contents. For example, the “Minerals” section displays an alphabetical list of the dataset’s minerals in a condensed view

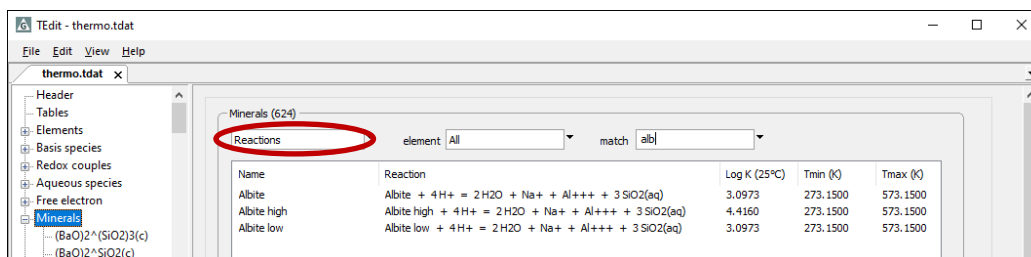


Double-click on an entry to go to its editing pane. Use the buttons or right-click menu to add or remove entries, control filters, and so on, as described later in this chapter.

Change the pulldown from “List” to “Details” to see properties of the entries, such as mole weights and formulae



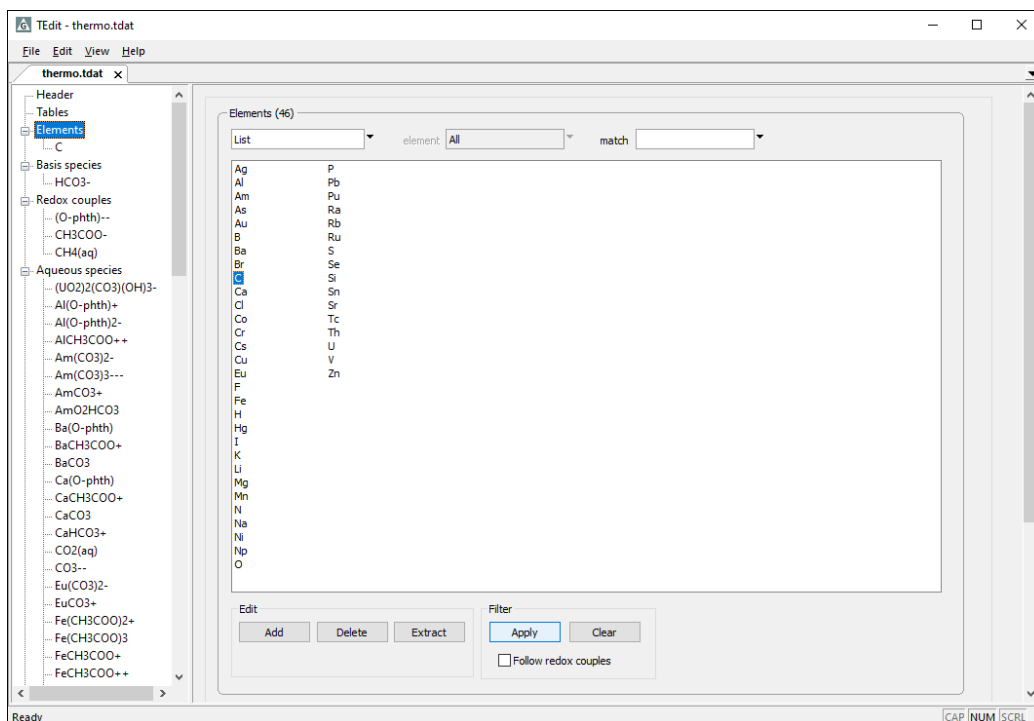
or to “Reactions” to see their reactions and log  $K$  values at 25°C



or “Redox reactions” to list only oxidation-reduction reactions. You can similarly identify “Non-redox reactions” within the “Redox couples” section.

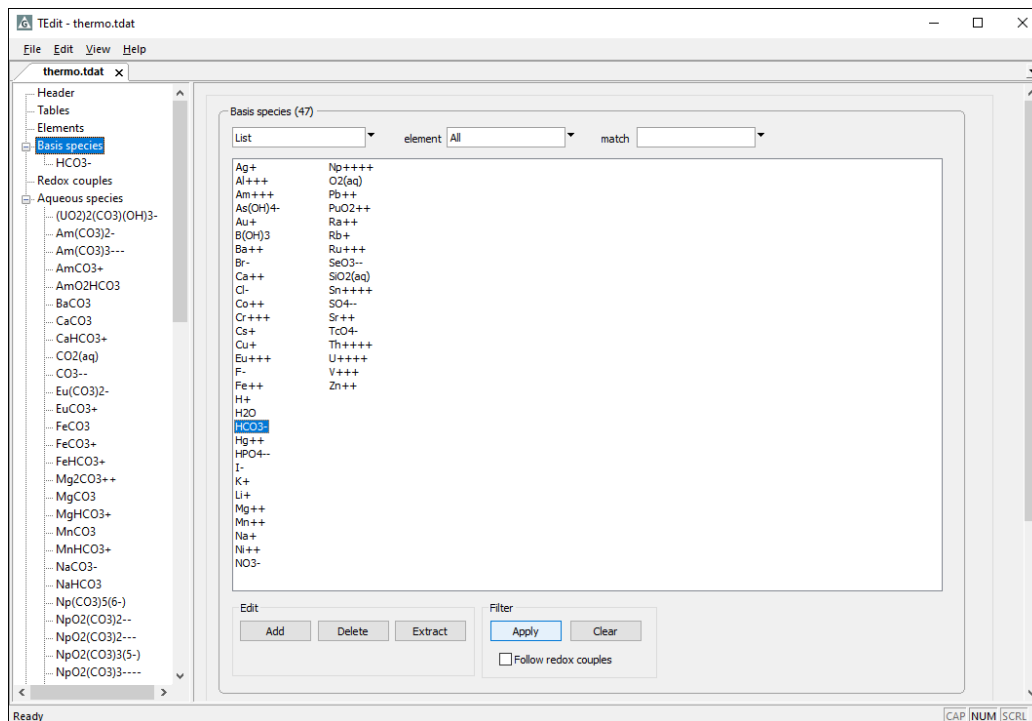
In any case, you can use the “element” pulldown or “match” box to limit the entries shown in the list. In the screenshot above, “alb” was typed into the “match” box to compare the stability of albite with its polymorphs.

To filter the species shown in the tree, go to one of the section headers, choose one or more options in the list, then click on the **Apply** button under “Filter”. By filtering on the element “C”, the tree shows only species containing that element



To show all the entries again, choose **Clear**.

Similarly, if you go to the “Basis species” section and filter on a species like “HCO<sub>3</sub>-”, you can set the tree structure to show only species containing inorganic carbon



If you check “Follow redox couples”, on the other hand, the filter would include redox couples linked to “HCO<sub>3</sub>-”, such as “CH<sub>3</sub>COO-” and “CH<sub>4</sub>(aq)”.

