# User Guide to the OpenCalphad software package version 5.0

DRAFT

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# Contents

# 17 Macro     42

# 18 Map     42

# 19 New     43

# 20 Optimize     43

# 21 Plot     43

# 22 Quit     45

# 28 Summary  56

# 1  Introduction

The OpenCalphad (OC) initiative aims to provide a free high quality software for thermodynamic calculations, including property and phase diagrams, assessment of databases and a thermodynamic library for simulations for inorganic systems i.e. gases. liquids, alloys and other materials using many different kinds of models for the phases. There are three papers published about OC [15Sun1, 15Sun2, 16Sun]. General information about thermodynamic models, calculations and assessments based on the Calphad technique can be found in the book by Lukas et al [07Luk]. The software is provided free with a GNU GPL license.

In OC there is also a framework to store different kinds of materials properties that depend on temperature, pressure and composition when such properties are related to the phases of the system. The OC software can also be used to assess model parameters for such properties from experimental and theoretical values.

Complimentary (and maybe sometimes contradictory, I am not perfect) information about the OC software can be found in getting-started.pdf, news-oc5.pdf and the other parts of the OC documentation.

# 2  Some general features

Oc is operated by commands typed by the user or read from a macro file. The command monitor has a menu of command and each of these usually has sub-menus and finally some questions may be asked like phase names, a value or an expression. In most cases a default answer is provided which can be selected by just pressing the RETURN key or by typing a comma, ",", on the same line as the command. At all levels the user should be able to type a ? and get some help, usually an extract from this manual, sometimes just a menu or examples of answers.

The different parts of the OC software are documented separately for each module: thermodynamic models (GTP), equilibrium calculations (HMS), step/map/plot routines (SMP) and the application software interface (OCASI/TQ). OC uses the free numerics packages LAPACK and BLAS and a free least square routine, LMDIF citelmdif, developed at Argonne 1980 for assessments. For graphics OC generates a command file which can be plotted with the free GNUPLOT [GNUPLOT] software. If GNUPLOT is properly installed this is done automatically by OC.

## 2.1  Names and symbols

There are many symbols and names used in this package. A symbol or name MUST start with a letter A-Z. It usually can contain digits and the underscore character after the initial letter. All names are CASE INSENSITIVE, i.e. fe, FE, fE and Fe is the same. Some special symbols are used:

- /- is used to denote the electron. /+ can be used for a positive charge.

- # are used to identify composition sets after a phase name or sublattice after a constituent name.

- & are used in some parameter identifiers to specify the constituent for the parameter, like for mobilities, the mobility of Fe in the BCC phase is denoted MQ&FE(BCC).

A name of an element is one or two characters, a species maximum 24 characters (note that a species name does not have to be its stoichiometric formula). A phase name is 24 characters but can also have a pre- and suffix 4 characters long and possibly a composition set number after a hash symbol, #.

State variable symbols and TP-fun symbols can be 16 characters long. TP-funs are expressions used to describe the $T$ and $P$ dependence of model parameters.

For user input it is possible to use abbreviations of names but one must be careful with names that have the same abbreviation and avoid names that are abbreviations of another name!

## 2.2 Phases, composition sets and phase tuples

Each phase in a system has a name and a thermodynamic model. The models are explained in a separate documentation. The phases can be entered interactivly or read from a database or a saved file together with the last calculation.

In some cases a phase can be stable with two ore more different compositions for example inside miscibility gaps or when the phase has order/disorder transitions. In such a case one use a composition set index to separate these. The composition set index is appended to the phase name preceeded by a hash "#" character, like liquid#2.

Composition sets can be created manually, see the command **AMEND PHASE** in section 5.11.3 or automatically by the grid minimizer or application software.

The phase tuple has been introduced to have a single index for both phases and composition sets in application software. The tuple index thus contain both the phase number and the composition set index. The array of tuple indices is updated internally whenever a new composition set is created or deleted.

## 2.3 The use of wildcards for names

In many cases one can use an asterix "*" as a name and this normally means "all". For setting status of phases one can use the special "*S" for all suspended phase, "*D" for all dormant phases.

## 2.4 Model parameters

All data is organized relative to a phase and the phase is identified by a name. Each phase can have a different model for the composition dependence but the way to enter model parameters is the same for all models. However, the meaning of a model parameter will depend on the model of the phase.

Many types of data can be stored as explained in the section on parameter identifiers. The parameter also has a constituent specification explained in the constituent array section and possibly a degree, the meaning of which is model dependent.

The basic syntax of a parameter is

"identifier" ( "phase name" , "constituent array" ; "degree" ) "expression" "bib.ref."

These parts are explained in more detail below.

### 2.4.1 Model Parameter Identifiers

The OC thermodynamic package can handle any phase property that depend on $T, P$ and the constitution of the phase using the models implemented. It is easy to extend the number of properties by declaring property identifiers in the source code. If the parameters should have an influence on the Gibbs energy (like the Curie temperature) or a diffusion coefficient (like the mobility) the necessary code to calculate this must be added.

