Visual MINTEQ 3.0 user guide
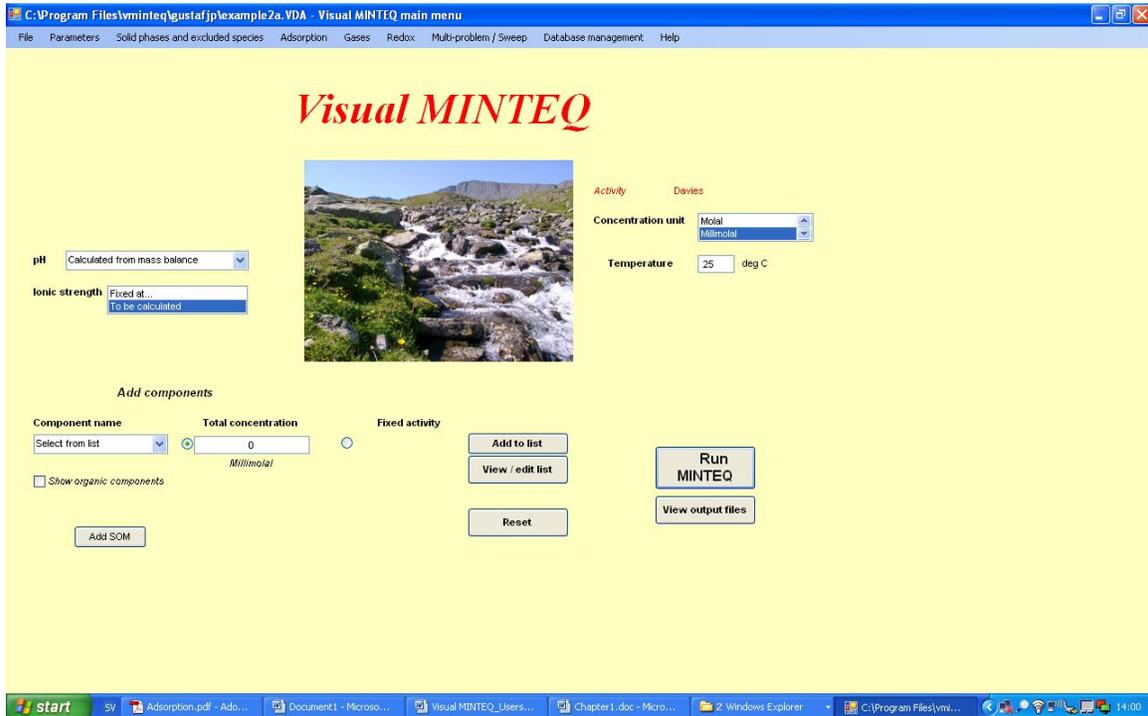
Jon Petter Gustafsson

This user guide is far from complete and at this stage it only contains information on the most basic aspects of the program, such as input/output file handling, pH options etc. I will extend it in the future with details on the more advanced options. / JPG 9/8 2011.

Contents

1. What is Visual MINTEQ?

1.1 History of the MINTEQ codes

Visual MINTEQ was first released in 2000 as a Windows user interface to the U.S. EPA model MINTEQA2. The original version of this model (called MINTEQ) was developed in the early 1980's at Battelle Pacific Northwest Laboratory (Felmy et al., 1984) as a cooperative effort funded by the U.S. Department of Energy and the U.S. EPA. The original MINTEQ developed by Felmy et al. (1984) was produced by combining the mathematical structure of MINEQL (Westall et al., 1976) with the thermodynamic database of the WATEQ3 model developed by the U.S. Geological Survey (Ball et al., 1981).

The MINTEQ model was then renamed to MINTEQA1 by the U.S. EPA Environmental Research Laboratory at Athens, Georgia (AERL) in 1985. The model was anticipated to diverge from the original as it was adapted to the special needs of the U.S. EPA, but in reality there were very few differences between MINTEQA1 and the original MINTEQ. The distribution package, available for DOS-based PC's or for Digital Equipment Corporation VAX machines, included a preprocessor program PRODEFA1 for the preparation of MINTEQA1 input files.

After more significant revisions were made in the late 1980's, the name was changed to MINTEQA2. With further development, version numbers were used to indicate new versions, and the model's formal name was left as MINTEQA2. The current version, released in 2005, is version 4.03.

Work with Visual MINTEQ began in 1998 with the code "MINTEQA2 For Windows 95", which was only a Windows interface to MINTEQA2 ver. 3.11. This code was never published. It was used for undergraduate teaching at the Swedish University of Agricultural Sciences (SLU). In the first Visual MINTEQ version (1.0), released in 2000 on the web, the code had been entirely rewritten in Visual Basic version 6.0. Still, however, Visual MINTEQ was essentially just a Windows interface to MINTEQA2 ver. 4.0.

