OpenCalphad version 5
summary of new and old features

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Contents

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 stable 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.
- Sufficently fast for practical calculations in multicomponent system.

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. 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 dependance 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 (VAX/VMS was a famous computer from DEC in the 80'ies). It can be used to read data, set conditions, calculate equilibria, property and phase diagram. Plotting is done by the free GNUPLOT software. It can also assess model parameters. If you prefer a Graphical User Interface you are welcome to develop 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. In collaboartion with CEA and the university in Toulouse a PhD student has started to work this year on implementing better statistical routines to estimate the validity of an assessment and the possible extrapolations.

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, phyton 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, a number of test macro files.
- UG, the user guide and manual (also used on-line)

There are also a number of publications as listed below.

5 Software updates

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

5.1 New 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 New 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 New 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 if conditions. It also include parallelization using OpenMP on the equilibrium level and a possibility to assess model parameters.

5.4 New 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%. Extensive use of the Valgrind software and compiling OC on different Fortran compilers has also improved the general performance and stability and there are no important memory leaks during parallel calculations.

During MAP and STEP OC now performs a global minimization as test At node points and a line is suspened in the plot if there is some other phase stable. OC can now calculate isothermal sections and plot tie-lines in these. 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.

5.5 New features in version 5

Due to user requests the speed has been improved significantly for multicomponent (more then 15 elements) systems. There has also been a revision of the user interface to make it simpler to understand how to enter a system interactivly and to perform an assessment. By request there is also a possibility to write a database in the FactSage (Solgasmix) format.

The calculation of phase diagrams with tie-lines in the plane (binary and isothermal sections) using MAP has also been improved. The steplength control and selection of independent axis can now handle most problems. But the user may still have to add several startpoints to have a complete diagram. Option B for handling ordering in a 4 sublattice

BCC phase has been implemented and also a special grid minimizer for FCC and BCC ordering taking into account the symmetry. For ionic crystal like the spinel phase there is also a special grid minimizer to generate gridpoints that are uncharged.

The interest in the development of new models for magnetism and heat capacity at low temperature has added some new features to OC.

Because there are many onging 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 allows 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_2/L1_0 and A2/B2/B32/D0_3/L2_1(Heusler) 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 Symbols and TP functions

In OC there are two different types of symbols that could be confused, one is called TP-functions or TP-symbols and are used to simplify expressing the model parameters as functions of T and P. These have a very strict syntax because during equilibrium calculations they maybe calculated millions of times together with their first and second derivatives with respect to T and P.

The other type of symbols are user defined functions of the general thermodynamic properties like Gibbs energy, denoted G, entropy, enthalpy etc. The values of these can be obtained after an equilibrium calculation. A user defined symbol can also refer to an already existing symbol or it can be a “dot derivative” of one state variable with respect to another. Currently the only such derivative implemented is H.T which represent the heat capacity (provided the conditions are T, P and the mass balance).

6.3 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
$x_{\mathrm{A}}^{\mathrm{liquid}} - x_{\mathrm{A}}^{\mathrm{Laves}} = 0$
in order to calculate a congruent melting and use expressions on for total amount like
$N_{\mathrm{U}} + N_{\mathrm{ZR}} = 1$
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.

6.3.1 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.

6.3.2 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.

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

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.

6.3.3 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:

$$M^\alpha = \begin{pmatrix} \frac{\partial G^\alpha_{\mathrm{A}}}{\partial x_{\mathrm{A}}} & \frac{\partial G^\alpha_{\mathrm{A}}}{\partial x_{\mathrm{B}}} \\ \frac{\partial G^\alpha_{\mathrm{B}}}{\partial x_{\mathrm{A}}} & \frac{\partial G^\alpha_{\mathrm{B}}}{\partial x_{\mathrm{B}}} \end{pmatrix}$$

and for a binary substitutional phase the chemical potential G^α_{A} is:

$$G^\alpha_{\mathrm{A}} = \left(\frac{\partial G^\alpha}{\partial N_{\mathrm{A}}}\right)_{T,P,N_{\mathrm{B}\neq\mathrm{A}}} = G^\alpha_M + \frac{\partial G^\alpha_M}{\partial x_{\mathrm{A}}} - \sum_{i=\mathrm{A,B}} \frac{\partial G^\alpha_M}{\partial x_i} \tag{2}$$

