

A quick introduction to MINEQL+
AQUATIC CHEMISTRY COURSE

Department of Geochemistry
Faculty of Earth Sciences
Utrecht University

Oktober 2000—2002 Niels Hartog
http://geocities.com/niels_hartog

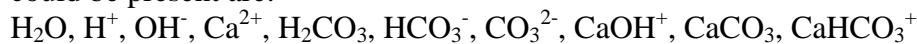
1.0 Introduction

MINEQL+ is a chemical equilibrium model capable of calculating aqueous speciation, solid phase saturation states, precipitation-dissolution, and adsorption. An extensive thermodynamic database is included in the model.

This document is a short overview of the program. Much more information, including the theoretical conditions of the model, can be found in the 318 pages of the User's Manual (Schecher & McAvoy, 1998). Section 2 briefly reviews the model fundamentals and, while in section 3 I try to explain the program routine operation.

2.0 MINEQL+ Model Fundamentals

In Mineql+, you start out by choosing components that define your system. Components are the basic building blocks from which all species are formed. The chemistry of system is organised using the **tableau method** (Morel & Hering, 1993). A tableau is a table of stoichiometric coefficients. Each column represents an individual component, and each row represents a separate species. The solution composition is written in terms of the components. For example, consider a 0.001 M solution of CaCO₃ in a closed system. The species that could be present are:



(Note: H₂O is always a component added automatically by the program. H⁺ is usually a component. The electron is a component in redox reactions.)

For this system, the components are: H₂O, H⁺, Ca²⁺, CO₃²⁻

Reactions are written with components on the left-hand side and products on the right-hand side. The stoichiometric matrix for the example can be written as:

Species	Components				(¹)K
	H ₂ O	H ⁺	Ca ²⁺	CO ₃ ²⁻	
H ₂ O	1	0	0	0	K ₁
H ⁺	0	1	0	0	K ₂
Ca ²⁺	0	0	1	0	K ₃
CO ₃ ²⁻	0	0	0	1	K ₄
OH ⁻	1	-1	0	0	K ₅
HCO ₃ ⁻	0	1	0	1	K ₆
H ₂ CO ₃	0	2	0	1	K ₇
CaOH ⁺	1	-1	1	0	K ₈
CaHCO ₃ ⁺	0	1	1	1	K ₉
CaCO ₃	0	0	1	1	K ₁₀

(1) Note that the equilibrium constant K, is defined differently from the more traditional definition in the text.

For example, the traditional expression is:

$\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-}$ $K_a = 10^{-10.3}$ However, following the format specified for MINEQL+, the expression should be written with components on the left hand side and species on the right hand side. Therefore: $\text{H}^+ + \text{CO}_3^{2-} = \text{HCO}_3^-$ $K_6 = 10^{10.3}$ where the notation K₆ is used to be consistent with the stoichiometry shown in the table.

The MINEQL+ program solves the mass balance. In this case, there are three equations (below) and three unknowns ($[Ca^{2+}]$, $[H^+]$, $[CO_3^{2-}]$)

$$Ca^T = f([Ca^{2+}], [H^+], [CO_3^{2-}])$$

$$CO_3^T = f([Ca^{2+}], [H^+], [CO_3^{2-}])$$

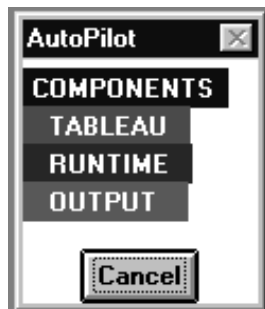
$$H^T = f([Ca^{2+}], [H^+], [CO_3^{2-}])$$

3.0 Routine Program Operation



Mineql+ basically consists of four subsequent software modules

- (1) Chemical Components Selection Module
- (2) Species Tableau Module
- (3) Runtime Manger
- (4) Output Manager



