

# **OpenCalphad version 4**

## **summary of new and old features**

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# Contents

<b>1</b>	<b>Background</b>	<b>4</b>
<b>2</b>	<b>Long term goals for the OC software</b>	<b>4</b>
<b>3</b>	<b>Dependencies</b>	<b>5</b>
<b>4</b>	<b>Structure of the OC software</b>	<b>5</b>
4.1	Utility and numerical routines . . . . .	5
4.2	Thermodynamic model software . . . . .	6
4.3	Equilibrium calculations . . . . .	6
4.4	Phase Diagrams and other diagrams . . . . .	6
4.5	Command line user interface . . . . .	6
4.6	Assessment of model parameters . . . . .	6
4.7	Application Software Interface . . . . .	7
4.8	Documentation . . . . .	7
<b>5</b>	<b>Software features</b>	<b>7</b>
5.1	Features in version 1 . . . . .	7
5.2	Features in version 2 . . . . .	8
5.3	Features in version 3 . . . . .	8
5.4	Features in version 4 . . . . .	8
<b>6</b>	<b>A general descripton</b>	<b>9</b>
6.1	Thermodynamic models and data . . . . .	9
6.2	Equilibrium calculations and conditions . . . . .	9
6.2.1	Parallelization of equilibrium calculation . . . . .	10
6.2.2	Calculation of partial derivatives . . . . .	10
6.2.3	Calculation of the Darken stability matrix and diffusion coefficients. . . . .	10
6.3	Calculation and plotting of diagrams . . . . .	11
6.4	Application software interface . . . . .	12
6.4.1	The phase tuple . . . . .	12

6.4.2	Multiple equilibria and parallelization . . . . .	12
6.5	The beginning of an assessment procedure . . . . .	13
6.6	Modeling other properties that depend on $T, P$ and phase composition . . . . .	13
6.7	Known bugs, problems and missing features . . . . .	13
<b>7</b>	<b>Short summary of all commands in OC3</b>	<b>14</b>
7.1	All top level commands . . . . .	14
7.2	Commands without subcommands . . . . .	15
7.3	Commands with subcommands . . . . .	15

# 1 Background

The Open Calphad (OC) initiative started in 2011 when a group of scientists decided that there was a need of a high quality open source software to gain wider acceptance of computational thermodynamics (CT) as a useful tool in materials science. The use of thermodynamic calculations in many applications is severely restricted by the cost as well as the hardware and software limitations imposed by most proprietary thermodynamic software. Providing a free software would simplify such implementations and open a much larger market also for the high quality databases provided by the commercial vendors.

Another aim was to support the scientific interest in new thermodynamic models and improved algorithms for multicomponent thermodynamic calculations and a better software for thermodynamic assessments as described in the book by Lukas et al.[07Luk]. At present such developments can only be done by scientists who are affiliated to the commercial software companies.

The last version of the OC software is available on [<http://www.opencalphad.org>].

The last development version, with more features but maybe less stable, is available on a repository called opencalphad at [<http://github.com>].

The OC software in its present state is mainly of interest for researchers, scientists and students with programming skills. It does not have any professional installation procedure and requires understanding of compilation and linking of software. It may be as stable as the commercial software in a few years time and it can be used for teaching computational thermodynamics and development of software using CT. There are three papers describing OC [15Sun1, 15Sun2, 16Sun].

This summary includes also the essential parts of the features of the previous versions.

## 2 Long term goals for the OC software

Several of the long term software goals with the OC initiative has now been reached

- A model package open for the implementation of new models.
- A stable minimizer calculating equilibria for a flexible set of conditions.
- Calculation of property and phase diagrams with graphics output.
- An assessment package for fitting model parameters.
- A software interface to different applications.

All of this in an open software free for non-commercial applications. But there are still many bugs and features missing or not fully implemented.

The aim of OC is to open a rich field for testing new thermodynamic models and applications for anyone interested. It will also be interesting to implement other minimizers and optimizers and to improve the graphics.

### 3 Dependencies

To install OC you need:

- a compiler for Fortran 95/08 like GNU gfortran 4.8 or later.
- For graphics the GNUPLOT software must be installed.
- For numerics versions of the LAPACK/BLAS libraries adapted to your hardware are recommended but default versions are provided.

If you need help to handle the installation please ask a local guru, the OC team provide this software for free and have no resources to help with this.

### 4 Structure of the OC software

The software is divided into packages. There are well defined software interfaces between the packages that makes it possible to extend and change them independently.

There are no databases provided with OC except with the examples. To obtain high quality databases please contact a commercial vendor.

#### 4.1 Utility and numerical routines

- The METLIB package is used mainly for the interactive user interface. Originally written in Fortran 77 and modified to the new Fortran standard but it includes features that are depreciated like ENTRY.
- OC needs numeric routines for inverting a matrix and solving a system of linear equations and calculate eigenvectors of the Darken stability matrix. With version 4 LAPACK and BLAS are used for this and if you have a LAPACK library adapted to your hardware please use that rather than the version provided with OC.
- The LMDIF1 package for least square fitting of model parameters is a free software developed at Argonne National Lab (1980).

## 4.2 Thermodynamic model software

The General Thermodynamic Package (GTP) has data structures for storing model parameters, conditions and calculated results and code to calculate the Gibbs energy and its first and second derivatives of phase when the  $T, P$  and constitution of the phase is known. At present the Compound Energy Formalism (CEF) and the partially Ionic two-sublattice liquid model (I2SL) are implemented. For more information on thermodynamic models see Lukas et al.[07Luk].

For describing the  $T$  and  $P$  dependence there is a TP function package for storing and calculating functions, including first and second derivatives of  $T$  and  $P$ .