You can additionally apply and clear filters through the right-click menus of entries in the tree structure or in the **Find...**, **Mole Weight...**, and **Troubleshoot...** dialogs, described later.

To search the dataset, go to **Edit → Find...** (Ctrl+F) and type in a character string. The dialog lists each occurrence of the string, along with its context. You can limit the search to specific sections (e.g. “Minerals”) or search fields (“Name”, “Formula”, “Reaction”, “End members”, “Comment”, or “Mineral type”). Double-click on an entry to go to its editing pane, or right-click for more options.

### 9.2.2 Adding and deleting entries


To add an element, species, solid solution, or virial interaction term to a dataset, right-click on the appropriate section heading in the tree and choose **Add**. The new entry will appear on the tree at the end of the selected section, as well as within the dataset when you save it. Or, add from an entry on the tree to place the new entry directly after it. Complete the data template that appears, as described in the next section.


To remove one or more entries from a dataset, select on the tree the entries to be deleted, then right-click on one and choose **Delete**. Alternatively, click on the **Delete** button within the section's summary pane. A popup dialog will appear listing the chosen entries, along with any dependent entries. You may choose **OK** to delete all the entries, or **Cancel** to retain them.

Alternatively, choose **Extract** to preserve your selected entries while deleting everything else from that section. If you extract the elements H, O, Na, and Cl, for example, all other elements (and their dependent species and reactions) will be deleted.

Anything you delete is temporarily stored in the "Deleted entries" section of the tree. From there you can restore entries to the dataset or clear them out permanently. All deleted entries will be discarded when you close the dataset.

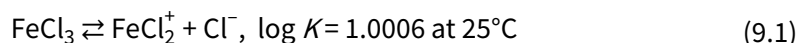
### 9.2.3 Completing entries in thermo datasets

When adding an element to a database, you enter a name, symbol, and mole weight. For basis species, fill in the species' name, charge, ion size parameter, *b* term, if applicable, mole weight, and chemical formula, if desired. Last, click the  button to build up the species' elemental composition.

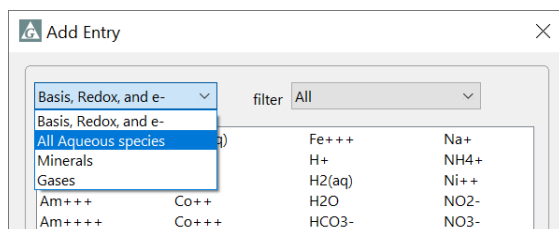
For the remaining species, set a balanced chemical reaction, in terms of any species in the dataset. Under "Species in reaction", click  to select the species. By default, the dialog that opens lists the basis and redox species, as well as the electron, but you can change the pulldown to show all aqueous species, minerals, or gases. Double-click on the entries to include in the reaction. You can also traverse the dialog with the keyboard; type one or more characters to find species beginning with that sequence, then hit the **Enter** key to add the species, and **Esc** to close the dialog. Next, supply a reaction coefficient in the space to the right of each species' name. Species with a negative reaction coefficient appear on the reaction's left-hand side; those with a positive coefficient are on the right. As you add coefficients, **TEdit** automatically writes the reaction out and checks for charge and mass balance.

In the fields below the reaction, set the log *K* temperature expansion for the reaction as written. For *T*-table datasets, specify values at the principal temperatures; use "500" to indicate "no data". If the log *K* is known at a different temperature, you can add to the *T*-table on the "Tables" pane. For polynomial datasets, set coefficients *a-f*, and optionally set a temperature range of validity. For more information, see **Temperature expansions** in the **Thermo Datasets** chapter of the *GWB Reference Manual*.

As an example, suppose we want to add the aqueous species FeCl<sub>3</sub>, as in the reaction below, to "thermo.tdat"




To do so, right-click on “Aqueous species” and choose **Add**. In the blank pane that opens, type “FeCl<sub>3</sub>(aq)” as the species name. Set the mole weight to “162.206” and the ion size to “4”. Click **add**, and in the dialog that opens, change the pulldown to “All Aqueous species”



then select “FeCl<sub>2</sub>+” and hit the **Enter** key, then repeat for “Cl-”, then close the dialog. The entry pane will look like

Set a reaction coefficient of “1” for each and enter the log *K* value above

For solid solutions, set the name, the activity model, the end-member minerals, and their “tags” (short labels). In binary solutions, you can specify a range for the second end member’s mole fraction. For solutions of more than two end members (this and certain other features are currently supported only for conversion to EQ3/6 format, see [Exporting EQ3/6 datasets](#)), set the maximum mole fraction for each end member. For site-mixing


solutions, set the site number  $b$ . For Guggenheim solutions, set the dimensionless parameters  $a_0$ ,  $a_1$ , and  $a_2$ . Alternatively, specify second-order temperature expansions for  $\text{J mol}^{-1}$  Guggenheim coefficients  $A_0$ ,  $A_1$ , and  $A_2$  by clicking the  button and setting values for  $p_1$ – $p_9$ . The sign of the  $a_1$  (or  $p_4$ – $p_6$ ) coefficient reflects the order in which end members appear, as well as the GWB's convention for setting out the Guggenheim equations. Note, if you reorder the end members, the range and Guggenheim  $a_1$  (or  $p_4$ – $p_6$ ) coefficients will be adjusted. For the various other models, supply coefficients  $p_1$ – $p_6$  as necessary. For more information, see [Solid solutions](#) in the **Configuring the Programs** chapter of this guide, as well as **Solid solutions** in the **Thermo Datasets** chapter of the *GWB Reference Manual*.

For virial datasets, also enter coefficients reflecting pair-wise and triplet interactions among the species, as necessary. For those invoking the SIT method, you can specify interaction terms for cation–anion pairs and ion–neutral species pairs, as well as their temperature ranges of validity. For those invoking the “Pitzer equations”, you can additionally specify interaction terms for cation–cation or anion–anion pairs and species triplets. You can see a summary of these terms (their values at 25°C) on the data pane for any basis, redox, or aqueous species, but you specify them under the subsections of the “Virial coefficients” heading. Click **Add** in the appropriate section and select species to form a pair or triplet from the pulldown list. Fill in values for some or all of the coefficients (see **Virial Coefficients** in the **Thermo Datasets** chapter of the *GWB Reference Manual*).

If you rename an entry, the change will propagate to reactions, solid solutions, and virial coefficient pairs or triplets within the dataset, but not to datasets of surface reactions that draw species from the thermo dataset, nor to ancillary datasets (for [electrical conductivity](#), [isotope fractionation](#), and [water quality standards](#)).

## 9.2.4 Completing entries in surface datasets

### 9.2.4.1 Two-layer datasets

Two-layer datasets are arranged much like thermo datasets. You start by adding one or more “Basis surface species”, for which you specify a name, charge, and mole weight. Each basis entry defines a sorbing site. Click  to define the site's elemental composition, drawing from the list of elements in the thermo dataset, which is named in the dataset “Header”.

Second, compile a list of surface complexes under “Surface species”. For each complex, set a reaction written in terms of a surface site, combined with basis, redox, and aqueous species drawn from the thermo dataset. Set an equilibrium constant as a log  $K$  for each reaction at 25°C (the  $a_{\pm}$  value), as well as the temperature expansion.