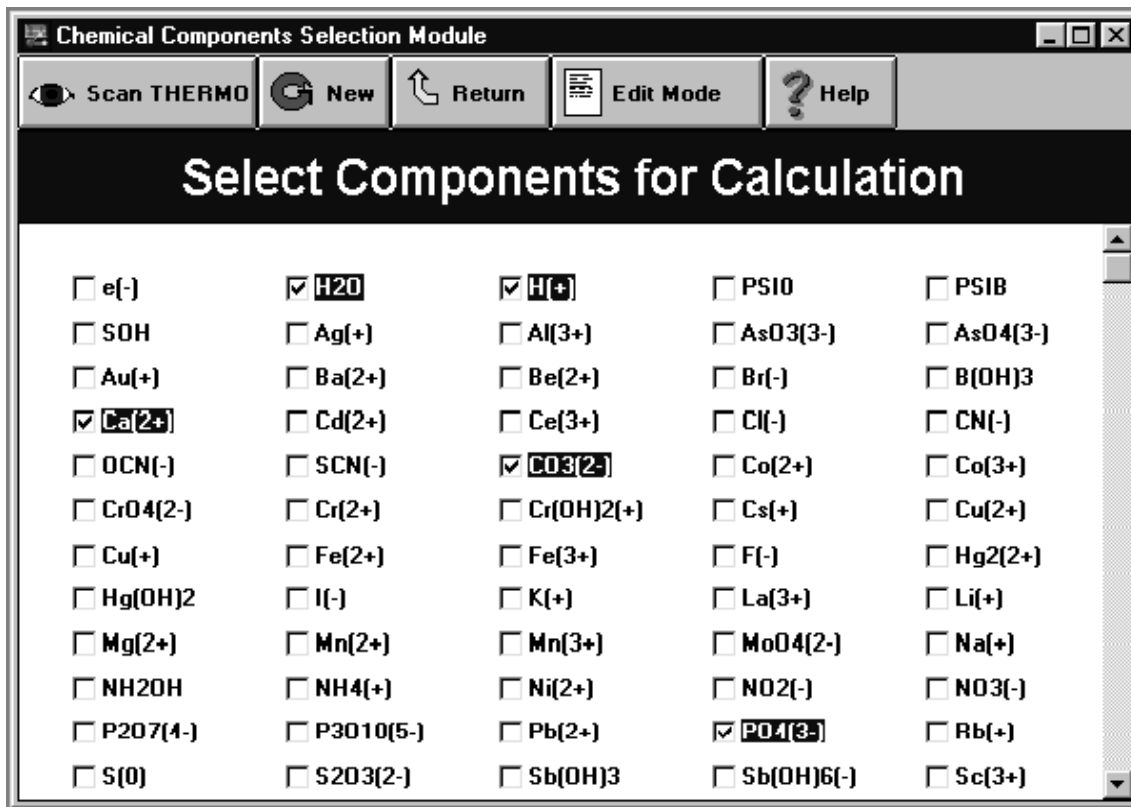
In default the AutoPilot (Alt-m + a) is "on" and the program automatically directs you through the modelling process from (1) to (4).

3.1 Selecting Chemical Components

Defining the components that describe the chemistry of a system in MINEQL+, involves the use of:

- (1) Chemical Components Selection Module,
- (2) Species Tableau Module

(1) Using the Chemical Components Selection Module



The Chemical Component Selection Module contains a list of all the chemical components available under MINEQL+. There are 145 pre-defined components and 55 NULL components. The NULL components are at the bottom of the list and are available to you for making your own components. To define a new problem, you can reset an existing problem by clicking the New button. This option will also de-select all components except H₂O and H(+). As you select chemical components from the Select Component tool, you are adding columns to the tableau. When you search the thermodynamic database (section 3.2), or add new reaction data manually, you are adding new rows to the tableau.

3.2 Scanning the Thermodynamic Database

Click the Scan THERMO button at the top of the screen and, depending on what options you have set under *preferences* (section 3.0), MINEQL+ will scan the default database and/or the personal database and create a tableau.

