

GRFIT

A PROGRAM FOR SOLVING SPECIATION PROBLEMS:
EVALUATION OF EQUILIBRIUM CONSTANTS,
CONCENTRATIONS AND OTHER PHYSICAL PARAMETERS.

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1. INTRODUCTION

GRFIT is a program written for IBM-PC computers working under DOS. It solves solution speciation problems in heterogeneous and in homogeneous systems. It is specially written for evaluating concentrations, thermodynamical equilibrium constants and - depending on the chosen double layer model - capacities or site densities as well. Today a lot of different programs exists, that are written in PASCAL, BASIC or FORTRAN. Most of them have been adapted to personal computers. The most favored by solution and surface chemists working on a personal computer are "LETAGROP"(1), "MICROQL"(2), "FITEQL"(3). For determining equilibrium constants, these programs have been very powerful tools during the last decade. However, the usefulness of these programs are limited, firstly because they are not user-friendly, secondly because they have no graphical support to compare the calculated model with their experimental data, thirdly because they are limited to experimental sets of observations, and fourthly because they do not have the possibility to test and to proof a model before making any calculations.

GRFIT is not a speciation-program with a database for modeling environmental systems and does not replace programs like "MINTEQA2"(4), but it supports solution-chemists by solving their speciation calculations.

GRFIT distinguishes between 6 different model types:

- A) Evaluation of equilibrium constants and equilibrium speciation in systems at constant ionic strength.
- B) Evaluation of equilibrium constants and equilibrium speciation of systems at variable ionic strength, with help of the Davies-Equation as given by Baes and Mesmer (5).
- Evaluation of equilibrium constants and equilibrium speciation involving both, surface equilibriums and equilibriums in homogenous solution. The surface potential are evaluated, C) on the bases of the Constant

Capacitance Model by Schindler, D) on the Diffuse Layer Model by Gouy and Chapman, E) on the Stern Layer Model, and F) on the Triple Layer Model.

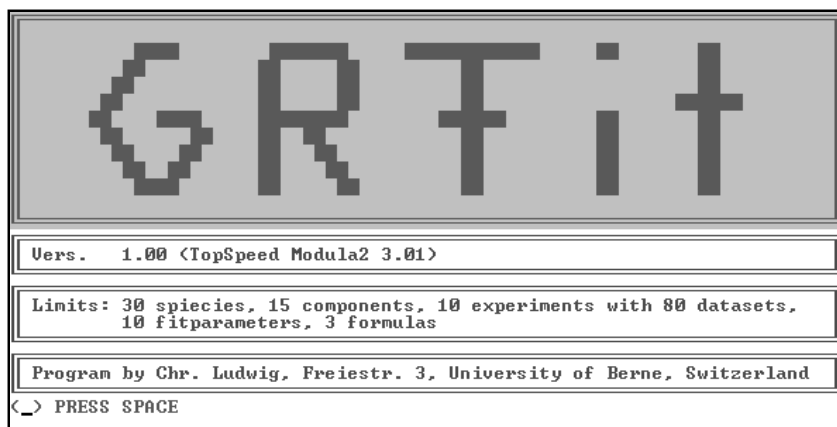
2. The Program Language

GRFIT is written in Modula2 and compiled by using the Top Speed Multi-Language Programming Environment by JPI (Jensen & Partners International). This language has been developed by N. Wirth the father of Pascal. Modula2 is a very powerful tool that allows you to program your own commands, procedures and to make your own libraries and objects. This has the advantage of writing programs that are easier to change, to expand, and to link with libraries from your colleagues, who are working in the same field. With Top Speed it's even possible to mix program languages.

3. How do I start the Program?

To start GRFIT two files are needed. On one hand the main-program "GRFIT.EXE" and on the other hand an ASCII-file with the name "STANDARD.GRF". "STANDARD.GRF" has to be in your working-directory. Some general parameters are loaded from this file while starting up the main-program. For the structure of this file look in the chapters "Set General Parameters" and "How to Define Functions". If there is no "STANDARD.GRF" or if you have lost it, then generate an empty ASCII file with the same name. "STANDARD.GRF" has to be in your working directory. You can start the program itself by giving a path. Having started the program the menu shown in Fig. 1 appears, in which some input limits are displayed. To reach the main menu one has to press any key (e.g. SPACE).

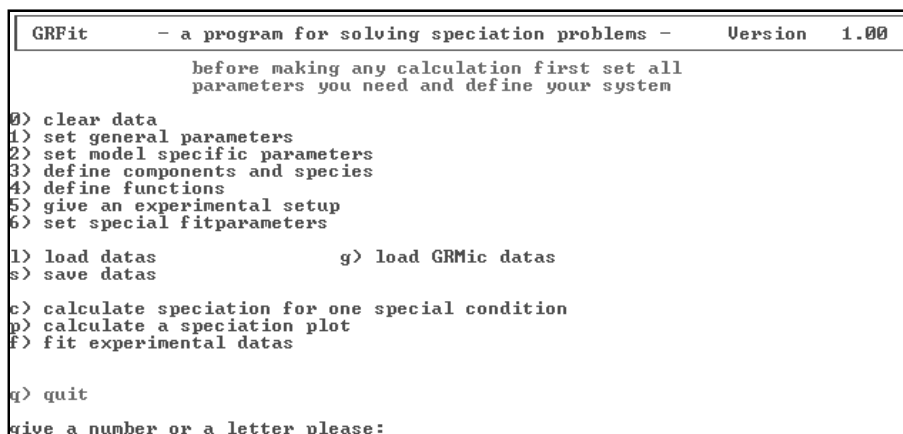
Fig. 1



Having pressed a key, Fig. 2 is displayed.

4. The Menu Structure of GRFIT

Fig. 2



The menu is split into three parts:








- I) The input of your speciation problem (0 to 6).
- II) Loading and saving features for all your input data (l, s and g)
- III) The calculation of your system (c, p, and f).


In general, if a new system has to be defined, one is working through one menu point item number after the other, starting with one. Menu point item number zero is already performed by starting up the program. The menus are nearly self explanatory.

