User's Guide

pHCali, version 1.32a-20070323

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CHAPTER 1

INTRODUCTION

The program pHCali has two objectives. *(1)* Firstly it makes possible the accurate calibration of *p*H-metric instruments, which is essential particularly for the quantitative investigation of complicated equilibrium systems in solution. The *p*H range to be calibrated can also be extended to the non-Nernstian ranges. *(2)* Secondly, pHCali is able to determine protonation constants of weak acids even if the analytical concentration of the weak acid is not exactly known.

1.1 Why *p*HCali is Useful?

The presently used *p*H-metric calibration methods have several problems despite the fact that they are being used for more than 50 years:

1. Each method applies some simplifications, but the theoretical grounding of them are the more dubious, the more precise the applied measurement devices are. For example, the applicability of the formulas derived in the Gran-method [1] requires the use of a monoprotic weak acid to determine the base concentration. The acid should be weightable precisely and must have small dissociation constant. In spite of these requirements, KH-phtalate is used in practice, which is a biprotic anion, its two protonation steps overlap and the simple buffer formula cannot be applied precisely for the first dissociation step in the frequently used concentration range.
2. It is not resolved to take into account or to indicate the carbonate content of the titrant solution, only practical advices are known.
3. Many methods suppose, that the electrode used during the measurements is ideal, i.e. the relationship between the measured signal and the negative logarithm of the hydrogen ion concentration is linear, and the slope of the straight line can be calculated from the Nernst-equation. These methods are not capable of taking either the deviation from the straight line or the deviation from the ideal slope into account, only empirical suggestions exist.[1]
4. The extension of the calibration range into the non-linear range is based on some old measurements [2–4], but their applicability to glass electrodes has neither been proved, nor it has been investigated!

These problems lead to the state that—in contrast to many other analytical methods—there is still no generally accepted calibration method in pH-metry. Many methods are being used, some of them are minor modifications of others [5–9], but the choice among the methods is based on local belief or trust rather than professional considerations.

The previously mentioned problems have already been known for very long time, and many practical solutions have been developed to avoid them. They work reasonably well as long as the studied chemical system is simple enough and the problems are not coupled. But nowadays there is no simple chemical system to study and the fact of coupling is extremely

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[1] In this document, an electrode is called a Nernstian one if the above mentioned linear relationship is true but small deviation from the ideal slope (i.e. 59.16 mV at 25 °C) may exist.

Table 1.1: The name of the executable program under different operating systems.

operating system	text mode	console mode	window mode
DOS	`phcalid.exe`	—	—
Windows	`phcalid.exe`	`phcalic.exe`	`phcaliw.exe`
Linux (statically linked)	—	`phcalit`	`phcalix`
Linux (dinamically linked)	—	`phcalit.shared`	`phcalix.shared`

hard to discover in practice. This may lead to identification of nonexistent species or ignoring existing ones in small concentration due to the lack of precise calibration.

*p*HCali intends to fill in these gaps by accomplishing the calibration without model simplifications in a single fitting step. Besides the determination of the calibration parameters it lets the user

- to utilize the maximum precision of measurements[2],
- to discover the possible experimental errors more easily,
- to indicate or even quantitatively determine the carbonate content of the titrant base and
- to extend the usable *p*H range in a trustable way.

Furthermore the program is able

- to handle multiprotic weak acids (that can be weighted accurately) as calibration material,
- to determine the protonation constants of any weak acid with composition of $\mathrm{H}_i A^{(q-i)-}$ $(i \le 9,\ q = 1, 2, \ldots)$,[3] even if the total concentration is not known precisely. Moreover,
- the program is capable to calculate the *p*H defined with the equilibrium *concentration* of the hydrogen ion in every measured point of the chemical system to be studied. These *p*[H] data are the most suitable input data of any equilibrium evaluation program.

1.2 Concisely about *p*HCali

To calibrate a *p*H-metric instrument, the program requires the same experiments as Gran's method [1], namely two titration curves are necessary: *(1)* a weak acid – strong base titration curve where the analytical concentration of the weak acid is exactly known and *(2)* a strong acid – strong base titration curve. Both curves are necessary to determine the instrumental parameters, the ion-product constant of water and the precise concentrations of the strong base and the strong acid stock solutions. During the experiments either potential or *p*H may be measured, the program is capable of handling both types of curves.

The titration data should be put in a text file. The program uses these input data and it applies the orthogonal distance regression to determine the data required for further work, that are then stored in text and image files. More titration curves and their repetitions can be put into a single input file. The program can handle up to 10 titration curves, 10000 experimental data pairs and 9 protonation constants simultaneously.

The program has been written in Fortran 77 with the use of GNU-Fortran (`g77`) compiler [10] and two libraries: the ODRPACK library [11] includes the subroutines for calculations and the DISLIN library [14] provides the graphics and user interface. They ensure that *p*HCali can be run under various operating systems in several modes. There are all together seven variants of the executable program in the following modes (the names are shown in Table 1.1):

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[2] At the time of writing this manual, the experimental uncertainty of the advanced, good quality *p*H-metric instruments are ~0,1 mV or ~0,002 *p*H unit.

[3] The precise definition of q can be found in *Notations and definitions* on page 75.

Text mode: This variant of *p*HCali can be used on a character-based full screen (e.g. pure DOS). It can only be used with keyboard and does not contain menu window before the work-window.

Console mode: This variant of *p*HCali can be run from a character-based window opened in graphical user interface (i.e. DOS-window in Windows or terminal in X-Window). Either mouse or keyboard can be used as input device. This variant has two menu windows beside the work window. The first one is called file-choosing window and the second one is called parameter-modifying window. All the input parameters can be altered through these two windows without the use of command line arguments. The messages of the program appear in the character-based window. If no such window is opened then the program automatically opens one at start and closes it before exiting. This mode is to be started mainly from command line, but may also be started via clicking on the icon.

Window mode: This variant of *p*HCali can be started from a graphical workspace as well as from command line. The only difference of this mode from the console one is that window mode creates a file called `phcali.msg` to store the program messages and it does not write them on the screen.

1.3 How to Read this Manual

The installation of the program and the example files under different operating systems are described in Section 1.4.

The program is expected to be used by people already familiar with the calibration procedure of *p*H-metric instruments and with the chemical and mathematical background. It is not the purpose of this manual to discuss these basics but for the sake of clarity of the notation system, the Appendix (*see* page 67) contains the mathematical description of titration curves in a fully detailed form. Every chapter of this manual uses the nomenclature defined in the appendix. Among others, the various definitions of the *p*H and the potential are of special importance. These are discussed in Subsection A.3.1. This section is worth to read even for those who are already completely familiar with the contents of the Appendix. Beside the Appendix, the short descriptions can also be found in the "Notations and definitions" part (*see* page 75).

This manual contains 3 main chapters:

- Chapter 2 contains the detailed description of *p*HCali. In fact, this chapter can be used as a reference handbook. It is suggested only to run through this chapter while getting acquainted with the program. The careful reading of this chapter is advised only if the user intends to use the program permanently. An exception is Section 2.1 which gives an overview about *p*HCali so this should be read at the very beginning.
- Chapter 3 is for getting familiar with the program. This chapter demonstrates every capability of the program through examples. The examples are not focused on the details rather than to help the user to learn the basic operation with the program. The examples adequately refer to necessary parts of Chapter 2 where more detailed information is to be found. The study of Example 3 can especially be useful because it describes a complete evaluation of an equilibrium investigation with the help of *p*HCali.
- Chapter 4 helps the user to master the program effectively and trustworthily. *p*HCali is not simply another method for evaluation of calibration measurements. The program has many other features. These capabilities, however, can only be used if the experimental data are accurate enough and carry appropriate amount of experimental information for the calibration. Furthermore, the orthogonal distance regression has some properties that are different from the conventional regression methods, and they may confuse the

inexperienced user a little bit. For these reasons, this chapter summarizes hints and the practical experience collected so far, which can improve the accuracy of the calibration and the determination of stability constants.

1.4 Installation

Minimum requirements:

- • 386DX 40 MHz processor,
- • 2 Mbyte (DOS, Windows) or 6 Mbyte (Linux) free disk space,
- • 4 Mbyte memory in text mode or 8 Mbyte in other modes,
- – VGA-compatible graphics card (but the calculation itself does not require graphics capability) and
- • MS-DOS 5.0, Windows 95 or Linux with kernel 2.0.

Acceptable configuration:

- • 486DX 100 MHz processor or better,
- • 2 Mbyte (DOS, Windows) or 6 Mbyte (Linux) free disk space (+4 Mbyte for each variant of the manual in PDF format),
- • 8 Mbyte memory in text mode or 32 Mbyte in other modes,
- – VESA-compatible graphics card with 800×600 resolution and 8bit color depth, and
- • MS-DOS 6.22, Windows 98SE or Linux with kernel 2.4.

The files installed on the user's computer:

Executables:
`phcalid.exe` (DOS and Windows)
`phcalic.exe`, `phcaliw.exe` (Windows)
`phcalit`, `phcalit.shared`, `phcalix`, `phcalix.shared` (Linux)

Documentation:
`00readme` (english, text file)
`change.log` (english, text file)

Documentation downloadable independently from InterNet:
`pHCalieo.pdf` (english, online)
`pHCaliep.pdf` (english, printable)
`pHCaliho.pdf` (hungarian, online)
`pHCalihp.pdf` (hungarian, printable)

Files for graphics:
`setgrx.bat`, `video.dat` (DOS)
`phcali.png` (Linux, it can be used as icon)

Confgiuration file with default values:
`phcali.cfg`

Confgiuration file with default values but with RGB-colors:
`phcali.rgb`

Example files:
`phcali.tid`
`kh1-13e.tid`, `kh1-13ph.tid`
`kh2-12e.tid`, `kh2-12ph.tid`
`aspph-a.tid`, `aspph-b.tid`, `aspph-c.tid`, `aspph-d.tid`, `aspph-e.tid`, `aspbeta.tid`,
`ox1-13e.tid`, `ox1-13ph.tid`, `oy1-13e.tid`, `oy1-13ph.tid`,
`ma1-13e.tid`, `ma1-13ph.tid`,

`su1-13e.tid`, `su1-13ph.tid`,
`kh113ej1.tid`, `kh113ej2.tid`

1.4.1 DOS Operating System

The freely downloadable `dphcali.zip` contains the executable program, a part of the documentation and the example files.[4] The installation itself is very simple. The user has to create a directory (or folder, in windows nomenclature) and the contents of `dphcali.zip` has to be extracted into that directory. In this directory, the program (`dphcali.exe`) is ready to use. If the user wants to access the program from other directories, then either *(1)* the installation directory should be inserted into the `PATH` environment variable or *(2)* the program name has to be called together with its path (e.g. `C:\PHCALI\PHCALID.EXE`). In the latter case the configuration file (*see* Subsection 2.2.2) must be copied into the specific directory if the user wants to use it there.

By default the graphical engine of *p*HCali does not utilize the capabilities of the computer's video cards thus the graphics is slow and the resolution is low. The `GRX20DRV` environment variable should be set to get fast and high resolution for the figures. It can be done, for example, with the `SETGRX.BAT` by running this batch file from the command line.[5] This file contains a command:

"`SET GRX20DRV=<driver> gw <width> gh <height> nc <colors>`",

where the value of the video card driver (`<driver>`) can be `stdvga`, `stdega`, `et4000`, `cl5426`, `mach64`, `ati28800`, `s3`, `VESA` or `memory`; the horizontal resolution (`<width>`) can be e.g. `640`, `800`, `1024`; the vertical resolution (`<height>`) can be e.g. `480`, `600`, `768` and the number of colors (`<colors>`) can be `2`, `16`, `256`, `64K` or `16M`. It is important to note, that *p*HCali uses only 16 colors but lower color depths are not always supported by present video cards, so at least the `64K` value should be set in these cases.[6]

1.4.2 Windows 95, 98, Millenium, 2000, XP and 2003 Operating Systems

The installation procedure of the program is the same as installing the program under DOS. The compressed archive `wphcali.zip` contains all three variants of the executables. It is important to note that the graphics of `phcalid.exe` works intrustably if it is started from the command line of Windows 2000, XP or 2003 operating system due to incompatibility issues. Nevertheless, `phcalic.exe` and `phcaliw.exe` run flawless under any Windows versions. Furthermore the graphical capabilities of the latter programs depend only on the specific operating system and do not require any preconfiguration.

*p*HCali does not write any information into the registry of Windows so the programs, data files or even the whole directory can be moved freely.

In case the user wants to start the program by clicking on an icon, then the icon should be created in one of the folders belonging to the Start menu or on the Desktop according to the followings:

- Right-click on an empty area of the opened folder or the Desktop. (A folder can be opened in a window by *(1)* highlighting the name of the folder through the «Start|Programs» or «start|All Programs» menu, *(2)* right-clicking the name, and *(3)* choosing the «Open» menu.)

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[4] Self-extracting archive is not distributed for security reasons. The `zip` file can be unpacked using e.g. `Unzip.exe` which can be downloaded from the `http://www.info-zip.org/pub/infozip/UnZip.html` web page.

[5] It is important to note that the environment variables *cannot be adjusted* through the command line interpreted by a file manager (e.g. Norton Commander, FAR Manager, etc.). Only the command line of the operating system can be used for this purpose.

[6] More information can be found through the `http://grx.gnu.de/` web page.

- The icon can be defined through the «Shortcut» option of the «New» menu.

If the user wants to register the `phcalic.exe` or `phcaliw.exe` program to the `tid` extension (i.e. file type) then it can be done as follows:

- The Windows Explorer should be started. In the «View» or «Tools» menu the «Folder Options» has to be opened.
- On the «File Types» tab there is a press button called «New» or «New type». After clicking on the button, the specific `tid` extension is to be registered, the program is to be linked and optionally the icon is to be defined. In older Windows versions, the Action must also be declared to be open.

1.4.3 Linux Operating System

It is important to note before all, that the Linux variants of the program are in experimental stage yet. They have been used successfully with several window managers[7] (KDE, GNOME, XCFE, Window Maker, IceWM and fvwm2) under two distributions: Debian Sarge v3.1r5 with 2.4.27-3-i386 kernel (XFree86's X11 system) and SuSE v10.0 with 2.6.13-i686 kernel (X.Org's X11 system). The successful running is not guaranteed under other systems, e.g. the program works only with mouse under Debian Etch with any architecture.

The executables, some parts of the documentation and the example files are to be found in the freely downloadable `lphcali.tgz` file. The installation is suggested to be done the following way:

- A directory should be created within the `/home/`*username* directory of the user in which *p*HCali will be installed.
- The file `lphcali.tgz` has be copied in the previously created directory and extracted with the

  ```
  tar -xzf lphcali.tgz
  ```

  command.
- The file `lphcali.tgz` can be deleted after extraction.

Certainly there are other means of the installation. If more than one users want to use the program and they do not want to have multiple copies of it on the fixed drives then the administrator (`root`) may copy the executables to the appropriate directories. The above described method, however, does not require the help of the system administrator, any user is able to carry out the installation alone.

After the installation, the programs are ready to use. In case the directory of the *p*HCali exists in the `PATH` environment variable then the program can be started from an X terminal window with the `phcalit`, `phcalix`, `phcalit.shared` or `phcalix.shared` commands. Otherwise `./phcalit`, `./phcalix`, etc. commands should be used. The programs can also be started by clicking on an icon. The creation procedure of an icon depends very much on the window manager or graphical desktop used. The file `phcali.png` can be used as the image file of the icon.

The executables `phcalit` and `phcalix` are compiled with static libraries, which means that the executables contain everything that is needed during runtime. These programs can be installed and run without the help of the root user, but their size is reasonably large. The file `lphcali.tgz` contains the executables compiled with shared libraries under the names `phcalit.shared` and `phcalix.shared`. These programs are significantly smaller in size, but they depend on libraries within the following packages: `libg2c0`, `libmotif3` and the DISLIN version 9.0 libraries.[8] The user may delete the not used executables.

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[7] The position of the program-window might slightly differ from the desired one under some window managers (e.g. under fvwm2).

[8] At file level, the following dynamic libraries are necessary during runtime to run the shared executables:

`libdislin_d.so.9`, `libg2c.so.0`, `libm.so.6`, `libgcc_s.so.1`, `libc.so.6`, `libXm.so.3`, `libXt.so.6`, `libX11.so.6`, `/lib/ld-linux.so.2`, `libXmu.so.6`, `libSM.so.6`, `libICE.so.6`, `libXext.so.6`, `libXp.so.6` and `libdl.so.2`.

Chapter 2

Reference Guide

This chapter demonstrates the usage of *p*HCali on a real experimental system. The experimental data consist of two titration curves:

- 6,035 cm^3 ~0,1 M HCl solution has been titrated with 0.2 M KOH solution for the first curve and
- 6,035 cm^3 0,1006 M KH-phtalate solution has been titrated with the same 0.2 M KOH solution for the second one.

In the titrant and each solution to be titrated, the ionic strength has been set to 1.0 M with KCl so the change of the ionic strength during the titrations has always been less than 6 %. Both potential and pH have been registered during the experiments, so both E_m–V_m and pH$_m$–V_m data series are available (*see* the reference files `kh1-13e.tid` and `kh1-13ph.tid` supplied). The explanations are based on the E_m–V_m titration curves but whenever the pH$_m$–V_m curves need to be handled differently, the difference is emphasized.

2.1 Overview of the Program

The different variants of the program, their execution and the data files required by them have already been described in Section 1.2.

*p*HCali reads the input data from and writes the results into text files during runtime. Figures representing the final results of the calculation can be saved as image files. The filenames of the text and image files cannot be chosen freely. The user must choose a name for each task to be evaluated. This will be called `TASKNAME` from now on. The `TASKNAME` must comply with the naming conventions of the used operating system and it *must not contain* spaces, the use of underline sign (_) is suggested instead. The name of each input and output file is started with the given `TASKNAME`. After the `TASKNAME`, the extension stands separated from the name with a period.

There are text files that are connected to *p*HCali rather than the actual task. The names of them begin with `phcali`, and their extension determines their function.

Figure 2.1 summarizes the names of the text files where

`TASKNAME.tid` contains all the data required for the calculations: the starting values of the parameters, the titration curves and the (V_m,E_m) or (V_m,pH$_m$) data pairs needed for the E_m/pH$_m \rightarrow p$[H] calculations. The `tid` extension is the abbreviation of 'titration data'. The fully detailed description of the structure of this file is given in Subsection 2.2.1.

`phcali.cfg` is the name of the configuration file. The operation of the program can be altered in this file. The fully detailed description of the structure of this file is given in Subsection 2.2.2.

`TASKNAME.cin` is a file written by the program after the calculations. Its structure and contents are identical to that of the file `TASKNAME.tid` (*see* Subsection 2.2.1) with the only difference that it contains the changes made during the last run which can be the following:

- handling of the parameters (they are to be fitted or fixed),

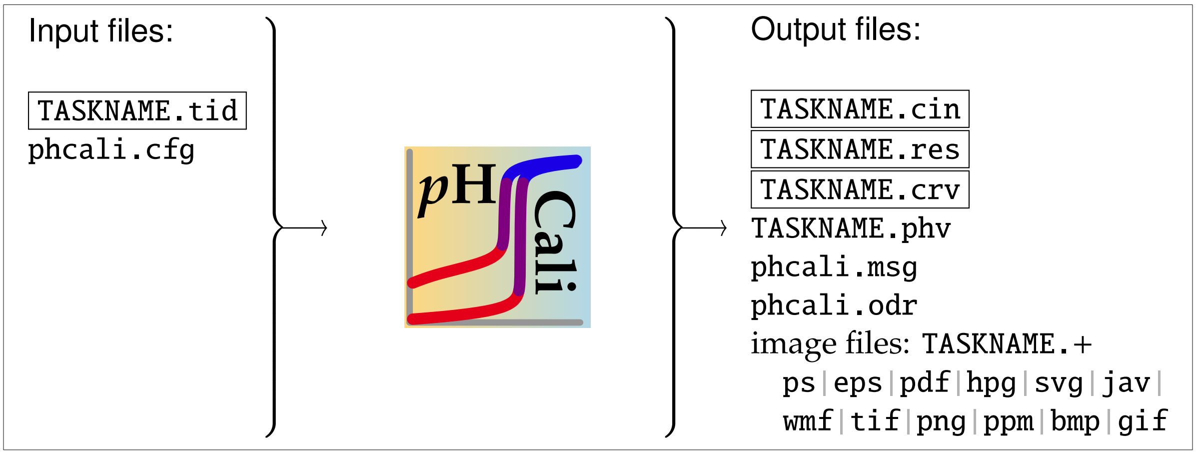


Figure 2.1: Input and output files of *p*HCali. The framed files are required or always created while the others are optional.

- final values of the fitted parameters and
- weighting factors of the individual data pairs (*see* Subsection 2.2.1 in detail).

The extension `cin` is the abbreviation of 'computed input'. *p*HCali is able to carry out the calculation either in a single step or in subsequent smaller steps allowing full user's controll. If the user wants to carry out the calculations in more steps or (s)he wants to continue the work later then it can be done by the help of this file. Changing the name of the file to another `TASKNAME` with `tid` extension, the calculation can be continued with the renamed file.

`TASKNAME.res` contains the final results of the calculations and parameters describing the circumstances of the calculation. The extension `res` is the abbreviation of 'results'. The fully detailed description of the structure of this file is given in Subsection 2.4.1.

`TASKNAME.crv` contains the measured and the calculated curves. The extension `crv` is the abbreviation of 'curves'. The user can create arbitrary figures with arbitrary programs using the data in this file. The fully detailed description of the structure of this file is given in Subsection 2.4.2.

`TASKNAME.phv` contains the results of the $\mathrm{E_m}/p\mathrm{H_m} \to p[\mathrm{H}]$ calculations based on the data pairs given in `TASKNAME.tid`. The extension `phv` is the abbreviation of 'pH-values'. At the end of the `TASKNAME.tid` file, the user can supply the titration curves of the equilibrium system to be studied after the calibration curves. In this case, the file `TASKNAME.phv` will contain the $(V,p[\mathrm{H}])$ data pairs for the system to be studied. This kind of data is the most practical input format for any further evaluation. The fully detailed description of the structure of this file is given in subsection 2.4.3.

`phcali.msg` contains the messages in case of windowed mode versions of the program. Originally, the console mode versions send these messages to the screen.

`phcali.odr` is the output file generated by the ODRPACK library and it contains a much more detailed description of the computation process and the results than the `TASKNAME.res` file. By default, the file `phcali.odr` is not created until the user requests it through line 33 of the `phcali.cfg`. The reason why the example files contain the numbers of the parameters besides their names is the more easily interpretable `phcali.odr`. This manual does not detail the structure of `phcali.odr`. The required information can be found in [11].

Beyond the text files, the figures created during the calculation can also be saved into image files under names `TASKNAME.*` where the extension can be one of the 12 supported image formats:

`*=ps` means PostScript file, which can be printed on PostScript printers directly, or can be converted to other image formats using other applications (e.g. Ghostscript and GSview[1]).[2]

`*=eps` means Encapsulated PostScript file, which is mainly for inserting graphics into LaTeX documents, but it can also be converted into other formats using other applications (e.g. Ghostscript and GSview programs mentioned above).[2]

`*=pdf` means Portable Document Format, which is mostly displayed in Adobe Acrobat Reader.[3]

`*=hpg` means Hewlett-Packard Graphics Language file. This can be used for printing on plotters.[4]

`*=svg` means Scalable Vector Graphics file.[5] This format is suitable for publishing vector graphics on the Web.

`*=jav` means Java Applet format.[6] This form is for displaying the figure on HTML pages.

`*=wmf` stands for the Windows Metafile format, which can directly be inserted into Word documents.

`*=tif` means Tagged Image File Format.[7]

`*=png` means the Portable Network Graphics[8] format which is suitable primarily for displaying graphics on HTML pages.

`*=ppm` means Portable Pixel Map format.[9] This format is to be displayed with special programs.

`*=bmp` means the Windows Bitmap format, which is mainly for specific purposes in Windows environment.

`*=gif` means the Graphics Interchange Format.[10] This format is to be displayed primarily on HTML pages.

If the name of the image file to be created is already exists, the program takes the first six characters of the `TASKNAME` and appends the string `_1`, `_2`, etc., together with the appropriate extension. The string created in this way will be the filename of the created image file. If more than ten image file names exist starting with the first six characters of the `TASKNAME` then the program continues with the numbering except the point that only the first five characters are taken from the `TASKNAME`.

The first seven of the above mentioned formats are vector graphics, which means that they can be enlarged or shrinked without loss of quality. The last five formats are bitmaps which may suffer loss of quality due to resizing. The resolution of the `svg`, `tif`, `png`, `ppm`, `bmp` and `gif` image files to be saved can be changed arbitrarily through the configuration file. The size of `ps` type image files corresponds to the size of an A4 paper. The size of the other image types inherits the ratio of the size of the work-window.

The following sections detail each step of the usage of the program: Section 2.2 describes the structure of the input files, Section 2.3 details the use of the program while in Section 2.4 the interpretation of the output files is given.

---

[1] Homepage: `http://www.cs.wisc.edu/~ghost/`

[2] Under pure DOS, this option is not working, probably due to a bug of the DISLIN library

[3] Homepage: `http://www.adobe.com`

[4] During the creation of such files the colors are lost, a greyscale image is saved.

[5] Homepage: `http://www.w3.org/Graphics/SVG`

[6] Homepage: `http://java.sun.com/applets/`

[7] Homepage: `http://www.awaresystems.be/imaging/tiff/faq.html`

[8] Homepage: `http://www.libpng.org/pub/png/`

[9] Homepage: `http://netpbm.sourceforge.net/doc/ppm.html`

[10] Information: `http://www.dcs.ed.ac.uk/home/mxr/gfx/2d/GIF89a.txt`

Table 2.1: Examples for the interpretation of lines containing real (R) and integer (I) types for input values.

variable names (and default values):	R_1(=0.00)	R_2(= 3.14)	I_1(= 365)	R_3(= 2.78)	I_2(= 999)
line to be read	value of the variables after reading				
`/`	0.00	3.14	365	2.78	999
`1.41 1.73 12 2.24   24`	1.41	1.73	12	2.24	24
`1.41,1.73,12,2.24,24`	1.41	1.73	12	2.24	24
`1.41 /`	1.41	3.14	365	2.78	999
`1.41,    ,12,    ,24`	1.41	3.14	12	2.78	24
`1.41,,12,,24`	1.41	3.14	12	2.78	24
`,,,,24`	0.00	3.14	365	2.78	24

2.2 Input Files

2.2.1 The Input Data File (`TASKNAME.tid` or `TASKNAME.cin`)

Each line of the input file contains one or more numbers that can be integers or reals. The data are separated by one or more spaces. Comma can also be used for separating data, however, only one comma can be placed betweeen two data. This comma can be combined with one or more spaces. After the data, remarks may appear which must be separated from the data with at least a space (or tabulator character) and a slash ('/').

Most data have default values so it is not required to give every data. In this case, however, either *(1)* the place of the missing datum must be indicated with two neighboring commas and only spaces can be put between the commas or *(2)* the line has to be closed with a slash. Both notations mean that there are missing data in the actual line and their default values must be used. Table 2.1 gives some examples for the syntax of input data. The detailed and precise rules of data reading can be found in FORTRAN 77 books (e.g. [12,13]).

For the titration data, the program supposes that the volumes are given in cm^3, the potentials are given in mV, the *p*H values are given in dimensionless *p*H units and the concentrations are given in mol/dm^3. If other units are used then the program will still calculate correctly, but the labels on the figures, in the text files and on the screen will be incorrect.

An input file consists of 3 sections, of which the first is compulsory (must not be omitted) and the second or the third is optional, one of them may be omitted:

- The first section (*see* Listing 2.1) contains the parameters that affect all titration curves.
- The second section (*see* Listing 2.2) contains the titration curves and those parameters that affect only the actual titration curve.
- The third section (*see* Listing 2.3) contains the (V_m,E_m) data pairs for which the *p*[H] values (i.e., the negative logarithm of [H^+]) should be calculated. Usually, this section contains the titration curves of the system to be studied after the calibration.

If *p*H rather than potential has been measured then the above statements are completely valid except that potential values should be replaced with *p*H values as it is shown in Listing 2.4. This listing contains Listings 2.1–2.3 together, but with *p*H values instead of potentials.

In the first section (*see* Listing 2.1 in case of the reference example, and Listing 2.4 if *p*H was measured), the following data should be given:[11]

Line 1 contains the the experimental uncertainty of the measured potential/*p*H (σ^y) expressed in mV (or in *p*H units). This value is around 0.1 mV/0.002 *p*H unit in case of high end devices.

---

[11] The next line number references will refer to the `kh1-13e.tid` data file, but the line numbers may differ in other systems.

Listing 2.1: Reference Data File with Potentials, Part I (`kh1-13e.tid`).

```
 1  0.1               / uncertainty of Em              (curve 1: HCl)
 2  0.002 0.0003      / uncertainty of Vm              (curve 2: KH-phthalate)
 3   1.38000E+01 1   / pKw                                      parameter  1
 4   3.77000E+02 1   / E0                                       parameter  2
 5   5.91600E+01 1   / m(=ln(10)RT/(zF))                        parameter  3
 6   0.00000E+00 0   / JH                                       parameter  4
 7   0.00000E+00 0   / JOH                                      parameter  6
 8   1.90000E-01 1   / c0 in mol/dm3 for the base solution      parameter 18
 9   1.00000E-03 1   / c(CO32-) in mol/dm3 for the impuritites  parameter 19
10   1.02000E+01 0   / log beta_1 for CO32-                     parameter 20
11   1.63000E+01 0   / log beta_2 for CO32-                     parameter 21
12   2               / number of given formation constants (<=9)
13   4.60000E+00 1   / log beta_1 for the weak acid             parameter 22
14   7.30000E+00 1   / log beta_2 for the weak acid             parameter 23
```

Using low end devices, this value can be as high as 1 mV/0.02 *p*H units.[12]

Line 2 gives the experimental uncertainty of the volume (σ^x) which may be considered either to be absolute or relative, depending on the type of burette used. Two real numbers must be given here. The first one gives the absolute value of uncertainty in cm^3-s, while the second number gives the relative error of the measured volume (V_m) expressed in ratio. In the first case, every measured volume has a constant uncertainty. In contrast, the error is linearly proportional to the measured volume in the second case. The program calculates the error in both ways for every measured data and it uses the bigger value for the further calculations. If only one method can be applied for the burette that is used, then the value belonging to the other method must be zero.