Type II - Aqueous Species					
Name	H2O	H(+)	Ca(2+)	Log K	Delta H
OH- (-1)	1	-1	0	-13.998	13.345
CaOH+ (+1)	1	-1	1	-12.598	14.535
CaHCO3+ (+1)	0	1	1	11.330	1.7900
CaHPO4 AQ	0	1	1	15.085	-0.23000
H2CO3 AQ	0	2	0	16.681	-2.2470
HCO3- (-1)	0	1	0	10.330	-3.6170
H2PO4- (-1)	0	2	0	19.553	-4.6200
HPO4-2 (-2)	0	1	0	12.346	-3.5300
H3PO4	0	3	0	21.710	0.0000
CaCO3 AQ	0	0	1	3.1500	4.0300
Total Conc. (M) -->					
	0.000E+00	0.000E+00	0.000E+00		

(2) Using the Species Tableau Module

The Tableau tool addresses chemical reaction data according to species type:

Species Type	Category	Accessed by Tableau Tool
I	Free, Aquo, or Unassociated	NO
II	Dissolved Complexes	YES
III	Fixed Entities: e.g., Solids, gases, pH	YES
IV	Precipitated Solids	NO
V	Dissolved Solids: Solids with the potential to precipitate	YES
VI	Species Not Considered	YES

The chemical components that are selected in the Chemical Components Selection Module (section 3.1), are automatically added as columns in the tableau. The tableau is a table of stoichiometric coefficients. The columns of the table represent chemical components, while the rows of the table represent chemical species. Essentially, this is an efficient way in which to represent chemical formation reactions. In addition to stoichiometry, a tableau will also include thermodynamic data that is associated with each individual chemical species plus the total concentrations associated with each chemical component.

3.3 Calculation Wizards Tool

The Calculation Wizards Tool is a collection of 5 input options to describe the chemistry of the system. The Calculation Wizard can be accessed from the Species Tableau Module (section 3.2) and the Runtime Manager (section 3.4).



(1) Input for Total Component Concentrations

The Totals Wizard allows you to input total molar concentrations for each component. The advantage of using this Wizard over the Tableau is that the Wizard focuses only on those components that require input. Components such as H_2O , H^+ , CO_3^{2-} , or e^- either do not require a total concentration or have their concentrations set in following Wizards.

(2) Setting the pH (fixed) or calculate the pH

The pH Wizard is designed to help set up pH calculations within MINEQL+. There are 2 general types of pH calculations. First, you can perform calculations where pH is a fixed, known value. In this case, the only thing you will have to define is the pH value itself. The second type of calculation is one where pH is calculated by MINEQL+.

(3) Setting Dissolved Inorganic Carbon and CO_2 Conditions

If you include CO_3^{2-} in your component list, the CO_2 Wizard will become active. Systems are assumed to be either open to atmospheric CO_2 or closed. If a system is open, you must supply it with the PCO_2 value. The value to input is a log value. Under normal atmospheric conditions, CO_2 has a partial pressure of $10^{-3.5}$ atm. This value would be input as -3.50.

(4) Moving Solids within the Tableau

In many situations, you may have several solids listed under the category of Type V (Dissolved Solids). Moving or deleting these solids can be tedious. The Solids Mover allows you to select only those solids that you wish to have included in the calculation. The result is that solids can be moved into, or out of, the Type V category individually or as a group.

(5) Setting Redox Options

The Redox Wizard allows you to choose various options that will help you to set the “free e^- concentration” in the system. To define the overall redox state in MINEQL+, a redox specie must be present. This species could be the pe, the dissolved O_2 (DO) concentration, or some other gas or ion pair.

