

Manual for CHEAQS Next,  
a program for calculating  
*C*hemical *E*quilibria in  
*A*quatic Systems

## Status box

This is the CHEAQS Next manual. This version of the manual corresponds with program version 2017.3 (released 7 July 2017). More topics may be added when appropriate.

Date of current version: 7 July 2017

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# 1 Introduction

## 1.1 CHEAQS Next's features

This is CHEAQS Next's manual. CHEAQS Next is a computer program that calculates the chemical speciation, given a set of total concentrations that is provided by the user. For instance, if you want to calculate the speciation of a 0.1 M CaCl<sub>2</sub>-solution at pH =7, the program will tell you that:

- 88% of the Ca is present as Ca<sup>2+</sup>;
- 12% of the Ca is present as CaCl<sup>+</sup>.

In addition, the user can specify that for some of the chemical elements, a concentration or activity of the *free species is given as input*. In that case, the total concentration is calculated for that element. This combination of options enables you to choose between calculations with fixed (=supplied by user) pH and calculate pH.

CHEAQS Next will not only calculate complexes formed from cations and ligands in solution, it will also calculate:

- redox equilibria such as:
  - $\text{Fe}^{3+} + e \rightleftharpoons \text{Fe}^{2+}$  or;
  - $\text{MnO}_2 (s) + 4 \text{H}^+ + 2 e \rightleftharpoons \text{Mn}^{2+}$
- precipitation of oversaturated solids (273 in the database);
- equilibria between gases and solution like:
  - $\text{CO}_2 (g) \rightleftharpoons 2 \text{H}^+ + \text{CO}_3^{2-}$
- adsorption to solid phases using the surface complexation model;
- complexation by natural organic matter such as fulvic and humic acids, by four different models.

## 1.2 How to read this manual

This chapter is a general introduction to the program. Chapter 2 discusses each menu command. Chapter 3 contains some in-depth topics, chapter 4 deals with the chemistry. Chapter 5 contains literature references. The Annex contains details about file formats.

## 1.3 Installing the program

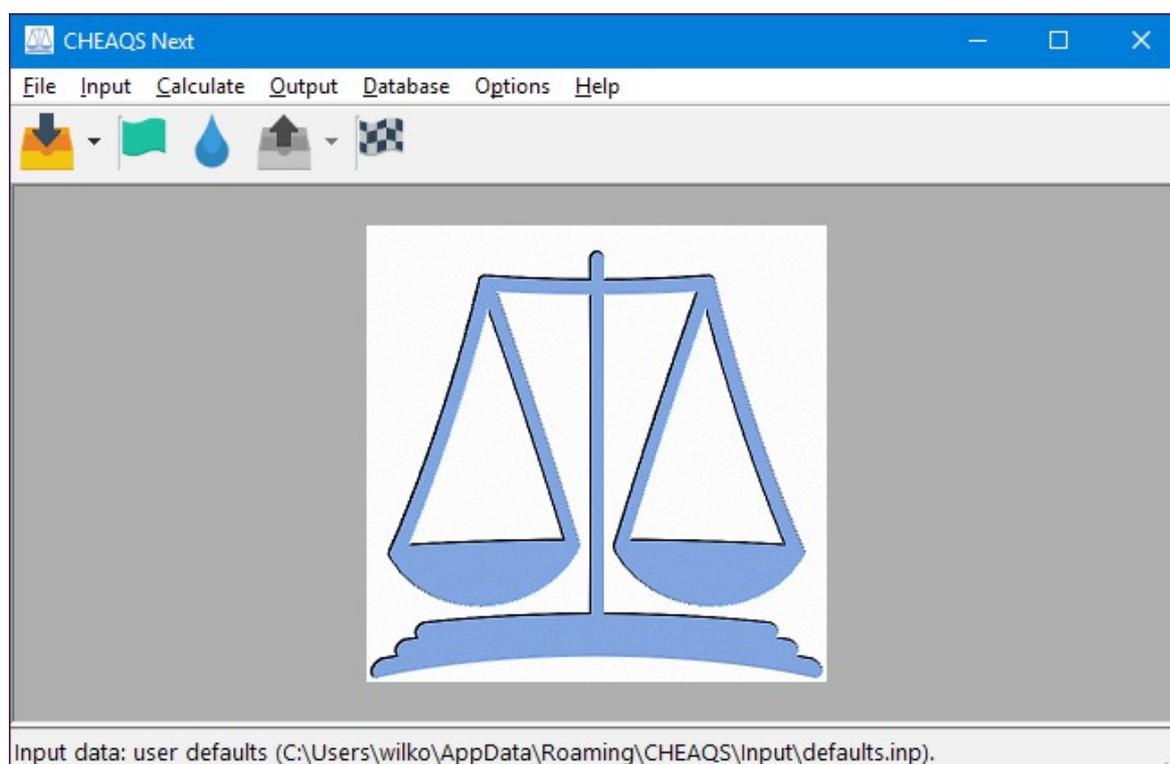
The program works on Windows computers from XP to Windows 10. To install the program, take the following steps.

1. Go to the website <http://www.cheags.eu> and download the latest version of SETUP.EXE in the download part of the website.
2. Run the program SETUP; the wizard will guide you through the installation procedure. You need sufficient rights for installing the program. During installation, a sub-directory called CHEAQS Next will be created in the directory for program files. That directory will contain the program CHEAQS2.EXE, and three other programs (OPTIONS.EXE, MANAGEDB.EXE, REGUNREG.EXE). You will also find an uninstallation program, the raw data files and a dll called CreateDat.dll. You should not delete any of these files.
3. Start the program.

During the first run, the program will create sub-directories in the application directory of the current user. In these sub-directories input files, output files and data files (including any user modifications of the database) will be stored. Also a file called CHEAQS.INI will be stored there containing user settings. Data files for each user will be created during the first run. You will also have the opportunity to open the help file with the Getting Started section during the first run. This is similar to what you can read in the next section.

## 1.4 Getting started

The program screen looks like the picture below. It has a classic Windows menu on top, a toolbar immediately below the menu and a statusbar at the bottom. When you browse through the menu, a tooltip will display information about the currently selected menu item.



*The program window*

To get started, you basically need to take three steps:

1. From the menu, choose Input - Edit input. When finished, return to the main window.
2. From the menu, select Calculate - Calculate speciation. After a short while, the output will appear on screen.
3. View (and optionally save or print) the output. When finished, return to the main window.

## 1.5 More information

You can find more information:

- on the website <http://www.cheaqs.eu>;
- on the twitter-page <https://twitter.com/cheaqs>;

- on the facebook-page <https://www.facebook.com/CheagsNext>;
- by sending an email to [info@cheags.eu](mailto:info@cheags.eu).

If you subscribe to the CHEAQS Newsletter (in the download area at <http://www.cheags.eu/download.html>), you will receive an email when news is available (approximately 2 to 4 times per year). You can use the same page to unsubscribe.



## 2 Menu commands

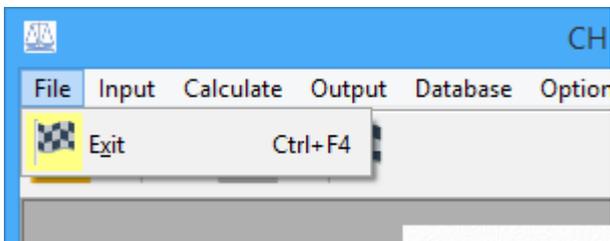
Using the menu, you can access the commands you need to control CHEAQS Next. Below you find the overview of the commands. Some often used commands are also available on the toolbar or via shortcuts.

### 2.1 The File Menu

The File Menu contains one item: Exit (see screenshot). By choosing that command you exit the program. If the current input data are not saved, you will be prompted to do so.

Alternative ways to invoke this command:

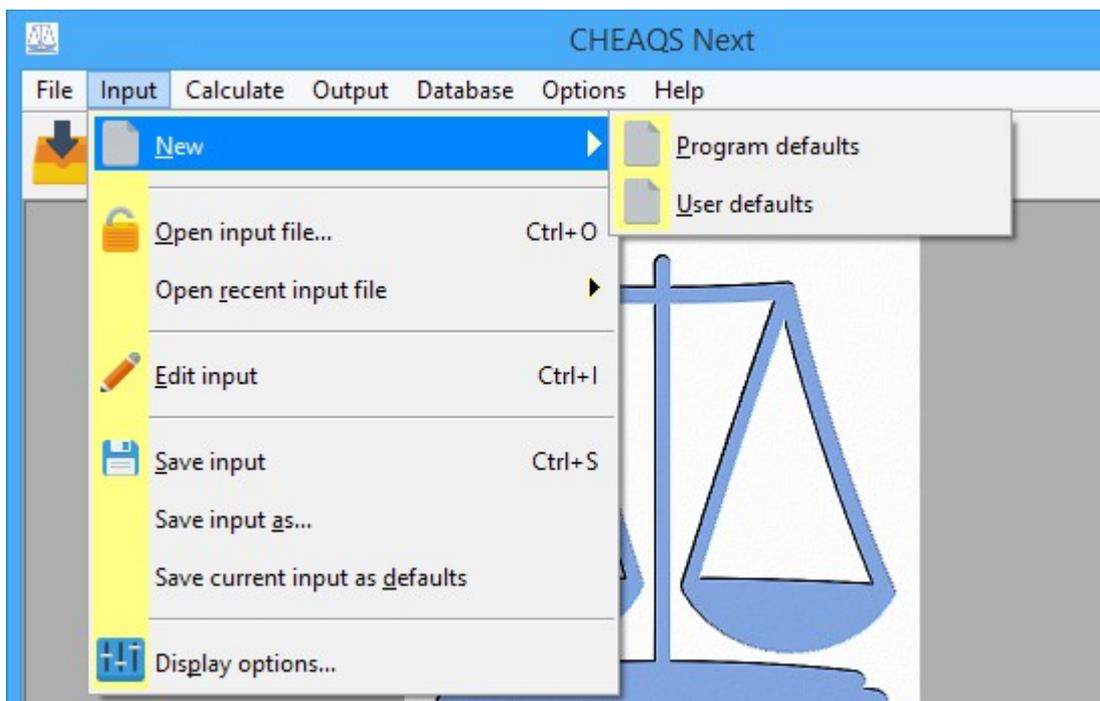
-  : press Ctrl-F4 or Alt-F4;
-  : click the most right button on the toolbar.



*The File Menu*

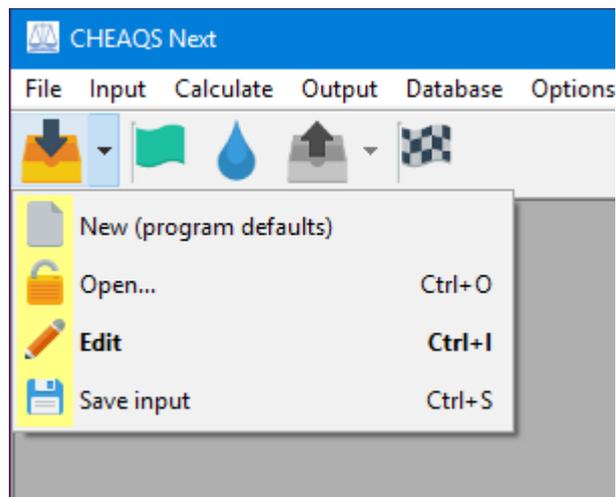
### 2.2 The Input Menu

The Input Menu contains eight items. See figure.



*The Input Menu*

Some of these items are also available from the toolbar. To access these items, you can click the small black triangle to open a dropdown menu with the most often used input commands. See figure.



*The Toolbar Input Menu*

## 2.2.1 Input – New

The program distinguishes two types of input defaults:

1. program defaults. They are defined by the program and therefore can not be changed by the user. All concentrations are set to zero, and pH is set to 7. All 'special' types of equilibria are set to *not* included. Ionic strength is set to 'calculated' and convergence criterion is  $1 \times 10^{-4}$  (0.01%).
2. user defaults. A user can create his or her own set of default input values. Simply create an input set using Edit - Input and store the input as defaults (see section 2.2.7). This will create an input file called DEFAULTS.INP in the default directory for input files. Each time the program starts, these defaults are loaded (visible on the status bar).

### 2.2.1.1 Input - New - Program defaults

This command sets all input values to the program defaults for input, as described above.

Alternative way to invoke this command:

☞ : open the menu from the toolbar and select 'New (program defaults)'.

### 2.2.1.2 Input – New - User defaults

User defaults: reads input file DEFAULTS.INP and replaces current input data with the one from that file. Only available if a file named DEFAULTS.INP is present in the default directory for input files. If no file with this name is present, this menu command is not available.

## 2.2.2 Input - Open Input file

This command allows you to open an input file you created previously. Input data currently in memory are erased (if not saved, you will be prompted to save or cancel). Initially, the program shows input files present in the default directory for input files but the user can change the directory to open files at a different location.

Alternative ways to invoke this command:

-  : press Ctrl-O;
-  : open the menu from the toolbar and select 'Open...'

## 2.2.3 Input - Open recent input file

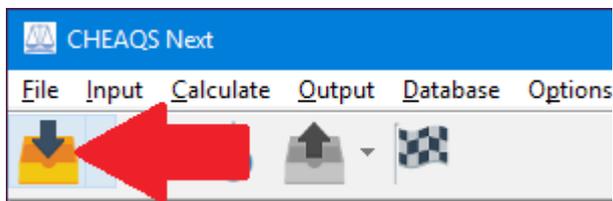
This command allows you to quickly open a file you recently opened or saved. Up to 9 files are remembered. To disable this feature, see section 2.6.3.

## 2.2.4 Input - Edit input

This command brings you to a window where you interactively specify your dataset. Editing input is explained in detail in section 3.1.

Alternative ways to invoke this command:

-  : press Ctrl-I;
-  : open the menu from the toolbar and select 'Edit';
-  : click the button on the toolbar (the button itself, as indicated by the arrow in figure below).



*The Default Toolbar Input action*

## 2.2.5 Input - Save input

Saves the current input data under latest filename (as displayed on the statusbar). If no name is available yet, the program will prompt you to provide one. In that case, the program will initially propose the default directory for input files, but the user can change that.

Alternative ways to invoke this command:

-  : press Ctrl-S;
-  : open the menu from the toolbar and select 'Save input'.

## 2.2.6 Save input as...

Saves current input data but first prompts for a location and filename to use.

## 2.2.7 Save current input as defaults

Saves current input in the file DEFAULTS.INP, in the default directory for input files. Next time the program starts, these data will be read automatically. Also, if you choose Input - New - User defaults, these data will be read.

## 2.2.8 Display options

This option allows you to control settings for editing input. Also available from Edit Input window and from Options Menu.

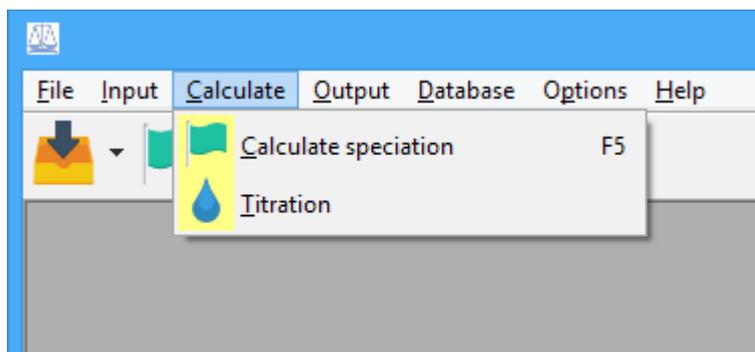
- units: M or g/L;
- order: normal, milli, micro or nano;
- number of decimals: 0 to 9;
- order in which to display cations and ligands: database order or alphabetically.

Notes:

- if you plan to use g/L, please check the molecular weights that the program uses, because the design choices that were made may influence the way you need to enter the data.
- if you want to use a different decimal character, you need to change you system settings (under 'Regional Settings'; the exact naming depends on the operating system).
- any changes to the settings are lost when you close a session, unless you check 'Input settings' at the tab 'Remember', which is the default setting.

## 2.3 The Calculate Menu

The Calculate Menu at present contains two items: 1) Calculate speciation and 2) Titration (see screenshot).



*The Calculate Menu*

### 2.3.1 Calculate - Calculate speciation

By choosing this command you instruct the program to calculate the speciation of the current input data set. When finished, the output will be sent to the default output location(s), i.e. either screen, one of the three output file types and/or the printer. You can change the default output location from the options menu. Default program setting for output location is screen.

Alternative ways to invoke this command:

 : press F5;

 : click the second button on the toolbar.

