

1999/25
copy 2

AGSO

HCh: a software package for geochemical equilibrium modelling. User's Guide

YURI SHVAROV & EVGENIY BASTRAKOV



RECORD 1999/25

Bme comp
1999/25
copy 2



AUSTRALIAN
GEOLOGICAL SURVEY
ORGANISATION

AUSTRALIAN GEOLOGICAL SURVEY ORGANISATION
DEPARTMENT OF INDUSTRY, SCIENCE & RESOURCES

AGSO RECORD 1999/25

HCh: a software package for geochemical equilibrium modelling. User's Guide

YURI SHVAROV¹ & EVGENIY BASTRAKOV²

¹Department of Geology, Moscow State University, Moscow, 119899, Russia

²Minerals Division, Australian Geological Survey Organisation, GPO Box 378, Canberra, ACT 2601
CANBERRA 1999

Department of Industry, Science & Resources

Minister for Industry, Science & Resources: Senator the Hon. Nick Minchin
Parliamentary Secretary: The Hon. Warren Entsch, MP
Secretary: Russell Higgins

Australian Geological Survey Organisation

Executive Director: Neil Williams

© Commonwealth of Australia 1999

This work is copyright. Apart from any fair dealings for the purposes of study, research, criticism, or review, as permitted under the *Copyright Act 1968*, no part may be reproduced by any process without written permission. Copyright is the responsibility of the Executive Director, Australian Geological Survey Organisation. Requests and enquiries should be directed to the Executive Director, Australian Geological Survey Organisation, GPO Box 378, Canberra, ACT 2601.

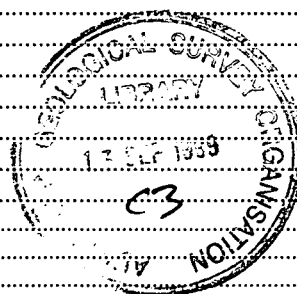
ISSN 1039-0073
ISBN 0 642 39784 8

Bibliographic reference: Shvarov, Yu.V. & Bastrakov, E.N., 1999. HCh: a software package for geochemical equilibrium modelling. User's Guide. Australian Geological Survey Organisation, Record 1999/25.
--

AGSO has tried to make the information in this product as accurate as possible. However, it does not guarantee that the information is totally accurate or complete. Therefore, you should not rely solely on this information when making a commercial decision.

Contents

ACKNOWLEDGEMENTS.....	v
OVERVIEW: GENERAL INFORMATION.....	1
INTRODUCTION.....	1
ABOUT THIS GUIDE.....	2
GUIDE CONVENTIONS.....	2
Keyboard Formats.....	2
Selecting and Choosing.....	2
Case Sensitivity.....	2
INSTALLATION OF THE PACKAGE.....	3
DOS Environment.....	3
Windows Environment.....	3
Windows 3.x.....	3
Windows 9x/NT.....	3
Specific features of work under the Windows NT operating system.....	4
HCh Directory Tree.....	4
Package Components.....	5
Package Upgrading.....	5
CHAPTER 1. THE UNITHERM PROGRAM AND DATABASE.....	6
ABOUT UNITHERM.....	6
Database Components.....	6
Database Capacity.....	6
Default Database.....	6
Database Files.....	7
Naming Conventions.....	8
Standard State Conventions.....	9
Calculation of Gibbs Free Energies.....	9
Water.....	9
Aqueous species.....	9
Basic species.....	9
Complexes.....	10
Pure phases (minerals, non-aqueous liquids and gases).....	11
Calculation of Coefficients of the Debye-Hückel Equation.....	12
WORKING WITH UNITHERM.....	13
To Start UNITHERM.....	13
Basic UNITHERM Commands.....	13
Modified Basic Commands.....	14
UNITHERM Reaction Commands.....	14
Additional UNITHERM Commands.....	15
Starting UNITHERM in a Specific Mode.....	16
Selecting components in the /SCOPY mode.....	16
CHAPTER 2. EQUILIBRIUM MODELLING.....	18
OVERVIEW.....	18
FILES REQUIRED FOR MODELLING.....	18
QUICK START: PREPARATION OF FILES.....	19
WORKING WITH MAIN.....	20
About MAIN.....	20
To start MAIN.....	20
Starting MAIN in a specific mode.....	20
To Quit MAIN.....	20
Creating and Changing Files.....	21
System Menu.....	22
Creating *.ST file.....	22
Viewing *.ST file.....	23
Editing *.ST file.....	23
Exporting *.ST files to ASCII files.....	24
Other operations on *.ST files.....	24



Blank Menu	25
Creating *.BL file	25
Viewing *.BL file	25
Editing *.BL file	26
Exporting *.BL files to ASCII files	26
Other Operations on *.BL files	26
Input Menu	27
Creating *.IN file	27
Viewing *.IN file	27
Editing *.IN file	27
Importing ASCII files	27
Other operations on *.IN files	28
Control Menu	29
Menu functions	29
Control file conventions	30
Expressions	30
Relations	30
Conditions	30
Operators and functions	31
Variables	31
Creating *.CT file	32
Viewing *.CT file	33
Editing *.CT file	33
Other operations on *.CT files	33
GIBBS Menu	34
Choosing the source file	34
Setting GIBBS options	34
Calling GIBBS	34
Result Menu	35
ASCII files	35
Binary file	35
Single points mode	35
Cross Sections mode	36
Options Menu	37
Change Directory Request switch	37
Shown Files switch	37
Delay Time switches	37
Set Paths switches	37
Screen Colours switches	38
Set Defaults switch	38
Saving settings	38
Restoring settings from file	38
WORKING WITH GIBBS	39
About GIBBS	39
Equilibrium Calculations	39
GIBBS reads Control file	39
GIBBS reads Input file	39
GIBBS reads Blank file	40
Tables of Results	41
Standard table of results	41
Tables extracted from binary files	43
GIBBS Options	44
REFERENCES	45
EMPLOYED MODELS AND ALGORITHMS	45
EXAMPLE HCH/GIBBS APPLICATIONS	46
Hydrothermal Geochemistry	46
Processing of Experimental Data	46
APPENDICES	47
APPENDIX 1. BRIEF SUMMARY OF HCH SPECIFICATIONS	48
APPENDIX 2. DEFINITION OF SOLID SOLUTION MODELS	50
APPENDIX 3. CALCULATION OF ACTIVITY COEFFICIENTS OF AQUEOUS SPECIES	52
Charged Aqueous Species	52

<i>Neutral Aqueous Species</i>	53
Examples of *.ST file modification	54
APPENDIX 4. EXAMPLES OF CONTROL FILES USAGE	55
<i>EXAMPLE 1: Titration and Mixing Calculations</i>	55
<i>EXAMPLE 2: Modelling of Processes at Steady-State Conditions</i>	56
<i>EXAMPLE 3: Modelling of Progressive Fluid-Rock Interaction by the "Flow-Through" Reactor Technique</i> ..	57
Special syntax of vector variables	58
APPENDIX 5. SUPPLEMENTARY UTILITIES	59
<i>LST2TAB: Conversion of *.LST Files for Export to Microsoft Excel</i>	59
<i>REX.XLS: Importing Results into Microsoft EXCEL</i>	60

Acknowledgements

The authors are grateful to Terry Mernagh, Roger Skirrow, and Greg Cameron for careful reviews and suggestions for improvement of the manuscript.

Overview: General Information

Introduction

The HCh program package was developed by Yu. Shvarov at the Department of Geology of the Moscow State University (Russia). It consists of several compatible programs and a thermodynamic database that provide a powerful tool for modelling of chemical and geochemical processes.

Using this program package you can:

Program	Functions
MAIN and GIBBS	Calculate chemical equilibria in chemical and geochemical systems using the GIBBS program; Define and calculate equilibrium-dynamic models of chemical and geochemical processes.
UNITHERM	Maintain an extensive thermodynamic database for aqueous species, minerals, gases and non-aqueous liquids; Calculate and tabulate thermodynamic properties of database components and chemical reactions over a wide range of T-P conditions.

The equilibrium compositions of multi-phase chemical systems are computed using the free-energy minimisation technique (Shvarov, 1976; 1978; 1981; 1987; 1989).

Model chemical systems can currently incorporate the following phases of constant and variable composition:

- Pure solids (minerals), liquids and gases
- An aqueous solution (including the supercritical aqueous phase)
- A gaseous mixture (ideal mixture of ideal gases)
- Liquid non-aqueous solutions (ideal or NRTL¹ model)
- Solid solutions (ideal multi-site mixing)

The model chemical systems can be either closed or open in respect to perfectly mobile components (Korzhinskii, 1965).

The HCh package was developed to simulate a broad variety of hydrogeochemical and geochemical processes. HCh can handle water-gas-rock interaction, fluid mixing, gas partitioning and boiling calculations. Possible calculations involving an aqueous solution cover the temperature range of 0 – 1000°C and pressure range of 1 – 5000 bar at water densities exceeding 0.35 g/cm³. The allowed salinity range is limited by the applicability of the extended versions of the Debye-Hückel equation.

The HCh package is user-friendly and quite self-explanatory. It can be used as a good starting point for learning computer modelling of geochemical systems. However, a novice user should have a reasonable knowledge of hydrothermal geochemistry and ability to formulate well-defined chemical and geochemical models.

It is recommended that the new users experiment with the provided examples and their own data. A basic knowledge of MS-DOS/Windows personal computers is assumed.

¹ Non-random two-liquid solution model

About This Guide

This manual has been compiled by the package developer (Yu. Shvarov, Moscow State University) and one of the long-term package users (E. Bastrakov, Australian Geological Survey Organisation). It represents the most comprehensive English version of the HCh documentation, providing instructions on the practical package usage and some brief information on the employed algorithms. You can also find additional information in the reference ASCII files (*.TXT and *.REF) located in your HCH and UNITHERM directories.

As the result of the ongoing HCh development this manual may contain minor omissions and undocumented options. Please refer to the WNEW*.TXT files for the most recent information. This manual covers version 3.3 of the HCh package.

Guide Conventions

Keyboard Formats

Key combinations and key sequences appear in this guide in the following formats.

Format	Meaning
KEY1, KEY2	A comma (,) between key names means to press and release the keys one after the other. For example, "press F3, F1" means to press and release the F3 key and then press and release the F1 key.
KEY1+KEY2	A plus sign (+) between key names means to press and hold down the first key while you press the second key. For example, "press CTRL+Q" means to press and hold down the CTRL key and press the Q key, and then release both keys.

Selecting and Choosing

The terms "select" and "choose" have different meanings in this guide. Selecting an item means marking it with the rectangular cursor or highlighting. Selecting alone does not start an action.

You choose an item to carry out an action.

- To select a single item

Use the arrow keys until you place the cursor on the item you want. The item is already highlighted.

- To select or cancel multiple items

Sometimes you need to select multiple items from an offered list.

1. Use the arrow keys to place the cursor on the item you want.
2. Press the SPACE BAR or INSERT key to highlight the item.
3. Use the arrow keys to proceed with further selection, pressing SPACE BAR or INSERT to select each item. Press SPACE BAR or INSERT again to cancel the selection of the item.

- To choose an item

1. Select the item(s).
2. Press ENTER. In menus it is also possible to press the UP or DOWN arrow keys, or simply a highlighted letter (Access key).

Case Sensitivity

Data entry in the HCh package may be case-sensitive. Case sensitivity is noted in the text where applicable.

Installation of the package

DOS Environment

1. Make sure that the computer is free from non-DOS resident programs and viruses.
2. Insert the HCh installation disk in a floppy disk drive.
3. At the command prompt, type the drive letter of the drive you are using, followed by a colon (:).
4. Type "INSTALL", and then press ENTER.
5. Type your password if required, and then press ENTER.
6. Follow the instructions on the screen. The default options are recommended for most users.
7. The message "Working version installed" tells you whether the installation has been completed successfully.
8. Move files UT.BAT and HCH.BAT to a directory mentioned in the PATH command of your AUTOEXEC.BAT file.

Note: By default the installation program activates an anti-virus program AIDSTEST. You can terminate this program by pressing CTRL+BREAK or CTRL+C if you find this virus scan unnecessary. You can also disable AIDSTEST completely during future upgrades of the HCh package. Simply delete the AIDSTEST.EXE file from the installation disk or rename it.

Windows Environment

If you are working in the Windows environment you can complete the installation by using MS-DOS prompt of Windows 3.x/ 9x/NT. You can also complete the installation by using the Windows Run command or using Windows EXPLORER (FILE MANAGER). However, we recommend the first (MS-DOS) option. This will immediately bring you to your ...HCH directory.

Windows 3.x

1. Insert the HCh installation disk in a floppy disk drive.
2. Run MS-DOS prompt (or a DOS shell, *eg*, Norton Commander) and follow the instructions for the DOS environment (see above, steps 3 – 8). Alternatively, choose the Run command from the File menu of Program Manager. Designate the drive letter from which you will be installing HCh, and type "INSTALL" (*eg*, **a:\install**). Click the OK button.
3. Type your password if required, and then press ENTER.
4. Follow the instructions on the screen. The default options are recommended for most users.
5. The message "Working version installed" tells you whether the installation has been completed successfully.
6. The MS-DOS window closes automatically when the installation has completed.
7. Move files UT.BAT and HCH.BAT to a directory mentioned in the PATH command of your AUTOEXEC.BAT file.

Windows 9x/NT

1. Insert the HCh installation disk in a floppy disk drive.
2. Run MS-DOS prompt (or a DOS shell, *eg*, Norton Commander) and follow the instructions for the DOS environment (see above, steps 3 – 8). Alternatively, click the Start button on the Taskbar and choose the Run command. Designate the drive letter from which you will be installing HCh, and type "INSTALL" (*eg*, **a:\install**). Click the OK button.
3. Type your password if required, and then press ENTER.
4. Follow the instructions on the screen. The default options are recommended for most users.
5. The message "Working version installed" tells you whether the installation has been completed successfully.
6. If necessary, click the Close button in the corner of the MS-DOS window.
7. Move files UT.BAT and HCH.BAT to a directory mentioned in the PATH command of your AUTOEXEC.BAT file (Windows 3.x/ 95) or your Environment System Variables (Windows NT).

You can create the HCh program group and program items in a conventional way (see your Windows manual or Help file). A number of icons (UT1.ICO, UT2.ICO and HCH.ICO) are usually provided on the installation disc for further customisation of the HCh program items.

Specific features of work under the Windows NT operating system.

During the installation you might get the message about the “non-standard DOS partition”, referring to the NTFS partition. Just press Y to proceed.

Note: If your computer has multiple operating systems, and you are planning to use HCh under all of them, run the installation program (INSTALL.EXE) from Windows NT only and choose a FAT partition for the HCh package.

If you prefer to work using both the full-screen and window modes, we recommend you always start HCh programs in a *full-screen* mode, or from a DOS prompt or a DOS-Shell program running in a full-screen mode. You can switch between the screen modes using Windows ALT+ENTER shortcut keys *after* starting an HCh program.

If you start an HCh program from a normal window and then change to the full screen, you might face a disruption of the program graphical interface. To fix this problem, follow the suggested sequence of actions:

For	Actions
MS-DOS prompt	<ol style="list-style-type: none"> 1. Quit the program (press F10 for UNITHERM; press Q for MAIN) 2. Minimize the DOS window, and then maximize it. 3. Re-start the program.
Norton Commander (a popular DOS-Shell)	<ol style="list-style-type: none"> 1. Quit the program (press F10 for UNITHERM; press Q for MAIN) 2. Press ALT+F9 (“EGA Lines”) twice. 3. Re-start the program.
Windows NT Explorer	<ol style="list-style-type: none"> 1. Quit the program (press F10 for UNITHERM; press Q for MAIN) 2. Edit the program properties (the Screen Tab; Usage: Full-screen) 3. Re-start the program.

Tip: Generally, we recommend to set the following properties for your HCh sessions:

- To change properties of the HCh programs
1. In My Computer or Windows NT Explorer, click the HCh program whose properties you want to change.
 2. On the File menu, click Properties.

