

Manual for CHEAQS Next
(64 bits), a program for
calculating CHemical
Equilibria in AQuatic
Systems

Status box

This is the CHEAQS Next (64 bits) manual. This version of the manual corresponds with program version 0.2.1.10 (released December 2023). More topics will be added when appropriate.

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Author: Wilko Verweij

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1. Introduction

1.1. CHEAQS Next's features

This is CHEAQS Next's manual, for the 64-bits version. 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 CaCl₂-solution at pH = 7, the program will tell you that:

- 88% of the Ca is present as Ca²⁺;
- 12% of the Ca is present as CaCl⁺.

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

1.3. Installing the program

The program works on 64-bits versions of Windows computers from Windows 7 to Windows 10. To install the program, take the following steps.

1. Go to the website <https://www.cheaq.eu> and download the latest version of SETUP64.EXE in the download part of the website.
2. Run the program SETUP64; 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 (64 bits) will be created in the directory for program files. That directory will contain the program CHEAQS64.EXE, and two other programs (CLEANUP64.EXE and REGUNREG64.EXE). You will also find an uninstallation program, the raw data files, one language file, the help file CHEAQS64.CHM, a license file and a file with release notes. 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 CHEAQS64.INI will be stored there containing user settings, as well as a language file called LANG.INI. Data files for each user will be created during the first run. The documentation (manual and background document about the database) will be downloaded on demand i.e. when you select the corresponding menu commands (see sections 2.4.4 and 2.6.7).

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. The six icons on top are the entries to a set of menu commands. You can point the mouse over one or press Alt+underlined character to open the menu. When you move the mouse over another icon, or press Alt+ another underlined character, the corresponding menu will appear, as shown for the Options-menu on the next page. Then click one of the buttons or items in the list. You can also 'fix' a menu by clicking on one of the icons. In that case, the menu will not change when you move the mouse over another icon. The program screen also has a statusbar at the bottom.



The program window (left) at startup or when (in this case) Options menu selected.

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 <https://www.cheags.eu>;
- by sending an email to info@cheags.eu;
- on the facebook-page <https://www.facebook.com/CheagsNext>;
- on the YouTube-channel <https://www.youtube.com/@cheagsnext>.

If you subscribe to the CHEAQS Newsletter (in the download area at <https://www.cheags.eu/download.html>), you will receive an email when news is available (approximately 2 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. To close the program, use Alt+F4 or click the [X] in the right top corner of the window.

2.1. The Input Menu

2.1.1. 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', the MSA-method is set as the default method for calculating activities, temperature is set to 25°C, temperature correction is switched off, neutralisation is turned off and convergence criterion is 1×10^{-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 2.1.7). This will create an input file called DEFAULTS.I64 in the default directory for input files. Each time the program starts, these defaults are loaded (visible on the status bar).

2.1.1.1. Input - New - Program defaults

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

2.1.1.2. Input - New - User defaults

User defaults: reads input file DEFAULTS.I64 and replaces current input data with the one from that file. Only available if a file named DEFAULTS.I64 is present in the default directory for input files. If no file with this name is present, this menu command is not available.

2.1.2. 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. This command accepts input files created with the 64-bits edition (*.i64) as well as files created with the 32-bits edition of CHEAQS Next (*.inp) in 2016 or later.

2.1.3. 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 and displayed in a list. To disable this feature, see section 2.5.1.

2.1.4. 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.

2.1.5. 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.

2.1.6. Input - Save input as...

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

2.1.7. Input - Save current input as defaults

Saves current input in the file DEFAULTS.I64, 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. The Calculate Menu

The Calculate Menu at present contains one item: Calculate speciation.

2.2.1. 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 shown on screen. From there, you can save or print the output.

2.3. 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 (but the list may be empty);
- View side by side (but only useful if two or more output files are present);

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).

2.3.1. Output - 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 section 3.2.

2.3.2. Output - 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.

2.3.3. Output - Open recent output file

This command allows you to quickly open a file you recently opened or saved. Up to 9 files are remembered and displayed in a list. To disable this feature, see section 2.5.1.

2.3.4. Output - Save output...

Saves the current output data in an internal format (with default extension .o64). 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... or the command View side by side), after which the user can view, save or print the output.

2.3.5. Output - 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.

2.3.6. Output - 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.

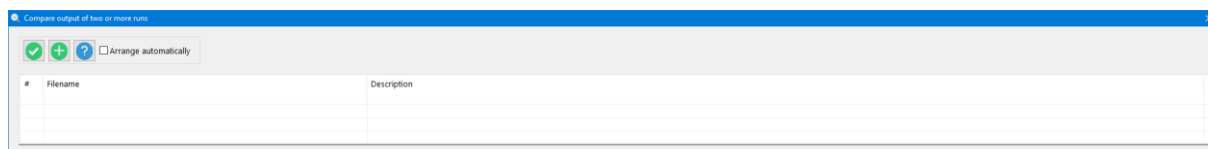
Both these file types can be read by many spreadsheet programs like EXCEL® or OpenOffice Calc®.

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.

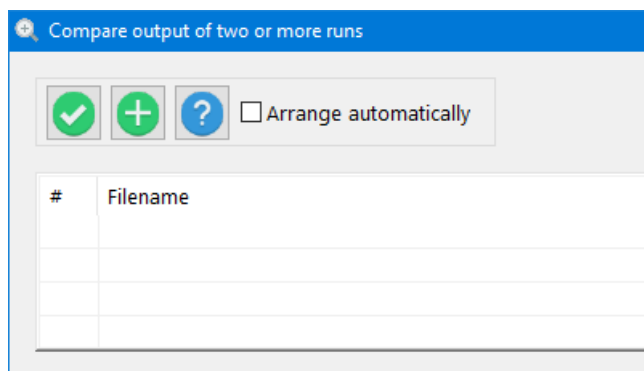
2.3.7. Output - View side by side

The new option 'View side by side' enables the user to view two or more output sets at the same time. Initially, the screen looks like in the figure below.




The window for viewing two or more output sets side by side.

The left part, when zoomed in, looks like in the next figure.



The window for viewing two or more output sets side by side, left part zoomed in.

You can add output sets from existing output files (*.o64) by clicking on the  -icon, after which you can select an output file to open. The filename and description will be displayed in the table. Below you see an example screen with two output sets chosen. In principle there is no limit to the number of output sets that you can view simultaneously.

#	Filename	Description
#1	C:\Users\wilko\AppData\Roaming\CHEAQ564\Output\vc1.o64	VC1
#2	C:\Users\wilko\AppData\Roaming\CHEAQ564\Output\vc2.o64	VC2

View output

Summary:

Fraction	Concentration	Unit	Percentage
Dissolved Ca	1.000E-003	M	100.00%
Total Ca	1.000E-003	M	100.00%

Details:

Species	Concentration	Unit	Percentage	Activity	Unit	Log10(intrinsic β)	Log10(cond)
free Ca 2+	9.892E-004	M	98.92%	7.980E-004	M		
Ca(OH) +	1.692E-009	M	0.00%	1.603E-009	M	1.300	
Ca(CO3) (aq)	4.796E-007	M	0.05%	4.796E-007	M	3.220	
CaH(CO3) +	1.031E-005	M	1.03%	9.770E-006	M	11.529	

View output

Summary:

Fraction	Concentration	Unit	Percentage
Dissolved Mg	1.000E-003	M	100.00%
Total Mg	1.000E-003	M	100.00%

Details:

Species	Concentration	Unit	Percentage	Activity	Unit	Log10(intrinsic β)	Log10(cond)
free Mg 2+	9.105E-004	M	91.05%	7.012E-004	M		
Mg(OH) +	2.866E-008	M	0.00%	2.685E-008	M	2.580	
Mg4(OH)4 4+	2.562E-024	M	0.00%	9.016E-025	M	16.560	
Mg(SO4) (aq)	8.948E-005	M	8.95%	8.948E-005	M	2.260	

Viewing two output sets side by side.