## 2.3.2 Calculate - Titration

The Calculate - Titration item of the menu enables you to set up a titration. More information about titrations can be found in section 3.5.

## 2.4 The Output Menu

Some items of the output menu (such as printing) are not always available. They become available after the first run or after opening an output file.

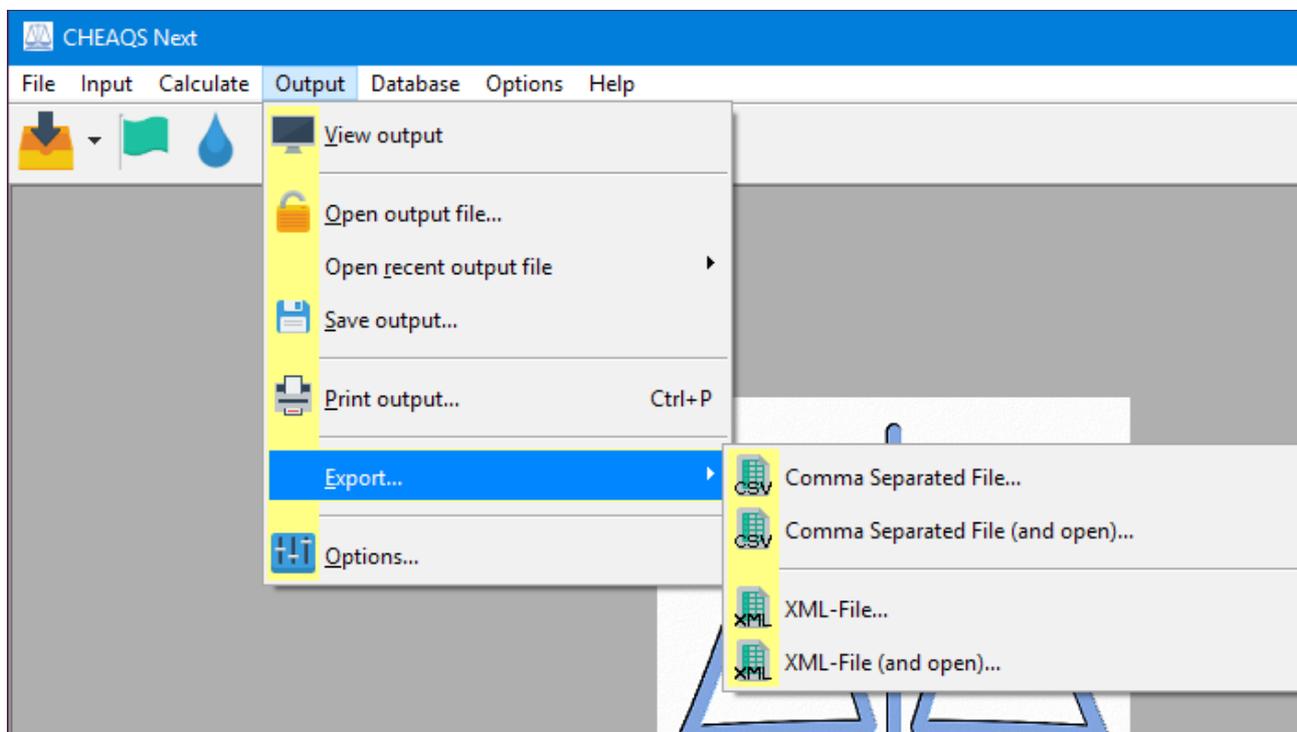
The following items are always available:

- Open output file;
- Open recent output file;
- Options.

The following items are only available after the first run or after opening an output file:

- View output;
- Save output;
- Print output;
- Export (with four sub-items).

In the figure below you see the items that you can choose from.



*The Output Menu*

## 2.4.1 View output

If you choose View output, a window will open that contains the output of the latest run or the latest opened output file. You can browse through the cations and ligands, save or print the output, or display additional info. This output window with its many functions is discussed in detail in Chapter 3.

Alternative ways to invoke this command:

-  : open the output menu from the toolbar and select 'View output';
-  : click the button on the toolbar (the button itself, not the part on the right with the black triangle).

## 2.4.2 Open output file...

This command allows you to open an output file you created previously. Output data currently in memory are erased. Initially, the program shows output files present in the default directory for output files but the user can change the directory to open files at a different location.

## 2.4.3 Open recent output file

This command allows you to quickly open a file you recently opened or saved. Up to 9 files are remembered. To disable this feature, see section 2.6.3.

## 2.4.4 Save output...

Saves the current output data in an internal format (with default extension .ofc2). The program will prompt you to provide a name. The program will initially propose the default directory for output files, but the user can change that.

These CHEAQS Next output files are not readable by users, but the program can read them (using the command Open output file...) after which the user can view, save or print the output.

Alternative way to invoke this command:

-  : open the output menu from the toolbar and select 'Save output...!'.

## 2.4.5 Print output...

This command brings you to the Print output form. From that form, you can set a variety of options determining what you print and how you print. This topic is discussed in more detail in Chapter 3.

Alternative ways to invoke this command:

-  : press Ctrl-P;
-  : open the output menu from the toolbar and select 'Print output'.

## 2.4.6 Export...

CHEAQS Next can export the output in two formats (in addition to its own internal format):

1. comma separated files with default extension .csv;
2. XML-files with default extension .xml.

Both these file types can be read by many spreadsheet programs like EXCEL® or OpenOffice Calc.

The export menu item allows you to:

- either save the file and return to the menu;
- or save the file and immediately open it. In that case, CHEAQS Next will determine which program on your computer is configured to open .csv or .xml-files and will open the file with that program.

## 2.4.7 Options...

This option allows you to control settings for displaying output. Also available from View Output window and from Options Menu.

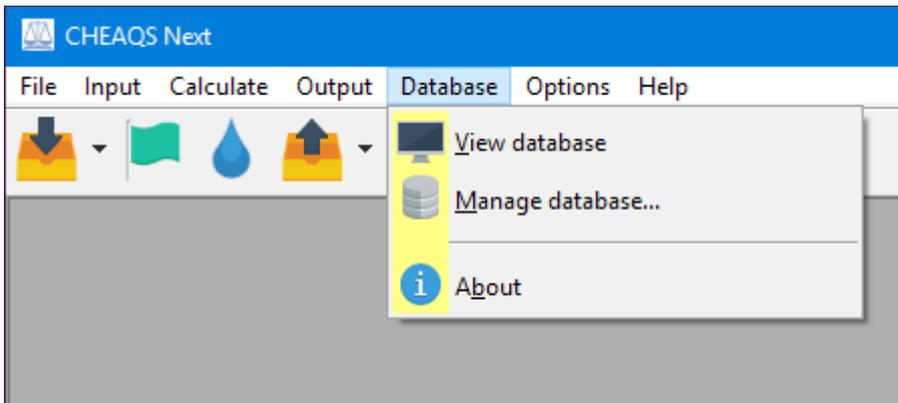
- units: M or g/L;
- order: normal, milli, micro or nano;
- number of decimals: 0 to 9;
- which species/fractions to display: by default only species or fractions which represent 0.01% of the total are being displayed (to prevent that many species are being displayed which are not significant) but here you can change that. If you want free species to be displayed also if they represent less than the threshold, you can indicate that too.
- the default output destination:
  - screen;
  - printer;
  - CHEAQS Next's internal file format;
  - .csv-file;
  - .xml-file.

Notes:

- if you plan to use g/L, please check the molecular weights that the program uses, because the design choices that were made may influence the way you need to enter the data.
- if you want to use a different decimal character, you need to change your system settings (under 'Regional Settings'; the exact naming depends on the operating system).
- any changes to the settings are lost when you close a session, unless you check 'Output settings' at the tab 'Remember', which is the default setting.

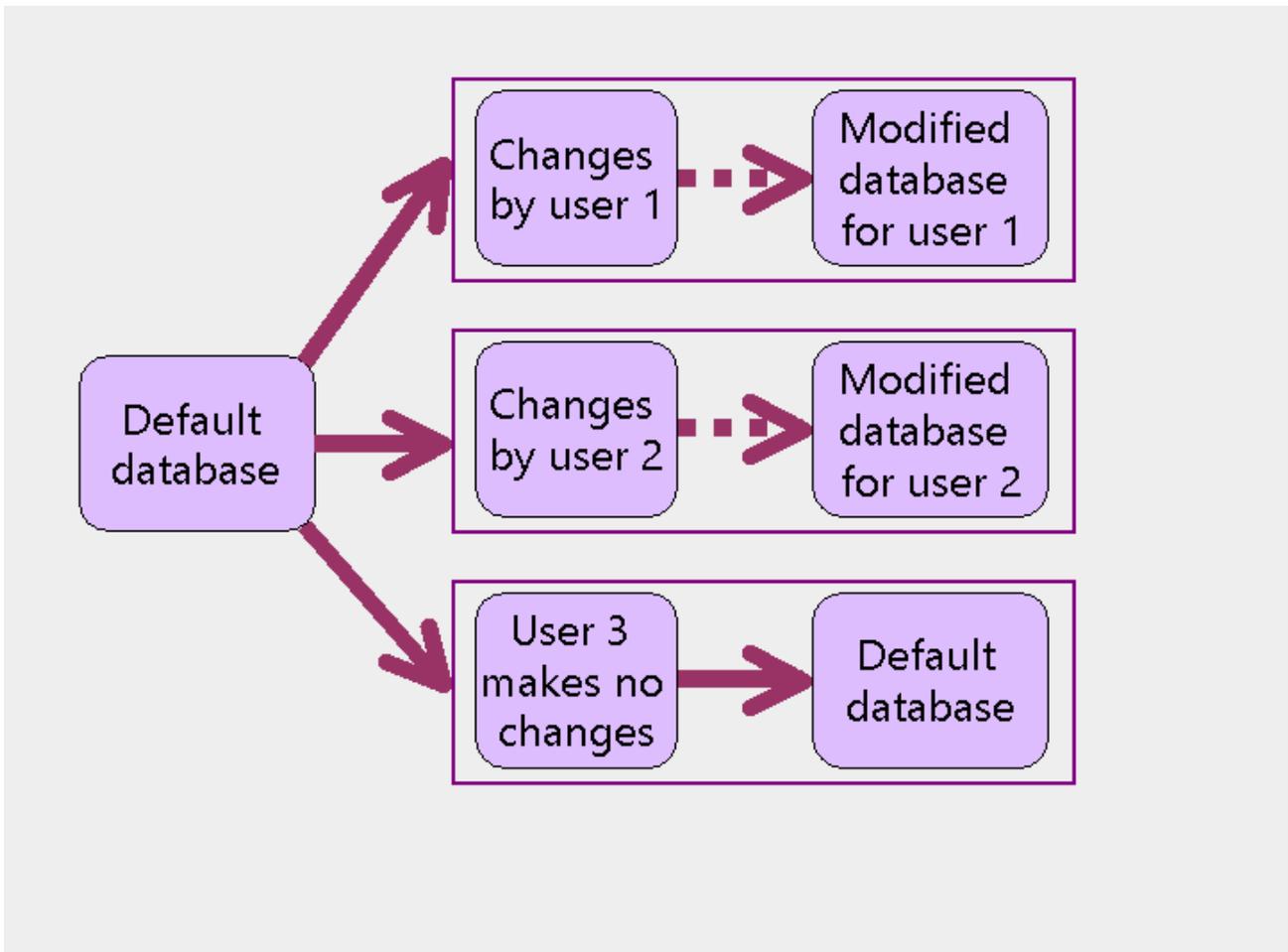
## 2.5 The Database Menu

The Database menu has three options (see figure). The first one (View database) enables you to view the contents of the current user database. Manage database allows you to make changes to the user database. The last one, About, displays meta-information (such as version number).



*The Database Menu*

CHEAQS Next always keeps the default database as installed during setup. In addition, user changes (if any) are stored. The default database plus any user changes are combined into the user database. This implies that on one computer each user can have a different database. See figure.



*The data model that CHEAQS Next uses*

## 2.5.1 View database

When you choose this option, you can view information about the contents of the database. There are three ways to create cross-sections of the database:

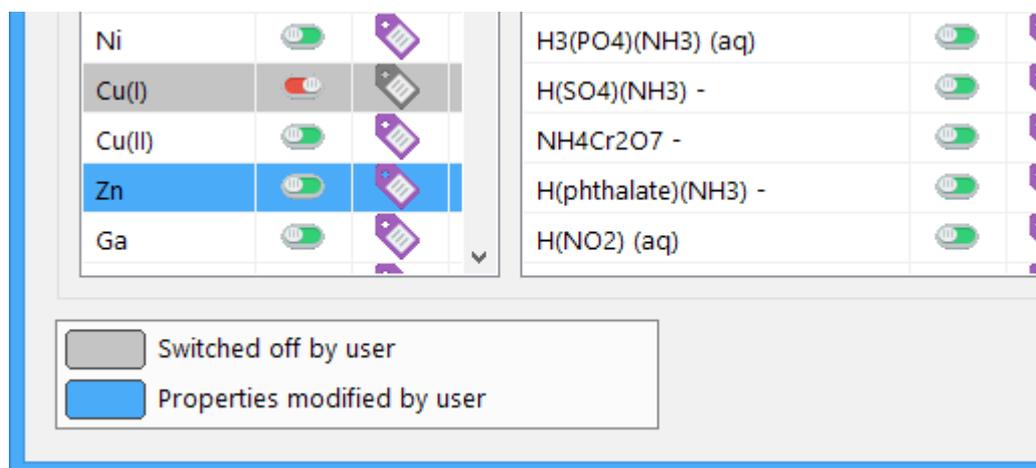
1. per component. Components are grouped in cations, ligands and 'other'. You can select a component from one of these three groups and the relevant species / equilibria will be shown on the right. When you click on one of these species / equilibria, the equilibrium definition will be shown in a separate window.
2. per type of equilibrium. Click a type on the left and the equilibria will be shown on the right.
3. per literature reference. Click a reference and all equilibria based on that particular reference will be shown.

## 2.5.2 Manage database

As already mentioned, CHEAQS Next enables you to make changes to the database. Once you select this option, a separate program (called ManageDB.exe) is launched. The program displays components on the left, and equilibria in the middle.

### 2.5.2.1 Changing items in the default database

Using the switch () you can switch off a component from the database. Click the tag () to modify properties; for components, you can change the name and the atomic mass. For equilibria, you can change the name, equilibrium constant and the literature reference. Deleted and modified items are marked with different colors. See example where Cu(I) is switched off and Zn properties were modified.



For equilibria it can be somewhat unpractical to find a certain item in the long list. For that reason a search facility was developed which can be accessed using the search button . For example, if you type NTA, all items containing that text are selected. See example on next page.

**Search form**

Search text:

Match case  Use arrows to point after click

Match only beginning of texts

Click in a cell to jump to result

default components	default equilibria	user components	user equilibria
(NTA)	H(NTA)		
	H2(NTA)		
	H3(NTA)		
	H4(NTA)		
	Li(NTA)		
	Be(NTA)		
	Na(NTA)		
	NaH(NTA)		
	Mg(NTA)		
	Al(NTA)		

*Search function at work*

### 2.5.2.2 Adding items to the database

In addition, you can add components and equilibria to the database using the buttons 'Add a component' and 'Add an equilibrium'. You can specify all necessary properties.

User additions:

Let us demonstrate this by adding citrate to the database followed by adding an acid-base reaction.

For citrate, we need to know its charge (-3) and molecular weight (189.0594). Initially the screen looks like shown here on the left. When you click the button 'Add a component', the following window appears. We select 'ligand' (left) and fill in the rest (right).