Property Tab	Selected Options		
Program	Command line: include your preferred command line options (see “Starting UNITHERM in a Specific Mode” on page 16) and “Starting MAIN in a Specific Mode” on page 20) Close on exit: ON	Working: preferred working directory	Batch file: NONE
Font	Available types: Bitmap only	Font size: Auto	
Memory	All lists: Auto	Protected Mode: OFF	Uses HMA: ON
Screen	Full-screen: ON		
Misc	All boxes (excluding shortcut keys): OFF	Idle sensitivity: Low	

HCh Directory Tree

After the initial installation your HCh directory tree should look approximately as follows:

[HCH

[EXAMPLES	Example files
[MAIN	Programs MAIN and GIBBS
[UNITHERM	UNITHERM program + database
[UNITHERM.EXT	Auxiliary programs for data fitting (free)
[UTIL	Supplementary items (utilities and program icons)
acknowlg.txt	Acknowledgements
faq.txt	Frequently asked questions
guide*.*	User's guide
licence*.txt	Licence agreement
readme.txt	Installation instructions
wnew*.txt	Latest information in ASCII format
hch.bat	Files for package customisation
ut.bat.	

Files UT.BAT and HCH.BAT are intended for package customisation. If these files are located in a directory mentioned in the PATH command of your AUTOEXEC.BAT file or your Environment System Variables, you will be able to call UNITHERM and MAIN from any of your working directories. Just type "UT" or "HCH" at the DOS prompt, and press ENTER.

Package Components

The installed HCh package consists of two parts:

The UNITHERM program + database (sub-directory UNITHERM).

The programs MAIN and GIBBS (sub-directory MAIN).

Program	Functions
UNITHERM	Thermodynamic database maintenance. Calculation of thermodynamic properties of the database components (aqueous species, minerals, gases and non-aqueous liquids) and chemical reactions.
MAIN	Maintenance and management of files and programs for equilibrium modelling.
GIBBS	Equilibrium calculations on chemical systems.

Note: The auxiliary programs in the optional UNITHERM.EXT directory (currently, UT-RYZ and UT-HEL) are not the part of the commercial HCh package. They are provided for your convenience to facilitate the development of the thermodynamic database for aqueous species. The program documentation is provided in the relevant text files.

Two additional utilities located in the UTIL directory (the program LST2TAB and the spreadsheet REX.XLS) are provided for import of the modelling results into spreadsheet programs. See Appendix 5, "Supplementary Utilities", for details.

Package Upgrading

To upgrade the package, you need to complete the following steps:

1. Copy the updated installation files (normally, HCH.AIN and *.TXT files) to your installation disk.
2. Re-run the installation program and follow the instructions. Choose the "Keep hard disk version" option to retain your own version of the database located in the ...HCH\UNITHERM directory.

During upgrading, informational text files (*.TXT) in the ...HCH directory are updated automatically.

Note: If you are upgrading from HCh version 3.2, the database file UT_RADII.REF will be automatically renamed to UT_SIZES.REF.

Chapter 1. The UNITHERM Program and Database

About UNITHERM

The UNITHERM program is designed for storage and retrieval of thermodynamic data and calculation of apparent Gibbs free energies of components (aqueous species, minerals, gases and non-aqueous liquids) required for equilibrium modelling. Using UNITHERM you can:

- Easily maintain and modify the provided thermodynamic database or create a new database of your own.
- Calculate apparent Gibbs free energies of the database components over a wide range of T-P conditions.
- Calculate pK and $\Delta G_r(T,P)$ values of a specified chemical reaction.
- Tabulate parameters of the extended Debye-Hückel equation for a number of electrolytes.
- Tabulate density, dielectric constant, fugacity and fugacity coefficients of pure water.

Database Components

The term "component" in the current manual and HCh programs means any chemical compound included in a model of a chemical system. Components may be represented by phases of constant composition or by components of phase-solutions (*eg*, aqueous species such as ions and complexes, or end-members of solid solutions). Thus the term "component" in this manual should be distinguished from an independent thermodynamic component.

Currently the database contains three types of components:

- Basic species (simple ions, some polyatomic ions and aqueous complexes)
- Complexes (aqueous complexes)
- Pure phases (minerals, gases, and non-aqueous liquids)

This subdivision is based on different algorithms employed to calculate the apparent Gibbs free energies (see "Calculation of Gibbs Free Energies" on page 9).

Database Capacity

The UNITHERM database can contain up to 1023 components of each type (basic species, complexes, and pure phases), *ie* 3069 components in total.

Default Database

The default database copied to your UNITHERM directory during the primary installation has been compiled from a variety of sources at the Department of Geochemistry of the Moscow State University. Despite the efforts to maintain a reasonable consistency it should be stressed that this is not a completely internally consistent thermodynamic data set. However, the default data provide a reasonable description of many hydrothermal equilibria in low- to medium-temperature hydrothermal conditions ($t < 350^\circ\text{C}$). They also provide a convenient starting point for building and expanding of your own database.

Browse the database references (see "Basic UNITHERM Commands" on page 13) and the reference text files (UT_*.REF) to familiarise yourself with the sources of thermodynamic data.

Note: Some of the records in the original UT_*.REF files are provided in a Cyrillic font. You can browse them in a UNITHERM session, or in a DOS session after UNITHERM execution. If you are running HCh under Windows, make sure you are working in a full-screen session - otherwise you will see an unreadable set of characters.

Database Files

The UNITHERM database consists of several data files which are normally located in the UNITHERM directory. Some of these files are binary and are maintained automatically by the UNITHERM program. Others are in the text (ASCII) format. As a rule ASCII files may be modified by an external text editor. All the binary files are mandatory and the text files are optional.

File	Format	Contents
UT.DIR	Binary	The list of the database components.
UT1.BIN	Binary	Parameters of the basic aqueous species (the revised HKF model).
UT2.BIN	Binary	Parameters of the aqueous complexes (the modified Ryzhenko-Bryzgalin model).
UT3.BIN	Binary	General parameters of the pure phases.
UT4.BIN	Binary	Heat capacity equations for the pure phases.
UT_BASIC.REF	Text	Extended references for basic species.
UT_COMPL.REF	Text	Extended references for complexes.
UT_ELECT.REF	Text	Parameters of background electrolytes (HKF) for calculation of activity coefficients of aqueous species.
UT_MINER.REF	Text	Extended references for pure phases.
UT_SIZES.REF	Text	Ion size parameters for calculation of activity coefficients of aqueous species.
(UT_RADII.REF in earlier versions)		
UT_REACT.REF	Text	Definition of a chemical reaction.
UT_TABLE.REF	Text	User-defined T-P table.
UT_USREL.REF	Text	User-defined "chemical elements".

Note: You can set the Read-Only attribute for any of the binary files to protect the database from inadvertent modifications.

Note: We do not recommended to modify the text file UT_USREL.REF with an external text editor. To edit this file start UNITHERM with the /UserElements command option (see "Starting UNITHERM in a Specific Mode" on page 16).

Naming Conventions

The UNITHERM database contains two groups of components with different naming conventions: (1) aqueous species (basic species and complexes) and (2) pure phases (minerals, gases, and non-aqueous liquids).

Group of components	Name (14 characters)		Examples
	<i>Mandatory part</i>	<i>Optional part (for names shorter than 14 characters)</i>	
(1) Aqueous species	Chemical formula in a conventional notation including the non-zero charge.	Any comment separated from the chemical formula by space or comma.	Fe++ FeOH+ Fe(OH)2 Fe(OH)3- Fe(OH)2 (aq) Fe(OH)2,aq
(2) Pure phases	Any string (eg, mineral name). The chemical formula of the component is defined inside the corresponding database record. Note: Special substrings in the comment field are used by modelling programs to distinguish gases and liquids from solid phases (see below).	Any comment separated from the main part of the name by space or comma.	Quartz Iron Hematite RH Hematite,RH

Tip: Use space as a comment separator (eg, Fe(OH)2 (aq)) if you do not wish the comment to appear in the output listing of modelling programs and in your System files. Use comma as a comment separator (eg, Fe(OH)2,(aq)) to retain the comment in the output listing.

Tip: If you want to truncate the comment in your routine output listing but to keep track of the exact species names used in your models, you can use the **Export ASCII** command of the System menu. Full comments will be printed in the *.STG text files (See "Exporting *.ST files to ASCII files" on page 24).

Special substrings in the comment field are used by modelling programs to distinguish gases and liquids from solid phases. This distinction is required to select a proper algorithm of calculating Gibbs free energies of species and defining gaseous, liquid and solid solutions.

Components	Substring	Purpose	Example
Pure phases: Gases	"g"	Specify a pure phase as a gas.	Hydrogen,g Hydrogen,gas 0
Pure phases: Liquids	"l"	Specify a pure phase as a liquid.	

A special substring is used to modify the selection of components in the MAIN program when you create a System file (see "Creating *.ST File" on page 22).

Components	Substring	Purpose	Example
All	"r"	Exclude a component from the default selection of components suggested for a specified chemical system.	HFeO2 (aq) /

Standard State Conventions

Component	Standard state convention
Stoichiometric minerals or pure liquids (including water)	Unit activity of the pure component at all temperatures and pressures.
Gases (including stable and metastable steam)	The hypothetical state of unit fugacity (1 bar) at any temperature.
Aqueous species (other than H ₂ O)	Unit activity of the species in a hypothetical 1 molal solution referenced to infinite dilution at any temperature and pressure.

Note: Fugacity and fugacity coefficients of water in liquid and gaseous phases are calculated by UNITHERM according to the gas standard state.

Calculation of Gibbs Free Energies

The standard molal Gibbs free energies of minerals, gases, and aqueous species are represented as **apparent** standard molal Gibbs free energies ($\Delta g(T, P)$) of formation from the elements at the given temperature and pressure. These apparent energies can be written as

$$\Delta g(T, P) = \Delta G_f + (G(T, P) - G(T_r, P_r)),$$

where ΔG_f denotes the standard molal Gibbs free energy of formation of the species from its elements in their stable phase at the reference temperature ($T_r = 298.15$ K) and pressure ($P_r = 1$ bar), and $G(T, P) - G(T_r, P_r)$ refers to differences in the standard molal Gibbs free energy that arise from changes in temperature ($T - T_r$) and pressure ($P - P_r$).

Further in the manual the apparent standard molal Gibbs free energies of formation ($\Delta g(T, P)$) are referred to as "Gibbs free energies".

Water

Thermodynamic properties of pure water are calculated according to the Haar-Gallagher-Kell (HGK) model (Kestin et al., 1984) using the modified algorithm of the program H2O (P.N. Kopylov, the Chernogolovka Institute of Experimental Mineralogy). This algorithm is consistent with the algorithms employed in the revised HKF model.

Aqueous species

Aqueous species are subdivided in UNITHERM into "basic species" and "complexes". This subdivision is purely conventional and is related to particular algorithms used to calculate Gibbs free energies of aqueous species. The "basic species" are self-sufficient, as their Gibbs free energies are calculated directly from an equation of state. In contrast, definition of the "complexes" and calculation of their energies require references to other aqueous species.

Note: An aqueous complex as a chemical compound can be optionally described either in terms of "basic species" or "complexes".

Basic species

Gibbs free energies of the "basic species" (simple ions, some polyatomic ions, and aqueous complexes) are calculated according to the revised Helgeson-Kirkham-Flowers equations of state (HKF) (Shock et al., 1992; Tanger and Helgeson, 1988). The calculation algorithm has been extracted from the SUPCRT92 software package (Johnson et al., 1992). See the referred publications for further details.

Note: The OH^- ion holds a unique position among other aqueous species. By default the free energy of formation of the OH^- ion is calculated from the Gibbs free energy of water and its dissociation constant calculated according to Marshall and Franck (1981):

$$\Delta g(T, P)_{\text{OH}^-} = \Delta g(T, P)_{\text{H}_2\text{O}} - R \cdot T \cdot \ln(10) \cdot pK_{\text{diss}}(T, P).$$

The built-in OH^- (OH^-) ion cannot be deleted from the database but you can add your own OH^- ion with a modified name (eg, “ $\text{OH}^- *$ ”).

Warning: At high temperatures and pressures the dissociation constant of water calculated according to Marshall and Franck (1981) is different from the dissociation constant of water calculated using SUPCRT (eg, the deviation can reach ~0.4 log units at 350°C and PSAT). If you are working with aqueous hydroxocomplexes at near-critical or supercritical conditions make sure that you are using the “proper” OH^- ion to preserve the internal consistency of your aqueous species database.

Complexes

Gibbs free energies of the “complexes” are calculated according to the modified Ryzhenko-Bryzgalin model (MRB) (Borisov and Shvarov, 1992) from their $pK_{\text{diss}}(T, P)$ values:

$$\Delta g(T, P) = \sum n_i \cdot \Delta g_i(T, P) - R \cdot T \cdot \ln(10) \cdot pK_{\text{diss}}(T, P),$$

where $\Delta g_i(T, P)$ are Gibbs free energies of basic species (and/or, H_2O , H^+ , and OH^-), and n_i are stoichiometric coefficients. Temperature and pressure dependence of $pK_{\text{diss}}(T, P)$ values is represented by the equation

$$pK_{\text{diss}}(T, P) = \frac{T_r}{T} \cdot pK_{\text{diss}}(T_r, P_r) + B(T, P) \cdot (zz/a)_{\text{eff}},$$

where $(zz/a)_{\text{eff}}$ is the effective property of the complex which depends on temperature:

$$(zz/a)_{\text{eff}} = A + \frac{B}{T}.$$

The parameter $B(T, P)$ does not depend on the complex type and is computed from the dissociation constant of water according to Marshall and Franck (1981). It is assumed that for H_2O $(zz/a)_{\text{eff}} = 1.0107$.

Note: If you exclude the default OH^- ion from your chemical system and replace it by an alternative OH^- ion, the parameter $B(T, P)$ in the MRB equation will still be calculated from the dissociation constant of water according to Marshall and Franck (1981).

Tip: You can use the “complex” representation of non-conventional aqueous species described according to the revised HKF model. For example, you can use $\text{Al}(\text{OH})_4^-$ instead of AlO_2^- . Just specify AlO_2^- and water as “basic species” and set $pK_{\text{diss}}(T, P)$, and A and B parameters of your complex to zero.

Note: UNITHERM does not provide facilities to calculate $\Delta g(T, P)$ or $pK_{\text{diss}}(T, P)$ values as simple power functions of temperature and pressure. However, you can re-fit available experimental data on $pK_{\text{diss}}(T, P)$ or $\Delta g(T, P)$ in terms of the MRB or HKF models using the auxiliary programs UT-RYZ and UT-HEL.

Pure phases (minerals, non-aqueous liquids and gases)

Gibbs free energies of minerals and non-aqueous liquids are conventionally calculated as:

$$\Delta g(T, P) = \Delta G(T_r, P_r) - S(T_r, P_r) \cdot (T - T_r) + \int_{T_r}^T Cp(t) dt - T \cdot \int_{T_r}^T \frac{Cp(t)}{t} dt + \int_{P_r}^P V(T, p) dP,$$

where $S(T_r)$, $V(T_r)$ and ΔG_f are the standard molal entropy, volume and Gibbs free energy of formation, and $Cp(t)$ is the molal isobaric heat capacity of the mineral at 1 bar. $Cp(t)$ is defined as a usual power function. If a mineral has phase transitions, every stable interval is described by its own $Cp(t)$ equation. The maximum number of the $Cp(t)$ equations allowed in UNITHERM is 5. Each phase transition is characterised by its temperature (at $P = 1$ bar), the reciprocal of the Clapeyron slope (dT/dP), and values of heat and volume effects. The temperature of the last phase transition can define the upper temperature limit of the mineral stability.

Gibbs free energies of gases are calculated as:

$$\Delta g(T, P) = \Delta G(T_r, P_r) - S(T_r, P_r) \cdot (T - T_r) + \int_{T_r}^T Cp(t) dt - T \cdot \int_{T_r}^T \frac{Cp(t)}{t} dt + R \cdot T \cdot \ln(P),$$

unless you have specified the /1bar command-line option (see "Starting UNITHERM in a Specific Mode" on page 16).