If the determinant of the matrix M^α:

$$\det(M^\alpha) = \frac{\partial^2 G^\alpha_M}{\partial x^2_{\mathrm{A}}}\frac{\partial^2 G^\alpha_M}{\partial x^2_{\mathrm{B}}} - (\frac{\partial^2 G^\alpha_M}{\partial y_{\mathrm{A}}\partial y_{\mathrm{B}}})^2 \tag{3}$$

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

$$\frac{\partial G^\alpha_{\mathrm{A}}}{\partial N_{\mathrm{B}}} = \frac{1}{N}\left(\frac{\partial^2 G^\alpha_M}{\partial x_{\mathrm{A}}\partial x_{\mathrm{B}}} - \sum_{\mathrm{C}} x_{\mathrm{C}}\left(\frac{\partial^2 G^\alpha_M}{\partial x_{\mathrm{A}}\partial x_{\mathrm{C}}} + \frac{\partial^2 G^\alpha_M}{\partial x_{\mathrm{B}}\partial x_{\mathrm{C}}}\right) + \sum_{\mathrm{C}}\sum_{\mathrm{D}} x_{\mathrm{C}} x_{\mathrm{D}} \frac{\partial^2 G^\alpha_M}{\partial x_{\mathrm{C}}\partial x_{\mathrm{D}}}\right) \tag{4}$$

and also the eigenvalues of this matrix. If there is a negative eigenvalue it means the phase is inside a spinodal. The derivation of eq. 4 can be found in the HMS documentation. It is interesting to note that eq. 4 is symmetrical, $\frac{\partial G_{\mathrm{A}}}{\partial N_{\mathrm{B}}} = \frac{\partial G_{\mathrm{B}}}{\partial N_{\mathrm{A}}}$.

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

6.4 Calculation and plotting of diagrams

The STEP procedure can calculate property diagram with a single axis variable and the user can plot how various state variables or model properties depend on this axis variable. In the plotting any two state variables can be used.

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 requires two independent axis variables and it calculates lines where the set of stable phases changes for different values of the axis variables. At present only two axis are allowed.

For examples of the graphics in OC please look at the documentation of the macro examples.

The mapping has been improved but it is very dependent on selecting a good equilibrium as a start point. If some lines are missing one may try to start at another equilibrium inside the diagram and merge the plots. The AMEND LINE command makes it possible to remove lines that are wrong.

Mapping of binary systems has been significantly improved in version 5 and mapping of multicomponent system is also reasonable. But there is still a missing feature in detecting exit lines from invariant equilibria for an isopleth. Additionally the present version of mapping will not discover miscibility gaps that occurs during mapping but it will check the global equilibrium at each node point and suspend lines that ends in a metastable equilibrium. 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 many different 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.

With version 5 the possibility to plot so called Gibbs triangle diagrams for isothermal sections of thernary diagrams has been added. For such diagrams it is also possible to plot tie-lines, i.e. a line between the composition of the phases in equilibrium in a two-phase region.

6.5 Saving results on a file

It is possible to save the current state of a calculation or assessment on an UNFORMATTED Fortran file. This will save all equilibria created but not results from a STEP or MAP command. The unformatted file can be read back into the program and used for future calculations. This means that the current state of an assessment can always be saved. However, the unformatted file may not be readable in a later version of OC so save also macro files and other documentation.

The reason step and map results are not saved is that sometimes they will exceed the available memory. For such cases one need to have a random access or DIRECT file which has not yet been implemented. The problem is to detect that the memory is exhausted and to stop the ongoing step or map procedure while saving the calculated equilibria to free up the memory.

6.6 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.

6.7 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 and listed below 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 from the user interface or by application software in the same way as thermodynamic state variables.

- G, the Gibbs energy parameter for an endmember or an interaction. G(LIQUID,FE;0) is the Gibbs energy for pure liquid Fe. Note that the parameter will be used also below the melting temperature of Fe for a liquid phase containing Fe. G(LIQUID,CR,FE;0) is the regular parameter for Cr and Fe in the liquid.
- TC, a parameter for the critical temperature for ferro or antiferro magnetic ordering using the Inden model.
- BMAG, a parameter for the average Bohr magneton number using the Inden model.
- CTA, a parameter for the Curie temperature for ferromagnetic ordering using a modified Inden model.
- NTA, a parameter for the Neel temperature for antiferromagnetic ordering using a modified Inden model.