Finally, specify one or more minerals to carry the surface. Right-click on “Sorbing minerals” and select **Add**. Each sorbing mineral may host an arbitrary number of sorbing sites, which are the basis species in the dataset. Next to “Name”, click “New Sorbing Mineral” → “Minerals...” and choose a mineral from the thermo dataset. Enter the



mineral's specific surface area, in  $\text{m}^2 \text{g}^{-1}$ . Under sorption sites, click  to pull in the surface's basis species; for each, set site density in mol (mol mineral) $^{-1}$  or sites  $\text{nm}^{-2}$ .

You can specify a value for constant capacitance or constant potential, but not both, in the Header section. You may prefer to leave these unset and allow the user to set values as desired from within **Rxn**, **SpecE8**, **React**, **Phase2**, **X1t**, or **X2t** (see [Two-layer surface complexation model](#) under **Configuring the Programs**).

#### 9.2.4.2 Triple-layer and CD-MUSIC datasets

The process for completing entries for triple-layer and CD-MUSIC datasets differs from that for the two-layer case above principally in the need to distribute surface charge across two or three planes. For triple-layer datasets, you enter separate values for  $z_0$  and  $z_\beta$ . Datasets for the CD-MUSIC method, in contrast, require you to enter values for  $\Delta z_0$ ,  $\Delta z_1$ , and  $\Delta z_2$ . Note that in current usage, the value for  $\Delta z_2$  is commonly taken to be zero.

Supply the required capacitance values  $C_1$  and  $C_2$  in the "Header" section.

#### 9.2.4.3 Langmuir datasets

Langmuir datasets contain a single basis entry, which represents the sorbing site. The Langmuir site is uncharged and carries no mass, so you need enter only a name. You can load any number of Langmuir datasets simultaneously into the GWB modeling programs, as long as each has a unique "type" set in the "Header", and a unique name for the basis entry.

To define the surface complexes, right-click on "Surface species" and choose **Add**. Then, click in the "Species" box and choose a species to complex with the surface site. **TEdit** will construct a balanced reaction including the Langmuir site and will fill in all the entries, except for the log  $K$  temperature expansion, which you must supply.

#### 9.2.4.4 $K_d$ and Freundlich datasets

$K_d$  and Freundlich surface datasets include surface complexes but not basis species. To define a surface complex, right-click on "Surface species" and choose **Add**. Click in the box to the right of "Species:" and choose from the basis, redox, and aqueous species in the thermo dataset. **TEdit** automatically completes the entry, except for the  $K_d$ , or the values of  $K_f$  and  $n_f$ , which you must also enter.

#### 9.2.4.5 Ion exchange

An ion exchange dataset contains a single basis species. To define it, right-click on "Basis species" and choose **Add**. In the box to the right of "Sorbed species", choose from the charged basis species in the thermo dataset. **TEdit** will automatically complete the entry.

To define the surface species that exchange with the basis species, right-click on "Surface species" and select **Add**. Click in the box to the right of "Species" and choose from the list of species of like charge in the thermo dataset. **TEdit** will construct a

balanced reaction following the activity convention you have chosen, and fill in all entries except for the selectivity coefficient, which you must enter as a linear value.

### 9.2.5 Adding references

From the “Header” section, you can add comments to appear at either the beginning of a dataset or at the end. Text you type into the “Preamble” appears just below the Header lines at the top of the dataset, whereas the contents of the “Bibliography” appear at the bottom. If you would like to add comments or a reference to an individual species in the dataset, open the species’ data pane and enter text in the “Reference” block. **TEdit** saves this text after the species’ block of thermodynamic data.

### 9.2.6 Reordering entries

Entries within each section of the dataset can appear in arbitrary order. You can move an entry by dragging it (as described below) within the same section. You can also right-click on any section heading (except “Header” and “Tables”) and click **Sort** to alphabetize the entries within that section. Use **Edit → Sort** to alphabetize the entire dataset. Keep in mind H<sub>2</sub>O must be the first basis species, so it will not be affected by dragging or sorting.

### 9.2.7 Transferring entries to other datasets

You can transfer data tables, elements, species, solid solutions, or virial coefficients from one dataset to another. Copy entries to the clipboard by selecting them on the tree structure, then right-click one and select **Copy**, or alternatively use **Edit → Copy**. **Edit → Cut** performs a similar function but removes the entries in question from the source dataset. Select multiple entries by holding the **Ctrl** or **Shift** key while making your selections.

To paste, go to the target dataset and select **Edit → Paste**. **TEdit** includes the type of entry (e.g. Element) in the information it copies to the clipboard, so the entry will be pasted in the appropriate section. If you select an entry within the correct section of the target dataset before pasting, **TEdit** will paste the copied entry immediately after it; otherwise, the entry will be added at the end of the list.

You can also drag entries (see [Drag and drop feature](#) under **Introduction**) from one dataset to another. Select one or more entries on the tree structure of the source dataset, then hold the left mouse button down and drag to the tree structure or current entry of the target dataset, and release. As with copying and pasting, if your cursor is within the correct section, **TEdit** will place the entry where you drop it. If not, **TEdit** will place it at the end of the appropriate section. If the source and target datasets are open in the same **TEdit** window, switch to the target dataset by hovering over its tab while dragging.

You should use your judgment when transferring thermodynamic data from one dataset to another. **TEdit** will issue a warning when activity models differ and will not allow you to transfer data in some cases. For example, you cannot transfer virial

coefficients from an SIT to an H-M-W dataset. Similarly, the program will not allow you to transfer surface species unless both datasets use the same surface model: you cannot transfer a reaction for sorbed  $\text{Pb}^{++}$  from a two-layer to a three-layer model dataset.

**TEdit** will issue a warning if you try to transfer an entry that would be undefined in the target dataset. For example, you would need to add the element Cadmium to “thermo.tdat” before you can paste in the basis species  $\text{Cd}^{++}$ . Similarly, a dataset utilizing the virial equations must include the  $\text{Ca}^{++}$  and  $\text{Cl}^-$  species before you can paste the  $\text{Ca}^{++} - \text{Cl}^-$  cation–anion pair interaction term.


When transferring log  $K$ s within a  $T$ -table to another  $T$ -table dataset, **TEdit** will check the principal temperatures of both datasets and transfer only values corresponding to exact temperature matches. When transferring log  $K$ s set as polynomial expansions to a dataset utilizing  $T$ -tables, **TEdit** will evaluate the polynomial at the principal temperatures of the target dataset and store the data as  $T$ -tables. It will not transfer data in  $T$ -tables to a polynomial dataset.

## 9.2.8 Rebalancing reactions

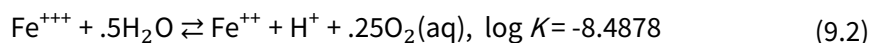
In the current release, reactions can be written in terms of any species in the dataset (see **Species and reactions** in the **Thermo Datasets** chapter of the *GWB Reference Manual*). Deprotonation reactions, for example, can be written equally validly in terms of the proton  $\text{H}^+$  or the hydroxyl ion  $\text{OH}^-$ , even though the latter is a secondary aqueous species. As a second example, the stability of aragonite might be defined relative to its polymorph calcite, rather than the basis species “ $\text{HCO}_3^-$ ”.