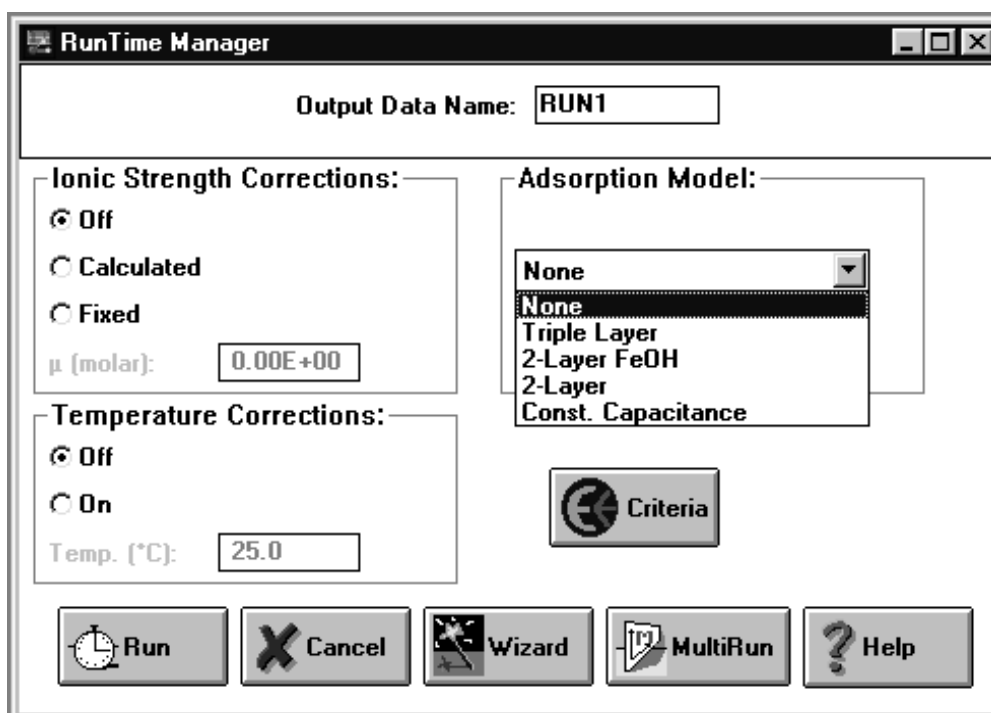
When performing a fixed pe calculation, the only information required is the pe value itself. For DO, you can either enter the DO concentration in mg/L or as the partial pressure of O_2 .

As with the CO₂ Wizard, the partial pressure is input as a log value. Under normal atmosphere conditions the PO₂ equal to 0.21. This translates to a log value of -0.68.

Using fixed pe or fixed O₂ options, the Type III tableau will be reset for the correct species, and the log K values will be altered to reflect the pe or DO levels.

3.4 Running the Calculation

(3) Using the Runtime Manager



The Runtime Manager represents the final stage before running the actual model calculations. This is also the final chance to check on the chemical conditions using the Calculation Wizards Tool (section 3.4).