2.4. The Database Menu

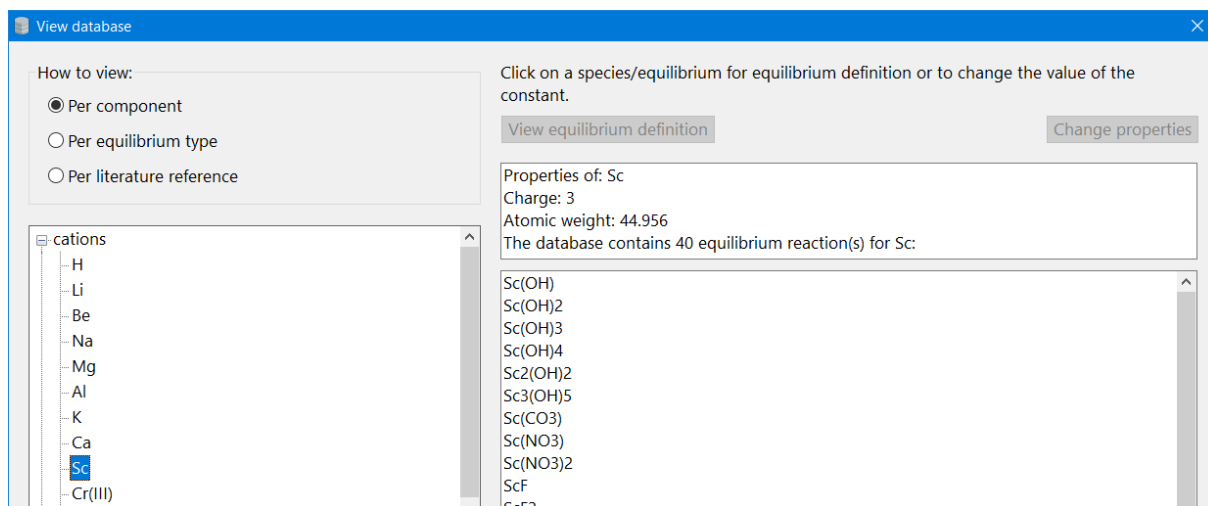
The database menu eventually contains four items; three of them are ready in a first version.

1. View database
2. Manage database [NOT READY YET]
3. About database
4. Database document

Below you will find details about these item.

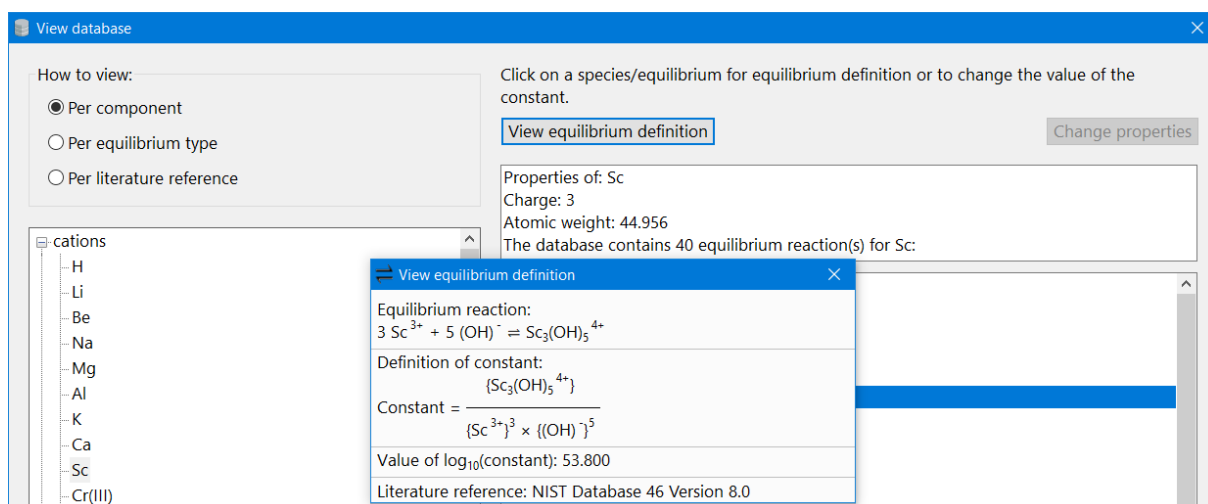
2.4.1. Database - View database

The option 'View database' enables a user to view the contents of the database. You can do this along three lines (see screenshot): per component, per equilibrium type or per literature



Window for viewing database.

reference. If you click on one of the equilibria/species in the list on the right, you can view its equilibrium definition.



Window for viewing database with one equilibrium definition shown.

Note: in future editions it will be possible to modify the properties of a species from here.

2.4.2. Database - Manage database

[NOT READY YET]

2.4.3. Database - About database

The option 'About database' enables a user to view meta-information about the database such as: location and version of original files, presence/absence of a file with user modification of the database, as well as number of elements in each data file, original and modified.

2.4.4. Database - Database document

This option enables you to view the background document about the database. This is easier than downloading the document manually from the website but basically the functionality is the same. In some more detail:

- The first thing the program does is creating a common (i.e. for all users) directory, usually C:\ProgramData\CHEAQ64 (unless the directory already exists).
- Next step is downloading the document from the website, so an active internet-connection is required. If the document already exists, and 'Options - Updates' is turned on (see section 2.5.2), a check is made if a newer version is available. If so, that one is downloaded first.
- The document is opened with the program according to your system's configuration.

2.5. The Options Menu

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

2.5.1. Options - 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.
- Recent folders

2.5.2. Options - Updates

On this page you can indicate whether CHEAQ64 Next should check for updates at start-up. An active internet connection is required to let this work.

2.5.3. Options - File associations

Here you have the option to register or unregister the file types that CHEAQ64 uses: input files (extension .i64) and output files (extension .o64). If you register these file types,

- the files will be shown in Windows Explorer with the CHEAQ64 icons for input resp. output.
- Double-clicking an input file will invoke CHEAQ64, 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.i64, the output file will be name FirstTest.o64. The location for this file is the default location for output files.
- Double clicking an output file will also invoke CHEAQ64, which will open the output file and display the output.
- Right-clicking an output file shows the option 'Print', which will CHEAQ64 print the output with current printing settings (e.g. printer).

2.5.4. Options - Language

At present, CHEAQ64 Next comes with one language file (English). If you (or somebody else) created a file with a different language, you can select that here.