4.1 How to Define Your Problem

Before one starts the program one should have an idea about what a speciation calculation is and how one can describe chemical equilibriums in a matrix form. The mathematical part of the program is discussed elsewhere (2). In the following sections all the features of the program will be discussed. As an example the speciation of copper(II) and of its adsorption onto TiO_2 (anatase) is used (6).

4.1.1 Masks and Tables

To simplify and to make the input more user-friendly special masks and tables have been defined. Masks are used to make an input of words and numbers like in the Fig. 3. If the program has already opened a mask, the user is allowed to move up and down using the cursor functions  and . Pressing the  key one can change from the OVERWRITE MODE into the INSERT MODE. The cursor functions  and  are used to move right or left in the text. To delete fields one can press "Ctrl Y". To delete only the letters behind the cursor position one can press "Ctrl Z". The  key or the BACKSPACE () key can also be used to delete. The program interprets every input as a string and transforms it into the correct form such as INTEGER-, CARDINAL-, REAL-, LONGREAL numbers or other useful TYPES. A mistake in the input field is indicated with a beep and one can not leave the field until the mistake is corrected. (Do not make spaces before, in between, or after an input, because the transformation into the correct TYPES is then not possible and you can not leave the input field).

A second user-friendly input form are the tables, shown in Fig. 5 and 6. They work in the same way as the masks, but the structure is in the form of a worksheet, with columns and rows. The commands used for the masks can also be used for the tables. To move from an input field to the next right, one uses the TAB () key and to go to the left, one presses SHIFT TAB. The RETURN (or ENTER) key moves the cursor to the beginning field of the next row, if there is a next one;

otherwise the cursor moves to the beginning of the same row. To insert and delete rows the keys **F1** and **F2** are used. Masks and tables can be left by pressing the "GO ON" key **F10**. The masks and tables can be left from every position. This position is stored in memory. When the mask is called up later the cursor position will be the same as before. If the mask has more columns than can be shown on the screen, the screen scroll utility is automatically used when you press the TAB or SHIFT TAB key to move to the next column that is not displayed on the screen.

4.1.2"1) set general parameters"

By choosing menu point item number one, Fig. 3 appears on the screen. Some of the following parameters are not independent of features, which will be discussed in later chapters.

Fig. 3

```

GRFit - parameter
help for adapting surface-model:
0) Solution Speciation
1) Davies-Equation after Baes & Mesmer (for 1:1 electrolyt.)
2) Constant Capacitance Model by Stumm & Schindler
3) Diffuse Layer Model by Gouy & Chapman
4) Basic Stern Model
5) Triple Layer Model by Stern

choose model : 2
filename for speciation :
startvalue x (-LOGICl, small) : 2.
endvalue x (-LOGICl, big ) : 10.
stepwidth : 0.3
nr. of the component on y-axis : 3
nr. of component on x-axis : 4
1 = %, 2 = [concl] : 1
1 = graphic, 2 = no graphic : 1
1 = no print, 2 = IBM, 3 = HP: 1
how many experiments ? : 2
draw multiplot (1-3-10-8 etc.) : 1-2
1 = mtot, 2 = dil, 3 = dilspline: 2

GO ON --> f10  SAVE PARAMETERS --> f3  LOAD PARAMETERS -->f4

```

choose model

There is some help on the screen for choosing the correct models. "Solution Speciation": this speciation calculation is specifically for homogenous solutions. That means there is no layer model used, which takes the electrostatic effects of a surface into account. Of course, precipitation curves can be calculated using the precipitate as a component. The "Davies Equation" uses the "A" and "B" factors to make an approximation for a Log(K) value at another ionic strength. Log(Q) is then the corrected Log(K):

$$\text{Log}(Q) = \text{Log}(K) + \frac{A\sqrt{I}}{1+\sqrt{I}} + BI \quad [1]$$

This formula should be used only for 1:1 electrolytes. The A and B factors are given in Baes and Mesmer (5). In the following the famous layer models can be chosen to do modelling work. The theory behind these models is well described by Westall (2,3).

filename for speciation

This field is used to write ASCII-files, which contain are the speciation results. This feature allows the user to transfer the results into other programs to make high resolution graphics or to make tables. The file is written if a name and the extension is given (name.prn). If the field is empty no file is created. Using twice the same name the older file is automatically overwritten. In general the structure of the ASCII output depends on the definition of the screen output. The results one gets by choosing the main menu "p) calculate a speciation plot" are identical with the results in the ASCII file. How the structure of the file is changed for the different features is discussed later for every feature itself.

startvalue x, endvalue x and stepwidth

With these parameters you define the x-range of your graphic. Usually on the x-axis the pH is plotted. The startvalue gives the limit at low pH and the endvalue at high pH. With the stepwidth, the pH increments are calculated to define at which pH a speciation calculation has to be done. That is the way to change the resolution of the speciation calculation.

nr. of the component on y-axis

This parameter has different effects. First it controls the range of the y-axis. Second, it is used to indicate which component for the plot is of special interest. The component numbers are defined in the main menu under "3) define species and components". The limits on the y-axis depend on the way the graphical output is defined. If the output is in percent, all species are calculated as a percent of the total amount of the defined component.

The limits of the y-axis are depending on different features. If the output is in percent it is fixed from 0 to 100 or else

the limit is given by the total concentration defined for the experiment number one. (How to work with different experimental setups is explained later). If a function is plotted, the limits are defined in the menu "4) define functions" and the parameter given here is neglected.

nr. of the component on x-axis

This parameter indicates, which component will be plotted on the x-axis. Normally this will be the component indicating H^+ . The negative logarithm is plotted (pH).

1 = %, 2 = [conc.]

If this parameter is set to "1" the output will be in percent of a component, as defined above under "nr. of the component on y-axis". The output into an ASCII file has then the following structure:

1. column: the pH (values on the x-axis).
2. column: the concentration of the 1. species in percent of the defined component
3. column: the concentration of the 2. species in percent of the defined component
- etc.