After the release of Visual MINTEQ ver. 2 in 2001, the model gradually diverged from MINTEQA2, for example by expanding and revising the thermodynamic database as well as including new options for modeling surface complexation and organic complexation. With version 3.0, the code has been completely transferred to the .NET environment relying on .NET Framework. Still, however, the numerical engine of the program still relies on the subroutines of MINEQL (Westall et al.,. 1976) with only small changes to accommodate the new options added later. As for its graphical structure, Visual MINTEQ has remained essentially the same since the 1998 version of "MINTEQA2 For Windows 95".

1.2 MINTEQA2 and Visual MINTEQ – Similarities and differences

Because Visual MINTEQ and MINTEQA2 have the same origins and largely the same procedures for calculations, there are many similarities between the two codes. For example, the same terminology is used in both codes (e.g., components, infinite and finite solids, etc.). Still, users of Visual MINTEQ may still find it useful to consult the manual for MINTEQA2 ver. 4.0, especially for background descriptions.

However, since Visual MINTEQ started to diverge from MINTEQA2 in 2000, there are now a number of differences between the codes. In most cases this is because a number of new options and features have been added. Here are some examples of enhancements in Visual MINTEQ:

1. Visual MINTEQ can account for the effects of mixing and dilution when a titrant of a given composition is added to a solution.

2. There are six different surface complexation models to choose from; Visual MINTEQ includes the Basic Stern, the Three Plane and the Non-Electrostatic models.

3. It is now possible to use different surface complexation models on different surfaces.

4. The charge of the reference surface component is now allowed to be different from zero. For one-pK models, the charge is typically –0.5 by default – this value can be changed by the user.

5. The surface can have a cylindrical or a spherical geometry.

6. Fixed-charge sites can be defined for ion-exchange calculations to permanently charged surfaces

7. Complexation to natural organic matter can be simulated with state-of-the-art models (SHM, NICA-Donnan)

8. In surface complexation models, each surface can have a maximum of six coordination sites and include one fixed-charge site for ion-exchange reactions.

9. Visual MINTEQ can consider counter-ion accumulation in the diffuse layer of charged surfaces

10. Interfacing with Microsoft Excel to facilitate the handling of input and output data.

11. The thermodynamic databases are different, as Visual MINTEQ contains updated and expanded data from the NIST Critical Stability Constants database. However, the database of MINTEQA2 ver. 4.0 can be downloaded and used as well.

1.3 Some technical specifications

Visual MINTEQ has been coded in Microsoft Visual Basic *.NET 2005. Microsoft *.NET Framework 1.1 or higher is required for Visual MINTEQ to run. The program will run on most Windows platforms (except ME). Other operating systems are not supported, but Visual

MINTEQ has been reported to run under a Windows emulator such as Wine. Microsoft Excel 2003 or higher is required for the interaction with Excel.

There are a number of executable (.EXE) files associated with the software. Of these there are two that can be considered being the core of Visual MINTEQ:

- The Vminteq EXE file (vminteq09.exe in Visual MINTEQ 3.0) provides most of the interface for Visual MINTEQ. Input files are created, sent to the Mintrun EXE file (see below) and the results are read and presented on the output pages.

- The Mintrun EXE file (mintrun08.exe in Visual MINTEQ 3.0) carries out all the calculations. It appears as a black box during runtime.

These two EXE files communicate with one another using ASCII text files. More specifically, when the user presses the **Run** button in the interface, the text file "minin.vda" is created. This file contains all information necessary for the simulation. Mintrun reads in "minin.vda" and when it terminates the calculations, the output will be written to two other ASCII text files, "vmint.out" and "vmint.ou2", where the former contains all detailed results for each problem, and the latter contains the information used to set up the table **Selected sweep results** for multi-problem / sweep files. This program structure is admittedly rather old-fashioned. It is inherited from MINTEQA2 ver. 4.0, where the two core .EXE files are "Prodefa2" and "Minteqa2".

Therefore, if the user opens the file "minin.vda", this represents the last simulation that was carried out by Visual MINTEQ. Also, when the user presses the **View output files** button from the main menu, Visual MINTEQ will always open the results from the last simulation, which are stored in "vmint.out" and "vmint.ou2".

1.4 Download and install

To install Visual MINTEQ, follow these steps:

1. If this is NOT the first time you install Visual MINTEQ ver. 3.0 on your computer, start with removing the previous installation (go to **Control Panel** – choose **Add or Remove Programs** – choose **Visual MINTEQ**).