Is is important to know that the success of orthogonal fitting depends largely on the accurately given experimental uncertainties. That is why the values of these data should be given with great caution.

Lines 3–14 contain those parameters that affect all titration curves. All lines except line 12 contain one real and one integer number. The real one is the initial value of the parameter. The integer indicates whether the corresponding parameter should be fitted (=1) or fixed (=`0`). Lines 3–11 define the following parameters: pK_w, E' or I_d, m_E or m_p, J_H or J_H^p, J_{OH} or J_{OH}^p, c_b, c_c, lg β_1^C and lg β_2^C, respectively. Line 12 gives the number of cumulative formation constants of the titrated weak acid. In case of KH-phtalate, this value is two so lines 13 and 14 contain the values of lg β_1^A and lg β_2^A.

It must be noted, that the cumulative formation constants of the carbonate ion are in lines 10–11. Theoretically, these parameters may be fitted but *they must not be fitted in practice*! The titrant base (hopefully) does not have that much carbonate contamination to get enough experimental information from the titrations to determine the cumulative formation constants correctly. The values of these constants at the actual ionic strength can be taken from databases or tables (*see* [19], for example).

In the second part of the input data files (shown in Listing 2.2 for the reference example and in the appropriate lines of Listing 2.4 if *p*H was measured), the titration curves should be entered. In the reference example, lines 15–89 define the strong acid – strong base titration curves, while lines 90–171 define the weak acid – strong base ones. Each titration curve begins with a header: five data (four of these are fittable parameters) before the measured points. They are the followings:

Line 15 contains a real number which

- must be `0.0` in case of strong acid – strong base titration and

---

[12] The experimental uncertainty of *p*H is 0.00169 *p*H unit in each installed data file. Theoretically, this value corresponds to 0,1 mV so the results of the analogue calculations become comparable. In practice, any similar value (e.g. 0.002) works perfectly.

Listing 2.2: Reference Data File with Potentials, Part II (`kh1-13e.tid`).

```
 1   0.00000E+00     / H:A ratio in the weighted material (or 0) for curve  1
 2   6.03500E+00 0   / V0 in cm3 for curve 1                    parameter 31
 3   1.00000E-01 1   / +T(H)0 in mol/dm3 for curve 1            parameter 32
 4   0.00000E+00 0   / T(A)0 in mol/dm3 for curve 1             parameter 33
 5   0.00000E+00 0   / shift in the measured E/pH for curve 1   parameter 34
 6   0.0000   317.4   1.0e-00
 7   0.1000   316.3   1.0e-00
 8   0.2500   314.6   1.0e-00 / the next 64 lines are omitted from the manual
 9  11.6280 -372.1   1.0e-00
10  12.0280 -372.7   1.0e-00
11  -1.00      0.0   0.0
12   1.00000E+00     / H:A ratio in the weighted material (or 0) for curve  2
13   6.03500E+00 0   / V0 in cm3 for curve 2                    parameter 35
14   0.00000E+00 0   / +T(H)0 in mol/dm3 for curve 2            parameter 36
15   1.00600E-01 0   / T(A)0 in mol/dm3 for curve 2             parameter 37
16   0.00000E+00 0   / shift in the measured E/pH for curve 2   parameter 38
17   0.0000   164.9   1.0e+00
18   0.1000   160.0   1.0e+00 / the next 71 lines are omitted from the manual
19  11.5790 -372.2   1.0e-00
20  11.9790 -372.9   1.0e-00
21  12.3790 -373.3   1.0e-00
22  -1000.0    0.0   0.0
```

- it gives the ratio of the stoichiometric numbers the hydrogen ion and the anion in the weighted form of the weak acid. For example, this number is `1.0`, `2.0` and `0.0` in cases of KH-phtalate (*see* line 90), oxalic acid and sodium oxalate, respectively. The meaning of this line is clarified and detailed more deeply in the explanations of lines 17 and 18.

Line 16 is the initial volume of the solution to be titrated. For **pHCali**, it is a fittable parameter so the line contains a real and an integer number (see explanations of lines 3–14.)

Line 17 contains a real and an integer too. The real number is a fittable parameter:

- In case of strong acid – strong base titration, this line gives the total concentration of the hydrogen ion (T_H) in the solution.
- In case of weak acid – strong base titration, this line gives how much strong acid was additionally added into the solution. Since line 18 gives the value of T_A then
  $$\underline{T_H = (\text{datum in line 17} + (\text{datum in line 15} \times \text{datum in line 18}))}\,.$$
  This method of calculating T_H becomes important when the exact value of T_A is not known[13] so it has to be fitted as well. The method used in this program makes it possible to fit the weak acid content and the acidic contamination of the weighted material independently.

Line 18 also determines a parameter that can be fitted so it contains a real and an integer.

- In case of strong acid – strong base titration both values are zero.
- In case of weak acid – strong base titration the real number is the total concentration of the anion of weak acid (T_A) in the titrated solution. If the calculation is for a calibration, then the value of the integer must be zero, so the parameter must be fixed.

Line 19 contains a shift parameter providing a—somewhat dangerous—correction method if the potential or *p*H values of the actual titration curve are accidentally shifted compared to the other curves. This problem may occur if the *p*H-meter was calibrated by one buffer before each titration and this calibration was not successful. The value of the parameter in line 19 may correct this shift. *Precise measurements, however, must not be replaced by any mathematical correction, thus this line must get a value of* `0.0` *in most cases!* A possible application of this parameter is described in Section 4.3.

---

[13] This situation might occur *only* for the determination of the cumulative formation constants of a weak acid. It must not be applied during calibration since it is based on an exactly known T_A value!

Lines 20–88 contain the complete titration curve. Each line describes one titration point. Their order is arbitrary, it is advisable but not compulsory to sort the data by the increasing volume of the titrant. Repeated measurements (that is where the contents of lines 15–18 are the same) can be given as a single titration curve, as it is shown in the example of Subsection 3.3.1 after the omission of the erroneous measured data.

Every titration point is given by three real numbers: the measured volume (V_m), the potential or pH (E_m or pH_m) and the relative weighting factor (w_R). The value of the last parameter is `1.0` by default so this value is valid if it is not given by the user explicitly. In this case, a slash (/) must be used to terminate a line (*see* second paragraph of Subsection 2.2.1 on page 18).

The relative weighting factor determines the contribution (importance, weight) of the specific titration point within the sum of squares function (*see* Section A.4). *w_R is not equal to any of the weighting factors defined in Section A.4 (w, w^x and w^y).* In fact, w_R is rather used to calculate them using the following equations:[14]

$$w^y = \frac{w_R}{(\sigma^y)^2} \qquad \text{and} \qquad w^x = \frac{w_R}{(\sigma^x)^2}\,.$$

The values of the relative weighting factors are handled by the program in the following way:

- The largest value of them is 1.0, this is means the greatest contribution.
- If the value of the relative weighting factor is ≤0.0 then the specific point is omitted, it will appear neither in the calculations, nor on the figures. These data are called deleted ones.
- If the weighting factor is a positive number but its value is <0.00001 then the program will remember the presence of the point and display it on the figures, but **pHCali** will not include that point in the calculations. These are the skipped data (against the deleted ones).
- If the $0.00001 \le w_R \le 1.0$ relations are true then the program will use the given weighting factor at the calculations for the specific titration point.

Line 89 declares the end of the first titration curve. A titration curve ends if

- the `TASKNAME.tid` file ends or
- the given value for the volume is a negative number. In this case, the potential/pH and the weighting factor should also be given or they should be replaced with a slash! The value of the negative number may be interpreted in three different ways:
  - `-1.0` (or precisely a number between `-0.99` and `-9.9`) means that a new titration curve follows in the input file.
  - `-10.0` (or precisely a number between `-9.91` and `-999.0`) means that the program terminates to read the input file regardless of anything that is beyond the actual line.
  - `-1000.0` (or precisely a number between `-999.1` and `-10000.0`) means that the program finishes the reading of titration curves and it supposes that the remaining part of the file contains only such titration points for which the $E_m/pH_m \rightarrow p[\mathrm{H}]$ calculation should be carried out based on the result of the calibration.

Lines 90–171 should be interpreted the same way as the previous ones, because they describe the weak acid – strong base titration.

The remaining lines of the reference data file contain the third part (*see* Listing 2.3 or the appropriate lines of Listing 2.4 in case of pH measurement). In these lines, the titration data

---

[14] These expressions require the really precise values from the first two lines of the input file.

Listing 2.3: Reference Data File with Potentials, Part III (`kh1-13e.tid`).

```
 0.0000  317.4
 0.1000  316.3
 0.2500  314.6           / the next 64 lines are omitted from the manual
11.6280 -372.1
12.0280 -372.7
```

Listing 2.4: Reference Data File with *p*H values (`kh1-13ph.tid`).

```
0.00169         / uncertainty of pHm          (curve 1: HCl)
0.002 0.0003    / uncertainty of Vm           (curve 2: KH-phthalate)
 1.38000E+01 1  / pKw                                  parameter  1
 0.00000E+00 1  / Id                                   parameter  2
-1.00000E+00 1  / m(=-1)                               parameter  3
 0.00000E+00 0  / JH^p                                 parameter  4
 0.00000E+00 0  / JOH^p                                parameter  6
 1.90000E-01 1  / c0 in mol/dm3 for the base solution  parameter 18
 1.00000E-03 1  / c(CO32-) in mol/dm3 for the impuritites    parameter 19
 1.02000E+01 0  / log beta_1 for CO32-                 parameter 20
 1.63000E+01 0  / log beta_2 for CO32-                 parameter 21
 2              / number of given formation constants (<=9)
 4.60000E+00 1  / log beta_1 for the weak acid         parameter 22
 7.30000E+00 1  / log beta_2 for the weak acid         parameter 23
 0.00000E+00    / H:A ratio in the weighted material (or 0) for curve  1
 6.03500E+00 0  / V0 in cm3 for curve 1                parameter 31
 1.00000E-01 1  / +T(H)0 in mol/dm3 for curve 1        parameter 32
 0.00000E+00 0  / T(A)0 in mol/dm3 for curve 1         parameter 33
 0.00000E+00 0  / shift in the measured E/pH for curve 1     parameter 34
 0.0000   1.094  1.0e-00
 0.1000   1.113  1.0e-00
 0.2500   1.142  1.0e-00 / the next 64 lines are omitted from the manual
11.6280  12.749  1.0e-00
12.0280  12.758  1.0e-00
-1.00           /
 1.00000E+00    / H:A ratio in the weighted material (or 0) for curve  2
 6.03500E+00 0  / V0 in cm3 for curve 2                parameter 35
 0.00000E+00 0  / +T(H)0 in mol/dm3 for curve 2        parameter 36
 1.00600E-01 0  / T(A)0 in mol/dm3 for curve 2         parameter 37
 0.00000E+00 0  / shift in the measured E/pH for curve 2     parameter 38
 0.0000   3.672  1.0e+00
 0.1000   3.755  1.0e+00 / the next 71 lines are omitted from the manual
11.5790  12.751  1.0e-00
11.9790  12.763  1.0e-00
12.3790  12.769  1.0e-00
-1000.0 /
 0.0000   1.094
 0.1000   1.113
 0.2500   1.142          / the next 64 lines are omitted from the manual
11.6280  12.749
12.0280  12.758
```

are entered: the measured volume and the measured potential or *p*H in each line.[15] It is important to note, that the values of V_m are not used during the $E_m/pH_m \rightarrow p[H]$ calculations. They are present for the easier identification of the data only.

2.2.2 The Configuration File (`phcali.cfg`)

The properties of *p*HCali can be adjusted by changing the contents of the `phcali.cfg` file. The presence of the configuration file is not required. If it is not present the program uses the default settings.

It is a text file with a simple structure: every line in it determines a property and every line except five ones contain one data. The data can be integer or real numbers, boolean values (`.TRUE.` or `.FALSE.` constants) or strings. The integers generally refer to the symbols and lines used in the figures. Their more important values are shown in Figure 2.2. The data

---

[15] For the sake of an example, the strong acid – strong base titration data are repeated in the third part of the reference data file. In practice, however, the titration curves of the equilibrium system to be investigated after the calibration should be included in the third part.

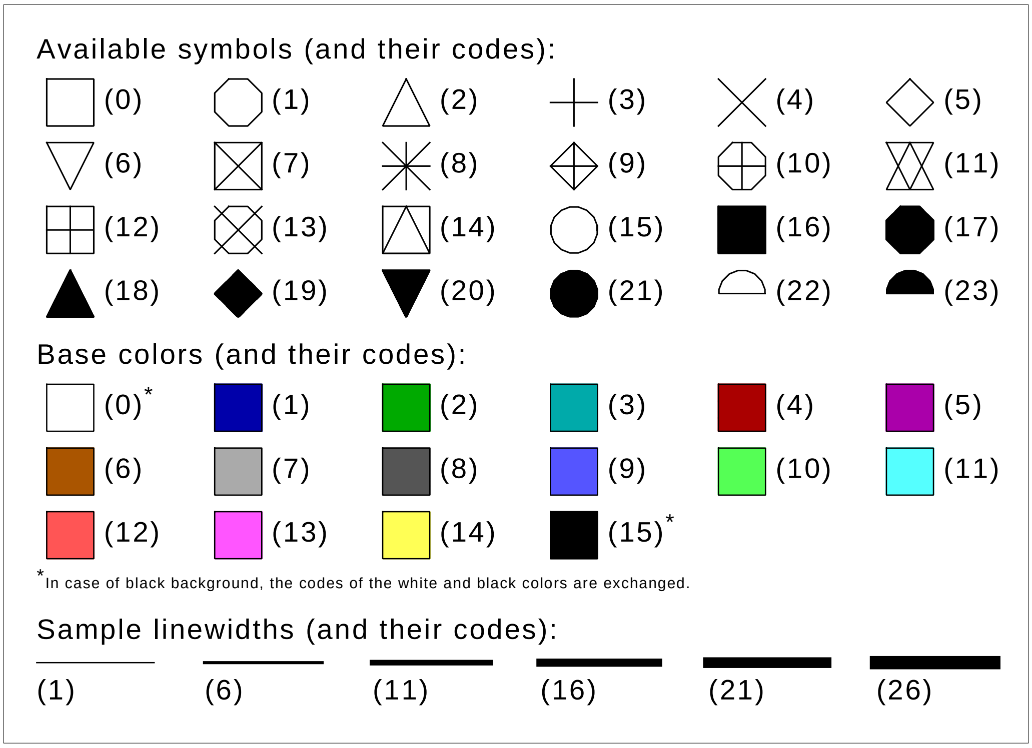


Figure 2.2: Symbols, base colors and line widths available on the graphics screen, as well as, their codes.

may be followed with remarks which must be started with a slash (/). Data and the leading slash of remarks must be separated at least one space or tabulator character.[16] Lines must not be omitted, *not even* if they are not being used by the specific variant of the program (e.g. the text mode variant does not contain the parameter modifying windows of the other variants). The file `phcali.cfg` (with the default settings) is shown in Listing 2.5.

If an integer number defines a color, this number can be replaced by four integer values in any line of the `phcali.cfg` file.[17] In this way, not only the colors listed in Figure 2.2 can be chosen, any color can be defined as an RGB-color. In this case, the first value of these four integer ones must be negative and the following three values are the intensities of the red, green and blue components, respectively. The intensity values must be in the 0–255 range. For example, the „`-1 0 255 0`" numbers defines the pure green color, or the black and white colors can be defined as „`-1 0 0 0`" and „`-1 255 255 255`", respectively.[18]

The meaning of the specific lines are the following:

Line 1 determines the colors of the background and the foreground (used for frames and texts). This line can have three different syntaxes:

1. The line includes only one logical value which can be `.TRUE.` (white background and black foreground) or `.FALSE.` (black background and white foreground).
2. The line includes one logical value followed by two integer ones. The meaning of the logical value corresponds to the previous syntax, but now it determines only the default color of the background for transparent PNG and GIF image files (*see* the second line). The two integer values give the colors for the background and foreground, respectively.
3. The line includes one logical value followed by six integer ones. The meaning of the

---

[16] The precise definition of those characters which can be used for data separation, can be found in the first part of Subsection 2.2.1.

[17] The file `phcali.rgb` is the same as the original configuration file, but the colors are given as RGB-values.

[18] Among the others, this method can also be used for defining colors in Windows operating systems.

Listing 2.5: The configuration file including the default values (`phcali.cfg`).

```
 1  .TRUE.  / background is white(.TRUE.) or black(.FALSE.) or VGA/RGB colors
 2  .FALSE. / disables(.FALSE.) or enables(.TRUE.) transparency for PNG/GIF files
 3  8       / color for axis, grids, labels and axis titles
 4  4       / color of curve 1  [Possible values and colors:
 5  1       / color of curve 2  [ 0:black     6:brown        12:light red
 6  5       / color of curve 3  [ 1:blue      7:light gray   13:light magenta
 7  2       / color of curve 4  [ 2:green     8:dark gray    14:yellow
 8  3       / color of curve 5  [ 3:cyan      9:light blue   15:white
 9  12      / color of curve 6  [ 4:red      10:light green
10  9       / color of curve 7  [ 5:magenta  11:light cyan
11  13      / color of curve 8  [0/15 may be reversed with the background color
12  10      / color of curve 9  [an RGB value should be given (0<=r,g,b<=255) after
13  11      / color of curve 10 [a negative integer, e.g.: -1 r g b.
14  21      / symbol for the fitted data  [The possible symbols and their values
15  15      / symbol for the skipped data [are in the documentation.
16  12      / size of symbols for the lower left (LL) graph [positive number
17  20      / size of symbols for the lower right (LR) graph [positive number
18  16      / size of symbols for the upper left (UL) graph [positive number
19  30      / height of all titles and the labels of the LL graph [positive number
20  25      / height of labels for the LR and the UL graphs [positive number
21  25      / height of texts in the legend [a positive number
22  1       / thickness of initially calculated curves [positive number
23  3       / thickness of finally calculated curves [positive number
24  1       / thickness of connecting lines for the LR/UL graphs [positive number
25  16      / length of major ticks [positive number
26  8       / length of minor ticks [positive number
27  14      / color of the calculate and point-selector buttons
28  12      / color of the save&quit button
29  13      / color of the working... button
30  11      / color of the file exporting buttons
31  .FALSE. 0.0 0.0 / if .TRUE. then xmin and xmax are given for LR graph
32  .FALSE. 0.0 0.0 / if .TRUE. then ymin and ymax are given for UL graph
33  .FALSE. / if .TRUE. then the report of ODRPACK is also written as "phcali.odr"
34  .TRUE.  / if .FALSE. then the image files does not inlcude the UR description
35  .FALSE. / if .TRUE. then the program returns to the modifying window after calc
36  'notepad.exe'   / name of the preferred editor
37  -1 -1 0 0       / place of menu windows in pixels: x0, y0, xwidth and ydepth
38  -1 -1 0 0       / place of work window in pixels: x0, y0, xwidth and ydepth
39  .FALSE. / if .TRUE. then the menu windows are skipped
40  853 603 / width and height (pixels) of TIFF, GIF, PNG, PPM, BMP and SVG images.
```

logical value corresponds to the first syntax, but now it determines only the default color of the background for transparent PNG and GIF image files (*see* the second line). The 2–4. and 5–7. integer values give the intensities of the red, green and blue components of the colors for the background and foreground, respectively.

Default: white background with black foreground.

Line 2 determines the background of the PNG and GIF image files. `.FALSE.` means that the background color is defined in the first line while `.TRUE.` means transparent background. In the latter case the background color is determined by the document in which the image file was inserted.
Default: as defined in the first line.

Line 3 defines the colors of the axes, grids, axis titles, and labels of the figures. The values can be between `0`–15 or can be given as RGB-color.
Default: dark gray.

Lines 4–13 define the colors of the ten possible curves, respectively. The values can be between `0`–15 or can be given as RGB-colors.
Default: 1: red, 2: blue, 3: magenta, 4: green, 5: cyan, 6: light red, 7: light blue, 8: light magenta, 9: light green and 10: light cyan.

Line 14 defines the symbol of the fitted data in the figure. The value can be between `0–23`.
Default: solid circle (●).

Line 15 defines the symbol of the experimental points excluded from the fitting. The value can be between `0–23`.

Default: empty circle (○).

Lines 16–18 define the sizes of the symbols used in the lower left, lower right and upper left figures of the graphical window, respectively. The value can be between `0–32768`, but it is meaningful only between `0–100`.
Default: lower left: 12, lower right: 20 and upper left figure:16.

Line 19 defines the sizes of the axis titles and axis labels in the lower left figure of the graphical window. The value can be between `0–32768`, but it is meaningful only between `0–100`.
Default: 30.

Line 20 is the same as line 19 except that it corresponds to the upper left and lower right figures.
Default: 25.

Line 21 defines the size of the legend text in the lower left figure of the graphical window. The value of the number can be between `0–32768` but it has practical meaning only between `0–100`.
Default: 25.

Line 22 defines the thickness of the lines in the lower left figure of the graphical window for the curves calculated from the initial parameter values. The value of the number can be between `0–32768` but it has practical meaning only between `0–50`.
Default: 1.

Line 23 is the same as line 22 except it regards to the curves calculated from the final parameter values of the fitting.
Default: 3.

Line 24 defines the thickness of lines connecting the points in the lower right and upper left figures. The value of the number can be between `0–32768` but it has practical meaning only between `0–50`.
Default: 1.

Lines 25–26 define the lengths of the major and minor ticks, respectively, in all figures of the graphical window. The value of the number can be between `0–32768` but it has practical meaning only between `0–30`.
Default: 16 (major ticks) and 8 (minor ticks).

Lines 27–30 determine the background colors of *(27)* the «Calculate» and the point-selector buttons, *(28)* the «save&quit» button, *(29)* the «working...» button and *(30)* the image file export buttons. The value of the number can be between `0–15` or can be defined as RGB-color.
Default: Calculate, save&Quit, working... and image files.

Line 31 determines the minimum and maximum values of the horizontal axis in the lower right figure of the graphical window. A logical value and two real numbers must be given here. If the first data is `.FALSE.` then the program automatically determines the minimum and maximum values, regardless of the given real numbers. If both reals are zero, the same happens, independently of the logical value. If the value of the logical variable is `.TRUE.` and at least one real number is different from zero then the real numbers determine the minimum and maximum, respectively.
Default: the program calculates the limits.

Line 32 is analogous to the previous line except it corresponds to the vertical axis in the upper left figure.
Default: the program calculates the limits.

Line 33 determines whether the original messages of the ODRPACK library (used for the

orthogonal regression) are to be available for the user. A logical value is required here. In case the value is `.TRUE.` the program stores the messages in the `phcali.odr` file. In case of `.FALSE.` this file is not created. The messages of the ODRPACK library are much more detailed than those of pHCali so those users, who are interested in orthogonal regression, are suggested to let this file created. This manual does not explain the ODRPACK library itself in detail so the document given in [11] should be downloaded from the InterNet in order to interpret the content of `phcali.odr`.
Default: `phcali.odr` is not created.

Line 34 contains a logical value which determines whether the image files created by the program contain an information block in the upper right part or not. If the value is `.TRUE.` then the information block is present, in the other case not.
Default: the information block exists.

Line 35 also contains a logical value which alters how the program runs. If the value is `.TRUE.` then pressing the «save&quit» button does not really terminate the program, rather it returns to the parameter modifying window where the values and the fitting state of the parameters can be modified and a new calculation can be started.[19]
Default: there is no return.
Limitation: This value does not affect the text mode variant of the program, because there is no parameter modifying window.

Line 36 contains the name of the preferred text (or ASCII-) editor between apostrophes. If the path of the editor is not listed in the `PATH` environment variable then the full path must be entered between the apostrophes.
Default: `'notepad.exe'` under Windows[20] and `'gvim'` under Linux. This option is not functional under DOS.

Line 37 contains four integers to determine the position and size of the file-chooser and parameter-modifier windows. All numbers must be given in pixels. The first two numbers determine how far the upper left corner of the window has to be placed from the upper and left edges of the screen. The third and fourth numbers determine the width and height of the windows.
Default: The width and height are 636 and 400 pixels, respectively. The window is centered in both directions on the screen. This option is not functional under DOS.

Line 38 contains four integers to determine the position and size of the work-window. All numbers must be given in pixels. The first two numbers determine how far the upper left corner of the window has to be placed from the upper and left edges of the screen. The third and fourth numbers determine the width and height of the windows.
Default: The weight and height of the window are 90 % of those of the screen, respectively. The window is centered in both directions on the screen. This option is not functional under DOS.

Line 39 contains a logical value. If it is `.TRUE.` the program skips the file-chooser and parameter-modifier windows and opens directly the work window. This option has the same effect as the second command line parameter (*see* Subsection 2.3.1).
Default: the above mentioned two windows appear when pHCali is executed. This option is not functional under DOS.

---

[19] This possibility may make the study of the examples in Chapter 3 easier if the user uses the console or window mode variant of the program.

[20] Although, Notepad is the default text editor in Windows, it is too simple even for the most basic editing tasks. For example, this editor does not display the actual character position. Notepad can be replaced by numerous free and/or commercial editors. Perhaps, the most obvious one is the Metapad (Homepage: `http://www.liquidninja.com/metapad/`).

Line 40 contains two integers to determine the horizontal and vertical size (given in pixels) of the savable image files. These values influence the image files only if their form is `svg`, `tif`, `png`, `ppm`, `bmp` or `gif`.
Default: 853 pixels horizontally and 603 pixels vertically.

2.3 Executing *p*HCali

*p*HCali can be run *(1)* from a command line by typing the name of the executable and the parameters,[21] *(2)* by clicking on the icon of the program or (3) by dragging one of the data files onto the icon of the program. After starting, the program

- interprets the command line parameters (in case of dragging, the name of the data file is interpreted as the first command line parameter),
- opens the file-chooser window in console and window mode in which the `TASKNAME` can be modified (this window does not exist in text mode),
- opens the parameter-modifier window (this window does not exist in text mode, as well), in which the initial values and the fitting status of the parameters can be modified, then
- it opens the work-window, in which the fitting, the inclusion/exclusion of the experimental points can be done. After completing the tasks in this window, the program stops running or returns to the parameter-modifier window, if the user requests this in line 35 of the `phcali.cfg` file.

2.3.1 Optional Command Line Parameters

The program can be started without any parameter but experienced users can use two command line parameters for using the program more efficiently:

1. If the value of the optional first parameter is "`?`", "`/?`", "`-H`", "`-h`", "`/H`" or "`/h`" then the program displays a brief help in text or console mode, or it writes this help into the file `phcali.msg` in windowed mode.

   In all other cases the first parameter can be the `TASKNAME` or a minus sign (`-`). If the first parameter is a minus sign or it is not given then the default value, i.e. `phcali` is used for the `TASKNAME`. If the end of the parameter contains the `.tid` extension (i.e. the user gave the name of the input file), the program detaches the extension from the string and uses the remaining characters as the `TASKNAME`.

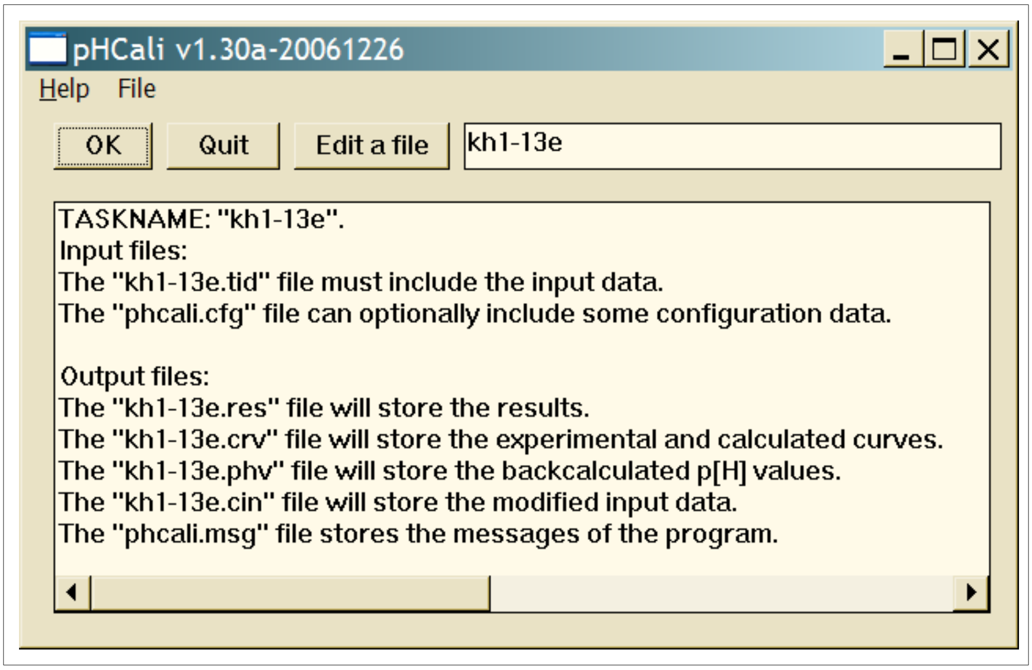
2. The value of the optional second parameter can be either a minus sign (`-`) or a colon (`:`). In case of minus sign the program skips each graphical window, it immediately carries out the fitting on the basis of the `TASKNAME.tid` file, it creates the result files and finally it stops running. This option lets the program to work without any interaction, so its usage can be automated with appropriate input files.