Reactions in the dataset can be rebalanced by various methods, described below. In each case, **TEdit** recalculates equilibrium constants automatically.

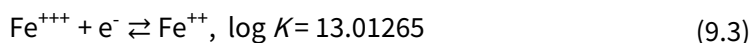
### 9.2.8.1 Basis swapping


To rebalance a reaction in **TEdit**, there’s no need to add or delete species manually. Instead, swap the basis to automatically rebalance reactions (see [Setting and constraining the basis](#) under **Configuring the Programs**). To do so, click the “swap” button  next to the species you’d like to remove, select the type of species to swap in, then choose the species from the pulldown list.

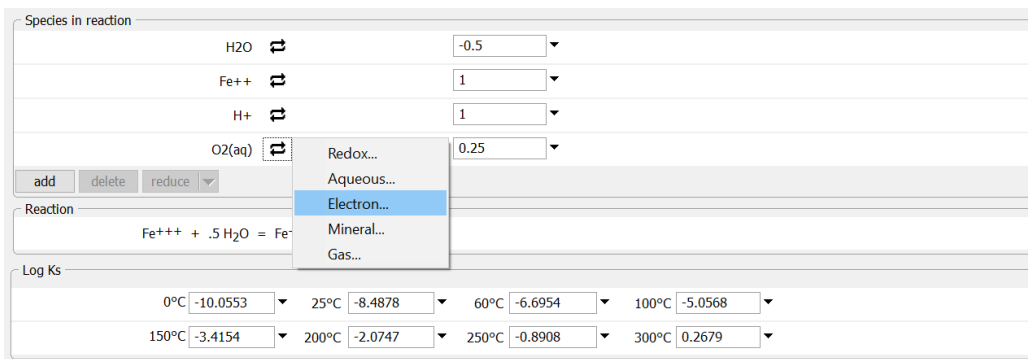
To recast the reaction for the redox species  $\text{Fe}^{+++}$  in “thermo.tdat”



as a half-cell reaction



click the “swap” button  next to “O2(aq)” and select **Electron... → e<sup>-</sup>**



Species in reaction

Species	Stoichiometry	Log Ks
H2O	-0.5	
Fe <sup>++</sup>	1	
H <sup>+</sup>	1	
O2(aq)	0.25	

add delete reduce

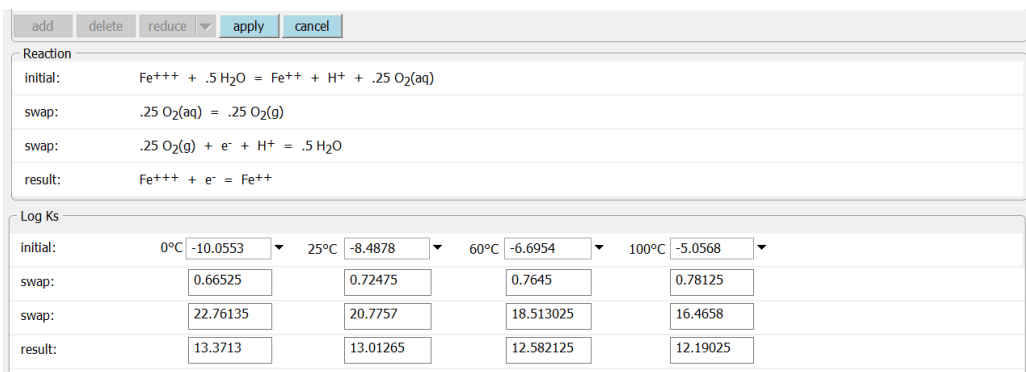
Reaction

Fe<sup>+++</sup> + .5 H<sub>2</sub>O = Fe<sup>+</sup>

Log Ks

0°C	25°C	60°C	100°C
-10.0553	-8.4878	-6.6954	-5.0568
150°C	200°C	250°C	300°C
-3.4154	-2.0747	-0.8908	0.2679

**TEdit** will display how it rebalances the initial reaction and recalculates log *K* values



add delete reduce apply cancel

Reaction

Initial: Fe<sup>+++</sup> + .5 H<sub>2</sub>O = Fe<sup>++</sup> + H<sup>+</sup> + .25 O<sub>2</sub>(aq)

swap: .25 O<sub>2</sub>(aq) = .25 O<sub>2</sub>(g)

swap: .25 O<sub>2</sub>(g) + e<sup>-</sup> + H<sup>+</sup> = .5 H<sub>2</sub>O

result: Fe<sup>+++</sup> + e<sup>-</sup> = Fe<sup>++</sup>

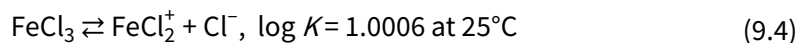
Log Ks

initial:	0°C	25°C	60°C	100°C
	-10.0553	-8.4878	-6.6954	-5.0568
swap:	0.66525	0.72475	0.7645	0.78125
swap:	22.76135	20.7757	18.513025	16.4658
result:	13.3713	13.01265	12.582125	12.19025

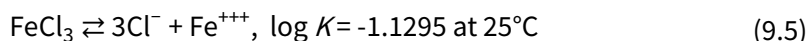
and will temporarily disable editing. Click **apply** to accept the changes, or **cancel** to revert to the original reaction.

### 9.2.8.2 Automatically reducing reactions

You can automatically reduce reactions written in arbitrary form to the set of redox and basis species, or the set of basis species alone. For example, the dissociation reaction for FeCl<sub>3</sub>(aq) might be written in stepwise fashion in terms of the aqueous species FeCl<sub>2</sub><sup>+</sup>

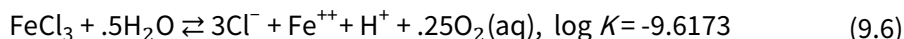


To automatically reduce that reaction to the set of redox and basis species, click the **reduce** pulldown button under “Species in reaction”, then select **Reduce to redox and basis**. Note how **TEdit** automatically swaps out the aqueous species FeCl<sub>2</sub><sup>+</sup> for the redox species Fe<sup>+++</sup> and recalculates the equilibrium constant to reflect the cumulative reaction



Click **apply** to accept the changes, or **cancel** to revert to the original reaction.