If this parameter is set to "2" the output will be in units of concentration. The output into an ASCII file has then the following structure:

1. column: the pH (values on the x-axis).
2. column: the total concentration of the 1. component
3. column: the total concentration of the 2. component
- etc.

and then, the total concentrations of the components and the free concentrations of all species are plotted in the order defined under the menu "3)define components and species"

1 = graphic, 2 = no graphic

If this parameter is set to "1" the output for a speciation-plot will be shown as a graphic. The program has a self detecting mode, which allows you to use the program with different graphic systems, like CGA, OLIVETTI, HERCULES, EGA

or VGA cards. However, the best is to work in the VGA mode whenever possible, because some fonts are bad readable in some other graphic modes and colors are used to distinguish between different species in the speciation plot. If the user of this program has no graphical support on his computer, he can work with the program setting this parameter to "2". A big advantage of this program is the adaptability of the graphics. Choose "1" whenever possible.

1 = no print, 2 = IBM, 3 = HP

If you have chosen to work with graphical support, the program supports HP Deskjet, IBM and EPSON compatible printers. If the parameter is changed to "2" or "3", after having made a graphic, the computer sends a screen-dump to your printer.

how many experiments

The computer can calculate several separate sets of data at the same time. Every set asks for a separate input. This feature is very important, when different titrations with different total concentration have been made or when the user wants to compare the influence of different parameters like capacities, site densities, the ionic strength, total concentrations and free concentrations. (One can also define more than one experiment, if there are no measured data available). Often experiments are produced in a way, that it is not necessary to have them stored separately as an experiment.

draw multiplot

Often, not all experiments can be printed at the same time on the screen. The user can choose, which experiments he wants to plot in the graphic at the same time. The first indicated experiment is also used to tell the program, which experimental setup is chosen for the feature "c" in the main menu.

1 = mtot, 2 = dil, 3 = dilspline

There are three different ways to define the total concentrations of the components. If "1" is chosen, the speciation plot is made by taking the concentrations given in the main menu under "2)" and "3)". For the whole plot the total concentrations of the components for the defined experiments are not

changed. If there is experimental data given in the main menu under "6)" it will not be plotted in that mode. Often the user wants to have a direct comparison with his experimental values. In order to compare the calculations with the measured data one has to choose the mode "2". This mode works only when the experimental data is given in the main menu under "6)". The speciation plot is then calculated taking the given experimental pH-values and the dilution factors given by the dilution at every titration point. The total concentrations (which are not fixed) are then multiplied with this factor. For example, if the total concentration (initial concentration) is given as 0.1 M and the initial volume has been doubled during the titration, the dilution factor is set to 0.5. The program takes then 0.05 M as the total concentration to calculate the speciation at this pH. In this mode ("2") the experimental values are plotted as squares and the calculated curves are displayed as linear linked dots. This allows very fast speciation plots to be made, which are directly comparable with the measured data. Often these plots do not look so nice because not enough experimental data is available. If there was no dilution this is no problem, because the total concentrations are the same for the whole pH range. If there is a dilution from one experimental datapoint to the next, one does not know, which total concentrations to take that the speciation calculation in between the experimental data points is reasonable. The following approach, mode "3", is a very successful way to solve this problem. A data point with a lower pH value, than that of the first measured point is calculated with the total concentration of the first experimental datapoint. A data point with a higher pH value, than that of the last measured point is calculated with the total concentration of the last experimental datapoint. To estimate the total concentrations in between, the program plots the dilution factor against the pH (only in memory). Then it lays a cubic spline through this curve. From that the program calculates for the given stepwidth (see above) a good

estimation for every dilution factor. This mode works only, when the experimental setup in the main menu "5)" is chosen. This mode is a very good tool for plotting curves, that will be published as a graphic.

SAVE PARAMETERS, LOAD PARAMETERS

All the parameters defined above, will be saved together with every other input in a binary file, using the save option in the main menu. With the saving and loading possibilities in this menu one can save the parameters in a separate ASCII file, which can be changed with any editor. This ASCII file has to have the name "STANDARD.GRF". "STANDARD.GRF" is loaded automatically, when the program is started. The structure of this file is the same as shown in Fig. 3 (and Fig. 10). Every option has to be on a new line. The line number corresponds to the option. One has to start with the first line in STANDARD.GRF. However it is easier to change this file with the here defined SAVE utility. The parameters are saved by pressing the **F3** key. If one has no "STANDARD.GRF" the program can also start, when no parameters are defined, but at least an empty file with the name "STANDARD.GRF" has to be created. Having changed the parameters, to return back to the parameters defined in "STANDARD.GRF" one can load the parameters from "STANDARD.GRF" by pressing the **F4** key.

4.1.3"2) set model specific parameters"

The masks in that menu are different for every model. In Fig. 4 one possibility is shown. This input is structured in experiments. If there is more than one experiment the **F10** key will move to the input of the next experiment. This is useful when different titrations are treated at the same time, or if it is of interest to see the differences by changing certain parameters.

model 0

For this model no parameters have to be defined.

model 1

This model needs the ionic strength to solve the Eq. [1].

model 2

This model is shown in Fig. 4.

Fig. 4

GRFit - input of parameters for the choosed Model

experiment no.: 1

surface site density [moles/g] : 0.000145
 fit site density ? :
 specific surface area [m²/g] : 90.
 concentration of solid [g/l] : 9.48125
 capacitance (inner) [F/m²] : 2.658
 fit capacitance (inner) ? :
 component-nr. of SOH : 1
 component-nr. of potentialterm 1 : 2

GO ON --> f10

Some of the inputs are separated in two mask blocks. The upper block contains only physical information like ionic strength, site densities, capacities etc. This information is important for calculating the exponential terms for the adsorption models. The lower block gives information to the program, as which components the exponential terms and sites are defined. The input for the components follows in the next main menu "3)". Some input fields ask if a certain parameter should be fitted. If one wants to fit this parameter, a star "*" is entered into the corresponding field. If the field is empty the parameter is not fitted. These fields have no influence on the options "c)" and "p)" in the main menu. One should be careful, choosing the fitparameters. For example, it is not wise to fit site densities and capacities at the same time, because these two parameters are strongly correlated.

model 3 to 5

These models are treated like model 2. The input is self explanatory.