   In case of colon the program skips the file-chooser and parameter-modifier windows and opens the work-window directly. This will speed up work if the user is sure that no changes are needed in the `TASKNAME.tid` file. This parameter has no effect in text mode since the mentioned windows are inaccessible and every change needed to be done in the input file should be done prior running.

   It can be seen from the above interpretations, that the two possible values of the second parameter exclude each other so they cannot be given together at the same time.

---

[21] Under Linux, it should not be forgotten that `./phcalit` or `./phcalix` must be typed instead of the simple file names if the actual directory is not given in the `PATH` environment variable.



kh1-13e

TASKNAME: "kh1-13e".
Input files:
The "kh1-13e.tid" file must include the input data.
The "phcali.cfg" file can optionally include some configuration data.

Output files:
The "kh1-13e.res" file will store the results.
The "kh1-13e.crv" file will store the experimental and calculated curves.
The "kh1-13e.phv" file will store the backcalculated p[H] values.
The "kh1-13e.cin" file will store the modified input data.
The "phcali.msg" file stores the messages of the program.

Figure 2.3: The file-chooser window in case of the reference example.

2.3.2 Usage of the File-Chooser Window

If *p*HCali has been started without any command line parameters (which is most likely when it is started from icon) the `TASKNAME` will be "`phcali`". This default string can be changed through the file-chooser window, which is shown in Figure 2.3 in case of the reference example. The window contains two menus, three buttons, an information line and an information box below the others. The functions can be accessed with the mouse or with the use of «Tab», «Space» and/or «Enter» keys as usual. The purpose of the menus and buttons are the following:

The Help menu displays the version number and the purpose of the program and it also informs how this manual can be accessed.

The File|Change TASKNAME item or the information line makes possible to change the name of the task. The button activates the open file dialog box of the operating system, and lists the files having `.tid` extension for the choice. The name of the chosen file will be the `TASKNAME` without its extension. The same name will be displayed in the information line as well. The `TASKNAME` can also be changed in the information line without using the open file dialog box.

The OK button goes forward to the parameter-modifier window.

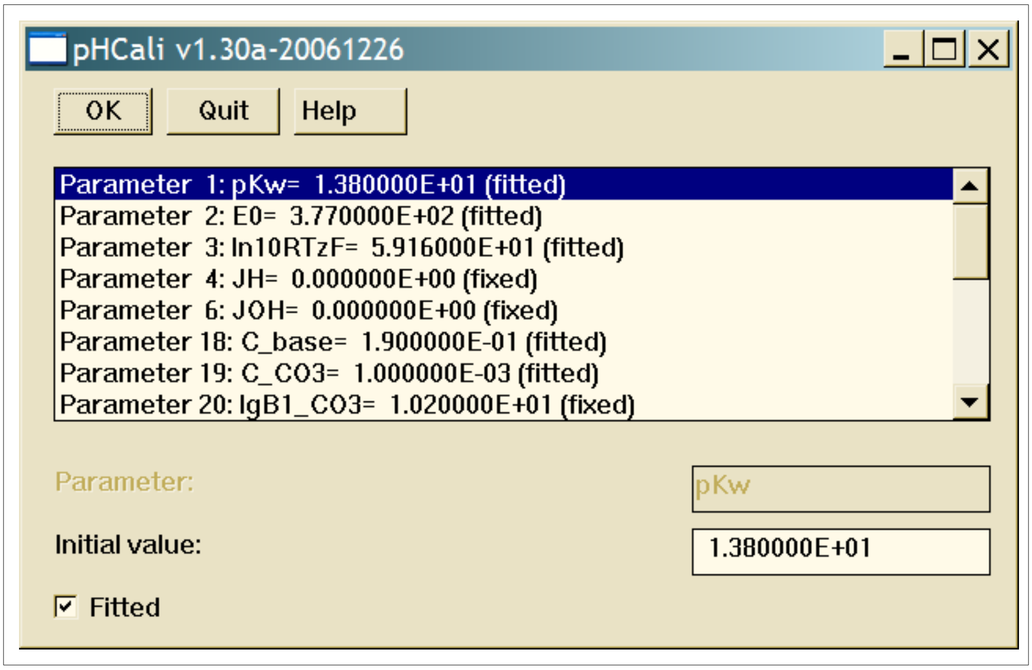
The Quit button terminates the program.

The Edit a file button lets the user to start the preferred text editor in order to modify an arbitrary text file. The preferred editor can be set in line 37 of the `phcali.cfg` file. The default is `notepad.exe` under Windows and `gvim` under Linux.

The information box displays detailed information about the files to be read and the files to be created. Its contents are actualized if `TASKNAME` is changed through either the «File|Change TASKNAME» menu item or the information line.

2.3.3 Usage of the Parameter-Modifier Window

The parameter-modifier window is shown in Figure 2.4 in case of the reference example. The initial values and the fitting state of the parameters can be modified before the calculations



Parameter 1: pKw= 1.380000E+01 (fitted)
Parameter 2: E0= 3.770000E+02 (fitted)
Parameter 3: ln10RTzF= 5.916000E+01 (fitted)
Parameter 4: JH= 0.000000E+00 (fixed)
Parameter 6: JOH= 0.000000E+00 (fixed)
Parameter 18: C_base= 1.900000E-01 (fitted)
Parameter 19: C_CO3= 1.000000E-03 (fitted)
Parameter 20: lgB1_CO3= 1.020000E+01 (fixed)

Parameter: pKw

Initial value: 1.380000E+01

☑ Fitted

Figure 2.4: The parameter-modifier window in case of the reference example.

by the help of this window. The window contains three buttons, a list box, an inactive text field, an active number field and a check box. They can be used either with mouse or with the help of «Tab», «Space» and/or «Enter» keys as usual. The functions of the OK and Quit buttons are the same as those described in the previous subsection, except that pressing the «OK» button the program goes forward to the work-window. The «Help» button outlines the usage of the window.

In order to modify a parameter, the specific item must be chosen in the list. For each parameter, the list shows the serial number attached by the program, the name, the initial value and the actual fitting state (fitted or fixed). By choosing one parameter, the values of the other fields are automatically updated. The initial value of the chosen parameter can be changed within the number field. The change is interpreted by the program after pressing the «Enter» key. If the syntax of the value is correct then it is also displayed in the list. The same stands for the check box. In case it is checked the specific parameter is to be fitted.

If the user requested the program to return to the parameter-modifier window in line 35 of the `phcali.cfg` file then the program can only be terminated from this window using the «Quit» button.

2.3.4 Usage of the Work-Window

Before opening the work-window, *p*HCali carries out the fitting with the initial parameter values and draws the results on the screen. The initial look of the work-window is shown in Figure 2.5 in case of the reference example. Figure 2.6 shows the appearance of the work-window when the measured *p*H values are fitted instead of potentials. The work-window is split into four parts:

1. The lower left part the figure shows the titration curves. Each curve is plotted with different colors. The symbols represent the measured data. The solid symbols are the points that were taken into account during the fitting and the empty symbols show data eliminated from the calculations. The dashed lines represent the curve calculated using the initial values of the parameters[22] while solid lines give the curves calculated using the

---

[22] Mainly the wrong initial values can be identified by the help of these curves.

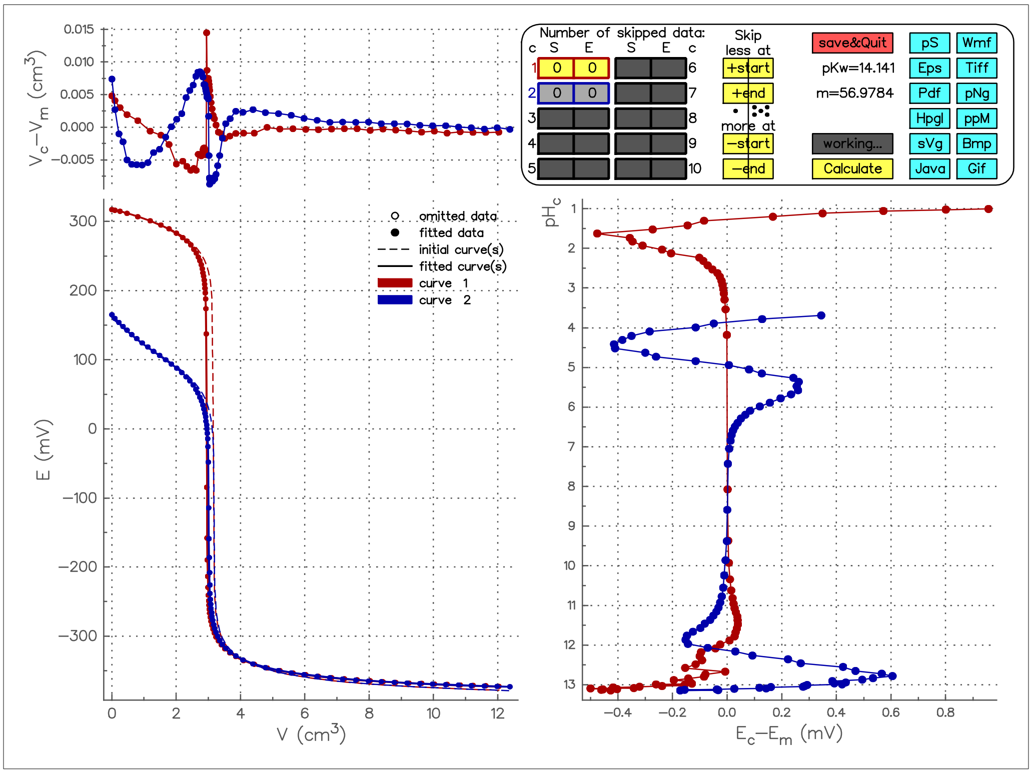


Figure 2.5: The initial work-window of the reference example if potential is fitted.

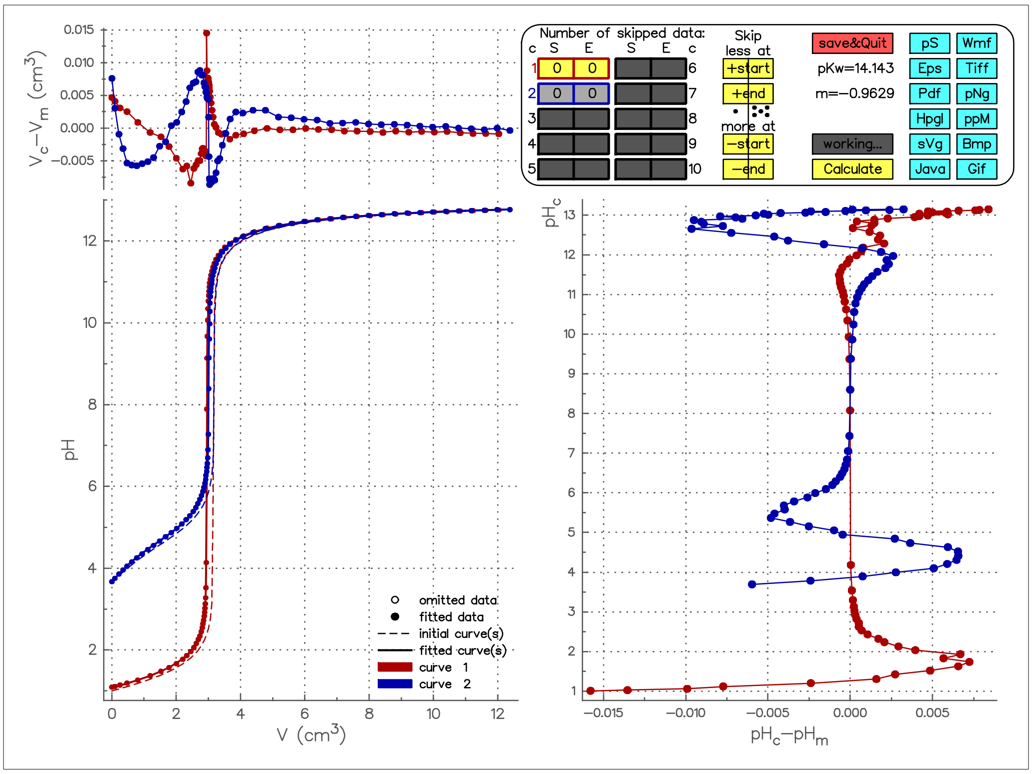


Figure 2.6: The initial work-window of the reference example if *p*H is fitted.

last parameter values. The scaling and labeling of the axes are done automatically by the program. The colors, type and size of the symbols together with the thickness of lines can be defined within the `phcali.cfg` file.

This figure also contains the legend. The symbols concerning all curves are written in black in this legend. Colored rectangles show the colors of specific curves. The order of the curves corresponds to the order within the `TASKNAME.tid` file. This legend corresponds to all figures of the work-window.

2. The lower right figure shows the differences between the calculated and measured potentials (or pHs) as a function of the calculated pH ($p\mathrm{H}_c$). The figure is rotated by 90 degrees so the $p\mathrm{H}_c$ axis of this figure precisely corresponds to the E (or pH) axis of the lower left figure. The line connecting the points has no specific meaning, it only provide better visibility for the trend of the curves. The range of the horizontal axis of the figure can be set to arbitrary values by the user in line 31 of the `phcali.cfg` file.
3. The upper left figure shows the differences between the calculated and measured volumes as the function of the volume. The line connecting the points have no meaning, it only provides better visibility for the trend of the curve. The volume (horizontal) axis of this figure is the same that of the lower left figure so it is not drawn again. The range of the vertical axis in the upper left figure can be set to arbitrary values in line 32 of the `phcali.cfg` file.
4. The operating panel can be found in the upper right corner. It makes possible *(1)* to exclude previously fitted points or to reinsert previously excluded points to both ends of the curves, *(2)* the fitting can be carried out multiple times according to the changes made and `(3)` the program can be terminated.

   The beginning and the end of a curve is to be understood as the following: titration points can be given in arbitrary order by the user. These data are sorted by the program along with increasing volume of the titrant prior to any calculation. According to this, the beginning means the point with the least volume and the end means the point with the greatest volume regardless of their position given in the input file. If data of multiple repeated titrations are given within one titration curve then the data of the experimentally different titrations are mixed. An example for this is shown in Section 3.3.

2.3.4.1 Use of the Operating Panel with Mouse

The look of the operation panel is shown in Figure 2.5. The tasks of the buttons are described next.

- Each of the 10 buttons on the left side (which are grouped in two columns) are connected to one titration curve. The frames, vertical divider lines and the serial numbers of the buttons are colored according to the appropriate curve settings. Clicking on one of the buttons put the connected curve into the focus so every further change affects this curve. The background color of the active curve is yellow by default while the others are light gray. If less than ten curves are present in the actual task (e.g., there are only two ones in the reference example), the buttons of the unavailable curves have black lines and dark gray background.

  Every button contains two numbers. The left one indicates how many points are to be excluded from the beginning of the curve. The right number indicates the number of data to be excluded at the end of the curve. These numbers change if the user excludes or includes points for the next fitting. Points cannot be excluded from the center of curves using the operation panel. Such changes have to be made manually by modifying the weighting factors within the `TASKNAME.tid` file. The interpretation of the relative weighting factors is described in Subsection 2.2.1 (*see* the description of lines 22–80).
- By clicking on the buttons in the third column (having yellow background by default), the number of those points can be changed which are taken into account in the fitting. The topmost (+start) button adds previously excluded points (if there is any) to the beginning

of the actual titration curve. The second upper botton (+end) adds previously omitted points to the end of the curve. The lower two buttons (–start and –end) do the opposite operation, i.e. they remove more points from the actual curves for the next fitting. By clicking on the left side of one of the buttons in the third column, the number of points is changed by one. On the other hand, clicking the right side changes the number of points by a maximum of five. This fact is emphasized by the displayed one and five dots in the operating panel. The different clicking areas are separated with a vertical line drawn through all the buttons within the third column.[23]

- The fourth column of the operating panel contains buttons with miscellaneous functions and labels:

  The Calculate button carries out the fitting, regarding the changes made through the operating panel. The work window is redrawn at the end of the calculations.

  The working... button is not a clickable one, it only changes its background color from dark gray to magenta until the calculations are finished.

  The two text legends contain the two most important results of the fitting, namely the $\mathrm{p}K_w$ and the slope of the Nernst-like equation.

  The save&Quit button creates the result files and either stops running or returns to the parameter-modifier window, depending on the setting in the 35th line of the `phcali.cfg` file.

- In the last two columns of the operating panel 12 buttons can be found with light blue background by default. The function of these ones are the same as that of the «save&quit» button, except that they also save the last work-window into an image file. The format of the file (*see* Section 2.1 in detail) is given on each button. The figures in the image file look alike as in the work-window but the operating panel is replaced by an information box which contains the most important parameters of the fitting. The information box can be omitted by changing the 34th line of the `phcali.cfg` file.

  If the user wants to save more phases of his/her work, it can be done in more steps using the `cin` files (*see* Section 2.1).

2.3.4.2 Use of the Operating Panel with Keyboard

The only accessible input device is the keyboard in text mode and it is an alternative device in console and window modes which can be combined with mouse. The following differences appear by using the operating panel from the keyboard:

- The acutal curve can be selected by pressing the appropriate number key(s) and pressing the «Enter» key afterwards. In console and window modes, the «Enter» key is not necessary.
- The combination of the `+`, `-`, `s`, `S`, `e` and `E` characters and typing the number of the points to be omitted/included can be used to change the number of the points to be fitted. E.g., the string "`+S13`" (or "`S+13`" excusively in text mode) and «Enter» includes 13 previously excluded points into the fitting at the beginning of the curve. If there were less previously excluded points then all of them will be included again. The string "`-E1`" (or alternatively "`E-1`" in text mode) excludes one point from the end of the curve after pressing the «Enter» key. The characters `S` and `E` stand for the words "Start" and "End". If the user wants to increase or decrease the number of points only by one then the number can be omitted from the string.
- The functions of the other buttons can be accessed by pressing the uppercase letter indicated

---

[23] These points and the vertical line are not drawn in the DOS version since the mouse cannot be used.

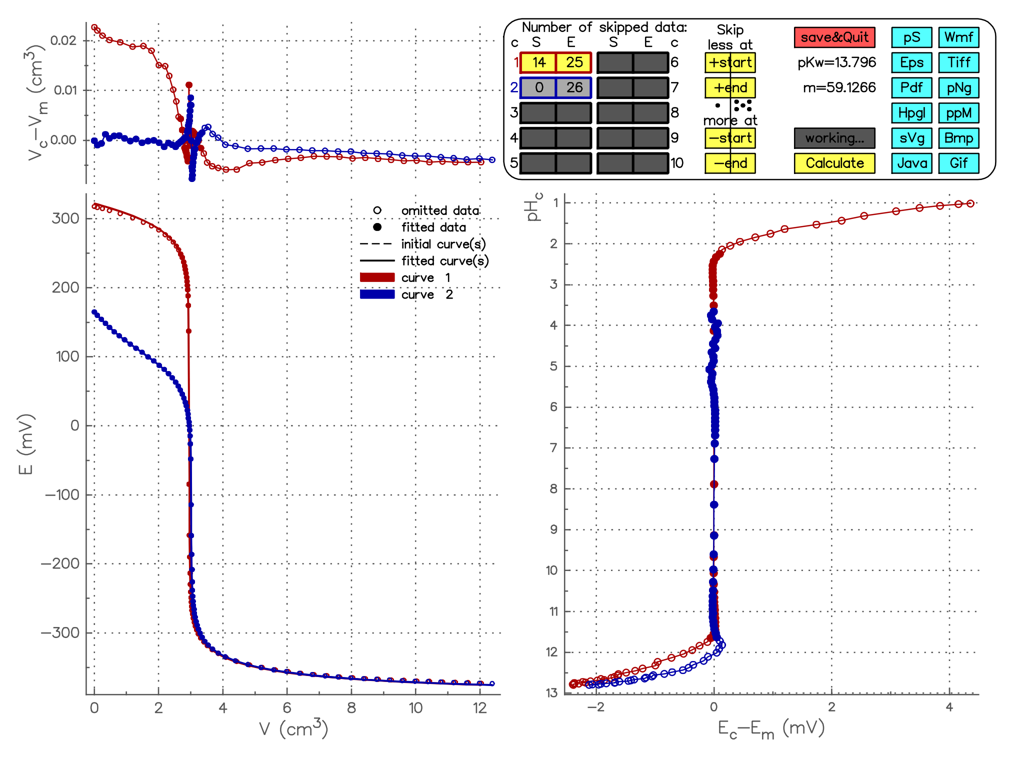


Figure 2.7: The final work-window of the reference example if potential is fitted.

on the appropriate button. In text mode variants of the program, the «Enter» should also be pressed. The «Enter» has to be pressed twice to terminate the program after entering the `Q` letter of the «save&Quit» button.

In the reference example, the main objective is to omit the points from the non-Nernstian area and get the calibration data of the used *p*H-metric instrument. By using the operation panel with keyboard, the final result can be achieved step by step if the

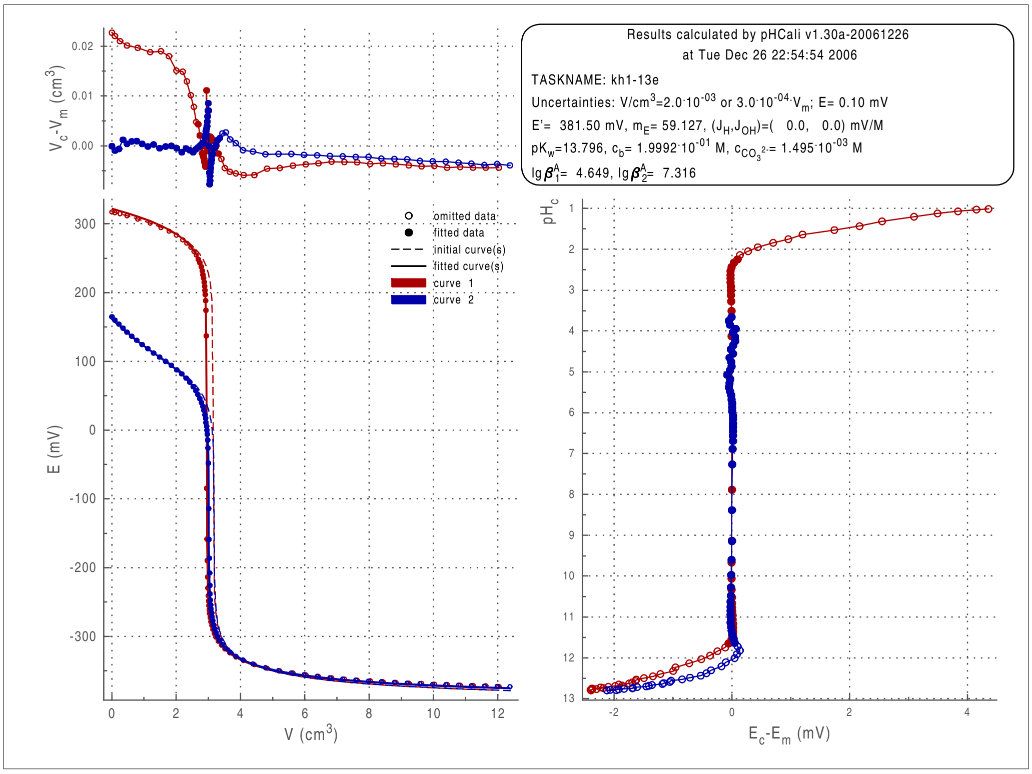
```
-S10 Enter                             C (Enter)
-E20 Enter   2  (Enter)   -E20 Enter   C (Enter)
-E5  Enter   1  Enter     -E5  Enter   C (Enter)
-S4  Enter                             C (Enter)
2    (Enter) -E Enter                  C (Enter)
```

commands are entered. Using the mouse, the same steps should be carried out in order to achieve the work-window displayed in Figure 2.7.[24] The savable image file corresponding to this work-window is shown in Figure 2.8. («Enter» keys inside parenthesis can only be given in text mode!)

Under Windows operating systems and in the console or window mode, the focus is not automatically set back to the work-window if the user switches between the windows of the running applications. After returning to the work-window, the user should left click on the work-window and should press the «Enter» key to give the focus back on the work-window of *p*HCali. In many cases, the same must be done if the mouse and keyboard are used in combination.

---

[24] In the reference example, the points to be omitted are denoted in the `kh1-13e.tid` file. For them, the relative weighting factor is given as `1.0e-00` instead of the usual `1.0e+00`.


Results calculated by pHCali v1.30a-20061226
at Tue Dec 26 22:54:54 2006

TASKNAME: kh1-13e
Uncertainties: V/cm^3=2.0·10^{-03} or 3.0·10^{-04}·V$_m$; E= 0.10 mV
E'= 381.50 mV, m$_E$= 59.127, (J$_H$,J$_{OH}$)=(0.0, 0.0) mV/M
pK$_w$=13.796, c$_b$= 1.9992·10^{-01} M, c$_{CO_3^{2-}}$= 1.495·10^{-03} M
lgβ_1^A= 4.649, lgβ_2^A= 7.316

Figure 2.8: The image file of the final fitting of the reference example if potential is fitted.

2.4 Output Files

In this section, the interpretation of the result files (having `res`, `crv` and `phv` extensions) can be found. The structure of the `TASKNAME.cin` file has already been discussed in Subsection 2.2.1. The difference between the `TASKNAME.tid` and `.cin` files is that the first one contains the initial values of the weighting factors and parameters while the second one contains the final values of them. The other text and image files have already been discussed in Section 2.1.

2.4.1 The Structure of the Result File (`TASKNAME.res`)

The contents of `TASKNAME.res` is shown in Listing 2.6 in case of the reference example after the data omission described in the previous section has been carried out. In the following, this file is referred to but the line numbers mentioned may change in other tasks. The contents of the result file can be divided into sections. Every section starts with a title line. It begins with five asterisks and then the name of the section comes. The `TASKNAME.res` consists of five sections:

`***** Used version` (line 1 in Listing 2.6):
This section gives the currently used version of *p*HCali.

`***** Input file` (lines 2–5 in Listing 2.6):
In this section, the name of the input file and some important parameters of the titration curves are displayed. For example, line 4 says that the first titration curve contains 69 points, of which the first 14 and the last 25 have been excluded from the fitting and the fitted data are in the *p*[H]=2.2–11.6 range.

`***** Estimated parameter values` (lines 6–26 in Listing 2.6):
In this section, the parameters are given. One parameter belongs to each line. The parameters that were not fitted are marked with the label fixed. In case of fitted parameters, the initial value before the last calculation and the standard deviation of it is displayed in

Listing 2.6: The content of `kh1-13e.res` file corresponding to Figures 2.7–2.8.

```
***** Used version: pHCali v1.27a-20051208
***** Input file: kh1-13e.tid
Curve(s):
 1: 30 fitted data (p[H]= 2.2-11.6), 14/ 25 omitted data from start/end.
 2: 50 fitted data (p[H]= 3.7-11.6),  0/ 26 omitted data from start/end.
***** Estimated parameter values:
     Name  Final value   Std. deviation  Initial value of the last calculation
      pKw  1.379553E+01  2.249750E-02    1.414066E+01
       E0  3.814998E+02  3.293109E-01    3.756276E+02
 ln10RTzF  5.912668E+01  1.308592E-01    5.697842E+01
       JH  0.000000E+00  fixed (Fitting is not recommended!)
      JOH  0.000000E+00  fixed (Fitting is not recommended!)
   C_base  1.999245E-01  5.755079E-05    2.000092E-01
    C_CO3  1.494589E-03  5.548072E-05    1.799731E-03
 lgB1_CO3  1.020000E+01  fixed
 lgB2_CO3  1.630000E+01  fixed
   lgB1_A  4.648838E+00  7.687519E-03    4.727018E+00
   lgB2_A  7.315919E+00  1.141487E-02    7.358921E+00
    V0_c1  6.035000E+00  fixed
  +TH0_c1  9.876698E-02  2.553896E-05    9.906755E-02  (TH0_base= 0.000000E+00)
   TA0_c1  0.000000E+00  fixed
  Shft_c1  0.000000E+00  fixed
    V0_c2  6.035000E+00  fixed
  +TH0_c2  0.000000E+00  fixed                         (TH0_base= 1.006000E-01)
   TA0_c2  1.006000E-01  fixed
  Shft_c2  0.000000E+00  fixed
***** Experimental uncertainties:
 2.000E-03 or 3.000E-04*Vm cm3 for the volume, whichever is larger
 1.000E-01 mV for E
***** Goodness-of-Fit statistics:
                    Number of iterations:    13
          Number of function evaluations:    66
          Number of Jacobian evaluations:    15
                         Rank deficiency:     0
 Average of weighted deviation of volume:  3.386902E-03
                      only for curve  1:  3.313719E-03
                      only for curve  2:  3.427576E-03
     Average of weighted deviation of E:  2.832030E-02
                      only for curve  1:  2.648744E-02
                      only for curve  2:  2.930560E-02
```

the specific lines. The names of the parameters in the program and their meanings are the following:

Name:	Meaning of name
`pKw`	pK_w
`E0` (or `Id`)	E' (or I_d)
`ln10RTzF` (or `m`)	m_E (or m_p)
`JH` (or `JH^p`)	J_H (or J_H^p)
`JOH` (or `JOH^p`)	J_{OH} (or J_{OH}^p)
`C_base`	c_b
`C_CO3`	c_c
`lgB1_CO3`	$\lg\beta_1^C$
`lgB2_CO3`	$\lg\beta_2^C$
`lgBi_A`	$\lg\beta_i^A$, $i=1\,..\,9$
`V0_ci`	V_0 value for the i^{th} experimental curve ($i=1\,..\,10$).
`+TH0_ci`	In case of the i^{th} experimental curve ($i=1\,..\,10$), it is the portion of the total hydrogen ion concentration in the solution to be titrated which is added as strong acid. A more detailed description can be found at the explanation of line 17 of the `kh1-13e.tid` file in Subsection 2.2.1.
`TA0_ci`	The total concentration of the anion of the weak acid in the solution to be titrated for the i^{th} experimental curve ($i=1\,..\,10$).
`Shft_ci`	The shift parameter of the potential (or *p*H) values for the i^{th} experimental curve ($i=1\,..\,10$). A more detailed description can be found at the explanation of line 19 of the `kh1-13e.tid` file in Subsection 2.2.1.