To reduce the reaction to the set of basis species, click **reduce** once again, then select **Reduce to basis**. This time, **TEdit** swaps out the redox species  $\text{Fe}^{+++}$  for the basis species  $\text{Fe}^{++}$  and again recalculates the equilibrium constant



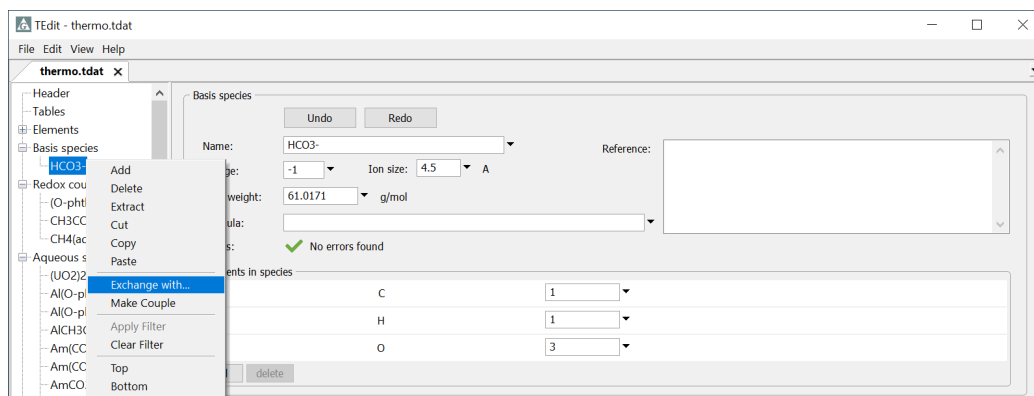
Note, the latter option limits the ability of the GWB programs to interactively decouple redox reactions.

### 9.2.8.3 Exchanging species positions

You can use **TEdit** to exchange the positions of basis, redox, and aqueous species within a thermo dataset. For example, you might replace the basis species “ $\text{HCO}_3^-$ ” with the aqueous species “ $\text{CO}_3^{--}$ ”. In this case, “ $\text{CO}_3^{--}$ ” will appear in the basis, and “ $\text{HCO}_3^-$ ” among the aqueous species; all of the reactions in the dataset that had been written in terms of “ $\text{HCO}_3^-$ ” will be rebalanced in terms of “ $\text{CO}_3^{--}$ ”.

To exchange the positions of two species, right-click on the entry for one of them on the tree structure and click **Exchange with...**, select the type of species to exchange with, then choose from the pulldown list the second of the species. **TEdit** exchanges the species’ position in the dataset, as you can see in the tree structure, and rewrites the reaction between them. In some cases, dependent reactions throughout the dataset will be rebalanced, as well.

To perform the “ $\text{CO}_3^{--}$ ” for “ $\text{HCO}_3^-$ ” swap described above, for example, right-click on “ $\text{HCO}_3^-$ ”, then select **Exchange with... → Aqueous... →  $\text{CO}_3^{--}$** , as shown below:



A dialog will open showing the species whose reactions will be rebalanced. Hover over any species to see how it will be rebalanced. Click **OK** to proceed, or **Cancel** to back out. The rebalanced reaction for “CH<sub>3</sub>COO<sup>-</sup>” is shown below

Reaction	
CH <sub>3</sub> COO <sup>-</sup> + 2 O <sub>2</sub> (aq) = 3 H <sup>+</sup> + 2 CO <sub>3</sub> <sup>-</sup>	
Log Ks	
0°C	139.3854
25°C	126.0609
60°C	110.2168
100°C	95.2545
150°C	79.9594
200°C	67.3483
250°C	56.5137
300°C	47.1757

You could accomplish the same thing in reverse, by selecting “CO<sub>3</sub><sup>-</sup>” from the tree and exchanging it with “HCO<sub>3</sub><sup>-</sup>”. If you were to exchange the same two species a second time, the dataset would revert to its original state.

The exchange feature provides a quick method for changing the redox pivot of a thermo dataset (see **Basis species** under the **Thermo Datasets** chapter in the *GWB Reference Manual*). In “thermo.tdat”, when you exchange the basis species O<sub>2</sub>(aq) for the redox species H<sub>2</sub>(aq), the latter becomes the redox pivot. All reactions written in terms of dioxygen, including the redox coupling reactions and that for the free electron, will be rebalanced in terms of dihydrogen.

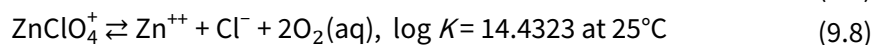
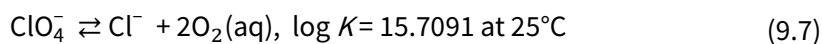
H<sub>2</sub>O and H<sup>+</sup> are required as entries in the basis and have therefore been excluded from the exchange feature. O<sub>2</sub>(aq) and H<sub>2</sub>(aq) can only be exchanged with each other.

## 9.2.9 Adjusting redox coupling

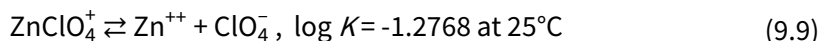
Besides changing the redox pivot of a dataset or otherwise rebalancing redox reactions (see previous section), you can couple or decouple redox reactions, and rebalance dependent reactions accordingly. You can also create or eliminate redox couples. For more information on how redox reactions are interactively enabled or disabled in the apps, see [Redox couples](#) in the **Configuring the Programs** chapter of this guide, and [Redox disequilibrium](#) under **Using SpecE8**.

### 9.2.9.1 Coupling and decoupling reactions

You can decouple an aqueous species to move it to the “Redox couples” section of the dataset. As an example, given a dataset with the following aqueous species



you might wish to decouple the perchlorate ion to allow for redox disequilibrium, and to rebalance the Zn-perchlorate complex in terms of the new couple as below



To do so, right-click on “ClO4-” and choose **Decouple**. A dialog will pop up asking you to confirm the decoupling. If any redox reactions within the “Aqueous species”, “Minerals”, and “Gases” sections of the dataset can be rebalanced with the new couple so as to eliminate the change in oxidation state, **TEdit** will open a second dialog offering to rebalance those entries. Mouse over an entry to see how it will be rebalanced, then click **OK** to continue, or **Cancel** to skip the rebalancing.

The opposite action, coupling a redox species, moves it to the “Aqueous species” section of the dataset. A redox species that invariably remains coupled in your calculations might benefit from permanent coupling in this way, as would any non-redox reaction that happens to be in that section of the dataset. To couple a reaction, right-click on the redox species and select **Couple**. Click **Yes** in the first dialog that pops up to confirm the move. A second dialog will offer to rebalance dependent reactions in terms of the remaining basis and redox species. Mouse over an entry to see the rebalanced reaction, and Click **OK** to continue, or **Cancel** to skip the rebalancing.

Coupling a redox species in the dataset limits the flexibility of calculations using that data, whereas decoupling an aqueous species increases flexibility.

#### 9.2.9.2 Making and breaking redox couples

You can turn a basis species into a redox couple by writing a reaction linking it to another basis or redox species. By making a redox couple, you can account for redox equilibrium or disequilibrium in your calculations as needed. In “thermo\_minteq.tdat”, for example, you might want to couple the basis species “Acetate-” and “CO3--”, with the former serving as the redox species. To do so, right-click on “Acetate-” and select **Make Couple**, which moves the entry to the “Redox couples” section. Complete the entry by providing reaction and log *K* expansion (see [Completing entries in thermo datasets](#) in this section).

Conversely, you can eliminate a redox coupling reaction that is unlikely to reach equilibrium under any circumstances. To do so, right-click on a redox species and select **Break Couple**. The redox species will be moved to the “Basis species” section and the reaction and log *K* expansion replaced with the species’ elemental composition.