4.1.4"3) define components and species"

Here the components, the total concentrations, the free concentrations, the identification of the fitparameters, the species, the stoichiometric matrix for the equilibriums and the corresponding constants in the logarithmic form will be

entered. When this menu is chosen, a first table is displayed as shown in Fig. 5.

Fig. 5

GRFit - input of the components			
experiment no.: 1			
name	tot. conc.	fr. conc.	fr/tot fit?
1:TiOHTiOH	1.374781E-3	0.	
2:EXP	0.	0.	
3:Cu	0.00085833	0.	
4:H+	0.	0.	*

GO ON --> f10 INS --> f1 DEL --> f2

Again as already explained for the main menu point item number "2)" this table is defined for several experiments. That allows us to study the influence of different concentrations on the defined system.

The table is organized into five columns:

1. the name of a component
2. the total concentration of a component
3. the free concentration of a component
4. a mark that tells the program, if the total or free concentration is known.
5. a mark that tells the program, if the total concentration should be fitted from experimental data.

fr./tot (column 4)

Here the user can fix either the free or the total concentration. If the total concentration is known the free concentration is calculated by a mass-balance iteration. If the free concentration is known this iteration is not necessary. For the program it is necessary to separate the two forms. The components with known free concentration have to be at the end. Often this is the case for the protons, when the behavior of the system at different pH is studied. If the free concentration is known one has to put a star "*" or else the field is kept empty. The program automatically sorts the components so that those marked with a star are at the end of

a table. This feature is also very practical, when one likes to delete or insert a new component. If the component is first sorted to the end of the field the deleting and inserting manipulations are much safer. After the manipulation the star is taken away and one turns back the components by putting the star to the correct component(s). One should not forget to put a star when using the option "p)" or "f)" in the main menu.

name (column 1)

The name is only used as a mnemonic for the user, when he wants to define the stoichiometric matrix; or as a help, when he has to identify species or formulas in the graphic. (Every species or formula has its color). The name can have a length of twelve characters.

total concentration (column 2)

The total concentration of a component is given in this column. If the component is identical with the defined site in the main menu "2)" then this value will be overwritten by doing the calculation. Therefore it is not important to give the correct value in Mol/l for the site densities. This treatment allows to fit the site densities from experiments with different site concentrations. The same is the case for the exponential terms. The "total concentration" is overwritten for every calculation.

free concentration (column 3)

This value is used as a first estimation for the iteration in the microql part, if the total concentration is given. If the free concentration is known, no iteration is necessary for that component. In that case this component should be at the end of the table.

fit ? (column 5)

If a star "*" is put into this field, the total concentration is fitted from the experimental data.

Do not set a star "*":

- when the component is the site, which is already used in the main menu "2". Use the possibility of fitting the site density directly.

- when the component is an exponential term.
- when the free concentration is fixed. The calculation of the total concentration is anyway available in the form of a function (see main menu point item number "4").

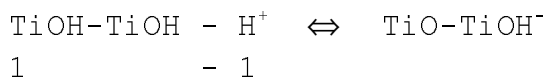
Having made all the input shown in Fig. 5 press the "GO ON" key **F10** and the next input sheet is displayed as shown in Fig. 6.

Fig. 6

name	TiOHTiOH	EXP	Cu	H+	log(K)	fit?
1:H+	0	0	0	1	0.	
2:OH-	0	0	0	-1	-13.8	
3:Cu 2+	0	0	1	0	0.	
4:TiOHTiOH2 +	1	1	0	1	5.404	
5:TiOHTiOH	1	0	0	0	0.	
6:TiO-TiOH	1	-1	0	-1	-7.747	
7:TiO-TiO-	1	1	1	-1	-17.21	
8:TiOCuTiOH+	1	1	1	-1	-1.	*
9:TiOHCuTiOH+2	1	2	1	0	5.	*
10:CuOH +	0	0	1	-1	-8.22	
11:Cu(OH)2	0	0	1	-2	-17.53	
12:Cu2(OH)2	0	0	2	-2	-10.6	
13:TiOCuTiO	1	0	1	-2	-7.	*

GO ON --> F10 INS --> F1 DEL --> F2 CONU. COMPONENT --> S-F10

The table shown in Fig. 6 contains the input of the species, the stoichiometric matrix, the equilibrium constants, and the mark for fitting the equilibrium constants. In the first column the name of the species is given. It is only a help, for identifying species in this table as well as to indentify them later in a speciation graphic. (Every species has its color in this graphic. The curves correspond then to the names written in this table). The name can have a length of twelve characters. The following columns belong to the components defined above. Every species in the system is defined as a product of its components. For example the 6th species in Fig. 6 is described in the following way:



because Cu²⁺ is not used, this term is zero. The exponential term "EXP" is used, because TiOH-TiOH describes the surface site and the deprotonated form TiO-TiOH⁻ is negatively charged the value is set to -1. Next to the last column the logarithmic values to the base 10 of the equilibrium constants for

the defined equilibrium in the corresponding line are entered into the table. The last column tells the program, which constants should be fitted, when using the option "f)" in the main menu. If the constants should be fitted, a star "*" is entered else the field stays empty.

CONV. COMPONENT --> S-F10

This command at the bottom has not been discussed so far. It allows one to convert a species into a component. Normally that is not necessary, but it is very useful when a precipitation curve should be plotted. The easiest way to do that is by defining the precipitated form as a component of the system, because the free concentration is then zero by definition. That has the consequence that every equilibrium has to be redefined. This redefinition can be done automatically, when the precipitated form first is defined as a species and then subsequently transformed into the component. Choosing this option the mask shown in Fig. 7 is displayed:

Fig. 7

```

GRFit - select an other species as component

select a species as new component, 0 = no change

nr. of old component      : 0
nr. of new component     : 0

GO ON --> F10
  
```

The number of the old component is the component number of the component that is transformed into a species. The number of the new component is the number of the species that will become the new component. Having pressed the "GO ON" key **F10** one turns back to the main menu. Choosing the option "3)", again one should see the changes in the menu of the components and the ones in the menu of the species. If one has made a mistake the components can be changed back in the same way. Care should be taken when changing components, when the

species that should become a component is a multiple of the component that will become a species, because the program can only treat INTEGER numbers as stoichiometric coefficients. For example the component Cu^{2+} should not be changed with $\text{Cu}_2(\text{OH})_2^{2+}$.