**Edit component's properties**

Type of component:  
Please select the type of component:

Cation  
Ligand  
Adsorption site  
Redox solid  
Gas

Charge:  
Enter charge:

Molecular weight:  
Enter weight:

**Edit component's properties**

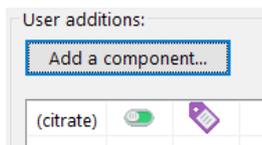
Type of component:  
Please select the type of component:

Ligand

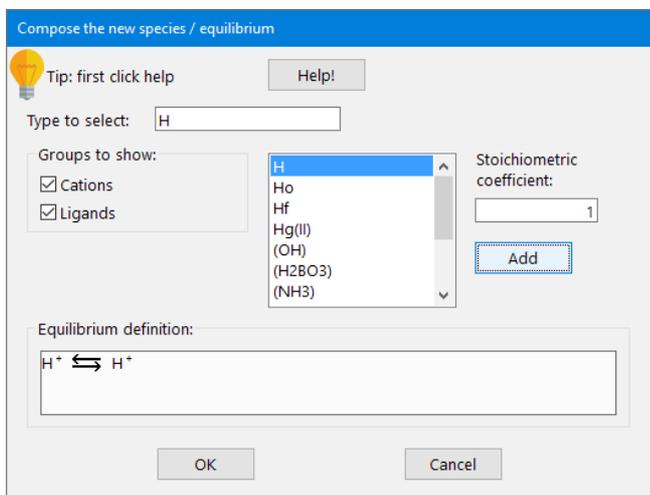
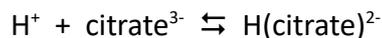
Name:  
Enter name: (citrate)

Charge:  
Enter charge: -3

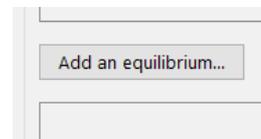
Molecular weight:  
Enter weight: 189.0594



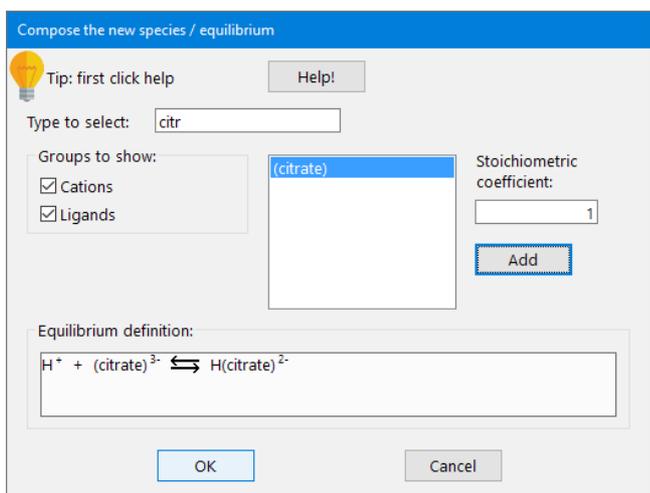
When we click the OK-button, citrate appears as new user added component (see picture on left). Now that citrate is added, we can add equilibria containing citrate. For the equilibrium reaction:



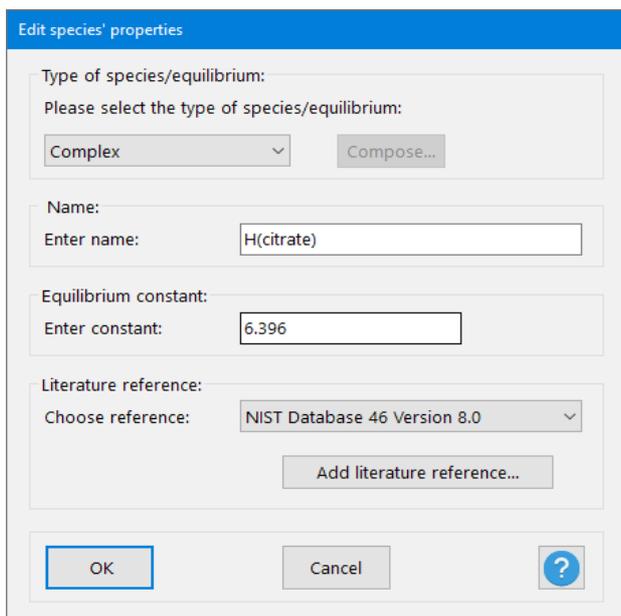
the  $\log_{10}$ -value of the equilibrium constant is 6.396 (NIST, 2004). To add this equilibrium to the database, we click the button 'Add an equilibrium'. See screenshot on right.



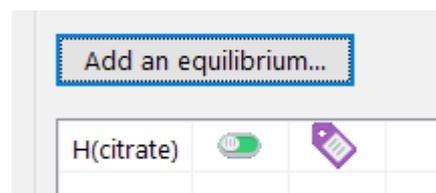
In the following window, we first choose 'Complex' from the dropdown list, then click the button 'Compose' to start composing the equilibrium reaction. Again a new window appears, shown on left. The first thing we do there is to select 'H'. We do that by starting to type in the box 'Type to select'. See screenshot. The listbox from that moment on only contains items with the text 'H'. We select the top one, type '1' in the box for stoichiometric coefficient, and click the button 'Add'. The screen will then look like show here on top left. We repeat this procedure for citrate. Once we type 'citr' in the text box, only one entry in the listbox remains. We select that one, stoichiometric coefficient is already OK, and click 'Add' again. See next screenshot.



At this stage, the equilibrium is defined and we can click OK to continue with the other properties of the equilibrium. We enter the constant (in  $\log_{10}$ ) and choose the reference from the dropdown list. Finally we click 'OK'.



The screen will be updated to reflect these changes, as shown.



### 2.5.2.3 Saving changes

When you are ready, click the 'Save'-button. The new files will be created (this may take some time; do NOT interrupt the program at that stage).

Note that conditions for use of the program include the obligation to mention any user changes to the default database in case you publish results obtained with CHEAQS Next.

## 2.5.3 About

This option will show a window with information about the user files, such as location on disk, version number and date.

## 2.6 The Options Menu

The options menu contains six items, some of which are also available from other locations. Once you have chosen one of these six commands, you can also go to the other tabs of the window, which give access to the other options.

### 2.6.1 Input display

This Item shows you a window where you can set the display options for editing input. Also available from the input menu (section 2.2.8; see that section for a more detailed description) and from the Edit-Input window (section 2.2.4).

### 2.6.2 Output

This item enables you to determine how you want to view the output. Also available from the output menu (see section 2.4.7 for a more detailed text).

### 2.6.3 Remember

Here you can indicate which settings you want to keep across program sessions.

- Input settings;
- Output settings;
- Size (and state) of program window and output window;
- Recent input files;
- Recent output files.

### 2.6.4 Updates

On this page you can indicate whether CHEAQS Next should check for updates at start-up. An active internet connection is required to let this work. This option is on the same tab as the file associations (see section 2.6.6).

## 2.6.5 Menu colors

This command enables you to choose the menu colors that CHEAQS Next uses.

Note: CHEAQS Next uses the system menu font. In order to change CHEAQS Next's menu font, change the system settings via your Control Panel.

## 2.6.6 File associations

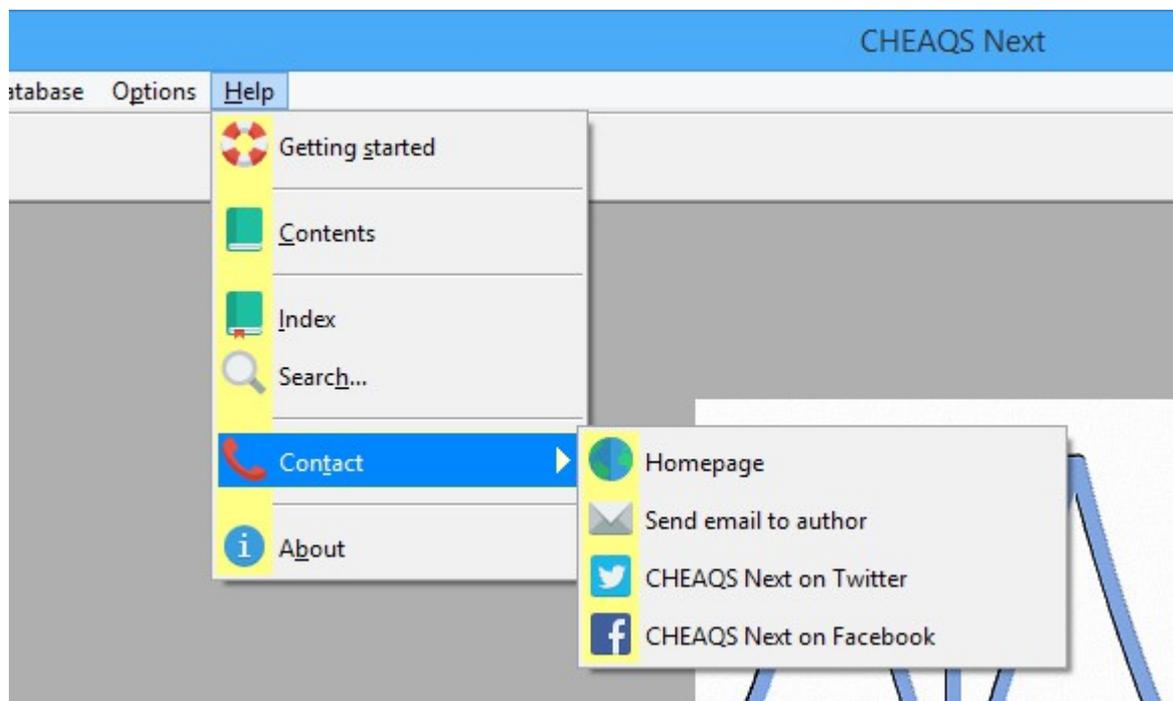
Here you have the option to register or unregister the file types that CHEAQS uses: input files (extension .inp) and output files (extension .ofc2). If you register these file types,

- the files will be shown in Windows Explorer with the CHEAQS icons for input resp. output.
- Double-clicking an input file will invoke CHEAQS, which will read the input file.
- Right-clicking an input file shows the option 'Open and Run', which will read the input file, run the calculation and save the output to a file with same base name. E.g. if you apply this option to a file called FirstTest.inp, the output file will be name FirstTest.ofc2. The location for this file is the default location for output files.
- Double clicking an output file will also invoke CHEAQS, which will open the output file and display the output.
- Right-clicking an output file shows the option 'Print', which will CHEAQS print the output with current printing settings (e.g. printer).

This option is on the same tab as the updates (see section 2.6.4).

## 2.7 The Help Menu

The help menu contains six items. See screenshot.



*The Help Menu*

## 2.7.1 Getting started

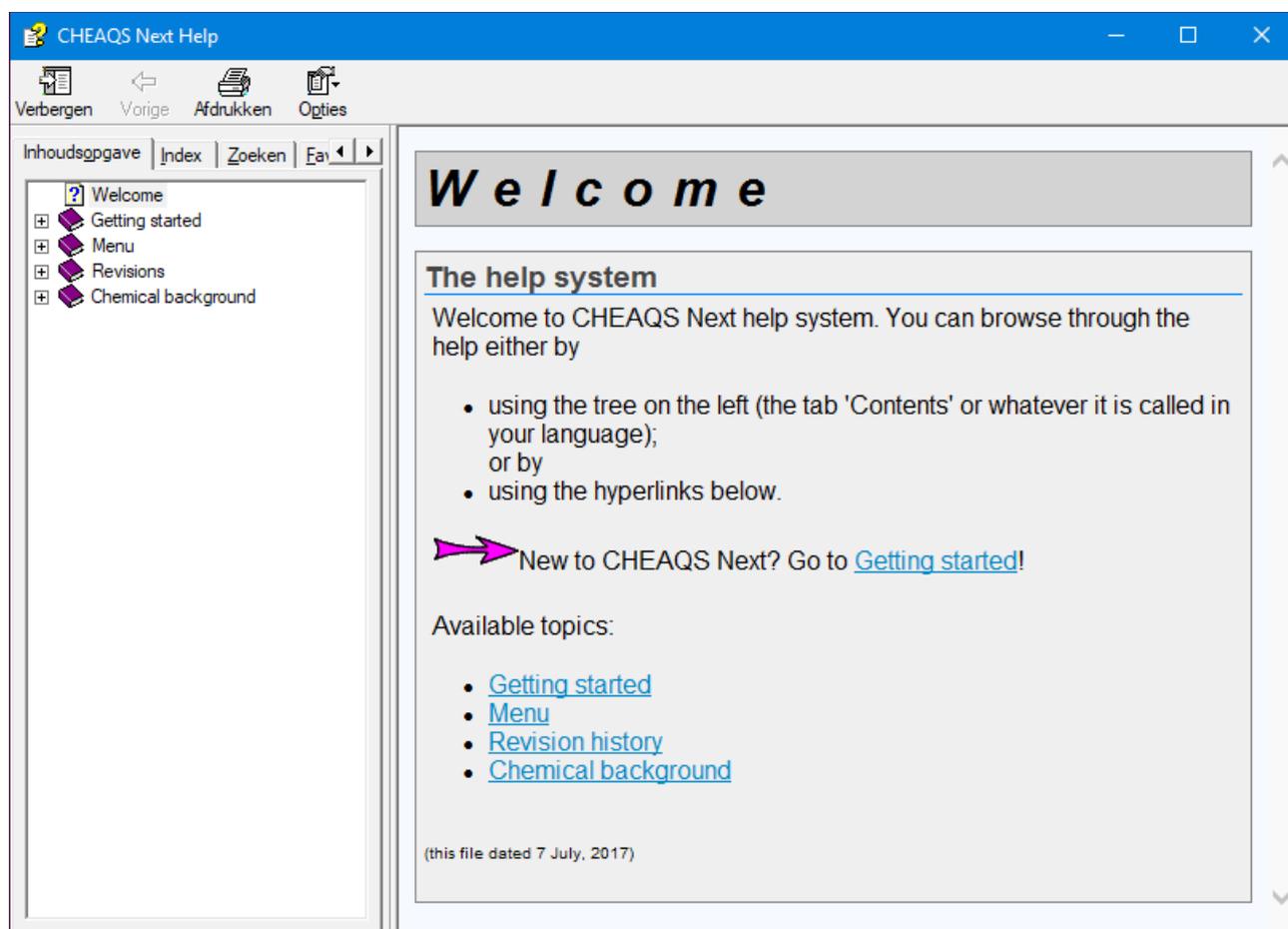
The first item of the help menu opens the help file CHEAQS2.CHM and selects the topic 'Getting started'. This is a set of help pages intended to help the user getting acquainted with the program.

## 2.7.2 Contents

This item also opens the help file and displays the Contents tab. See figure below. The figure is a screendump of the Dutch help system. In a different language the headings will be adjusted accordingly.

## 2.7.3 Index

The Index item also opens the help file but brings you to the index page. There you can select a topic on the left and the topic will be displayed on the right.



*The contents page of the help file.*

## 2.7.4 Search

The Search item also opens the help file but brings you to the search page. There you can enter any keyword; the corresponding help pages will be displayed.

## 2.7.5 Contact

This item contains a variety of items to get in touch with CHEAQS Next's author or community:

- the CHEAQS Next homepage <http://www.cheaqs.eu>;
- send an email to the author (a pop3-email client needs to be configured);
- the CHEAQS twitter page;
- the CHEAQS facebook page.

## 2.7.6 About

This command displays a dialog box with the version number and acknowledgements.



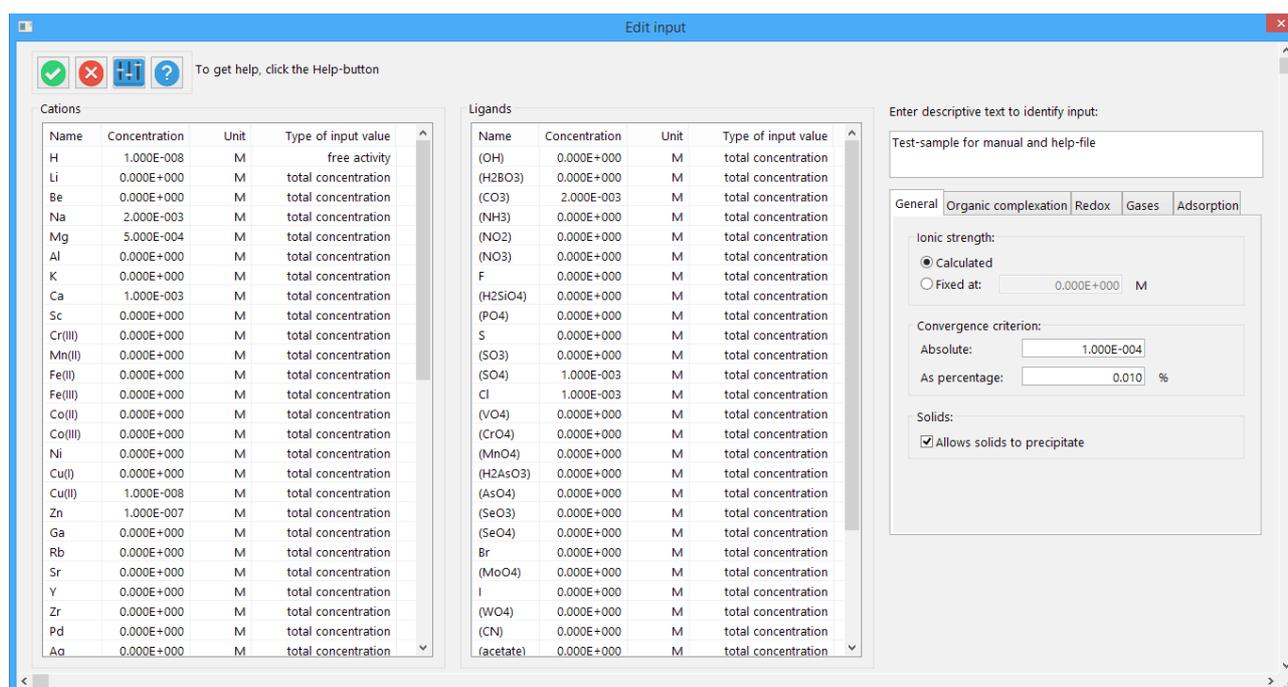
## 3 In-depth topics

This chapter contains five topics that are discussed in more details than fits in the previous chapter. These topics are:

1. editing input;
2. handling output;
3. printing output;
4. pH-calculations;
5. titrations.