- IBM&C, a parameter for the individual Bohr magneton number for constituent C using a modified Inden model. For example IBM&FE(BCC,FE) is the Bohr magneton number for BCC Fe. The identifier IBM&FE(BCC,CR) means the Bohr magneton number of a single Fe atom in BCC Cr. An identifier IBM&FE(BCC,CR,FE) can be used to decribe the composition dependence of the Bohr magneton number for Fe in BCC.
- THET, a parameter for the Debye or Einstein temperature.
- MQ&C, a parameter for the logarithm of the mobility of constituent C.
- RHO, a parameter for the electrical resistivity.
- MSUS, a parameter for the magnetic susceptibility.
- G2, a parameter for the two-state liquid model.
- VISC, a parameter for the viscosity.
- LPX, a parameter the lattice parameter in X direction.
- LPY, a parameter the lattice parameter in Y direction.
- LPZ, a parameter the lattice parameter in Z direction.
- LPTH, a parameter the angle between lattice directions.
- EC11, a parameter for the elastic constant C11.
- EC12, a parameter for the elastic constant C12.
- EC44, a parameter for the elastic constant C44.
- FHV
- V0, a parameter for the volume at 298.15 K and 1 bar.
- VA, a parameter for the integrated thermal expansion.
- VB, a parameter for the Bulk modulus.
- LAMB, a parameter for the thermal conductivity.
- HMVA, a parameter for the enthalpy of vacancy formation.

6.8 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 reecent 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 form an OC calculation without using calls to subroutines.

6.8.1 The phase tuple

In the OCASI interface a new method was introduced in version 4 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. Thus OC has a variable called "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 compostion set of a phase follow after those for the first composition set. This feature was introduced in version 3 of OC and was slightly changed in version 4. The phase tuple has 5 integer indices:

1. is the location of the phase record,
2. is the composition set number,
3. is the alphabetical phase index (i.e. the normal phase index),
4. is an index to the array of "phase_varres" records where conditions and results are stored
5. the last is zero or an index in the phase tuple array of the next composition set of the same phase.

The phase tuple is an array provided by OC to the application software and updated internally whenever there is a change. The user interface of OC sometimes 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.

6.9 Multiple equilibria and parallelization

The user can enter several equilibria from the application software (as well as interactively) 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 node points during step/map results and when OC is used assess model parameters from experimental data. Each equilibrium is independent and they be calculated in parallel if OC is compiled with OpenMP.

6.10 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 now fairly stable but it may be changed in future releases.
- 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 ochelp5.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	EXIT	MAP	SELECT
AMEND	FIN	NEW	SET
BACK	HELP	OPTIMIZE	SHOW
CALCULATE	HPCALC	PLOT	STEP
DEBUG	INFORMATION	QUIT	
DELETE	LIST	READ	
ENTER	MACRO	SAVE	

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
- DEBUG not implemented
- 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
- SHOW a property value for a state variable like $T, MU(C), G$ or a user defined symbol or a model parameter identifier (always with a phase specification!).

7.3 Commands with subcommands

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

7.3.1 AMEND

Amend should change something already entered or set. But sometimes it creates something so one should be careful if a subcommand should be changed to 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.
- 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 remve 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. Many of the things that formely were part of "set bit phase" have been moved here because they represent permanent modification which are never "reset".
  - 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.
  - AQUEUS_MODEL not implemented yet.
  - BCC_PERMUTATIONS for the 4 sublattice BCC ordered model. Only unique permutations of model parameters needed.
  - DEFAULT_CONSTITUTION allows to set min and max of constituents.
  - DISORDERED_FRACS adds a disordered fraction set for an ordered phase.
  - ELASTIC_MODEL_1 adds an elastic model (not implemented).
  - FCC_CVM_TETRAHDR the FCC tetrahedron model including SRO. Not implemented yet.
  - FCC_PERMUTATIONS for the 4 sublattice FCC ordered model. Only unique permutations of model parameters needed.
  - FLORY_HUGGINS model for polymers (not implemented).
  - GADDITION a Gibbs energy value can be added to a phase.
  - LIQUID_2_STATENDL adds a Gibbs energy for the glas transition model (not implemented).
  - LOWT_CP_MODEL adds an Einstein or Debye Cp model
  - MAGNETIC_CONTRIB adds an Inden-Hillert or Inden_Xiong magnetic model.
  - QUASICEM_MODEL specifies a quasichemical model for SRO without any LRO. (not implemented).
  - QUIT You did not want to amend anything for the phase
- 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.