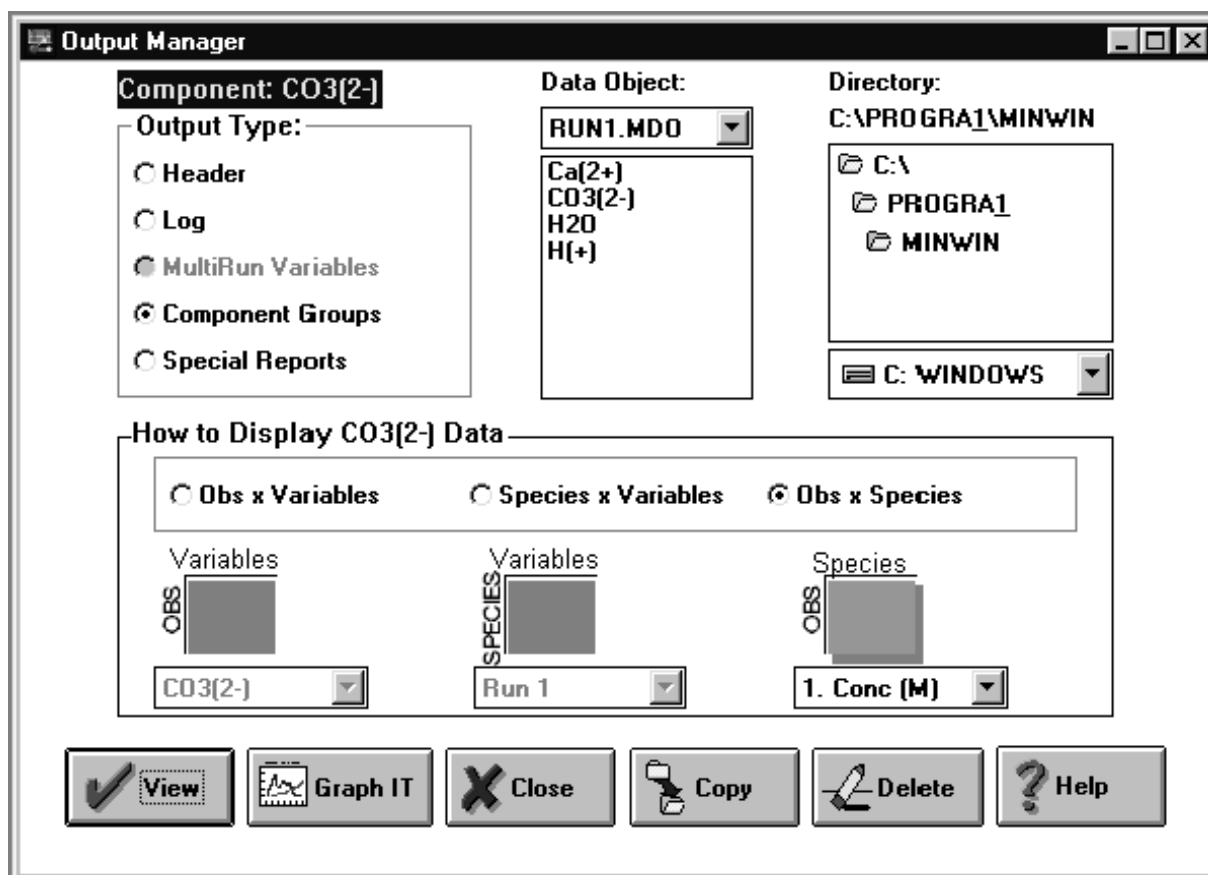
Here is a checklist of options to consider before running the calculation:

Option	Default
Ionic Strength Correction	Off (on recommended)
Temperature Correction	Off / 25 °C
Electrostatic adsorption models	None
Multirun (titration, 2-way analysis, field data)	Single run

To run the calculation, enter a output data name. The name should be 8 characters long or less. Don't put a file extension after the name. MINEQL+ will chop the extension off and add the *.MDO extension.

Once the output object is set, click the Run button to run.

3.5 The Output Manager



MINEQL+ provides the Output Manager as a way in which you can have full access to MDO output and extract data in the form you want. The Output Manager allows you to:

- (1) Extract speciation output from any perspective and display it in a tabular format
- (2) Display the header, log, and the multirun files
- (3) Graphical options are limited in Mineql+, but graphical output of speciation data can be generated (Graph IT – button)
- (4) Generate special reports (e.g., calculate alkalinity, or extract special types of data like ionic strength or saturation index)

4.0 References

William D. Schecher and Drew C. McAvoy, *MINEQL+ A Chemical Equilibrium Modeling System: Version 4.0 for Windows User's Manual*, 1998, Environmental Research Software, Hallowell, Maine

François M. M. Morel and Janet G. Hering, *Principles and Applications of Aquatic Chemistry*, 1993, John Wiley & Sons, Inc.