## 4.3 Equilibrium calculations

The HMS minimizer implementing the algorithm by Hillert[81Hil] for finding the equilibrium state in a multicomponent system for many different kinds of external conditions. It makes use of GTP for calculating the Gibbs energy and its derivatives for each phase. The algorithm is described in [15Sun2].

## 4.4 Phase Diagrams and other diagrams

The step/map/plot (SMP) package for calculating and plotting diagrams. It uses HMS for calculating equilibria for conditions varying along the axis and the free software GNUPLOT for plotting on various devices.

## 4.5 Command line user interface

The PMON command line user interface has a VAX/VMS flavour. It can be used to read data, set conditions, calculate equilibria, property and phase diagram. Plotting is done by GNUPLOT. It can also assess model parameters. If you prefer a graphics user interface you are welcome to add that.

## 4.6 Assessment of model parameters

An assessment software using a least square routine (LMDIF1) to fit model parameters to experimental and theoretical data.

## 4.7 Application Software Interface

The OC Software Application Interface (OCASI) to make it possible to integrate OC in general application software for various simulations. This has now been equipped with an iso-C binding which makes the data structures defined in the Fortran package available to programs in C++, java, python and other software languages. There is a recent paper describing this [16Sun].

## 4.8 Documentation

A fairly extensive documentation of the code, a user guide and additional examples as macro files including graphics is provided with the software.

- GTP, the thermodynamic model package.
- HMS, the implementation of Hillert's equilibrium algorithm.
- SMP, the Step, Map and Plot package.
- MACRO, the test macro files.
- UG, the user guide and manual.

There are also a number of publications as listed below.

## 5 Software features

The main features in OC is summarized below in a historical order.

### 5.1 Features in version 1

The version 1 release of OC in 2013 could calculate multicomponent equilibria using Hillert's algorithm[81Hil] for models based on the Compound Energy Formalism (CEF)[01Hil, 07Luk]. It included a possibility to read unencrypted TDB files and a simple command interface with macro facilities to set conditions, calculate equilibria and list results. It had a grid minimizer to ensure finding the global minimum and detect miscibility gaps. There was also a limited application software interface called OC-TQ.

## 5.2 Features in version 2

The most important facilities added was generating property and phase diagrams. However, these and many of the other features are still incomplete and fragile and may not work properly in some cases. Feedback from users (providing the data and a macro file reproducing the problem) is the best way to obtain a more stable and error free software.

## 5.3 Features in version 3

The main aim of OC version 3 is to provide a stable and accurate calculation of single multicomponent equilibria for a very flexible set of conditions. It also includes parallelization using OpenMP on the equilibrium level and a possibility to assess model parameters.

Other important features like property and phase diagram are available in about the same form as in version 2.

## 5.4 Features in version 4

One of the main changes has been to use LAPACK and BLAS for inverting the phase matrix and solve the equilibrium equation. That has reduced the time for an equilibrium calculation almost 20%. But there are some cases when the old routines were more stable. Using LAPACK made it also possible to calculate eigenvalues and thus obtain the phase stability. A calculation of the whole matrix of derivatives of the chemical potentials for all components with respect to the amount of the components has been implemented. This matrix is needed also for transforming mobilities to diffusion coefficients.

Using valgrind and some other Fortran compilers with check of uninitialized variables has improved the general performance and stability. OC now releases all used memory with the NEW command and there are no important memory leaks. By default OC is compiled with check of array bounds and initialization of local variables, removing these and compiling with -O2 option works and can sometimes reduce the calculation time with a factor 3. But it may cause untested errors.

The step length control in the MAP command has been improved and that has made the phase diagrams slightly better but more testing is needed. The problem is that if a change improves one diagram some other diagram becomes worse. At node points OC now performs a global minimization as test and the line is removed if there is some other phase stable. This change has removed most metastable lines.

OC can now calculate isothermal sections and plot tie-lines. But there are a few things with the STEP calculation that has not yet been improved. There are new options for plotting like adding a text label (which can be calculated as the set of stable phases) or overlaying several plots.

It is now possible to have other components than the elements. But quasi-binary sections



are still difficult.

It is also possible to set conditions on the volume,  $V$ , and allow  $P$  to vary. In materials science that is not so important but these variables are fundamental in thermodynamics.

Because there are many ongoing developments the documentation of the source code is not completely updated and there are several features that have incomplete or no description.

## 6 A general descripton

### 6.1 Thermodynamic models and data

The thermodynamic models include the Compound Energy Formalism (CEF) with up to 9 sublattices and allowing for molecules, ions and vacancies as constituents. For liquids with strong short range ordering the partially ionic 2 sublattice liquid model (I2SL) is implemented. For a detailed description of these (and other) models see the book [07Luk].

The Gibbs energy can be partitioned for phases with long range ordering (sublattices) in an ordered and a substitutional part. The implementation of this for phases with order/disorder transformations, like A1/L1<sub>2</sub>/L1<sub>0</sub> has been revised and simplified.

The thermodynamic data can be entered interactively or read from a database. OC can read most database files following the TDB format as defined by the SGTE organization.

There are a few free but not very high quality databases provided with the OC software. For use of high quality databases please contact the commercial vendors.

### 6.2 Equilibrium calculations and conditions

The equilibrium calculations follows the algorithm proposed by Hillert [81Hil] and recently explained in more detail by Sundman et al[15Sun2]. It allows a very flexible set of conditions on amounts or fractions of components, chemical potentials or activities, enthalpies, fix phases etc.