Whereas making a couple increases the flexibility of the calculations you can consider, breaking a couple limits you. It is generally preferable to decouple a reaction in the apps than to break a redox couple in the thermo dataset.

#### 9.2.9.3 Identifying redox and non-redox reactions

Redox reactions should ideally be limited to the “Redox couples” section of the dataset. As such, reactions for “Aqueous species”, “Minerals”, and “Gases” should be written without species O<sub>2</sub>(aq), O<sub>2</sub>(g), H<sub>2</sub>(aq), H<sub>2</sub>(g), and e<sup>-</sup>, and without pairs of species of different

valences, such as  $\text{Mn}^{++}$  and  $\text{MnO}_4^-$ , to the extent practical. In other words, reactions are ideally balanced in terms of species of the same oxidation state as the species in question.



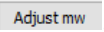
You can identify “Redox reactions” or “Non-redox reactions” by selecting the appropriate pulldown option from the summary panes of the aforementioned sections (see [Summaries, filtering, and searching](#)).



In some cases, you may be able to rebalance redox reactions by swapping in an existing basis or redox species that eliminates the change in oxidation state. Or, lacking an appropriate species, you might copy one from another dataset, or add one from the literature, and then rebalance with it (see previous sections).

In other cases, you might find that an aqueous species might be utilized to the same effect. That species, then, could serve well as a redox couple and might benefit from decoupling, as described above.

## 9.2.10 Troubleshooting

**TEdit** will open the **Troubleshoot...** dialog if it finds any issues when you open or save a dataset, and when you go to **File → Troubleshoot....** The dialog lists warnings for specific entries that can typically be fixed within **TEdit**, such as charge or mass imbalances. Double-click on an entry to go to its editing pane. A second box describes omissions, broader dataset problems, and errors that may need to be fixed in a text editor, and additionally indicates when a new dataset format is available. Click **Refresh** to recheck for issues after making updates, or after changing focus to another open dataset. Finally, you can click **View Errors** to open an error log generated when **TEdit** first reads a dataset. The log indicates the line numbers on which errors are found and is intended as a guide for fixing errors in a text editor. The log does not refresh, so reopen an updated dataset to continue troubleshooting.

Each entry’s editing pane includes its own troubleshooting status. A  indicates that no problems have been found, while a  symbol flags one or more problems. A message provides more details. If the reaction is not mass-balanced, you can adjust the mole weight, assuming the reaction is correct, by clicking .

To check the entire dataset for mass imbalances, go to **Edit → Mole Weight....** The dialog lists all imbalances exceeding a threshold (0.9 g/mol by default) in descending order. Double-click any row to go to that species’ entry pane. Or, select one or more rows in the dialog and click  to recalculate using the mole weight expected from the elemental composition. Clicking  recalculates the mole weights of all species exceeding the specified threshold.

If **TEdit** cannot open a corrupted dataset, you will need to fix it in a text editor. The error messages from **TEdit** or the other apps should help you locate the approximate line or entry that needs to be fixed. Formatting details are given in the **Thermo Datasets** and **Surface Datasets** chapters in the *GWB Reference Manual*.



## 9.3 Importing and exporting databases for other modeling programs

### 9.3.1 Importing PhreeqC datasets

TEdit can convert datasets for the PhreeqC program (see [Further Reading](#)) to GWB-format thermo and surface datasets. To do so, go to **File** → **Import** → **PhreeqC...** and browse to open a PhreeqC “.dat” file, or drag a dataset into TEdit.

Depending on the keywords encountered in the PhreeqC dataset, TEdit will produce a GWB dataset using either the `phreeqc`, `b-dot`, `sit`, or `h-m-w` activity model (see [Thermodynamic datasets](#) under **Configuring the programs**, and [Activity coefficients](#) under **Using SpecE8**), corresponding to PhreeqC’s default, LLNL, SIT, and PITZER models, respectively.

The GWB programs enforce an operable temperature range, as constrained by the lower and upper principal temperatures of the dataset in use (see **Thermo Datasets** in the *GWB Reference Manual*). Unless laid out in the PhreeqC dataset with the `LLNL_AQUEOUS_MODEL_PARAMETERS` data block, you must specify an appropriate range for the imported dataset so that TEdit can construct a principal temperature grid. Pressure defaults to one atmosphere up to 100°C, and above that follows a correlation for the vapor pressure of water.

For the `phreeqc`, `sit`, and `h-m-w` models, polynomial coefficients for Debye-Hückel parameters  $A$  and  $B$  are taken from the THEREDA project’s dataset (see [Further Reading](#)). If the `-APHI` keyword is used in a PITZER dataset, however, Debye-Hückel  $A$  polynomial coefficients are calculated according to the relation  $A^{\phi} = 2.303A/3$ . For the `b-dot` model,  $A$ ,  $B$ , and  $\dot{B}$  are read from the `LLNL_AQUEOUS_MODEL_PARAMETERS` data block, and the remaining “CO2” and “H2O” header variables are taken or fit from the tables spanning 0–300°C in “thermo.tdat” but are not used by default, as described below.

For the `b-dot` model, TEdit sets “ion size” of each neutral aqueous species for which the `-CO2_llnl_gamma` keyword is encountered to -0.6; the flag triggers the Drummond (1981) activity coefficient equation used in PhreeqC. You can change the setting to -0.5 to apply Helgeson’s method, using the “CO2” tables described above. H2O’s “ion size” parameter is similarly used as a flag; the default setting of -1 for imported `b-dot` datasets triggers the Garrels and Christ (1965) water activity calculation used in PhreeqC. To revert to the standard Helgeson (1969) model using the “H2O” tables, change “ion size” of H2O to 0. More options are described in **Species and reactions** under **Thermo Datasets** in the *GWB Reference Manual*.

TEdit contains an internal list of elements and their mole weights, along with a list of common organic compounds, which it compares to the elements and master species laid out in the PhreeqC dataset. Whereas a PhreeqC dataset might contain a fictitious element “Ac” corresponding to its master species Acetate-, TEdit will create a basis species Acetate- composed of true elements: 2 C, 3 H, and 2 O, rather than 1 Ac. When TEdit

encounters an element it does not recognize, it will prompt you to substitute a known element, use the fictitious element, or define the elemental composition of a compound.

The temperature dependence of  $\log K$ s in GWB datasets is described with a polynomial containing up to six coefficients  $a-f$ , (see **Temperature expansions** under **Thermo Datasets** in the *GWB Reference Manual*). GWB polynomial coefficients were converted from coefficients  $A_1$ - $A_6$  in PhreeqC's analytic expression as follows:

$$\begin{aligned} a &= \log K_{T_r} = A_1 + A_2 T_r + \frac{A_3}{T_r} + A_4 \log T_r + \frac{A_5}{T_r^2} + A_6 T_r^2 \\ b &= A_2 \\ c &= A_6 \\ d &= A_3 \\ e &= A_5 \\ f &= \frac{A_4}{\ln(10)} \end{aligned}$$

where  $T_r$  is 298.15 K. Lacking an analytical expression, the  $\log K$  at 25°C in PhreeqC was used, with the standard enthalpy change when available, as follows:

$$\begin{aligned} a &= \log K_{T_r} \\ b &= 0 \\ c &= 0 \\ d &= \frac{-\text{delta\_h}}{R \ln(10)} \\ e &= 0 \\ f &= 0 \end{aligned}$$

where  $\text{delta\_h}$  is the standard enthalpy of reaction in kJ/mol and  $R$  is the gas constant in kJ/(mol K).