2.5.5. Options - Screen colors

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

2.6. The Help Menu

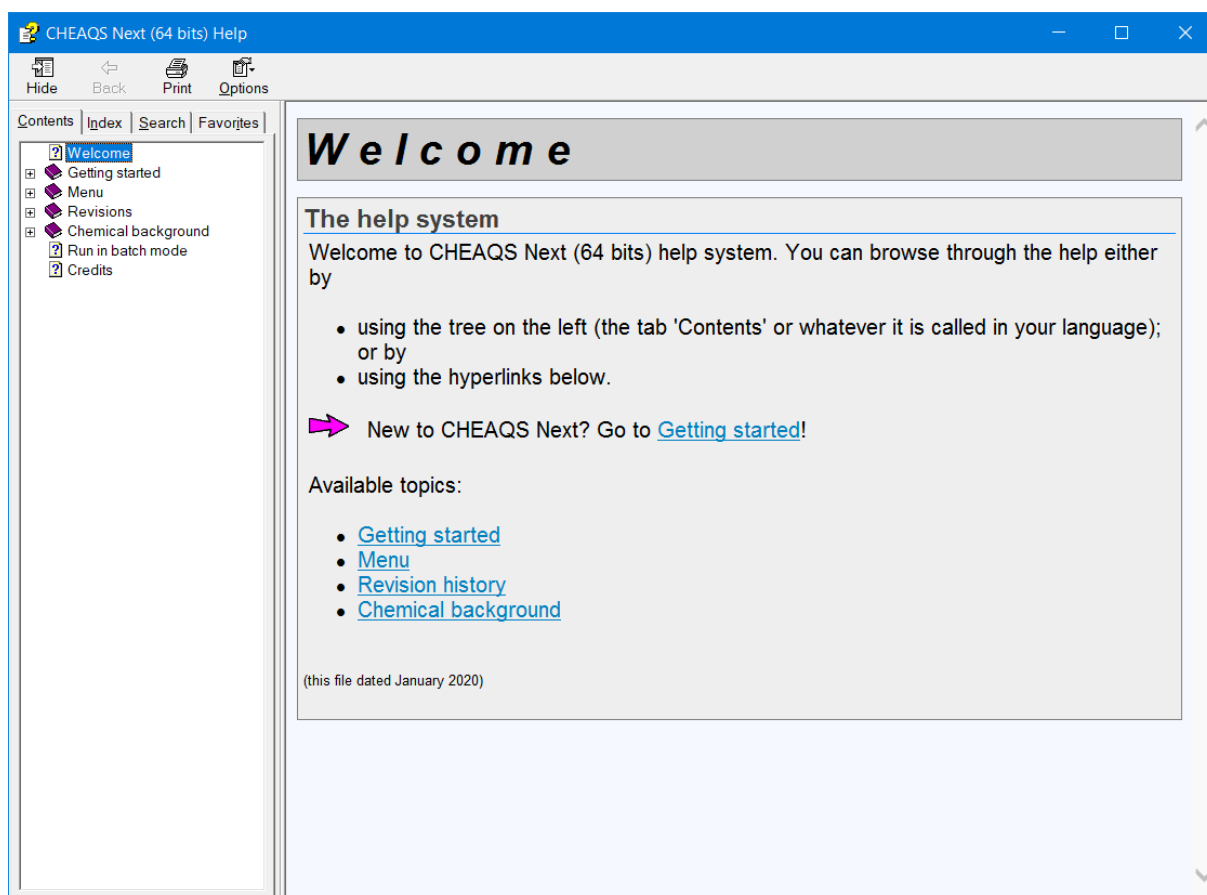
The help menu contains seven items.

2.6.1. Help - Getting started

The first item of the help menu opens the help file CHEAQS64.CHM and selects the topic 'Getting started'. This is a set of help pages intended to help the user getting acquainted with the program.

2.6.2. Help - Contents

This item also opens the help file and displays the Contents tab. See figure below.



The contents page of the help file.

2.6.3. Help - 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.

2.6.4. Help - 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.

2.6.5. Help - Contact

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

- the CHEAQs Next homepage <https://www.cheaqs.eu>;
- send an email to the author (a pop3-email client needs to be configured);
- the CHEAQs facebook page <https://www.facebook.com/CheaqsNext>.
- the YouTube-channel <https://www.youtube.com/@cheaqsnext>.

2.6.6. Help - About

This command displays information about the version number and acknowledgements.

2.6.7. Help - Manual

This option enables you to view the manual. This is easier than downloading the document manually from the website but basically the functionality is the same. See section 2.4.4 for more info about what the program exactly does.

3. In-depth topics

This chapter contains seven 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;
6. batch mode;
7. creating your own language file.

3.1. Editing input

After you click Input - Edit from the menu, 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.

The screenshot shows the 'Edit input' window. On the left, there are two tables: 'Cations' and 'Ligands'. Each table has columns for Name, Concentration, Unit, and Type of input value. The 'Cations' table lists various elements like H, Li, Be, Na, Mg, Al, K, Ca, Sc, Cr(III), Mn(II), Fe(II), Fe(III), Co(II), Co(III), Ni, Cu(I), Cu(II), Zn, Ga, Rb, Sr, Y, Zr, Pd, Ag, Cd, In, Sn(II), and Sn(IV). The 'Ligands' table lists various chemical species like (OH), (H2BO3), (CO3), (NH3), (NO2), (NO3), F, (H2SiO4), (PO4), S, (SO3), (SO4), Cl, (VO4), (CrO4), (MnO4), (H2AsO3), (AsO4), (SeO3), (SeO4), Br, (MoO4), I, (WO4), (CN), (acetate), (catechol), (salicylate), and (phthalate). On the right, there is a text box for 'Enter descriptive text to identify input:' with the value 'testfile for manual'. Below this are tabs for 'General', 'Organic complexation', 'Redox', 'Gases', and 'Adsorption'. The 'General' tab is active, showing options for 'Ionic strength/salt concentration' (Use MSA-model, Use Davies-equation, Calculated, Fixed at: 0.000E+000 M), 'Convergence criterion' (Absolute: 1.000E-004, As percentage: 1.000E-002 %), 'Solids' (Allow solids to precipitate), 'Temperature conversion' (Do not apply, Apply anyhow, Only if ΔH is available for all equilibria, Temperature: 25 °C), and 'Adjusting charge balance' (Do not apply, Choose cation and anion).

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 editing input.



The search button will show a search form where you can enter text to search for a component.



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. There are three items that you can change viz. concentration, unit and type of input value. See figure.

Cations			
Name	Concentration	Unit	Type of input value
H	1.390E-003	M	total concentration
Li	0.000E+000	M	total concentration
Be	0.000E+000	M	total concentration
Na	1.190E-003	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 but you may. 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

Cations			
Name	Concentration	Unit	Type of input value
H	1.390E-003	M	total concentration
Li	0.000E+000	M	total concentration
Be	0.000E+000	g/L	total concentration
Na	1.190E-003	mM	total concentration
Mg	7.300E-004	mg/L	total concentration
Al	0.000E+000	μM	total concentration
K	2.000E-004	μg/L	total concentration
Ca	1.360E-003	nM	total concentration
		ng/L	total concentration

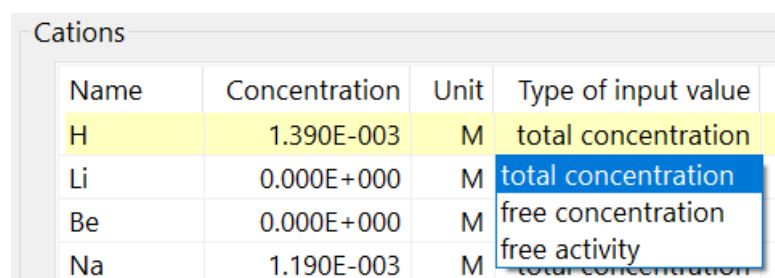
The unit dropdown list.

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.

You can also use the options-button to change units.

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.



Name	Concentration	Unit	Type of input value
H	1.390E-003	M	total concentration
Li	0.000E+000	M	total concentration
Be	0.000E+000	M	free concentration
Na	1.190E-003	M	free activity

The 'type of input value' dropdown list.

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.

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 CO₃, the program will consider the necessity of forming solid CaCO₃. In that case the dissolved concentration of both Ca and CO₃ will decrease and hence the free concentration of Ca and CO₃. That works fine. If you specify 'free concentration' for Ca and 'total concentration' for CO₃, the program will only decrease the dissolved concentration for CO₃, not for Ca. That works fine too. However, if you specify 'free concentration' for both Ca and for CO₃, 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⁻, 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 identify calculation output.