2. Double-click on the installation zip file (Vminteq3_setup.zip, available from the Visual MINTEQ webpage). Then double-click on the icon **Setup**.

3. Follow the instructions during the setup process. It is highly recommended that you install Visual MINTEQ in the default folder.

4. When setup is completed, click on the new icon **Visual MINTEQ** on the desktop. The main menu will open. If this is the first time you install Visual MINTEQ ver. 3.0, a dialog box will appear (see Fig. xx), prompting the user to select the folder for the user-editable files. Select one of the alternatives, save the settings, and return to the main menu.

5. For best performance, decimal points should be used as the decimal symbols instead of decimal commas. Users in non-English-speaking countries may need to change their Windows settings accordingly (choose **Control Panel** – **Regional and language options** – **Customize** – **Decimal Symbol**).

6. The software is now fully installed and Visual MINTEQ can be used.

NOTE: Visual MINTEQ uses an ASCII text file, "userfolder.txt", present in My Documents, to locate the folder with user-editable files. If this text file is destroyed, Visual MINTEQ will not be able to locate the user-editable files and will prompt the user to supply this path the next time Visual MINTEQ is started. The same thing happens if the folder with user-editable files is moved or deleted.

1.5 Common problems

If the specifications in section 1.3 are not met, Visual MINTEQ will not start at all. Check, for example, that .NET framework is installed on the computer.

There are also many situations when errors will occur when running a problem. Often this is because the calculations do not result in a sensible result. There may be different reasons for this; incorrect data input, or a too complex or ill-posed problem are two common types of reasons. When an error occurs during run-time, the error will often be traced and reported to the user on the output page. However, this is not always the case – in some cases the error handling will not work and a dialog box will appear. Usually this dialog box will display either of two messages:

1. When Error 53 ("file not found") is displayed, it means that there are one or more files of Visual MINTEQ that are not present in the correct path. Check that all files that the problem uses (databases etc.) really exists. In some extreme cases, reinstallation may be necessary.

2. Error 62 ("input past end of file") is a very general error that occurs whenever an error occurs in the calculation part of the code. It frequently occurs when the problem is ill posed so that the calculations do not converge. Please check that the problem is correctly configured – activity guesses may also need to be changed.

1.6 Acknowledgments

2. Introduction to Visual MINTEQ

2.1 First look at Visual MINTEQ

Visual MINTEQ can be started in either of two ways:

1. Double-click on the program icon for Visual MINTEQ
2. Double-click on a Visual MINTEQ input file (a .vda file)

In the former case, Visual MINTEQ will open in its default mode, with no components added etc (see Figure 2.1.1). In the latter case, the main menu will look different depending on the input file opened.
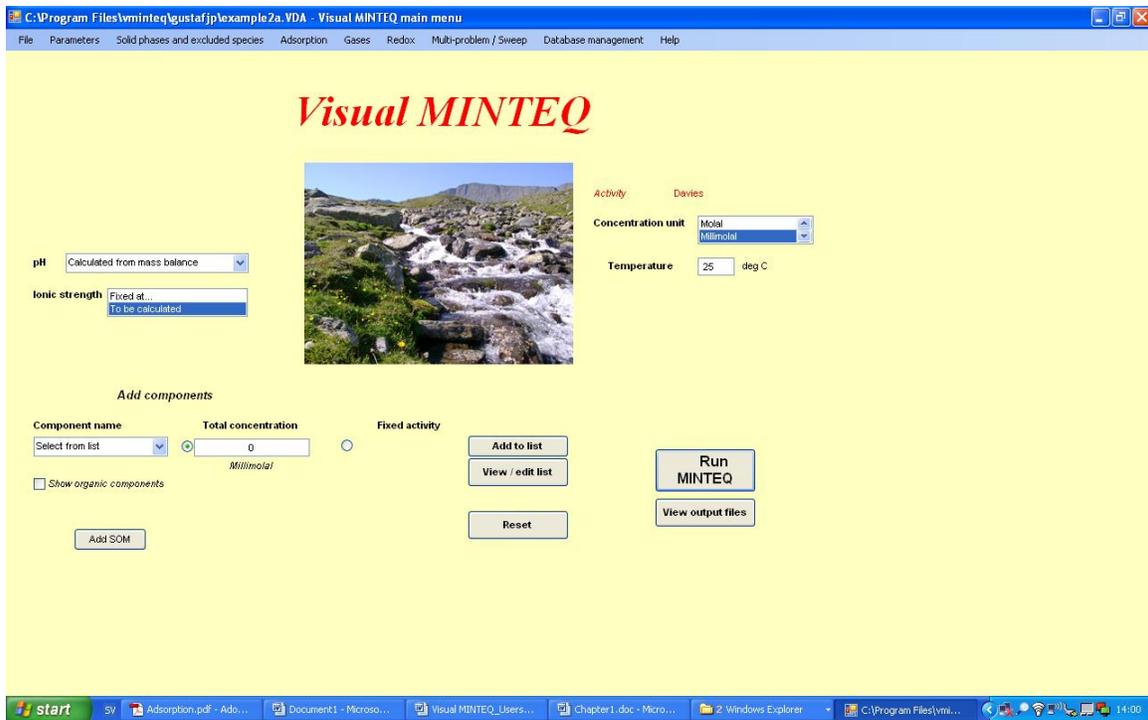
Figure 2.1.1. The Visual MINTEQ main menu in its default mode.