It is possible to set condition on the enthalpy,  $H$ , or the volume,  $V$ , of a system or phase. For mole fractions one can also set an expression as condition like

$$x_A^{\text{liquid}} - x_A^{\text{Laves}} = 0$$

in order to calculate a congruent melting and use expressions on for total amount like

$$N_U + N_{\text{ZR}} = 1$$

to specify that the sum of moles of U and Zr should be unity.

To ensure that the global equilibrium is calculated there is an initial grid minimizer described in the paper by Sundman et al[15Sun2]. The grid minimizer can automatically detect miscibility gaps, i.e. that a phase will be stable with two or more composition, called composition sets. It can optionally be turned off to speed up calculations or one can set a higher

density of gridpoints if there are problems finding the stable set of phases.

### 6.2.1 Parallelization of equilibrium calculation

Parallelization is possible on several levels in OC. For example one can calculate several equilibria with different sets of conditions in parallel using the OpenMP library. This is particularly important when OC is used for simulations, for example in a phase field software as the calculation time is divided by the number of CPU's available.

### 6.2.2 Calculation of partial derivatives

OC calculates all second derivatives with respect to  $T, P$  and all constituents of all phases. This improves stability during equilibrium calculation and makes it possible to calculate for example the stability function as part of an equilibrium calculation.

It also makes it possible to implement The “dot derivative” method to calculate derivatives of state variables has been implemented. This allows calculation of properties like the heat capacity without resorting to numerical derivation.

$$C_P = \left( \frac{\partial H}{\partial T} \right)_{P, N_i} \quad (1)$$

The calculation makes use of the analytical first and second derivatives of the Gibbs energy for  $T, P$  and all constituent fractions calculated in the model package.

### 6.2.3 Calculation of the Darken stability matrix and diffusion coefficients.

The matrix of all second derivatives of the Gibbs energy for a phase is often known as Darken stability matrix. For a binary substitutional system this matrix is simply:

$$M = \begin{pmatrix} \frac{\partial G_A^\alpha}{\partial x_A} & \frac{\partial G_A^\alpha}{\partial x_B} \\ \frac{\partial G_B^\alpha}{\partial x_A} & \frac{\partial G_B^\alpha}{\partial x_B} \end{pmatrix}$$

and if the determinant of this matrix

$$\det(M) = \frac{\partial^2 G_M}{\partial y_1^2} \frac{\partial^2 G_M}{\partial y_2^2} - \left( \frac{\partial^2 G_M}{\partial y_1 \partial y_2} \right)^2 \quad (2)$$

is negative the composition of the phase is inside a spinodal and the phase would like to separate into two different composition, i.e. a miscibility gap.

For larger systems the determinant may be more complicated but as the model package calculates all second derivatives analytically the software provides a command to calculate

the matrix of the derivatives of all chemical potentials with respect to all components

$$\frac{\partial G_A}{\partial N_B} = \frac{1}{N} \left( \frac{\partial^2 G_M^\alpha}{\partial x_A \partial x_B} - \sum_C x_C \left( \frac{\partial^2 G_M^\alpha}{\partial x_C \partial x_B} + \frac{\partial^2 G_M^\alpha}{\partial x_A \partial x_C} \right) + \sum_C \sum_D x_C x_D \frac{\partial^2 G_M^\alpha}{\partial x_C \partial x_D} \right) \quad (3)$$

and also the eigenvalues of this matrix. If the lowest eigenvalue is negative it means the phase is inside a spinodal. The derivation of eq. 3 can be found in the HMS documentation. It is interesting to note that eq. 3 is symmetrical.  $\frac{\partial G_A}{\partial N_B} = \frac{\partial G_B}{\partial N_A}$

This matrix is also important to convert the mobilities of the components to diffusion coefficients.

### 6.3 Calculation and plotting of diagrams

The STEP procedure for property diagram. Such diagrams are calculated with a single axis variable and the user can calculate and plot how various state variables or model properties depend on the axis variable. A primitive version of the step procedure was available already in version 1 but has been gradually improved in the later versions.

There is also a “step separate” option for Gibbs energy curves and similar things when each phase is calculated separately along the axis variable.

The MAP procedure for phase diagrams calculates lines where the set of stable phases changes for different values of the axis variables. At present only two axis are allowed.

The mapping has been improved somewhat but it is very dependent on selecting a good start point. If some lines are missing one may try to start at another point in the diagram and merge the plots. The AMEND LINE command makes it possible to remove lines that are wrong or as an emergency one can remove lines that are wrong by editing the input file to GNUPLOT.

Mapping of binary systems is fairly stable although there are problems at the top of miscibility gaps. Mapping of multicomponent system is possible but frequently some lines are missing. There is an unresolved problem to exit from certain node points. The present version of mapping will not discover miscibility gaps that occurs during mapping but things will improve gradually. Feedback from users are welcome.

During both MAP and STEP all calculated equilibria are saved and it is possible to plot various properties. All node points are saved as equilibria which can be inspected individually and it is also possible to copy equilibria along a line to a current equilibria and extract values.

The results from a STEP or MAP command can only be saved graphically or as a GNUPLOT file. It is not possible to save the results on a file for later use by the OC software but we are working on that. The user can always create MACRO files for calculations he would like to repeat.

GNUPLOT version 4.6 or later is needed to generate the graphics. In the user interface of OC some additional graphics options, like a title and ranges of the x and y axis, has been

added. It is also possible to edit the output files from OC to take advantage of the extensive graphics facilities of GNUPLOT.

## 6.4 Application software interface

For use in application software there is an OC Software Application interface, OCASI. This follows the TQ standard[95Eri]. There are some examples to use this interface provided with the software, both for Fortran and C++ and a recent paper [16Sun].

A full Fortran/C++ application software interface including the use of compatible data structures has been implemented using the isoC binding. This means that software written in C++ as well as Fortran can directly access results from an OC calculation without using calls to subroutines.