### 3.1 Editing input

Section 2.2.4 explains how to start editing input. After you choose one of the commands described in that section, you will see a screen that looks like the screenshot below. On top left you see a row of buttons. Below it you see a table for cations. Adjacent there is a similar table for ligands. On the right, you find a text box for entering a descriptive text and below it a tab with pages called General, Organic complexation, Redox, Gases and Adsorption. Each of these elements will be discussed in more detail below.



Overview of input screen

#### 3.1.1 The buttons

The picture below shows the buttons on top in some more detail.



Buttons on input screen

-  Click this button when you are ready editing and want to confirm all changes you made. You will return to the main menu.
-  Click this button if you want to cancel all changes you made and return to the menu.
-  This button will bring up the Options window. For more information see section 2.2.8.
-  This button will display the page from the CHEAQS Next help file about editing input.

### 3.1.2 Cations

Below the buttons, you find a table with information about cations. Note that in the example the default display order of the program is used i.e. database order, not alphabetically. There are three items that you can change viz. concentration, unit and type of input value. See figure.

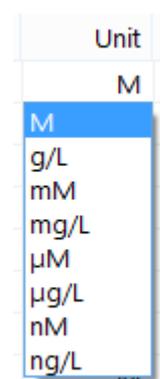
Name	Concentration	Unit	Type of input value
H	1.000E-008	M	free activity
Li	0.000E+000	M	total concentration
Be	0.000E+000	M	total concentration

*Cation information on input screen*

To change the *concentration*, click in the table cell containing the current value. You can then type the new value. You do not have to press Enter to complete the new value. You can use any valid numeric format. For example: 0.1 or 1E-1. Do take care of using the decimal character that your system is using (in the figure “.”, not “;”).

To change the *unit* that the program uses to display concentrations, click in a cell that contains the current unit. A dropdown menu will appear as shown in the figure, with the currently selected unit highlighted. See figure. You can select a different unit from the list after which the program will calculate the new values for the concentrations. For gases (see further down) the situation is different because gas pressures will always be shown in atm. The order (normal, milli, micro, nano) that you choose does apply to gases: if you choose mM rather than M, pressures will be displayed as m-atm.

If you plan to use g/L, please check the molecular weights that the program uses, because the design choices that were made may influence the way you need to enter the data.

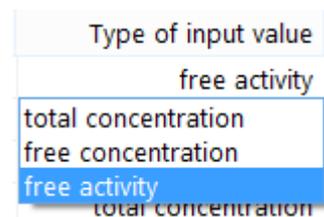


*The unit dropdown list*

Changing the input value works similarly: click in the cell containing the current type, a dropdown list will appear from which you can choose. See figure on next page. Unlike the unit discussed above, you change the type of input value of each cation and ligand separately.

Now what do these types mean?

- If you enter 'total concentration' for a cation or ligand, the free concentration and free activity will be calculated.
- If you enter 'free concentration', the total concentration and free activity will be calculated.
- If you enter 'free activity', the total concentration and free concentration will be calculated.



The 'type of input value' dropdown list

If you specify 'total concentration' for H, you can calculate the pH. See discussion later in this chapter.

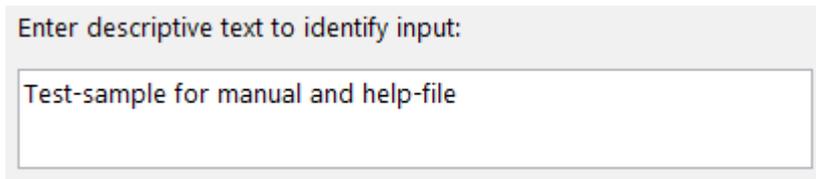
If you want to calculate the 'concentration' of solids, you should take care not to 'lock' the system. E.g. if you specify 'total concentration' for Ca and for CO<sub>3</sub>, the program will consider the necessity of forming solid CaCO<sub>3</sub>. In that case the dissolved concentration of both Ca and CO<sub>3</sub> will decrease and hence the free concentration of Ca and CO<sub>3</sub>. That works fine. If you specify 'free concentration' for Ca and 'total concentration' for CO<sub>3</sub>, the program will only decrease the dissolved concentration for CO<sub>3</sub>, not for Ca. That works fine too. However, if you specify 'free concentration' for both Ca and for CO<sub>3</sub>, the program will not be able to decrease the dissolved concentration. In such a case, the program will warn you that the dataset you provided is inconsistent.

### 3.1.3 Ligands

For ligands, the situation is very much similar to cations. For OH<sup>-</sup>, you can not specify 'free activity' or 'free concentration'; only 'total concentration' is enabled. To perform calculations at fixed pOH, use free activity or free concentration for cation H instead.

### 3.1.4 Description

On top right, you find a text box where you can enter a description of your sample. See figure. It is not necessary to provide a text here, but it can be practical to avoid situations where you wonder what kind of sample it was that you see the output of.



Edit input: text box for description

### 3.1.5 Tab: general

Below the description you find a tab window with five pages. The first one contains a few general characteristics of the calculation settings. See figure. First of all, you can indicate whether the ionic strength of the sample needs to be calculated or fixed. If you select 'fixed', you can enter a value in the text box. Secondly, you can specify the convergence criterion. For most situations, the default value of  $1 \times 10^{-4}$  will be OK. In rare cases, you may find that e.g. fractions do not sum up to 100% but instead to 99.99%. In those cases, you may want to set the convergence criterion to a lower value.

In general, it is not a good idea to set the convergence criterion to a higher value if the calculations do not converge. Usually lack of convergence points to an error in the input data.

Finally, you can indicate whether oversaturated solids are allowed to precipitate. If you check this option, solids will be added to the calculations and dissolved concentrations may be lower than total concentrations. If you do not check this option, no solids will be formed but you can still check the saturation state of each solid.

General Organic complexation Redox Gases Adsorption

Ionic strength:  
 Calculated  
 Fixed at:  M

Convergence criterion:  
 Absolute:   
 As percentage:  %

Solids:  
 Allows solids to precipitate

*Edit input, tab: general*

### 3.1.6 Tab: organic complexation

The second tab allows you to turn on organic complexation. See figure. It is turned off by default. If you select one of the four buttons of one of the available models, the frame 'Specifications' will appear. There you can enter a concentration for the dissolved organic carbon (in mg/L of C). For the Tipping-models 5, 6 and 7, you can also specify which part of this concentration consists of fulvic acids and which part consists of humic acids. Example: if you have 4 mg/L fulvic acids and 6 mg/L humic acids, enter a concentration of 10 mg/L of C, and for 'Fraction of Fulvic Acids' enter 0.4.

For Cabaniss & Shuman's model, you can specify the number of sites per mg C, as well as whether or not to extrapolate to other metals with charge +2 or higher. This extrapolation is described by Janssen & Verweij (2003).

General Organic complexation Redox Gases Adsorption

Organic complexation:  
 Include organic complexation?  
 No  
 Yes, use Model 7 (Tipping, 2011)  
 Yes, use Model 6 (Tipping, 1998)  
 Yes, use Model 5 (Tipping & Hurley, 1992, 1994)  
 Yes, use Cabaniss & Shuman (1988)

Specifications:  
 Concentration:   
 (in mg/L of C)  
 Sites per mg C (in M):   
 (Default value: 8E-6 M)  
 Extrapolate to metals with charge +2 or more

*Edit input, tab: organic complexation*

### 3.1.7 Tab: redox

The third tab is for redox. See figure. As soon as you click the check box 'Include redox equilibria', the text boxes for specifying redox as well as the table for redox solids are enabled. To specify redox, you can choose between entering as pE (negative log of electron activity) or in mV. If you type in one text box, the other one will be updated. pE and mV are related as:

$$\text{mV} = \text{pE} \times 59.159$$

Specifying 'concentration' for redox solids works the same as for cations and ligands; changing units as well.

Redox:

Include redox equilibria

as pE:

in mV:  mV

Redox solids:

Name	Concentration	Unit
MnO2 (s)	0.000E+000	M
Cu (s)	0.000E+000	M
PbO2 (s)	0.000E+000	M
S (s)	0.000E+000	M

'Type of input value' is always 'total concentration'.

*Edit input, tab: redox*

### 3.1.8 Tab: gases

The fourth tab enables you to specify gas pressures. See figure. Editing the values for pressures works the same as for cations and ligands. For units, you can choose between, atm, milli-atm, micro-atm and nano-atm. This is applied to cations and ligands as well.

Gases:

Name	Partial pressure	Unit
CO2 (g)	0.000E+000	atm
NH3 (g)	0.000E+000	atm
H2S (g)	0.000E+000	atm
SO2 (g)	0.000E+000	atm

'Type of input value' is always 'partial pressure'.

*Edit input, tab: gases*

### 3.1.9 Tab: adsorption

The most-right tab is for entering concentrations of adsorption site. This works the same as for cations and ligands. See figure.

Adsorption:

Name	Concentration	Unit
(=S-OH)	0.000E+000	M

'Type of input value' is always 'total concentration'.

*Edit input, tab: adsorption*

## 3.2 Handling output

This section gives more details about the screen that you see after the program completes a run (see section 2.3). You see an example screenshot of that screen below. On top you find a row of buttons. Below that on the left, you find a so-called treewiew that you use to select the cation or ligand that you want to see the output of (in the screenshot, the cation Ca). On the right, you find a summary, at the bottom you find details.

The screenshot shows the 'View output' window with the following components:

- Buttons:** A row of icons for file operations (check, save, CSV, XML, print, zoom, refresh, help) and an 'Other info' button.
- Treewiew:** A tree structure on the left with 'cations' expanded to show H, Na, Mg, Ca (selected), Cu(II), and Zn. Below it, 'ligands' is expanded to show (CO3).
- Summary Table:**

Fraction	Concentration	Unit	Percentage
Dissolved Ca	1.360E-004	M	13.60%
Solid Ca	8.508E-004	M	85.08%
Organic bound Ca	1.324E-005	M	1.32%
Total Ca	1.000E-003	M	100.00%
- Details Table:**

Species	Concentration	Unit	Percentage	Activity	Unit	Intrinsic K	Conditional K	Literature reference
free Ca 2+	1.184E-004	M	11.84%	8.616E-005	M			
Ca(CO3) (aq)	5.493E-006	M	0.55%	5.498E-006	M	3.220	2.943	NIST Database 46 Version 8.0
CaH(CO3) +	1.212E-005	M	1.21%	1.120E-005	M	11.529	11.252	NIST Database 46 Version 8.0
Ca(CO3) (s)	8.508E-004	M	85.08%			8.480	8.203	NIST Database 46 Version 8.0
FA-monodentates	1.560E-006	M	0.16%					Tipping (1998)
FA-bidentates	2.258E-006	M	0.23%					Tipping (1998)
FA-tridentates	2.077E-007	M	0.02%					Tipping (1998)
FA-DDL	4.369E-006	M	0.44%					Tipping (1998)
HA-monodentates	9.492E-007	M	0.09%					Tipping (1998)
HA-bidentates	6.388E-007	M	0.06%					Tipping (1998)
HA-DDL	3.191E-006	M	0.32%					Tipping (1998)
Total Ca	1.000E-003	M	100.00%					

Overview of example output screen

You can change the size of the panes by dragging the vertical and horizontal bar, like shown in the following figure.



Move the vertical bar

### 3.2.1 The buttons

The buttons on top of the output screen are shown in the picture below. Below the picture each button will be discussed.



*Buttons on output screen*



Click this button when you are ready viewing the output and want to return to the main menu.



Click this button to save the output in an internal CHEAQS Next format. You can not directly read such internal files, but once you created one, you can later open it, and then view it, export it or print it. The command will bring up a File - Save dialog where you can specify directory and filename. The program will initially propose the default directory for output files, but the user can choose a different directory for saving output. Default extension is .ofc2 but you can change that.



This button will create a so-called 'comma separated value' file. Spreadsheet programs like Excel® or OpenOffice Calc® can import this type of files. That enables you to perform further analyses of the output data.



This button will create an XML-file. Such a file can be read by spreadsheet programs like Excel® (starting from version 2002) or OpenOffice Calc® (starting version 4.1). XML-files contain formatting in addition to the numbers that CSV-files contain.



This button will bring up the 'Print output' form that is discussed in the next paragraph.



This button will bring up the Options window. For more information see section 2.4.7.



Click this button to display pie graphs for the selected component, one for the summary, one for the details. Clicking the button again hides the graphs.



This button will display the page from the CHEAQS Next help file about viewing output.

Other info

The button 'Other info' will bring up a new window which contains information not directly linked to a specific cation or ligand. See section 3.2.4.

### 3.2.2 The summary

The summary window pane contains four elements:

1. Fraction: this can be dissolved (light yellow), solid (light pink), organic bound (light green)

or adsorbed (light blue). Total is always displayed (light gray). In the example displayed in the screenshot, you see dissolved Ca, solid Ca, organic bound Ca and total Ca.

2. Concentration: the concentration of each fraction (if above the display limit).
3. Unit: the unit corresponding to the concentration.
4. Percentage: the percentage of each fraction relative to the total. In the example, dissolved Ca represents 72.64% of total Ca.

### 3.2.3 The details

The window pane with the details contains nine columns.

1. Species: the name. Note that the colour corresponds with the colour of the fraction. So dissolved Ca (light yellow) consists of
  - free  $\text{Ca}^{2+}$ ;
  - $\text{CaCO}_3 (aq)$ ;
  - $\text{CaH}(\text{CO}_3)^+$
  - and so on...

For some species, you see a symbol indicating equilibrium arrows ( $\rightleftharpoons$ ). If you click on such a species (first column), information about that equilibrium reaction will be shown.