The main menu contains some of the most common options that may be reviewed when creating a problem. For example, the pH and ionic strength can be changed (sections 2.4 and 2.5), components can be added (section 2.2), as well as units for input and temperature. The **Reset** button is a useful feature that will erase everything from the present problem and return Visual MINTEQ to its initial default state (remember, however, to save anything of importance before you do this).

Just as any other Windows program you can open and save input files. The input files will always have the filename extension .VDA and customarily they are saved into the folder with user-editable files (usually My Documents \ Vminteq30), but they can of course be saved elsewhere, too.

2.2 Visual MINTEQ terminology

There are some terms that are used in Visual MINTEQ that may be unfamiliar to new users. Some of the most frequently asked questions by new users are about the meaning of the concepts component, problem and infinite, finite and possible solid. Below these concepts are summarized:

A **component** is the form of a chemical compound that Visual MINTEQ uses as a building block in chemical reactions. Some examples of components in MINTEQ are: H^+, Cl^-, Ca^{2+}, SO_4^{2-}, CO_3^{2-} and PO_4^{3-}. Many ions are not components, *e.g.* HCO_3^- and $H_2PO_4^-$. The reason is that they may be expressed from other components:

$HCO_3^- \ \rightleftharpoons \ H^+ + CO_3^{2-}$
$H_2PO_4^- \ \rightleftharpoons \ 2H^+ + PO_4^{3-}$
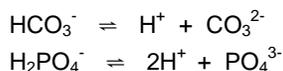
The choice of the component species is rather arbitrary, so it is possible to use HCO_3^- as a component rather than CO_3^{2-}. If so, CO_3^{2-} would be defined in the following way:

$CO_3^{2-} \ \rightleftharpoons \ HCO_3^- - H^+$

However, since all reactions are defined with a given component, it is heavy work to edit the databases should you wish to change a component, so this is normally not done.

When the concentration of, for example, PO_4^{3-} is stated in the Main Menu, it is important to note that you in fact state the total concentration of all PO_4 species (*e.g., TOT*PO_4). In the output lists of the results section however, the concentrations of the different PO_4 species will be shown separately, except on the page "Equilibrated mass distribution", in which the total concentration of phosphate will be given.

Remember that you should always define more components than fixed species in Visual MINTEQ. In some cases you may receive a message that tells you that Visual MINTEQ has added Cl^- at a concentration of 10^{-16} M. This is to ensure that there are more components than fixed species.

A **problem** is a user-defined composition of a water sample or water suspension to be speciated by Visual MINTEQ. A Visual MINTEQ input file may consist of several problems, if one of the multi-problem/sweep options is used.

Visual MINTEQ calculations may involve different kinds of solids. In Visual MINTEQ usage, a solid is a species, the activity of which is determined by a constant value. Typically, this applies to solid precipitates. Solids at equilibrium may be entered in three different ways in Visual MINTEQ:

An **infinite solid** is a precipitate for which there is no mass constraint, *e.g.* the concentration of the solid is sufficient to maintain equilibrium in solution at all times. This is the most common option.

A **finite solid** is a precipitate with a known initial mass. This means that it may dissolve completely during equilibration. When a finite solid is defined, the concentration of it (in mol / l suspension) needs to be supplied by the user. If the solid is not completely dissolved after equilibrium, Visual MINTEQ will report its concentration on the output page.

A **possible solid** is a precipitate that is not present initially, but that may be formed if Visual MINTEQ finds that the water sample is oversaturated with respect to the relevant precipitate. Visual MINTEQ will then re-equilibrate the solution assuming equilibrium with this precipitate. As for finite solids, Visual MINTEQ will report the concentration of any formed solid on the output page.