4.1.5"4) define functions"

This feature is one of the most useful tools in the program. Normally the species in a system are not directly measurable. Often only certain relations between species in solution or suspension are known. For example, a ternary system like the simultaneous adsorption of a metal and an organic ligand on a mineral surface is studied. In the programs used today the free concentration of the components and their total concentration both have to be given to the program as experimental data. But for the system described above, that is very difficult, because the free concentration of the metal and the ligand are normally not measurable. Sometimes they do not exist; e.g. the metal occurs only in different complexed forms. Often only the total amount of the adsorbed metal and the adsorbed ligand is accessible. With the features discussed here one can formulate relations of total (components) and free concentrations (species). For example the amount of adsorbed metal or ligand (in percent) can then be calculated by the summation of the corresponding surface species divided by the total amount times 100. There is also a feature, which allows one to transform concentrations defined in Mol/l into Mol/g corresponding to the sites of oxide, by using the parameter "a". This tool is very useful, because such expressions are then independent of the solid concentrations used for different experiments. The uses of the different possible parameters, that are allowed to be used in formulas are explained on the help lines displayed together with the input table. The program can treat up to three functions at the same time. They can be entered with a table as discussed above. As shown in Fig. 8 the table has two columns. The first one is used to define the formula. The help on the top of the screen

explains, in which form the formula has to be defined. The second column ("detach?") is used to put a mark in the form of a star "*". If a star is set, the formula is not displayed (detached), when using the option "p)" in the main menu. If all formulas are detached, instead of the formula, the speciation will be plotted. If the option "f)" in the main menu is used, only the formulas and the corresponding experimental data, that are not detached will be used for the fitting procedure. If a formula field is empty the formula has to be detached.

Fig. 8

GRFit - input of formulas	
help for defining a formula: - A formula can be defined with normal mathematical operators as: $+, -, *, /, ^, \text{SQRT}, \text{SQR}, \text{EXP}, \text{LN}, \text{LOG}, \text{SIN}, \text{COS}, \text{TAN}, \text{ASIN}, \text{ACOS}, \text{ATAN}$ - The operators above can connect parameters and numbers. - The parameters 't1, t2, ...', 'c1, c2, ...' and 'a' are allowed. 'T1' or 't1' is then the given or calculated total concentration of the component number one. 'C3' or 'c3' is then the given or calculated free concentration of the species number three. 'A' or 'a' is then the amount of solid in [g/l] times the dilutionfactor.	
formula	detach?
1:100-c3/t3*100	
GO ON --> f10 INS --> f1 DEL --> f2 SAVE F(X) --> f3 LOAD F(X) --> f4	

All parameters that have been set in 4.1.2 have the same effect on the function plot as on the speciation plot, except the limits of the y-axis, which have to be entered in the next mask. That will appear when the "GO ON" key **F10** is pressed as shown in Fig. 9.

Fig. 9

GRFit - input of formulas	
help for defining a formula: - A formula can be defined with normal mathematical operators as: $+, -, *, /, ^, \text{SQRT}, \text{SQR}, \text{EXP}, \text{LN}, \text{LOG}, \text{SIN}, \text{COS}, \text{TAN}, \text{ASIN}, \text{ACOS}, \text{ATAN}$ - The operators above can connect parameters and numbers. - The parameters 't1, t2, ...', 'c1, c2, ...' and 'a' are allowed. 'T1' or 't1' is then the given or calculated total concentration of the component number one. 'C3' or 'c3' is then the given or calculated free concentration of the species number three. 'A' or 'a' is then the amount of solid in [g/l] times the dilutionfactor.	
formula	detach?
1:100-c3/t3*100	
ymin when formula used: 0. ymax when formula used: 100.	
GO ON --> f10 INS --> f1 DEL --> f2 SAVE F(X) --> f3 LOAD F(X) --> f4	

At the bottom line two new commands have not been discussed so far:

SAVE F(X) --> f3

Pressing the **F3** key the actual functions will be written to the "STANDARD.GRF" file (see also in 4.1.2). The functions are written directly after the general parameters as shown in Fig. 10.

Fig. 10

2	<----- first line
2.0000000E+0	
1.0000000E+1	
3.0000000E-1	
3	
4	
1	
1	
1	
2	
1-2	
2	
1	<----- amount of functions
100-c3/t3*100	<----- function
0.0000000E+0	<----- lower limit of the y-axis
1.0000000E+2	<----- higher limit of the y-axis

If more than one function is defined for every function a new line has to be chosen. If functions are deleted in the table and the functions are saved again, the ascii file will become shorter and at the end of the file some numbers will not be overwritten, this has no effect on the correct working of the program. Of course the functions will be saved also as a part of the binary worksheet file using the option "s)" in the main menu.

LOAD F(X) --> f4

This option loads the functions and the corresponding limits of the y-axis stored in "STANDARD.GRF" into the actual table.

4.1.6"5) give an experimental setup"

In this part of the program the experimental data will be entered. In Fig. 11 the table of an input is shown.

Fig. 11

GRFit - input of the components		
experiment no.: 1		
x-values	f1(x)	Dilution
1:2.979	0.	1.
2:3.332	4.007	0.932
3:3.398	5.359	0.9231
4:3.468	3.686	0.9143
5:3.543	5.812	0.9057
6:3.619	6.422	0.8972
7:3.703	9.228	0.8889
8:3.786	11.25	0.8807
9:3.869	19.23	0.8727
10:3.956	21.05	0.8649
11:4.043	24.05	0.8571
12:4.13	23.98	0.8496
13:4.217	26.87	0.8421
14:4.301	29.67	0.8348
15:4.383	33.95	0.8276
16:4.461	37.98	0.8205
17:4.541	42.69	0.8136
18:4.617	47.463	0.8067

GO ON --> f10 INS --> f1 DEL --> f2 LOAD --> f4 DEL SHEET --> f5

Again the input is structured in experiments. Every experiment has its own table. Pressing the "GO ON" key **F10** the program will go to the input of the next experiment. In the table every line is contained the information of one experimental data point. The data point contains an x-value (normally the pH), for every function defined in the feature "4)" of the main menu the corresponding y-values ($f_1(x)$, $f_2(x)$, $f_3(x)$) and in the last column the dilution factor. If there is no dilution the dilution factor is set to unity. GRFIT calculates the total concentrations of the components (when the free concentration is not fixed) by taking the total concentration given in the main menu under option "3)" for the corresponding experiment and multiplying them with the dilution factor. Often, the results of experiment are already in form of an ASCII file on a disk. Then, the results do not have to be retyped, and can be loaded directly by using the load option **F4** in this menu. The pop up menu then asks for a filename as shown in Fig. 12.