In the lines 11–12 of Listing 2.6 a remark can be found which notifies the user not to fit the parameters J_H and J_{OH}. The reason of this advice is also mentioned in Subsection 2.4.3, and the detailed explanation can be found in Section 4.8.

Lines 20 and 24 also contain remarks. They make the calculation of the total hydrogen ion concentration easier in the solutions to be titrated. On the basis of line 20 in the reference example, the concentration of the strong acid is $\approx 0{,}0988$ M in case of the first titration curve. Since no weak acid is added to the solution, this value corresponds to the total hydrogen ion concentration. In line 24, it is found that no strong acid is added into the second solution to be titrated but there is hydrogen ion bounded to the weak acid in the solution, so the total hydrogen ion concentration is ≈ 0.1 M. A more detailed explanation is given in the discussion of line 17 of the `kh1-13e.tid` file within Subsection 2.2.1.

`***** Experimental uncertainties` (lines 27–29 in Listing 2.6):

This section only repeats the experimental uncertainties of the measured potential (or *p*H) and the measured volume originally given in the `TASKNAME.tid` file.

`***** Goodness-of-Fit statistics` (lines 30–40 in Listing 2.6):

In the last section, the most important statistical parameters are listed. In the reference example, lines 31–33 give the number of iterations, the number of function evaluations based on the equations (A.14) and the number of Jacobi-matrix calculations. If any of these numbers is larger than 200–300 then the user can be sure that *(1)* either wrong initial values have been entered or *(2)* the task is badly conditioned and the correlation of the parameters is unacceptably high. The same should be told if the value in line 34 is greater than zero.

Lines 35-40 give the average deviations of the measured and calculated points for both the potential (or *p*H) values and the volumes. The average deviation is not only calculated at once for all points but also independently for each titration curve.

In case the user wants more detailed information concerning the fitting, *p*HCali should be set to generate the `phcali.odr` file also (*see* Section 2.1 and the description of line 33 of the `phcali.cfg` file).

2.4.2 The Structure of the Curves File (`TASKNAME.crv`)

The `TASKNAME.crv` text file contains all the titration curves of all titrations. The purpose of this file is to allow the user either to evaluate the results by further calculations or to make figures based on the output data. The file consists of 11 columns. The first row of the file contains the titles of the columns and the titration curves follow in the next rows. The first line of every titration curve contains 11 asterisks (separated with spaces) and the serial number of the titration curve. The purpose of this leading line is to separate the individual curves. After the title line of the curve, the titration data can be found. The 11 columns contain the following data:

Column	Column name	Content of the column
1.	`Vm`	The measured volumes: V_m.
2.	`Em` (or `pHm`)	The measured potentials (or *p*H-s): E_m (or pH_m).
3.	`Ec0` (or `pHc0`)	Calculated potentials (or *p*H-s) using the initial values of the parameters.
4.	`Vc`	Calculated volumes using the final values of the parameters: V_c.
5.	`Ec` (or `pHc`)	Calculated potentials (or *p*H-s) using the final values of the parameters: E_c (or pH_c).
6.	`Verr`	$V_c - V_m$.
7.	`Eerr` (or `pHerr`)	$E_c - E_m$ (or pH_c–pH_m).
8.	`p[H]`	Negative logarithm of $[H^+]$: $p[H]$.

9.	`Vm`	This column is the same as the first one but asterisks replace data omitted from the fitting.
10.	`Em` (or `pHm`)	This column is the same as the second one but asterisks replace data omitted from the fitting.
11.	`-JH*[H]-JOH*[OH]` (or `-JH^p*[H]-JOH^p*[OH]`)	Extent of the deviation from the Nerst equation expressed in potential or pH: $-J_H{\cdot}[H^+]-J_{OH}{\cdot}\frac{K_w}{[H^+]}$ (or $-J^p_H{\cdot}[H^+]-J^p_{OH}{\cdot}\frac{K_w}{[H^+]}$).

2.4.3 The Structure of the *p*H-values File (`TASKNAME.phv`)

The back-calculated p[H] values are stored in the `TASKNAME.phv` file for the titration points given in the third part of the file `TASKNAME.tid`. In the reference example, the contents of the `kh1-13e.phv` file is shown in Listing 2.7. For this, the calculations were carried out according to the point exclusions shown in Figure 2.7 and 2.8 and the values of J_H and J_{OH} have been fixed to 0.0. Listing 2.8 displays the resulted `TASKNAME.phv` file when every point was included in the fitting and the values of J_H and J_{OH} were fitted too, together with the previously fitted parameters.

The structure of `TASKNAME.phv` is rather simple, it consists of a total four columns containing the V_m values, the p[H] values, the E_m (or pH_m) values and the back-calculated E_c (or pH_c) values from the equation (A.8), respectively (*see* equation (A.11) on page 71 for the relationship of p[H] and pH_c).

The first three columns need no further discussion.[25] Column 4 have no significance if the Nernst equation is valid for the whole calibrated range. If it is not true, column 4 contains the expected value of the given titration point if the Nernst equation is suspected to be valid. The difference between columns 3 and 4 shows the extent of the deviation from the Nernstian behavior. *p*HCali is able to calculate the values of the fourth column in two ways:

1. If at least one of the values of J_H and J_{OH} is fitted or one of them is fixed to a nonzero value then the program uses equation (A.9) (in case of potential is measured) or equation (A.12) (if pH is measured) to calculate the values of the fourth column. In such case, it is not advisable to exclude experimental points because this omission may decrease the experimental information required for the correct fitting of the parameters. Listing 2.8 contains the results of the calculation carried out this way.
2. The strictly Nernstian range must be found by systematic exclusion of the non-Nernstian points. The program then will compare the calculated points with the points of the first strong acid – strong base titration, and it uses interpolation to correct the measured data. The data calculated by this interpolation will be written into the fourth column.

   For example, let's consider the `kh1-13e.crv` file belonging to Figure 2.7. In columns 1, 2 and 5 of this file, the data of V_m, E_m and E_c can be found.[26] Since both J_H and J_{OH} are zero in this fitting, the value of E_c is nothing else than the potential calculated assuming that the Nernst equation is valid for the actual point. In other words, E_c is the expected value of the measured data. In the second and third lines of this data file (*see* Listing 2.7), it is shown that the measured data are 317.4 and 316.3 mV instead of the expected 321.758 and 320.450 mV, due to the deviation from the Nernst equation. If the user needs the value

---

[25] It is worth to mention that columns 1 and 2 can be used in the input files of the program PSEQUAD [18] (or other programs for calculating stability constants) without any further modification.

[26] The same data can be found in columns 1, 3 and 4 of a `*.phv` file. The data in a `*.crv` file, however, regard to the fitted points (from the second part of the corresponding `*.tid` file) while the data in a `*.phv` file regard to the data (from the third part of the corresponding `*.tid` file) for which p[H] values must be calculated.

Listing 2.7: The content of `kh1-13e.phv` file corresponding to Figures 2.7–2.8.

```
 Vm            p[H]     Em           Ec,Nernstian (from interpolation)
0.0000E+00    1.0841  3.17400E+02  3.21758E+02
1.0000E-01    1.1027  3.16300E+02  3.20450E+02
2.5000E-01    1.1315  3.14600E+02  3.18440E+02
4.7500E-01    1.1788  3.11800E+02  3.15289E+02
2.4530E+00    1.9534  2.66000E+02  2.66444E+02
2.5510E+00    2.0532  2.60100E+02  2.60375E+02
2.6250E+00    2.1445  2.54700E+02  2.54837E+02
2.6900E+00    2.2494  2.48500E+02  2.48599E+02
2.7340E+00    2.3323  2.43600E+02  2.43640E+02
2.9280E+00    3.5094  1.74000E+02  1.73995E+02
2.9380E+00    4.1318  1.37200E+02  1.37199E+02
2.9480E+00    7.8848 -8.47000E+01 -8.46994E+01
2.9580E+00    9.1295 -1.58300E+02 -1.58299E+02
3.3130E+00   11.6445 -3.07000E+02 -3.07053E+02
3.4030E+00   11.7426 -3.12800E+02 -3.12914E+02
3.5160E+00   11.8373 -3.18400E+02 -3.18644E+02
3.6650E+00   11.9354 -3.24200E+02 -3.24570E+02
3.8520E+00   12.0301 -3.29800E+02 -3.30315E+02
4.0990E+00   12.1248 -3.35400E+02 -3.36119E+02
1.0428E+01   12.7117 -3.70100E+02 -3.72467E+02
1.0828E+01   12.7252 -3.70900E+02 -3.73195E+02
1.1228E+01   12.7354 -3.71500E+02 -3.73870E+02
1.1628E+01   12.7455 -3.72100E+02 -3.74498E+02
1.2028E+01   12.7557 -3.72700E+02 -3.75085E+02
```

Listing 2.8: The content of `kh1-13e.phv` file if J_H and J_{OH} are also fitted.

```
 Vm            p[H]     Em           Ec,Nernstian (from JH & JOH)
0.0000E+00    1.0668  3.17400E+02  3.21106E+02
1.0000E-01    1.0855  3.16300E+02  3.19824E+02
2.5000E-01    1.1144  3.14600E+02  3.17864E+02
4.7500E-01    1.1619  3.11800E+02  3.14681E+02
2.4530E+00    1.9398  2.66000E+02  2.66436E+02
2.5510E+00    2.0400  2.60100E+02  2.60446E+02
2.6250E+00    2.1317  2.54700E+02  2.54980E+02
2.6900E+00    2.2370  2.48500E+02  2.48719E+02
2.7340E+00    2.3202  2.43600E+02  2.43780E+02
2.9280E+00    3.5023  1.74000E+02  1.74011E+02
2.9380E+00    4.1272  1.37200E+02  1.37204E+02
2.9480E+00    7.8959 -8.47000E+01 -8.47000E+01
2.9580E+00    9.1459 -1.58300E+02 -1.58300E+02
3.3130E+00   11.6713 -3.07000E+02 -3.07147E+02
3.4030E+00   11.7698 -3.12800E+02 -3.12986E+02
3.5160E+00   11.8649 -3.18400E+02 -3.18632E+02
3.6650E+00   11.9634 -3.24200E+02 -3.24491E+02
3.8520E+00   12.0585 -3.29800E+02 -3.30162E+02
4.0990E+00   12.1536 -3.35400E+02 -3.35854E+02
1.0428E+01   12.7430 -3.70100E+02 -3.71964E+02
1.0828E+01   12.7566 -3.70900E+02 -3.72827E+02
1.1228E+01   12.7667 -3.71500E+02 -3.73476E+02
1.1628E+01   12.7769 -3.72100E+02 -3.74128E+02
1.2028E+01   12.7871 -3.72700E+02 -3.74781E+02
```

of the p[H] for a titration point where the measured value is 316.9 mV then the expected value from the Nernst equation can be calculated from the

$$\frac{317,4-316,9}{317,4-316,3}=\frac{321,758-x}{321,758-320,450}$$

interpolation equation. The solution of this equation is x=321.163 mV. This is the potential corrected by interpolation that can be found in the fourth column of all `*.phv` files. The p[H] values (found in the second column of `*.phv` files) are calculated from these values based on equation (A.8) (in case of potential measurement) or based on equation (A.11) (if pH is measured). The result of such calculations is shown in Listing 2.7.

In practice, the first approach has been used so far. The big advantage of the second method is that it does not hypothesize any relationship for the deviation from the Nernst equation. There is also a disadvantage, namely, that no extrapolation is possible, only interpolation is permitted. A careful user is able to note that the two methods do not give the same p[H] values and their difference is larger than the experimental uncertainty. The reason of this is not to be searched within the program, rather than in the technique of the measurement. That is why, this problem is discussed deeply in Section 4.8.

CHAPTER 3

GETTING STARTED THROUGH EXAMPLES

This chapter introduces the abilities of the program through three examples. The aim of the chapter is to help the user to gain experience as quickly as possible therefore detailed use of the program is not given here. The examples refer to the appropriate parts of Chapter 2 if it is needed. Before reading this chapter, it is presupposed that the user has studied Chapter 1 and Section 2.1. Additionally, the description of an example supposes that the reader has got through the previous ones.

Since the commands to be used differ due to the various names of the executables, the name of the program is denoted with the `PROGNAME` word from now on. The `PROGNAME` can be one of those described in Table 1.1.

3.1 Calibration in the Nernstian Range

This example shows how the most common calibration measurement can be evaluated by *p*HCali. The next two titration curves were measured:

1. 6,035 cm^3 ~0,012 M HCl solution was titrated with ~0,025 M KOH solution and
2. 6,035 cm^3 0,1201 M KH-phtalate solution was titrated with the same ~0,025 M solution of KOH.

The ionic strength was adjusted to 1.0 M with KCl both in the titrant and in the solutions to be titrated. The change of the ionic strength during titrations was less than 1.2%. Both the potential and the *p*H were measured during the experiments so the titration curves are available in both E_m–V_m and $p\mathrm{H}_m$–V_m formats in the `kh2-12e.tid` and `kh2-12ph.tid` data files, respectively. These plain text files include all the input data required for the calculation, namely, the initial values of the parameters and the titration data. The structure of the `*.tid` files is rather simple, it can be understood easily, but the detailed description can also be found in Subsection 2.2.1.

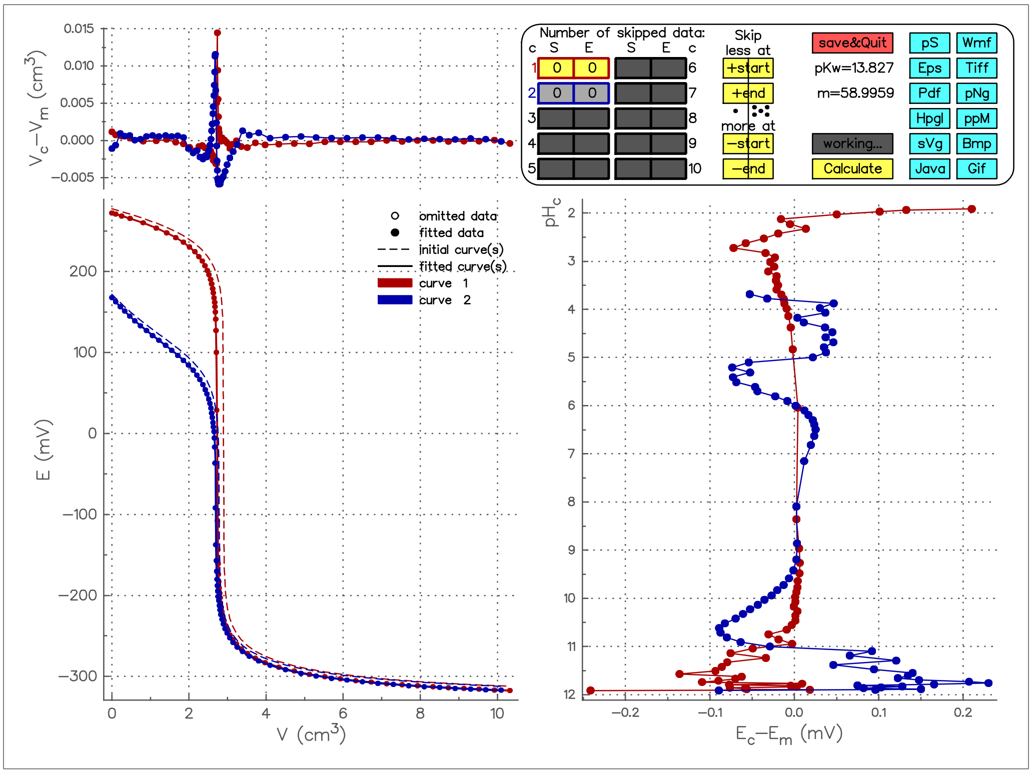
The goal of calculation based on the two titration curves is to get the calibration parameters of the used instrument (E' and m_E from equation (A.8)), negative logarithm of the ion-product constant of water ($\mathrm{p}K_w$), as well as the precise concentrations of the strong base in the burette and the strong acid to be titrated (c_b and c_s). In addition, the program fits the two formation constants of KH-phtalate (β_1^A and β_2^A) and also determines the carbonate content of the titrant (c_c). As it can be seen below, *p*HCali solves these tasks in a single step.

In order to solve the task of the first example, the program can be started in two ways: *(1)* by typing the command

```
"PROGNAME kh2-12e.tid"     «Enter»
```

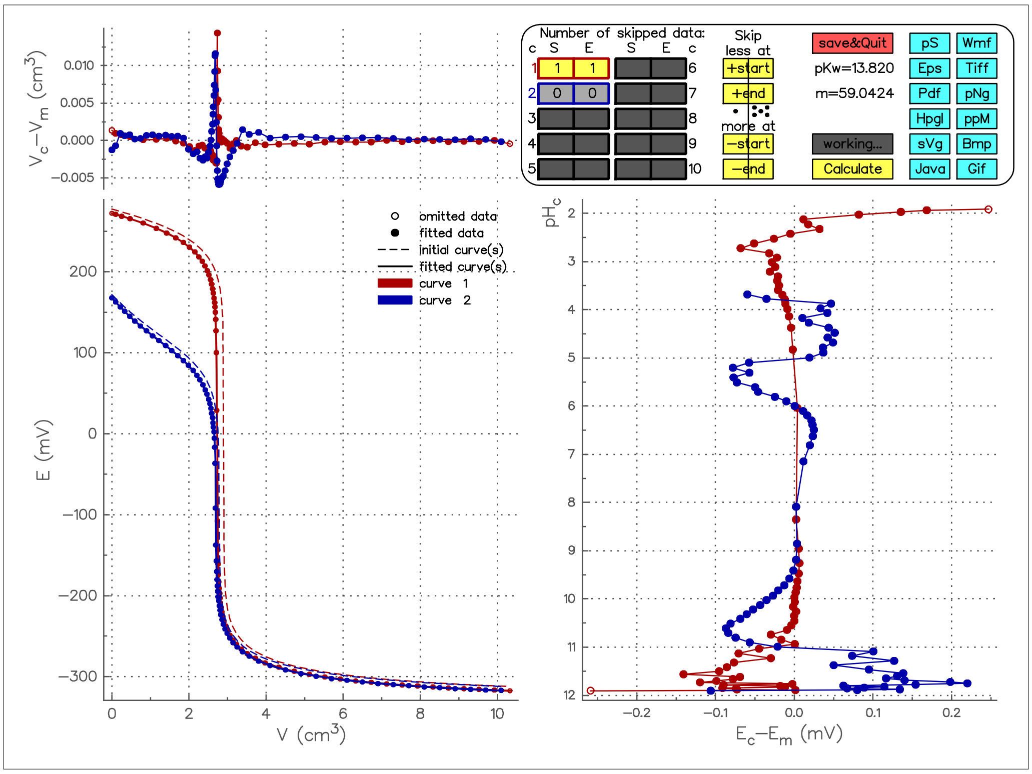
or *(2)* by clicking on the icon of the program. In the latter case, the file-chooser window appears (*see* Subsection 2.3.2) and the user can choose the file `kh2-12e.tid` from this window. After pressing the «OK» button, the parameter-modifier window appears which can also be closed by clicking on the «OK» button.

After these steps, all variants of the program open the work-window. The detailed interpretation of the figures in the work-window can be found in the first part of Subsection 2.3.4,



pKw=13.827
m=58.9959

Figure 3.1: The initial work-window of the `kh2-12e.tid` file if potential is fitted.



pKw=13.820
m=59.0424

Figure 3.2: The final work-window of the `kh2-12e.tid` file if potential is fitted.

while the usage of the operating panel is described in Subsubsections 2.3.4.1 and 2.3.4.2. Figure 3.1 shows the work-window.

In the lower right figure of the work window, the differences between the measured and calculated potentials are displayed. These values are rather small, considering that the experimental uncertainty of the used instrument was ~0.1 mV. Extremely erroneous points to be excluded cannot be found. Perhaps, the first and the last points of the strong acid – strong base titration curve might be excluded with the help of the operating panel. After omitting these two points, the state of the work-window is shown in Figure 3.2. After clicking the «save&quit» button, the program creates the result files and terminates. Three result files have been created:

1. The `kh2-12e.cin` is the same as `kh2-12e.tid` except for two differences. *(1)* The `.cin` file contains the fitted values of the parameters instead of the initial ones and *(2)* it includes the changed weighting factors according to the modifications done via the operation panel. The program uses the relative weighting factors for the exclusion/inclusion of the experimental points. This topic is discussed in Subsection 2.2.1 where choosing the titration point to be fitted is detailed.

   The purpose of this result file is to save the modifications in the form of input data and let the user carry out further evaluations by using this file. Since there are no further calculations in the first example, this file has no significance at this moment.
2. The `kh2-12e.res` file contains the essential results of the fitting. The detailed discussion of this file is given in Subsection 2.4.1 but for users familiar with curve fitting, the file itself may seem self-explanatory. Maybe the names of the parameters inside *p*HCali should be identified. These names can be found in the second part of Subsection 2.4.1 in detail.
3. The `kh2-12e.crv` file contains the measured and calculated curves. The interpretation of the individual columns can be found in Subsection 2.4.2.

The calibration can be carried out with the $p\mathrm{H}_m$–V_m titration curves, as well. In this case, the objective is the same but the values of I_d and m_p defined in equation (A.11) are determined instead of E' and m_E. The `kh2-12ph.tid` file (provided during the installation) contains the input data needed. For this case, the look of the work-window is shown in Figure 3.3. The files created during the calculation can be interpreted the same way as potentials were measured.

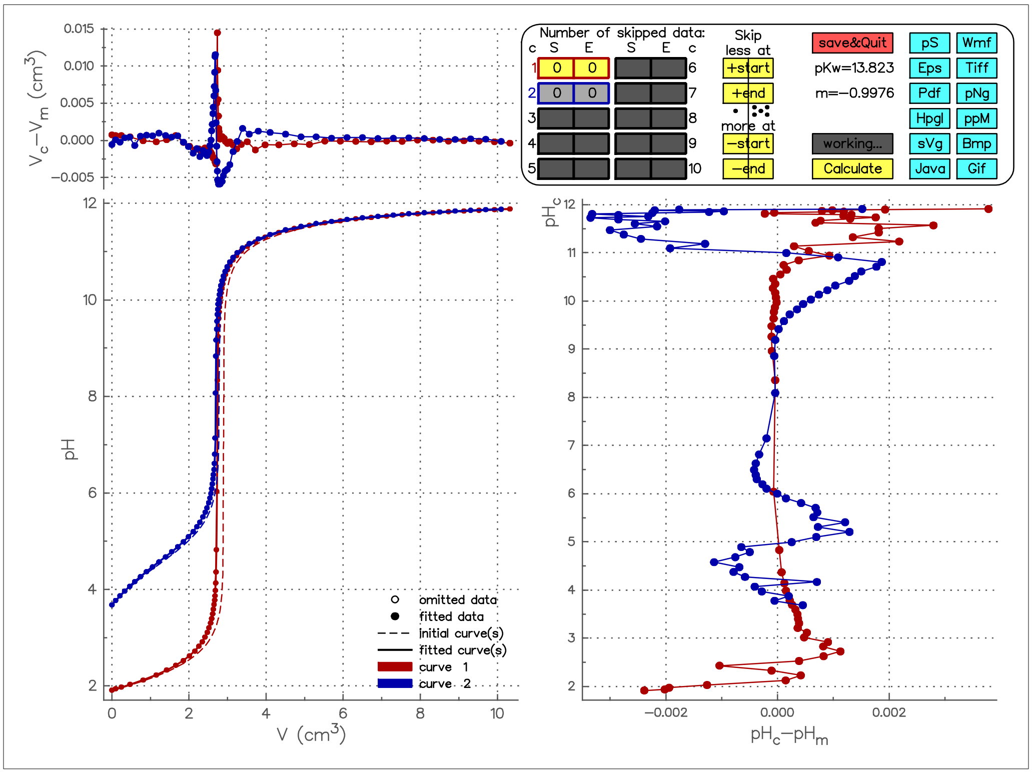
3.2 Calibration in Extended Measurement Range

The second example demonstrates the capabilities of *p*HCali when the calibration also required outside of the Nernstian ranges. This example is the same as the reference example throughout the guide so the experimental conditions of this measurement are described in the introductory part of Chapter 2.

The program provides three methods for taking the deviation from the Nernstian behavior into account.

1. The user fits the values of J_H and J_{OH} together with the usual calibration parameters. It can be done by changing the `0`-s to `1`-s in the 14th column of lines 6 and 7 in the `kh1-13e.tid` file (*see* Listing 2.1). After saving these modifications, either *(1)* the command "`PROGNAME kh1-13e.tid`" or clicking the icon of *p*HCali starts the program to calculate the required values. If the program is started from icon then the appropriate file should be chosen from the file-chooser window.

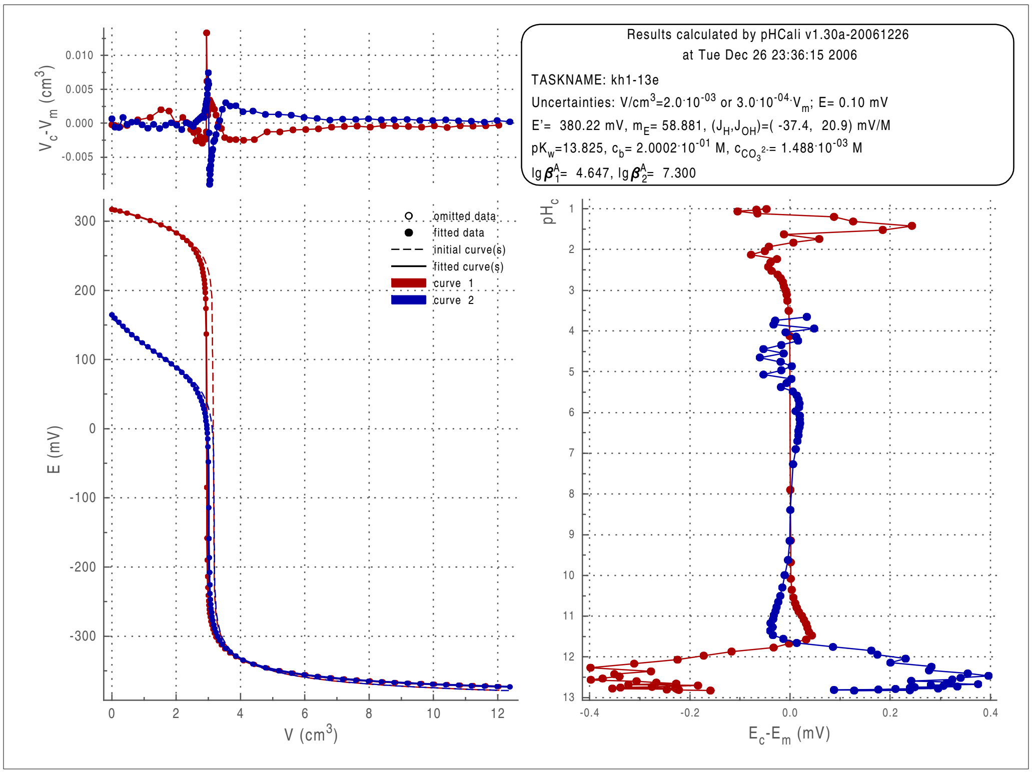
   This method is the most simple one but it may most easily lead to wrong values so *the usage of this method is not suggested*! The reasons are analyzed more deeply in Section 4.8 but as it can also be seen from the result of the fitting here (*see* the lower right graph of Figure 3.4), this method leads to large and systematic deviations at high *p*H.
2. The calculations are carried out in several successive steps:
   - The program should be started as in case of the first method. The experimental points in the non-Nernstian ranges (typically the $p\mathrm{H}_m \lesssim 2$ and $p\mathrm{H}_m \gtrsim 12$ values) should be omitted



pKw=13.823

m=−0.9976

Figure 3.3: The work-window of the `kh2-12ph.tid` file if *p*H is fitted.


Results calculated by pHCali v1.30a-20061226
at Tue Dec 26 23:36:15 2006

TASKNAME: kh1-13e

Uncertainties: $V/cm^3=2.0 \cdot 10^{-03}$ or $3.0 \cdot 10^{-04} \cdot V_m$; E= 0.10 mV

$E' =$ 380.22 mV, $m_E =$ 58.881, $(J_H, J_{OH}) =$(-37.4, 20.9) mV/M

$pK_w=13.825$, $c_b= 2.0002 \cdot 10^{-01}$ M, $c_{CO_3^{2-}}= 1.488 \cdot 10^{-03}$ M

$\lg \boldsymbol{\beta}_1^A =$ 4.647, $\lg \boldsymbol{\beta}_2^A =$ 7.300

Figure 3.4: The image file belonging to the final fit in the second example if J_H and J_{OH} are also fitted together with the usual parameters.

using the operating panel and only the usual calibration parameters (listed in the previous example) should be determined by fitting at first. The technical details of this fitting are given in Chapter 2: Figure 2.5 shows the initial work-window of this example while the final work-window (achievable by using the operation panel) is shown in Figure 2.7.