2.3 Input / output file handling

Just as any other Windows program, files can be opened and/or saved using the File – Open and File – Save commands available on the menu bar of the main menu. These files are referred to as input files, as they contain all data necessary to run a Visual MINTEQ simulation. Some further information:

- A Visual MINTEQ input file has the filename extension *.VDA

- By default, Visual MINTEQ expects input files to be in the folder of user-editable files (see section 1.4). However, other locations are also possible.

- The input files are ASCII files. Therefore, in principle they can also be edited using a text editor. However, this requires experience and familiarity with the formatting rules Visual MINTEQ use (these are not detailed in this manual).

- Output files (i.e., results from Visual MINTEQ simulations) can also be saved or read from the main output page (these have .OUT as their filename extension). However, because output files are much larger in size, users are recommended to primarily save input files (and then run these to generate the results) rather than output files.

- Many input files contain links to various other files such as database files. This can create problems when, for example, one user mails an input file to a second user. If the file names and/or their paths do not match, an error may result when reading or running these input files.

2.4 Options for setting the pH value

There are three options for setting the pH value:

1. **Calculated from mass balance** (default option). Choose this option when you are interested in calculating the pH in a solution for which you know the exact composition.

To understand how Visual MINTEQ calculates the pH, some knowledge on how the Mintrun EXE file carries out the equilibrium calculations is useful. Briefly, Visual MINTEQ solves the mass action equations and calculates the mass balance for all components including H^+, but no explicit consideration of charge balance is made. This means that for this option to work, the net charge balance for all entered components needs to be zero, otherwise this option will not yield correct results. To check the charge balance, choose **Parameters – Show initial charge balance** to show the sum of cation and anion charges on the main menu.

2. **Calculated from mass and charge balance.** When the pH value is calculated with this option, the H^+ activity is fixed and then adjusted until the solution is perfectly charge-balanced. In other words, Visual MINTEQ assumes that any charge imbalance is due to an imbalance of H^+. Also in this option, the composition of the water needs to be known, but the total H^+ concentration can be entered simply as 0. This option requires much more numerical work by Visual MINTEQ and convergence is not always obtained. The initial guess of the pH can be varied to aid convergence. This is done on the **List of fixed species**, which is available from the main menu by first clicking **View / edit list**. A value of the log activity of H^+ is given here; this is interpreted by the code as the initial guess of log $\{H^+\}$. Therefore, if you change the initial pH guess to pH 4.5 you should enter -4.5 here (=log $\{H^+\}$), see Figure 2.4.1.
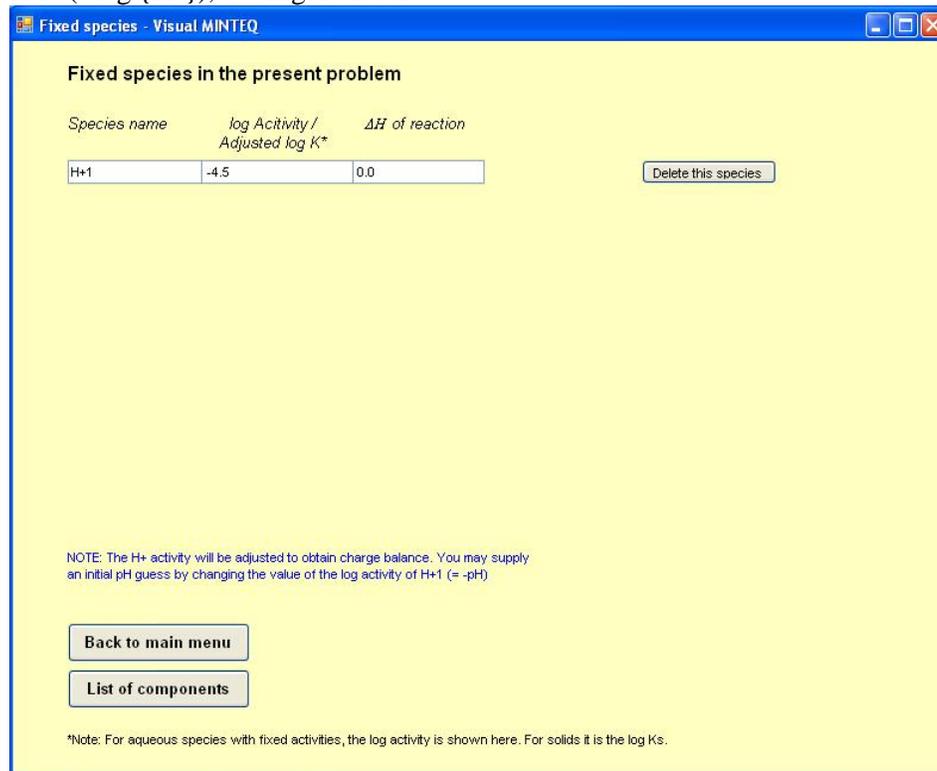
Figure 2.4.1. The initial pH guess in the calculated from mass and charge balance option.