### 6.4.1 The phase tuple

In the OCASI interface a new method has been introduced to identify phases called “phase tuples”. Initially each phase has a single “composition set” representing its constitution. Phases with miscibility gaps will have two or more “composition sets” representing the two different constitution. However, using a separate index for the phase and another for the composition set is rather clumsy. In OC we have introduced what is called a “phase tuple” as a Fortran 95 structure (TYPE). The array of phase tuples have a unique index for each combination of phase and composition set and the phase tuples for the second composition set of a phase are ordered after those for the first composition set. This was introduced in version 3 of OC but has been slightly changed in version 4. The phase tuple has 4 integer indices, one is the original phase index, the second is the composition set number, the third is an index to where the model parameters are stored and the fourth is the record where the constitution as well as calculated results are stored. The user interface of OC also displays the phase tuple index when listing phases and composition sets.

When a phase is entered it has one composition set with index 1 and a phase tuple is created with the same index as the phase and the composition set index equal to 1. When a new composition set is entered for a phase, either by the user or by the software itself, for example by the grid minimizer, the phase tuple index for the new composition set will be higher than any of the existing phases and have as values the phase number and a composition set number 2 or higher. Redundant phase tuples created by the grid minimizer are normally removed automatically after a calculation.

### 6.4.2 Multiple equilibria and parallelization

The user can enter several equilibria for the same system and have different conditions in each and calculate them separately and in parallel and transfer data between them. This facility is used also for storing step/map results and is a preparation for the software to

assess model parameters from experimental data. Each equilibrium is independent and they be calculated in parallel.

## 6.5 The beginning of an assessment procedure

The beginnings of an assessment procedure has been implemented is a straightforward least square fit of experimental data to the same data calculated by the model. The experimental data can be entered as equilibria (using the feature described in the previous item). In fact very little had to be done in the OC software for this purpose as we use as a free optimizing subroutine called LMDIF from the MINPACK software developed at Argonne National Lab 1980.

In OC some subroutines were added to allow this least square routine to change model parameters in the GTP package and to calculate the difference between the experimental data provided by the user and the same property calculated from the models of the phases. We would also like to develop additional statistical analysis of the results like estimating uncertainties using the assessment results for extrapolations. There is a separate documentation of this module.

## 6.6 Modeling other properties that depend on $T$ , $P$ and phase composition

OC has a flexible way to handle properties that may depend on  $T$ ,  $P$  and the phase constitution for example mobilities, elastic constants etc. Some properties are predefined but a skilled programmer can easily add a specific property and a model to use it in a calculation. The values of such properties can be obtained interactively or by application software in the same way as thermodynamic state variables.

## 6.7 Known bugs, problems and missing features

Some things are problematic and from the long list of things we wanted to implement but did not manage this time, these are a few:

- There is a problem with the STEP procedure in a binary system using a composition as axis. The STEP will stop at a phase boundary as it does not understand that nothing changes in a two-phase region except the amount of the phases.
- There is no check on miscibility gaps during a step or map command except at node points.
- Saving results from step and map on a file is not possible except graphically with GNUPLOT.

- The mapping is very fragile, lines are sometimes missing or metastable lines plotted.
- Conditions are not restored after finished step/map.
- The Scheil-Gulliver solidification model is not implemented in OC but there is an application software written in C++ that can do this. T-zero lines and para equilibria are also on the list to be implemented.
- The data structure is still volatile and likely to be changed in the next release.
- The OCASI subroutine set have not been designed yet. The earlier OC-TQ application software interface has been revised to use phase tuples.

As OC is open source anyone who is interested to help implementing a particular feature is welcome to start working on it.

## 7 Short summary of all commands in OC3

See also the PDF file ochelp4.pdf for a more extensive documentation. The commands for assessment are also explained in the assess.pdf file.

### 7.1 All top level commands

ABOUT	ENTER	LIST	QUIT
AMEND	EXIT	MACRO	READ
BACK	FIN	MAP	SAVE
CALCULATE	HELP	NEW	SELECT
DEBUG	HPCALC	OPTIMIZE	SET
DELETE	INFORMATION	PLOT	STEP

One restriction I have applied to commands and subcommands is that one should not need to type more than 3 characters to have a unique abbreviation.

Directly after the top level command the user can give some options preceded by a slash like /output=filename or /append=filename. The output that would normally appear on the screen will instead be listed on this file with extension DAT. The output option will delete any previous content on the file but the append will add the new output at the end of the file. The output is reset to the screen after the command.

A frequent Thermo-Calc user must disable his tendency to put hyphens or underscore characters between the command and subcommand.

## 7.2 Commands without subcommands

- ABOUT the software
- BACK to calling software (or exit) after confirmation
- EXIT, terminate the software (in Swedish) after confirmation
- FIN, terminate the software (in French) without confirmation
- HELP gives explanations about a (few) commands from the user guide
- HPCALC starts the inverse polish calculator
- INFORMATION is not implemented yet
- MACRO asks for name of macro file and executes it. A macro file can call another macro five levels deep.
- MAP a phase diagram with 2 or more independent axis.  
If the user already given a MAP command he is asked if he wants to keep the previous results.
- NEW asks for confirmation and if so removes all data.
- OPTIMIZE asks for the maximum number of iterations and then use a least square routine to obtain the best fit to experimental data by varying the set of model parameters specified by the user.
- QUIT terminates the software (in English) after confirmation

## 7.3 Commands with subcommands

Many subcommands are not implemented, I have indicated some but not all.