Calculation of Coefficients of the Debye-Hückel Equation

Using UNITHERM you can calculate coefficients necessary for estimation of activity coefficients of charged aqueous species according to the extended Debye-Hückel equation:

$$\log \gamma_i = -\frac{Az_i^2 \sqrt{I}}{1 + B\bar{a}\sqrt{I}} + \Gamma_\gamma + B \bullet (T) \cdot I$$

or

$$\log \gamma_i = -\frac{Az_i^2 \sqrt{I}}{1 + B\bar{a}\sqrt{I}} + \Gamma_\gamma + b_\gamma I.$$

$B \bullet (T)$ represents the extended term parameter for the NaCl-dominated solutions, which is a function of temperature (Helgeson, 1969).

b_γ represents the extended term parameter for the electrolyte MX , which is a function of temperature and pressure (Helgeson et al., 1981; Oelkers and Helgeson, 1990). Equation of state coefficients for computing extended term parameters b_γ for a number of electrolytes are provided by the UT_ELECT.REF database file.

Using UNITHERM you can calculate and tabulate the A , B , $B \bullet (T)$, and b_γ parameters.

Parameter of the Debye-Hückel equation	UNITHERM notation	UNITHERM menu key
A	A	A
B	B	B
$B \bullet (T)$	b-dot	C
b_γ	b-gamma	X

b_γ parameters are calculated for a specified "background" electrolyte (see "Additional UNITHERM Commands" on page 15).

Activity coefficients of charged aqueous species for your model system are calculated by GIBBS (See Appendix 3, "Calculation of Activity Coefficients of Aqueous Species").

Note: UNITHERM does not support any options to calculate Setchénow coefficients to estimate activity coefficients of neutral aqueous species. However, they can be calculated by GIBBS (See Appendix 3, "Calculation of Activity Coefficients of Aqueous Species").

Working with UNITHERM

To Start UNITHERM

At the command prompt, type "UT" and then press ENTER.

The UNITHERM window is displayed. Use the cursor control keys for browsing the database contents and selecting components of your interest.

The key bar with the list of the available commands is positioned at the bottom of the screen. The key bar operates in 3 modes when used in conjunction with the SHIFT and ALT keys.

Note: Some additional commands are not listed on the key bar. Press the F1 key to get brief information on these commands (see "Additional UNITHERM Commands" on page 15 for details).

Basic UNITHERM Commands

The following table describes the available commands on the main key bar.

Use		To
F1	Info	Get general information about UNITHERM. You can use UP and DOWN arrow keys to scroll through the help text; Get the extended reference for the selected component in the View mode (F3, F1). Note: Short references about Aqueous complexes and Pure phases in the UNITHERM "Info" window (F1) are read from the UT_COMPL.REF and UT_MINER.REF text files. You can change these references by editing the top lines of these files immediately after the exclamation mark (!).
F2	Input	Add a new component to the database. The new component is added to the end of the components list (use SHIFT+F2 to insert a new component immediately above the current position of the cursor bar).
F3	View	Examine the stored data for the selected component.
F4	Edit	Modify the data for the selected component.
F5	Move	Move the component to a different location in the UNITHERM table of contents.
F6	RenDel	Rename the selected component or delete it from the data base.
F7	Search	Find a component in the table of contents by a string of characters (the search is case-sensitive!).
F8	DefTab	Define temperatures and pressures for calculation of Gibbs free energies.
F9	Energy	Calculate Gibbs free energies for the selected component (kJ/mol by default). Note: The Gibbs free energies of the components are tabulated by the F9 command for their standard state except for the ideal gases. For ideal gases UNITHERM tabulates the values of $\Delta g(T,P) = \Delta g(T,1 \text{ bar}) + R \cdot T \cdot \ln(P)$. To calculate Δg values for the gas standard state ($T_f = 1 \text{ bar}$) start UNITHERM with the /1bar option (see "Starting UNITHERM in a Specific Mode" on page 16).
F10	Quit	Quit UNITHERM; Terminate the program Subset mode (S, F10) (see further).

Note: Operations that modify database (Input, Edit, Move, RenDel) are blocked in the Subset mode or when the Read-Only attribute is set for any of the data files (UT.DIR, UT#.BIN).

See "Additional UNITHERM commands" (page 15) and "Starting UNITHERM in a Specific Mode" (page 16) on how to print your data.

Modified Basic Commands

The SHIFT key modifies some of these basic commands. Pressing the SHIFT key displays the modified commands on the key bar.

Use		To
SHIFT + F2	Insert	Add a new component to the database. The new component is inserted immediately above the current position of the cursor bar.
SHIFT + F5	Copy	Duplicate the record. A copy of the selected component is inserted immediately below the current position of the cursor bar. You will be prompted to input a new unique name for the duplicated record.
SHIFT + F7	Next	Find the next component matching the previously defined search string.

Note: Operations that modify database (Insert, Copy) are blocked in the Subset mode or when the Read-Only attribute is set for any of the data files (UT.DIR, UT*.BIN).

UNITHERM Reaction Commands

The ALT key activates a special "Reaction" mode of UNITHERM. The relevant commands are displayed on the key bar by pressing and holding the ALT key.

Using this option you can calculate pK and $\Delta G_r(T,P)$ values of a specified chemical reaction. The reaction name and stoichiometry can be saved in the UT_REACT.REF file for a future reference.

Use		To
ALT + F2	Input	Input a new chemical reaction.
ALT + F3	View	View the title and stoichiometry of the current reaction.
ALT + F4	Edit	Edit the title and stoichiometry of the current reaction.
ALT + F5	Save	Save the reaction stoichiometry in the UT_REACT.REF file.
ALT + F8	pK	Calculate pK values of the specified chemical reaction.
ALT + F9	ΔG_r	Calculate $\Delta G_r(T,P)$ values of the specified chemical reaction (kJ/mol by default).

Note: Start UNITHERM in the /1bar mode to calculate pK and $\Delta G_r(T,P)$ values of chemical reactions involving gases (see "Starting UNITHERM in a Specific Mode" on page 16).

See "Additional UNITHERM commands" (page 15) and "Starting UNITHERM in a Specific Mode" (page 16) on how to print your data.

Additional UNITHERM Commands

Some additional commands are not listed on the key bar and can be activated by pressing one of the following keys.

Use	To
A	Calculate the <i>A</i> parameter of the Debye-Hückel equation.
B	Calculate the <i>B</i> parameter of the Debye-Hückel equation.
C	Calculate the extended parameter of the Debye-Hückel equation ($B\phi(T)$) for NaCl-dominated solutions according to Helgeson (1969).
X	Calculate the extended parameter of the Debye-Hückel equation (b_γ) according to Helgeson et al. (1981) and Oelkers and Helgeson (1990) for a selected "background" electrolyte (see command F11).
D	Calculate density of pure water.
E	Calculate dielectric constant of pure water.
F	Calculate fugacity of pure water and gases ² .
G	Calculate fugacity coefficients of pure water and gases.
	Note: D, E, F and G commands return the properties of water in its stable phase for any given temperature and pressure. However, you can specify a metastable water phase using the W command (see below).
P	<ol style="list-style-type: none"> 1. Print the table of the database contents; 2. Print the stored data for the selected component in the View mode (F3, P); 3. Print the tabulated parameters (eg, F9, P; ALT+F9, P).
	Note: You can redirect all the program output to the UT.PRN ASCII file instead of to the printer using the command-line /PTF option (see "Starting UNITHERM in a Specific Mode" on page 16).
S	Select the subset of components for a specified chemical element (filter the database).
W	Switch between stable and metastable phases of water.
	Note: In the "metastable" mode the HGK model equations for the chosen phase ("Vapor" or "Liquid") are extrapolated into the metastable phase region across the vapor saturation curve. An error string (*Error*) will be printed for an attempt to tabulate water properties (energy, density, dielectric constant, etc) outside the area of reasonable extrapolation.
F11	Switch between electrolytes available for computation of the extended parameter of the Debye-Hückel equation according to Helgeson et al. (1981) and Oelkers and Helgeson (1990).
F12	Switch between energy units (cal vs J) for pure phases. You can also use this key in the Input (F2, F12), View (F3, F12), and Edit (F4, F12) modes.

Quick reference for most of the UNITHERM commands can be obtained from the UNITHERM Info window (F1).

² The F and G options for pure gases other than water are included as a provision for the description of real gases. The relevant algorithms are yet to be incorporated.

Starting UNITHERM in a Specific Mode

At times you might want to run UNITHERM in a specific mode. To ensure that UNITHERM runs in a particular mode, specify one of the following options after the "UT" command. For example, type "UT /PrintToFile" to redirect all the program output to the UT.PRN file.

Note: The command-line options are case-insensitive. Some of them can be abbreviated to the letters shown here in the uppercase.

Use	To
/lbar	Calculate free energies for gases according to their standard state ($T_f = 1 \text{ bar}$). The option will affect only tabulation of $\Delta G(T,P)$, $\Delta G_r(T,P)$, and pK values.
/copy	Copy the data files UT.DIR and UT*.BIN with optimisation. The optimised database is copied into the WT.DIR and WT*.BIN files in the same directory. To make the copy of your database usable you have to rename them to UT.DIR and UT*.BIN files (eg, using the DOS command ren w*. * u*.*).
/kcal	Calculate free energies of components and chemical reactions in kcal/mol instead of kJ/mol.
/scopy	Create a new database from the selected components of the current database.
/tab	Save a user-defined T - P definition table (F8, ESC) in the UT_TABLE.REF file. Retrieve a user-defined T - P definition table (F8, ESC) from the UT_TABLE.REF file.
/PrintToFile or /PTF	Redirect all the program output to the UT.PRN ASCII file instead of to the printer.
/UserElements or /UE	Define or change your own "chemical elements" if the periodical system is insufficient for your purposes. The definitions are stored in UT_USREL.REF ASCII file. Tip: You can specify your own "chemical elements" for special problems including non-equilibrium geochemical processes (eg, with blocked redox reactions for a particular chemical element), or processes with isotopic exchange.

Note: If you want to use specific modes (eg, /lbar, /PTF or /tab) on a day-to-day basis you can add the necessary options to your UT.BAT file (eg, ... \UNITHERM\UNITHERM.EXE /PTF) or to the Command line of the UNITHERM Program Properties of Windows (eg, ... \HCH\UNITHERM\UNITHERM.EXE /PTF).

Selecting components in the /SCOPY mode

When you start UNITHERM in this mode all the components of the current database will be selected for copying. You should start to prepare your reduced data set by *deselecting* unnecessary components. Note that all the selected components are designated with the default UNITHERM colour.

Use	To
INSERT or SPACE BAR	Select/Deselect the current component.
-	Deselect all the components below the current position of the cursor bar.
+	Select all the components below the current position of the cursor bar.
*	Reverse the present selection below the current position of the cursor bar. Note: If you switch to and from the UNITHERM subset mode (S), your current selection will be preserved.

Note: During the program session you can work with UNITHERM as usual, but the commands that modify the original database will be disabled.

The data are copied when you complete your selection and quit the program. The new database is copied into the WT.DIR and WT*.BIN files in the same directory. To make the copy of your database usable you have to rename them to UT.DIR and UT*.BIN files (eg, using the DOS command **ren w*.* u*.***).

Chapter 2. Equilibrium Modelling

Overview

Using the HCh package you can calculate the equilibrium compositions of chemical systems containing an aqueous solution, a gaseous mixture, non-aqueous liquid solutions, solid solutions, and any number of pure individual phases (minerals). You can consider either closed systems or open systems with perfectly mobile components (PMC) (Korzhinskii, 1965).

The package also provides powerful tools for automated equilibrium-dynamic modelling of geochemical processes (see "Control Menu" on page 29).

Preparation and maintenance of the necessary modelling files are performed with the assistance of the MAIN program.

The equilibrium calculations on systems are performed by the GIBBS program.

Files Required for Modelling

To proceed with calculations you must prepare several binary files to define the chemical system and formats of the input data. There are four different types of binary files used for calculations. Each of them has a specific fixed extension.

The following table describes the files required for modelling.

File type	Extension	Status	Purpose
System	*.ST	Mandatory	Definition of a chemical system. These files contain stoichiometric data for all possible components of the system and some additional data such as ion charges and ion size parameters, Setchénov coefficients for neutral aqueous species, and parameters for solid and liquid solution models.
Blank	*.BL	Mandatory	Definition of the input data and their formats. These files define the substances used for the description of the total system composition(s) and the corresponding measurement units.
Input	*.IN	Optional	Description of the total system composition(s). You can describe up to 3 system compositions according to the format defined in a *.BL file.
Control	*.CT	Optional	Definition of the modelling algorithm. These files contain the information necessary for automated equilibrium calculations for a number of system compositions.

Note: The *.IN and *.CT files are not mandatory for equilibrium calculations in the "manual" (non-automated) mode. You can define the total system composition(s) in the direct interactive mode of GIBBS using a *.BL file and calculate the equilibrium composition immediately.

Note: For special purposes you might find it necessary to create a special *.STG ASCII file complimenting your *.ST binary file (see "System Menu" on page 22 for details).

Quick Start: Preparation of Files

The following flow chart illustrates:

- A normal sequence of file preparation for equilibrium modelling;
- Interaction between different package programs during a MAIN session.

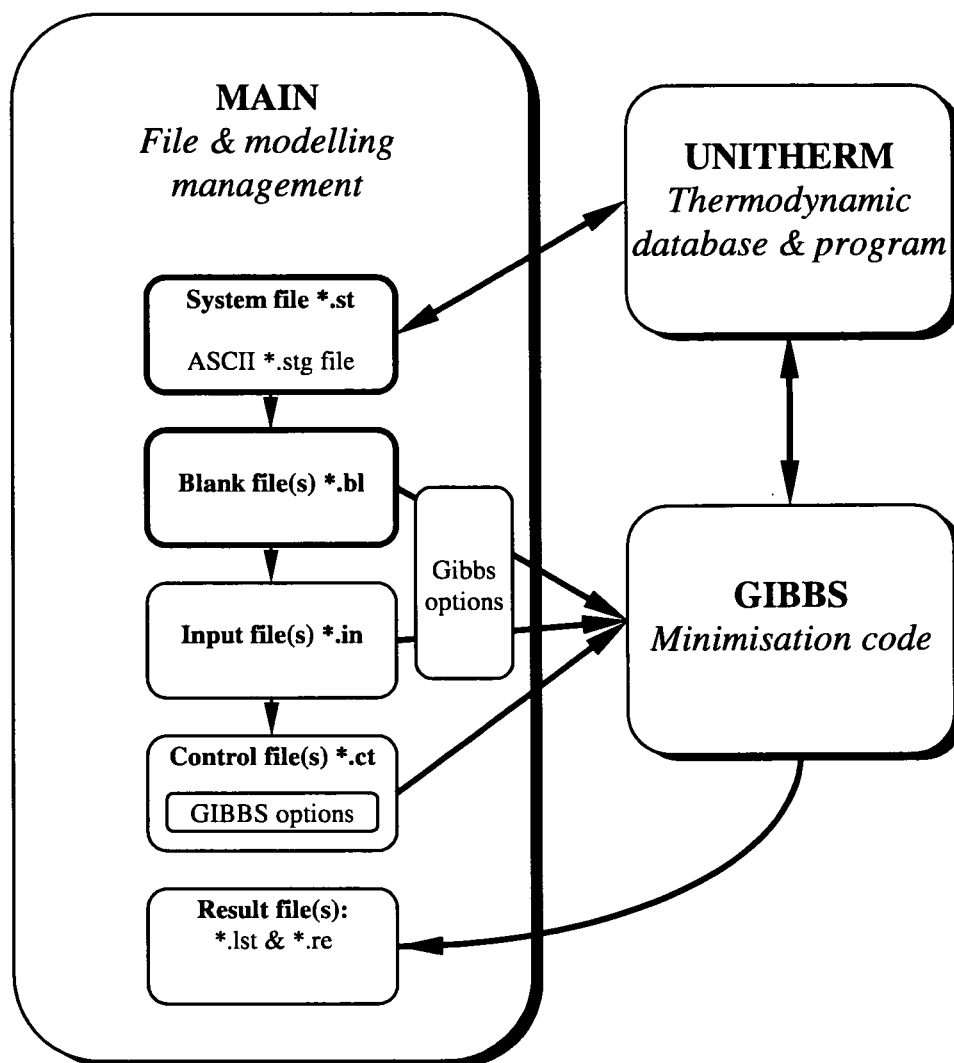


Figure 1. Interaction of HCh components and a general sequence of file preparation.