A list of the model parameter identifiers currently defined can be obtained by the command **LIST MODEL_PARAM_ID**:

```
Indx Ident T P Specification              Status Note
   1 G     T P                                 0 Energy
   2 TC    - P                                 2 Combined Curie/Neel T
   3 BMAG  - -                                 1 Average Bohr magneton numb
   4 CTA   - P                                 2 Curie temperature
   5 NTA   - P                                 2 Neel temperature
   6 IBM   - P &<constituent#sublattice>;     12 Individual Bohr magneton num
   7 THET  - P                                 2 Debye or Einstein temp
   8 MQ    T P &<constituent#sublattice>;     10 LN mobility1 of component
   9 MF    T P &<constituent#sublattice>;     10 LN mobility2 of component
  10 MG    T P &<constituent#sublattice>;     10 LN mobility3 of component
  11 RHO   T P                                 0 Elect resistivity
  12 MSUS  T P                                 0 Magn suseptibility
  13 G2    T P                                 0 Liquid two state parameter
  14 VISC  T P                                 0 Viscosity
  15 LPX   T P                                 0 Lattice param X axis
  16 LPY   T P                                 0 Lattice param Y axis
  17 LPZ   T P                                 0 Lattice param Z axis
  18 LPTH  T P                                 0 Lattice angle TH
  19 EC11  T P                                 0 Elastic const C11
```

```
20 EC12  T P                                 0 Elastic const C12
21 EC44  T P                                 0 Elastic const C44
22 FHV   T P &<constituent#sublattice>;     10 Flory-Huggins volume ratio
23 V0    - -                                 1 Volume at T0, P0
24 VA    T -                                 4 Thermal expansion
25 VB    T P                                 0 Bulk modulus
26 LAMB  T P                                 0 Thermal conductivity
```

Many of these identifiers have no supporting software implemented, this is an ongoing project. The columns T P indicate if the parameter may depend on $T$ or $P$. Some identifiers require additional specification of the constituent and sublattice, like the mobility of a constituent. Currently it is not yet clear if mobilities should depend on the sublattice or not but the notation allows that.

A slightly more detailed explanation of the identifiers are:

- 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, a parameter for the Flory-Huggins volume ratio

- 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.

The current value of any of these parameter identifiers can be obtain by the command **LIST STATE_VARIABLE** using the identifier and appropriate phase and component specifiers, see section 16.16.

For details of the meaning of the model identifier refer to the model documentation. As already mentioned many of the identifiers, like the mobility, does not influence the Gibbs energy but as they depend on the $T, P$ and constitution of the phase it is convenient to model them in the same way as the thermodynamic data.

### 2.4.2   Constituent array and degrees

A constituent array specifies one or more constituent in each sublattice. A constituent must be entered as a species with fixed stoichiometry. Between constituents in different sublattices one must give a colon, ":", between interacting constituents in the same sublattice one must give a comma, ",," or a space. A constituent array with exactly one constituent in each sublattice is also called an "endmember" as it give the value for a "compound" with fixed stoichiometry. Constituent arrays with one or more interaction constituents describe the composition dependence of the property. Without such parameters the property will vary linearly between the endmembers.

If there are no sublattices, like in the gas, one just give the phase and the constituent

G(GAS,C1O2)

If no degree is specified it is assumed to be zero. For endmembers the degree must be zero but it may sometimes be useful to specify the zero in order to distinguish the parameter from the expression for the calculated value of the property, like the chemical potential of a component. In the gas phase one normally assumes there are no interactions but it is possible to add such parameters. For an fcc phase with 4 sublattice for ordering and one for interstitials an endmember parameter is

G(FCC,AL:NI:NI:NI:VA;0)

This would be the Gibbs energy of an fcc AL1NI3 ordered compound.

An interaction between vacancies and carbon in the austenite is

G(FCC,FE:C,VA;0)

For an interaction parameter one should always specify a degree but also in this case an omitted degree is interpreted as zero.

### 2.4.3 The TPFUN expression and bibliographic reference

The expression for a parameter can be a single value or a function of $T$ and $P$. It must start with a low temperature limit, usually 298.15 K and must finish with a high temperature limit. These expressions as well as their first an second derivatives will be calculated by the TP-fun package. To simplify that there is a strict syntax for the expression. A term in the expression is

"numeric value" * "name of TP function" *T** "power" *P** "power"

You can construct very complex expression by referring to other functions. If "power" is zero the corresponding *T** or *P** can be omitted. If it is negative it must be surrounded by parenthesis like (-1). If it is unity the **1 can be skipped.

Several terms, seperated by signs, forms an expression and it must be terminated by a semi-colon, ";". After the semicolon there must be a high temperature limit or a breakpoint in temperature. A breakpoint must be followed by the letter "Y" and then a new expression for temperatures above the breakpoint.