- AMEND should change something already entered or set. But sometimes it creates something so one should be careful if it should be an ENTER or SET command.
  - ALL.OPTIM\_COEFF means you can rescale or recover previous set of the optimizing coefficients.
  - BIBLIOGRAPHY asks for a bibliographic id and amends its text.
  - COMPONENTS changes the set of components.
  - CONSTITUTION asks for a phase and the user can amend the amount and current constitution of a phase. I have put this here and not as part of AMEND PHASE to avoid confusion with adding a composition set.

- CP\_MODEL not implemented and probably redundant.
- ELEMENT amends data for an element (not implemented).
- EQUILIBRIUM is not implemented and probably redundant.
- GENERAL can name of current equilibrium, the user can specify if he is a beginner (the software can provide more help (not implemented)), or expert, if global gridminimizer should be used and if it can merge composition sets, if composition sets can be created automatically and if redundant composition set can be deleted after an equilibrium calculation. The latter questions are mainly interesting for debugging.
- LINE make it possible to remove a line calculated for a STEP or MAP command. A part of the line can be removed by editing the GNUPLOT file.
- PARAMETER amends a parameter expression for a phase (not implemented, use ENTER PARAMETER to enter the new function).
- PHASE (default) asks for phase name and amends data for this phase like:
  - \* COMPOSITION\_SET (default) adds or deletes a composition set. Composition sets are needed for miscibility gaps when a phase can be stable with two or more compositions. A composition set can be identified with a hash symbol “#” followed by a number or by a user specified prefix or suffix. Deleting a set will always be the one with the highest number. When adding a set the user can provide a prefix and suffix and the default constitution for this set.
  - \* MAGNETIC\_CONTRIB adds an Inden-Hillert magnetic model.
  - \* DISORDERED\_FRACS adds a disordered fraction set for an ordered phase.
  - \* GLAS\_TRANSITION adds a glas transition model (not implemented).
  - \* QUIT You did not want to amend anything for the phase
  - \* DEFAULT\_CONSTIT amends the default constitution for a composition set of the phase. Same as SET PHASE “name” DEFAULT\_CONSTITU.
  - \* DEBYE\_CP\_MODEL adds a Debye Cp model (not implemented).
  - \* EINSTEIN\_CP\_MDL adds a Einstein Cp model (not implemented).
  - \* INDEN\_WELMAGMOD adds a magnetic model according to Wei (not implemented).
  - \* ELASTIC\_MODEL\_A adds an elastic model (not implemented). Note the LIST MODEL\_PARAM\_ID how to enter  $T$ ,  $P$  and composition dependent elastic constants and lattice parameters.
- QUIT you did not want to amend anything.
- SPECIES amends data for a species (not implemented).
- SYMBOL the user can specify if the symbol can only be calculated when explicitly named (usually all symbols are evaluated when any symbol is evaluated as they



can depend on each other). This is needed for symbols used as conditions. The user can also specify that a symbol should be local to a specific equilibrium. In this way one can store the value of a symbol from one equilibrium and calculate differences with respect to other equilibria.

- TPFUN\_SYMBOL replaces an existing TPfun with a new expression.
- CALCULATE various things like:
  - ALL\_EQUILIBRIA all equilibria within the range set for experimental equilibria with non-zero weight are calculated. This is useful for testing if there are any problems before optimizing.

If you are running the version compiled with OpenMP the equilibria will be calculated in parallel. Additional experimental or other symbols and properties can be calculated.
  - EQUILIBRIUM (default) is the normal equilibrium calculation command which first calls the grid minimizer (if the conditions allow) and then the iterative minimizer.
  - GLOBAL\_GRIDMIN Only the grid minimizer is called to find the gridpoints that represent the lowest Gibbs energy. These are normally used by the iterative minimizer to find the real equilibrium. If followed by COMPUTE NO\_GLOBAL one will have the same result as COMPUTE EQUILIBRIUM.
  - NO\_GLOBAL calculates the equilibrium for the current set of conditions starting from the current set of stable phases and their constitutions. No grid minimizer called.
  - PHASE ask for phase name, amount and constitution and at current  $T$  and  $P$  calculates either:
    - \* ONLY\_G Gibbs energy and first and second derivatives with respect to  $T$  and  $P$ .
    - \* G\_AND\_DGDY calculates also all first derivatives with respect to the phase constituents.
    - \* ALL\_DERIVATIVES Also all second derivatives with respect to the phase constituents.
    - \* CONSTITUTION\_ADJust You will be asked to enter a new composition (default is current) of the phase and this command will then calculate  $G$  and all chemical potentials after adjusting the constitution of the phase to have the minimum Gibbs energy for the given overall composition. It is interesting when one or more components are parts of several constituents for example in a gas or phases with order/disorder transitions.
    - \* DIFFUSION\_COEFF You will be asked to enter a new composition (default is current) of the phase and this command will then calculate the Darken

stability matrix

$$\frac{\partial G_A}{\partial N_B}$$

for all components (see eq. 3) and also all mobility values (if there are any).

- QUIT if you did not really want to calculate anything.
- SYMBOL Calculate the value of one or all symbols at the current equilibrium.
- TPFUN\_SYMBOLS all TP functions values and their first and second derivatives with respect to T and P (6 values).
- TRANSITION asks for a phase to be stable with zero amount and a condition to be released to calculate the equilibrium. The phase must not have the FIX status. After the calculation the phase is set to be entered and the released condition set to the calculated value. If calculation fails the status is not reset (sorry I have not had time to do all). No grid minimizer called.
- DEBUG Nothing of this works
  - FREE\_LISTS
  - STOP\_ON\_ERROR
  - ELASTICITY
- DELETE Only composition sets and equilibria can be deleted. To delete a parameter you can amend its expression to be zero.
  - PHASE (default) but not allowed
  - ELEMENTS not allowed
  - SPECIES not allowed
  - QUIT you did not want to delete anything
  - COMPOSITION\_SET The highest set is deleted (one cannot delete the first). Must be used with great care.
  - EQUILIBRIUM must be used with great care.
- ENTER is the main command to enter data interactively. Note that in most cases data are read from a TDB file.
  - BIBLIOGRAPHY enter a bibliographic reference id and text.
  - COMMENT enter a text that is saved and listed with the equilibrium.
  - CONSTITUTION to enter the constitution of a phase (same as AMEND CONSTITUTION).
  - COPY\_OF\_EQUILIB the current equilibrium is copied to a new one with a name specified by the user.