Listing 3.1: The rows of `kh1-13e2.tid` file to be changed in examle 2.

```
 1.37955E+01 1  / pKw                                      parameter  1
 3.81500E+02 1  / E0                                       parameter  2
 5.91267E+01 1  / m(=ln(10)RT/(zF))                        parameter  3
 0.00000E+00 0  / JH                                       parameter  4
 0.00000E+00 0  / JOH                                      parameter  6
 1.99925E-01 1  / c0 in mol/dm3 for the base solution      parameter 18
 1.49459E-03 1  / c(CO32-) in mol/dm3 for the impuritites  parameter 19
 4.64884E+00 1  / log beta_1 for the weak acid             parameter 22
 7.31592E+00 1  / log beta_2 for the weak acid             parameter 23
 9.87670E-02 1  / +T(H)0 in mol/dm3 for curve 1            parameter 32
0.00000E+00  3.17400E+02  1.0E-20 / the next 12 lines are also to be changed
...
2.62500E+00  2.54700E+02  1.0E-20
3.40300E+00 -3.12800E+02  1.0E-20 / the next 23 lines are also to be changed
...
1.20280E+01 -3.72700E+02  1.0E-20
3.43700E+00 -3.11900E+02  1.0E-20 / the next 24 lines are also to be changed
...
1.23790E+01 -3.73300E+02  1.0E-20
```

Listing 3.2: The changed rows of `kh1-13e2.tid` file in examle 2.

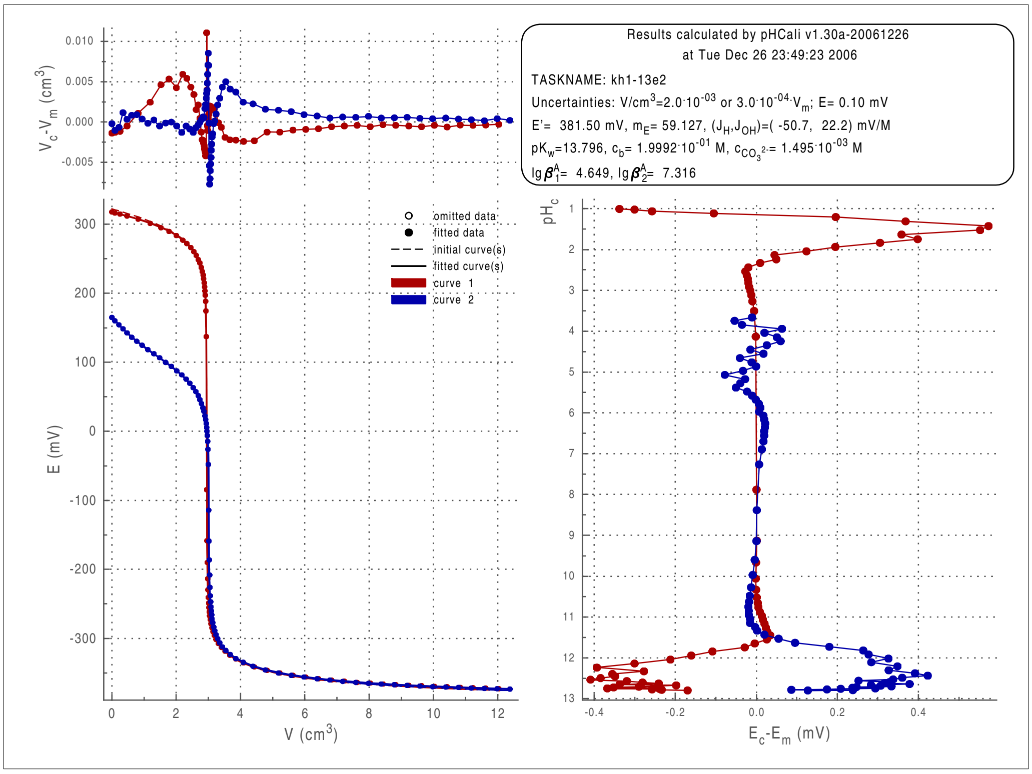
```
 1.37955E+01 0  / pKw                                      parameter  1
 3.81500E+02 0  / E0                                       parameter  2
 5.91267E+01 0  / m(=ln(10)RT/(zF))                        parameter  3
 0.00000E+00 1  / JH                                       parameter  4
 0.00000E+00 1  / JOH                                      parameter  6
 1.99925E-01 0  / c0 in mol/dm3 for the base solution      parameter 18
 1.49459E-03 0  / c(CO32-) in mol/dm3 for the impuritites  parameter 19
 4.64884E+00 0  / log beta_1 for the weak acid             parameter 22
 7.31592E+00 0  / log beta_2 for the weak acid             parameter 23
 9.87670E-02 0  / +T(H)0 in mol/dm3 for curve 1            parameter 32
0.00000E+00  3.17400E+02  1.0E-00 / the next 12 lines have also been changed
...
2.62500E+00  2.54700E+02  1.0E-00
3.40300E+00 -3.12800E+02  1.0E-00 / the next 23 lines have also been changed
...
1.20280E+01 -3.72700E+02  1.0E-00
3.43700E+00 -3.11900E+02  1.0E-00 / the next 24 lines have also been changed
...
1.23790E+01 -3.73300E+02  1.0E-00
```

The latter figure shows that the calculations are based only on the points within the Nernstian range. After clicking «save&quit» button, the result files are created and the program stops running.

- One of the result files (`kh1-13e.cin`) should be renamed to `kh1-12e2.tid`. In this file, the following changes have to be made: *(1)* The parameters fitted in the previous run must be fixed now on by changing the `1`-s in the 14th character of the appropriate lines to `0`-s. `(2)` The weighting factors having `1.0E-20` value should be changed to `1.0E-00`. *(3)* The previously fixed values of J_H és J_{OH} must be fitted so the `0`-s in the 14th character position of lines 6–7 should be changed to `1`-s.

  The affected lines are shown in Listing 3.1 before and in Listing 3.2 after the above detailed modifications.
- After starting the program—with either the "`PROGNAME kh1-13e2.tid`" command or by clicking on the appropriate icon and choosing the `kh1-13e2.tid` file—, it calculates the values of J_H and J_{OH} along with the other parameters kept fixed. The image file of the final work-window of the fitting is shown in Figure 3.5.

The comparison of Figures 3.4 and 3.5 may lead to the opinion that the second method is worse than the first one. The second one does not enhance the fitting in the basic range, moreover, it increases the deviation in the acidic range in a small extent. Figure 2.7 can ensure, however, that the values of the usual calibration parameters (describing the



Results calculated by pHCali v1.30a-20061226
at Tue Dec 26 23:49:23 2006

TASKNAME: kh1-13e2
Uncertainties: $V/cm^3=2.0\cdot10^{-03}$ or $3.0\cdot10^{-04}\cdot V_m$; E= 0.10 mV
E'= 381.50 mV, m_E= 59.127, (J_H,J_{OH})=(-50.7, 22.2) mV/M
pK_w=13.796, c_b= $1.9992\cdot10^{-01}$ M, $c_{CO_3{}^{2-}}$= $1.495\cdot10^{-03}$ M
$\lg\beta_1^A$= 4.649, $\lg\beta_2^A$= 7.316

Figure 3.5: The image file belonging to the final fit in the second example if J_H and J_{OH} are fitted and the other parameters are fixed after a previous fitting.

Nernstian range) are correct. To resolve this virtual contradiction, some facts should be considered. Fitting J_H together with the other parameters results smaller deviation in the pH=1–2 range at the expense of worsening the other calibration parameters. This worsening is hidden by the first method if the user is not careful enough. A more detailed description of the problem can be found in Section 4.8.

3. The last method offered by pHCali is the interpolation. If the value of both J_H and aJ_{OH} are fixed to zero, the program automatically chooses this option, i.e. the command "`PROGNAME kh1-13e.tid`" automatically uses the interpolation in this example.[1] The essence of the interpolation is that the first strong acid – strong base titration curve is taken from the input file, and accordingly to the deviations of this curve from the Nernstian behavior, the program corrects the titration data for the calculation of the p[H] values. More information concerning the interpolation can be found in Subsection 2.4.3 and in Section 4.8.

The limitations of the above methods are that *(1)* at least one strong acid – strong base titration curve must be present, *(2)* the ionic strength must be the same (and set by the same medium) in this titration and in the titrations belonging to the system to be studied after the calibration and *(3)* the response sign of the used electrode must be reproducible in the non-Nernstian ranges, too. Measurements carefully planned and carried out usually fulfill these conditions.

3.3 Complete Evaluation of Equilibrium Measurements

The last example presents a complete investigation of an equilibrium reaction, starting with the calibration and ending with the determination of the cumulative protonation constants of the conjugated base of an unknown weak acid (in the present case, the aspartate). The experimental data have been measured in a student's laboratory on a device with 0.2 mV

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[1] If the user had modified the `kh1-13e.tid` file before then these modifications must be canceled first.

Table 3.1: Weak acid – strong base titration data in example 3.

Curve 4						Curve 5						Curve 6					
V /cm^3	pH_m	E_m /mV	V /cm^3	pH_m	E_m /mV	V /cm^3	pH_m	E_m /mV	V /cm^3	pH_m	E_m /mV	V /cm^3	pH_m	E_m /mV	V /cm^3	pH_m	E_m /mV
0.00	3.842	182.2	4.40	5.708	71.6	0.00	3.852	181.6	4.81	6.433	28.6	0.00	3.823	183.4	4.82	6.362	33.1
0.42	4.043	170.2	4.60	5.920	59.1	0.40	4.048	170.0	5.12	10.416	–206.7	0.43	4.038	170.7	5.00	9.397	~~–148.4~~
0.81	4.223	159.6	4.80	6.295	37.0	0.80	4.228	159.4	5.43	10.950	–238.5	0.80	4.212	160.4	5.20	10.565	~~–215.5~~
1.21	4.387	150.1	5.00	8.991	~~–146.6~~	1.19	4.386	150.1	5.62	11.107	–247.5	1.21	4.375	150.6	5.40	10.882	~~–234.2~~
1.40	4.458	145.8	5.21	10.609	~~–218.7~~	1.64	4.550	140.3	5.82	11.227	–254.5	1.60	4.522	141.9	5.63	11.080	~~–245.8~~
1.60	4.530	141.5	5.40	10.908	–236.1	2.00	4.681	132.7	6.03	11.322	–260.2	1.98	4.655	134.0	5.82	11.196	~~–252.9~~
1.80	4.601	137.3	5.60	11.092	–246.8	2.20	4.745	128.8	7.12	11.608	–277.3	2.20	4.731	129.6	6.02	11.282	–258.2
2.00	4.672	133.1	5.80	11.222	–254.4	2.41	4.816	124.7	7.40	11.660	–280.3	2.41	4.802	125.2	6.47	11.433	–267.1
2.19	4.735	129.3	6.00	11.314	–259.8	2.60	4.877	120.9	7.86	11.726	–284.2	2.60	4.866	121.6	6.81	11.517	–272.2
2.40	4.806	125.3	6.20	11.422	–266.2	2.81	4.950	116.7	8.02	11.769	–286.9	2.85	4.959	116.2	7.03	11.563	–275.0
2.60	4.872	121.4	6.81	11.557	–274.3	3.00	5.017	112.7	8.43	11.797	–288.2	3.05	5.025	112.2	7.43	11.634	–279.1
2.79	4.936	117.5	7.20	11.635	–279.0	3.22	5.098	107.9	8.69	11.820	–289.8	3.22	5.085	108.8	7.80	11.671	~~–282.5~~
3.00	5.012	113.1	7.63	11.707	–283.1	3.48	5.198	101.9	9.00	11.848	–291.6	3.42	5.163	104.1	8.23	11.745	–285.7
3.20	5.081	109.0	8.01	11.758	–286.2	3.61	5.257	98.4	9.29	11.873	–293.0	3.60	5.240	99.5	8.80	11.805	–289.4
3.40	5.159	104.3	8.42	11.807	–289.1	3.83	5.357	92.3	9.62	11.898	–294.6	3.81	5.338	93.7	9.24	11.845	–291.6
3.61	5.245	99.1	8.82	11.848	–291.5	4.02	5.467	86.0	10.00	11.927	–296.4	4.01	5.445	87.4	9.62	11.877	–293.6
3.80	5.333	94.0	9.20	11.883	–293.6	4.20	5.581	79.3				4.23	5.582	79.1	10.00	11.899	~~–295.4~~
4.01	5.443	87.5	9.60	11.915	–295.5	4.42	5.763	68.5				4.42	5.738	70.0			
4.20	5.556	80.8	9.99	11.946	–297.3	4.64	6.028	52.7				4.63	5.979	55.5			

Table 3.2: Strong acid – strong base titration data in the third example.

Curve 1						Curve 2						Curve 3					
V /cm^3	pH_m	E_m /mV	V /cm^3	pH_m	E_m /mV	V /cm^3	pH_m	E_m /mV	V /cm^3	pH_m	E_m /mV	V /cm^3	pH_m	E_m /mV	V /cm^3	pH_m	E_m /mV
0.00	1.816	302.7	5.00	9.575	~~–158.7~~	0.00	1.826	302.2	4.90	4.054	170.2	0.00	1.829	302.0	5.00	8.441	~~–97.9~~
0.40	1.862	300.2	5.22	10.649	–220.1	0.40	1.868	299.7	5.03	9.889	~~–175.3~~	0.40	1.870	299.5	5.20	10.519	–212.2
0.81	1.909	297.3	5.40	10.909	–235.2	0.80	1.914	297.0	5.20	10.629	–218.8	0.80	1.919	296.3	5.42	10.889	–234.0
1.24	1.965	294.0	5.60	11.081	–245.5	1.20	1.965	294.0	5.41	10.945	–237.2	1.20	1.970	~~294.8~~	5.62	11.084	–245.7
1.63	2.022	290.8	5.80	11.203	–252.6	1.60	2.023	290.6	5.61	11.116	–247.5	1.61	2.026	290.4	5.80	11.202	–252.7
2.01	2.081	287.2	5.94	11.270	–256.7	2.00	2.084	286.8	5.80	11.231	–254.3	2.00	2.086	286.8	5.92	11.267	–256.4
2.20	2.115	285.3	6.50	11.460	–268.1	2.22	2.124	284.6	5.92	11.290	–257.7	2.20	2.120	284.6	6.51	11.480	–269.1
2.40	2.151	283.0	6.62	11.492	–269.8	2.40	2.156	282.7	6.47	11.481	–269.3	2.40	2.157	282.7	6.70	11.530	–272.0
2.61	2.191	280.6	6.82	11.536	–272.5	2.60	2.195	280.3	6.80	11.566	–274.2	2.61	2.196	280.2	7.00	11.598	–276.1
2.80	2.232	278.2	7.00	11.575	–274.6	2.81	2.239	277.7	7.00	11.606	–276.5	2.81	2.237	277.8	7.20	11.637	–278.3
3.00	2.279	275.4	7.21	11.616	–277.1	3.00	2.281	275.1	7.20	11.644	–278.8	3.00	2.282	275.2	7.40	11.671	–280.3
3.21	2.331	272.4	7.41	11.652	–279.2	3.20	2.333	272.0	7.43	11.681	–281.1	3.20	2.330	272.4	7.60	11.701	–282.3
3.42	2.391	268.7	7.60	11.682	–281.0	3.40	2.389	268.7	7.62	11.711	–282.7	3.40	2.386	268.7	7.80	11.728	–283.8
3.63	2.460	264.7	7.80	11.712	–282.7	3.62	2.458	264.6	7.81	11.737	–284.2	3.60	2.442	~~265.2~~	8.00	11.755	–285.4
3.80	2.526	260.8	8.00	11.738	–284.4	3.82	2.531	260.3	8.03	11.765	–286.0	3.80	2.520	260.9	8.41	11.806	–288.4
4.01	2.615	255.5	8.41	11.787	–287.2	4.00	2.614	255.4	8.40	11.809	–288.6	4.00	2.604	256.0	8.80	11.843	–290.7
4.20	2.728	248.7	8.80	11.829	–289.7	4.20	2.724	249.0	8.80	11.849	–291.0	4.24	2.734	248.3	9.24	11.885	–293.1
4.40	2.870	240.5	9.22	11.867	–291.9	4.40	2.862	240.8	9.20	11.885	–293.3	4.40	2.847	241.7	9.63	11.915	–295.1
4.60	3.079	228.0	9.60	11.898	–293.9	4.60	3.072	228.4	9.61	11.921	–295.3	4.60	3.035	230.5	9.98	11.941	–296.6
4.81	3.536	200.9	10.00	11.932	–295.8	4.80	3.467	204.9	10.00	11.951	–297.1	4.81	3.408	208.4			

(~0.004 pH unit) uncertainty. The titrations were carried out with a conventional, calibrated 10 cm^3 burette in a cell thermostatted to 25 °C. The order of the experiments is given below:

- The used instrument was preliminarily adjusted using one buffer solution (0.05 M KH-phtalate) assuming that the slope is Nernstian.[2]
- 25 cm^3 of 0.02000 M KH-phtalate solution was titrated with ~0.1 M KOH solution and this experiment was repeated two more times. These experiments are given as curves 4–6 in this example. The measured $V_m - pH_m - E_m$ data points are shown in Table 3.1.
- The device was again adjusted with the same buffer solution.
- 25 cm^3 ~0.02 M HCl solution was titrated three times with the same ~0.1 M KOH solution. These are curves 1–3 in the current example. The measured $V_m - pH_m - E_m$ data points are

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[2] In everyday terminology, this procedure is called one-point calibration but it is not enough for precise pH-measurement. This procedure is called adjustment in this guide to distinguish it from the precise calibration.

Table 3.3: Titration data in the third example for determining the formation contants of aspartate ion.

Curve 7						Curve 8						Curve 9					
V /cm^3	pH$_m$	E$_m$ /mV	V /cm^3	pH$_m$	E$_m$ /mV	V /cm^3	pH$_m$	E$_m$ /mV	V /cm^3	pH$_m$	E$_m$ /mV	V /cm^3	pH$_m$	E$_m$ /mV	V /cm^3	pH$_m$	E$_m$ /mV
0.00	2.111	285.2	5.50	4.199	161.7	0.00	2.123	284.4	5.40	4.157	164.0	0.00	2.115	285.1	5.60	4.275	157.2
0.42	2.179	281.0	5.60	4.283	156.7	0.21	2.155	282.6	5.50	4.237	159.5	0.20	2.147	282.9	5.86	4.545	141.5
0.80	2.244	277.5	5.70	4.377	151.0	0.40	2.188	280.5	5.63	4.355	152.5	0.40	2.179	281.2	6.06	4.910	119.8
1.22	2.328	272.4	5.80	4.492	144.3	0.60	2.223	278.8	5.80	4.558	140.2	0.60	2.213	279.2	6.20	5.980	56.3
1.60	2.409	267.7	5.92	4.655	134.6	0.80	2.255	276.8	5.91	4.716	130.8	0.81	2.249	277.1	6.34	8.339	–83.5
2.00	2.512	261.5	6.00	4.780	127.3	1.10	2.312	273.5	6.00	4.951	117.0	1.03	2.292	274.5	6.58	8.851	–113.6
2.20	2.564	258.4	6.40	8.497	–92.6	1.40	2.378	269.5	6.10	5.401	90.4	1.20	2.325	272.4	6.80	9.109	–128.9
2.40	2.624	255.0	6.53	8.786	–109.7	1.60	2.424	266.4	6.20	7.733	–47.9	1.40	2.365	270.1	7.00	9.285	–139.3
2.60	2.687	251.1	6.60	8.889	–115.9	1.80	2.473	263.6	6.31	8.411	–87.7	1.61	2.413	267.6	7.21	9.437	–148.1
2.80	2.755	247.0	6.70	9.023	–123.5	2.00	2.525	260.6	6.43	8.705	–105.2	1.82	2.465	264.3	7.40	9.563	–155.9
3.00	2.835	242.4	6.84	9.155	–131.7	2.20	2.580	257.5	6.61	8.974	–121.0	2.02	2.518	261.3	7.62	9.695	–163.5
3.20	2.915	237.7	6.90	9.211	–134.7	2.40	2.640	253.8	6.80	9.170	–132.7	2.20	2.563	258.6	7.80	9.812	–170.5
3.40	3.001	232.6	7.00	9.292	–139.7	2.60	2.704	250.1	7.00	9.335	–142.6	2.41	2.626	254.7	8.00	9.928	–177.2
3.60	3.098	226.8	7.14	9.401	–146.1	2.84	2.786	245.4	7.20	9.474	–151.0	2.60	2.686	251.3	8.20	10.056	–185.0
3.80	3.195	221.0	7.28	9.493	–151.6	3.01	2.854	241.1	7.40	9.605	–158.6	2.80	2.755	247.1	8.40	10.183	–192.3
3.98	3.289	215.5	7.40	9.573	–156.1	3.20	2.938	236.3	7.60	9.724	–165.6	3.00	2.830	242.7	8.60	10.335	–201.4
4.10	3.353	211.6	7.50	9.633	–159.7	3.33	2.992	233.1	7.80	9.846	–172.7	3.20	2.910	237.6	8.82	10.512	–211.6
4.22	3.418	207.8	7.60	9.694	–163.3	3.50	3.072	228.3	8.00	9.974	–180.2	3.40	2.996	232.8	9.00	10.675	–221.6
4.32	3.470	204.8	7.80	9.810	–170.4	3.62	3.132	224.9	8.20	10.103	–187.7	3.61	3.095	227.5	9.20	10.842	–231.4
4.44	3.538	200.7	8.00	9.930	–177.4	3.82	3.230	219.1	8.40	10.244	–196.4	3.80	3.189	221.5	9.40	10.987	–239.8
4.60	3.626	195.5	8.20	10.053	–184.5	3.94	3.291	215.6	8.60	10.408	–206.1	4.00	3.297	215.0	9.60	11.105	–246.8
4.72	3.691	191.7	8.55	10.303	–199.5	4.02	3.339	212.5	8.84	10.609	–218.0	4.20	3.401	208.9	9.81	11.211	–253.1
4.80	3.736	189.0	8.80	10.499	–210.9	4.26	3.465	205.0	9.06	10.806	–229.8	4.41	3.514	202.4	9.98	11.282	–257.4
4.90	3.795	185.4	9.21	10.853	–232.0	4.40	3.543	200.6	9.26	10.957	–238.6	4.60	3.619	195.9			
5.00	3.857	182.0	9.60	11.116	–247.5	4.60	3.650	194.2	9.46	11.089	–246.7	4.81	3.736	189.1			
5.12	3.928	177.6	9.98	11.284	–257.5	4.80	3.765	187.4	9.60	11.166	–251.0	5.00	3.849	182.5			
5.20	3.980	174.6				5.00	3.889	179.8	9.81	11.260	–256.5	5.20	3.969	175.3			
5.34	4.074	168.9				5.20	4.011	172.8	10.00	11.336	–261.0	5.40	4.113	166.8			

shown in Table 3.2.

- The device was again adjusted with the same buffer solution.
- 25 cm^3 solution containing ~0.015 M HCl and 0.0102 M aspartic acid was titrated with the same ~0.1 M KOH solution. The three parallel measurements are given as curves 7–9 in the present example. The measured $V_m - pH_m - E_m$ data points are listed in Table 3.3. The aspartic acid content is derived from the exactly known concentration of the aspartic acid stock solution. The HCl content came from the HCl stock solution, the concentration of which was determined from the previous titrations.

During the experiments, the ionic strength was set to 0.5 M using more concentrated KCl stock solutions.

3.3.1 Calibration

The first step of the evaluation is to check if the technical parameters were constant during the measurement. In order to do this, linear regression has to be carried out for the $pH_m - E_m$ data pairs of each titration curve (the points omitted from the regression are striked out in the tables). The fitted straight lines are

Curve 4: $pH_m = -0.016900 \cdot E_m + 6.9214$, Curve 1: $pH_m = -0.016898 \cdot E_m + 6.9330$,
Curve 5: $pH_m = -0.016903 \cdot E_m + 6.9213$, Curve 2: $pH_m = -0.016900 \cdot E_m + 6.9319$,
Curve 6: $pH_m = -0.016889 \cdot E_m + 6.9198$, Curve 3: $pH_m = -0.016901 \cdot E_m + 6.9315$,
Curve 7: $pH_m = -0.016905 \cdot E_m + 6.9318$, Curve 8: $pH_m = -0.016887 \cdot E_m + 6.9278$, and
Curve 9: $pH_m = -0.016901 \cdot E_m + 6.9319$.

The comparison of the intercepts suggests that there was an experimental problem during the one buffer calibration of the pH-meter. The intercept values are smaller by ~0.01 pH unit

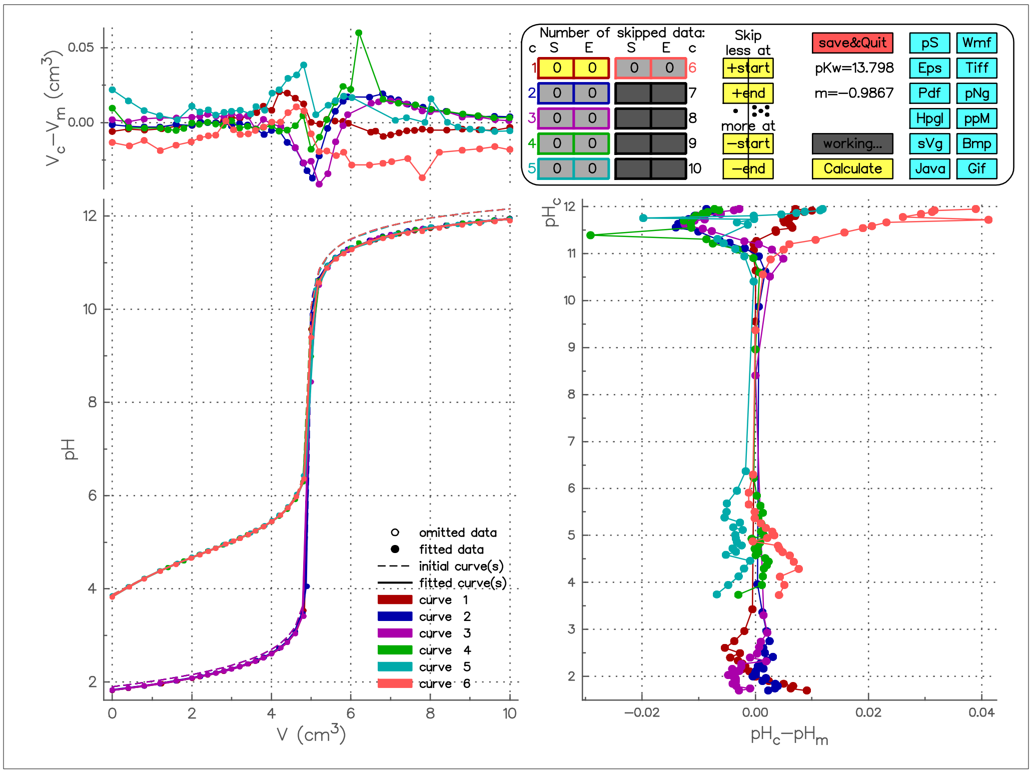
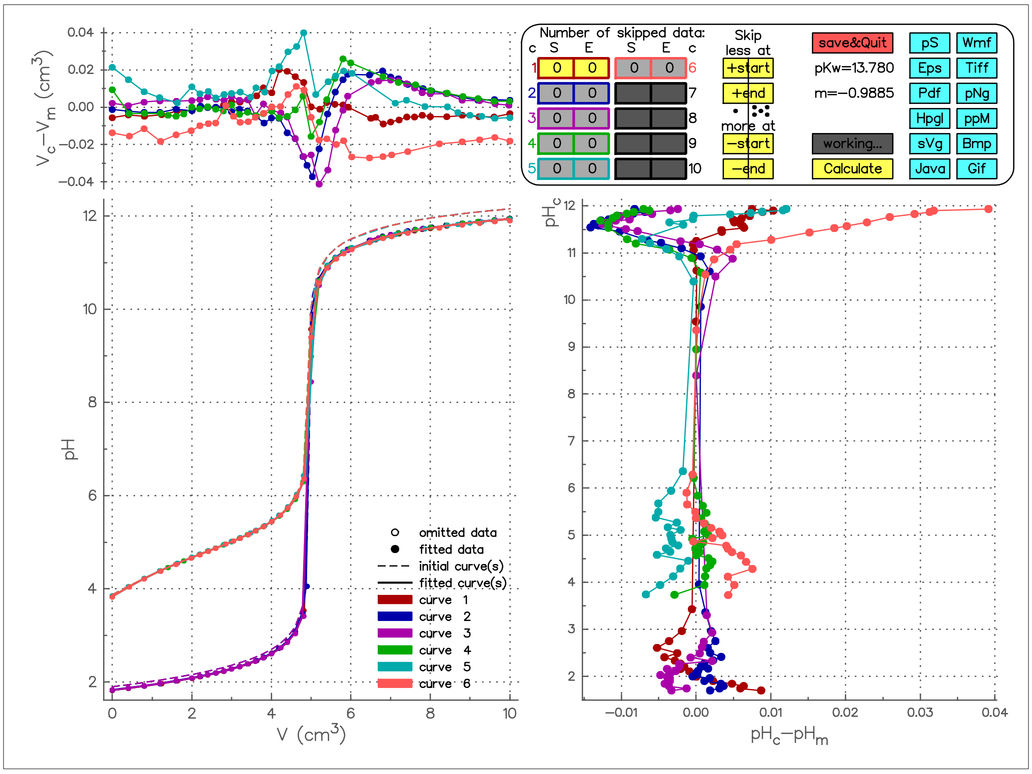


Figure 3.6: The work-window of the `aspph-a.tid` file in the third example.

after the first one-buffer calibration than after the others. This value is significantly greater than the experimental uncertainty.