Enter descriptive text to identify input:

Text to describe sample.

Text box for description.

3.1.5. Tab: general

Below the description you find a tab window with five pages. The first one contains several general characteristics of the calculation settings. See figure. Below these options will be discussed.

GeneralOrganic complexationRedoxGasesAdsorption

Ionic strength/salt concentration:
☐ Use MSA-model
☒ Use Davies-equation

☒ Calculated

☐ Fixed at: M

Convergence criterion:

Absolute:

As percentage: %

Solids:

☐ Allow solids to precipitate

Temperature conversion:

☒ Do not apply
☐ Apply anyhow
☐ Only if ΔH is available for all equilibria

Temperature: °C

Neutralisation:

☒ Do not apply
☐ Choose cation and anion:

Tab: general.

Ionic strength/salt concentration

First of all, you can indicate which model should be used for correction at non-zero ionic strength. You can either use the MSA-model or the Davies-equation. If you choose the MSA-model, this model will be used whenever there are sufficient data in the database; if data are missing, the Davies-equation will be used. In case you choose the Davies-equation, you can also 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.

Convergence criterion

Secondly, you can specify the convergence criterion. For most situations, the default value of 1×10^{-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.

Precipitation of solids

Thirdly, 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.

Temperature correction

For temperature correction, three settings are available.

1. No correction
2. Apply anyhow: this means that if for part of the equilibria in your dataset information (ΔH) is available but not for all, temperature correction will be applied for those equilibria for which it is possible and not for the others.
3. Only if ΔH is available for all equilibria: this means that if for part of the equilibria in your dataset information (ΔH) is available but not for all, temperature correction will NOT be applied.

If you select 2 or 3, you can also specify a temperature (in °C) .

Neutralisation

This option allows you to automatically add a cation or anion in case the solution is not electroneutral. If you select this option, you need to specify both a cation and an anion. Note that uncharged components are not allowed.

3.1.6. Tab: organic complexation

The second tab is for specifying organic complexation. You can turn on or off organic complexation. If you turn it on, you can choose from three models. Each of them requires two input parameters: the concentration of DOC (in mg/L of C), as well as the fraction of fulvic acids (these models distinguish fulvic acids and humic acids). For more details please read section 4.6.

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)

Concentration:
(in mg/L of C)

Fraction of fulvic acids:

Tab: organic complexation.

3.1.7. Tab: redox

The third tab is for specifying redox equilibria, See figure on next page. You can in- or exclude redox equilibria; if you include them, you can specify the redox either as pe or in mV. If you type in one, the other one will be updated automatically. If you include them, you can also specify 'concentrations' for redox solids, solids that take part in a redox reaction such as MnO₂.

General Organic complexation Redox Gases Adsorption

Redox:

☒ Include redox equilibria

Redox as pE:

Redox in mV: mV

Redox solids:

Name	Concentration	Unit
MnO ₂ (s)	0.000E+000	M
Cu (s)	0.000E+000	M
PbO ₂ (s)	0.000E+000	M
S (s)	0.000E+000	M

<Type of input value> is always <total concentration>

Tab: redox.

3.1.8. Tab: gases

The fourth tab is for specifying gas pressures. See figure. The unit for gas pressures is atm, so you will not find M or g/L here.

General	Organic complexation	Redox	Gases	Adsorption
---------	----------------------	-------	-------	------------

Gases:

Name	Partial pressure	Unit	
CO2 (g)	3.300E-004	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>

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.

General	Organic complexation	Redox	Gases	Adsorption
---------	----------------------	-------	-------	------------

Adsorption:

Name	Concentration	Unit	
(=S1-OH)	0.000E+000	M	

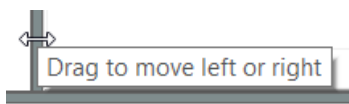
<Type of input value> is always <total concentration>

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 2.2). You see an example screenshot of that screen below (next page). On top you find a row of buttons. Below that on the left, you find a so-called treeview 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.

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, also at next page. Below the picture each button will be discussed.

View output

Do not display graphs

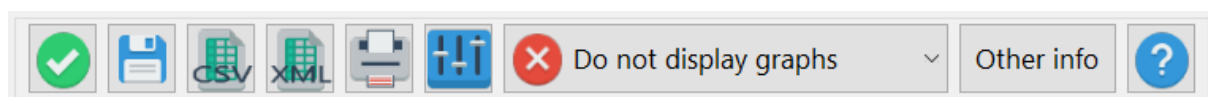
Summary:

Fraction	Concentration	Unit	Percentage
Dissolved Ca	9.815E-004	M	72.17%
Solid Ca	3.785E-004	M	27.83%
Total Ca	1.360E-003	M	100.00%

Details:

Species	Concentration	Unit	Percentage	Activity	Unit	Log10(intrinsic β)	Log10(conditional β)	Literature reference
free Ca 2+	8.983E-004	M	66.05%	6.326E-004	M			
\rightleftharpoons Ca(CO ₃) (aq)	5.496E-006	M	0.40%	5.496E-006	M	3.220	2.915	NIST Database 46 Version 8.0
\rightleftharpoons CaH(CO ₃) +	9.681E-006	M	0.71%	8.868E-006	M	11.529	11.224	NIST Database 46 Version 8.0
\rightleftharpoons Ca(SO ₄) (aq)	6.370E-005	M	4.68%	6.370E-005	M	2.360	2.055	NIST Database 46 Version 8.0
\rightleftharpoons CaCl +	4.306E-006	M	0.32%	3.945E-006	M	0.400	0.248	NIST Database 46 Version 8.0
\rightleftharpoons Ca(CO ₃) (s)	3.785E-004	M	27.83%			8.480	8.175	NIST Database 46 Version 8.0

Example output screen.



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 .o64 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.



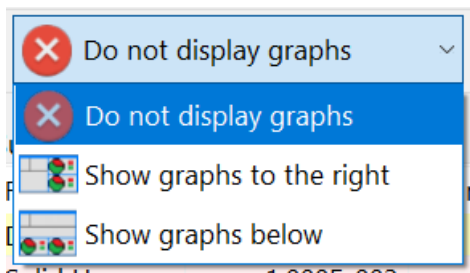
This button will create an XML-file. Such a file can be read by spreadsheet programs like Excel® (starting from version 2002) or OpenOffice Calc® (starting version 4.1). XML-files contain formatting in addition to the numbers that CSV-files contain.



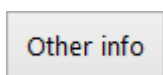
This button will bring up the 'Print output' form that is discussed in the next section.



This button will bring up the Options window.



Open the dropdown-list to display pie graphs for the selected component, one for the summary, one for the details. You can choose to show the graphs on the right of the screen or at the bottom.



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.



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

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 'Example output screen' on previous page, 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.

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. 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. See example below.
2. Concentration: concentration of the species.
3. Unit: unit used for the concentration.
4. Percentage: percentage of the species compared to the total.

\rightleftharpoons View equilibrium definition ×
Equilibrium reaction: $\text{H}^+ + \text{Ca}^{2+} + (\text{CO}_3)^{2-} \rightleftharpoons \text{CaH}(\text{CO}_3)^+$
Definition of constant: $\text{Constant} = \frac{\{\text{CaH}(\text{CO}_3)^+\}}{\{\text{H}^+\} \times \{\text{Ca}^{2+}\} \times \{(\text{CO}_3)^{2-}\}}$
Value of $\log_{10}(\text{constant})$: 11.529
Literature reference: NIST Database 46 Version 8.0

Example of 'view equilibrium definition'.