Example:

The screenshot shows a window titled "Information about equilibrium reaction" with a close button (X) in the top right corner. The window content is as follows:

Information about  $\text{CaH}(\text{CO}_3)^+$

---

Equilibrium reaction:  
 $\text{H}^+ + \text{Ca}^{2+} + (\text{CO}_3)^{2-} \rightleftharpoons \text{CaH}(\text{CO}_3)^+$

---

Definition of K:  

$$K = \frac{\{\text{CaH}(\text{CO}_3)^+\}}{\{\text{H}^+\} \times \{\text{Ca}^{2+}\} \times \{(\text{CO}_3)^{2-}\}}$$

---

Value of  $\log_{10}(K)$ : 11.529

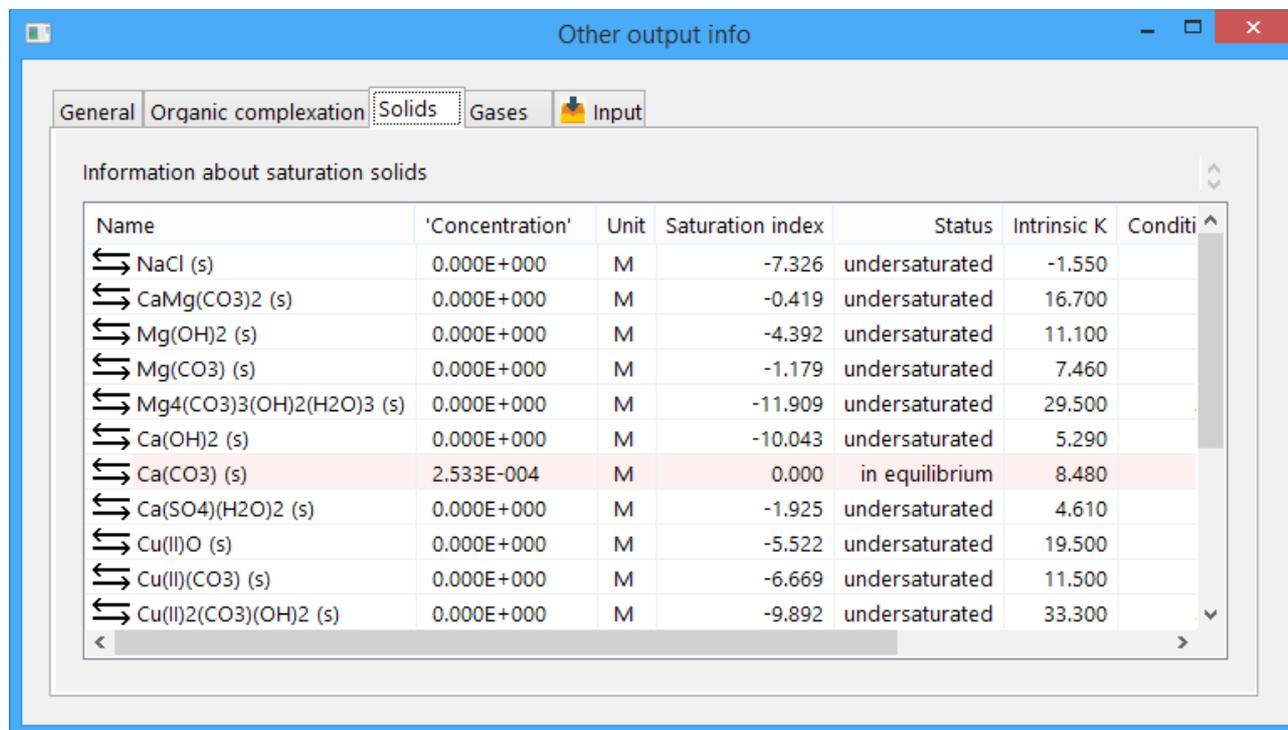
---

Literature reference: NIST Database 46 Version 8.0

2. Concentration: concentration of the species.
3. Unit: unit used for the concentration.
4. Percentage: percentage of the species compared to the total.
5. Activity: activity of the species. The activity of a species is the "effective concentration" under non-ideal conditions, i.e. ionic strength  $> 0$ . The activity is calculated as a product of the concentration and an activity coefficient  $f$ . CHEAQS Next uses the Davies-equation to calculate activity coefficients. See section 4.3.
6. Unit: unit used for the activity.
7. Intrinsic K: equilibrium constant under ideal conditions (ionic strength is zero, temperature is 25 °C). Intrinsic and conditional K's are displayed as  $\log_{10}$ -values.
8. Conditional K: equilibrium constant under non-ideal conditions. Note that CHEAQS Next assumes that temperature is always 25 °C.
9. Literature reference: literature source where equilibrium information comes from.

### 3.2.4 Other info

Clicking the button 'Other info' brings up a new window that contains information not specifically linked to one cation or ligand. See a screenshot for how a window like that may look like.



Name	'Concentration'	Unit	Saturation index	Status	Intrinsic K	Condi
↔ NaCl (s)	0.000E+000	M	-7.326	undersaturated	-1.550	
↔ CaMg(CO <sub>3</sub> ) <sub>2</sub> (s)	0.000E+000	M	-0.419	undersaturated	16.700	
↔ Mg(OH) <sub>2</sub> (s)	0.000E+000	M	-4.392	undersaturated	11.100	
↔ Mg(CO <sub>3</sub> ) (s)	0.000E+000	M	-1.179	undersaturated	7.460	
↔ Mg <sub>4</sub> (CO <sub>3</sub> ) <sub>3</sub> (OH) <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> (s)	0.000E+000	M	-11.909	undersaturated	29.500	
↔ Ca(OH) <sub>2</sub> (s)	0.000E+000	M	-10.043	undersaturated	5.290	
↔ Ca(CO <sub>3</sub> ) (s)	2.533E-004	M	0.000	in equilibrium	8.480	
↔ Ca(SO <sub>4</sub> )(H <sub>2</sub> O) <sub>2</sub> (s)	0.000E+000	M	-1.925	undersaturated	4.610	
↔ Cu(II)O (s)	0.000E+000	M	-5.522	undersaturated	19.500	
↔ Cu(II)(CO <sub>3</sub> ) (s)	0.000E+000	M	-6.669	undersaturated	11.500	
↔ Cu(II) <sub>2</sub> (CO <sub>3</sub> )(OH) <sub>2</sub> (s)	0.000E+000	M	-9.892	undersaturated	33.300	

Example of 'Other output info' window

This window contains up to six tabs depending on the types of equilibria that were included (in the example, five tabs are included). These are discussed and explained below.

1. General: contains information like number of iterations, ionic strength and charges.
2. Organic complexation: contains information about fraction of organic sites that is occupied by metals (and which metals).
3. Solids (see example screenshot):
  - when solids are allowed to precipitate: shows which solids were included in the calculations and whether or not they are formed. Row is marked pink if a solid has non-zero concentration like CaCO<sub>3</sub> in the example;
  - when solids are NOT allowed to precipitate: shows relevant solids and their state (oversaturated or undersaturated).
4. Gases: shows relevant gas-solution-equilibria.
5. Adsorption: contains information about fraction of adsorption sites that is occupied by metals (and which metals).
6. Input: contains input (for verification).

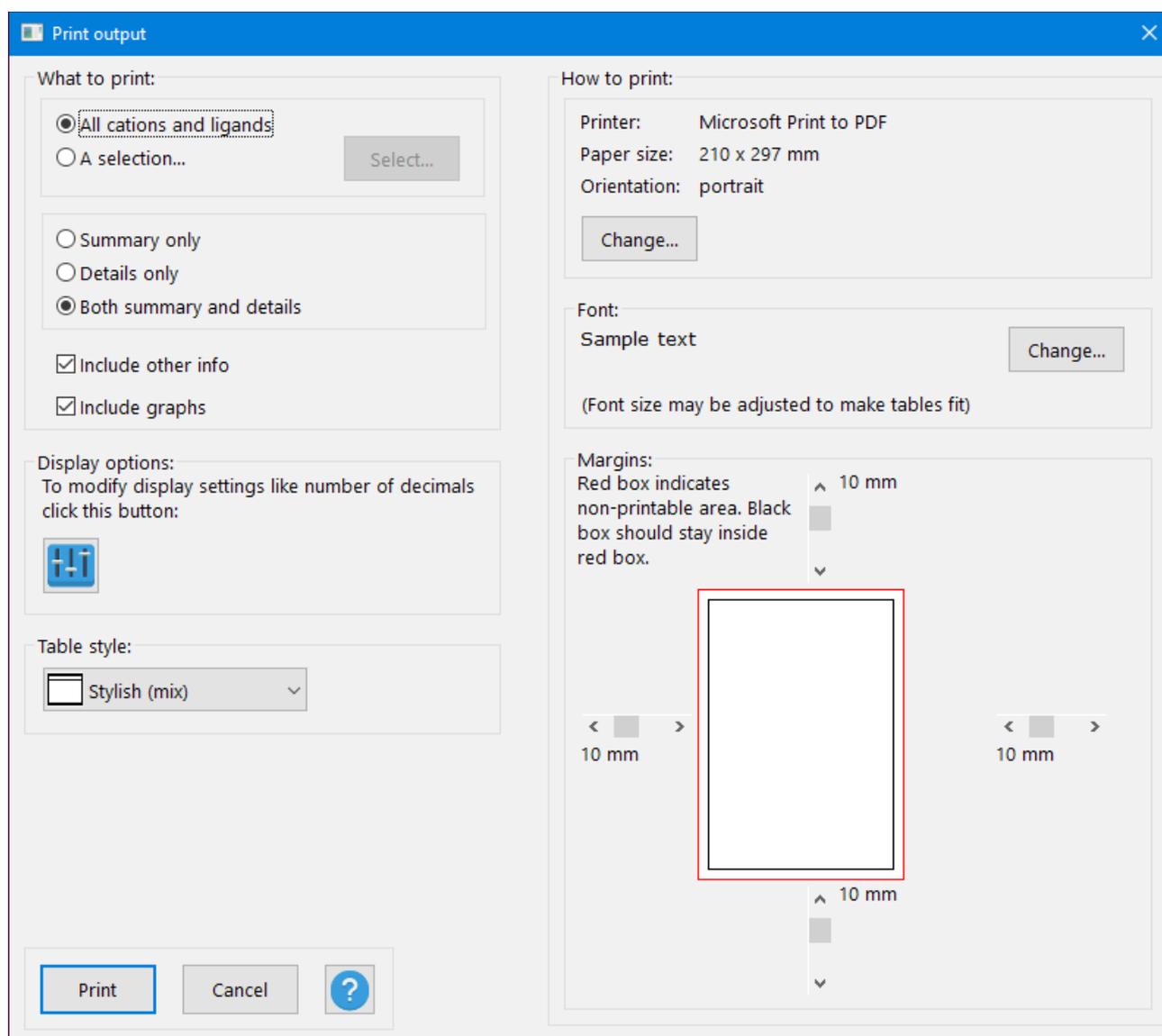
### 3.3 Printing output

Printing output is one of the features that is greatly improved compared to the older CHEAQS Pro. When you have clicked the Print-button on the 'View output'-screen, a window like shown below will appear. The window enables you to determine what will be printed and how.

In the left column you can choose

- *what* will be printed;
- *print options* as discussed earlier in section 2.4.7;
- styles for printed tables.

In the right column you can select *printer settings*.



The 'Print output' window

### 3.3.1 What to print

The items in the left column allow you to select *what* to print. Here is some more detail.

- First you can select which cations and ligands you want to appear in the printed output. Select the appropriate radio button (all or a selection). In the latter case, a window appears where you can select which ones to include in the output. Cations and ligands not included will only be mentioned at the beginning of the printed output.
- You can also indicate whether you want to see summary, details, or both.

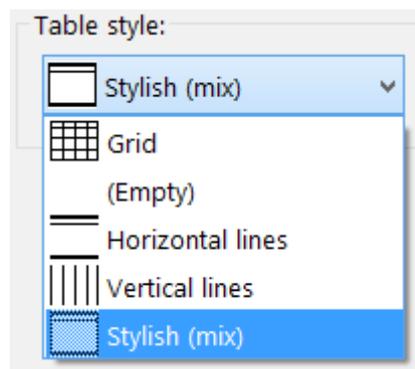
- In addition, you can choose whether other info should be included.
- Finally, you can indicate whether graphs should be included.

### 3.3.2 Options

You can also change print options (same as Output - Options from the main menu; see section 2.4.7).

### 3.3.3 Table styles

Unlike in previous versions of CHEAQS Next where only a grid-like table style was provided, now you can choose from five different styles, depending on your taste and mood. See figure.



### 3.3.4 Printer settings

In the right column you can choose printer settings.

- First the printer, paper size and orientation (portrait/landscape);
- Secondly the font you want to use. The text 'Sample text' shows your current selection. Note that, in order to make width of tables fit, the font size will be reduced automatically where necessary.
- Finally the margins you want to apply. Red lines indicate minimum printer margins; you can change the margins to be applied (shown in black). Please leave some space between the black and red lines because sometimes the printer margins are not correctly reported by the printer and results will be unpredictable.

## 3.4 pH-calculations

Of all the questions I receive about CHEAQS, many are dealing with pH-calculations. For that reason, I decided to devote a special section to this topic. The main issues are:

1. how to instruct the program to calculate pH rather than using a fixed pH;
2. how to interpret the output in case of calculated pH, and check whether the calculations were performed correctly.

#### *Sample 1*

Now we start with a sample that is obviously wrong: a 1 mM solution of  $\text{Na}_2\text{CO}_3$  at a pH of 7. Wrong, because we know that this is an alkaline solution, yet we force a pH of 7.

Step 1: calculate the speciation of such a solution at fixed pH of 7.

Start CHEAQS Next, set input to program defaults (see section 2.2.1.1).

Specify the following values and types of input value:

- H: 1E-7, free activity (the default);
- Na: 2E-3, total concentration;
- $\text{CO}_3$ : 1E-3, total concentration.

Return to the main menu, run the calculation (F5) and view the output. For H, you will see (in the summary window) a total concentration of 1.177E-3 M. Where does that come from? You also see

(general part of 'Other info') a charge of positive ions of 1.999E-3 eq, and a charge of negative ions of 8.226E-4 eq. Difference: 1.177E-3 eq. Charge ratio is 2.431. In the input tab of 'Other info' we see that pH was fixed. These anomalies are the result of the poor input data. If this was a chemically sound calculation,

- the total concentration of H would be the same as in the input;
- the positive charge would be the same as the negative charge.

Both conditions are not met here. The program had to 'generate' H (1.177E-3 M) to calculate results at a pH of 7.

We are now repeating the same calculation but have the program calculate the pH. Choose Edit - Input, then specify:

- H: 0, total concentration

(leave the values for Na and CO<sub>3</sub> as they were) and run again.

You will see a total H of 3.232E-8 M. To understand this better, have a look at the output screen.

There are four species with H:

free H <sup>+</sup>	3.234E-11 M	
HCO <sub>3</sub> <sup>-</sup>	3.487E-4 M	
H <sub>2</sub> CO <sub>3</sub>	2.268E-8 M	(note stoichiometric coefficient of 2!)
NaHCO <sub>3</sub>	3.094E-7 M	

When you sum these values, you obtain 3.491E-4 M.

Similarly for OH:

free OH <sup>-</sup>	3.483E-4 M
NaOH	7.763E-7 M

This sum is 3.490E-4 M.

Now you see an almost equal value for total H as for total OH. The difference can be calculated when the output is shown with more digits and turns out to be 3.232E-8 M and therefore negligible compared to the values of 3.491E-4 or 3.490E-4.

If you view the other info, first of all you will see ('input' tab) that pH was calculated. At the 'general' tab you will see that both the positive and negative charges are 1.980E-3 eq, so we now have the same value! Of course, the charge ratio is therefore 1.

If you go back to the underlying window, you will see an activity for H of 3.058E-11 M, corresponding to a pH of  $-\log_{10}(3.058E-11) = 10.515$ . So it is not strange that in the previous calculation (where we forced the solution to have a pH of 7) unlogical results were obtained.

If you wish, you can repeat the first calculation with a fixed pH value of 10.515. Then you will see a negligible concentration of H as well as equal charges.

### Sample 2

Now we are repeating the above steps for NaHCO<sub>3</sub>. First we reset the input (Input - New - Program defaults). Specify the following values and types of input value:

- H: 1E-3, total concentration
- Na: 1E-3, total concentration
- CO<sub>3</sub>: 1E-3, total concentration

Go back to the menu and run the calculation. At the 'input' tab of the 'Other info' check that pH was calculated. At the 'general' tab, you will see that both the positive and negative charge are  $9.994\text{E-}4$  eq. This is how it should be! If you close the 'Other info', you can see that total H is  $1\text{E-}3$  which is exactly what you entered. (If you sum all the species as above, you will find  $1.002\text{E-}3$  of  $\text{H}^+$  and  $2\text{E-}6$  of  $\text{OH}^-$ ).

The pH is  $-\log_{10}(5.416\text{E-}9) = 8.266$  so slightly alkaline.

### Sample 3

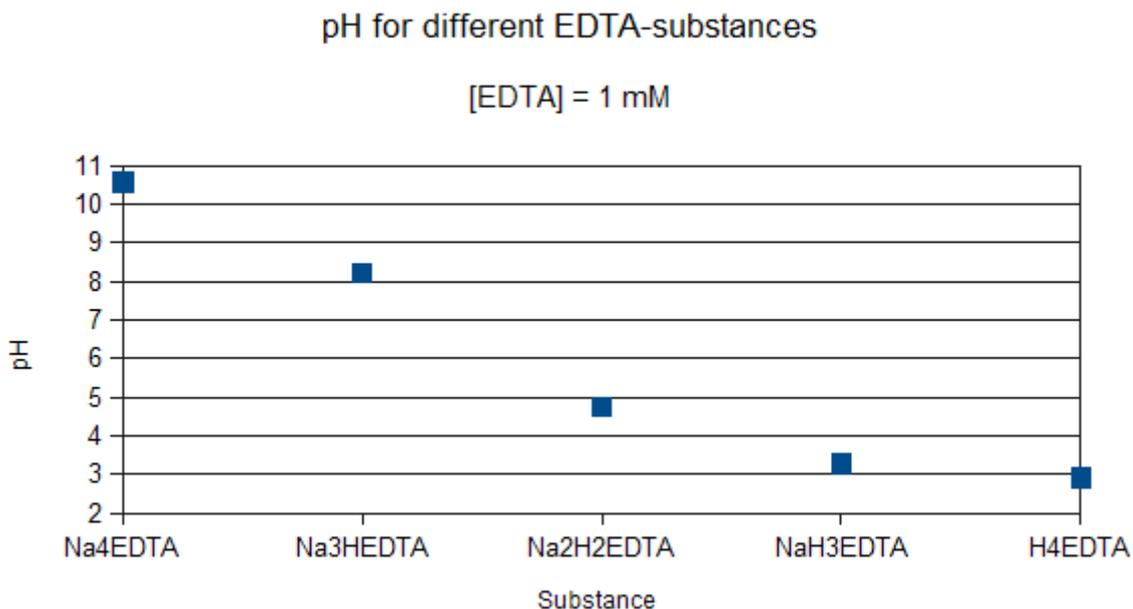
For sample 3 we are going to calculate the pH of EDTA-solutions, starting with  $\text{Na}_4\text{EDTA}$ , step by step replacing each Na by a H. Because the deprotonated EDTA-ion has a charge of -4, we need 4 Na ions for each EDTA-ion. In the table below we find the required input for the five cases. Note that 'type of input value' for H always has to be set to 'total concentration'.