3. **Fixed at…** Choose this option when the pH value is known. Enter the relevant pH value in the text box that appears. As a result, the H^+ activity will be fixed and added to the list of fixed species in Visual MINTEQ.

Why, then, does Visual MINTEQ include the option to calculate the pH from mass and charge balance, when optimization using mass balance only is much easier numerically? The answer is that it is tricky to set the total H^+ concentration correctly when variably charged surfaces including dissolved organic matter (DOM) are included in the calculations. In these situations, the second option is preferred since it avoids complicated book-keeping of the total H^+ concentration inherent in surface components and in the diffuse layer.

The Visual MINTEQ input files of examples 1a, 1b, 1c and 1d illustrate the difference in how the two options for calculating pH works. In these four input files, the pH is calculated in solutions of 0.01 M Na_2CO_3 or 0.01 M $NaHCO_3$, at 25^oC. The pH value in these two cases is 10.96 and 8.22, respectively.

- *Example 1a:* Use of the "Calculated from mass balance" option to calculate the pH in 0.01 M Na_2CO_3.
- *Example 1b:* Same, but with 0.01 M $NaHCO_3$. Note that the total concentration of H^+ (0.01 M) should be given.
- *Example 1c:* Use of the "Calculated from mass and charge balance" option to calculate the pH in 0.01 M Na_2CO_3. Note the larger number of iterations required to solve the problem compared to example 1a (194 instead of 11).
- *Example 1d:* Same, but with 0.01 M $NaHCO_3$. Here the total concentration of H^+ is set to 0. In this case, 42 iterations were required, compared to 5 for example 1b.

2.5 Creating a problem

In this section we describe the general procedure for how to set up a very simple Visual MINTEQ simulation that does not involve any choices from the menu bar (i.e. adsorption, redox, surface complexation, solid phases, gases etc.). We show how to set up, run and interpret the results. The question is:

Example 2. In a 0.01 M $CaSO_4$ solution at pH 7.0 and at 25^oC, what is the speciation? In other words, what are the relative proportions of Ca^{2+}, SO_4^{2-} and $CaSO_4^0$ in solution? Is the solution oversaturated with respect to any solid phase, such as gypsum?

1. Start Visual MINTEQ. The main menu will appear.

2. Change the pH option to "Fixed at" and make sure that the value in the text box is 7.0.

3. The ionic strength option should be **To be calculated**, as is the default option.

4. The concentration unit should be **Molal** (mol/kg solvent, equal to mol/l or M for most water solutions unless they are very concentrated, see here).

5. The temperature is given as $25^{\circ}C$, so the default value should not be changed.

6. Now add components. In this case there are two components, Ca^{2+} and SO_4^{2-}, both with a concentration of 0.01 M. Therefore, locate Ca^{2+} in the dropdown list to the left. Then enter 0.01 in the **Total concentration** text box. Next, click **Add to list** to add Ca^{2+} to the problem.

7. Add SO_4^{2-} by following the same procedure as for Ca^{2+}.

**Figure 2.5.1.** The list of components in example 1 with 0.01 M $CaSO_4$.

8. Click **View / edit list** to ensure that all components have been added, with the right concentrations. If everything is correct the list will look as Figure 2.5.1. Note that there are three components in the problem: H^+, which is fixed by the pH value, is set to 0 on the component list. Ca^{2+} and SO_4^{2-} are added with a concentration of 0.01 M each.

9. Click **Run** to calculate the speciation.

10. After the calculation, the main **Output** page will be shown, see next page. On the top of this page, it is seen that the pH at equilibrium is 7.00 (same as what we entered). The calculated ionic strength is 0.0277 M, and there is an almost perfect charge balance, as judged from the fact that the **Sum of cations** and **Sum of anions** are equal. These sums

are shown in the unit eq / kg (equivalents of charge per kg solvent). The **charge difference (%)** is calculated as:

$$\text{Charge difference (\%)} = 100 \cdot \text{Abs}\left(\frac{\text{SumA} - \text{SumC}}{\text{SumA} + \text{SumC}}\right)$$

, where SumA is the sum of anions (eq/kg solvent) and SumC the sum of cations (eq/kg solvent).