PhreeqC's polynomial for virial coefficients in the PITZER and SIT models differs from its  $\log K$  polynomial. GWB polynomial coefficients for virial coefficients were converted from coefficients  $A_0$ - $A_5$  in PhreeqC's PITZER/SIT expansion as follows:

$$\begin{aligned} a &= A_0 \\ b &= A_3 \\ c &= A_4 \\ d &= A_1 \\ e &= A_5 \\ f &= A_2 \end{aligned}$$

GWB datasets invariably contain destruction reactions, so formation reactions within PhreeqC SOLUTION\_SPECIES, SURFACE\_SPECIES, and EXCHANGE\_SPECIES blocks are reversed and  $\log K$  coefficients are negated.

**TEdit** converts charged species' names to the GWB convention. For example,  $\text{Ca}^{++}$  replaces  $\text{Ca}^{+2}$ . The suffix (aq) is appended to species  $\text{O}_2$  and  $\text{H}_2$ . Additionally, suffixes (aq) and (s) are added where species names are duplicated. **TEdit** expects gases to end in "(g)" or ",g" to differentiate them from minerals in the PHASES block; ",g" is changed to "(g)".

A PhreeqC dataset might contain surface complexation and ion exchange reactions in addition to those involving aqueous species, minerals, and gases. Upon reading a PhreeqC dataset, **TEdit** splits the surface reactions into separate ".sdat" files, one for each ion-exchange, two-layer, or CD-MUSIC model surface it finds (see [Sorption onto mineral surfaces](#) under **Configuring the Programs**).

In converting ion-exchange data, **TEdit** combines PhreeqC's half-reactions into full reactions following the Gaines-Thomas convention, and transforms  $\log K$  values to linear selectivity coefficients. No temperature dependence is carried over.

In PhreeqC, information about sorbing minerals, such as the specific surface area and concentration of sites, is specified in the input file, rather than the dataset, as in GWB. To complete surface complexation datasets imported from PhreeqC, you should identify the sorbing mineral(s), and for each, specify its specific surface area along with the site density of each sorbing site. If the original data was for a non-electrostatic model, you should set surface potential to 0 from the Header pane. Or, for a constant capacitance model, set surface capacitance. For a CD-MUSIC surface, set capacitance values  $C_1$  and  $C_2$ .

### 9.3.2 Importing EQ3/6 datasets

**TEdit** can convert thermo datasets for Version 8 of the EQ3/6 package (see [Further Reading](#)) to GWB-format. To do so, go to **File** → **Import** → **EQ3/6...** and browse to open an EQ3/6 "data0.xxx" file, or drag the dataset into **TEdit**.

Depending on the EQ3/6 dataset, **TEdit** will produce a GWB dataset using either the b-dot or h-m-w activity model (see [Activity coefficients](#) under **Using SpecE8**). EQ3/6 "Temperature limits (degC)" values are written explicitly as GWB "TminC" and "TmaxC" fields only if the values differ from the first and last principal temperatures. For the b-dot model, the "CO2" and "H2O" tables are filled in as described in the previous section. For the h-m-w model, Debye-Hückel  $A$  is calculated from  $A^\phi$  as described previously.

For the b-dot model, **TEdit** sets "ion size" of each neutral aqueous species for which the "neutral ion type" equals "-1" to "-0.6"; the flag triggers the Drummond (1981) activity coefficient equation used in EQ3/6.  $\text{H}_2\text{O}$ 's "ion size" parameter is set to "-2" to trigger the water activity calculation currently used in EQ3/6. For more information, see **Species and reactions** under **Thermo Datasets** in the *GWB Reference Manual*. For any species missing an ion size parameter, the value is set to "4" in the GWB dataset, following EQ3/6.

EQ3/6 datasets require a "strict basis species"  $\text{O}_2(\text{g})$ , whereas GWB datasets require aqueous basis species. Thus, if the EQ3/6 dataset contains  $\text{O}_2(\text{aq})$  in its "auxiliary basis species" section, **TEdit** makes it the basis species and moves  $\text{O}_2(\text{g})$  to the gases section. The reaction for  $\text{O}_2(\text{aq})$  is reversed and the  $\log K$ s are negated. The remaining auxiliary

basis species are mapped to GWB redox couples, whether or not they actually involve oxidation and reduction (see [Identifying redox and non-redox reactions](#)). The EQ3/6 "Eh reaction" is rebalanced and used for the "free electron" reaction in the GWB dataset, and its log  $K$ s are divided by "–4". Various spellings for aqueous O<sub>2</sub> (e.g. O<sub>2</sub>, O<sub>2</sub>,aq, O<sub>2</sub> (aq), and so on) are changed to O<sub>2</sub>(aq).

Reactions and log  $K$ s are factored as necessary so that the left-hand side species has a coefficient of "–1". If the EQ3/6 dataset is flagged with "INTERPRET 500 AS NO DATA= NO", any 500 log  $K$  value is considered an actual value and will be changed to 500.0002 within the GWB dataset. The change allows the GWB apps to distinguish actual data from "no data" 500 values but has an insignificant effect on stability. Any mineral mole volumes set to 500 are assumed to mean "no data" and are changed to "0". Any pure liquids (e.g. Hg(l)) are appended to the list of minerals.

All EQ3/6 solid solutions will be imported to GWB format, although not all are currently supported in the GWB modeling programs. For the Guggenheim, regular (binary), cubic Maclaurin, third-order Maclaurin, and ternary regular solution models, model coefficients  $p_{1\psi}$ – $p_{9\psi}$  are converted from cal mol<sup>–1</sup> to J mol<sup>–1</sup>. Additionally, coefficients  $p_{4\psi}$ – $p_{6\psi}$  in the Guggenheim model are negated because of the different conventions followed by EQ3/6 and the GWB programs. Solid solution "tags" default to the first six characters from each end member, but you might wish to update them, and in some cases, you might be required to (e.g. an end member Albite's tag cannot match its name). For more information, see [Solid solutions](#) under the **Configuring the Programs** chapter of this guide, as well as **Solid solutions** under **Thermo Datasets** in the *GWB Reference Manual*.

In virial datasets that follow the Version 7 format (i.e., with keywords "single-salt parameters" and "mixture term parameters"), only the virial coefficient values at 25°C are carried over. The coefficients  $a_1$ – $a_5$  in the high-temperature Pitzer treatment introduced in Version 8 are converted to the new GWB format virial polynomial (see **Virial coefficients** under **Thermo Datasets** in the *GWB Reference Manual*) according to:

$$\begin{aligned} a &= a_1 \\ b &= a_4 \\ c &= a_5 \\ d &= a_2 \\ e &= 0 \\ f &= a_3 \end{aligned}$$

Any text encountered before either the "Miscellaneous parameters" block or any type of "Configuration data" is stored as a comment in the GWB dataset between the initial lines and the list of principal temperatures. Text from the "References" block is added as comments to the end of the GWB dataset. The comments are visible in **TEdit** in the "Preamble" and "Bibliography" sections, respectively, of the "Header" pane.