Compound	Na	H	EDTA
$\text{Na}_4\text{EDTA}$	$4\text{E-}3$ M	0	$1\text{E-}3$ M
$\text{Na}_3\text{HEDTA}$	$3\text{E-}3$ M	$1\text{E-}3$ M	$1\text{E-}3$ M
$\text{Na}_2\text{H}_2\text{EDTA}$	$2\text{E-}3$ M	$2\text{E-}3$ M	$1\text{E-}3$ M
$\text{NaH}_3\text{EDTA}$	$1\text{E-}3$ M	$3\text{E-}3$ M	$1\text{E-}3$ M
$\text{H}_4\text{EDTA}$	0	$4\text{E-}3$ M	$1\text{E-}3$ M

In the table below you will find the calculated free activity for H as well as the pH.

Compound	{H+}	pH
$\text{Na}_4\text{EDTA}$	$2.755\text{E-}011$ M	10.56
$\text{Na}_3\text{HEDTA}$	$6.157\text{E-}009$ M	8.21
$\text{Na}_2\text{H}_2\text{EDTA}$	$1.803\text{E-}005$ M	4.74
$\text{NaH}_3\text{EDTA}$	$5.425\text{E-}004$ M	3.27
$\text{H}_4\text{EDTA}$	$1.213\text{E-}003$ M	2.92

This is also shown in the graph.



So, to calculate the pH of a solution:

- make sure to set 'type of input value' for H to 'total concentration';
- check the output to see if charges are equal;
- calculate pH as  $-\log_{10}(\text{activity of free H})$ .

## 3.5 Titrations

### 3.5.1 Introduction to titrations

Basically, a titration is just a series of calculations where one or two input variables are systematically changed. Five types of titrations are implemented. Note that a single and double titration are not chemically correct. You can e.g. titrate Cu(II) without any counterions. Therefore these types should only be used if the concentration of the counterions can be neglected. If you are not sure whether this is allowed, you should use the chemically correct type.

Compared to the older CHEAQS Pro, you can now plot 40 variables during the titration instead of just one. In addition, you can plot the X- and Y-axis either in log-mode or in normal mode. Finally, you need to decide about where and how to output the results only when the titration is finished. The first titration type, a single titration, will be dealt in more detail than the others. So if you are new to titrations, read that part first.

When you have chosen Calculate - Titration from the menu, you see the window as shown here.

Select type of titration

Welcome to the titration wizard. This wizard guides you through the steps of setting up a titration modelling experiment.

At this first form, you can indicate the type of titration that you would like to perform. The four types on the left are without volume change (only the solution composition changes), on the right you can choose a real-world-chemical titration, so including volume change.

When you have you made your choice, click 'Next step'.

Without volume change:

- Single titration
- Double titration
- "Replace" titration
- Chemically correct titration

With volume change:

- Real chemical titration

Next step    Cancel    ?

Here you can choose the desired titration type. Each type will be discussed in a separate section.

### 3.5.2 Single titration

For this titration, let us assume you want to add Cu(II) to a solution containing 1  $\mu\text{M}$  of EDTA, at pH = 7. For now, we ignore any cations associated with the EDTA, as well as any anions associated with the Cu(II). We proceed as follows.

At the screen shown in the previous section, we click 'Single titration' as well as 'Next step'. A message tells us we are going to define the starting solution. If we chose Input - New - Program defaults before we started, pH is set to 7 and all concentrations are zero. So the only thing we need to do here is to set the total concentration of EDTA to 1  $\mu\text{M}$  ( $1\text{E-}6$ ). Then we click the green 'OK'-sign on top left.

#### *Independent variable*

We now proceed to the next step, where the window is called 'Variable to change'. In this example, it is the total Cu(II)-concentration. For other examples, you could choose:

- A cation
  - Total concentration
  - Free concentration
  - Free activity
- A ligand: same as for a cation
- Other
  - Adsorption site
  - Redox solid such as  $\text{MnO}_2 (s)$
  - Gas pressure such as  $\text{CO}_2 (g)$
  - Redox (as pE; see section 3.1.7 for conversion formula from mV)
  - Ionic strength
  - Equilibrium constant for each included equilibrium (based on your input set)
  - Organic complexation
    - total concentration of organic acids
    - for Tipping's models (model 5, 6 and 7): division over fulvic and humic acids (0 – 100%)
    - for Cabaniss & Shuman's model: the number of sites per mg C

For our example, we choose 'A cation', click Cu(II) in the list, and click 'Total concentration'.

We also specify an initial Cu(II)-concentration of zero, final of  $2\text{E-}6$  (twice the EDTA-concentration) and a stepsize of  $1\text{E-}8$ . This will result in 200 calculations. See figure on next page.

Click 'Next step' to proceed. Note that if you choose to multiply by a factor rather than adding a fixed term, the X-axis will be shown in log-mode by default.

#### *Dependent variables*

This next step enables you to choose the variables that you would like to be recorded during the titration. You can choose

- Species
  - Concentration
  - Activity
  - Saturation index
  - Conditional constant

Depending on the species you click, some choices will be disabled.

**Variable to change**

 In this step you select the variable you would like to change. Start at the top, the form will be constructed depending on your choices. Please start by selecting the type of parameter you would like to change.

A cation  
 A ligand  
 Other:

Please select one from the list below

<div style="border: 1px solid gray; padding: 2px;"> <p>Ni</p> <p>Cu(I)</p> <p style="background-color: #007bff; color: white;">Cu(II)</p> <p>Zn</p> <p>Ga</p> <p>Rb</p> <p>Sr</p> </div>	<p>Please select the type of value below.</p> <p><input checked="" type="radio"/> Total concentration</p> <p><input type="radio"/> Free concentration</p> <p><input type="radio"/> Free activity</p>
--	--

Values:

Initial value:	<input type="text" value="0"/>	<i>Unit: M</i>
Final value:	<input type="text" value="2e-6"/>	
How to get there:	<input checked="" type="radio"/> Add a number <input type="radio"/> Multiply by a number	
Stepsize:	<input type="text" value="1e-8"/>	
Number of runs:	<input type="text" value="200"/>	

*'Variable to change' window*

- Fraction: this can be dissolved, organic, precipitated etc, also depending on your input
- Other
  - ionic strength
  - negative or positive charge of ions in solution

For our example, we select 'Species', 'free Cu(II)<sup>2+</sup>', then 'concentration'<sup>1</sup>. When we click the 'Add'-button, this variable will be added to the list which can be found at the tab 'Already selected'. Then click 'Next step' again. The titration will be started.

#### *Export Titration Data*

When the titration is finished, a window is shown where you can indicate what to do with the output:

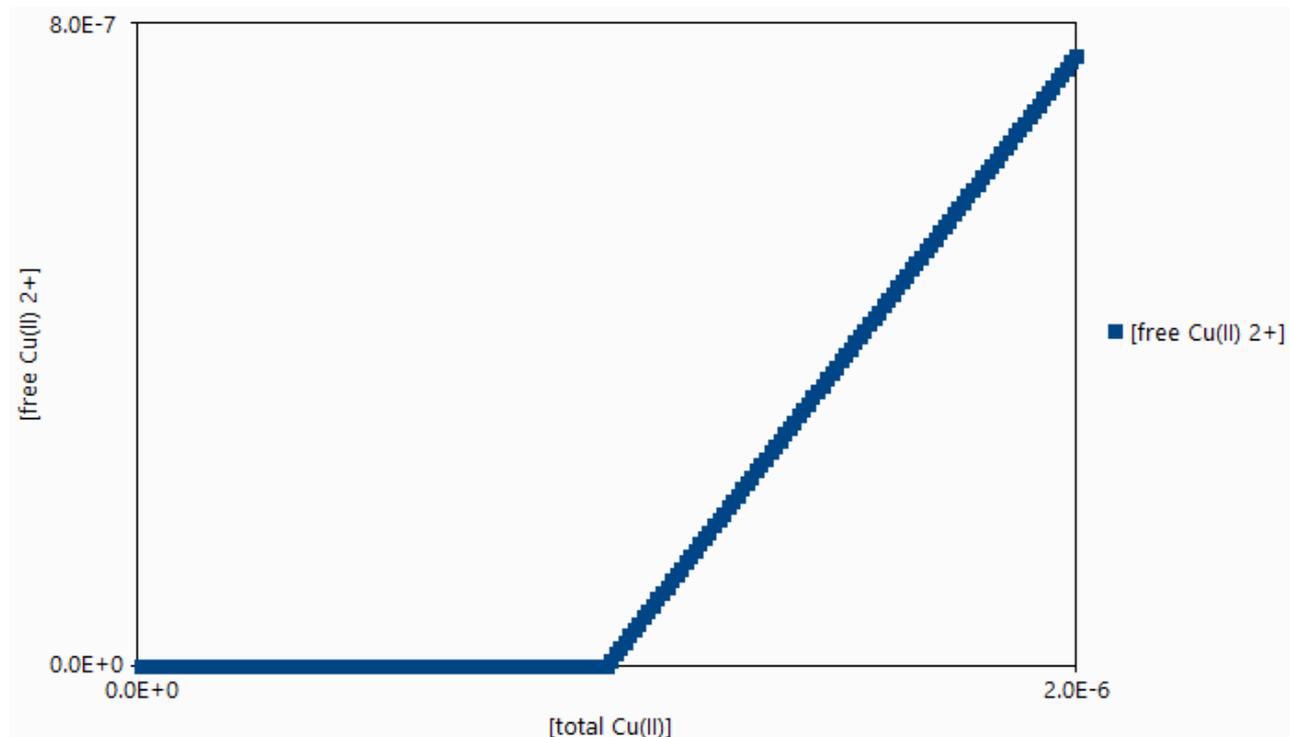
- save as a bitmap
- save as a text file
  - choose text qualifier: single or double quote or nothing
  - choose field separator: comma, tab or space

<sup>1</sup> CHEAQS Next uses “[ ]” for concentrations, “{ }” to denote activities.

For a csv-file, you would typically choose the double quote and the comma.

- save as an XML-file.

The result of this titration example is shown in the graph below.



### 3.5.3 Double titration

For a double titration, the procedure is very similar. The main difference is that you have to select two independent variables instead of one. You can use this option e.g. to create pH-pE-diagrams.

### 3.5.4 Replace titration

A 'replace titration' is a titration where a cation is replaced by another cation or an anion with another anion. (Since most ligands are anions, this is almost equivalent.)

First, you choose the type of component: cation or ligand. Subsequently, the list boxes will be filled. In the left list box, you click the component to be replaced; in the right list box you choose to component to replace. Finally, add initial and final values for concentrations, plus stepsize or factor. The program automatically calculates the final concentration for the component to replace. Please keep in mind that, because the concentration of the first one will typically decrease, you should specify a negative stepsize or a factor smaller than 1.

In the figure below, you see a typical example. As you see, the program takes into account the charges of the cations to determine a chemically correct final concentration.

**What to replace**

In this step you select the cation or ligand that you want to replace, and what to replace it with.

Replace:

Replace a  cation  ligand

Replace: with:

H	H
Li	Li
Be	Be
Na	Na
Mg	Mg
Al	Al
K	K

Concentrations:

	Initial value (in M):	Final value (in M):	
Na	1e-3	0	✓
Al	0.000E+000	3.333E-004	

How to get there:  Add a number  Multiply by a number

Stepsize:  (Take care if initial > final...)

Number of runs: 100 ✓

Previous step Next step Cancel ?

### 3.5.5 Chemically correct titration

As noted before, a single or double titration is not chemically correct. A 'replace titration' is, but if you want to *add* a compound to a solution, you need to use the 'chemically correct titration'. The first step for this titration is to create the compound you want to add. In the figure below, the user already pointed Na as the first component, with stoichiometric coefficient 2, and also already selected (CO<sub>3</sub>) as the second component. The stoichiometric coefficient of 1 was already typed in the text box but the button 'Confirm' was not clicked yet. Once clicked, the icon for charge changes into a green check mark and the OK-button is enabled. Clicking OK returns you to the previous form, shown below. Note that you are not limited to two components; e.g. to add NaHCO<sub>3</sub>, you add Na, H and CO<sub>3</sub>, each with a stoichiometric coefficient of 1. Similarly, to add Na<sub>2</sub>H<sub>2</sub>EDTA, add Na and H with a stoichiometric coefficient of 2 and EDTA with a stoichiometric coefficient of 1.

**Compose compound**

1) Click each cation and ligand, 2) specify a stoichiometric coefficient, 3) click confirm, 4) click OK when ready.

Cations:   
 H  
 Li  
 Be  
 Na  
 Mg  
 Al  
 K  
 Ca  
 Sc  
 Cr(III)  
 Mn(II)  
 Fe(II)  
 Fe(III)  
 Co(II)

Ligands:   
 (OH)  
 (H2BO3)  
 (CO3)  
 (NH3)  
 (NO2)  
 (NO3)  
 F  
 (H2SiO4)  
 (PO4)  
 S  
 (SO3)  
 (SO4)  
 Cl  
 (C2O4)

Enter stoichiometric coefficient for (CO3):

Charge = 2

Charge: 

When done, click OK.

In the figure below, the user specified that Na should increase from 0 till  $10^{-3}$  M and that  $\text{CO}_3$  should start at 0 too. The program then calculates the final concentration of  $5 \times 10^{-4}$  M, based on the charges.

**Compound to add**

 In this step you select the compound you want to add. First compose the compound, then fill in values for concentration. The form will be constructed depending on your choices.

Compose compound:  Chosen:  $\text{Na}_2(\text{CO}_3)$

Concentrations:

	Initial value (in M):	Final value (in M):	
Na	<input type="text" value="0.000E+000"/>	<input type="text" value="1e-3"/>	
(CO3)	<input type="text" value="0.000E+000"/>	5.000E-004	

Route:

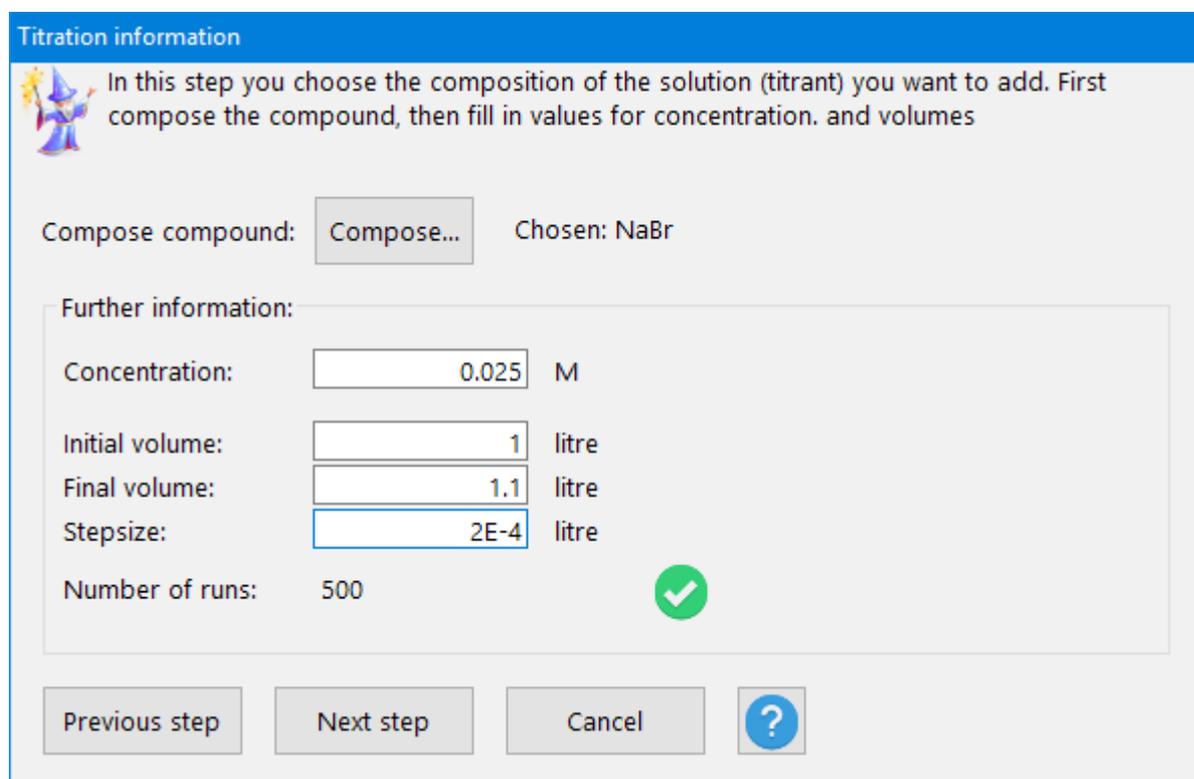
How to get there:  Add a number  Multiply by a number

Stepsize:

Number of runs: 250 

### 3.5.6 Real chemical titration with volume change

For a real chemical titration (including volume change), the first step is also to compose a compound, using the same procedure as in the previous paragraph. Subsequently, the window as shown below is displayed. In this example, the user wants to add a solution of 0.025 M of NaBr to a erlenmeyer or other flask. The initial volume, before starting to add, is 1 litre here. The user wants to add 0.1 litre so that the final volume becomes 1.1 litre.