Working with MAIN

About MAIN

The program is developed for preparation and maintenance of files necessary for equilibrium modelling. Using MAIN you can:

1. Create and modify files defining your model chemical systems.
2. Define algorithms for equilibrium-dynamic geochemical modelling.
3. Calculate equilibrium compositions of your chemical systems using GIBBS.

To start MAIN

At the command prompt, type "HCH", and press ENTER. The MAIN window appears. Initially, the MAIN window displays the contents of your current directory.

Note: The exact list of the displayed files depends on the setting of the "Shown Files" switch in the Options menu (see page 37).

The program is menu-driven. The menu bar is displayed at the top of the screen.

- To choose a menu

Press the RIGHT arrow or LEFT arrow key to select the menu you want, and then press ENTER (or UP arrow, or DOWN arrow). Or press the highlighted letter for the menu you want.

Press F1 to get Help on the selected menu.

- To choose a command from a menu

Use the UP arrow or DOWN arrow key to select the command you want, and then press ENTER.

Or press the highlighted letter for the menu you want. The status bar at the bottom of the screen will contain the list of keys for currently available commands.

Starting MAIN in a specific mode

At times you might want to run MAIN in a specific mode. To ensure that MAIN runs in a particular mode, specify one of the following options after the "HCH" command. For example, type "HCH /PrintToFile" to redirect all the program output to the MAIN.PRN file rather than to a printer.

Note: The command-line options are case-insensitive. Some of them can be abbreviated to the letters shown here in the uppercase.

Use	To
/PrintToFile (or /PTF)	Redirect all the program output to the ASCII file MAIN.PRN in the current directory.
/IgnoreError (or /IE)	To ignore the error message about excluding the default OH ⁻ ion from the aqueous species list (see "System Menu" later on page 22).

Note: If you want to use specific modes (eg, /IE or /PTF) on a day-to-day basis you can add the necessary options to your HCH.BAT file (eg, ...\\MAIN\\MAIN.EXE /IE) or to the Command line of the MAIN Program Properties of Windows (eg, ...\\HCH\\MAIN\\MAIN.EXE /IE).

To Quit MAIN

To exit the program, choose **Quit (Q)** on the main menu bar. Press ALT+Q to quit MAIN when the menu bar is not accessible.

Creating and Changing Files

To create and change the files necessary for the modelling, use the following menus.

Use	To
System	Create and edit files defining the chemical system (*.ST files).
Blank	Create and edit files defining the formats of the input data (*.BL files).
Input	Create and edit files describing the total system compositions (*.IN files).
Control	Create and edit files defining the algorithms for equilibrium modelling (*.CT files).

System Menu

Creating *.ST file

1. From the System menu, choose **New**.
2. If the information about the database contents appears, press any key to skip the message.
3. If the "Set directory for System file" directive is displayed, set the directory where you want to save the file. Press the drive letter to choose the drive, and select the necessary directory using the ENTER and arrow keys. Press ESC to accept the selected directory. Just press ESC if no changes are required.
4. Define the type of your system. Select one or more of the following possible phases:
 - "Perfectly mobile components" (for an open system with perfectly mobile components, PMC).
 - "Individual phases" (for a system containing individual phases – solids, liquids and gases that will not mix).
 - "Solid solution(s)" (for a system containing solid solutions).
 - "Liquid solution(s)" (for a system containing non-aqueous liquid solutions).
 - "Gaseous mixture" (for a system containing a gaseous phase).
 - "Aqueous solution" (for a system containing an aqueous phase).

To select an item use the SPACE BAR or INSERT key. To complete the selection press ENTER.

5. Select the chemical elements making up your system, then press ENTER.
6. Put the elements in a suitable order, then press ENTER.
7. Select PMC (for an open system) and minerals from the offered lists. You can use the F1 key to view chemical formulas of these components.

For a system containing solid solutions:

- Enter the number of solid solutions.
- Select end-member minerals from the offered list (you can use the F1 key to view chemical formulas of minerals). Press ENTER.
- Input the name of the solid solution, then press ENTER.
- Press ENTER to confirm the Ideal mixing model.
- Fill in the table with the parameters of the appropriate ideal site-mixing model (see Appendix 2, "Definition of Solid Solution Models in HCh"). Just leave this table empty to define the simplest "molecular" solution). Press ESC to finish.
- Repeat these steps for the rest of the solid solutions.

For a system containing non-aqueous liquid solutions:

- Repeat the initial steps for a system with solid solutions.
- Select either Ideal or Non-random two-liquid solution model (NRTL) for your liquid solution. Press ENTER.
- If you chose NRTL, enter parameters of your model. Press ESC to finish.

Note: If you know that your liquids can form N partially immiscible phases, you need to create N copies of your solution in the System file. For each copy of such solution we recommend you to use *one and the same solution name*. As the result of calculations you will obtain N equilibrium liquid solutions, although their definitions and names in the System file are identical.

Select gases and aqueous species from the offered lists. Press ENTER.

8. Input the title of the system, then press ENTER.
9. Input the filename (without the extension). When ENTER is pressed, the new System file is saved and ready for use.

Note: The maximum number of chemical elements allowed in your model is 30.

Note: If you need to include in your aqueous system OH^- ion other than the default UNITHERM ion, you must start MAIN with the /IgnoreError (/IE) option (see "Starting UNITHERM in a Specific Mode" on page 20). The built-in OH^- ion cannot be excluded from the aqueous species list in a normal MAIN mode.

Tip: You can add the /IE option to your HCH.BAT file or to the Command line of the MAIN Program Properties of Windows.

Viewing *.ST file

1. From the System menu, choose **View**.
2. Select the necessary *.ST file, and press ENTER.
3. Use the cursor keys for scrolling the file if necessary. If the System file contains pure phases with non-integer stoichiometric coefficients (eg, pyrrhotite $\text{Fe}_{0.877}\text{S}$), the ALT key highlights them, and the ALT+L combination shows their real values.
4. Press ESC to quit.

Editing *.ST file

Using the **Edit** command of the System menu you can:

- Delete unnecessary components from the file.
- Edit names and parameters of solid and liquid solutions.
- Edit effective diameters (a) of the charged aqueous species.
- Add individual Setchénou coefficients for neutral aqueous species (see Appendix 3, "Calculation of Activity Coefficients of Aqueous Species").
- Alter the system title.

Using the **Edit** command of the System menu you cannot:

- Edit stoichiometry or names of the components in System files – they are defined in the UNITHERM database.
- Add new components to your System file or change them.

1. From the System menu, choose **Edit**.
2. Select the necessary *.ST file, and press ENTER.
3. Use the cursor keys to select the necessary line. Press DELETE if you wish to delete the current component. A minus sign (–) is displayed after the component number. To cancel deletion, press the DELETE key again.
4. To rename a solid or liquid solution, select any of its end-member components. Press ALT+N, enter the new name, and press ENTER.
5. To edit parameters of a solid or liquid solution, select any of its components. Press ALT+E, edit the parameters, and press ESC.
6. To alter the diameter of the selected aqueous species, press ALT+S³. Enter the new value, then press ENTER.
7. To alter the system title press ALT+T, edit the title, and press ENTER.
8. Press ESC to complete editing. The new data are saved in the existing *.ST file.

³ ALT+R in earlier HCh versions

Exporting *.ST files to ASCII files

Use this command to substitute free energies of specified components with your own non-database values, or to fix their activity coefficients at arbitrary constant values.

1. From the System menu, choose **Export ASCII**.
2. Select the necessary *.ST file, and press ENTER. An ASCII file with the same name as the specified *.ST file and the extension *.STG is created in the same directory. It contains the names of all the system components (except PMC) and allocates the fields for their energies and activity coefficients.

You can edit this file using the **ASCII Files** command of the Result menu (see “Result Menu” on page 35).

Note: To use *.STG files for equilibrium modelling you **must** run GIBBS with the /g option (see “Gibbs Options” on page 44).

Tip: You might need *.STG files for processing experimental data when the accuracy of the Gibbs free energies of components provided by UNITHERM is not sufficient.

Other operations on *.ST files

The System menu provides some other commands to manage System files. You can print, copy, rename, and delete files. When you choose one of these commands you are asked to select a System file, and the command is performed if you follow the program's directives.

Blank Menu

*Creating *.BL file*

1. From the Blank menu, choose **New**. The directive "Choose System (*.st) file" appears.
2. Select the System file that describes your system, and press ENTER.
3. If the "Set directory for Blank file" directive appears, set the directory in which you wish to save the file. Press the drive letter to choose the drive, and select the necessary directory using the ENTER and arrow keys. Press ESC to accept the selected directory. Just press ESC if no changes are required.
4. If the system is open, select the fugacity units for the PMC⁴ (bars, their decimal or natural logarithms). Press ENTER.
5. Select the way to define the total system compositions. The following options for input substances are available:
 - Chemical elements (for theoretical modelling).
 - Ions and complexes (for processing hydrogeochemical data).
 - Other substances (the default option; convenient in most cases of geochemical modelling).

Press ENTER.

6. If the system is open, choose the type of each PMC:
 - Constant (you must specify the fugacity value(s) in the current *.BL file)
 - Variable (you will input the fugacity value(s) later in an *.IN file)
 - Computed (the fugacity value(s) will be calculated by GIBBS program using the formulas defined in a *.CT file).
7. If the system contains an aqueous solution, choose the measurement unit for water (kg by default). Use the DOWN or UP arrow keys to make your selection. Select the unit and press ENTER.
8. If you have chosen chemical elements for definition of the total system composition, choose units for each element.

If you have chosen "ions and complexes" or "other substances" for definition of the total system composition, input their chemical formulas followed by the appropriate measurement units. You can define any number of ions or substances. To finish the list press ENTER when the input field for a formula is empty.

9. Input the filename (without the extension). When ENTER is pressed, the new Blank file is saved and ready for use.

Note: Each Blank file points to one particular System file, but there can be any number of different Blank files that point to the same System file.

*Viewing *.BL file*

1. From the Blank menu, choose **View**.
2. Select the necessary *.BL file and press ENTER.
3. Use the cursor keys for scrolling the file if necessary. The top line of the file contains the reference to the source System file.
4. Press ESC to quit.

⁴ If fugacity values of your PMC can drop below 10^{-39} bars, we recommend you to specify these values using logarithmic units.

Editing *.BL file

1. From the Blank menu, choose **Edit**.
2. Select the necessary *.BL file and press ENTER.
3. Use the cursor keys to select the necessary data line.
4. To switch between the data column and the unit box press TAB.
5. To change the formula in the current data line press ENTER and edit the formula.
6. Press ESC to complete editing. The new data are saved in the existing *.BL file.

Note: You cannot change the number of ions or substances in your Blank file. The only way to do this is to create a new *.BL file. You can change the types of the PMC, formulas of ions and substances, and their measurement units.

Exporting *.BL files to ASCII files

From the Blank menu, choose the **Export ASCII** command if you need your Blank file in the ASCII format. The specified Blank file is copied as a text file with the same name and the extension *.BLK. This file can be used by external programs for the automatic creating of Input files in the ASCII format (see the **Import ASCII** command of the Input menu on page 27).

Other Operations on *.BL files

The Blank menu provides some other commands to manage Blank files. You can print, copy, rename, and delete files. When you choose one of these commands you are asked to select a Blank file, and the command is performed if you follow the program's directives.

Input Menu

*Creating *.IN file*

1. From the Input menu, choose **New**. The directive "Choose Blank (*.bl) file" appears.
2. Select the necessary Blank file, and press ENTER.
3. If the "Set directory for Blank file" directive appears, set the directory in which you wish to save the file. Press the drive letter to choose the drive, and select the necessary directory using the ENTER and arrow keys. Press ESC to accept the selected directory. Just press ESC if no changes are required.
4. Fill in the columns with the required data:
 - Fugacities of PMC (if the system is open and their type is variable).
 - Quantity of water (for a system with an aqueous solution).
 - Quantities of chemical elements, ions or other substances.
 - Titles for each composition of the system.

Measurement units for all the data are shown to the right of input fields. After completing the input, press ESC.

5. Input the filename (without the extension). When ENTER is pressed, the new Input file is saved and ready for use.

Note: If you use ions to define the system composition, you might get the error message on non-zero charge balance. In this case, correct the composition in one of the three suggested ways and press ESC again.

Note: Each Input file points to one particular Blank file, but there can be any number of different Input files that point to the same Blank file.

*Viewing *.IN file*

1. From the Input menu, choose **View**.
2. Select the necessary *.IN file and press ENTER.
3. Use the cursor keys for scrolling the file if necessary. The top line of the file contains the reference to the source Blank file.
4. Press ESC to quit.

*Editing *.IN file*

1. From the Input menu, choose **Edit**.
2. Select the necessary *.IN file and press ENTER.
3. Move to the field that requires editing:
 - Use the DOWN arrow or UP arrow keys to move along the column.
 - Use the TAB or SHIFT+TAB keys to switch between columns.
 - Press ENTER to shift the edit box one field down.
 - Clean all the fields in the column to delete a composition completely.
 - Press CTRL+C⁵ to copy the contents of the current field to the right column, and ALT+C to copy the entire column to the right.
4. Press ESC to complete editing. The new data are saved in the existing *.IN file.

Importing ASCII files

From the Input menu, choose the **Import ASCII** command if you need to create an *.IN file from an existing ASCII file. The source ASCII file must have the fixed extension .INP and is created by filling in the table presented in a *.BLK file (see the **Export ASCII** command from the Blank menu on page 26). You can edit the loaded data as usual (see "Editing *.IN File"). Press ESC to save the data into a new *.IN file.

⁵ CTRL+TAB and ALT+TAB (or ALT+T) in previous HCh versions. These keys are now disabled.

Other operations on *.IN files

The Input menu provides some other commands to manage Input files. You can print, copy, rename, and delete files. When you choose one of these commands you are asked to select an Input file, and the command is performed if you follow the program's directives.

Control Menu

Menu functions

The Control menu enables you to create and maintain files defining the automatic equilibrium calculations for a number of system compositions⁶. Using Control file instructions, the GIBBS program can perform the entire series of calculations without your intervention. During these calculations the results of any computational step can be used as input data for the subsequent calculations.

Although the application area of the algorithmic approach implemented in HCh is very wide, it has been used mostly for local equilibrium modelling by the "step-flow-through reactor" technique. This practice has resulted in adoption of a specific terminology for the definition of modelling algorithms. A single equilibrium calculation is called "step"; a series of steps related by a single common rule is called a "wave". A numerical model defined in a Control file can include one or more waves each containing an arbitrary number of steps. If your model includes a single wave, it is one-dimensional; if the number of waves is more than one, the model is two-dimensional. The steps can also be referred to as "blocks", "reactors" or "points" depending on the model context.

As in all equilibrium calculations, each reactor must be characterized by its own temperature, pressure, chemical potentials of PMC, and bulk chemical composition. In a Control file you can define these parameters for all the reactors as functions of relative time, distance or other conditions.

A single-wave model can represent a unit stage of a geochemical process. It may be visualised as a one-dimensional (either in terms of space or time) sequence of reactors. Equilibrium compositions of consecutive reactors are calculated through a single pass. For example, in the case of a "flow-through" reactor model one wave corresponds to a single batch of fluid passing through a reactor sequence.

A multi-wave model can represent a multi-stage geochemical process. It may be visualised as a two-dimensional (either in terms of time or space) sequence of reactors. Equilibrium compositions of consecutive reactors are calculated through a number of passes (waves). For example, in the case of a "flow-through" reactor model a number of waves correspond to a number of fluid batches passing through a reactor sequence.

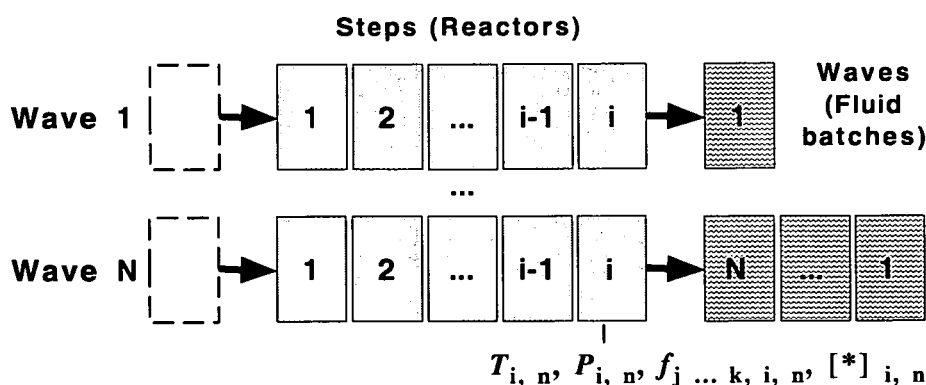


Figure 2. Geometric concept of the "step-flow-through reactor" technique.