Fig. 12

GRFit - input of the components

experiment no.: 1

X-values	f1(X)	Dilution
1:2.979	0.	1.
2:3.332	4.007	0.932
3:3.398	5.359	0.9231
4:3.468	3.686	0.9143
5:3.543	5.812	0.9057
6:3.619		
7:3.703		
8:3.786		
9:3.869		
10:3.956		
11:4.043		
12:4.13		
13:4.217		
14:4.301		
15:4.383	33.95	0.8276
16:4.461	37.98	0.8205
17:4.541	42.69	0.8136
18:4.617	47.463	0.8067

load experimental datas

filename ?

GO ON --> f10 INS --> f1 DEL --> f2 LOAD --> f4 DEL SHEET --> f5

For this option to work successfully the ASCII format has to be structured in the following way:

1.line
2.line
3.line
etc.

number of datasets		
x_1	y_1	dilfac ₁
x_2	y_2	dilfac ₂

The values in one line have to be separated at least by one SPACE. In general the columns, which are shown in the table have to be represented in the ASCII file and the first line in this file contains the amount of datasets (= total amount of lines minus one). The feature "DEL SHEET" deletes the actual table.

4.1.7"6) set special fitparameters"

The options of this menu are shown in Fig. 13. The parameters are controlling the fit of the experimental data. For fitting the Newton Raphson method with Gauss Elimination is used. This method needs the derivation of the function, that is fitted. Because the user defined functions depend on a Microql algorithm the derivations are calculated numerically, which is opposite to the Newton Raphson iteration for the massbalance equation used for the Microql part, which has been solved analytically. The parameter "dx" is used twice. First as the step to calculate the derivation and second as a convergence criteria to stop the iteration in the microql part. The

relative convergence is then reached, when the value becomes smaller than "dx" times 10^{-3} . The parameters "chitol" and "deltatol" are the convergence conditions for the iteration in the fitting routine for the experimental data. The fitting is based on χ^2 , the sum of the errors in the square of all the data points. If χ^2 is smaller than "chitol", or if "deltatol"

is smaller than $\frac{\chi_{\text{new}}^2 - \chi_{\text{old}}^2}{\chi_{\text{old}}^2}$, the iteration stops. The parameters

above only should be changed, when the user has problems with fitting. They have been tested for a lot of different cases in our research group and they have worked in all cases.

Fig. 13

```
GRFit - fitparameter

help for settings:
- dx is the derivationstep in a function with:
  f(x) lim(x -> 0) = (f(x+dx)-f(x))/dx
  with x as a fitparameter.
- chitol is the absolute value for the breakcondition
  after an iterationloop in the Newton Raphson algorithm.
- deltatol is the relativ value for the breakcondition
  after an iterationloop in the Newton Raphson algorithm.

dx          (default = 1.E-8):0.00000001
chitol      (default = 1.E-8):0.00000001
deltatol    (default = 1.E-6):0.000001
1 = fit M.K., 2 = fit LOG(M.K.):1

GO ON --> f10
```

The last parameter in the mask determines, whether the parameters for the fit of experimental data will be treated in the non-logarithmic form ("1") or in the logarithmic form ("2"). If the option is set to "2" often the fit is faster, but because the logarithmic values are fitted, the change of the value could be too big and the procedure will never find the minimum. Therefore the change is limited to one logarithmic unit. If the change is bigger, the change is one logarithmic unit. However another advantage of fitting the parameters in logarithmic forms, is that the routine is allowed to produce negative values. The non-logarithmic form must be a positive number and for instance negative concentrations are not possible. If one chooses the option "1" the program treats every parameter that should be fitted in the non-logarithmic

form. To avoid negative values, the program divides the parameter ten times, if it would become negative.

Both possibilities of fitting parameters should give the same results. If a small change of a parameter has a big effect on the system, or if a system has problems to get converged, it is better to fit this parameter in the non logarithmic form (option "1"). But the possibility ending up in a local minimum using option "1" is bigger than for option "2". However, if a fit is possible, normally the fit can be done with both options.

4.1.8"loading and saving the given input"

s) save data

When this menu is chosen, the program asks for a filename. Enter a name with extension (e.g. "name.fit") and press the ENTER key. The program then saves all actual data in the memory to a file on the disk. If there is a filename on your disk with the same name, this file will be overwritten without any checkback!

l) load data

The input for that menu is the same as for the saving part. The program deletes the actual parameters and loads the new parameters from the disk into the computers memory. Before loading parameters, one has to be certain that the old parameters have been saved already. If the menu is chosen by accident press the ENTER key. The program gives then the error "wrong filename", when the ENTER key is pressed a second time, the program goes back to the main menu without loosing data in the actual memory. The same is the case when the program does not find a file with that name.

g) load GRMic data

This option is not necessary to work with the program. It is only provided for users, who worked with the program "GRMic", an older version of Microql. Most of the input used in that program can be loaded into "GRFit". The option is treated as discussed above.

4.2 The Calculation Features

Some examples are presented in the following chapters.

4.2.1 "c) calculate speciation for one special condition"

This option is used to check quickly some numerical facts of a speciation. In Fig. 15 and Fig. 16 the output for a copper(II) speciation using model "1" after Baes and Mesmer (5) is plotted. The total concentration of copper(II) was set to 0.8 mM and the ionic strength was set to $I = 0.1$. The stoichiometric matrix and the constants have been set as shown in Fig. 14.