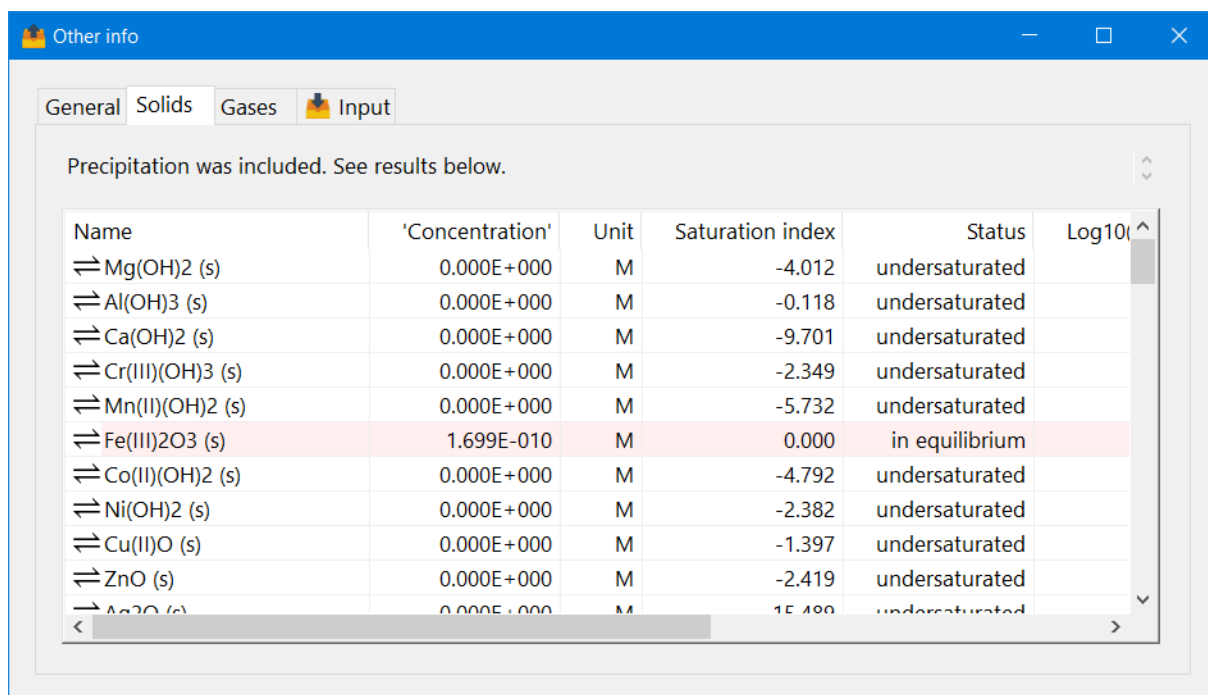
5. Activity: activity of the species. The activity of a species is the "effective concentration" under non-ideal conditions, i.e. ionic strength > 0. The activity is calculated as a product of the concentration and an activity coefficient f . CHEAQS Next uses the Davies-equation or the MSA-model to calculate activity coefficients. See section 4.3.
6. Unit: unit used for the activity.
7. $\text{Log}_{10}(\text{intrinsic } \beta)$: 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. $\text{Log}_{10}(\text{conditional } \beta)$: equilibrium constant under non-ideal conditions i.e. corrected for ionic strength/salt concentrations and temperature.
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.

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

1. General: contains information like number of iterations, ionic strength and charges.
2. MSA-details: contains detailed background information about MSA-model:
 - for each salt, the calculated MSA;
 - for each species, the activity coefficient γ , $\ln(\gamma)$, $\ln(\gamma\text{-Hard Sphere})$, $\ln(\gamma\text{-electrostatic})$;
 - supporting variables, like x (free volume fraction) etc..



Name	'Concentration'	Unit	Saturation index	Status	Log10
$\rightleftharpoons \text{Mg}(\text{OH})_2 \text{ (s)}$	0.000E+000	M	-4.012	undersaturated	
$\rightleftharpoons \text{Al}(\text{OH})_3 \text{ (s)}$	0.000E+000	M	-0.118	undersaturated	
$\rightleftharpoons \text{Ca}(\text{OH})_2 \text{ (s)}$	0.000E+000	M	-9.701	undersaturated	
$\rightleftharpoons \text{Cr}(\text{III})(\text{OH})_3 \text{ (s)}$	0.000E+000	M	-2.349	undersaturated	
$\rightleftharpoons \text{Mn}(\text{II})(\text{OH})_2 \text{ (s)}$	0.000E+000	M	-5.732	undersaturated	
$\rightleftharpoons \text{Fe}(\text{III})_2\text{O}_3 \text{ (s)}$	1.699E-010	M	0.000	in equilibrium	
$\rightleftharpoons \text{Co}(\text{II})(\text{OH})_2 \text{ (s)}$	0.000E+000	M	-4.792	undersaturated	
$\rightleftharpoons \text{Ni}(\text{OH})_2 \text{ (s)}$	0.000E+000	M	-2.382	undersaturated	
$\rightleftharpoons \text{Cu}(\text{II})\text{O} \text{ (s)}$	0.000E+000	M	-1.397	undersaturated	
$\rightleftharpoons \text{ZnO} \text{ (s)}$	0.000E+000	M	-2.419	undersaturated	
$\rightleftharpoons \text{Ag}_2\text{O} \text{ (s)}$	0.000E+000	M	15.488	undersaturated	

Example 'other info' output screen.

- ### 3.3. Printing output

Print output
X

What to print:

☐ Summary only
☐ Details only
☒ Both summary and details

☒ Include other info
☒ Include graphs ☒ Color ☐ B&W

Pages (e.g. 2;5-7;12):

How to print:

Paper size: width: 210 mm
height: 297 mm

Margins: left: 10 mm; right 10 mm;
top: 10 mm; bottom: 10 mm.

Table style:

Font: Cambria 11 pt
 (Sample text)

Print preview
X

What to print:

☐ Summary only
☐ Details only
☒ Both summary and details

☒ Include other info
☒ Include graphs ☒ Color ☐ B&W

Pages (e.g. 2;5-7;12):

How to print:

Paper size: width: 210 mm
height: 297 mm

Margins: left: 10 mm; right 10 mm;
top: 10 mm; bottom: 10 mm.

Table style:

Font: Cambria 11 pt
 (Sample text)

Example of window for printing output.

The 'what'-area enables you:

- to print summary only, details only or both;
- to include other info (see sub-section above);
- to include graphs and to choose between color and black/white;
- to select the range of pages you want to print. Use - to set ranges (for example: 2-4) or ; to separate ranges (for example 2-4; 6-9; -3; 2-).

The 'how'-area enables you:

- to select a different printer
- to select printer properties (including portrait/landscape);
- to change printer margins;
- to select a table style;
- to select a font and font size for printing.

On the right you see a print preview, with buttons for selecting a different page to preview.

3.4. pH-calculations

CHEAQS Next can either perform calculations at a fixed pH, or it can calculate the pH for you. This section deals with the latter situation. 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 Na_2CO_3 at a pH of 7. Wrong, because we know that this is a 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 2.1.1.1).

Specify the following values and types of input value:

- H: 1E-7, free activity (the default);
- Na: 2E-3, total concentration;
- CO_3 : 1E-3, total concentration.

Return to the main menu, run the calculation 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 CO₃ 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 ⁺	3.234E-11 M	
HCO ₃ ⁻	3.487E-4 M	
H ₂ CO ₃	2.268E-8 M	(note stoichiometric coefficient of 2!)
NaHCO ₃	3.094E-7 M	

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

Similarly for OH:

free OH⁻ 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 NaHCO₃. 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
- CO₃: 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 9.994E-4 eq. This is how it should be! If you close the 'Other info', you can see that total H is 1E-3 which is exactly what you entered. (If you sum all the species as above, you will find 1.002E-3 of H⁺ and 2E-6 of OH⁻).