The next step is the calibration of the instrument using pHCali and the first six titration curves. This task requires an input file (it is named `aspph-a.tid` in the present case) created from the data of these curves. The second section of this file (*see* Subsection 2.2.1) contains the six curves in the order of their serial numbers, and titration curves 7–9 are put into the third section of the `aspph-a.tid` file for the $p\mathrm{H_m} \rightarrow p[\mathrm{H}]$ calculations. By running the appropriate pHCali variant with the `aspph-a.tid` file, the work-window visible in Figure 3.6 appears on the screen. The upper left and lower right graphs show that there are some bad points on the curves: the 10th data before the last one in curve 4, the 7th data before the last one in curve 5 and the 6th data before the last one in curve 6. These points must be excluded but it cannot be done with the help of the operating panel since the erroneous data are not at the beginning or at the end of the curves. The user must quit pHCali by pressing the «save&quit» button and edit the file with an ASCII editor. A relative weighting factor of `0` must be given to the points to be excluded.

The necessary changes detailed above has been already done in the `aspph-b.tid` file. By running the program with this file, the work-window visible in Figure 3.7 appears. The comparison of the three weak acid – strong base curves suggests that the whole curve 6 should be excluded because it differs significantly from the others. This fact can clearly be seen either from the figure or in table 3.1, as well. The same comparison for the strong acid – strong base curves suggests that curve 1 should also entirely be excluded from the further calculations (although its deviation is smaller than that of curve 6) as it can be seen either from the figure or in Table 3.2. In order to omit the erroneous curves only from the calculations and to leave them on the graphs, all relative weighting factors for curves 1 and 6 must be set to $1.0{\times}10^{-20}$. In this way, these points do not contribute to the sum of squares function (*see* equation (A.14)) practically thus they do not influence the fitting. These points, however, remain detectable for the program and they are displayed on the figures.



pKw=13.780

m=−0.9885

Figure 3.7: The work-window of the `aspph-b.tid` file in the third example.

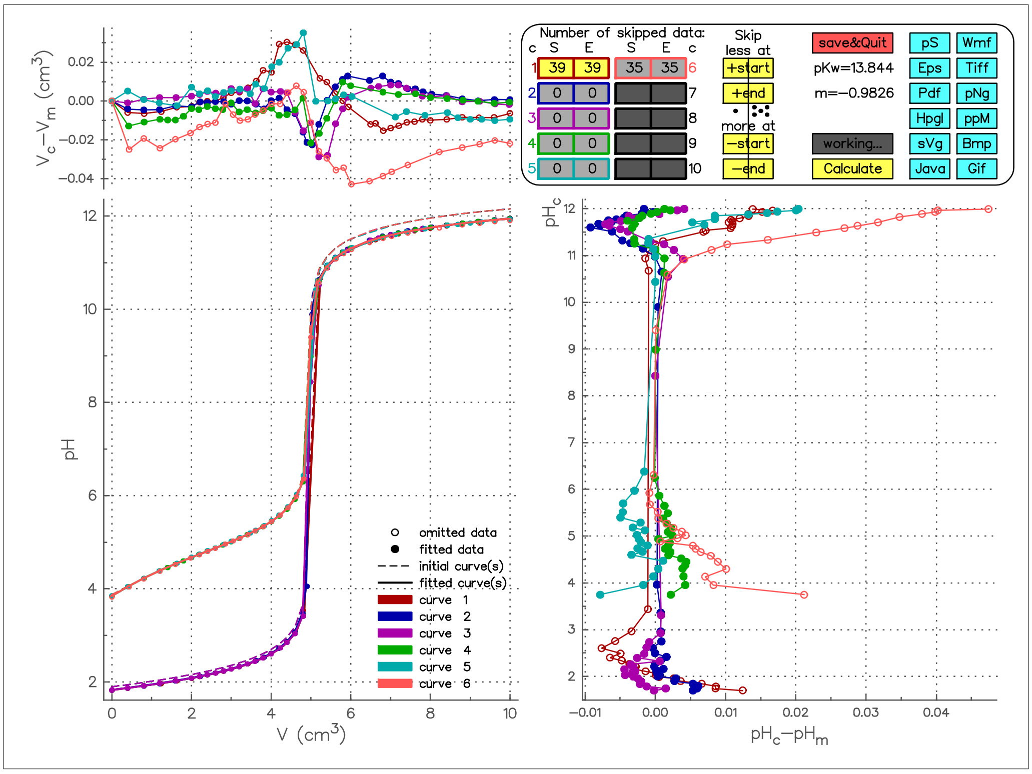
In order to change the relative weighting factors, *p*HCali has to be terminated with the «save&quit» button and the data file has to be modified with a text editor. The changes detailed above have already been made in `aspph-c.tid` file. Running the program with this file results in the work-window visible in Figure 3.8. The numbers in the upper-right part of the window indicate that curves 1 and 6 are completely excluded.

The next step of the evaluation is to exclude points outside the Nernstian range. As the lower right part of Figure 3.8 shows, there are systematic deviations between the measured and calculated data at both ends of the strong acid – strong base curves. The same is valid for the basic ends of the weak acid – strong base titration curves. Using the operating panel, the erroneous points can be excluded in multiple steps and refitting. The remaining data do not show significant systematic deviation between the experimental and calculated points as it is shown in Figure 3.9.[3] After terminating the program with the «save&quit» button, the current state is stored in the `aspph-c.cin` file. Renaming it to `aspph-d.tid` and running *p*HCali with this file, the work-window shows this state initially.

The goal in the previous phase of the evaluation was to separate and exclude questionable experimental data. Till this point, it was practical to handle the curves separately because the points to be omitted were easier to find. The fitting of the remaining points gives those parameters which are required for further equilibrium calculations. For this fitting, it is expedient to handle the repeated curves together by *p*HCali as a single one. The reason for this treatment comes from the nature of parameter estimation. By fitting the repeated experiments separately, more than one value should be fitted for some parameters (e.g. the exact concentration of the strong acid). The over-parametrization of the task certainly leads to unnecessary correlations. It is even more serious problem in case of orthogonal fitting than in the usual parameter estimation procedures (*see* Section 4.1). To avoid this failure, it is highly suggested to contract curves 1–3 and 4–6 of `apph-d.tid` into one-one curve before the final fitting. This change has already been made in the `aspph-e.tid` file.

---

[3] The first point of the fifth curve is also omitted on this figure as an erroneous one.

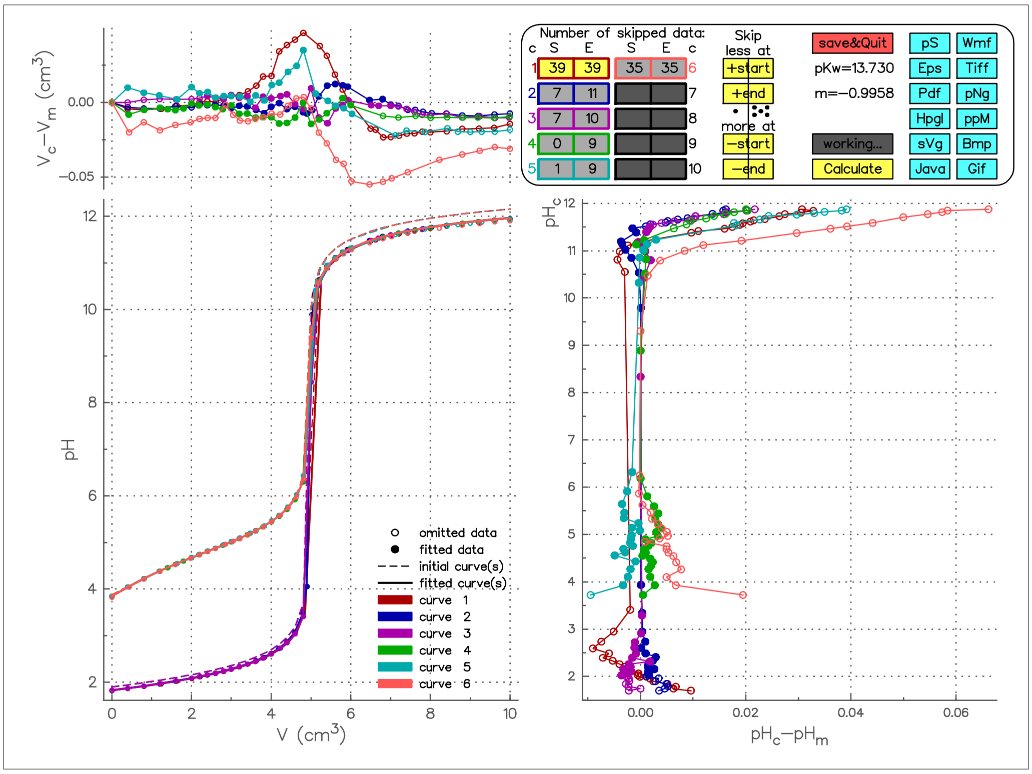


Number of skipped data:

c	S	E	S	E	c
1	39	39	35	35	6
2	0	0			7
3	0	0			8
4	0	0			9
5	0	0			10

pKw=13.844
m=−0.9826

Figure 3.8: The work-window of the `aspph-c.tid` file in the third example.



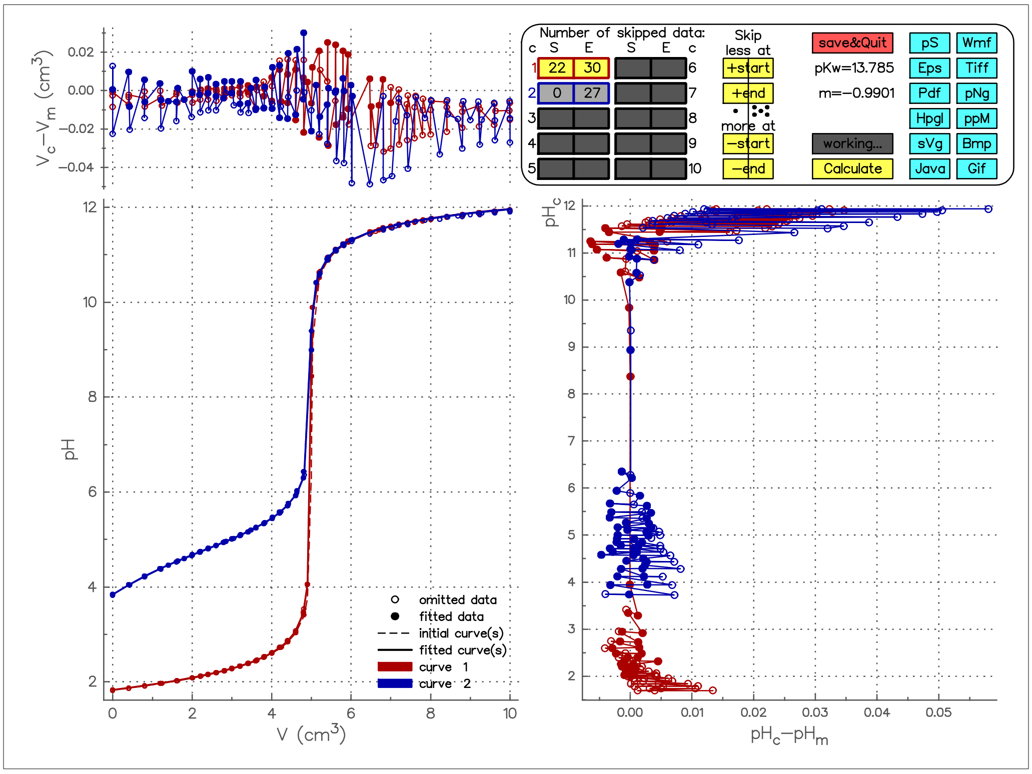
Number of skipped data:

c	S	E	S	E	c
1	39	39	35	35	6
2	7	11			7
3	7	10			8
4	0	9			9
5	1	9			10

pKw=13.730
m=−0.9958

Figure 3.9: The final work-window of the `aspph-c.tid` file in example 3 (or the initial work-window of the `aspph-d.tid` file).

This file contains one more change in line 143: the shift parameter of the contracted weak acid – strong base titration curve is also fitted. The usage of this parameter corrects the problem indicated by the initial linear fitting on the $pH_m - E_m$ points, that is the significant



pKw=13.785

m=−0.9901

Figure 3.10: The work-window of the `aspph-e.tid` file in the third example.

differences in the intercepts of the straight lines (*see* page 20 in Subsection 2.2.1). From the two possible parameters, the one belonging to curves 4–6 should be fitted, because these curves are shifted compared to the others, as shown by the values of the intercepts. In this case, the titration curves belonging to the aspartic acid solutions are not influenced by this parameter during the further calculations.

By running the program with the `aspph-e.tid` file, the work-window visible in Figure 3.10 appears. This figure illustrates the final results of the calibration. After pressing the «save&quit» button, the final results are stored in the result files created by the program. Two files can always have importance for the user:

- The `aspph-e.phv` file contains the $V_m - p[H]$ values calculated from the original aspartic acid titration curves. These data can be the starting data set for further equilibrium calculations for various programs (e.g. [18]). The structure of the file is detailed in Subsection 2.4.3.
- The `aspph-e.res` file contains the final results of the calibration which is also shown in Listing 3.3. The contents of the `*.res` files described in full detail in Subsection 2.4.1.

The calibration is completed by the evaluations done so far. Comparing the method of the program to other usual calibration methods, the following advantages of pHCali can be mentioned:

- All titration curves can be handled simultaneously.
- Despite the fact that there are no any neglection during the evaluations, the cumulative formation constant(s) of the calibration material is/are not needed to be known. The(se) value(s) can be determined during the calculations(e.g., lines 16–17 in Listing 3.3).
- The carbonate content of the titrant base can be determined and it can be taken into account during further evaluations. It is not available with the conventional calibration procedures used so far. Line 13 in Listing 3.3 indicates that the titrant is contaminated with ~1% carbonate anion which is a significant amount when precise measurements are required.

Listing 3.3: The content of `aspph-e.res` file.

```
 1  ***** Input file: ASPPH-e.tid
 2  Curve(s):
 3   1: 66 fitted data (p[H]= 2.0-11.6), 22/ 30 omitted data from start/end.
 4   2: 79 fitted data (p[H]= 3.7-11.3),  0/ 27 omitted data from start/end.
 5  ***** Estimated parameter values:
 6       Name  Final value   Std. deviation  Initial value of the last calculation
 7        pKw  1.378540E+01  3.984947E-02    1.372830E+01
 8         Id  1.498100E-01  8.726922E-03    1.369870E-01
 9          m -9.900779E-01  4.091968E-03   -9.959890E-01
10       JH^p  0.000000E+00  fixed (Fitting is not recommended!)
11      JOH^p  0.000000E+00  fixed (Fitting is not recommended!)
12     C_base  9.945512E-02  9.304050E-05    9.940650E-02
13      C_CO3  1.103565E-03  8.882159E-05    1.007220E-03
14   lgB1_CO3  1.020000E+01  fixed
15   lgB2_CO3  1.630000E+01  fixed
16     lgB1_A  4.718486E+00  1.232788E-02    4.696890E+00
17     lgB2_A  7.425175E+00  1.776282E-02    7.391980E+00
18      V0_c1  2.500000E+01  fixed
19    +TH0_c1  2.007876E-02  1.872289E-05    2.016670E-02  (TH0_base= 0.000000E+00)
20     TA0_c1  0.000000E+00  fixed
21    Shft_c1  0.000000E+00  fixed
22      V0_c2  2.500000E+01  fixed
23    +TH0_c2  0.000000E+00  fixed                          (TH0_base= 2.000000E-02)
24     TA0_c2  2.000000E-02  fixed
25    Shft_c2 -7.997806E-03  3.722839E-03    0.000000E+00
26  ***** Experimental uncertainties:
27   1.000E-02 or 1.000E-03*Vm cm3 for the volume, whichever is larger
28   4.000E-03 unit for pH
29  ***** Goodness-of-Fit statistics:
30                      Number of iterations:     7
31            Number of function evaluations:    63
32            Number of Jacobian evaluations:     9
33                           Rank deficiency:     0
34   Average of weighted deviation of volume:  1.107074E-02
35                        only for curve  1:  1.245299E-02
36                        only for curve  2:  9.639059E-03
37       Average of weighted deviation of pH:  2.575632E-03
38                        only for curve  1:  2.937330E-03
39                        only for curve  2:  2.198632E-03
```

- The deviation in the slope of the electrode used from the ideal Nernstian value can be corrected (*see* line 9 in Listing 3.3).
- It is not needed to know (or to believe) the *p*H range in which the Nernst equation is valid for the electrode used. The appropriate range can simply be determined visually by omitting/including points at the beginning and at the end of the titration curves. It is highly important to know this range when the user investigates the equilibrium system the measuring device should be calibrated for!
- The possible errors during the experiments can be either corrected (*see* the shift parameter in line 25 of Listing 3.3) or indicated (e.g., the carbonate content of the strong base). These errors usually remained hidden using the conventional calibration procedures so far.

3.3.2 Determination of Formation Constants

If only protonation equilibria are present in the system to be studied by the user, another program is not necessary for calculating the cumulative formation constants since *p*HCali can determine them. The great advantage of using the program is the ability of fitting the initial concentrations too, which can be important if the material to be investigated is hard to weight precisely.

For determining the cumulative formation constants, a `*.tid` file has to be created which is similar to that of used during the calibration. The only difference is that the third section of the file (*see* Subsection 2.2.1) has no meaning and therefore should be omitted. The data file to be created contains the values of the parameters determined during the calibration so these parameters must be fixed. The only parameters to be fitted are the cumulative formation constants of the investigated material. The initial values of the cumulative formation constants of the material should be given in the place of that of the calibration material. The second section of the `*.tid` file contains the titration curves the same way as for calibration. The necessary file for the actual example is supplied in the aspbeta.tid file (and corresponds

Listing 3.4: Partial content of `aspbeta.tid` file.

```
 1 4.000E-03         / uncertainty of Em or pHm
 2 1.0E-02 1.0E-03 / uncertainty of V
 3  1.37854E+01 0  / pKw                                          parameter  1
 4  1.49813E-01 0  / Id                                           parameter  2
 5 -9.90078E-01 0  / m(=-1)                                       parameter  3
 6  0.00000E+00 0  / JH^p                                         parameter  4
 7  0.00000E+00 0  / JOH^p                                        parameter  6
 8  9.94551E-02 0  / c0 in mol/dm3 for the base solution          parameter 18
 9  1.10366E-03 0  / c(CO32-) in mol/dm3 for the impuritites      parameter 19
10  1.02000E+01 0  / log beta_1 for CO32-                         parameter 20
11  1.63000E+01 0  / log beta_2 for CO32-                         parameter 21
12  3              / number of given formation constants (<=9)
13  9.00000E+00 1  / log beta_1 for the weak acid                 parameter 22
14  1.20000E+01 1  / log beta_2 for the weak acid                 parameter 23
15  1.50000E+01 1  / log beta_3 for the weak acid                 parameter 24
16  2.00000E+00    / H:A ratio in the weighted material (or 0) for curve  1
17  2.50000E+01 0  / V0 in cm3 for curve 1                        parameter 31
18  1.46000E-02 0  / +T(H)0 in mol/dm3 for curve 1                parameter 32
19  1.02000E-02 0  / T(A)0 in mol/dm3 for curve 1                 parameter 33
20  0.00000E+00 0  / shift in the measured E/pH for curve 1       parameter 34
21  0.00  2.111 1.0e-20
22  0.42  2.179 1.0e+00
23  9.60 11.116 1.0e+00
24  9.98 11.284 1.0e+00
25  0.00  2.123 1.0e-20
26  0.21  2.155 1.0e-20
27  9.81 11.260 1.0e-20
28 10.00 11.336 1.0e-20
29  0.00  2.115 1.0e+00
30  0.20  2.147 1.0e+00
31  9.81 11.211 1.0e+00
32  9.98 11.282 1.0e+00
```

to Listing 3.4).[4]

Lines 3–11 of this file correspond to the values determined during the calibration (*see* lines 7–15 in listing 3.3) but they are now fixed. Lines 12–15 of Listing 3.4 contain the initial values of the cumulative formation constants of the aspartate ion. Line 16 shows that the material was weighted in form of H_2A. Line 18 shows the concentration of the strong acid added independently into the solution to be titrated. The three repeated curves are given for the program as a single curve. It can be seen from Table 3.3 that the 8th curve is different from the other two (the 7th and the 9th) ones, therefore, 1.0×10^{-20} relative weighting factor should be given for the titration points of the 8th curve. It is shown in lines 71–130 of the `aspbeta.tid` file. The last fact to be mentioned is that the first point of curve 7 is treated to be an erroneous one as line 21 shows this fact.

Running the program with the `aspbeta.tid` file leads to the work-window seen in Figure 3.11. The differences in the lower right and upper left parts clearly indicate that the fitting is not acceptable in the basic range. The same can be read from the titration curves in the lower left part. It is visible that the equivalence point is different in a small extent from the expected value (which can be calculated precisely in this specific example).

If the concentration of the total anion is also given as a fitted parameter as seen in line 19 of the `aspbeta.tid` file (which means that the `0` is to be replaced with a `1` in the 14th character position of the line) and the fitting is repeated, the resulted work-window is the one seen in Figure 3.12. In this window, systematic deviation significantly exceeding the experimental uncertainty cannot be found which, while the initial concentration of the anion has been increased from 0.0102 M to 0.01086 M. In the specified experiments, the weighted material was $C_4H_7O_4N \cdot H_2O$ where an additional gravimetric measurement clarified that the weighted material has lost its crystalline water partially so the obtained results are acceptable: $\lg\beta_1 = 9{,}67$, $\lg\beta_2 = 13{,}29$ and $\lg\beta_3 = 15{,}16$. For the sake of comparison,

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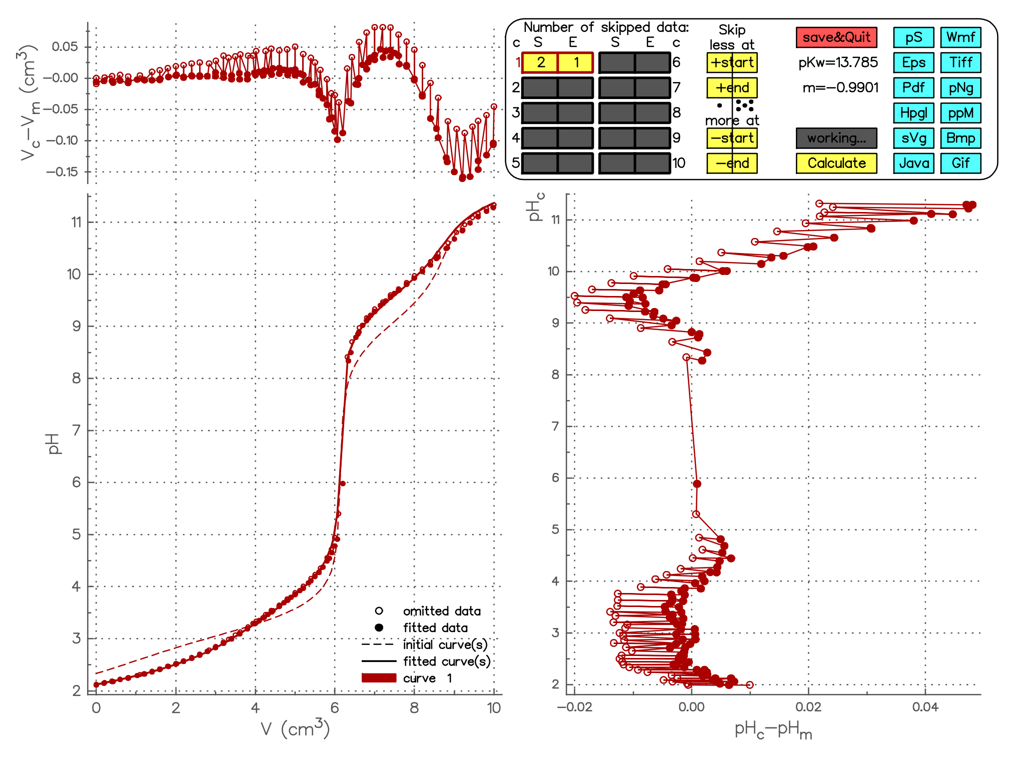
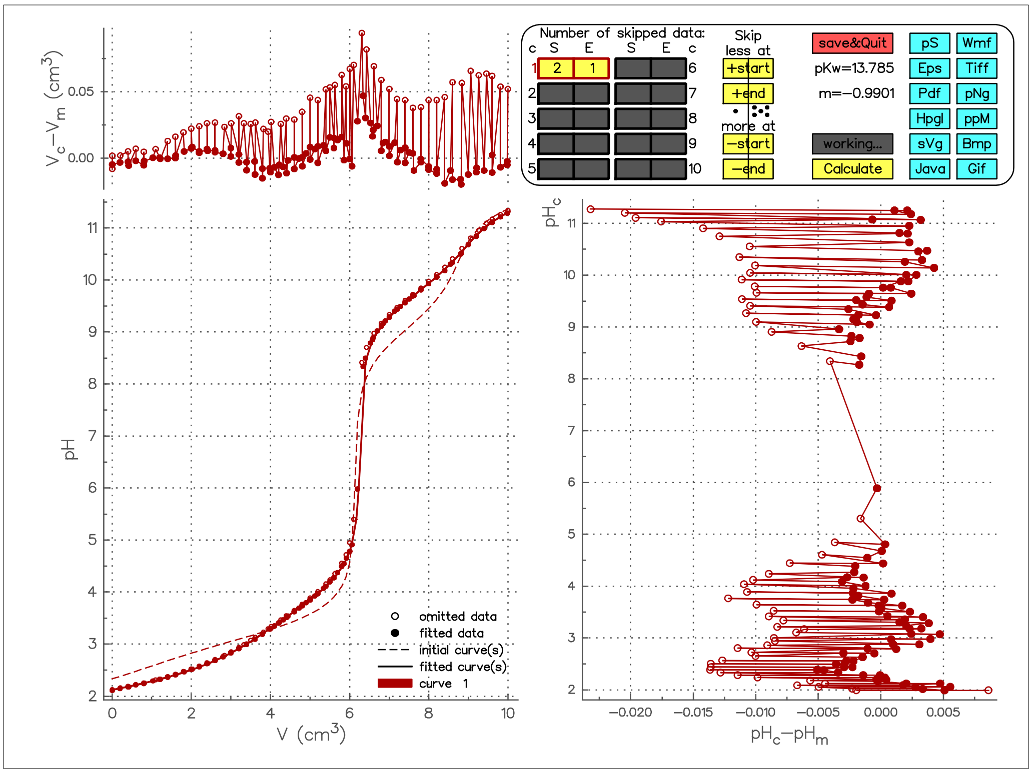
[4] This file also illustrates that parallel titration curves can be given together with the same header lines since the parameters included in the header are identical for these curves.



pKw=13.785

m=−0.9901

Figure 3.11: The final work-window of the `aspbeta.tid` file in the third example if the total concentration of aspartate ion is fixed.



pKw=13.785

m=−0.9901

Figure 3.12: The final work-window of the `aspbeta.tid` file in the third example if the total concentration of aspartate ion is fitted.

the literature data according to [19]: $pK_w = 13,73 - 13,81$, $\lg \beta_1 = 9,63$, $\lg \beta_2 = 13,31$ and $\lg \beta_3 = 15,26$.

CHAPTER 4

PRACTICAL GUIDE

During creation of *p*HCali, the authors carried out more than 40 calibration measurements besides the evaluation of earlier measured data, in order to test the program. These measurements included testing of various calibration materials, systematic changing of the carbonate content of the strong base solutions, measurements at various ionic strengths and using different *p*H ranges. In the course of the evaluation of the experimental data, large amount of empirical knowledge was collected which may help the precise calibration. It is not closely related to the usage of the program, rather to the chemistry of the calibration systems. This knowledge is discussed in this chapter.

4.1 Sensitivity of the Orthogonal Regression for the Initial Values and Correlation of the Parameters

The success of orthogonal regression depends more on the correct initial values of the fitted parameters and the experimental errors than in case of the usual parameter estimation procedures. The reason of this is that the orthogonal curve fitting treats the volume data as to be fitted (although with some constraints) together with the other parameters. Thus, the number of the fitted parameters is more than usual. This feature greatly increases the correlation between the parameters (i.e., how the parameters can be substituted with each other). Moreover the mathematical equations describing the titration curves (equation (A.6) and equation (A.9) or (A.12)) contain parameters that are already in large correlation with each other. From mathematical aspect, the fitting of the parameters in such equations is a very difficult task.

The following advices are able to aid the successful fitting:

1. The parameters with already known exact values are not fitted. They can be for example, the concentrations or cumulative formation constants exactly known from independent measurements.
2. The obviously erroneous experimental points must be excluded. An example is shown in the first step of the calibration task described in Section 3.3.
3. The initial values of the parameters must be estimated with great caution. *Differences in the order of magnitude are not tolerated by the orthogonal fitting usually!* A good approximation is satisfactory in most cases but in extreme situations, the fitting might miss the minimum even when the best initial values are entered. This fact can be illustrated on the reference example of Chapter 2. The inital work-window of the `kh1-13e.tid` file is shown in Figure 2.5 while the final work-window after omitting the points outside of the Nernstian range is displayed in Figure 2.7. The exclusion of the points, however, is not needed to be done from the graphical work-window. By suitably choosing the values of the relative weighting factors, the `*.tid` file can be written so that *p*HCali is able to distinguish between the points even before the fitting procedure. It can be simply done for the reference example in the following way:
    - The `kh1-13e.tid` file should be copied to `k.tid`.