Fig. 14

name	Cu2+	H+	log(K)	fit?	A-fak.	B-fak.
1:Cu 2+	1	0	0.	0.	0.	0.
2:H +	0	1	0.	0.	0.	0.
3:OH -	0	-1	-13.78	0.	0.	0.
4:Cu(OH) +	1	-1	-8.	-1.022	0.25	
5:Cu(OH)2	1	-2	-17.3	-1.022	0.2	
6:Cu(OH)3 2+	1	-3	-27.8	0.	-0.04	
7:Cu(OH)4 3+	1	-4	-39.6	2.044	-0.16	
8:Cu2(OH)2 +	2	-2	-10.36	-1.022	0.08	

GO ON ==> f10 INS ==> f1 DEL ==> f2 CONU COMPONENT ==> S-f10

Fig. 15

	LOG(conc.)	(conc.)	% of Cu2+	LOG(Q)
Cu 2+	-3.096938E+0	7.999486E-4	9.999358E+1	0.000000E+0
H +	-4.000000E+0	1.000000E-4	0.000000E+0	0.000000E+0
OH -	-9.780000E+0	1.659587E-10	0.000000E+0	-1.378000E+1
Cu(OH) +	-7.317477E+0	4.814193E-8	6.017741E-3	-8.220539E+0
Cu(OH)2	-1.262248E+1	2.385193E-13	2.981491E-8	-1.752554E+1
Cu(OH)3 2+	-1.890094E+1	1.256210E-19	1.570262E-14	-2.780400E+1
Cu(OH)4 3+	-2.622186E+1	5.999836E-27	7.499795E-22	-3.912492E+1
Cu2(OH)2 +	-8.791414E+0	1.616537E-9	4.041342E-4	-1.059754E+1

balance-difference of:
Cu2+= 1.340535E-20
H+= 9.994846E-5

The output is structured in five columns. In column 1 are the name of the species. In column 2 are the logarithmic forms of the free concentrations of every species. In column 3 the species are plotted in percent of a component. This component is indicated by the parameter "nr. of the component on y-axis" defined in the menu "1)". In the last column the log K values are displayed, that have been used for the calculation. In the

displayed case they have been transformed after the Eq. [1]. If more than one experiment has been defined, the experiment, that is indicated as first in the "draw multiplot" command line of menu "1)", is chosen as setup for the calculation. This speciation calculation can be done with or without fixed free concentration, and allows us to calculate the speciation at a certain pH (Fig. 15, pH = 4) or the buffering pH of the system (Fig. 16).

Fig. 16

OUTPUT				
=====				
	LOG(conc.)	<conc.>	% of Cu2+	LOG(Q)
Cu 2+	-3.098908E+0	7.963274E-4	9.954092E+1	0.000000E+0
H +	-5.434467E+0	3.677332E-6	0.000000E+0	0.000000E+0
OH -	-8.345533E+0	4.513020E-9	0.000000E+0	-1.378000E+1
Cu(OH) +	-5.884980E+0	1.303227E-6	1.629034E-1	-8.220539E+0
Cu(OH)2	-9.755513E+0	1.755850E-10	2.194813E-5	-1.752554E+1
Cu(OH)3 2+	-1.459951E+1	2.514741E-15	3.143426E-10	-2.780400E+1
Cu(OH)4 3+	-2.048596E+1	3.266162E-21	4.082703E-16	-3.912492E+1
Cu2(OH)2 +	-5.926421E+0	1.184620E-6	2.961550E-1	-1.059754E+1
balance-difference of:				
Cu2+=	1.783995E-19			
H+=	-6.196203E-21			

4.2.2)p) calculate a speciation plot" and "f) fit experimental data"

Pressing "p" in the main menu the program plots the speciation diagram. The form in which the plot will be made depends on the features which have been discussed in this manual. In the following, only some examples will be shown. One should not forget that this menu only works, if at least one free concentration is fixed (see 4.1.4). The system as it is defined by Fig. 1 to Fig. 13 is shown in the form of a function with the experimental datapoints of two experiments. The log(K)-values are used as shown in Fig. 6. The experimental data are not represented (Fig. 17), but it is a good estimation for a fit. Pressing any key leads back to the main menu, when option "f" for fitting is selected, the output shown in Fig. 18 is displayed on the screen. Every parameter to be fitted is shown on the screen. The first set of parameters represent the guessed values. In addition for every loop χ^2 and χ per datapoint is calculated. The last iteration loop is repeated, even when the procedure has converged already. If the last two

lines have the same result the fit seems to be correct. The values before the indication "Newton Raphson has successfully converged" are the fitted values.