On the lower part of the page, the calculated concentrations and activities of all considered species at equilibrium are shown. The concentration unit on the main **Output** page is always mol / l, regardless of the unit used for the added components.
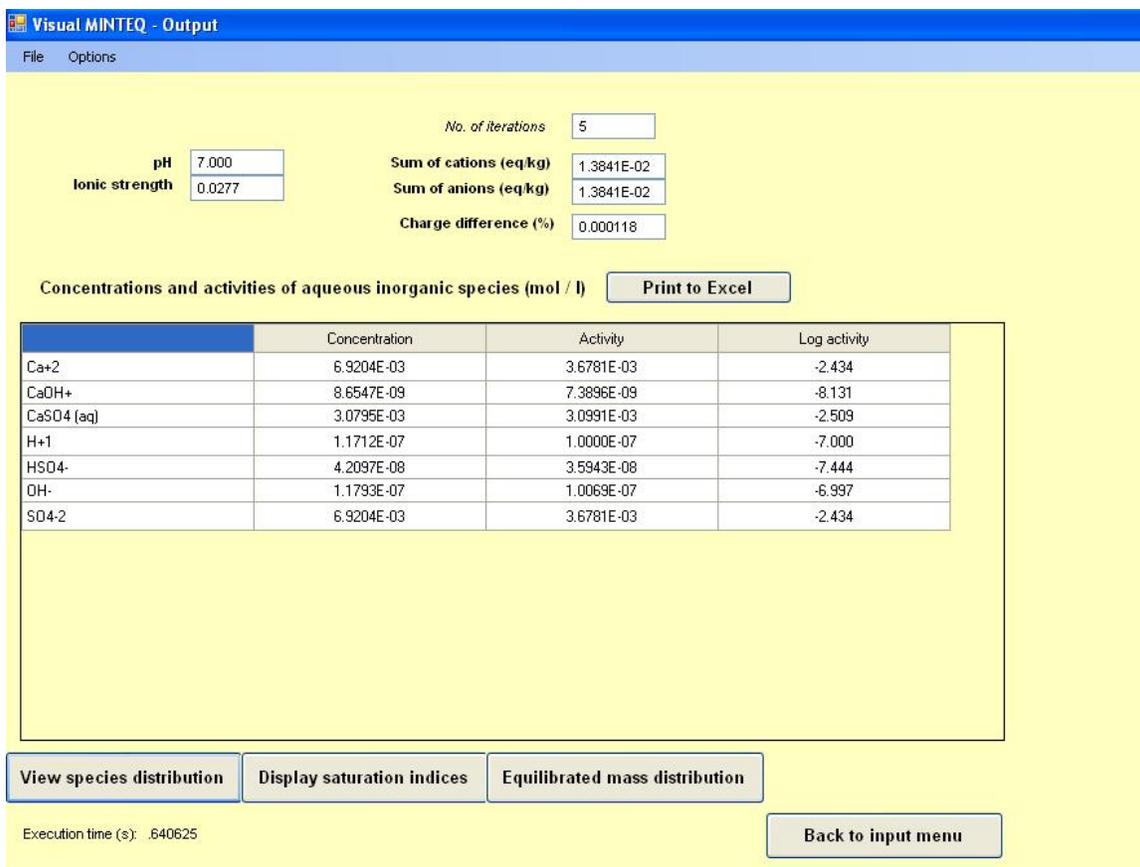
Figure 2.5.2. The main output page in example 1 with 0.01 M CaSO₄.

11. Below the table with concentrations and activities there are buttons with links to other results. Start reviewing these by clicking the **View species distribution** button.

12. A new menu is shown with the **Species table**, i.e. the calculated distribution among dissolved and adsorbed species, see Figure 2.5.3. This table does not show the distribution of H⁺, so in this case there are results only for two components, Ca^{2+} and

SO_4^{2-}. These results show that free Ca^{2+} ions account for 69.2 % of all dissolved Ca, with the uncharged $CaSO_4^0$ complex making up the rest. Identical results are obtained for SO_4^{2-}.

Fig. 2.5.3. The species table showing the distribution of the components.

13. Click **Back to main menu** to get back to the main **Output** page.

14. To check whether the water sample is over- or undersaturated with respect to any solid phases, click the **Display saturation indices** button.