Titration information

In this step you choose the composition of the solution (titrant) you want to add. First compose the compound, then fill in values for concentration, and volumes

Compose compound:  Chosen: NaBr

Further information:

Concentration:  M

Initial volume:  litre

Final volume:  litre

Stepsize:  litre

Number of runs: 500 



## 3.6 Batch mode

CHEAQS Next can also be run in batch mode. Of course you can use these options to call CHEAQS from a DOS-like environment (such as after choosing Start - Run, then 'CMD' ) but you will probably find these opportunities more useful when you can call CHEAQS from another application where you manage your chemical data. For instance, from the application that you use to manage your chemical data, you can create your own input file (using the file specifications in Annex I), then instruct CHEAQS to start, read that file, save the output and quit. You may find the information on the Microsoft-site useful, about launching applications (<https://msdn.microsoft.com/en-us/library/windows/desktop/bb776886%28v=vs.85%29.aspx>).

You may also want to review the section on file associations (section 2.6.6).

There are three ways to run CHEAQS in batch mode. Note that, if a file name contains one or more spaces, it needs to be enclosed with double quotes.

1. You can instruct CHEAQS to start, read one input file, perform the calculations, save the output and quit. Syntax: **cheaqs2.exe /RUN:<input file name> <output file name>** (without the "<" and ">"). Both file names may include full paths. If only a file name and no path is given, CHEAQS assumes the default directory for input and output file. The only visual clue that CHEAQS is running is the default progress box.

2. You can also instruct CHEAQS to start, run a series of input files, save the output for each input file, and quit. Syntax: **cheaqs2.exe /BATCH:<name of batch file>**. This batch file can be a text file that you create, and that consists of as many lines as you want input files to be run, in the syntax:
  - <input file name 1> < output file name 1>
  - <input file name 2> < output file name 2>
  - <input file name 3> < output file name 3>
  - etc.It is strongly recommended to use full paths for both input and output files.
3. You can also instruct CHEAQS to start and read one input file. Syntax: **cheaqs2.exe <input file name>** (without the "<" and ">").



## 4 The chemistry

This chapter deals with the chemistry that is incorporated into CHEAQS Next. You will find a short description, together with literature references and suggestions for further reading.

### 4.1 Solving procedure

The calculation of the speciation of a sample consists of several steps.

- First, initial (highly arbitrarily) values are assigned to program variables like ionic strength and free concentration for each cation and ligand.
- These values are used to calculate intermediate results for the speciation of the sample. (This includes adsorption, redox equilibria and organic complexation.)
- Subsequently, for each cation and ligand the total calculated mass is compared to the input mass, and the difference is used to make better estimates of the ionic strength and free concentrations.
- These steps are repeated until the mass balance differences decrease to acceptable differences (set by user as convergence criterion).

In case the user chose to allow solids to precipitate, an additional check is done to see if any solids are oversaturated. If so, some of the dissolved cations and ligands is precipitated and calculations are resumed using these new values. This is repeated until all solids are either undersaturated or in equilibrium.

### 4.2 Ionic strength calculation

The ionic strength  $I$  is calculated using the formula:

$$I = \frac{1}{2} \times \sum (c \times z^2)$$

where:

- $c$  refers to the concentration of the ions;
- $z$  stands for the charge of the ions.

Literature: e.g.: Stumm & Morgan, 1981.

### 4.3 Activity correction

Activity corrections are necessary because the intrinsic equilibrium constants are valid only for standard conditions, i.e. a temperature of 25°C and  $I=0$  (dilute solution). Activity correction is done by using the Davies equation which yields activity coefficients  $f$ :

$$\log f = -0.5079 \times z^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3 \times I \right)$$

where:

- $z$  is the charge of the species;
- $I$  is the ionic strength.

Note that sometimes a factor of 0.2 rather than 0.3 is used.

The activity coefficients for the current ionic strength are used to calculate activities of species which in turn are used to calculate conditional equilibrium constants. The Davies-equation is often said to be usable up to  $I = 0.5$  M, but it has been suggested that it may be used for values of  $I$  up to 1 M (Dyrssen et al., as cited in Mattigod and Sposito, 1979).

## 4.4 Temperature correction

Temperature corrections are necessary because the intrinsic equilibrium constants are valid only for standard conditions, i.e. a temperature of 25°C and  $I=0$  (dilute solution). In principle, it is possible to adapt the equilibrium constants for non-standard temperatures, but this requires knowledge of heat capacity data of each equilibrium (Verweij, 1991). That knowledge is often not available (Stumm & Morgan, 1981). Therefore, CHEAQS Next does not perform any temperature corrections.

## 4.5 Modelling adsorption

In addition to the "normal" variations in reported values for equilibrium constants, adsorption equilibrium constants have special uncertainties related to the variation in composition of different adsorbentia. Therefore, it is not possible to model adsorption equilibria the way you can model other types of equilibria. You can use the adsorption equilibria in CHEAQS Next only to make a first, rough estimate of the potential relevance of adsorption in your system. To do more specific calculations, you will either have to do measurements to determine the values of the adsorption constants in your system, or calculate a series of realistic values (scenario-approach).

### 4.5.1 Modelling adsorption in CHEAQS Next

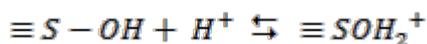
CHEAQS Next models adsorption by using the surface complexation model (Schindler & Stumm, 1987). This model uses many aspects of coordination chemistry and equilibrium theory which are so essential to equilibrium modelling in aquatic systems. The model supposes that adsorption sites can be represented as =S-OH where S stands for "site". In its most basic form, there are two types of acid-base-equilibria and two types of metal-adsorption equilibria.

### 4.5.2 Acid-base-equilibria

Relevant acid-base-equilibria:



and:



The values in the database of CHEAQS Next were arbitrarily taken from Schindler & Stumm (1987) for sites on aluminium (hydr-)oxides (page 97).

### 4.5.3 Metal adsorption equilibria

It is rather generally accepted that there is some relationship between hydrolysis constants and adsorption constants. Schindler & Stumm, 1987 used this relationship to derive adsorption constants for metals from their hydrolysis constants, for metals with a valency of two or three. This approach was used to fill the database of CHEAQS Next with a set of metal adsorption constants, for metals with a valency of two or more. For more details, please refer to the database document, available at the website.

### 4.5.4 Fixed concentration or linked?

[Note: not in current version yet but expected soon]

CHEAQS Next introduces the option to link adsorption. By default, CHEAQS Next assumes you want to specify the concentration of adsorption sites (fixed concentration). Now suppose you would like to model adsorption to solid Fe(III)-hydroxide. But what concentration to use for the solid? The concentration depends on the system (competing ligands e.g.). Exactly for such a situation, you can have CHEAQS Next calculate (1) the "concentration" of solid Fe(III)-hydroxide; (2) then use that value to calculate adsorption.

## 4.6 Modelling organic complexation

### 4.6.1 General introduction

Organic complexation by natural organic matter can not be calculated the same way as "normal", inorganic complexation or organic complexation with well-defined compounds such as acetate or EDTA. Inorganic complexation can be calculated relatively straightforward but organic complexation by natural organic matter can not. For that reason, special attention is required for including organic complexation in the program.

Complexation with Dissolved Organic Carbon (DOC) is different from inorganic complexation or complexation with well-defined compounds such as acetate or NTA. The reasons for that difference are as follows (see also Morel & Hering, 1993).

- DOC is very heterogeneous; DOC isolated at two sites may be very different (not to talk about the difficulty of selecting isolation procedures).
- Complexation with DOC generally shows a continuous range of equilibrium constants, due to chemical and steric differences in neighbouring groups.
- Increased cation binding and/or the ionic strength of the solution change electrostatic interactions among the functional groups in DOC-molecules.
- In addition, changing electrostatic interactions may cause conformational changes of the molecules.

At present four models are used in CHEAQS. Three models are designed by Tipping and co-workers (Model V, VI and VII), one model was designed by Cabaniss and Shuman, in the eighties.

- The first model (Model V, also known as WHAM-Water) was designed to deal with several metals. This model is much more sophisticated in the way electrostatic interactions are dealt with than Cabaniss & Shuman's model. See Tipping & Hurley, 1992 and Tipping, 1994.
- The second model (Model VI) is essentially the next step in the development by Tipping and co-workers. Model VI is described in an article from 1998.
- The third model (Model VII) is again a step forward in the development by Tipping and co-workers. Model VII is described in an article from 2011.
- The fourth model (actually the first one that was implemented in CHEAQS Pro and the last one implemented in CHEAQS Next) is a model for copper(II), published in 1988 by Cabaniss and Shuman (1988a, 1988b). For details see the original papers.

At present, there are no plans to include more models but I am open for suggestions.

## 4.6.2 Model V

### 4.6.2.1 Introduction

Model V was published by Tipping & Hurley in 1992. In 1994, Tipping published WHAM. WHAM comes in two flavours: WHAM-W(ater) which was basically Model V and WHAM-S(oils and sediments). CHEAQS Next includes WHAM-W.

Model V distinguishes fulvic acids (FA) and humic acids (HA) which are treated separately. For each acid, eight different discrete binding sites are used in the model. Site 1 to 4 (type "A") have twice as high concentrations as sites 5 to 8, type "B". The sites have a range of acid-base-properties. Metals bind to these sites, either to one site alone (monodentate) or to two sites (bidentate). A selection of the theoretically possible combinations is used (12 out of 36). Binding constants depend on ionic strength and electrostatic interactions. In addition to specific binding, species can accumulate in the diffuse double layer.

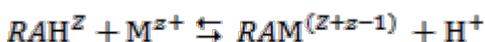
### 4.6.2.2 Equilibria included

For each gram of fulvic acids,  $4.73 \times 10^{-3}$  mol type A groups occur and  $2.37 \times 10^{-3}$  mol type B groups. For humic acids, these numbers are  $3.29 \times 10^{-3}$  and  $1.65 \times 10^{-3}$  respectively. Acid-base reactions for each site are expressed as:



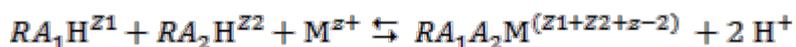
where RA is FA or HA.

Metal complexation on monodentate sites is expressed as:



where M represents a free metal ion or its monohydroxide. Tipping lists values for constants for several metals. These are included in CHEAQS Next's database.

Metal complexation on bidentate sites is expressed as:



A fraction of the sites is allowed to form bidentate complexes. In the original Model V (Tipping & Hurley, 1992), 40% of the sites was allowed to form bidentate complexes. In WHAM-W(ater) (Tipping, 1994), this value was changed to 50% for humic acids (still 40% for fulvic acids). CHEAQS Next uses the values from WHAM-W(ater).

### 4.6.3 Model VI

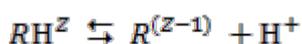
#### 4.6.3.1 Introduction

Model VI was published by Tipping in 1998. Model VI, just like Model V, distinguishes fulvic acids (FA) and humic acids (HA) which are treated separately. For each acid, eight different discrete binding sites are used in the model. Site 1 to 4 (type "A") have twice as high concentrations as sites 5 to 8, type "B". The sites have a range of acid-base-properties. Metals bind to these sites, either to one site alone (monodentate), to two sites (bidentate) or to three sites (tridentate). Tridentates are new in Model VI compared to Model V. Also new is that for each bidentate and tridentate group there are three sub-groups assumed to be present.

For bidentates and tridentates, a selection of the theoretically possible combinations is used (bidentates: 8 out of 36; tridentates: 16 out of 120). In total, 80 sites are assumed to be present. Binding constants depend on ionic strength and electrostatic interactions. In addition to specific binding, species can accumulate in the diffuse double layer.

#### 4.6.3.2 Equilibria included

For each gram of fulvic acids,  $4.8 \times 10^{-3}$  mol type A groups occur and  $2.4 \times 10^{-3}$  mol type B groups. For humic acids, these numbers are  $3.3 \times 10^{-3}$  and  $1.65 \times 10^{-3}$  respectively. Acid-base reactions for each site are expressed as:



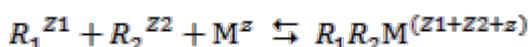
where R is FA or HA.

Metal complexation on monodentate sites is expressed as:



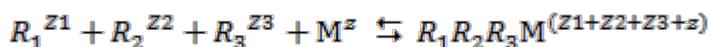
where M represents a free metal ion or its monohydroxide. Tipping lists values for constants for several metals. These are included in CHEAQS Next's database.

Metal complexation on bidentate sites is expressed as:



A fraction of the sites is allowed to form bidentate complexes. For fulvic acids this fraction is 0.42, for humic acids 0.50.

Metal complexation on tridentate sites is expressed as:



Again, a fraction of the sites is allowed to form tridentate complexes. For fulvic acids this fraction is 0.03, for humic acids 0.065.

#### 4.6.4 Model VII

##### 4.6.4.1 Introduction

Model VII was published by Tipping, with co-workers, in 2011. Model VII is very much similar to Model VI. It also distinguishes fulvic acids (FA) and humic acids (HA) which are treated separately. For each acid, eight different discrete binding sites are used in the model. Site 1 to 4 (type "A") have twice as high concentrations as sites 5 to 8, type "B". The sites have a range of acid-base-properties. Metals bind to these sites, either to one site alone (monodentate), to two sites (bidentate) or to three sites (tridentate). Tridentates are new in Model VI and VII compared to Model V. Also new, compared to Model V, is that for each bidentate and tridentate group there are three sub-groups assumed to be present.

For bidentates and tridentates, a selection of the theoretically possible combinations is used (bidentates: 6 out of 36; tridentates: 8 out of 120). In total, 50 sites are assumed to be present. Binding constants depend on ionic strength and electrostatic interactions. In addition to specific binding, species can accumulate in the diffuse double layer.

##### 4.6.4.2 Equilibria included

For each gram of fulvic acids,  $5.2 \times 10^{-3}$  mol type A groups occur and  $2.6 \times 10^{-3}$  mol type B groups. For humic acids, these numbers are  $3.4 \times 10^{-3}$  and  $1.7 \times 10^{-3}$  respectively. Acid-base reactions for each site as well as mono-, bi- and tridentates are expressed in the same way as for model VI. A fraction of the sites is allowed to form bidentate complexes. For fulvic acids this fraction is 0.42, for humic acids 0.50. For tridentate complexes these numbers are 0.03, resp. 0.065.

#### 4.6.5 Conditional constants for Model V, VI and VII

Conditional constants are calculated in quite the same way in Model V, VI and VII. Conditional constants for *acid-base equilibria* are calculated as follows:

$$K(Z) = K \times e^{2wZ}$$

where:

- Z is the charge of the organic acid;
- w is calculated by :  

$$w = P \times \log_{10}(I)$$

where:

- P is a constant term (different for FA and HA, and different for each model);
- I is the ionic strength.