7.3.2 CALCULATE

One can calculeate many 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

    $$\frac{\partial G_{\mathrm{A}}}{\partial N_{\mathrm{B}}}$$

    for all components (see eq. 4) 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 calculates 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.
- WITH_CHECK_AFTER calculates the equilibrium using the current compositions and checks afterwards with the grid minimizer if it has found a glocal equilibrium. Mainly for testing.

7.3.3 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.

7.3.4 ENTER

ENTER is the main command to enter data interactivly. 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 coped 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¿1200:1 X(liq,mo)=.2:.01 HM(fcc)=-30000:5000
- GNUPLOT_TERMINAL allows the user to change or add the terminal used for plotting.
- 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.
- MATERIAL the user can specify a database and a composition and temperature to calculate an equilibrium. If there are already data the user can enter a new composition for calculation.
- 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.
- PLOT_DATA the user can add data to be plotted for the cirrent equilibrium. Used for equilibria with experimental data for assessments.
- 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.

7.3.5 LIST

There are many things to LIST

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 equilibra 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.
  - C writes data for all elements.
  - M writes models for all 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 it value. **replaced by the SHOW command**

- SYMBOLS lists all entered state variable symbols (same in all equilibria). To list the values of symbols use **calculate symbol** or **show**.

- TPFUN_SYMBOLS lists one or all TP function symbols and expressions (same in all equilibria).

7.3.6 PLOT

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.

- APPEND you can add a GNUPLOT file that will be added to the current plot.
- AXIS_LABELS set text on X or Y axis.
- FONT-AND-COLOR select font and text color (not implemented).
- GIBBS_TRIANGLE set diagram to be a Gibbs triangle. Can only be used for isothermal sections.
- GRAPHICS_FORMAT set type of terminal. See **enter gnuplot-terminal** for possible terminals.
- LOGSCALE the X or Y axis or both can have logarithmic scaling.
- MANIPULATE-LINES to select color order for some lines.
- OUTPUT_FILE set name of plot file (default is ocgnu.dat).
- 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.
- QUIT you do not want to plot.
- RATIOS-XY the ratios of X and Y axis can be set.
- RENDER (default) finally plot when all options set.
- SCALE-RANGE of X and Y axis.

- TEXT allows adding a text in the plot at a apecific point and for phase diagrams also to calculate the set of stable phases at that point.
- TIE-LINE index for isothermal sections, 1 means all, 2 every second, 3 every third, 0 means none.
- TITLE set title of plot.

7.3.7 READ

READ data from a file.

- 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 TDB file. The user can select which elements he wants to read from the file.
- PDB Is a new format developed for data interchange.
- UNFORMATTED an unformatted file with model parameters and results for a single equilibrium calculation. Beware that an unformatted file may be unreadable in a future version.
- QUIT you did not want to read anything.
- DIRECT will save results from STEP and MAP on a random access file (not implemented).

7.3.8 SAVE

Ther are several possibilities to save data and results

- DIRECT not implemented yet (intended for STEP and MAP results).
- PDB writing an editable database file in PDB format
- QUIT do not save anything.
- SOLGAS writing a database in FactSage format.
- TDB same as **LIST TDB**
- 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.

7.3.9 SELECT

There are a few things to SELECT.

- 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).

7.3.10 SET

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).
- BIT can affect GLOBAL, EQUILIBRIUM and PHASE records. The bit is toggled, i.e. if already set it will be cleared. See the user guide for more information.
- 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 you can declare yourself as an expert.
- 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 toggled.
    - QUIT (default) no bit is changed.
    - EXTRA_DENSE_GRID to have more gridpoints in this phase
    - 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_2 or O_3 the most stable 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.
- T-AND-P is NOT to set conditions but just change local values used for example in calculate phase.
- 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.

7.3.11 STEP

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).

That is all (puuh)

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