An equilibrium-dynamic model can be defined using expressions, relations, and conditions, as follows:

⁶ The number of calculation steps is theoretically unrestricted and is limited only by the size of the output file accessible for processing by MAIN. In practice, a model cannot contain more than 64,000 calculation points, with the exact number depending on a particular computer configuration.

Control file conventions

Expressions

The expressions enable you to write formulae defining all the state variables of your system: temperature, pressure, chemical potentials of PMC and the bulk chemical composition of an equilibrium reactor.

To write formulae you can use the usual arithmetic operators and functions, any numerical constants, special variables, and relations. For example, to specify the temperature, pressure and chemical potential of the PMC for your calculation step you can write

```
T = 400-i*50
P = 3*T
lg(f) = 8.7-23560/(T+273.15),
```

where T is temperature in °C, i is the number of the current calculation step, P is pressure in bars, and f is fugacity of the PMC in the user-specified units.

To define the bulk chemical composition of an equilibrium reactor ([*]) you can write

```
[*] = [1]+100*[2]
[*] = [1]+[2]*10^(i-6)
[*] = [A],
```

and so on. [1] and [2] are the bulk system composition specified in the source *.IN file, and [A] is the bulk composition of the aqueous phase obtained at the preceding calculation step. The full list of the permissible special variables is provided on page 31. For further details, see Appendix 4, "Examples Of The Control Files Usage".

Relations

A relation is a pair of expressions connected by relational operators, which are = (equal to), <= (less than or equal to), >= (greater than or equal to), < (less than), > (greater than), <> (not equal to). When used in expressions, relations should be surrounded by parenthesis (). For these relations HCh generates the value of +1 for true and the value of 0 for false. For example, the formula

```
[*] = ([A]+100*[2])*(i<5)+([A]+100*[3])*(i>=5)
```

will be equivalent to

```
[*] = [A]+100*[2]
```

for calculation steps from 1 to 4, and to

```
[*] = [A]+100*[3]
```

for calculation steps greater than or equal to 5.

Conditions

The conditions are relations used to define the number of calculation steps or waves. See Appendix 4, "Examples Of The Control Files Usage" for details.

Operators and functions

To define your modelling algorithms use the following arithmetic operators: +, -, *, /, ^ or ** (raise to a power). The available functions are: log, exp, and sqr (square root).

Variables

To define your modelling algorithms use the following variables in the Control files:

Symbol	Variable
T	Current temperature (°C).
P	Current pressure (bars).
f, lg(f), or ln(f)	Current fugacity of PMC in selected units.
i	Current step number.
N	Current wave number.
W	Current quantity of water (moles).
[1]	1st composition from *.IN file.
[2]	2nd composition from *.IN file.
[3]	3rd composition from *.IN file.
[A]	Bulk composition of the aqueous phase of the system (current wave, preceding step).
[G]	Bulk composition of the gaseous phase of the system (current wave, preceding step).
[L]	Bulk composition of liquid non-aqueous phases of the system (current wave, preceding step).
[S]	Bulk composition of solid phases of the system (current wave, preceding step).
[*]	Current total system composition ([*]=[A]+[G]+[L]+[S]).
{A}	Bulk composition of the aqueous phase of the system (same step, preceding wave).
{G}	Bulk composition of the gaseous phase of the system (same step, preceding wave).
{L}	Bulk composition of liquid non-aqueous phases of the system (same step, preceding wave).
{S}	Bulk composition of solid phases of the system (same step, preceding wave).
{*}	Total system composition ({*}={A}+{G}+{L}+{S}) of the same equilibrium reactor obtained in the preceding wave.

A special syntax for the {} vector variables {*|G|A|L|S(expression)} allows you to refer to any step of the preceding wave. The value of the expression defines the step number. For example, {A(i-1)} means "the bulk composition of the aqueous phase from the preceding step of the preceding wave". See Appendix 4, Examples of Control Files Usage, for details.

Note: The [*] designation has double meaning:

1. Current total system composition;
2. Total system composition obtained at the preceding step.

This convention follows the usual convention adopted in computer programming. If the variable is to the left from the assignment operator ("="), it represents the new value. If the variable is to the right from the assignment operator, it represents the old (preceding) value. For example, the formula $[*] = [*] - [G]$ means "let the total system composition at the current step be equal to the total system composition at the preceding step minus the bulk composition of the gaseous phase obtained at the preceding step".

Note that T and P have the same "double meaning" (eg, you can write $T = T + 1$, which means that at each calculation step the temperature is incremented by 1).

Creating *.CT file

Modelling of geochemical processes in HCh involves circular calculations of equilibrium compositions of a chemical system (reactor) under changing input condition. To define an algorithm for such circular calculations you are provided with an on-screen chart of a computation loop. The loop consists of several blocks defining loop initialisation, an algorithm for setting the state variables for a calculation step, GIBBS run-time options, and a termination condition. Using this graphical interface you can select, view and edit each block of the model loop:

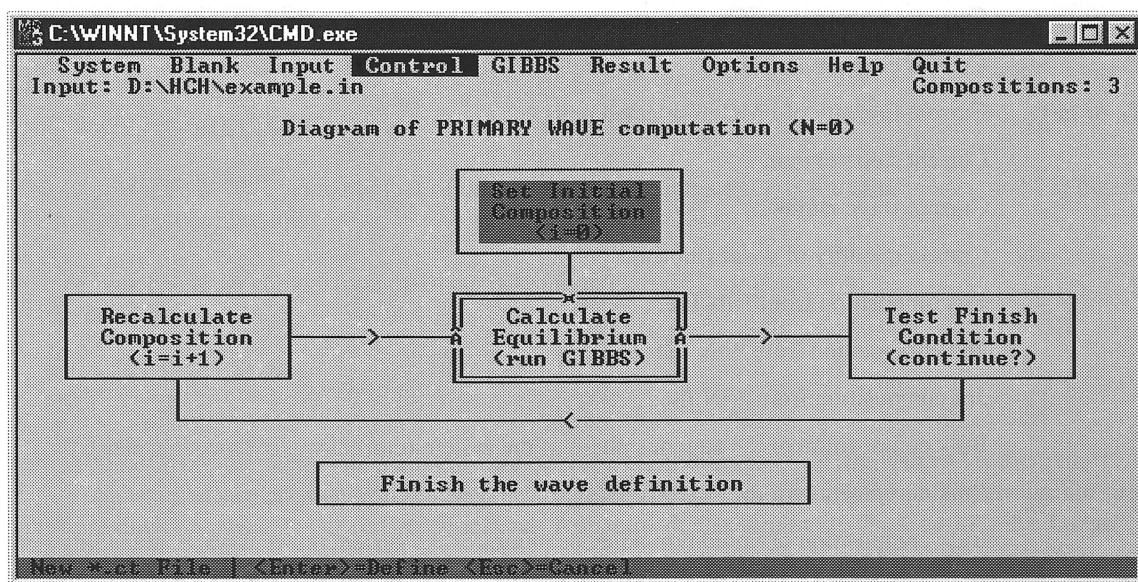


Figure 3. HCh graphical interface for model definition. Use arrow keys to navigate within the window.

1. From the Control menu, choose **New**.
2. The directive "Choose Input (*.in) file" appears.
3. Select the necessary Input file, and press ENTER.
4. If the "Set directory for Control file" directive appears, set the directory where you wish to save the file. Press the drive letter to choose the drive, and select the necessary directory using the ENTER and arrow keys. Press ESC to accept the selected directory. Just press ESC if no changes are required.
5. Using the graphical interface define the algorithm for computation of the Primary ($N = 0$) wave. Use arrow keys to select the necessary definition block.
 - Choose the block "Set Initial Composition ($i = 0$)". Input temperature, pressure, fugacities of computed PMC (if any), and the total system composition for the initial state of the system (this block is optional; see Appendix 4, "Examples of Control Files Usage"). Press ESC.
 - Choose the block "Recalculate Composition ($i = i + 1$)". Input the expressions that define changes of temperature, pressure, fugacities of PMC (if any), and the total system composition on the i -th ("general") step of the Primary wave ($i = 1, 2, \dots$) computation. Press ESC.
 - Choose the block "Calculate equilibrium". If necessary, input options for GIBBS (see "GIBBS Options" on page 44). Press ENTER.
 - Choose the block "Test Finish Condition". Input the condition that defines the length of the Primary wave. Press ENTER.
 - Choose the block "Finish the wave definition". If you have omitted the "Set Initial Composition" step, the warning is displayed; choose "Yes" if the initial step is not required by your model.
6. Answer the question "Should the SECONDARY WAVE be defined also?":
 - choose "Yes" if your model is multi-wave.
 - choose "No" to complete the model definition.
 - choose "Return" (or press ESC) to cancel the question.

7. Define the algorithm of the Secondary ($N = 1, \dots$) wave computation:

- Choose the block "Set Initial Composition ($i = 0$)". Input temperature, pressure, fugacities of computed PMC (if any), and the total system composition on the initial step of the secondary wave (this block must be omitted if it was not used in the Primary wave). Press ESC.
- Choose the block "Recalculate Composition ($i = i + 1$)". Input the expressions which describe the changes of temperature, pressure, fugacities of computed PMC (if any), and the total system composition on the i -th ("general") step of the Secondary wave ($i = 1, 2, \dots$) computation. Press ESC.
- Choose the block "Test Finish Condition". Input the condition which defines the length of the Secondary wave. Press ENTER.
- Choose the block "Finish the wave definition". If no errors are detected, input the condition defining the number of secondary waves. Press ENTER.

8. Input the description of the model (any text), then press ENTER.

9. Input the filename (without the extension). When ENTER is pressed, the new Control file is saved and ready for use.

Note: Each Control file points to one particular Input file, but there can be any number of different Control files that point to the same Input file.

Note: You can omit an optional block of the loop initialisation, ("Set Initial Composition ($i = 0$)") from your Primary wave definition. In this case, calculations by GIBBS will start from the "Recalculate Composition ($i = i + 1$)" block. However, you will not be able to use the block of the loop initialisation in subsequent calculation waves, either.

Viewing *.CT file

1. From the Control menu, choose **View**.
2. Select the necessary *.CT file, and press ENTER.
3. Use the cursor keys for scrolling the file if necessary. The top line of the file contains the reference to the source Blank file.
4. Press ESC to quit.

Editing *.CT file

1. From the Control menu, choose **Edit**.
2. Select the necessary *.CT file, and press ENTER.
3. Use the DOWN arrow or UP arrow keys to move along the column.
4. Press ENTER to modify the current step of your algorithm, the model title, or GIBBS options.
5. Press ESC to complete editing. The new data are saved in the existing *.CT file.

Other operations on *.CT files

The Control menu provides some other commands to manage Control files. You can print, copy, rename, and delete files. When you choose one of these commands you are asked to select a Control file, and the command is performed if you follow the program's directives.

GIBBS Menu

Normally the GIBBS program is called by MAIN.

To calculate the equilibrium composition of a chemical system GIBBS requires information on the total system composition, the possible components of the system and their thermodynamic properties, the temperature and pressure of equilibration. Most of this information is provided by MAIN. Before calling GIBBS, MAIN creates a special file GIBBS.INI that contains:

1. The source files specification and the list of options for GIBBS;
2. The path to the database in use;
3. The path to the MAIN program (this path is required when GIBBS returns the control to MAIN and is included automatically).

Choosing the source file

You can pass either Blank (*.BL), Input (*.IN), or Control (*.CT) file to GIBBS. When you pass an Input file, GIBBS calculates equilibria for the total system composition(s) from this file; when you pass a Blank file you have to define the total system compositions manually during GIBBS execution. In both cases you need to define the temperature and pressure before the calculations begin. When you pass a Control file, no additional input is required.

1. From the GIBBS menu, choose **Source File**.
2. Select the required *.BL, *.IN, or *.CT file and press ENTER. MAIN keeps your choice in memory for further use.

Note: If you call GIBBS without choosing a source file, MAIN passes to GIBBS the file used on the previous call, or the source file specified in its setup file (MAIN.INI). If no file was specified previously, MAIN will ask you to define it.

Setting GIBBS options

MAIN program does not know options for GIBBS. It can only pass to GIBBS a string of characters. See the list of the available options in the "GIBBS Options" section on page 44.

1. From the GIBBS menu, choose **Set Options**.
2. Edit the option list, and press ENTER. MAIN keeps the options in memory for further use.

Note: If you call GIBBS without setting options, MAIN passes to GIBBS the list of options used on the previous call or the options specified in its setup file (MAIN.INI).

Note: GIBBS options for automated equilibrium modelling must be defined within *.CT files. The options defined in *.CT files will override any options defined by means of the "GIBBS" menu.

Calling GIBBS

From the "GIBBS" menu, choose **Run GIBBS**.

If source file has been already specified, the GIBBS.INI file is created and GIBBS is loaded and started. Otherwise you will be requested to choose the source file (see above).

Note: This sequence of operations is available if MAIN knows the path to the GIBBS program. If not, you are requested to specify the GIBBS location prior to the call (see also the **Set Paths** command in the Options menu on page 37).

Result Menu

There are two types of files generated by MAIN and GIBBS programs: ASCII files (their extensions always consist of 3 letters) and binary files (their extensions always consist of 2 letters). All the ASCII files can be used by any external text viewer or editor, but also can be browsed from inside MAIN. The binary files can be processed by means of MAIN only.

ASCII files

Using this command you can work with the following ASCII files: *.PRN, *.STG, *.BLK, *.INP, *.RES, *.REX (generated by MAIN), *.LST (generated by GIBBS), and *.TXT (DOS text files).

1. From the Result menu, choose **ASCII Files**.
2. Select the required ASCII file and press ENTER.
3. Use the arrow keys to browse the file.
4. To delete the file from the disk, press ALT+D.
5. To rename the file, press ALT+R.
6. Press ESC to complete browsing.
7. To edit the file (*.STG only!), press ALT+E. Input or modify Gibbs free energy and/or activity coefficient for the necessary component(s) and press ESC. Confirm that you want to save the modified data.

Warning: If you substitute an energy of an aqueous "basic species" using an *.STG file, the free energies of the related "complexes" will still be calculated by HCh using the energies provided by UNITHERM. Thus, you will need to replace energies of the "daughter" complexes as well.

Binary file

This command allows you to view the contents of the *.RE binary files that are created by GIBBS in the modelling mode. You can also export selected data to .RES and .REX ASCII files (See Appendix 5 on page 59 for details).

1. From the Result menu, choose **Binary File**.
2. Select the required *.RE file and press ENTER.
3. Choose the mode to view the file.

Modelling results in a binary file are represented by a set of points, where each point corresponds to a single equilibrium computation. The points are graphically arranged by MAIN either in a one-dimensional array, or in a table, where rows will correspond to waves, and columns will correspond to steps. Using the graphical interface of MAIN you can examine your equilibrium compositions point by point (Single Points mode) or series by series (Cross Sections mode).

Single points mode

Use the arrow keys to navigate within the table. To view or process the data, use the following keys:

Use		To
Esc	ESC=Exit	Change the browsing mode or terminate the View command.
F	F=File	Change the name of the file (extension .RES) for saving selected results.
P	P=Print	Print the equilibrium composition of the selected point ("reactor").
S	S=Save	Save the equilibrium composition of the selected point in an ASCII file (extension .RES).
ENTER or V	V=View	Show the equilibrium composition of the current point.

Cross Sections mode

Using the Cross Sections mode you can examine your equilibrium compositions series by series.

- Select a particular cross-section mode to examine the modelling results. Press ENTER.

Use	To
Horizontal	To examine the evolution of your points within a computational wave.
Vertical	To examine the evolution of your points for a given reactor (step).
Diagonal (/)	To examine the state of your system at a particular "moment" (a "system shot").