Therefore, the conditional constant depends on the charge on the organic acids as well as on the ionic strength.

Values for P are listed below.

P	Fulvic acids	Humic acids
Model V	-103	-374
Model VI	-115	-330
Model VII	-119	-196

For the *other equilibria*, the calculation of the conditional constant occurs in a similar way.

## 4.6.6 Diffuse double layer

### 4.6.6.1 Volume of the diffuse double layer

Calculations for the diffuse double layer are the same for Model V as for Model VI and Model VII. The volume of the diffuse double layer is calculated separately for each type of acid, as follows:

$$V_D = \frac{10N_{Av}}{M} \times \frac{4\pi}{3} \times \left[ \left( r + \frac{1}{\kappa} \right)^3 - r^3 \right]$$

where:

- $N_{Av}$  is Avogadro's number;
- M is molecular weight of acid;
- r is the radius of the molecule (0.8 nm for Fulvic acids, 1.72 for Humic acids);
- $\kappa$  is the Debye-Hückel parameter, which is dependent on ionic strength.

Simply applying this formula in situations of low ionic strength and high content of organic acid would lead to artifacts (where volume of diffuse layer can be calculated to be more than 1 liter/liter). Therefore, some "tricks" are implemented to limit the volume of the diffuse double layer to 25% of the total.

### 4.6.6.2 Concentrations in the diffuse double layer

In case the acid has a negative charge (as it has in most cases), positive and neutral species are allowed to be in the diffuse double layer, just enough to make the diffuse double layer electrically neutral. When the acid has a positive charge, negative and neutral species are present. Concentration of species in the diffuse double layer is calculated by assuming that the concentration of that species in the diffuse double layer depends on the concentration in the bulk solution and the charge.

In formula:

$$\frac{[X^{z}]_{DDL}}{[X^{z}]_{solution}} = R^{|z|}$$

where R is calculated iteratively, to ensure the diffuse double layer is electrically neutral.

## 4.7 The database

### 4.7.1 Equilibrium constants

An often underestimated aspect of speciation modelling is the composition of the database with equilibrium constants. The first reason is that values in the literature may vary considerably, even up to a factor of 100 to 1000 (Zuehlke & Byrne, 1984; Giesy & Alberts, 1989). Selecting equilibrium constants is therefore a critical step. To ensure that the database of CHEAQS Next contains a consistent set of correct constants, values were taken from the NIST database 46 (version 8) where available (NIST database 46, 2004). This database has been compiled by the ultimate experts in this field, A.E. Martell and R.M. Smith, and is the electronic follow-up of their printed compilations (Martell & Smith, 1974, 1977, 1982; Smith & Martell, 1975, 1976, 1989).

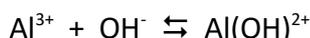
A few other sources were used as well, but only after it was confirmed that for matching constants comparable values were given as in the NIST database.

For the inclusion of constants in the NIST database, fairly critical criteria were applied. However, if a constant has not been selected for the NIST database, it does not necessarily mean that the value is not correct; possibly the information to check the correctness is just incomplete.

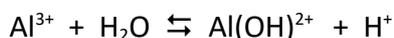
Therefore, it can be assumed that the values taken from the NIST database are most likely correct (within certain uncertainty limits), but this does not mean that the database is complete!

Details about the selection criteria and any conversions made, can be found in the background document about the database, available at the website <http://www.cheaqs.eu>.

A second reason why equilibrium constants often cause confusion is the different formats of equilibrium reactions. Compare e.g.



with



In both equilibria  $\text{Al}(\text{OH})^{2+}$  is formed. In the literature you can find values of  $\log_{10}$  around 9 and around -5. This is because of the difference in the way the equilibria are formulated, the K's differ by a factor of  $10^{14}$  (logs differ by 14). Indeed, because of the water constant. This is the reason you can view equilibrium information as explained in section 3.2.3.

## 4.7.2 Molecular weights

Molecular weights can also be a source of confusion, particularly for multi-atom ions like  $\text{NO}_3^-$ . Nitrate concentrations are sometimes expressed as mg/L  $\text{NO}_3^-$ , sometimes as mg/L N. So 1 mole of nitrate per liter is (rounded) 62 mg/L  $\text{NO}_3^-$  and 14 mg/L N. In CHEAQS Next's database, the atomic weights of ALL atoms in the ion are summed, in this example 62. If you have data of nitrate in mg/L, make sure the molecular weights correspond with CHEAQS Next's. See the previously mentioned database document for details.



## 5 Literature references

- Giesy, J.P & J.J. Alberts (1989). Conditional stability constants and binding capacities for copper(II) by ultrafilterable material isolated from six surface waters of Wyoming, USA. *Hydrobiologia* 188/189, 659 – 679.
- Janssen, R.P.T. & W. Verweij (2003). Geochemistry of some rare earth elements in groundwater, Vierlingsbeek, The Netherlands. *Water Research*, 37, 1320 - 1350.
- Martell, A.E. & R.M. Smith (1974). *Critical stability constants. Volume 1. Amino acids.* Plenum Press, New York.
- Martell, A.E. & R.M. Smith (1977). *Critical stability constants. Volume 3. Other organic ligands.* Plenum Press, New York.
- Martell, A.E. & R.M. Smith (1982). *Critical stability constants. Volume 5. First supplement.* Plenum Press, New York.
- NIST Standard Reference Database 46 Version 8.0 (2004). A.E. Martell & R.M. Smith (eds.), NIST, Gaithersburg, USA.
- Smith, R.M. & A.E. Martell (1975). *Critical stability constants. Volume 2. Amines.* Plenum Press, New York.
- Smith, R.M. & A.E. Martell (1976). *Critical stability constants. Volume 4. Inorganic complexes.* Plenum Press, New York.
- Smith, R.M. & A.E. Martell (1989). *Critical stability constants. Volume 6. Second supplement.* Plenum Press, New York.
- Zuehlke, R.W. & R.B. Byrne (1984). Thermodynamic and analytical uncertainties in trace metal speciation calculations. In: *Complexation of trace metals in natural waters*, C.J.M. Kramer & J.C. Duinker (eds.). Nijhoff/Junk, The Hague.



# Annex I. File specifications

## Input files

Here you find the specifications for the input file. Element # 1 – 3 always must be the first three lines in the file. The other elements can be specified at arbitrary order, but the order given below is best tested.

Regardless of your system settings, always use the decimal point.

Element #	Text	Remarks
1	CHEAQS input file	Must be first line.
2	Version description: CHEAQS Pro (Release P2016.1.0.0)	<ul style="list-style-type: none"> <li>• For compatibility with the older CHEAQS Pro, CHEAQS Next creates the text "CHEAQS Pro".</li> <li>• When creating an input-file, CHEAQS stamps the input file with the current version. In most cases, older files can be read but newer ones never.</li> <li>• Must be line #2.</li> <li>• Depending on the program version the number can be different. Check Help – About.</li> <li>• Do not insert a line break.</li> </ul>
3	Version code: P2016.1.0.0	Must be line #3. Depending on the program version this can be a different number. Check Help – About.
4	Description: <text>	Maximum length of description: 1024 characters.
5	Adsorption: not included <i>or:</i> Adsorption: included; fixed concentration <i>or:</i>  <i>(continued on next page)</i>	<p>This line means adsorption equilibria are not included in the calculations.</p> <p>This line means adsorption equilibria are included in the calculations. Enter a concentration for (=S-OH) in the list of components.</p>

	<p>Adsorption: included; linked to one solid (Al(OH)<sub>3</sub> (s)); ratio 0.05; site (=S-OH) <i>or:</i></p> <p>Adsorption: included; linked to sum of all solids; ratio 0.05; site (=S-OH)</p>	<p>This example show how to include adsorption, and make the concentration of the adsorbens dependent on solution properties. You can link this to a saturation solid as in the example of Al(OH)<sub>3</sub> (s) (in that case, include precipitation equilibria for useful results) or a redox solid (in that case, include redox equilibria for useful results). In this example stands 0.05 for the number of sites per mole of solid. Finally, it should be specified for which adsorbens the equilibrium constants should be used. In the default database, there is one adsorbens called (=S-OH).</p> <p>Similar to above but here the sum of concentrations of all solids is used.</p>
6	<p>Precipitation equilibria: not included <i>or:</i></p> <p>Precipitation equilibria: included</p>	<p>This line means precipitation equilibria are not included in the calculations. Do not insert a line break.</p> <p>This line means precipitation equilibria are included in the calculations. Do not insert a line break.</p>
7	<p>Redox equilibria: not included <i>or:</i></p> <p>Redox equilibria: included</p>	<p>This line means redox equilibria are not included in the calculations.</p> <p>This line means redox equilibria are included in the calculations. Specify the value for the redox in element 11.</p>
8	<p>Ionic strength: calculated <i>or:</i></p> <p>Ionic strength: fixed at 0.1 M</p>	<p>This line means that ionic strength will be calculated based on the composition of the solution.</p> <p>Means that ionic strength is fixed. Number of 0.1 is an example.</p>
9	<p>Organic complexation: not included <i>or:</i></p> <p><i>(continued on next page)</i></p>	<p>This line means organic complexation is not included in the calculations. No line break.</p>

	<p>Organic complexation: included  Model to use: 1  Concentration of C: 2.6  Sites per mg C: 0.000008  Concentration of sites:  0.0000208  Extrapolate: -1  <b>where -1 stands for 'true', 0 for 'false'.</b>  <b>or:</b>  Organic complexation: included  Model to use: 2  Concentration (mg/L C): 3.4  Fraction of fulvic acids: 0.64  <b>or:</b>  Organic complexation: included  Model to use: 3  Concentration (mg/L C): 3.4  Fraction of fulvic acids: 0.64  <b>or:</b>  Organic complexation: included  Model to use: 4  Concentration (mg/L C): 3.4  Fraction of fulvic acids: 0.64</p>	<p>This means organic complexation is included, with model Cabaniss &amp; Shuman. Numbers are examples. In the line "Concentration", do not add a line break.</p> <p>This means organic complexation is included, with Tippings's model 5. Numbers are examples.</p> <p>This means organic complexation is included, with Tippings's model 6. Numbers are examples.</p> <p>This means organic complexation is included, with Tippings's model 7. Numbers are examples.</p>
10	Convergence criterion: 1.0001	Convergence criterion normally should be set to this value ( $1.0001 - 1 = 1E-4 = 0.01\%$ ). More stringent is possible, less stringent is generally not a good idea.
	<i>(continued on next page)</i>	

<b>11</b>	<pre> &lt;name of component&gt;: &lt;number&gt; &lt;(type of input value)&gt; H: .00139 (total concentration) Na: .00119 (total concentration) Mg: .00073 (total concentration) K: .0002 (total concentration) Ca: .00136 (total concentration) e: 1 (free activity) (CO3): .00139 (total concentration) (SO4): .00073 (total concentration) Cl: .00272 (total concentration) </pre>	<p>Element 11 contains the input data for the components. Syntax is given in the column left.</p> <p>Type of input value can be:</p> <ul style="list-style-type: none"> <li>• total concentration;</li> <li>• free concentration;</li> <li>• free activity;</li> <li>• partial pressure (for gases);</li> <li>• not specified; for OH only (occurs when total concentration for OH is given. and must be enclosed by brackets.</li> </ul> <p><b>Example:</b>  Ca: .00136 (total concentration)  (no line break)</p> <p>To enable calculation of pH, specify total concentration for H.</p> <p>Even if you do not include redox equilibria, always specify redox, e.g. as  e: 1 (free activity)  Type of input value for e is always free activity.</p>
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## Output files

Here you find the specifications for the output file. Some elements are not discussed in detail because they are probably not interesting for users. However, if you need more information than given here, please contact me.

Regardless of your system settings, always the decimal point is used

Element #	Text	Remarks
1	CHEAQS output file	
2	Do NOT manually edit this file	
3	Format version: 3	Version 3 is in use since CHEAQS Next version 2015.2. May be increased in the future.
4	<number>	Number of components used in calculations.
	<i>(continued on next page)</i>	

5	<p>For example:  "H", "H", 1, 1, .00139, 3, .00139,  1.5517150132229E-8,  1.39001148370303E-3,  0, 0, 0, 0, 0, 0, 0,  1.39001148370303E-3</p>	<ul style="list-style-type: none"> <li>• Name (between double quotes)</li> <li>• Name to display (differs for redox; between double quotes)</li> <li>• Charge (in this case 1)</li> <li>• Type of component (in this case 1, for cation)</li> <li>• Input value (in this case .00139; note that no leading zero is written to the file)</li> <li>• Input type (in this case 3, total concentration)</li> <li>• Total concentration: .00139 M</li> <li>• Free concentration: 1.5517150132229E-8 M</li> <li>• Calculated mass in solution: 1.39001148370303E-3 M</li> <li>• Ibid. adsorbed: 0</li> <li>• Ibid. precipitated: 0</li> <li>• Ibid. in diffuse double layer for <i>fulvic</i> acids: 0</li> <li>• Ibid. specifically bound to <i>fulvic</i> acids: 0</li> <li>• Ibid. in diffuse double layer for <i>humic</i> acids: 0</li> <li>• Ibid. specifically bound to <i>humic</i> acids: 0</li> <li>• Ibid. sum of organic fractions: 0</li> <li>• Calculated total mass: 1.39001148370303E-3 M</li> </ul>
6	<number>	Number of species used in calculations.
	<i>(continued on next page)</i>	

7	<p>For example:  "<math>\text{H}(\text{CO}_3^-)</math>", 2, 8,  -1, 1, 1, 1, 6, 4, 10.329, 1,  1.2916745359097E-3,  0, 0, 0, 10.1693151686877, 10.329,  1.1782349203521E-3, 0</p>	<ul style="list-style-type: none"> <li>• Name (between double quotes)</li> <li>• Number of 'building blocks'; in this case because <math>\text{HCO}_3^-</math> is formulated as product of two components, H and <math>\text{CO}_3^{2-}</math>.</li> <li>• Type of species (in this case 8, complex)</li> <li>• Charge: -1</li> <li>• The stoichiometric coefficient and number of components: here 1 time component 1 (H) and 1 time component 6 (<math>\text{CO}_3^{2-}</math>).</li> <li>• The number used for the Davies-correction: 4</li> <li>• The equilibrium constant (as <math>\log_{10}</math>): 10.329</li> <li>• The literature reference: 1 (from the list of literature references)</li> <li>• Concentration in solution: 1.2916745359097E-3 M</li> <li>• Concentration in diffuse double layer of fulvic acids: 0</li> <li>• Ibid. humic acids: also 0</li> <li>• If applicable: pointer to the inorganic hydride (for Model 5, 6 and 7): here 0</li> <li>• Conditional equilibrium constant (as <math>\log_{10}</math>): 10.1693151686877</li> <li>• Original equilibrium constant (as <math>\log_{10}</math>): 10.329 (needed because internally conversions are made before the calculations start)</li> <li>• Activity of species: 1.1782349203521E-3 M</li> <li>• If applicable: pointer to the equilibrium in the full dataset.</li> </ul>
8	<number>	Total number of literature references
9	<number>	Number of literature references present in dataset
10	<p>For example:  1, "NIST Database 46 Version 8.0"</p>	Number of reference in list of references and text (between double quotes).
11	Number followed by input information per component plus molecular mass and type of input value.	Input data
12	<(number)>	Number of iterations
	(continued on next page)	

13	<2 numbers>	Charges (first positive charge, then negative charge)
14	<3 numbers>	Volumes: first volume of diffuse double layer of fulvic acids, then volume of diffuse double layer of humic acids, then volume of water (as fraction).
15	(number)	Term used for Davies correction
16	<text>	Description supplied by user
17	<boolean number>	Is ionic strength fixed (-1) or not (0)?
18	<one or two numbers>	If fixed, the fixed value and the calculated value; if not fixed the calculated value.
19	<number>	Convergence criterion e.g. 1.0001 for the default value.
20	<boolean number>	Adsorption included?
21	<boolean number>	Precipitation included?
22		If not included, information about saturation solids that could have been considered.
23	<boolean number>	Redox included?
24	<boolean number>	pH calculated?
25	<boolean number>	Organic complexation included
26	For example: .000234 .000766 -2.73527973343604E-3 3.55271222643213 -1.48716725762096E-3 7.26997475987953 16	Gram fulvic acids per L Gram humic acids per L Charge on fulvic acids (eq/g) Ratio DDL/solution for humic acids Charge on fulvic acids (eq/g) Ratio DDL/solution for humic acids Literature reference
27		Information about gases
28		Several internal links to reconstruct the output information.