- ELEMENT an element with data.
- EQUILIBRIUM an equilibrium record with the specified name is created. Each equilibrium record has an independent set of conditions. Will be used for assessments and is already used to store node points during step and map.
- EXPERIMENT data for assessments. These are a state variable of symbol followed by an equal sign, =, larger than, > or lesser than, < and a value and uncertainty separated by a colon. For example:  
 experiment T<sub>i</sub>1200:1 X(liq,mo)=.2:.01 HM(fcc)=-30000:5000
- MANY\_EQUILIBRIA allows the user to enter a table with conditions for many equilibria with similar conditions. It is intended for assessments but can be used also to calculate various properties that for a range of conditions not suitable for a STEP calculation. The user must give a general “head” of the table specifying phase status and all conditions including some that are different in the different equilibria. For those familiar with Thermo-Calc it replaces the POP file in assessments but is more flexible.
  - \* This command will first ask Table head::  
 and the user must specify conditions and other things for the table. The user can refer to values (or text) in the table by giving an “@” character followed by a digit 1 to 9. In the examples below user input is **in bold** and explanations in *italics*.  
 By default all phases are suspended for the equilibria so the user must specify the phases that should be entered, dormant or fixed.  
 Table head:: **entered 0** \* *all phases should be entered*  
 Table head:: **fix 0 liquid** *liquid should be fix with 0 moles*  
 Table head:: **fix 1 @2** *the phase in column 2 should be fix with 1 moles*
  - \* The conditions can be given using the @ character to indicate vaules that are given in the specified column in table to follow.  
 Table head:: **condition t=@1 p=1e5 n=1 w(cr)=@3 w(mo)=@4**
  - \* Optional calculations of entered symbols  
 Table head: **calculate cp**
  - \* Optinonal listing of state variables  
 Table head: **list HM tc(bcc)**
  - \* Optional experimental data  
 Table head: **experiment x(liquid,cr)=@5:.01, x(bcc,cr)=@6:.02**
  - \* Optional reference state  
 The reference state for a component can be set.  
 Table head: **reference O gas \* 1e5**
  - \* Optional plot data

You can create up to 9 datasets with data that can be overlaid on calculated diagrams. Each dataset is stored on a file called oc\_manyj.PLT where j is the

dataset number. The first integer is the dataset, the following two are plot coordinates and the last integer the symbol typ.

Table head: **plot 1 @1 @2 5**

\* Optional comment

Table head: **Sykes in Zeit.Metallkde Bd 69 (1927) p 1313**

\* The table head is finished by an empty line or “table\_start”

\* For the rows in the table the user must first provide a unique name for each equilibrium (that is counted as column 0 (zero)) and values for all columns referred to in the table head.

Table row: **EQ1 1573 BCC 0.3 0.05 0.18 0.35**

Table row: **EQ2 1623 BCC 0.3 0.11 0.22 0.29**

\* The table is finished by

Table row:**table\_end**

- OPTIMIZE\_COEFF the coefficients for use in assessments are entered. They have the symbols A00 to A99. If the user wants fewer than 100 coefficients he can specify a number.
- PARAMETER the expression of a parameter of a phase. The phase, the constituent array and degree must be specified.
- PHASE a phase with sublattices, site ratios and constituents. The parameters are entered individually with ENTER PARAMETER.
- QUIT you did not want to enter anything.
- SPECIES a species with name and stoichiometry. Its name must be unique but one can have several with the same stoichiometry.
- SYMBOL (default) name and expression of a state variable function.
- TPFUN\_SYMBOL The name and expression of a function of T and P that can be used in parameters.

- LIST of many things ...

Note the possibility to direct output to a file using /output=filename or /append=filename directly after the command, as mentioned in the beginning.

- AXIS lists current axis set by the user.
- BIBLIOGRAPHY lists bibliographic text for specific id or all.
- CONDITIONS lists all conditions in current equilibrium.
- DATA lists all parameters on different devices and ways:
  - \* SCREEN (default) Writes all parameters for all phases on the screen including the bibliographic information.
  - \* TDB Writes all parameters on file in TDB format.

- \* MACRO Writes all parameters on file as a macro file (not implemented).
- \* LATEX Writes all parameters on file as a LaTeX file (not implemented).
- EQUILIBRIA lists all entered equilibria with name and number (use LIST RESULTS to list the results).
- ERROR\_MESSAGE lists the error message associated with an error code.
- LINE\_EQUILIBRIA lists all equilibria stored during STEP or MAP. With the SET ADVANCED command one can copy one of these to the current equilibrium.
- MODEL\_PARAM\_ID lists all implemented model parameter identifiers like G, TC, BMAGN, elastic constants etc. that can depend on  $T, P$  and constitution of a phase. The use of such parameters require implementation of the model in the software.
- MODEL\_PARAM\_VAL lists the calculated value of a model parameter identifier for a phase.
- OPTIMIZATION the result of an optimization is listed.
- PARAMETER lists the expression for a single parameter.
- PHASE asks for phase name and then lists for option
  - \* CONSTITUTION (DEFAULT) lists constitution for this phase.
  - \* DATA lists parameter for this phase (no bibliography).
  - \* MODEL lists some model information for this phase.
- QUIT You do not want to list anything.
- RESULTS (default) from an equilibrium calculation. the program asks for a number how to format the phase information.
  1. stable phases with mole fractions in value order
  2. stable phases with mole fractions and constitution in value order
  3. stable phases with mole fractions and constitution in alphabetical order.
  4. stable phases with mass fractions in value order
  5. stable phases with mass fractions in alphabetical order.
  6. stable phases with mass fractions and constitution in value order
  7. all phases with mass fractions in value order
  8. all phases with mole fractions and constitutions in alphabetical order
  9. all phases with mole fractions and constitution in value order