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

Sample 3

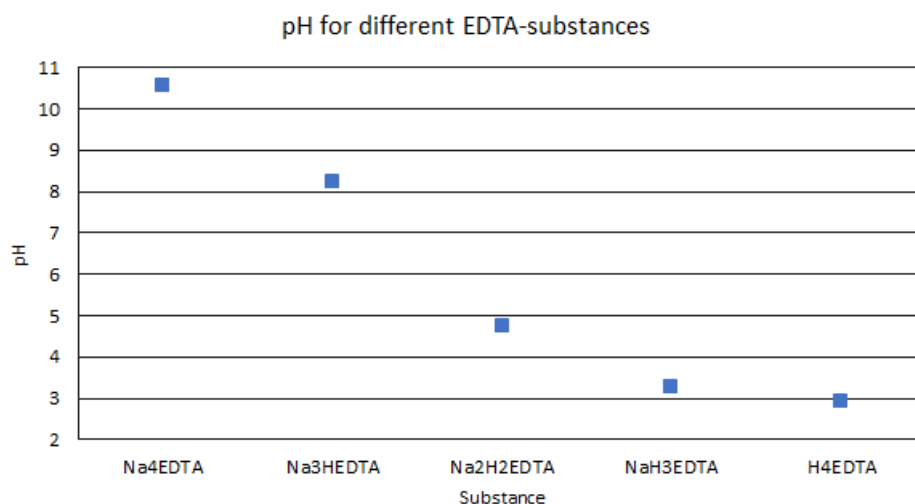
For sample 3 we are going to calculate the pH of EDTA-solutions, starting with Na₄EDTA, step by step replacing each Na by a H. Because the deprotonated EDTA-ion has a charge of -4, we need 4 Na ions for each EDTA-ion. In the tabel below we find the required input for the five cases. Note that 'type of input value' for H always has to be set to 'total concentration'.

Compound	Na	H	EDTA
Na ₄ EDTA	4E-3 M	0	1E-3 M
Na ₃ HEDTA	3E-3 M	1E-3 M	1E-3 M
Na ₂ H ₂ EDTA	2E-3 M	2E-3 M	1E-3 M
NaH ₃ EDTA	1E-3 M	3E-3 M	1E-3 M
H ₄ EDTA	0	4E-3 M	1E-3 M

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

Compound	{H+}	pH
Na ₄ EDTA	2.755E-011 M	10.56
Na ₃ HEDTA	6.157E-009 M	8.21
Na ₂ H ₂ EDTA	1.803E-005 M	4.74
NaH ₃ EDTA	5.425E-004 M	3.27
H ₄ EDTA	1.213E-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

[NOT READY YET]

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 2.5.3).

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: `cheaqs64.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. You can specify three types of output files: the internal format o64 (default), .csv or .xml-files.
2. You can also instruct CHEAQs to start, run a series of input files, save the output for each input file, and quit. Syntax: `cheaqs64.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.You need to use full paths for both input and output files. If one of the filenames contains spaces, both filenames have to be embedded between double quotes.
3. You can also instruct CHEAQs to start and read one input file. Syntax: `cheaqs64.exe <input file name>` (without the "<" and ">").

3.7. Changing language

3.7.1. How it works

During installation

During installation, a directory is created under the Program Files, like C:\Program Files\CHEAQs Next. The directory contains a sub-directory 'Languages', by default with two files, ODEFAULT.LANG and the Czech file LANG_CZ.LANG.

During first run

During the first run, a directory is created like C:\Users\<UserName>\AppData\Roaming\CHEAQs64; the file ODEFAULT.LANG is copied to this directory and renamed LANG.INI. To use the Czech file, please refer to paragraph 2.5.4.

During any run

The program reads all texts from the file LANG.INI. The only exception is the text that you see when you click Help - About. There is no way to change this text.

3.7.2. How you can make your own file

Before you start, choose a text editor that can handle Unicode-files. Open the file LANG.INI and familiarise with how it looks. The first line contains a description of the language in the file; by default 'English (default)'. In addition, you see the names of sections in the file e.g.:

[MAINMENU]

[INPUTMENU]

[CALCMENU]

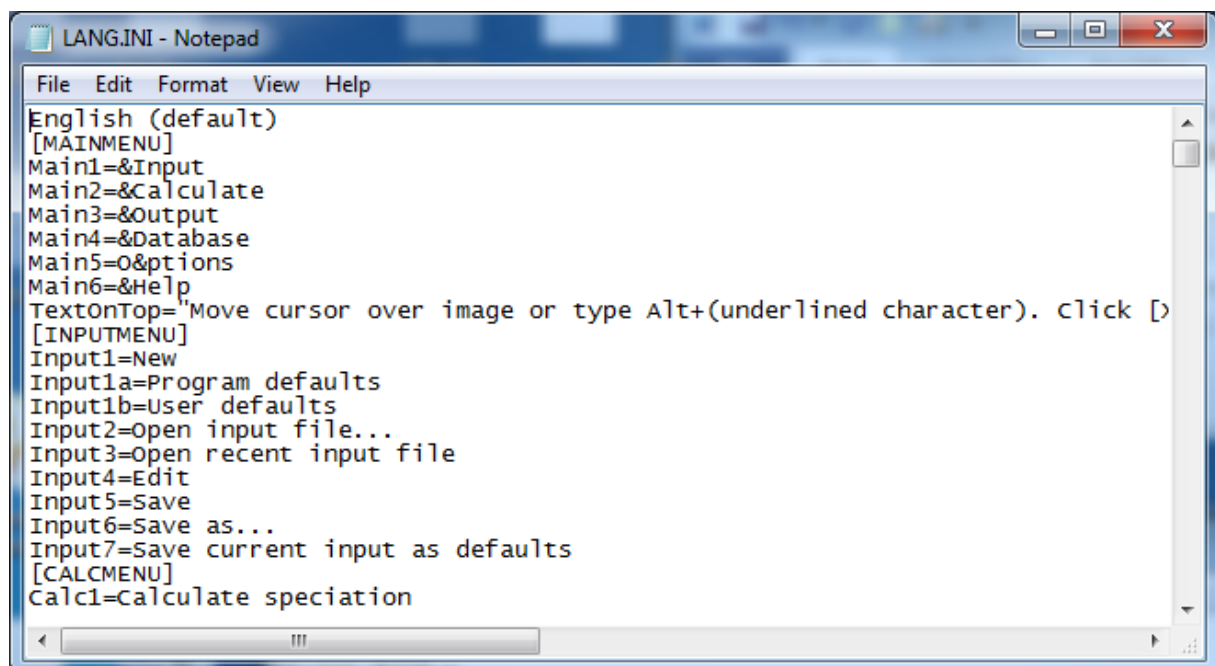
These sections contain keys and values e.g. in the section [MAINMENU]:

Main1=&Input

Main2=&Calculate

Main3=&Output

Etc. See the Figure below.



LANG.INI when edited with Notepad.

The three texts given in the example above are the texts on the main screen, where the '&' sign implies that the following character is displayed as underlined and can be invoked by pressing Alt + the underlined character. Another example: the window to change your language looks like shown below (next page).