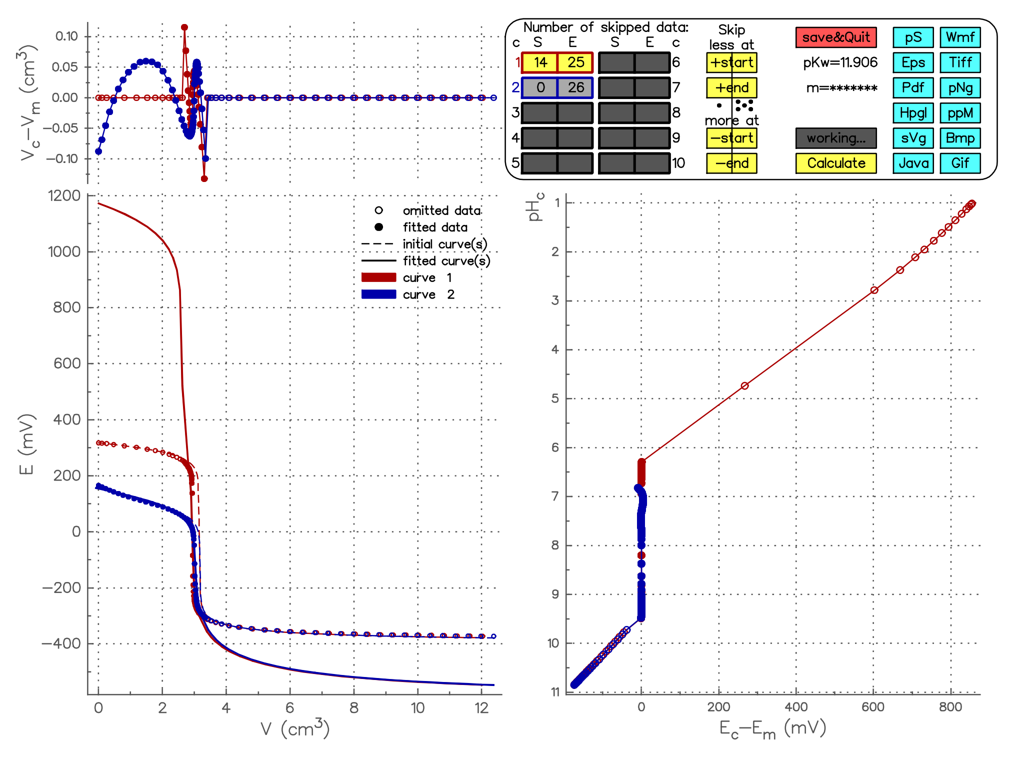


Figure 4.1: The final work-window of the reference example in case of a bad fitting.

- In the `k.tid` file, all weighting factors are set to 1.0 but they are written in two forms: `1.0e-00` or `1.0e+00`. The first form is connected to the points which are excluded from the fitting in Figure 2.7. If the strings `1.0e-00` in the `k.tid` file are changed to `1.0e-20` then the execution of the program would directly lead to the work-window seen in the referenced figure. But the real result can be seen in Figure 4.1 which illustrates the issue of an obviously failed calculation.

If the fitting described above is carried out in two steps then good results can be obtained:[1]

- Not only the values of the relative weighting factors have to be changed in the `k.tid` file. The status of the parameters E' and m_E should also be changed from fitted (`0`) to fixed (`1`) by changing the characters in the 14th character position in lines 4 and 5. After this modification, the program has to be run with the `k.tid` file.
- The `k.cin` file created at the end of the running has to be renamed to `k1.tid`. In this file, the status of two parameters (E' and m_E) have to be changed back (from fixed to fitted) by replacing the `0`-s with `1`-s. Now, the execution of the program with the `k1.tid` file leads to the work-window displaying the good results.

The good results can be obtained in one step also if the user does not change the status of the above mentioned parameters, rather (s)he gives better initial value for the concentration of the strong base. In this case, beside the weighting factors to be modified, the initial values of the base concentration should also be changed to `2.00000E-01` (from 0.19 M to 0.2 M) in the eighth line of the `k.tid` file. The calculation with the modified file instantly supplies the correct result so the two-step procedure is not necessary. This shows that 5 % difference between the initial value and the real one may lead to a poor estimation! This example is indeed an extreme one which may only occur if KH-phtalate is used, as it is

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[1] The followings work with every variant of *p*HCali but the necessary modifications can be carried out most simply through the parameter-modifier window.

described in Section 4.6.

The latter considerations can be summarized so that it is a good idea to modify the initial values to be fitted in case of wrong results. The lower left graph of the work-window gives a great help. Here the curves calculated with the initial parameter values are drawn with dashed lines. Using these curves, it can be estimated which parameter has to be modified and to which direction. But before doing any changes, it is advised to press the «calculate» button several times, and check if the result improved or not. The number of iterations is maximized in the program so the too slow convergence may alone cause the error for a poorly conditioned task. In such cases, the use of «calculate» button skips the maximum number of iterations. An example can be seen using the `ox1-13ph.tid` if the `1.0e-00` strings are changed to `1.0e-20` (*see* Section 4.6).

Besides wrong final results, it may also occur that the fitting is perfect but the volume data of an excluded point is misfitted resulting in distorted figures on the work-window. In most cases, the reason for this behavior is the too small weighting factor (i.e., it is less then one by many magnitudes of order), therefore even an irrealistic change in the calculated volume and/or *p*H is not able to influence the average deviation. In such case, the most expedient solution is to increase the value of the weighting factor of the point in question or—if the specific point is not necessary—it should completely be removed. The latter solution technically means that a weighting factor of 0.0 should be ordered to the point.

4.2 Importance of the Constant Ionic Strength

It is a common rule if the equilibrium is studied in solutions that the ionic strength in the titrated solution must be constant. This rule cannot be fulfilled with mathematical strictness because the reactions change the ionic strength themselves. But using an appropriate salt to set the ionic strength in both the titrant and the titrated solutions, the change of the ionic strength can be kept to be constant within 4–5 % error. It is practically enough to avoid varying values for the cumulative formation constants during the measurement. This practice also helps to keep the additivity of volumes to be valid.[2] If the density and the viscosity of both the titrant and the titrated solution are determined by the same ionic-strength-setting salt, the problem of dilatation or contraction can safely be neglected.

The practice of pH-metry is often in direct contradiction to these considerations. Titration of very dilute solutions with very concentrated bases is a commonly used technique. In such cases, the relative change in volume is rather low ($V_m/V_0 \ll 1.0$) thus it is suspected that the change in the ionic strength can be neglected due to the tiny dilution. This is not true, however! The variation of the ionic strength depends not only on the ratio of the volumes but on the ratio of the concentrations too, and the concentration in the titrant is much higher than that in the titrated solution. It is also suspected that the dilatation or contraction can be neglected because their contribution to the volume of the titrated solution is very small. But the independent variable of the titration curves is not the $V_0 + V_m$, but the V_m itself which has very small values due to the high concentration of the titrant base! Using *p*HCali, these errors can be caught on the upper left graph of the work-window: the curves after the equivalence points have systematic deviation which exceed the experimental uncertainty.

4.3 Potential or *p*H should be Measured?

The answer: both if possible, otherwise, the measurement of the potential is suggested. It is bad news for chemists, who prefer thinking in *p*H units rather than in potential. But the

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[2] Do not forget that strictly additive volumes are supposed for the formulae used for the calculations (*see* the Appendix)!

exceptional measurement of pH makes the recognition and the elimination of some classes of experimental errors difficult or even impossible.

The reason of this advice is rather simple. In fact, the measurement devices always measure potential directly. The pH displayed on the screen of the device is only the result of a previous one-, two- or three point adjustment/calibration through which the user has taught the device how to calculate pH from the measured potential. It is a common procedure that the device is set to a specific pH value of a buffer solution before the measurement of every titration curve. Any failure in this operation may cause that not the same $pH_m(E_m)$ function describes all the titration curves. In this way, the basic assumption is not fulfilled for devices calibrated to pH values! The measured potential is not influenced by this adjustment so the potential data can still be evaluated.

The third example of Chapter 3 details how such problems can be identified, and (in some cases) how the pHCali can take the change in the $pH_m(E_m)$ curves into account.

4.4 How Closely the Titration Points should be Measured?

In practice the titrant is dosed in two ways:

1. The added volume is independent from the measured potential, but the added volume portions are approximately constant. The reason of this technique is that measured data around the equivalence point carry much more uncertainty in potential (or pH) than the other data so it is not worth to measure many points here, these data would be excluded from the evaluation anyway. This method enables the user to carry out the titration faster.
2. The principle of the second procedure is that the bigger the change in the potential is the smaller the next added volume should be. At the most steep ranges of the titration curve, as dense the measurements should follow each other as the burette is capable for within its technical limitations. Using this method, certainly more time is required to carry out a titration.

For pHCali, definitely the second method is preferable. The orthogonal curve fitting is capable to evaluate the points around the equivalence point too. On the other hand, the equations, on which the program is based, do not apply any approximations. These two facts together make it possible to evaluate the complete titration curve without any preliminary exclusion. Using pHCali, experimental data should be excluded only if *(1)* the data is erroneous or *(2)* some of the points are in the non-Nernstian range.

It is extremely important to measure around the equivalence point during a calibration measurement. Independent experimental information to determine the carbonate content can only be found on the strong acid – strong base titration curves near the equivalence point. If this range is skipped during the measurement, the program is less capable to determine the carbonate content. Considering this fact, the strong acid – strong base titration of the first example in Chapter 3 is a completely suitable one (*see* Figure 3.1) while the curve in case of the third example seems a bit rough-and-ready around the equivalence point (*see* Figure 3.6).

4.5 Question of the Quantitative Determination of the Total Carbonate Concentration

To determine the carbonate content of the titrant base is a very difficult task form the experimental aspect. The equations derived in the appendix suspect that the actual total carbonate concentration can always be calculated using the volume ratios (*see* equation (A.3c)). But this is not true if the studied solution is stirred. In practice the stirring is carried out in two ways:

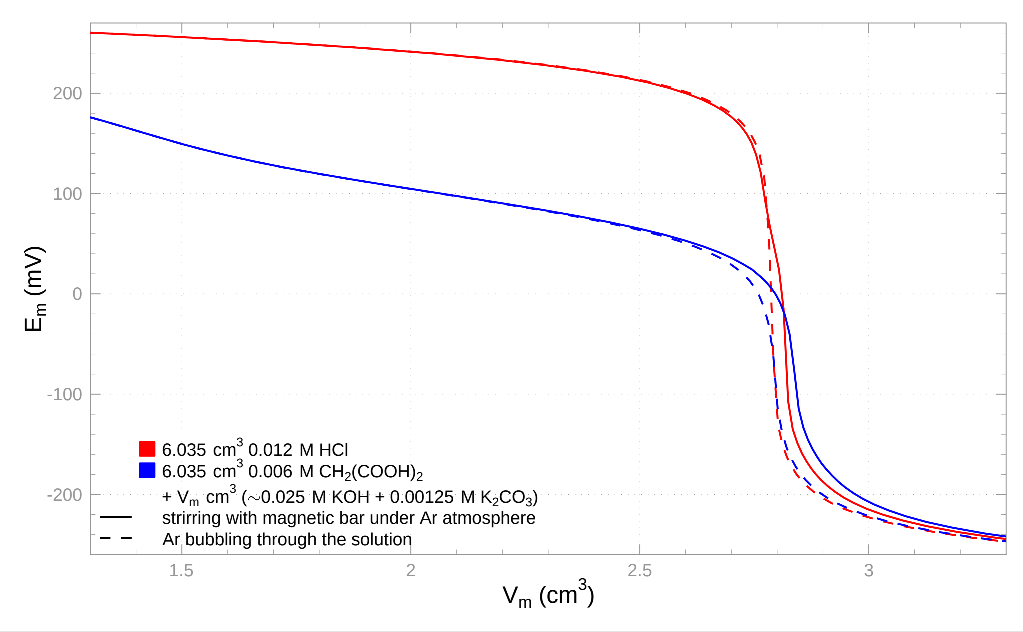

Figure 4.2: Titration of hydrochloride and malonic acid solutions with KOH contaminated by ~5 % carbonate.

1. An inert gas is led into the titrated solution. In the acidic range, the gas purges the carbonate as carbon-dioxide from the solution. In basic medium, it does not happen.
2. An inert gas is led above the solution and the stirring is done, for example, with a magnetic stirrer. In this case, the loss of CO_2 is much less but it cannot be completely stopped since CO_2 has relatively poor solubility in water.

These stirring methods lead to different titration curves at higher carbonate concentrations as it is illustrated in Figure 4.2. In case of bubbling through the solution, the curvature caused by the carbonate content vanishes from the titration curve. It results significant shifting of the formally detectable equivalence point.

Modeling the extent of the evaporation of carbon-dioxide is practically impossible. This fact required to carry out systematic study of how much the different conditions influence the CO_2 leaving. The experiences coming from the calculations with *p*HCali are the following:

- In case of bubbling inert gas through the solution, the program was not able to determine the carbonate concentration quantitatively in any of the measurements. The fitting of the carbonate concentration gave the 10–50 % of the real value.
- In case of mechanical stirring, the program was able to determine the carbonate concentration quantitatively if the following conditions were valid:
  - $T_{CO_3^{2-}}/T_{OH^-} \leq 2\,\%$ and $T_{OH^-} \leq 0.025\,M$, or
  - $T_{CO_3^{2-}}/T_{OH^-} \leq 1\,\%$ and $T_{OH^-} \leq 0.25\,M$.
- Independently of the stirring method, the badly determined carbonate concentration did not influence the other parameter values so the calibration of the device was possible.[3]

It is obvious from the above observations that *p*HCali cannot be used for the quantitative determination of the carbonate content if the titrant base is strongly contaminated with carbonate. But this contamination can be indicated clearly, and it cannot be smeared by the function transformations!

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[3] This fact is a surprising but unambiguous experience!

Table 4.1: Comparison of the possible standard compounds for the calibration. The data given in percent mean the largest ratio of the concentration of H_2A species in the solutions to be titrated. The points of the aspects are within a 1–5 range in which 5 is the best value so the largest total point corresponds to the most appropriate compound.

data and aspects	KH-phtalate	oxalic acid	malonic acid	succinic acid

data files
(without the extension `.tid`)
	`kh1-13e`
	`kh1-13ph`
		`ox1-13e`
		`ox1-13ph`
		`oy1-13e`
		`oy1-13ph`
			`ma1-13e`
			`ma1-13ph`
				`su1-13e`
				`su1-13ph`

lg K_1	4.7	3.6	5.1	5.2
lg K_2	2.7	1.1	2.6	4.0
max. c_{H_2A}/T_A at T_H=0.2 M	8 %	42 %	85 %	97 %
max. c_{H_2A}/T_A at T_H=0.02 M	8 %	10 %	61 %	90 %
1. solubility	5	5	5	5
2. quantitatively weightable	5	5	5	5
3. the protonation processes are inside the Nernstian range	5	2	5	5
4. lg K_2 can accurately be determined	2	3	5	5
5. the protonation processes are not overlapped	3	4	4	2
6. there is no overlap with the protonation of HCO_3^-	4	5	3	3
Total point:	24	24	27	25

Another important experience is that the carbonate content must always be fitted, even if the level of the contamination is less than 0.1 %! Fixed 0.0 M value of carbonate concentration always resulted wrong slope and wrong ionic product of water during the calculations. This phenomenon can be understood by the fact that even very little carbonate concentration changes the shape of the strong acid – strong base titration curves significantly. The hydrogen ion concentration is very low around the equivalence point thus small amount of carbonate will be able to form a buffer system according to the Henderson-Hasselbach equation, and it can be indicated by the orthogonal regression.

4.6 How to Choose a Standard Compound for the Calibration?

In traditional calibration methods (such as Gran's method [1]), KH-phtalate is used almost exclusively as the calibration standard compound. In this practice, the only point considered is that the calibration compound must be suitable to be weighted precisely, the other possible criteria are neglected. Subsection 1.1 has already detailed what problems arose with KH-phtalate. Indeed, the necessity of simplified evaluation procedures in the pre-computer era led to the fact that no other compound is used.

By using pHCali, there are no necessary restrictions. Compounds having more complicated protonation processes can also be used as calibration material, so the authors examined more compounds, as applicable calibration materials. The aspects of the selection and the comparison of the evaluation are summarized in Table 4.1. The four rows following the header row and the names of the data files, show the values needed to apply the aspects. The lower part of the table contains six criteria and the points gathered by each compound. The interpretation of the points are given in the caption of the table. The order of the aspects

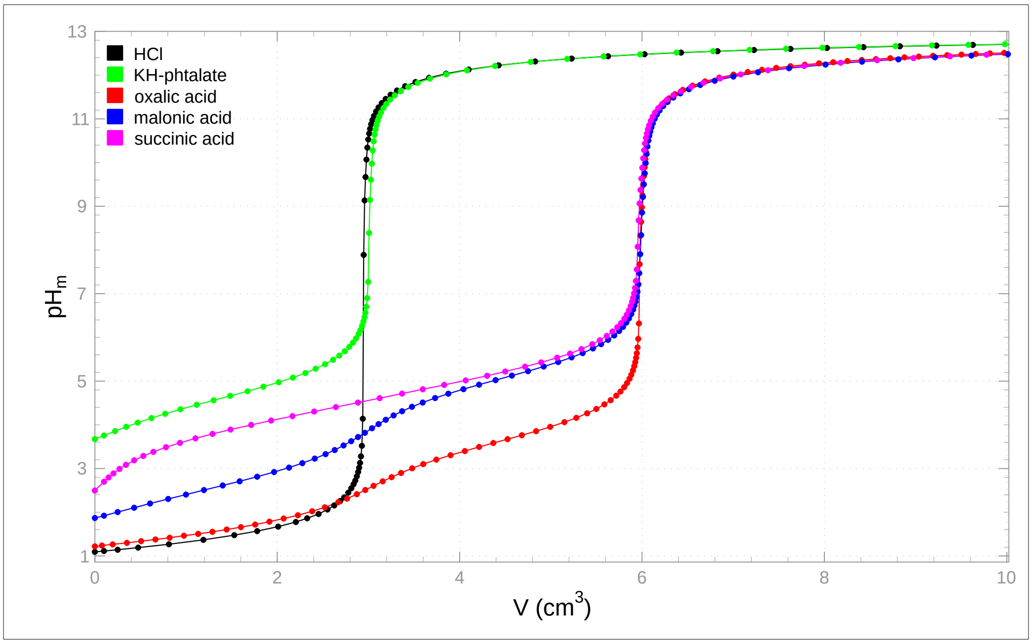

Figure 4.3: Titration of 6.035 cm^3 ~0.1 M acid solutions with ~0.2 M KOH solution.

represents their order of importance, too.

- The first two aspects, the solubility and the capability to be weighted precisely are obligatory. If a compound got less than five points for any of these criteria then it was not suitable for calibration. The authors examined more compounds those listed in the table but those which did not fulfill the above mentioned conditions are not discussed here.

  Four compounds have remained after the first selection. Their typical titration curves are shown in Figure 4.3 together with a typical strong acid – strong base titration curve. With the help of the figure, the points given for the further aspects can be understood more easily.

- The importance of the third aspect is that the too low or too high value of a stability constant must be determined together with the J_H (or J_{OH}) from the same sections of the titration curves. It certainly leads to (otherwise avoidable) correlations. If the calibration only covers the Nernstian range, the protonation processes in the J_H- (or J_{OH}-) influenced range will be disturbing but the appropriate cumulative formation constants cannot be determined quantitatively.

- The fourth aspect applies a general principle, i.e. the stability constant of a species can only be determined quantitatively if the concentration of the species is at least 20 % of the total anion concentration in one or more points of the titration. From this point of view, the KH-phtalate is not a suitable calibration compound. The H_2A form is present in 8 % or less which is highly disturbing but this value is too low for precise determination of β_2^A.[4] This is one reason why the success of the fitting is so sensitive to the initial concentration of the strong base if the `k1-13e.tid` file is used (*see* the appropriate part of Section 4.1). By running the supplied data files, the user can try that the sensitiveness is not experienced that much using the other calibration materials.

- The importance of the fifth and sixth aspects is that the smaller the overlap of the protonation processes the smaller the correlation between the corresponding cumulative stability constants is.

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[4] Experienced users know that the reason of the 8% is that the weighting did not happen in the form of H_2A. Phtalic acid is poorly soluble in water, precluding it as a calibration material.

It can be stated on the basis of the table and the figure that malonic acid seems to be a more suitable calibration compound if either the sum of the scores is viewed or by ranking the compounds according to the order of their first-non maximal score (the later a compound gets non-maximal score for an aspect the better position is achieved). The table certainly contains the subjective opinion of the authors too, but it is definitely informative for the user either if (s)he is looking for a calibration material or (s)he is searching a new compound.

This book shows the usage of *p*HCali through titrations based on KH-phtalate since this compound is the most known. During the installation, the files belonging to the other possible calibration materials (given in Table 4.1) are also installed on the user's computer, so they can be studied, as well. These files can be interpreted in the same way as `kh1-13e.tid` and `kh1-13ph.tid` detailed previously. The only exceptions are the files `oy1-13e.tid` and `oy1-13ph.tid`. These are created to demonstrate how can the oxalic acid be treated as a monoprotic acid by excluding the points influenced by the second protonation process. The denoting convention in these files: the values of the relative weighting factors are 1.0 for each point, but for the points outside the Nernstian range, this value is given in `1.0e-00` while for the ones within the Nernstian range the string is `1.0e+00`.

4.7 Signs Suggesting the Existence of Experimental or Calculation Problems

The practical knowledge accumulated during the evaluation of the measurements detailed in the introduction of this chapter can be summarized in one simple rule. Any fitting or experimental problem significantly modifies the fitted value of the negative logarithm of the ion-product constant of water (pK_w) and/or the slope of the Nernst equation (m_E or m_p). By checking these two values, the user can easily verify the goodness of the fitting, therefore, these values are displayed in the work-window of the program. Any other parameter value or statistical number may suggest some information for the user even in a very detailed form (see the `phcali.odr` file in Section 2.1) but these pieces of information did not prove to be always valid according to the experience obtained so far.

4.8 Extending of the *p*H-Range to be Calibrated: J_H and J_{OH} or interpolation should be used?

*p*HCali offers two methods to extend the calibration to the non-Nernstian ranges: *(1)* fitting J_H and J_{OH} (or J^p_H and J^p_{OH}) defined in equation (A.9) (or (A.12)) or *(2)* the interpolation. In practice, almost exclusively the first method is used presently but the theoretical foundations of this method have not been elaborated for the glass electrode (*see* [2]). It has been pointed by the use *p*HCali that systematic errors can certainly be committed if J_H and/or J_{OH} is fitted. These risks are detailed in the following.

The final result of the reference example is shown in Figure 2.7 if the calibration was carried out within the Nernstian range. The lower right part of the figure shows the first sign of the applicability of J_{OH}. If equation (A.9) were applicable then the deviations in the potentials of both titration curves should be the same in the non-Nernstian range at the basic end of the curves. It is obviously not the case in the figure, and the difference between the deviations is much larger than the experimental uncertainty of the potential.

The same phenomenon can be experienced if the user evaluates the titrations with oxalic acid, malonic acid or succinic acid instead of the KH-phtalate titration.[5] The oxalic acid and malonic acid titrations also show that such differences do not exist in acidic medium. The

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[5] The user can check it by using the installed `ox1-13e.tid`, `ma1-13e.tid` and `su1-13e.tid` files.

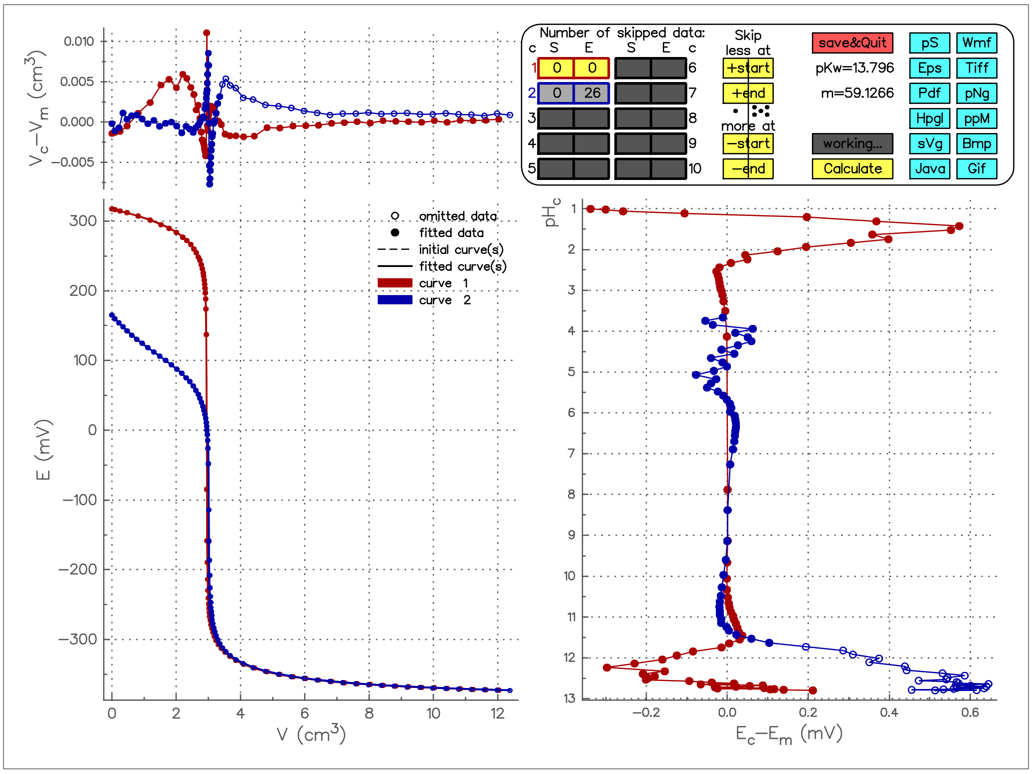

pKw=13.796
m=59.1266

Figure 4.4: The work-window of using the `kh113ej1.tid` file.

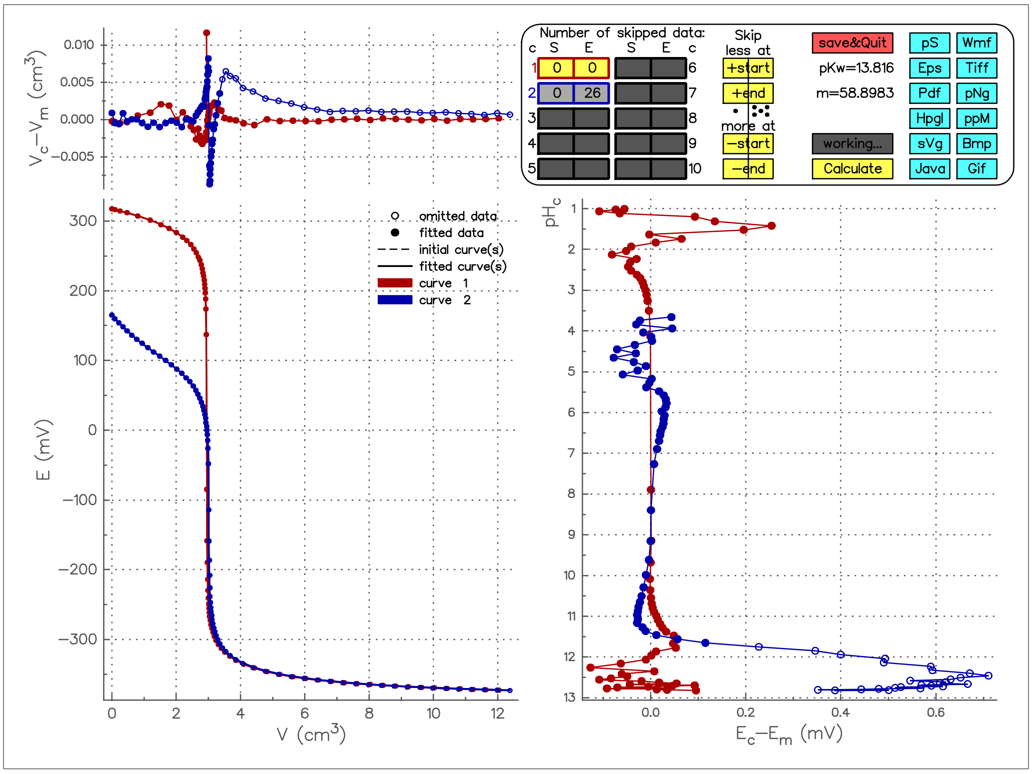
deviations from the Nernstian behaviour are the same for both the strong acid – strong base and the weak acid – strong base titrations as well.

The different quality and quantity of the ionic strength determining ions can explain this behavior. The twice protonated anions of the weak acids do not have charge thus the ionic strength is determined by the KCl in the acidic part of all titration curves. In basic medium, however, this fact is not valid. If strong acid is titrated then the ionic strength is determined by both the KCl and the excess of KOH. In case of weak acid, the concentration of its completely deprotonated anion is also significant. This anion significantly contributes to the ionic strength with its two negative charges. It follows that equation (A.9) cannot be generally valid but it may still be applied if the ionic strength is constant and the ionic strength setting salt does not change during titrations. This limited validity must be studied next.

It is generally true in an equilibrium system that the ionic strength setting salt and the value of the ionic strength are the same in the system to be investigated as they were during the strong acid – strong base titration of the calibration. On the basis of this fact, it can be said that J_H and J_{OH} may be fitted, but the non-Nernstian points at the basic end of the weak acid – strong base titration must be omitted from the calibration. In case of the reference example, the results of the fitting of J_H and J_{OH} are shown on figures 4.4 and 4.5.