Note: The meaning of particular cross-sections can change if you use a *special* syntax for the Control file vector variables. See pages 31 and 58 for details.

Use the arrow keys to navigate within the table of points and select a series of interest. To view or process the data, use the following keys:

Use	To
C	C=Component Select a system component to show.
Esc	ESC=Exit Change the browsing mode or terminate a command.
O	O=CutOff Truncate the records in the current result (*.RE) file beyond the selected cross-section. Use this command to recalculate a part of your equilibrium-dynamic model starting from a particular reactor/wave. For horizontal cross-sections the command also allows you to delete preceding waves. Use this option to reduce the size of the result file prior to adding additional waves.
S	S=Save Save the table with calculation results for specified components of the selected cross-section. The table is saved in an ASCII file with .REX extension.
TAB	TAB=Unit Switch between quantity and concentration for the solution components in the "View" mode.
V	V=View Show the component variance along the cross-section.

Note: The ASCII *.REX files are ready for import by a spreadsheet program (eg, EXCEL).

Options Menu

There are several internal switches in MAIN which you can change to make working with the program more convenient for you. Their values are stored in the MAIN.INI file and used for setting the program modes when MAIN starts. MAIN.INI also contains the paths to the UNITHERM database and the GIBBS program, and the data required for GIBBS calls - the source file specification and the list of GIBBS options.

Change Directory Request switch

1. From the Options menu, choose **ChDir Request**.
2. Select one of the following answers, and press ENTER.

Answer	Meaning
All	The directive "Set directory for ... file" is displayed whenever you create *.ST, *.BL, *.IN, or *.CT file (the default setting).
*.st only	The directive "Set directory for ... file" is displayed only on the creation of System files.
None	All files are created in the current directory without additional requests.

Shown Files switch

1. From the Options menu, choose **Set Shown Files**.
2. Select one of the following answers, and press ENTER.

Answer	Meaning
Specific...	MAIN displays only the files relevant to a chosen menu.
All files	MAIN displays all files in the current directory (the default setting).

Delay Time switches

This switch sets the display time for instructions and messages guiding your work.

1. From the Options menu, choose **Set Delay Times**.
2. Select the display time for instructions, and press ENTER.
3. Select the display time for messages, and press ENTER.

The default values are 3 sec for instructions and 2 sec for messages.

Set Paths switches

If you have different versions of thermodynamic databases or GIBBS programs, you might need this command to switch between them. You will also need to use this command if you lose your old MAIN.INI file.

1. From the Options menu, choose **Set Paths**.
2. Select the path you wish to define, and press ENTER.
3. To set path to a UNITHERM database, set the directory with the required version of the database, and press ESC. This database will be used for further work.
4. To set path to a GIBBS program, set the directory with the required version of GIBBS, and press ESC. The selected version of GIBBS will be used for further work.

Note: The ESC key does not terminate execution of the command if the selected directory does not contain the database or the GIBBS program. In this case an error message appears. You can terminate execution of the command by pressing CTRL+Q.

Screen Colours switches

If you want to change the colour palette of MAIN:

1. From the Options menu, choose **Set Colours**.
2. Select the text item for which you want to change the colours, and press ENTER.
3. Change the foreground and/or background colours of the selected item by pressing the arrow keys. The example box enables you to see the results.
4. Press ENTER to accept the colours for the selected item.
5. Press ESC to finish the colour definition session.
6. Accept the changes, or restore the old or default settings.

Note: GIBBS uses the same colour palette as MAIN.

Set Defaults switch

You can use this switch to restore the default settings of the MAIN program.

1. From the Options menu, choose **Set Defaults**.
2. Select the setting you wish to restore, and press ENTER.

Saving settings

By default all the customised settings are lost when the MAIN session is completed. To make them permanent you must save them in the MAIN.INI file.

1. From the Options menu, choose **Save Setup**.
2. Select location for the customised MAIN.INI file, and press ENTER.

Option	Directory
in the current directory	The directory from which MAIN was started.
where MAIN.EXE located	The MAIN directory (common setting).
in another directory	Any directory you like.

Note: When MAIN starts it searches for the MAIN.INI file in the current directory, then (if it is not found) in the MAIN directory.

Tip: The most convenient way to work is probably as follows:

1. Create a separate directory for your data files.
2. Save your MAIN.INI file with the appropriate settings in this directory.
3. Start MAIN from this directory.

Restoring settings from file

At times you might need to restore the MAIN settings from a MAIN.INI file located in a directory other than your current directory or the MAIN directory. To read the settings from this file and set the corresponding modes:

1. From the Options menu, choose **Load Setup** command.
2. Select the required MAIN.INI file, and press ENTER. The file is read and the modes are set.

Working with GIBBS

About GIBBS

GIBBS performs equilibrium calculations on chemical systems using a free energy minimisation technique.

Equilibrium Calculations

When GIBBS starts it reads the GIBBS.INI file, loads the source file (*.BL, *.IN, or *.CT), and reads the corresponding System (*.ST) file. The subsequent procedure differs depending on the type of the source file.

GIBBS reads Control file

In this automated mode the calculations begin immediately. The results of calculations are always saved in a file in the current directory.

If the model is multi-wave, the results will be automatically written into a binary file with the extension .RE. The file will have the same name as the source Control (*.CT) file.

If the model is single-wave, you will be requested to choose between the binary (*.RE) and the ASCII (*.LST) output files. If you select an ASCII file option, you will be able to edit the name of the output *.LST file.

Note: In the modelling mode GIBBS uses the options defined in the *.CT source file.

GIBBS reads Input file

1. Input the value of temperature in °C (default is 25) and press ENTER, or press ESC to quit the program.
2. Input the value of pressure in bars (default is Sat. – saturated vapour pressure for the defined temperature) and press ENTER, or press ESC to return to the previous step.

Calculations begin immediately after pressing the ENTER key. If the Input file contains more than one system composition, the compositions are sequentially processed for the same T and P. The title of the processed composition is displayed in the third screen line. If you think that the calculations are too long and do not want to wait longer, press ESC to terminate them. The message "Process terminated..." appears, and the calculations proceed for the next composition. When all the compositions are processed, the table of results is displayed (see "Table of Results" on page 41).

3. Use the cursor keys for scrolling the table of results if necessary. Press ESC to finish.
4. Choose one of the following answers:

Choose	To
Print	Send the table of results to the printer.
Save in file	Add the table to a file in the current directory.
None	Skip the results (default).
Add as initial values	Save the first equilibrium composition in the source *.IN file. This option is available if (1) calculations for the first composition were not terminated, and (2) the source *.IN file does not already contain initial values.

The program performs the chosen action and returns to the start. Now you may change temperature and/or pressure and repeat the calculations for the same system compositions. If the *.IN file contains a single system composition and you did not change the temperature and pressure, you may modify the system composition from keyboard and then repeat calculations.

Note: If you start GIBBS using an *.IN file with the previously saved initial values, the corresponding T and P will be offered for input.

GIBBS reads Blank file

1. Input the value of temperature in °C (default is 25) and press ENTER, or press ESC to quit the program.
2. Input the value of pressure in bars (default is Sat. – saturated vapour pressure for the defined temperature) and press ENTER, or press ESC to return to the previous step.
3. If the system is open, input fugacities of all variable PMC (measurement units are displayed on the screen), or press ESC to return to the start.
4. Input quantities of water and elements, ions or substances as specified in the *.BL file (units are displayed on the screen), or press ESC to return to the start.

If you input quantities of ions, you might get the message on non-zero charge balance. If this is the case, choose one of three offered ways for correction of the system composition.

5. Input the composition title and press ENTER (to return to start press the ESC key as usual). Calculations begin immediately.

If you think that the calculations are too long and do not want to wait longer, press ESC to terminate them. The message "Process terminated..." appears, and the program returns to the start. If the job is successfully completed, the table of results is displayed (see "Table of Results" on page 41)

6. Use the cursor keys for scrolling the table of results if necessary. Press ESC to finish.
7. Choose one of the following options: "Print", "Save to file", "None", and "Add as initial values" (see the previous section).

After returning to the start, you can modify temperature, pressure, and/or total system composition and repeat calculations for the new values.

Note: If you start GIBBS using a *.BL file with the previously saved initial values, the first cycle of calculations begins immediately.

Tables of Results

Standard table of results

This table is displayed when GIBBS calculations in non-automated mode are successfully completed. It can be saved in a text file with the fixed extension .LST. If the file with the specified name already exists, the table will be added to its end. The tables of results within the *.LST file will be separated by the page separator code (ASCII 12). In the general case the table of results is structured as follows:

Data	Quantity and Concentration units	Activity coefficients
System title Temperature Total pressure		
Compositional data (columns 1 - 3)		
Input data		
Composition titles		
Total system compositions (including fugacities of PMC for open systems) in user specified substances	User-specified	
Output data		
• Pure phases		
Equilibrium assemblage of pure phases	Moles + Mass fractions (%) in the bulk solid phase*	
Total number of moles of pure phases	Moles	
Bulk composition of pure phases in terms of chemical elements	Moles**	
Total number of moles of chemical elements	Moles	
• Solid solutions		
Equilibrium composition of a solid solution	Mole fractions	Rational ⁷
Total number of moles of end-member substances + mass fraction (%) of the solid solution in the bulk solid phase	Moles + Mass fraction (%) in the bulk solid phase**	
Bulk composition of the solid solution in terms of chemical element	Moles**	
Total number of moles of chemical elements	Moles	
• Non-aqueous liquid solutions		
Equilibrium composition of a liquid solution	Mole fractions	Rational
Total number of moles of end-member substances	Moles	
Bulk composition of the liquid solution in terms of chemical element	Moles**	
Total number of moles of chemical elements	Moles	

See next page

⁷ Mole fraction basis

Data	Quantity and Concentration units	Activity coefficients
● Gaseous mixture		
Equilibrium composition of the gaseous mixture	Mole fractions	Rational
Total number of moles of gases	Moles	
Bulk composition of the gaseous mixture in terms of chemical element	Moles**	
Total number of moles of chemical elements	Moles	
● Aqueous solution		
Equilibrium concentration of water	Mole fraction	Rational
Equilibrium concentrations of aqueous species	Molality	Molal
Ionic strength	Molality	
pH		
Eh ***		
Bulk composition of the aqueous solution in terms of:		
Water	Moles**	
Chemical elements in the aqueous phase excluding water	Moles**	
● GIBBS run options (optional)		

* Bulk solid phase comprise pure phases (minerals) and solid solutions.

** Moles by default. You can specify your own output units using the /o GIBBS option (see "GIBBS Options" on page 44 for details).

*** Eh value is output only if you included the H₂ (aq) species in your aqueous speciation model.

Note: The activity coefficients of components of ideal solutions are always set to one. See Appendix 2, "Definition of Solid Solution Models", for clarification.

Note: Tables of results produced by GIBBS in the modelling mode are not displayed when calculations are completed. Instead they are automatically written into the file that you have specified at the start of the calculations.

In comparison with the tables of results produced by GIBBS in a non-automated mode, they do not contain information on the initial system compositions (except the fugacities of the PMC).

Tables extracted from binary files

Tables of results can also be extracted from the binary *.RE files produced by GIBBS in a modelling mode (see "Result Menu" on page 35). However, these tables contain reduced information in comparison with the text *.LST files.

Data	Quantity and Concentration units
Step information	
Wave number	
Step number	
Temperature	
Total pressure	
Fugacities of PMC for open systems	
Compositional output data	
• Pure phases	
Equilibrium assemblage of pure phases	Moles
• Solid solutions	
Equilibrium composition of a solid solution	Mole fractions
Total number of moles of end-member substances	Moles
• Non-aqueous liquid solutions	
Equilibrium composition of a liquid solution	Mole fractions
Total number of moles of liquids	Moles
• Gaseous mixture	
Equilibrium composition of the gaseous mixture	Mole fractions
Total number of moles of gases	Moles
• Aqueous solution	
Equilibrium concentration of water	Mole fraction
Equilibrium concentrations of aqueous species	Molality
pH	
Eh	
Bulk composition of the aqueous solution in terms of:	
Water	Moles
Chemical elements in the aqueous phase excluding water	Moles

Note: Data on the activity coefficients of the solution components are not provided.

Note: Data from the binary *.RE files can be exported to text files (*.REX) ready for import by a spreadsheet program (eg, EXCEL). The structure of these files is very similar to the structure of the *.RES text files, but the bulk compositions of phases in terms of chemical elements are omitted.

GIBBS Options

At times you might want to run GIBBS in a specific mode. To this end you should specify one or more GIBBS options, which are defined as a string of characters (*eg*, */i/s/t/c=@1/b=@1*). The options can be passed to GIBBS using (1) the Gibbs menu of MAIN or (2) the Calculate Equilibrium block of a Control file.

Use	To
	Modify the output listing (*.LST files only):
<i>/i</i>	Add the list of options to the output listing.
<i>/o=<value></i>	Output bulk compositions in specified units where <value> = mol (default) kg g mg mkg.
<i>/t</i>	Output calculation time.
<i>/x</i>	Exclude concentrations of aqueous species from the listing.
	Change the calculation mode:
<i>/b=@n</i>	Specify the algorithm for reading and/or calculation of Setchénow coefficients of neutral aqueous species. See Appendix 3 for details. You can change the @n value at run time by pressing ALT+B when you define or change temperature or pressure.
<i>/b=<value></i>	Set the common Setchénow coefficient for all the neutral species equal to <value>. You can change the <value> at run time by pressing ALT+B when you define or change temperature or pressure.
<i>/c=@n</i>	Set the extended parameter of the Debye-Hückel equation equal to <i>bγ</i> value for the specified background electrolyte (Oelkers and Helgeson, 1990) (<i>eg</i> , <i>/c=@1</i> defines NaCl) and to replace all the default ion size parameters (Å) with the ion size parameters calculated for the given electrolyte (Shock et al., 1992). See Appendix 3 for details. You can change the @n value at run time by pressing ALT+C when you define or change temperature or pressure.
<i>/c=<value></i>	Set the extended parameter of the Debye-Hückel equation equal to <value>. You can change the <value> at run time by pressing ALT+C when you define or change temperature or pressure.
<i>/g</i>	Use an *.STG file for free energies and/or activity coefficients substitution. The string “(Subst On)” is added to the system title to indicate that the substitution mode is active. If the *.STG file is not found in the same directory as the corresponding *.ST file, the <i>/g</i> option will be ignored without any warning messages. Warning: If you substitute an energy of a “basic species” using an *.STG file, the free energies of the related “complexes” will still be calculated using the default energies provided by UNITHERM. Thus, you will need to replace energies of the “daughter” complexes as well.
<i>/s</i>	Compute sequentially. When you set this option, the program uses the equilibrium composition obtained at the previous step as an initial approximation for the next step. This makes computations faster if the differences between total system compositions are small. Without this option all the compositions are processed independently. Do not set this option if the compositional differences between computation steps are significant.
<i>/<value></i>	Re-set the internal numerical threshold for mass-conservation equations balance (the default value is /6). Note: this is an emergency switch! You do not need to change this value in your routine practice. Decrease this value (<i>eg</i> , set it to /5) if you have convergence problems; Increase this value (<i>eg</i> , set it to /7 or /8) if you are “loosing” minor components from your modelling jobs.
<i>/w</i>	Calculate the activity of water according to the revised HKF model (Helgeson et al., 1981). This option must be used together with the <i>/c=@n</i> option (<i>/c=@n /w</i>).