The corresponding parts in the file LANG.INI are:

[Options]

OptCaption=Options

CaptionTab1=Remember

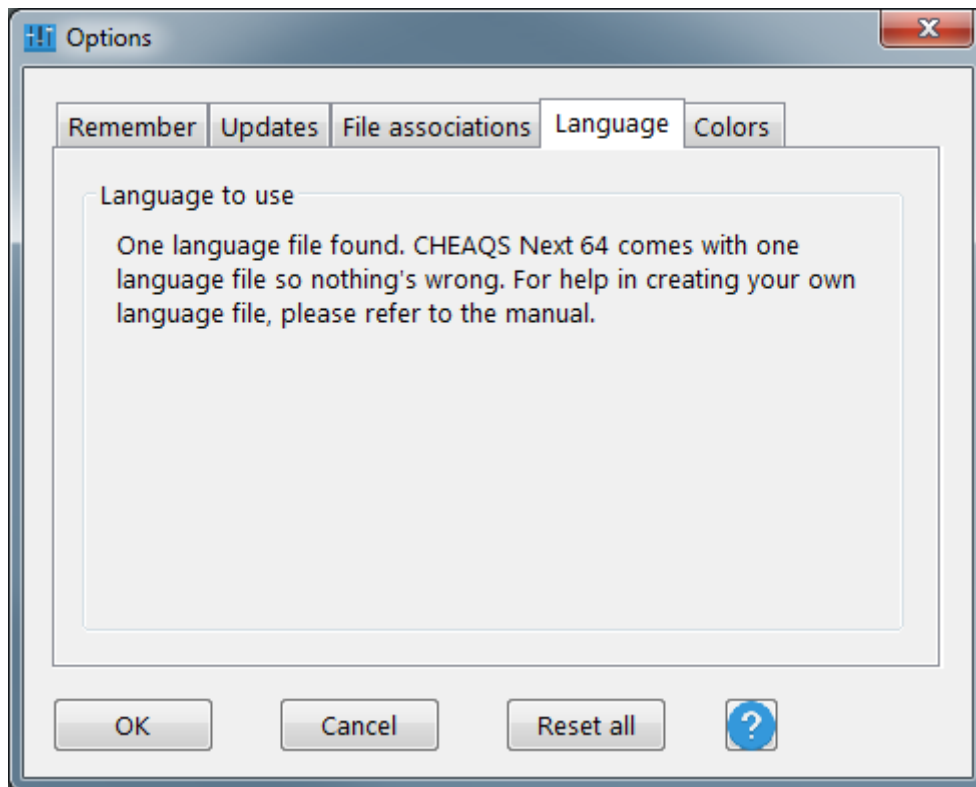
CaptionTab2=Updates

CaptionTab3=File associations

CaptionTab4=Language

CaptionTab5=Colors

GroupBox4=Language to use



Options window as built up using the texts from LANG.INI.

LangFileOne=One language file found. CHEAQS Next 64 comes with one language file so nothing's wrong. For help in creating your own language file, please refer to the manual.

CmdBtn-1=OK

CmdBtn-2=Cancel

CmdBtn-3=Reset all

To create your own file, proceed as follows:

1. change the description of the language in the first line;
2. change all other texts after the '='-sign; leave everything before up to and including the '='-sign exactly as it was;
3. save the file;
4. test it. For displaying the new texts the texts on the main screen it is necessary to restart the program.
5. copy the file to C:\Program Files\CHEAQS Next\Languages with extension .LANG;
6. start the program and choose Options-Language to use.

It is important not to use double quotes in your texts.

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). CHEAQS offers two ways for activity corrections: the Davies-equation and the MSA-model.

In summary:

- The Davies-equation is a semi-empirical extension of the Debye-Hückel-equation. It can be applied to all ions but at higher ionic strengths the calculated values may not be correct anymore.

- The MSA-model has a solid theoretical background, gives reliable data up to high salt concentrations but the required data are not yet available for all salts.

4.3.1. The Davies-equation

The Davies equation yields activity coefficients γ (sometimes called f):

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

where:

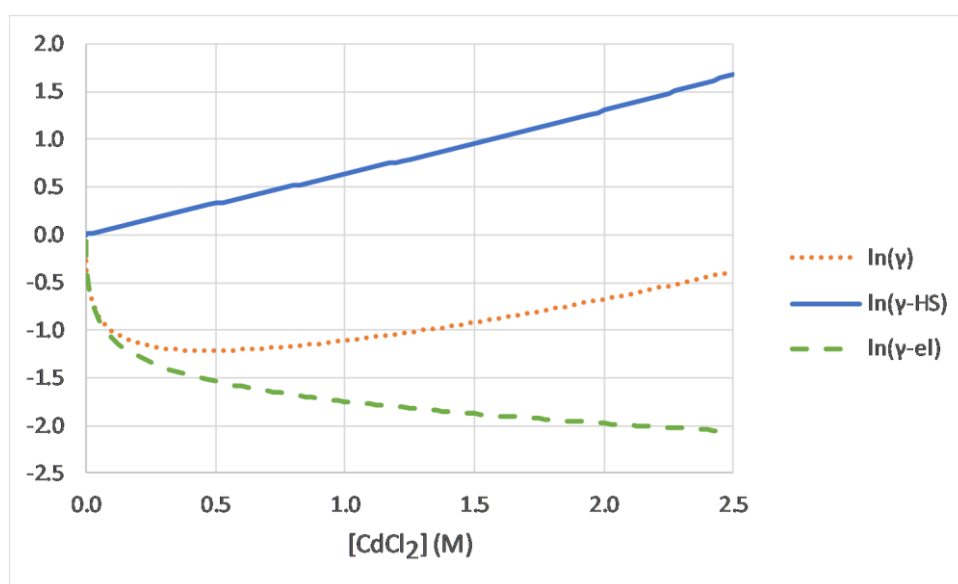
- z is the charge of the species;
- I is the ionic strength.

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).

4.3.2. The MSA-model

The MSA-model calculates the activity coefficients γ with this formula $\ln(\gamma_i) = \ln(\gamma_i^{\text{HS}}) + \ln(\gamma_i^{\text{el}})$ where γ_i consists of a hard-sphere part and an electrostatic part. The hard-sphere part describes effects due to excluded volume, while the electrostatic part takes into account effects of Coulomb interactions between ions. When the salt concentration increases, the term $\ln(\gamma_i^{\text{HS}})$ increases more or less linearly, while the term $\ln(\gamma_i^{\text{el}})$ decreases sharply initially, and then decreases slowly at higher concentration. The sum term $\ln(\gamma_i)$ decreases initially, and then increases (see figure for CdCl_2 with on the X-axis the concentration of CdCl_2 in M). Details about the method can be found in Simonin, 2017. The implementation of this model in CHEAQS is described by Verweij & Simonin (2020).



Elements of $\ln(\gamma)$ for Cd^{2+} .

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). 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). For those equilibria for which ΔH data could be found, it was added to the CHEAQS database. The program can convert the constants from 25°C to other temperatures using the Van 't Hoff-equation (Van 't Hoff, 1884):

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

When you edit the input you can specify the temperature. If you select a temperature different than 25°C, you can choose between:

- no correction for temperature;
- only correction if ΔH is available for all equilibria in the dataset;
- correct always if ΔH is available. That means that for some equilibria (those with ΔH available) the constant will be corrected, for others it will not.

4.5. Modelling adsorption

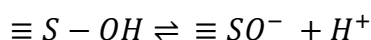
In addition to the "normal" variations in reported values for equilibrium constants, adsorption equilibrium constants have special uncertainties related to the variation in composition of different adsorbentia. Therefore, it is not possible to model adsorption equilibria the way you can model other types 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

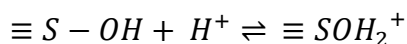
CHEAQS Next models adsorption by using the surface complexation model (Schindler & Stumm, 1987). This model uses many aspects of coordination chemistry and equilibrium theory which are so essential to equilibrium modelling in aquatic systems. The model supposes that adsorption sites can be represented 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 later]

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.