The first figure belongs to a two step fitting. At first, only the parameters influencing the Nernstian range were fitted. In the second step, the previously determined values were fixed, all the points of the strong acid – strong base titration curve were included and only J_H and J_{OH} were fitted. This stage can be found in the `kh113ej1.tid` file. In case of the second figure, all parameters were fitted together in the second step. This stage is stored in the `kh113ej2.tid` file.

It is obvious from Figure 4.4 that J_H and J_{OH} cannot describe the deviation from the Nernstian behaviour.There are still significant and systematic deviations on the strong acid – strong base titration curve. In Figure 4.5, this deviation is closer to the experimental uncertainty



pKw=13.816

m=58.8983

Figure 4.5: The work-window of using the `kh113ej2.tid` file.

but the slope has changed significantly which means that J_H and m_E are in unacceptable correlation with each other.

If J_H and/or J_{OH} is fitted, the user would certainly expect that the $|J_H \cdot [H^+]|$ and $\left|J_{OH} \cdot \frac{K_w}{[H^+]}\right|$ expressions do not influence the Nernstian range. It can be checked very simple. The **kh1-13e.crv** file contains the calculated final curves of the reference example (*see* Figure 2.7). It can be seen from the 7th and 8th columns of the file that the range in which the differences of the measured and calculated potentials are smaller than the experimental uncertainty (i.e. 0.1 mV) is $2.2<p[H]<11.6$. It follows that J_H and J_{OH} do not influence the Nernstian range only if the relationships $|J_H \cdot [H^+]|<0.1$ mV and $\left|J_{OH} \cdot \frac{K_w}{[H^+]}\right|<0.1$ mV are valid. If the `kh113ej1.tid` input file is used then J_H=–50.7 mV/M and J_{OH}=26.0 mV/M, and the above mentioned relations are valid only within the $2.7<p[H]<11.4$ range. Even if the other parameters are fixed, the fitting of J_H and J_{OH} unnecessarily constricts the availability of the Nernst equation! This effect can significantly affect the results of $p[H]$ calculations (at the edges of the Nernstian range) causing a shift of several hundredth pH units! In case of the `kh113ej2.tid` file, similar calculations lead to the result that the valid range of the Nernst equation decreased to $2.6<p[H]<11.5$, so the effect is the same: *The fitting of* J_H *and* J_{OH} *decreases the precision of the calibration instead of improving it!*

These considerations are based on the experimental data measured by the authors with their electrodes, but it is enough to warn the user to check the validity of equation (A.9) for the used instrument before applying J_H and J_{OH}.

As an alternative extension of the calibration, *pHCali* offers an interpolation method for the calculation of $p[H]$ values in the non-Nernstian ranges to eliminate the above problems with J_H and J_{OH}. This method has already been detailed in Subsection 2.4.3. It is very important to emphasize that this method can only be successfully used if two conditions are true:

1. The value of the ionic strength and the salt used for setting it in the strong acid – strong

base titration curve must practically be the same as those in the system to be investigated.

2. The deviation from the Nernst equation in the non-Nernstian ranges are reproducible.

APPENDIX

MATHEMATICAL DESCRIPTION OF TITRATION CURVES

During the calibration, the experimental data of strong acid – strong base and weak acid – strong base titration curves are being evaluated. For this procedure, the calculated analogue data must be created by suitably changing the parameters of the mathematical equations. Ideally, the goal is to get smaller differences between the experimental and calculated data than the experimental uncertainty. The required equations are derived within this appendix in detail.

The equations describing the strong acid – strong base and weak acid – strong base titrations can be treated similarly as described below (on the basis of [15]).

A.1 Description of the Equilibrium State at any Point of Titration

During the titration, only those species must be taken into account which can be built from the components of the hydrogen ion, the anion of the weak acid and/or the carbonate ion. The following species[1] (and their cumulative formation constants) must be taken into account in every titration point:

$$H^+ + OH^- \rightleftharpoons H_2O \qquad K_w = [H^+] \cdot [OH^-] \tag{A.1a}$$

$$i\,H^+ + A^{q-} \rightleftharpoons H_iA^{(q-i)-} \qquad \beta_i^A = \frac{[H_iA^{(q-i)-}]}{[H^+]^i \cdot [A^{q-}]} \quad (i = 1 \ldots n) \quad \text{and} \tag{A.1b}$$

$$j\,H^+ + CO_3^{2-} \rightleftharpoons H_jCO_3^{(2-j)-} \qquad \beta_j^C = \frac{[H_jCO_3^{(2-j)-}]}{[H^+]^j \cdot [CO_3^{2-}]} \quad (j = 1 \ldots 2), \tag{A.1c}$$

where

$[X]$ is the equilibrium concentration of X species,
H^+ is the hydrogen ion,
OH^- is the hydroxide ion,
K_w is the ion-product constant of water defined with concentrations (its negative logarithm (pK_w) is used more frequently),
q is the charge number of the completely deprotonated anion of the weak acid,
A^{q-} is the completely deprotonated anion of the weak acid,
$H_iA^{(q-i)-}$ is the i times protonated form of the anion of the weak acid,
n is the number of protonation steps concerning the anion of the weak acid,[2]
β_i^A is the cumulative formation constant of the i times protonated anion of the weak acid defined by concentrations,
CO_3^{2-} is the carbonate ion,

---

[1] For the sake of simplicity, hydrogen ion will be written everywhere even where hydroxonium ion (H_3O^+) should be written.

[2] Just for the sake of unambiguity: n does not necessarily equals to q, e.g. q=1 and n=2 for glycinate.

$H_jCO_3^{(2-j)-}$ is the hydrogen carbonate ion (j=1) or the carbonic acid (j=2) and

β_j^C is the cumulative formation constant (defined by concentrations) of the hydrogen carbonate ion (j=1) or the carbonic acid (j=2).

In the given titration point, the equilibrium concentrations of all species can be expressed according to the equations (A.1) if the equilibrium concentrations of the components ($[H^+]$, $[A^{q-}]$, $[CO_3^{2-}]$) and the formation constants are known:

$$[OH^-] = K_w \cdot [H^+]^{-1} \tag{A.2a}$$

$$[H_iA^{(q-i)-}] = \beta_i^A \cdot [H^+]^i \cdot [A^{q-}] \quad (i = 1 \ldots n) \qquad \text{and} \tag{A.2b}$$

$$[H_jCO_3^{(2-j)-}] = \beta_j^C \cdot [H^+]^j \cdot [CO_3^{2-}] \quad (j = 1 \ldots 2). \tag{A.2c}$$

The total concentrations of the components in the titration point corresponding to V_m *(1)* can be given with the experimental volumes and the analytical concentrations and *(2)* can also be expressed using the equilibrium concentrations:

$$T_H = \frac{(r \cdot c_a + c_s) \cdot V_0 - c_b \cdot V_m}{V_0 + V_m} = \sum_{i=1}^{n} i \cdot [H_iA^{(q-i)-}] + \sum_{j=1}^{2} j \cdot [H_jCO_3^{(2-j)-}] + [H^+] - [OH^-] \tag{A.3a}$$

$$T_A = \frac{c_a \cdot V_0}{V_0 + V_m} = [A^{q-}] + \sum_{i=1}^{n} [H_iA^{(q-i)-}] \qquad \text{and} \tag{A.3b}$$

$$T_C = \frac{c_c \cdot V_m}{V_0 + V_m} = [CO_3^{2-}] + \sum_{j=1}^{2} [H_jCO_3^{(2-j)-}], \tag{A.3c}$$

where

T_H is the total concentration of the hydrogen ion,
T_A is the total concentration of the anion of the weak acid,
T_C is the total concentration of the carbonate ion,
V_0 is the initial volume of the solution to be titrated,
V_m is the total volume of the titrant base added at a given titration point,
c_b is the analytical concentration of hydroxide ion in the titrant base,
c_c is the analytical concentration of carbonate ion in the titrant base,
c_a is the analytical concentration of weak acid in the solution to be titrated,
c_s is the analytical concentration of *additional* strong acid in the solution to be titrated[3] and
r is the protonation degree of the weighted form of weak acid.[4]

---

[3] Additional strong acid means that this amount of hydrogen ion *was not* originally connected to the weighted weak acid, it was added into the initial solution indepentently.

[4] It means, that the anion of the weak acid was weighted in $H_rA^{(q-r)-}$ form, e.g. in case of KH-phtalate q=2 but r=1.

The equilibrium concentrations from equations (A.2) can be substituted into equations (A.3), and both $[A^{q-}]$-t and $[CO_3^{2-}]$-t are set off then the

$$T_H = \sum_{i=1}^{n} i \cdot \beta_i^A \cdot [H^+]^i \cdot [A^{q-}] + \sum_{j=1}^{2} j \cdot \beta_j^C \cdot [H^+]^j \cdot [CO_3^{2-}] + [H^+] - K_w \cdot [H^+]^{-1} \tag{A.4a}$$

$$T_A = [A^{q-}] \cdot \left(1 + \sum_{i=1}^{n} \beta_i^A \cdot [H^+]^i \right) \tag{A.4b}$$

$$T_C = [CO_3^{2-}] \cdot \left(1 + \sum_{j=1}^{2} \beta_j^C \cdot [H^+]^j \right) \tag{A.4c}$$

equations will be the result. They contain three unknown quantities (the equilibrium concentrations of the three components) if the total concentrations and the cumulative formation constants are known. The values of $[H^+]$, $[A^{q-}]$ and $[CO_3^{2-}]$ can be determined from equations (A.4) with appropriate numerical methods, and the equilibrium concentration of any species can be calculated using equations (A.2).

A.2 Calculation of Hydrogen Ion Concentration at a Point of Titration Curve

Rearranging equation (A.4b) for $[A^{q-}]$ and equation (A.4c) for $[CO_3^{2-}]$, substituting these values into equation (A.4a), transforming the right side of the resulted equation to zero and multiplying the rearranged equation by $[H^+]$, the

$$T_A \cdot \frac{\sum_{i=1}^{n} i \cdot \beta_i^A \cdot [H^+]^{i+1}}{1 + \sum_{i=1}^{n} \beta_i^A \cdot [H^+]^i} + T_C \cdot \frac{\sum_{j=1}^{2} j \cdot \beta_j^C \cdot [H^+]^{j+1}}{1 + \sum_{j=1}^{2} \beta_j^C \cdot [H^+]^j} + [H^+]^2 - T_H \cdot [H^+] - K_w = 0 \tag{A.5}$$

equation will be the result. If the total concentrations are substituted with the experimental volumes and the analytical concentrations from equations (A.3) the equation (A.5) will take its final form:

$$\begin{aligned} 0 \; = & \frac{c_a \cdot V_0}{V_0 + V_m} \cdot \frac{\sum_{i=1}^{n} i \cdot \beta_i^A \cdot [H^+]^{i+1}}{1 + \sum_{i=1}^{n} \beta_i^A \cdot [H^+]^i} + \frac{c_c \cdot V_m}{V_0 + V_m} \cdot \frac{\sum_{j=1}^{2} j \cdot \beta_j^C \cdot [H^+]^{j+1}}{1 + \sum_{j=1}^{2} \beta_j^C \cdot [H^+]^j} + \\ & [H^+]^2 - \frac{(r \cdot c_a + c_s) \cdot V_0 - c_b \cdot V_m}{V_0 + V_m} \cdot [H^+] - K_w \, . \end{aligned} \tag{A.6}$$

Equation (A.6) is an implicite equation giving the exact relation between the volume (V_m) and the concentration of the hydrogen ion ($[H^+]$) at a point of the titration. If the other parameters (β_i^A-s, β_j^C-s, K_w, V_0, c_a, c_s, c_b and c_c) are known then the $[H^+]$ can be calculated from the value of the volume.

From equation (A.6), the hydrogen ion concentration cannot be expressed in an explicit form by any rearrangement, therefore numerical methods must be used to solve the equation. It can be proved quite easily that the equation has one and only one positive solution for $[H^+]$ at a given value of V_m. It can be determined with the help of either the bisection or the modified secant method [16] with arbitrary precision.

A.3 Calculation of a Point of the Titration Curve

A titration curve means measured potentials or measured pH values as the function of the volume of the titrant ($E_m - V_m$ or $pH_m - V_m$). The potentials or pH values of a calculated titration curve are computed from the experimentally determined volumes ($E_c - V_m$) or $pH_c - V_m$).

A.3.1 Various Definitions of *p*H and Potential

The definition of pH has been given by Sørensen at the beginning of the 20th century as the negative logarithm of the activity of the hydrogen ion. The analytical methods (like pH-metry), however, aim to determine concentrations, thus more interpretations of pH have been used in practice since the original definition was given. These interpretations are more widely used than the original one, and unfortunately, they are not equivalent to each other. Like pH, potential also have more interpretations. This situation causes several problems nowadays, thus the following notations are introduced in order to avoid misunderstanding:

pH_a stands for the negative logarithm of *the activity* of the hydrogen ion ($pH_a{=}-\lg a_{H^+}$).

p[H] stands for the negative logarithm of the *concentration* of the hydrogen ion ($p[H]{=}-\lg[H^+]$).

pH_m stands for the *measured value* of pH, i.e. this value is displayed and/or stored by the instrument.

pH_c denotes the *calculated* pH value which can be determined from the volume and other parameters of the titration curve. In others words, it is the calculated analogue of pH_m.[5]

pH means the general use of the concept, e.g., in words like pH-metry, pH-sensitive, etc.

E_m stands for the *measured value* of potential, i.e. this value is displayed and/or stored by the instrument.

E_c denotes the *calculated value of the potential* which can be determined from the volume and other parameters of the titration curve. In others words, it is the calculated analogue of E_m.

A.3.2 Calculation of the Potential

The theoretical electrode potential (E_t) from the Nernst equation can be given with the

$$E_t = E^{\ominus} + \frac{\ln 10 \cdot R \cdot T}{z \cdot F} \cdot \lg a_{H^+} \tag{A.7}$$

equation where

$E^{\ominus}$ is the standard electrode potential of the hydrogen electrode, its value is 0 V by definition,

R is the molar gas constant,

T is the absolute temperature,

z is the charge number of hydrogen ion, i.e. its value is +1,

F is the Faraday constant, its value is 96485,31 C/mol and

a_{H^+} is the activity of the hydrogen ion. Its defining equation is $a_{H^+}{=}\gamma_\pm \cdot [H^+]$, where $\gamma_\pm$ is the mean activity coefficient.

In practice, the calculated potentials are treated on the analogy of equation (A.7) with the

$$E_c = E' + m_E \cdot \lg[H^+] \quad \left(= E_c^N\right) \tag{A.8}$$

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[5] pH_c does not equal to p[H] as (A.11) and (A.12) equations will show below.

equation where E' and m_E are empirical constants. They can be considered as formal standard potential and the actual slope, respectively. Where it is needed, the notation E_c^N emphasizes that the calculation was carried out using the Nernst equation *only* without the empirical extension terms (*see* equation (A.9) below).

E' includes the reference electrode potential, the diffusion potential and the mean activity coefficient of the investigated solution, so their values should be kept to be constant during the measurement. The constant values can generally be achieved by choosing an appropriate reference electrode and by setting up constant ionic strength with a suitable salt. On the other hand, m_E—which can be calculated from the experimental data—shows how ideal is the used hydrogen ion selective electrode. The more the relation $m_E=\frac{\ln 10 \cdot R \cdot T}{z \cdot F}$ is true the more the Nernstian characteristics of the electrode is valid.

In practice, E' and m_E are strictly constant only within a specific *p*H range, and E_m and $\lg [H^+]$ are linearly proportional only in this range. The deviation from this behavior is taken into account according to [2], even nowadays. This work suggests that equation (A.8) is to be extended with additive terms:

$$E_c = E' + m_E \cdot \lg [H^+] + J_H \cdot [H^+] + J_{OH} \cdot \frac{K_w}{[H^+]}, \tag{A.9}$$

where J_H and J_{OH} are empirical constants, although their values can be approximated with theoretical calculations [2].

Briefly, every point of the titration curve ($E_c - V_m$) can be calculated on the basis of equations (A.6) and (A.9): $E_c=f(\text{parameters}, V_m)$ where the parameters can be β_i^A-s, β_j^C-s, K_w, V_0, c_a, c_s, c_b, c_c, E', m_E, J_H ans J_{OH}.

A.3.3 Calculation of *p*H

*p*H-metric instruments usually give a *p*H value and not the directly measured potential. This pH_m is calculated from the measured potential according to a previous calibration (based on one or two buffer solutions), and this value is stored or displayed. No matter how the calibration happens the instrument calculates pH_m according to a

$$pH_m = a_1 + a_2 \cdot E_m \tag{A.10}$$

type equation where a_1 and a_2 are constants determined and stored by the instrument during the previous calibration. In ideal case, $a_2=-\frac{z \cdot F}{\ln 10 \cdot R \cdot T}$.[6]

The value of pH_c can be calculated on the analogy of equation (A.10) by substituting equation (A.8):

$$pH_c = a_1 + a_2 \cdot E_c = (a_1 + a_2 \cdot E') + (a_2 \cdot m_E) \cdot \lg [H^+] = I_d + m_p \cdot \lg [H^+] \quad \left(= pH_c^N\right), \tag{A.11}$$

where the value of m_p is -1 in case of ideal Nernstian behavior and I_d is an empirical constant. The first one can be considered as the actual relative slope and the last one is called Irving factor in the literature [17].[7] These parameters can also be calculated if potential was measured: $I_d=a_1 + a_2 \cdot E'$ and $m_p=a_2 \cdot m_E$. Where it is necessary, the notation pH_c^N of the calculated *p*H emphasizes that the calculation was carried out on the basis of the Nernst equation *only* without the extension terms (*see* equation (A.12) below).

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[6] The values of a_1 and a_2 can easily be determined if both pH_m and E_m are stored.

[7] It must be mentioned that the derivation of the Irving factor given in [17] supposes that the behavior of the electrode is ideally Nernstian (m_p=−1) and the derivation takes only the diffusion potential into account. It has to be noted, however, that the value of I_d is also influenced by the value of $\gamma_{\pm}$.

In case of pH measurement, the pH range to be studied can be extended too, on the analogy of equation (A.9):

$$pH_c = I_d + m_p \cdot \lg [H^+] + J_H^p \cdot [H^+] + J_{OH}^p \cdot \frac{K_w}{[H^+]}, \tag{A.12}$$

where J_H^p and J_{OH}^p are empirical constants. It can easily be proved that $J_H^p = a_2 \cdot J_H$ and $J_{OH}^p = a_2 \cdot J_{OH}$.

The calculation of pH can be summarized briefly: on the basis of equations (A.6) and (A.12), an arbitrary point of the calculated titration curve ($pH_c - V_m$) can be determined using the function $pH_c = f(\text{parameters}, V_m)$ where the parameters can be β_i^A-s, β_j^C-s, K_w, V_0, c_a, c_s, c_b, c_c, I_d, m_p, J_H^p and J_{OH}^p.

A.4 Calculation of Parameter Values

The accurate calibration of a pH-metric instrument can be divided into two parts. *(1)* At first, the accurate values of the calibration parameters have to be determined and then *(2)* the ($p[H] - V_m$) data can be calculated using the determined parameter values for those titration curves which belong to the equilibrium system to be investigated and not to the calibration. These calculated points can serve as input data for equilibrium data evaluation programs (e.g. [18]).

On the basis of the above mentioned calibration parameters, any titration curve can be calculated. The necessary parameters can be calculated by the minimization of the sum of squares functions defined by the

$$S(\beta_i^A, \beta_j^C, K_w, V_0, c_a, c_s, c_b, c_c, E', m_E, J_H, J_{OH}) = \sum_{k=1}^{p} w_k \cdot (E_{m,k} - E_{c,k})^2 \quad \text{or} \tag{A.13a}$$

$$S(\beta_i^A, \beta_j^C, K_w, V_0, c_a, c_s, c_b, c_c, I_d, m_p, J_H^p, J_{OH}^p) = \sum_{k=1}^{p} w_k \cdot (pH_{m,k} - pH_{c,k})^2 \tag{A.13b}$$

$$(i = 1 \ldots n,\ j = 1 \ldots 2)$$

equations. In these equations, p stands for the total number of titration points in all titration curves used for the calibration, w_k is the weighting factor of the kth measured point (E_m or pH_m) and the index k generally points to the kth titration point.

The sum of squares function defined by equations (A.13) can take into account only the experimental errors of the measured potential or pH, not those of the volume. In order to take also the uncertainty of the volume into account, the definition of the sum of squares function has to be modified according to the following equations:

$$S(\beta_i^A, \beta_j^C, K_w, V_0, c_a, c_s, c_b, c_c, V_{c,l}, E', m_E, J_H, J_{OH}) =$$

$$\sum_{k=1}^{p} \left(w_k^y \cdot (E_{m,k} - E_{c,k})^2 + w_k^x \cdot (V_{m,k} - V_{c,k})^2 \right) \quad \text{or} \tag{A.14a}$$

$$S(\beta_i^A, \beta_j^C, K_w, V_0, c_a, c_s, c_b, c_c, V_{c,l}, I_d, m_p, J_H^p, J_{OH}^p) =$$

$$\sum_{k=1}^{p} \left(w_k^y \cdot (pH_{m,k} - pH_{c,k})^2 + w_k^x \cdot (V_{m,k} - V_{c,k})^2 \right) \tag{A.14b}$$

$$(i = 1 \ldots n,\ j = 1 \ldots 2,\ l = 1 \ldots p),$$

where V_c is the calculated volume, w^x is the weighting factor of the volume and w^y is the weighting factor of the potential or pH. Equations (A.14) make it possible to carry out the calculation by orthogonal regression.

In usual calibration procedures, the values of β_j^C-s, V_0, c_a and probably those of β_i^A-s are well known, so the aim is to determine the values of K_w, c_s, c_b, c_c (and perhaps those of β_i^A-s). Besides them, the values of E', m_E, J_H and J_{OH} can be determined in case of potential measurement or those of I_d, m_p, J_H^p and J_{OH}^p in case of pH measurement. If these parameters are accurately known, an arbitrary E_m or pH_m value can be transformed into a p[H] value for which the equations describing chemical equilibria can be applied.

Notations and Definitions

The number in parentheses gives the page number where the most important usage of the notation or definition can be found or there is a more detailed explanation on the referred page.

Notations:

a_1 …… (page 71)
A constant used by the pH-metric instrument to calculate the displayed pH from the measured potential.

a_2 …… (page 71)
A constant used by the pH-metric instrument to calculate the displayed pH from the measured potential.

a_{H^+} …… (page 70)
The activity of the hydrogen ion.

A^{q-} …… (page 67)
The completely deprotonated anion of the weak acid.

β_i^A …… (page 67)
The cumulative formation constant of the i times protonated anion of the weak acid defined by concentrations.

β_j^C …… (page 68)
The cumulative formation constant (defined by concentrations) of the hydrogen carbonate ion (j=1) or the carbonic acid (j=2).

c_a …… (page 68)
The analytical concentration of weak acid in the solution to be titrated.

c_b …… (page 68)
The analytical concentration of hydroxid ion in the titrant base.

c_c …… (page 68)
The analytical concentration of carbonate ion in the titrant base.

CO_3^{2-} …… (page 67)
The carbonate ion.

c_s …… (page 68)
The analytical concentration of additional strong acid in the solution to be titrated.

E' …… (page 71)
Empirical constant (formal standard potential).

$E^{\ominus}$ …… (page 70)
The standard electrode potencial of the hydrogen electrode.

E_c …… (page 70)
The calculated analogue of E_m.

E_c^N …… (page 71)
The calculated analogue of E_m, emphasizing the fact that Nernst-like equation was used for the calculation.

E_m …… (page 70)
The measured value of the potential displayed and/or stored by the instrument.

F …… (page 70)
The Faraday constant.

$\gamma_\pm$ …… (page 70)
The mean activity coefficient.

H^+ …… (page 67)
The hydrogen ion.

$H_iA^{(q-i)-}$ …… (page 67)
The i times protonated form of the anion of the weak acid.

$H_jCO_3^{(2-j)-}$ …… (page 68)
The hydrogen carbonate ion (j=1) or the carbonic acid (j=2).

I_d …… (page 71)
Empirical constant (Irving factor).

J_H …… (page 71)
In case of potential measurement, it is an

empirical constant for taking into account the deviation from the Nernstian equation in the acidic range ($p\mathrm{H}\lesssim 2$).

J_{OH} .... (page 71)
In case of potential measurement, it is an empirical constant for taking into account the deviation from the Nernstian equation in the basic range ($p\mathrm{H}\gtrsim 12$).

$\mathrm{J}^{\mathrm{p}}_{\mathrm{H}}$ .... (page 72)
In case of pH measurement, it is an empirical constant for taking into account the deviation from the Nernstian equation in the acidic range ($p\mathrm{H}\lesssim 2$).

$\mathrm{J}^{\mathrm{p}}_{\mathrm{OH}}$ .... (page 72)
In case of pH measurement, it is an empirical constant for taking into account the deviation from the Nernstian equation in the basic range ($p\mathrm{H}\gtrsim 12$).

K_w .... (page 67)
The ion-product constant of water defined with concentrations.

m_{E} .... (page 71)
Empirical constant (actual slope of the Nernst-like equation).

m_{p} .... (page 71)
Empirical constant (actual relative slope of the Nernst-like equation).

n .... (page 67)
The number of protonation steps concerning the anion of the weak acid.

OH^- .... (page 67)
The hydroxide ion.

p .... (page 72)
The number of titration points of all titration curves used for the calibration.

$p\mathrm{H}$ .... (page 70)
The general use of the pH-concept.

$p\mathrm{H}_a$ .... (page 70)
The negative logarithm of the *activity* of the hydrogen ion.

$p[\mathrm{H}]$ .... (page 70)
The negative logarithm of the *concentration* of the hydrogen ion.

$p\mathrm{H}_c$ .... (page 70)
The calculated analogue of $p\mathrm{H}_m$.

$p\mathrm{H}_c^{\mathrm{N}}$ .... (page 71)
The calculated analogue of $p\mathrm{H}_m$, emphasizing the fact that Nernst-like equation was used for the calculation.

$p\mathrm{H}_m$ .... (page 70)
The measured pH value displayed and/or stored by the instrument.

pK_w .... (page 67)
Negative logarithm of the ion-product constant of water defined with concentrations.

q .... (page 67)
The charge number of the completely deprotonated anion of the weak acid. Only compounds having really small q can be used for calibration purposes.

R .... (page 70)
The molar gas constant.

r .... (page 68)
The protonation degree of the weighted form of weak acid.

S .... (page 72)
The weighted sum of squares to be minimized.

σ^x .... (page 19)
Experimental uncertainty of the measured volume.

σ^y .... (page 19)
Experimental uncertainty of the measured potential or pH.

T .... (page 70)
The absolute temperature.

T_{A} .... (page 68)
The total concentration of the anion of the weak acid.

T_{C} .... (page 68)
The total concentration of the carbonate ion.

T_{H} .... (page 68)
The total concentration of the hydrogen ion.

V_0 .... (page 68)
The initial volume of the solution to be titrated.

V_c .... (page 72)
The calculated volume.

V_m .... (page 68)
The total volume of the titrant base added at a given titration point.

w .... (page 72)
The weighting factor.

w_R .... (page 21)
The abbreviation of relative weighting factor.

w^x .... (page 72)
The weighting factor of the volume.

w^y .... (page 72)
The weighting factor of the potential or pH.

[X] .... (page 67)
The equilibrium concentration of X species.

z .... (page 70)
The charge number of hydrogen ion.

Definitions:

console mode .... (page 8)
This variant of *p*HCali can be started from character-based windows opened in graphical user interface (i.e. Windows or X-Window).

data file .... (page 8)
See text file.

file-chooser window .... (page 28)
A window for the modification of the basename of the given task (*see* `TASKNAME`)

file .... (page 8)
Whole bulk of data that can be referred together by one name and it is placed in a storage media (usually in a hard drive) of a computer.

image file .... (page 8)
A file including the data of a picture. It can be displayed on the screen and/or can be printed on a printer.

operating panel .... (page 31)
The upper right part of the work-window. It makes possible the inclusion/exclusion of data, as well as, the recalculations with the modifications.

orthogonal distance regression .... (page 8)
Procedures used for parameter estimation usually take into account only the experimental error of the dependent variable and the values of the indpendent variable are considered as exact ones. On the other hand, the orthogonal distance regression is able to take into account the errors of both variables if the experimental uncertainty is known for both variables.

parameter-modifier window .... (page 28)
A window for modifying the initial values and fitting state of the parameters.

`PROGNAME` .... (page 39)
The name of the executables to be used.

relative weighting factor .... (page 21)
It determines the contribution of the specific titration point.

RGB-color .... (page 23)
It is a method for defining colors. The method resolves each color to its three components (red, green and blue ones) and the intensities of these pure colors should be given.

`TASKNAME` .... (page 15)
It is the base name of the actual task chosen by the user.

text file .... (page 8)
This type of file includes (almost) only displayable characters found on the keyboard, i.e. letters, numbers and punctuation marks. Text files are generally used for storing numbers or simple text. They can be changed by editors (e.g. `edit.com` under DOS, Notepad under Windows and `gvim` under Linux). *Word processors, like Word, should not be used to change them.*

text mode .... (page 8)
This variant of *p*HCali can be used on character-based screen so it can be started from pure DOS.

window mode .... (page 8)
This variant of *p*HCali can be started on a graphical user interface (i.e. Windows or X-Window).

work-window .... (page 29)
A window for adjusting the state of measured data (omitted/fitted) and carrying out the calculations.

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