The conditions are listed first, then some global properties, then some data for each component and then the stable phases with amount and composition and possibly constitution.
- SHORT
  - \* A writes one line for all elements, species and phases.

- \* P writes one line for all phases sorted with stable first, then max 10 entered phases in decreasing stability, finally the dormant in decreasing stability.
- STATE\_VARIABLES asks for state variable symbol and lists its value. For the value of model parameter identifiers like the Curie temperature, TC(BCC), mobility, MQ&FE(FCC), etc. use the LIST MODEL\_PARAM\_VAL.
- I will try to merge list state\_variables and compute symbol to a SHOW command**
- SYMBOLS lists all entered state variable symbols (same in all equilibria).
- TPFUN\_SYMBOLS lists one or all TP function symbols and expressions (same in all equilibria).
- PLOT asks for state variables or symbols for x and y axis and after that the user can plot directly or change anything in the submenu below.

OC generates a command file for GNUPLOT and a data file with the values to plot and then executes this in a separate shell. The user can edit the command file to add options and execute it again inside gnuplot. But beware not to overwrite the files you want to edit. There are 10 colors for the lines to plot. If more than 10 lines to plot the colors are repeated cyclically.

OC keeps the previous values set of all options set (except the scaling of an axis with a new variable and the output file which is always reset to the default “ocgnu”) unless changed explicitly.

I have no idea how to overlay a calculated result with for example experimental data. Hopefully some GNUPLOT expert will tell me how to do that.

- RENDER (default) finally plot when all options set.
- X RANGE set plot range on x axis.
- Y RANGE set plot range on y axis.
- X TEXT set text on x axis.
- Y TEXT set text on y axis.
- TITLE set title of plot.
- TIE-LINE index for isothermal sections, 1 means all, 2 every second, 3 every third, 0 means none.
- LOGSCALE the X or Y axis or both can have logarithmic scaling.
- TEXT allows adding a text in the plot at a specific point and for phase diagrams also to calculate the set of stable phases at that point.
- APPEND you can add a GNUPLOT file that will be added to the current plot.
- KEEP spawn the plot window and continue the program. Not implemented yet.

- POSITION\_OF\_KEYS select position of the labels (identification) of the lines in the plot. The labels can be placed inside/outside of the plot, to the left/center/right and top/bottom. See the explanation of “set key” in GNUPLOT.
- GRAPHICS\_FORMAT set type of terminal (P for postscript, G for gif). You will also be asked for output file.
- OUTPUT\_FILE set name of plot file (default is ognu.dat).
- GIBBS\_TRIANGLE set diagram to be a Gibbs triangle (not implemented).
- QUIT you do not want to plot.

**More options will be added when I understand GNUPLOT better**

- READ At present only TDB is implemented.
  - TDB (default) an unencrypted TDB file can be read. Many TYPE\_DEFS are not handled correctly and warning are given. For partitioned phases you may have to edit the parameters. The user can select which elements he wants to read.
  - UNFORMATTED an unformatted file with model parameters and results for a single equilibrium calculation. It was implemented in version 2 but due to changes in the data structure it does not work any longer.
  - QUIT you did not want to read anything.
  - DIRECT will save results from STEP and MAP on a random access file (not implemented).
- SAVE This is not yet implemented.
  - UNFORMATTED (default) A file is written with unformatted data for all thermodynamic data and conditions and results for a single equilibrium. There is no guarantee an unformatted file will be readable in a later version of OC.
  - DIRECT not implemented yet (intended for STEP and MAP results).
  - QUIT do not save anything.
- SELECT a few things.
  - EQUILIBRIUM (default) change the current equilibrium to the selected one (number or name or next or previous).
  - MINIMIZER there is only one.
  - OPTIMIZER there is only one.
  - GRAPHICS there is only one.
  - LANGUAGE there is only one (English).
- SET can be used for many things. The most important is conditions.

- ADVANCED This is a command for very special things.
  - \* DENSE\_GRID\_ONOFF toggles the grid minimizer to use denser grid or normal. A dense grid is better to ensure the global equilibrium is found but will also take longer to calculate. About 10 times more gridpoints are calculated compared to the normal grid.
  - \* EQUILIB\_TRANSF transfer an equilibrium calculated along a line in STEP or MAP to the current equilibrium.  
*this is probably the most awkward command of all. But I do not want to have a TRANSFER or COPY command on the top level as that will certainly be misunderstood and misused*
  - \* QUIT you did not want to set anything advanced.
- AS\_START\_EQUILIB use current equilibrium as start for step or map. Not necessary if there is only one start equilibrium.
- AXIS axis “number” to an independent variable (must be a condition).
- Some status BITS in the GLOBAL, EQUILIBRIUM and PHASE records can be toggled.
  - \* The global record bits are listed below. Most of them are set or reset automatically by the software or by other commands.
    - 0 you are a beginner (set by default)
    - 1 you are experienced
    - 2 you are an expert
    - 3 gridminimizer must not be used
    - 4 gridminimizer must not merge comp.sets. (set by default)
    - 5 there are no data (cleread automatically)
    - 6 there are no phases (cleared automatically)
    - 7 comp.sets must not be created automatically
    - 8 comp.sets must not be deleted automatically
    - 9 data has changed since last save (set automtically)
    - 10 means verbose is on (not implemented)
    - 11 means verbose is permanently on (not implemented)
    - 12 means be silent (supress warnings)
    - 13 no cleanup after an equilibrium calculation
    - 14 use denser grid in grid minimizer (see also ADVANCED)
    - 15 calculations in parallel is not allowed
    - 16 do not test global equilibrium at node points
    - 17 components are not the elements
    - 18 check calculated equilibrium with grid minimizer
  - \* The EQUILIBRIUM record bits are listed below