15. A new menu is shown with information for different relevant solid phases that were found in the database, see Fig. 2.5.4. For each mineral, the calculated log IAP (Ion activity product) is given, together with the saturation index, which is defined as the difference between log IAP and log K_s (solubility constant of the mineral at the given temperature). In this particular example, when undersaturation prevails, the saturation indexes are negative and given in blue. Positive values (oversaturation) will result in red values. The table also shows the stoichiometry of the solid phases, as they are given in the database.
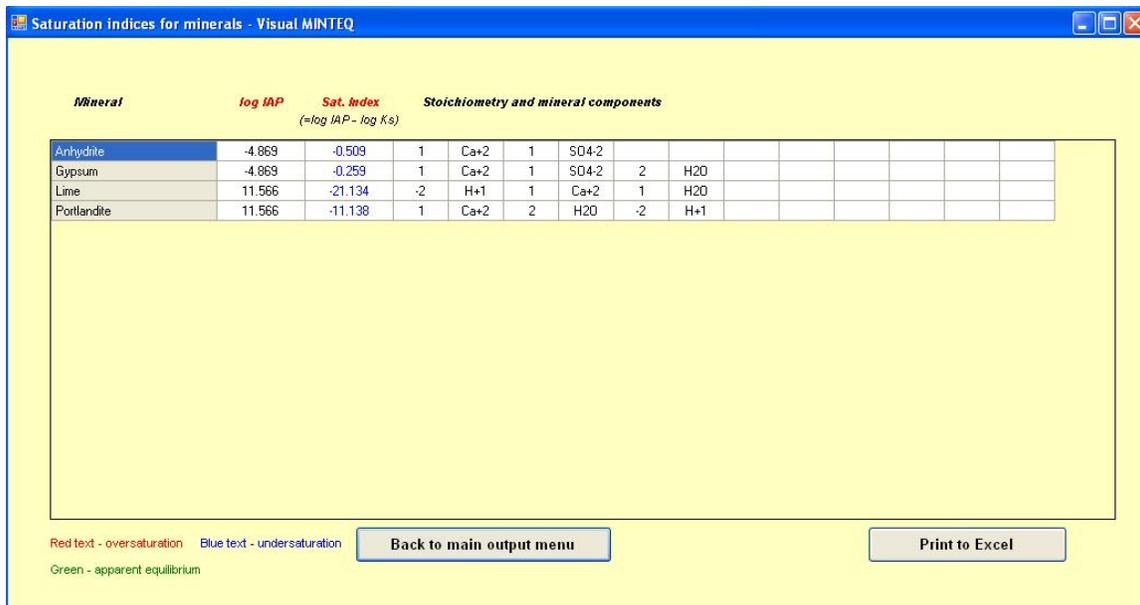
Fig. 2.5.4. Saturation indexes for different relevant minerals (= solid phases) in example 1.

16. Click **Back to main menu** to get back to the main **Output** page.

17. By clicking the **Equlibrated mass distribution** button, we will be brought to a page that shows the total dissolved, adsorbed and precipitated concentrations of each component.

18. In this example, this menu does not contain anything that we did not already know (Fig. 2.5.5). The total dissolved concentrations of Ca^{2+} and SO_4^{2-} are the same as we already entered, and nothing is adsorbed or precipitated (as we have not defined any such reactions).
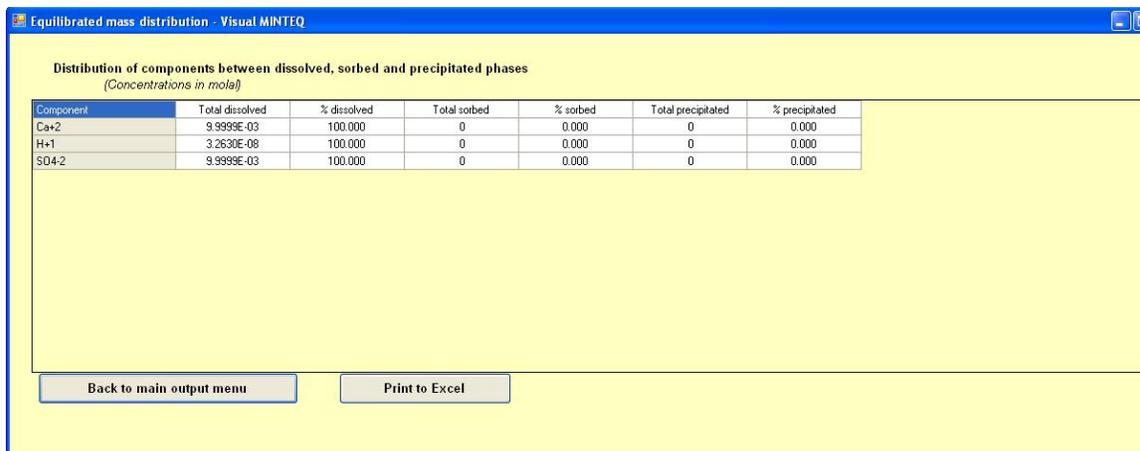
**Fig. 2.5.5.** Equilibrated mass distribution of the components in example 1.

2.6 Multi-problem / sweep options