References

Employed Models and Algorithms

- Borisov, M. V., and Shvarov, Yu. V., 1992, Thermodynamics of geochemical processes: Moscow, Moscow State University Publishing House, 254 p (in Russian).
- Ding, K., and Seyfried, W. E., 1990, Activity coefficients of H_2 and H_2S in NaCl solutions at 300°-425°C, 300-500 bars with application to ridge crest hydrothermal systems: EOS, v. 71, 43, p. 1680.
- Helgeson, H. C., 1969, Thermodynamics of hydrothermal systems at elevated temperatures and pressures: American Journal of Science, v. 267, 7, p. 729-804.
- Helgeson, H. C., Kirkham, D. H., and Flowers, G. C., 1981, Theoretical prediction of the thermodynamic behaviour of aqueous electrolytes at high pressures and temperatures: Calculation of activity coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 600°C and 5 kb: American Journal of Science, v. 281, 10, p. 1249-1516.
- Johnson, J. W., Oelkers, E. H., and Helgeson, H. C., 1992, SUPCRT92: a software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bars and 0 to 1000°C: Computers and Geosciences, v. 18, 7, p. 899-947.
- Kestin, J., Sengers, J. V., Kamgar-Parsi, B., and Levelt Sengers, J. M. H., 1984, Thermophysical properties of fluid H_2O : Journal of Physical & Chemical Reference Data, v. 13, 1, p. 175-183.
- Korzhinskii, D. S., 1965, The theory of systems with perfectly mobile components and processes of mineral formation: American Journal of Science, v. 263, 3, p. 193-205.
- Marshall, W. L., and Franck, E. U., 1981, Ion product of water substance, 0-1000°C, 1-10000 bars new international formulation and its background: Journal of Physical & Chemical Reference Data, v. 10, 2, p. 295-304.
- Nordstrom, D. K., and Munoz, J. L., 1994, Geochemical thermodynamics, Blackwell Scientific Publications, 493 p.
- Oelkers, E. H., and Helgeson, H. C., 1990, Triple-ion anions and polynuclear complexing in supercritical electrolyte solutions: Geochimica et Cosmochimica Acta, v. 54, 3, p. 727-738.
- Powell, R., 1977, Activity-composition relation for crystalline solutions, in Fraser, D. G., editor, Thermodynamics in geology: Dordrecht, D. Reidel Publishing Company, p. 57-65.
- Shock, E. L., Oelkers, E. H., Johnson, J. W., Sverjensky, D. A., and Helgeson, H. C., 1992, Calculation of the thermodynamic properties of aqueous species at high pressures and temperatures: J. Chem. Soc. Faraday Trans., v. 88, 6, p. 803-826.
- Shvarov, Yu. V., 1976, Calculation of equilibrium composition in a multicomponent heterogeneous system: Transactions (Doklady) of the U.S.S.R. Academy of Sciences: Earth Science Sections, v. 229, 1-6, p. 223-225.
- Shvarov, Yu. V., 1978, Minimization of the thermodynamic potential of an open chemical system: Geochemistry International, v. 15, 6, p. 200-203.
- Shvarov, Yu. V., 1981, A general equilibrium criterion for an isobaric-isothermal model of a chemical system: Geochemistry International, v. 18, 4, p. 38-45.
- Shvarov, Yu. V., 1987, Use of the electrical neutrality equation in calculations on the equilibrium compositions of geochemical systems: Geochemistry International, v. 24, 2, p. 131-135.
- Shvarov, Yu. V., 1989, A numerical criterion for existence of the equilibrium state in an open chemical system: Sciences Geologiques (Bulletin), v. 42, 4, p. 365-369.
- Suleimenov, O. M., and Krupp, R. E., 1994, Solubility of hydrogen sulfide in pure water and in NaCl solutions, from 20 to 320°C and at saturation pressures: Geochimica et Cosmochimica Acta, v. 58, 11, p. 2433-2444.
- Tanger, J. C. I., and Helgeson, H. C., 1988, Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Revised equations of state for the standard partial molal properties of ions and electrolytes: American Journal of Science, v. 288, 1, p. 19-98.

Example HCh/GIBBS Applications

A few recent references to case studies that employed the HCh program package or the GIBBS program:

Hydrothermal Geochemistry

- Pokrovskii, V. A., and Helgeson, H. C., 1991, Unified description of incongruent reactions and mineral solubilities as a function of bulk composition and solution pH in hydrothermal systems: *The Canadian Mineralogist*, v. 29, 4, p. 909-942.
- Grichuk, D. V., 1996, Ore elements in midoceanic ridge hydrothermal systems: *Geochemistry International*, v. 35, 7, p. 586-606.
- Ryzhenko, B. N., Barsukov, V. L., and Knyazeva, S. N., 1996, Chemical characteristics (composition, pH, and Eh) of a rock-water system: 1. The granitoids-water system: *Geochemistry International*, v. 34, 5, p. 436-454.
- Kolonin, G. R., Pal'yanova, G. A., Shironosova, G. P., and Morgunov, K. G., 1997, The effect of carbon dioxide on internal equilibria in the fluid during the formation of hydrothermal gold deposits: *Geochemistry International*, v. 35, 1, p. 46-57.
- Ryzhenko, B. N., Barsukov, V. L., and Knyazeva, S. N., 1997, Chemical characteristics (composition, pH, and Eh) of the rock-water system: II. Diorite (andesite)-water and gabbro (basalt)-water systems: *Geochemistry International*, v. 35, 12, p. 1227-1254.
- Borisov, M. V., and Shvarov, Yu. V., 1998, Mobilization of ore components during the formation of Pb-Zn hydrothermal lodes: a thermodynamic model: *Geochemistry International*, v. 36, 2, p. 134-149.

Processing of Experimental Data

- Pokrovskii, V. A., and Helgeson, H. C., 1995, Thermodynamic properties of aqueous species and the solubilities of minerals at high pressures and temperatures: the system $\text{Al}_2\text{O}_3\text{-H}_2\text{O-NaCl}$: *American Journal of Science*, v. 295, 10, p. 1255-1342.
- Bastrakov, E. N., Pokrovskii, V. A., and Heinrich, C. A., 1997, Gold in hydrothermal solutions: thermodynamic properties of $\text{Au}(\text{HS})_2^-$ and solubility of gold at high pressures and temperatures, Seventh Annual V.M.Goldschmidt Conference, LPI Contribution No. 921: Tucson, Arizona, Lunar and Planetary Institute, Houston, p. 19.
- Suleimenov, O. M., and Seward, T. M., 1997, A spectrophotometric study of hydrogen sulphide ionisation in aqueous solutions to 350°C: *Geochimica et Cosmochimica Acta*, v. 61, 24, p. 5187-5198.

Appendices

Appendix 1. Brief Summary of HCh specifications

Note: Specifications are provided for HCh v. 3.3, May 1999

Hardware Requirements

IBM PC AT-compatible computers; 640Kb RAM; EGA monitor and better; hard disk; floppy disk; keyboard. Math co-processor not necessary but highly recommended.

HD space: 1 Mb for the initial installation.

Operating Systems

MS-DOS 3.3 and higher, Windows 3.x, Windows 9x/NT;
DOS-emulating packages for the Macintosh computers.

Databases

Number of user-defined databases: Unlimited

Database usage: One at a time

Database components and capacity

Stoichiometry units:	Chemical elements	105	Standard (conventional)
		≤150	User-defined (see page 16)

Database components	Database capacity	Chemical compounds	Equation of state	Comment	Guide Page
Pure water		Pure water	Haar-Gallagher-Kell model (Kestin et al., 1984).		9
Basic species	1023	Simple ions, some polyatomic ions, and aqueous complexes	The revised Helgeson-Kirkham-Flowers equations of state (MHKF) (Shock et al., 1992; Tanger and Helgeson, 1988).		9
Complexes	1023	Aqueous complexes	The modified Ryzhenko-Bryzgalin model (Borisov and Shvarov, 1992).		10
Pure phases	1023	Minerals, gases, and non-aqueous liquids	Conventional integration of heat-capacity equations *.	Allowed number of phase transitions in minerals: 4; the maximum number of the $C_p(t)$ equations: 5.	11
Total	3069				

*** Note:**

1. $C_p(t) = a + b \cdot T + c \cdot T^{-2} + d \cdot T^{-0.5} + e \cdot T^2 + f \cdot T^3 + g \cdot T^4 + h \cdot T^{-3} + i \cdot T^{0.5} + j \cdot T^{-1}$.
2. No provisions for calculation of mineral compressibilities.

Allowed Model Phases and Solution Models

Phases	Maximum number of phases	Solution model and calculation of activities	Maximum number of components in the solution phase	Guide Page
Pure solids (minerals), liquids and gases	255			
An aqueous solution (including the supercritical aqueous phase)	1	Water: $\gamma=1$ or according to the HKF model (Helgeson et al., 1981). Charged species: extended versions of the Debye-Hückel equation (Helgeson, 1969; Helgeson et al., 1981; Oelkers and Helgeson, 1990). Neutral species: Setchénow equation (eg, Oelkers and Helgeson, 1990).	255	44 52 53
A gaseous mixture	1	Ideal	255	
Liquid non-aqueous solutions	Unlimited *	1. Ideal 2. Non-random two-liquid (NRTL)	50 6	
Solid solutions (ideal multi-site mixing)	Unlimited *	Ideal: 1. Molecular 2. Mixing-on-sites (MOS, 4 sites allowed) 3. Local charge balance (LCB)	50 20 20	50 50

* **Note:** The maximum total number of phases and components in a system is restricted by the available conventional memory (DOS), and will vary depending on a particular problem and computer configuration.

Special Notes

Recommended T-P range for systems containing aqueous solution:	0 – 1000°C, 1 – 5000 bar at water densities exceeding 0.35 g/cm ³ (according to the MHKF model; see above)
Allowed salinity range for systems containing aqueous solution:	Limited by the applicability of the extended versions of the Debye-Hückel equation (see above).

Limitations of Chemical models

The maximum number of chemical elements allowed in models: 30

Limitations of Equilibrium-Dynamic Models

The number of calculation steps in model definition loops:	Unrestricted; the convenient range is 1..73.
The number of waves (loops):	Limited by the size of the output file accessible for processing by the package. The theoretical maximum is constrained by 64,000 calculation points, but in practice might be less. The exact number will vary depending on a particular computer configuration. This limitation is not critical due to the MAIN CutOff command (see page 36).

Appendix 2. Definition of Solid Solution Models

Currently you can specify in the HCh package ideal mixing-on-sites (MOS) models for solid solutions. The maximum number of mixing sites allowed in the program is 4.

To specify an ideal mixing-on-site model for a given solid solution, fill in the table which is displayed when you create a new System (*.ST) file. The columns numbers (1..4) correspond to different mixing sites. Coefficients in the upper column cells represent the stoichiometric coefficients for the sites. Other cells are allocated for chemical elements (ions) mixing on the specified sites.

For example, consider garnets of the generalised formula $X_3Y_2(SiO_4)_3$ in which mixing can occur independently on the eightfold X sites and the sixfold Y sites (Nordstrom and Munoz, 1994). The mixing is restricted to Al^{+++} and Fe^{+++} in the octahedral site and Mg^{++} , Fe^{++} , and Ca^{++} in the cubic site. The end-member components and their compositions are andradite ($Ca_3Fe_2(SiO_4)_3$), grossular ($Ca_3Al_2(SiO_4)_3$), pyrope ($Mg_3Al_2(SiO_4)_3$) and almandine ($Fe_3Al_2(SiO_4)_3$). To specify the ideal MOS model in HCh you need to fill in the solid-solution table as follows:

Solid solution: Garnet (ideal)				
	1	2	3	4
Coefficient	3	2		
1. Andradite	Ca	Fe		
2. Grossular	Ca	Al		
3. Pyrope	Mg	Al		
4. Almandine	Fe	Al		

As mixing occurs only on two sites, the columns 3-4 are left blank.

Note: If you ignore this table (just by pressing ESC), the end-members of the solid solution will be treated as "molecular" species.

When the mixing ions have different charges, it is also possible to specify a local charge balance (LCB) model. In this case, because of the charge balance, a group of atoms exchanges as a whole, *eg*, $CaAl - NaSi$, and should be formally considered as mixing on one site. Thus you can ascribe to these complexes separate single ions (*eg* Al for $CaAl$, and Si for $NaSi$), and use them in the solution definition table. Note that the specified ions will not have any physical meaning, but will be used by the program only to determine whether pairs of exchanged ions are different or not.

For example, to specify a LCB model for the albite-anorthite solid solution ($NaAlSi_3O_8 - CaAl_2Si_2O_8$) you need to fill in the solid-solution table as follows:

Solid solution: Plagioclase (ideal)				
	1	2	3	4
Coefficient	1			
1. Albite	Si			
2. Anorthite	Al			

The activities of the end-member components are calculated by GIBBS according to the expression:

$$a = \tilde{\gamma} \cdot \tilde{X},$$

where \tilde{X} is an appropriate function of the concentration of the end-member component in the solution ("thermodynamic" mole fraction of (Powell, 1977), and $\tilde{\gamma}$ is the corresponding activity coefficient. For ideal solid solutions $\tilde{\gamma} = 1$ and $a_{ideal} = \tilde{X}$. The thermodynamic mole fraction for the ideal multi-site mixing is calculated as the product of mole fractions of the *site* components (elements) raised to the power of the site stoichiometric coefficients:

$$\tilde{X} = \prod_i X_i^{N_i}.$$

Note: The composition of a given solid solution in the GIBBS output listing is expressed in terms of the chosen end-member minerals on the conventional mole fraction basis. The activity coefficients of the end-member minerals are always set to 1 according to the provided definition of the ideal solid solution.

Note: You may assign any activity coefficient (γ) for an end-member component by using the /g option of GIBBS (see "Exporting *.ST files to ASCII files" on page 24 and "GIBBS Options" on page 44). In this case the activity of the component will be calculated as the product of the ideal activity and the specified activity coefficient:

$$a = \gamma \cdot a_{ideal} = \gamma \cdot \prod_i X_i^{N_i} .$$

Appendix 3. Calculation of Activity Coefficients of Aqueous Species

Activity coefficients of all aqueous species are calculated for the molality scale of concentration.

Charged Aqueous Species

Activity coefficients of charged aqueous species are calculated by GIBBS according to the extended Debye-Hückel equation. The necessary parameters for their calculation are provided by the UT_SIZES.REF and UT_ELECT.REF database files.

By default activity coefficients of charged aqueous species are calculated according to Helgeson (1969):

$$\log \gamma_i = -\frac{Az_i^2 \sqrt{I}}{1 + B\tilde{a}\sqrt{I}} + \Gamma_\gamma + B \bullet (T) \cdot I,$$

where Γ_γ designates the mole fraction to molality conversion factor given by $\gamma = -\log(1 + 0.0180153 \cdot m^*)$, and m^* symbolises the sum of the molalities of all solute species in solution. This expression is equivalent to $\Gamma_\gamma = \log(X_w)$, where X_w represents the mole fraction of water in solution.

Ion size parameters (\tilde{a}) for particular ions are considered to be temperature-independent and are kept in the UT_SIZES.REF file (UT_RADII.REF in earlier HCh versions). If there is no specified individual value for a particular ion, the ion size parameter is set to the default value of 4.5 Å.

Using a special GIBBS option (*/c = <value>*) you can also set the extended parameter of the Debye-Hückel equation to a common arbitrary value (eg, */c = -0.2*).

Using a special GIBBS option (*/c = @n*) you can choose the calculation of activity coefficients of charged aqueous species according to Oelkers and Helgeson (1990) for a specified background electrolyte *MX*:

$$\log \gamma_i = -\frac{Az_i^2 \sqrt{I}}{1 + B\tilde{a}\sqrt{I}} + \Gamma_\gamma + b_\gamma I.$$

In this case the ion size parameters for all the ions are calculated by GIBBS according to Shock et al. (1992):

$$\tilde{a} = r_{e,M+} + r_{e,X-},$$

where r_e is an effective electrostatic radius of an ion depending on temperature and pressure.

- To specify electrolytes from the default UT_ELECT.REF database file

Set	For	Set	For
<i>/c = @1</i>	NaCl-dominated solutions.	<i>/c = @3</i>	KOH-dominated solutions.
<i>/c = @2</i>	NaOH-dominated solutions.	<i>/c = @4</i>	KCl-dominated solutions.

Note: All these options can be changed at GIBBS run-time by pressing ALT+C when you define or change temperature or pressure (just omit the slash from the option definition). You can also remove them by specifying the "c=" option.

For information about setting GIBBS options, see Chapter 2, "Gibbs Options" (page 44).

Neutral Aqueous Species

Activity coefficients of neutral aqueous species are calculated by GIBBS according to the Setchénow equation (eg, Oelkers and Helgeson, 1990):

$$\log \gamma_n = \Gamma_\gamma + b_n \cdot I,$$

where b_n is the Setchénow coefficient (b-Setch in HCh notation). By default, $b_n = 0$, and

$$\log \gamma_n = \Gamma_\gamma.$$

Note: By default, activity coefficients of neutral aqueous species in HCh versions prior to 3.3 were calculated according to the degenerative version of the extended Debye-Hückel equation:

$$\log \gamma_n = \Gamma_\gamma + B \bullet (T) \cdot I, \text{ or}$$

$$\log \gamma_n = \Gamma_\gamma + b_\gamma \cdot I.$$

You can still use this algorithm by specifying the GIBBS command-line option `/b=@0` (see below).