- 0 No threads allowed (no parallel calculation)
- 1 No global minimization allowed for this equilibrium
- 2 No equilibrium has been calculated (there are no results)
- 3 Conditions and results not consistent
- 4 Last equilibrium calculation failed
- 5 No automatic generation of composition sets
- 6 Equilibrium tested by grid minimizer
- 7 Current results are from a grid minimization
- \* To change the phase status word use SET PHASE ... bit
- CONDITION (default) the state variable and value of a condition. Normally set a state variable equal to a value. Only a few expressions are allowed for mole fractions and amounts of moles.
- ECHO echo of the input from macro files on the screen. There is no way to turn off echo.
- FIXED\_COEFF to set an optimizing coefficient to a fixed value.
- INPUT\_AMOUNTS amount of species in moles. These will be added together and used for conditions of the components.
- INTERACTIVE at the end of macro files.
- LEVEL I am not sure what this was intended for.
- LOG\_FILE the name of a file with a copy of all input and defaults. Useful for documenting errors!
- NUMERIC\_OPTIONS maximum number of iterations (default 500) and convergence limit (default  $10^{-6}$ ).
- OPTIMIZING\_COND depending on the optimizer used for assessment some conditions can be set.
- PHASE the user must specify a phase name and can then ...
  - \* STATUS (default) the status of a single phase, or all using an asterisk “\*”, can be set. See also SET STATUS PHASE with a more flexible way to specify phases.
  - \* DEFAULT\_CONSTITU the default constitution of the phase can be set. Same as AMEND PHASE name DEFAULT\_CONSTITU.
  - \* AMOUNT the amount of the phase (redundant).
  - \* QUIT nothing is set for the phase.
  - \* BITS some special bits for a phase can be set. At present there is no way to “UNSET” these bits ... so be careful. Most of these are set automatically by the software.
    - QUIT (default) no bit is changed.

- FCC\_PERMUTATIONS to indicate 4 sublattice fcc or hcp permutations. Only one parameter stored for each unique permutation. Must be set before any parameters are entered.
  - BCC\_PERMUTATIONS to indicate 4 sublattice bcc permutations. Must be set before any parameters are entered (when implemented).
  - IONIC\_LIQUID\_MDL to indicate ionic liquid model. A phase with the ionic liquid model that is entered interactively must currently have the name ionic\_liquid and this bit is automatically set. If read from a TDB file the :Y after the phase name assigns this model. Setting this bit interactively has no function at present.
  - AQUEOUS\_MODEL to indicate aqueous model (not implemented).
  - QUASICHEMICAL to indicate quasi-chemical model (not implemented).
  - FCC\_CVM\_TETRADRN to indicate CVM fcc tetrahedron model (not implemented).
  - FACT\_QUASICHEMCL to indicate FACT quasi-chemical model (not implemented).
  - NO\_AUTO\_COMP\_SET to prevent automatic creations of composition sets for this phase. One can forbid creating automatic composition sets (by the grid minimizer) for all phases with the AMEND GENERAL or SET BIT GLOBAL commands.
- \* QUIT nothing is set.
  - \* RANGE\_EXP\_EQUIL is needed for the CALCULATE ALL command. The first and last equilibrium included in an assessment or a CALCULATE ALL command must be specified. The first (default) equilibrium, number 1, cannot be included.
  - \* REFERENCE\_STATE the reference state of a component. The phase,  $T$  and  $P$  must be specified. The phase must exist with the component as its only component. When the phase can exist with the component in different ways, like O in a gas can be O, O<sub>2</sub> or O<sub>3</sub> the most molecule at current  $T$  is selected.
  - \* SCALED\_COEFF can be used to set a coefficient to be optimized with a specified scaling factor and possibly a min and max value.
  - \* STATUS
    - PHASE (default) one or more phases can be set as suspended, dormant, entered or fixed. You can use \* to mean all phases, \*S for all suspended, \*D for all dormant and \*E for all entered and \*U for all entered and unstable. The list of phases is terminated by an equal sign "=" or an empty line.  
If the new status is not already given after the equal sign it is asked for. If the new status is entered or fixed the amount is asked for.
    - ELEMENT an element can be entered or suspended.
    - SPECIES a species can be entered or suspended.

- CONSTITUENT not implemented.
- UNITS like energy Joule/cal or mass kg/lb ... but not implemented yet.
- VARIABLE\_COEFF an optimizing parameter is specified.
- VERBOSE the software will write extra output. Not implemented
- WEIGHT to be used for assessments.
- STEP is used to calculate along a single independent axis variable.
  - NORMAL follow the axis variable from low to high limit.
  - SEPARATE calculate each phase separately.
  - QUIT do nothing.
  - CONDITIONAL follow the axis variable and update s symbol after each step (to be used for Scheil-Gulliver simulations, not yet implemented).

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