### 9.3.3 Exporting EQ3/6 datasets

**TEdit** can convert GWB thermo datasets using the *b-dot* or *h-m-w* models to EQ3/6 format. To do so, go to **File** → **Export** → **EQ3/6...**, then choose a folder and supply a name for the EQ3/6 “data0.xxx” file.

**TEdit** will supply tables of header variables appropriate for either model. The “Temperature limits (degC)” are taken from the global “TminC” and “TmaxC” if specified. Otherwise, they are taken from the first and last principal temperatures. For *h-m-w* datasets, Debye-Hückel  $A^\phi$  is calculated according to  $A^\phi = 2.303A/3$ . The log  $K$ s for the “Eh reaction” are converted from the “free electron” reaction, if present, as long as **TEdit** can rewrite the reaction in terms of  $H^+$  and  $O_2(g)$ . If not, log  $K$ s from thermo.tdat are used.

For *b-dot* datasets, uncharged species with an “ion size parameter” of “-.5” or “-.6” (flagging the Helgeson and Drummond “CO2” equations, respectively) are set with a value of “-1” for “neutral ion type”. For all other species, the flag is set to “0” and “azer0” set to the “ion size” value in the GWB dataset.

EQ3/6 requires a one-to-one mapping of elements and strict basis species, beginning with  $O:H_2O$ , continuing, for example, with  $H:H^+$ ,  $C:HCO_3^-$ , and so on, and concluding with an unpaired basis species  $O_2(g)$ . No strict basis species can contain more than one element beyond H and O. If a GWB dataset contains multiple basis species that would map to the same element (e.g.  $HCO_3^-$  and  $CH_3COO^-$  both contain C) you will be alerted (see description of the **EQ3/6 Export Errors...** dialog at the end of this section). To make the dataset workable in EQ3/6, you might make one of them a redox couple so that it is exported as an auxiliary basis species (see [Making and breaking redox couples](#)). For disequilibrium calculations in EQ3/6, it is acceptable to supply all 500 (“no data”) log  $K$  values. If you leave multiple basis species paired with the same element, the first such species encountered will be the strict basis species, and subsequent species will become auxiliary basis species, but with an incomplete reaction and no log  $K$  data in the data0 file.

Various spellings for aqueous and gaseous  $O_2$  (e.g.  $O_2$ ,  $O_{2,aq}$ ,  $O_2(g)$ , and so on) are changed to  $O_2(aq)$  and  $O_2(g)$ , respectively. Since EQ3/6 requires reactions to be written in terms of strict and auxiliary basis species, any arbitrarily written reactions are rebalanced in terms of their GWB analogues, the basis and redox species (see [Automatically reducing reactions](#)). Although redox reactions in EQ3/6 are often balanced in terms of  $O_2(g)$ , the GWB programs will rebalance such reactions in terms of  $O_2(aq)$ . Reaction log  $K$ s are limited to four digits after the decimal place.

The various expansion coefficients  $p_1$ – $p_9$  for solid solution models are converted from  $J\ mol^{-1}$  to  $cal\ mol^{-1}$ . In the Guggenheim model, coefficients  $p_4$ – $p_6$  are negated. GWB ideal and site\_mixing models map to EQ3/6 ideal site-mixing models. The  $p_7$  site parameter is taken to be unity, in the former case, or equal to  $b$ , in the latter. The various  $p_n$  parameters are limited to three digits after the decimal place in EQ3/6 datasets, so the conversion can be somewhat lossy.

GWB virial coefficient temperature expansions ( $a$ – $f$  for the new polynomial and  $\beta_{25}$ – $c_5$  for the legacy polynomial; see **Virial coefficients** under **Thermo Datasets** in the *GWB Reference Manual*) are mapped to EQ3/6 coefficients  $a_1$ – $a_5$  according to:

$$a_1 = a \text{ or } \beta_{25}$$

$$a_2 = d \text{ or } c_2$$

$$a_3 = f \text{ or } c_3$$

$$a_4 = b \text{ or } c_1$$

$$a_5 = c \text{ or } c_4$$

If any virial coefficient contains an  $e$  (or  $c_5$ ) value, **TEdit** will warn you that EQ3/6 will not be able to reproduce the temperature expansion (see next paragraph). **TEdit** writes out an extra  $a_6$  coefficient in this case, although it will cause an error in EQ3/6.

**TEdit** will launch the **EQ3/6 Export Errors...** dialog, a version of the **Troubleshoot...** dialog described previously (see [Troubleshooting](#)), if it detects certain issues. The dialog lists species-specific as well as global issues, allowing you to make changes before proceeding with the export. For example, species names in EQ3/6 datasets are limited to 24 characters, so the dialog will flag species with longer names. If you continue without renaming, **TEdit** will simply truncate the problematic species names in the data0.xxx dataset, without regard for any duplicates it creates in the process. As a second example, **TEdit** expects datasets treating redox reactions to use  $O_2(aq)$  as the redox pivot. If  $H_2(aq)$  is the pivot, **TEdit** will alert you. In this case, you can use the “Exchange” feature to make  $O_2(aq)$  the pivot before re-exporting (see [Exchanging species positions](#)).

## 9.4 TEdit command line

You can start **TEdit** by clicking the icon on the GWB dashboard, opening a “.tdat” or “.sdat” file, or entering the command `tedit.exe` from the Windows “Command Prompt.”

When you start **TEdit** from the command line, you can specify an optional argument. For example, the command

```
tedit -touch my_thermo.tdat
```

causes **TEdit** to silently open the “my\_thermo.tdat” thermodynamic database and save it again with the same name.

The following options are available from the command line:

<code>-touch &lt;dataset&gt;</code>	Silently read in the specified thermo or surface dataset and save it with the same name.
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<code>-mw &lt;dataset&gt;</code>	Open the specified dataset and recalculate the mole weight of all species directly from their elemental composition, then save it with the same name.
----------------------------------	---

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**Table 9.1**                      **Keyboard shortcuts in TEdit**

---

Ctrl+A	Select all
Ctrl+C	Copy
Ctrl+F	Find
Ctrl+N	Open the dialog to add species to a reaction
Ctrl+O	Open a thermo or surface dataset
Ctrl+Q	Quit TEdit
Ctrl+S	Save
Ctrl+Shift+S	Save As
Ctrl+V	Paste
Ctrl+X	Cut
Delete	Delete
F1	Open GWB Essentials Guide

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# Appendix: Further Reading

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The following literature references, from the many hundreds that have been published, provide a starting point for further reading on various aspects of geochemical modeling and its applications. Additional references are available in the *GWB Reaction Modeling Guide* and the *GWB Reactive Transport Modeling Guide*.

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