Fig. 17

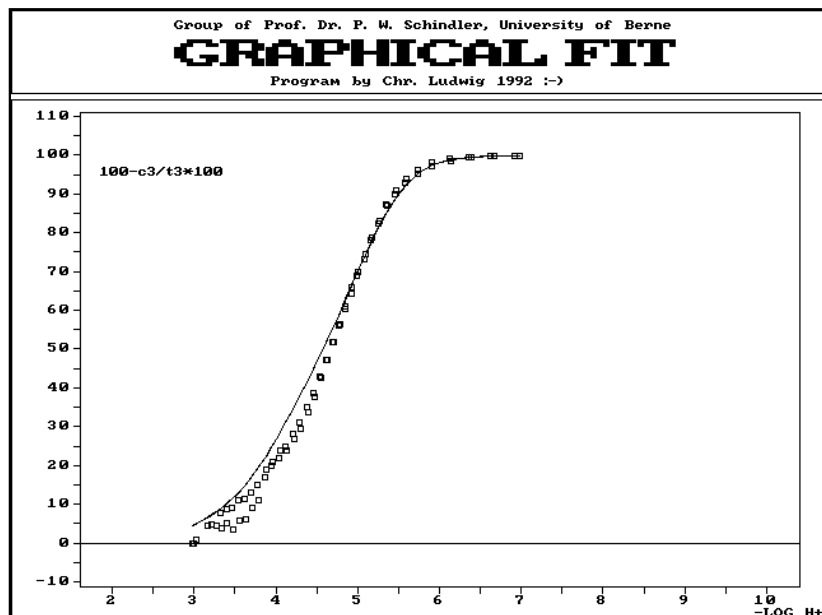


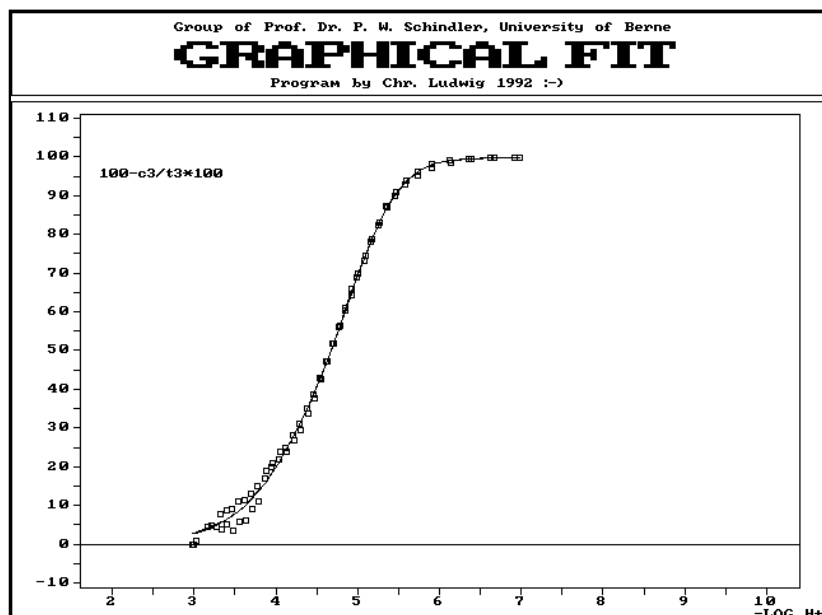
Fig. 18

Newton-Raphson-Fit:			
log(K 8)	log(K 9)	log(K13)	
-1.000E+0	5.000E+0	-7.000E+0	
	$\sqrt{\text{chi}^2}/\text{nr}$	$= 5.08526682329379\text{E-}1$	$\text{chi}^2 = 1.41609024124570\text{E+}3$
-1.101E+0	4.677E+0	-6.783E+0	
	$\sqrt{\text{chi}^2}/\text{nr}$	$= 2.26188698859855\text{E-}1$	$\text{chi}^2 = 2.80159429345722\text{E+}2$
-1.101E+0	4.749E+0	-6.750E+0	
	$\sqrt{\text{chi}^2}/\text{nr}$	$= 1.69568517278191\text{E-}1$	$\text{chi}^2 = 1.57454067716337\text{E+}2$
-1.093E+0	4.751E+0	-6.752E+0	
	$\sqrt{\text{chi}^2}/\text{nr}$	$= 1.69383152813096\text{E-}1$	$\text{chi}^2 = 1.57110012854009\text{E+}2$
-1.092E+0	4.751E+0	-6.752E+0	
	$\sqrt{\text{chi}^2}/\text{nr}$	$= 1.69383145600525\text{E-}1$	$\text{chi}^2 = 1.57109999474083\text{E+}2$
-1.092E+0	4.751E+0	-6.752E+0	
	$\sqrt{\text{chi}^2}/\text{nr}$	$= 1.69383145598460\text{E-}1$	$\text{chi}^2 = 1.57109999470251\text{E+}2$
Newton Raphson has successfully converged_			

If the procedure does not converge the calculation can be aborted by pressing a key. The program displays the indication: "you have pressed a key during the calculation". If the procedure is diverging the procedure stops. The comment "Newton Raphson has not converged" will be displayed on the screen.

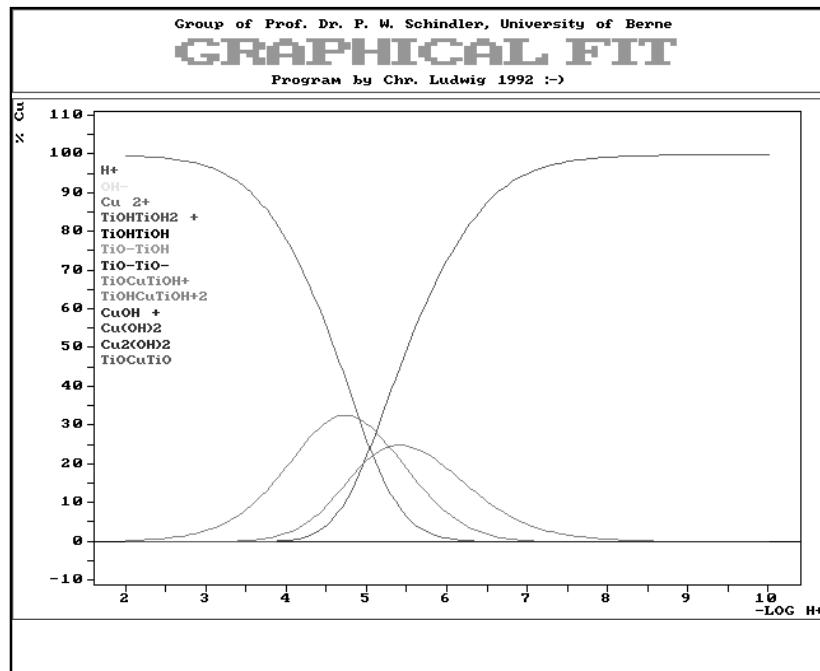
After the comment, one can press a key and the program returns back to the main menu. Pressing "p" the speciation (function) will be displayed as shown in Fig. 19.

Fig. 19



The fitted curve lays now on the data points. The fitted values have been replaced automatically in the corresponding tables and masks. When all formulas (4.1.5, Fig. 3) are detached and the last input of the general parameters is set to "1" the speciation for the setup of experiment "1" is presented as shown in Fig. 20. The relation of the curves and the species is not visible here, because the figure is only in black and white. On a color screen every species has another color and the color of the names are corresponding to the color of the curves. Only a few curves are plotted in this figure, because only the species with copper are represented.

Fig. 20



5. Errors

The error handling of the tables and masks have been discussed in earlier sections. Apart from that, the program does some checks to minimize the danger of breaking down the system, before it starts the calculations. All detected errors will be displayed on the screen, with some hints to correct the input.

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