Three models are used in CHEAQS. These models are designed by Tipping and co-workers (Model V, VI and VII).

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.

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



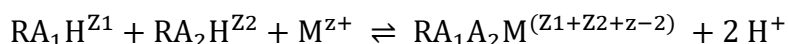
where RA is FA or HA.

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

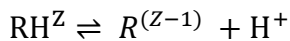
Model VI was published by Tipping in 1998. Model VI, just like Model V, distinguishes fulvic acids (FA) and humic acids (HA) which are treated separately. For each acid, eight different discrete binding sites are used in the model. Site 1 to 4 (type "A") have twice as high concentrations as sites 5 to 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.

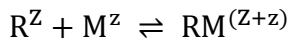
4.6.3.2. Equilibria included

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



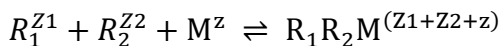
where R is FA or HA.

Metal complexation on monodentate sites is expressed as:



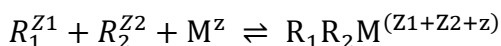
where M represents a free metal ion or its monohydroxide. Tipping lists values for constants for several metals. These are included in CHEAQS Next's database.

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, 5.2×10^{-3} mol type A groups occur and 2.6×10^{-3} mol type B groups. For humic acids, these numbers are 3.4×10^{-3} and 1.7×10^{-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);
- κ 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).

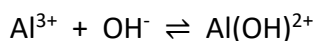
A few other sources were used as well, but only after it was confirmed that for matching constants comparable values were given as in the NIST database.

For the inclusion of constants in the NIST database, fairly critical criteria were applied.

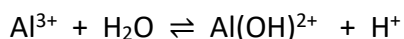
However, if a constant has not been selected for the NIST database, it does not necessarily mean that the value is not correct; possibly the information to check the correctness is just incomplete. Therefore, it can be assumed that the values taken from the NIST database are most likely correct (within 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.

See also Twiss *et al.* (2001) for an interesting paper on where calculation of constants can go wrong.

4.7.2. Molecular weights

Molecular weights can also be a source of confusion, particularly for multi-atom ions like NO_3^- . Nitrate concentrations are sometimes expressed as mg/L NO_3^- , sometimes as mg/L N. So 1 mole of nitrate per liter is (rounded) 62 mg/L 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

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6. Credits

I like to thank the following people and communities:

- Jean-Pierre Simonin (CNRS, Paris, France) for help in implementing the Mean Spherical Approximation model;
- The Pelles C community, FreeBasic community and in earlier days the Powerbasic community;
- paomedia for most of the icons (<https://github.com/paomedia/small-n-flat>);
- Pat Russell for the Newton Raphson method (link no longer working);
- Someone who wishes to stay anonymous for the Czech translation;
- and of course the CHEAQs community for all their suggestions over the years...

Annex I. File specifications

I.1. Input files

Here you find the specifications for the input file. Element # 1 and 2 always must be the first two lines in the file. The other elements can be specified at arbitrary order, but the order given below is the only order which is tested.

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

Input files can be read by CHEAQS in both Unicode and ANSI-format (but CHEAQS creates only files in Unicode)

Element #	Text	Remarks
1	CHEAQS NEXT (64 bits) input file	Must be first line.
2	Format version: 1	In the future this version number may increase.
3	Description: <text>	Maximum length of description: 1024 characters.
4	Ionic strength: calculated	This line means that ionic strength will be calculated based on the composition of the solution.
	Ionic strength: fixed at 0.1 M	Means that ionic strength is fixed. Number of 0.1 is an example.
5	Ionic strength model: 1 'Davies	Model used for ionic strength correction; 1 is Davies, 2 is MSA
	Ionic strength model: 2 'MSA	
6	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.
7	Temperature: 25 °C	Temperature used for calculations. Number of 25 is an example. Should be between 0 and 100 (but reliability above 40 is questionable).
8	Temperature correction: 0	• 0: no correction;
	Temperature correction: 1	• 1: only if possible for all included equilibria;

	Temperature correction: 2	<ul style="list-style-type: none"> 2: apply to equilibria for which it is possible; skip for other equilibria
9	Force neutral solution: 0	No charge balance adjusting is done
	Force neutral solution: 1 Cation to neutralise: Na Anion to neutralise: Cl	Will add cation or anion to adjust the charge balance. Names of cation and anion must match exactly the names in the file COMPON.D64 and do not include charges.
10	Precipitation equilibria: not included	This line means precipitation equilibria are not included in the calculations.
	Precipitation equilibria: included	This line means precipitation equilibria are included in the calculations.
11	Redox equilibria: not included	This line means redox equilibria are not included in the calculations.
	Redox equilibria: included	This line means redox equilibria are included in the calculations. Specify the value for the redox in element 14.
12	Adsorption: not included	This line means adsorption equilibria are not included in the calculations.
	Adsorption: included; fixed concentration	This line means adsorption equilibria are included in the calculations. Enter a concentration for (=S-OH) in the list of components.
	Adsorption: included; linked to one solid (Al(OH) ₃ (s)); ratio 0.05; site (=S-OH)	<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)₃ (s) (in that case, include precipitation equilibria for useful results) or a redox solid (in that case, include redox equilibria for useful results).</p> <p>In this example stands 0.05 for the number of sites per mole of solid.</p>

		<p>Finally, it should be specified for which adsorbents the equilibrium constants should be used. In the default database, there is one adsorbents called (=S-OH). Should be one line in the file (so no line breaks).</p>
	Adsorption: included; linked to sum of all solids; ratio 0.05; site (=S-OH)	Similar to above but here the sum of concentrations of all solids is used. Should be one line in the file (so no line breaks).
13	Organic complexation: not included	This line means organic complexation is not included in the calculations.
	Organic complexation: included Model to use: 2 Concentration (mg/L C): 3.4 Fraction of fulvic acids: 0.64	This means organic complexation is included, with Tippings's model 5. Numbers are examples.
	Organic complexation: included Model to use: 3 Concentration (mg/L C): 3.4 Fraction of fulvic acids: 0.64	This means organic complexation is included, with Tippings's model 6. Numbers are examples.
	Organic complexation: included Model to use: 4 Concentration (mg/L C): 3.4 Fraction of fulvic acids: 0.64	This means organic complexation is included, with Tippings's model 7. Numbers are examples.
14	<name of component>: <number> <(type of input value)> H: 0.00139 (total concentration) Na: 0.00119 (total concentration) Mg: 0.00073 (total concentration) K: 0.0002 (total concentration) Ca: 0.00136 (total concentration) e: 1 (free activity) (CO3): 0.00139 (total concentration) (SO4): 0.00073 (total concentration) Cl: 0.00272 (total concentration)	<p>Element 14 contains the input data for the components. Syntax is given in the column left. Type of input value can be:</p> <ul style="list-style-type: none"> • total concentration; • free concentration; • free activity; • partial pressure (for gases); • not specified; for OH only (occurs when total concentration for OH is given). <p>and must be enclosed by brackets.</p> <p>Example:</p>

		<p>Ca: 0.00136 (total concentration)</p> <p>To enable calculation of pH, specify total concentration for H, even if it is 0. For example, to calculate the pH of a 0.1 M NaOH-solution, specify:</p> <p>H: 0 (total concentration) Na: 0.1 (total concentration) (OH): 0.1 (total concentration)</p> <p>Type of input value for e is always free activity; activity of e needs to be specified only if redox equilibria are included.</p>
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I.2. Output files

No specification of the output file format is given here. Easier to understand are the also supported .csv and .xml-files.