Note: The old `/0` option for calculation of activity coefficients of neutral species is now disabled.

Using the GIBBS command-line options `/b=@n` and `/b=<value>` you can specify direct reading or calculation of Setchénow coefficients by GIBBS in a number of possible ways.

Option	Algorithm
<code>/b = @0</code>	The common "Setchénow" coefficient for all the neutral species is equal either to b-dot or b-gamma values of the extended Debye-Huckel equation (the old default option).
<code>/b = @1</code>	The individual Setchénow coefficients are read from the ion "size" fields of the neutral species in a relevant System (*.ST) file.
<code>/b = @2</code>	The common Setchénow coefficient for all the neutral species is calculated as a function of temperature ($0 < t < 374^\circ\text{C}$) according to (Suleimenov and Krupp, 1994) approximation for H_2S (aq). Any values entered in the "size" fields of the neutral species in your *.ST file will be ignored.
<code>/b = @3</code>	The common Setchénow coefficient for most of the neutral species is calculated as a function of temperature and pressure according to an empirical fit for H_2S (aq) based on Ding and Seyfried (1990) and Suleimenov and Krupp (1994) (Bastrakov and Pokrovskii, personal communication). Any non-zero values entered in the "size" fields of the neutral species will be used as "scaling" factors to calculate individual Setchénow coefficients relative to the Setchénow coefficients of H_2S : $b_n = a \cdot b_n(\text{H}_2\text{S})$. For further clarification see examples provided below.
<code>/b = <value></code>	The Setchénow coefficients for all the neutral species are set to a common arbitrary value (eg, <code>/b = 0.46</code>). Any Setchénow values entered in the "size" fields of the neutral species in your *.ST file will be ignored, and any other built-in algorithms suppressed.

Note: All these options can be changed at GIBBS run-time by pressing ALT+B when you define or change temperature or pressure (just omit the slash from the option definition). You can also remove them by specifying the "b=" option.

For information about setting GIBBS options, see Chapter 2, "Gibbs Options" (page 44).

Examples of *.ST file modification

To specify direct reading or calculation of Setchénow coefficients by GIBBS, you might need to modify your System file in one of the following ways:

/b=@0:

Not applicable. Any individual values entered in the "size" fields of your *.ST file will be ignored.

/b=@1:

```

      H O Cl  S Na  z  a
* * * Aqueous solution * * *
0.  2  1  0  0  0  0  0.00  H2O
1.  1  0  0  0  0  1  9.00  H+
2.  1  1  0  0  0 -1  3.50  OH-
3.  0  2  0  0  0  0  0.46  O2      # Individual value
4.  2  0  0  0  0  0  0.60  H2      # Individual value
5.  2  0  0  1  0  0  0.46  H2S     # Individual value
6.  1  0  0  1  0 -1  3.50  HS-
7.  0  0  0  2  0 -2  4.50  S2--
8.  0  3  0  2  0 -2  4.50  S2O3--
9.  0  2  0  1  0  0  0.46  SO2     # Individual value

```

/b=@2:

Not applicable. Any individual values entered in the "size" fields of your *.ST file will be ignored.

/b=@3:

```

      H O Cl  S Na  z  a
* * * Aqueous solution * * *
0.  2  1  0  0  0  0  0.00  H2O
1.  1  0  0  0  0  1  9.00  H+
2.  1  1  0  0  0 -1  3.50  OH-
3.  0  2  0  0  0  0  1.00  O2      # Scaling factor re H2S
4.  2  0  0  0  0  0  1.30  H2      # Scaling factor
5.  2  0  0  1  0  0  1.00  H2S     # Scaling factor
6.  1  0  0  1  0 -1  3.50  HS-
7.  0  0  0  2  0 -2  4.50  S2--
8.  0  3  0  2  0 -2  4.50  S2O3--
9.  0  2  0  1  0  0  0.00  SO2     # Scaling factor; Note that
                                     # 0.00 = 1.00 (!)

```

/b=<value>:

Not applicable. Any individual values entered in the "size" fields of your *.ST file will be ignored, and any other built-in algorithms for calculation of Setchénow coefficients suppressed.

Appendix 4. Examples of Control Files Usage

See "Control File Conventions" on page 30 for the list of the variables permissible for model definitions. The example files provided below are commented by the hash sign (#).

- EXAMPLE 1 Calculation of diagrams, titration and mixing calculations.
- EXAMPLE 2 Modelling of dynamic processes at steady-state conditions.
- EXAMPLE 3 Modelling of progressive fluid-rock interaction by the
"flow-through" reactor technique, *eg* metasomatic zoning.

EXAMPLE 1: Titration and Mixing Calculations

Geological model

Rock of a given composition is equilibrated with an aqueous solution at constant temperature and pressure. The object of the modelling is to define the equilibrium alteration assemblages and aqueous solution compositions at increasing rock-to-water ratios, R/W (*eg*, from 10^{-5} to 10^5) with a step of 1 log units.

Preparation steps

After the routine preparation of the files defining a chemical system of interest (*.ST and *.BL) you should create an Input file (*.IN) with two separate bulk compositions for the aqueous solution [1] and the rock [2] (*eg*, 1 kg of each).

Numerical model

The numerical model of the titration can be represented by a number of reactors of variable bulk composition defined as a function of the titration step (i) in terms of the initial rock and solution:

$$[*] = [1] + [2] * 10^{(i-6)},$$

where [*] is the bulk chemical composition of the reactor at the i-th step. To characterise the rock-to-water ratios as within the specified limits (from 10^{-5} to 10^5) you should define the power of the multiplier of the rock amount as (i-6).

Now you can prepare your Control file. Note that for this particular problem you do not need to use the block of the loop initialisation ("Set Initial Composition (i=0)").

```
Input file: Filename
Wave model: Titration
GIBBS options: /S
* * * Primary wave * * *
      Initial step...      # Not required for this problem
      General step...      # Model definition
Temperature,C  T = 300     # Titration at constant temperature
Pressure,bar   P = 500     # Titration at constant pressure
Composition [*] = [1]+[2]*10^(i-6) # Calculation of increasing R/W
      Stop when: i=11      # Loop until i = 11 (R/W = 1E+05)
* * * End of file * * *
```

Now you are ready to run GIBBS.

File of results

The modelling results can be optionally written either into an ASCII (*.LST) or binary (*.RE) output file. On the basis of your Control file instructions GIBBS will output the sequence of 11 equilibrium compositions defining the overall direction of the particular water – rock interaction.

EXAMPLE 2: Modelling of Processes at Steady-State Conditions

Geological model

An aqueous solution is equilibrated with a rock of a given composition at some temperature and pressure at rock-buffered conditions ($R/W \gg 1$). The resulting solution saturated with all the rock components is ascending along a fault zone towards the Earth's surface. The object of the modelling is to define the mineral composition of the resulting vein material.

Preparation steps

After the routine preparation of the files defining a chemical system of interest (*.ST and *.BL) you should create an Input file (*.IN) with two separate bulk compositions for the initial aqueous solution [1] and the rock [2] (eg, 1 kg of each).

Numerical model

The bulk chemical composition of the reactor ([*]) at a general computation step can be defined in terms of the aqueous solution isolated from the equilibrium rock at the preceding step:

$$[*] = [A].$$

Thus the outlined algorithms requires sequential computation of the reactor composition.

Note: To define the bulk chemical composition of an equilibrium reactor using sequential computation you **must** specify the initial step in your wave model. In the general case the initial step is not mandatory.

Now you can prepare your Control file:

```
Input file: Filename
Wave model: Modelling of the vein mineral composition
GIBBS options: /S
* * * Primary wave * * *
    Initial step...      # Modelling of the initial equilibration:
    Temperature,C  T = 300      # Temperature at the initial depth
    Pressure,bar   P = 0        # Pressure = PSAT for a given temperature
    Composition [*] = [1]+[2]*100 # Initial rock-to-water ratio is set to 100
    General step...      # Modelling of precipitating minerals:
    Temperature,C  T = T-2      # Step of the temperature change (-2°C)
    Pressure,bar   P = 0        # PSAT for the new temperature
    Composition [*] = [A]      # Only the solution is ascending
    Do while: T>0          # Loop until the complete cooling
* * * End of file * * *
```

Now you are ready to run GIBBS.

File of results

The modelling results can be optionally written either into an ASCII (*.LST) or binary (*.RE) output file. On the basis of your Control file instructions GIBBS will output the sequence of 150 equilibrium compositions defining the mineral zoning of the model vein.

EXAMPLE 3: Modelling of Progressive Fluid-Rock Interaction by the "Flow-Through" Reactor Technique

Geological model

Progressive fluid-rock interaction in an open geochemical system at near-surface conditions (eg, the formation of roll-front U deposits by U leaching and re-deposition). An initially "fresh" aqueous solution percolates through a rock at constant temperature and pressure. The object of the modelling is to define the spatial and temporal evolution of the rock and solution compositions.

Preparation steps

After the routine preparation of the files defining a chemical system of interest (*.ST and *.BL) you should write into the input file (*.IN) two bulk compositions characterising the initial aqueous solution [1] and the unaltered rock [2].

Numerical model

The numerical model of the progressive fluid-rock interaction can be defined as number of reactors of variable bulk composition defined in terms of specified amounts of pre-reacted rock and solution:

[*] = [A] + [2] (interaction of the solution with unaltered rock), and

[*] = [A] + {S} (interaction of the solution with rock pre-altered in the previous wave).

Now you can prepare your control file:

```
Input file: Filename
Wave model: Flow-through reactor technique
GIBBS options: /S
* * * Primary wave * * *
    Initial step...
    Temperature,C  T = 25          # Earth surface conditions
    Pressure,bar   P = 1           # Earth surface conditions
    Composition [*] = [1]          # initial solution
    General step...
    Temperature,C  T = T           # isothermic system
    Pressure,bar   P = P           # isobaric system
    Composition [*] = [A] + [2]    # solution interaction with fresh rock
    Do while: i < 50               # 50 reactors are sufficient
* * * Secondary wave * * *
    Initial step...
    Temperature,C  T = 25          # initial conditions are the same
    Pressure,bar   P = 1           # initial conditions are the same
    Composition [*] = [1]          # the leaching solution is the same
    General step
    Temperature,C  T = T           # isothermic system
    Pressure,bar   P = P           # isobaric system
    Composition [*] = [A] + {S}    # solution interaction with altered rock
    Do while: I < 50               # the same length of the wave
* * * Completion condition * * *
    Do while: N < 50               # 50 waves are sufficient
* * * End of file * * *
```

Now you are ready to run GIBBS.

File of results

The modelling results will be written into a binary (*.RE) output file. On the basis of your Control file instructions GIBBS will output the sequence of more than 2500 calculated compositions of the system. They will describe the results of water-rock interaction along the filtration path (parameter i) at different stages of interaction (parameter N). The calculation results can be browsed using the **Binary File** command of the Result menu of MAIN. All the computed points will be graphically represented by MAIN as a 51 by 51 table where rows will correspond to waves, and columns will correspond to steps. You can examine your equilibrium compositions point by point (Single Points mode) or series by series (Cross Sections mode). To see the evolution of the fluid composition within the j-th wave choose the j-th horizontal cross-section; to see the evolution of rock composition in the i-th reactor, choose the i-th vertical cross-section; to see the state of your system at a particular moment choose a diagonal (/) cross-section. See "Result menu" on page 35 for details.

Special syntax of vector variables

A special syntax for the {} vector variables {*|G|A|L|S(expression)} allows reference to any step of the preceding wave. The value of the expression defines the step number. For example, {A(i-1)} means "the bulk composition of the aqueous phase from the preceding step of the preceding wave". This syntax allows the definition of a flow-through reactor model as follows:

```

Input file: Filename
Wave model: Special syntax
GIBBS options: /S
* * * Primary wave * * *
    Initial step...
    Temperature,C  T = 25
    Pressure,bar   P = 1
    Composition [*] = [1]+[2]          # [1] is fluid, [2] is rock
    General step...
    Temperature,C  T = T
    Pressure,bar   P = P
    Composition [*] = [2]              # the other blocks are initially dry
    Do while: i<50
* * * Secondary wave * * *
    Initial step...
    Temperature,C  T = 25
    Pressure,bar   P = 1
    Composition [*] = [1]+{S}          # new fluid batch
    General step...
    Temperature,C  T = T
    Pressure,bar   P = P               # below the example of the special syntax:
    Composition [*] = {A(i-1)}+{S}    # solution interaction with altered rock
    Do while: I<50
* * * Completion condition * * *
    Do while: N<1000                  # 1000 waves are sufficient
* * * End of file * * *
```

In such a model a "system shot" (the state of the system at the particular time) will be represented by the corresponding *horizontal* cross-section. Vertical cross-sections will represent evolution of the static part of the system (rock). The evolution of the fluid during the filtration will be represented by diagonal (\) cross-sections that cannot be shown by the program.

Appendix 5. Supplementary Utilities

Two additional utilities (the program LST2TAB and the spreadsheet REX.XLS) are provided to assist in processing of the modelling results and the relevant data analysis.

Utility	Functions
LST2TAB	Simplifies the import of *.LST files into Microsoft EXCEL by converting them into ASCII files in a "Tab Delimited" format: *.LST file → *.TAB file.
REX.XLS	Simplifies the import of *.REX files into Microsoft EXCEL (version 5.0 and higher): *.REX file → *.XLS file.

LST2TAB: Conversion of *.LST Files for Export to Microsoft Excel

To take the full advantage of this utility we recommend using it under the MS-DOS prompt or a DOS shell (*eg*, Norton Commander). Copy the program to a directory mentioned in the PATH command of your AUTOEXEC.BAT file (DOS, Windows 3.x/9x), or Environment System Variables (Windows NT), or create an appropriate batch file. You will be able to call the program from any of your working directories.

1. Run the program in the command-line mode from your current working directory. Type the program name followed either by the name of your input *.LST file or the asterisk (*). You do not need to type the file extension.
2. Press ENTER. When the job has been completed, you will receive a confirmation message. The output file(s) will have the same name(s) as the source file(s) followed by the extension *.TAB.

Type	To
lst2tab [filename]	Process a single required file.
lst2tab *	Process <i>all</i> *.LST files located in the current directory.
lst2tab /h (or /? or ?)	Display a brief help information.

You can also run the program in a dialog mode:

1. Type the program name, and press ENTER.
2. Enter the name of the input file in the provided edit box. Press ENTER.
3. Repeat step 2 if necessary.
4. Press ESC to finish.

You can run LST2TAB in the batch command-line (**lst2tab ***) or dialog modes in a normal Windows session (just double-click the program icon). Edit the program properties in a conventional way to customise your working directory and program mode (see your Windows manual or Help file).

Note: The program is sensitive to the exact format of the input data. The *.LST file is processed line by line. If the program encounters a line that cannot be recognised, it will print an error message (***Error***) in the relevant line of the output file. The subsequent lines will be copied without conversion until the next page separator symbol delimiting calculation steps. After this the program will resume the conversion for a new series of calculations as usual.

To import data into Microsoft EXCEL:

1. Using the EXCEL Open File Wizard choose the required *.TAB file.
2. Choose the "Delimited" file type. Set the delimiter as "Tab".
3. Click the FINISH button.

REX.XLS: Importing Results into Microsoft EXCEL

The *.REX files produced with the **Binary File** command of the Result menu of MAIN can be directly loaded into Microsoft EXCEL. To complete this task:

1. Start Microsoft EXCEL. Open the REX.XLS file.
2. Press the import button. Choose a *.REX file for import.
3. When the *.REX file is loaded, you will be prompted to save it in the Microsoft EXCEL format. Click SAVE to proceed.

Note: If you cancel this step and try to save this file later, the file format offered by EXCEL will be the "Tab Delimited" text.

4. The data are ready for processing and analysis.

Note: To take the full advantage of this utility we recommend copying it in your Microsoft EXCEL Startup directory.

Notes