**It is the responsability of the database manager to ensure the expression is continuous at the breakpoint. If there are jumps in the value at a breakpoint strange things will happen when calculating equilibria.**

After the high temperature limit the letter "N" must be given followed by a bibliographic reference for the parameter. Use the commands AMEND or ENTER BIBLIOGRAPHIC to give the reference.

**The database manager should always add a bibliographic reference even if it is just his or her name and a date. This avoids people to mistake a value inspired by your experience for a carefully validated parameter.**

A term can be used inside a natural logarithm, LN, or exponential, EXP. And the LN or EXP can be multiplied with a term. On the other hand you are not allowed to have any parenthesis,

except around powers or arguments to LN and EXP. A valid expression is

```
298.15 -8856.94+157.48*T-26.908*T*LN(T)+.00189435*T**2
       -1.47721E-06*T**3+139250*T**(-1); 2180 Y
       -34869.344+344.18*T-50*T*LN(T)-2.88526E+32*T**(-9); 6000 N 91Din
```

where 91Din is the reference to the SGTE unary database.

## 2.5 The reference state of a component

The values of most thermodynamic data must have a welldefined reference state. By default the reference state for the components is SER (Stable Element Reference) which is the stable state of the element at 298.15 K and 1 bar. (NOTE: the default reference state is defined by the database but today almost all databases have SER as reference state.)

For each component (also for other components than the elements) one can specify a phase at a given temperature and pressure as reference state, see section 26.17. The phase must exist for the component as pure.

A state variable like the chemical potential, MU(O), will refer to the user defined reference state if set. To obtain the value for the SER state one can use a suffix S, i.e. MUS(O) to obtain the chemical potential refered to SER.

Note that the value of integral properties like Gibbs energy, $G$, enthalpy, $H$, etc. may have mixed reference states unless all components have the same phase as reference state. In order to have the enthalpy of mixing of a phase all components must have that phase as reference state. For the volume, $V$, SER is always used as reference state unless all components have the same reference state.

## 2.6 Macro files

The macro command is very useful for preparing complex calculations and to remember how you did them. A macro file is simplest to create staring from a log file (created by the **SET LOG** command). See the macros directory for examples.

You can insert stops in the macro file with "@&" at the beginning of a line. This can be useful to inspect the output. The macro continues after pressing the ENTER/RETURN key. Depending on the graphical driver you use the program will normally pause after each plot and you must use the mouse to click on the graphical window to continue.

You can insert comments in the macro file with "@$" at the beginning of the comment line.

A macro file should be terminated with the command **SET INTERACTIVE** which gives back control to the keyboard (or the calling macro file) otherwise the program will terminate at the end of the macro.

Macro files can be nested 5 levels deep.

## 2.7 Environment and startup macro file

The OC program will look for an environment variable called OCHOME and if it finds this it will look for a file start.OCM which will be executed before the user gets control. This can typically be useful to set some variables like the plot terminals, see section 10.8. If there is no OCHOME environment variable the current directory will be searched.

If the OCHOME directory has a subdirectory called "data" this will be searched when the user tries to read a TDB file.

## 2.8 User interface feedback

OC has grown organically and although the basic concepts has been quite clear several of the implementations of these has become rather confusing. This will eventually require some cleaning up of the user interface.

If you like a Graphical User Interface you are welcome to write it.

A central part of any thermodynamic software is the modeling of the phases. The new PDB format for databases may help a little with the specification of the models. An attempt has been made in this version to clean up the way a model is specified and used. At present one must first ENTER the phase to give a name, basic model, sublattices and constituents. The AMEND command is then used to add magnetism, a disordered fraction set or to use of BCC/FCC permutations. Previously some of these things were set by the command SET PHASE ... BIT and that was not very clear.

Some computational options like for the grid minimizer are also set with several different commands. It is useful to have some feedback from users to organize this better.

# 3    All commands

The commands in alphabetical order as listed with the ?

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

Many of the commands have "subcommands" and usually there is a default (listed within slashes //) which is selected by pressing return. One can type commands and subcommands and other parameters on the same line if one knows the order, using a comma, "," to select the default.

## 3.1    Options

There some options that can be set for the whole session or for just a single command. The options are identified by a / in front like /output=myfile.dat.

The options can be specifies directly after a command. Only a few are implemented.

- /OUTPUT=*file name* open a file and write

- /APPEND=*file name* append output to a file, any previous content is kept.

- /ALL apply for all

- /FORCE override normal restrictions

- /VERBOSE write information while executing

- /SILENT do not write anything except fatal error messages

# 4    About

Some information about the software.

# 5    Amend

Intended to allow changes of already entered data. Only some of the subcommands are implemented.

| ALL_OPTIM_COEFF | CP_MODEL | LINE | SPECIES |
| BIBLIOGRAPHY | ELEMENT | PARAMETER | SYMBOL |
| COMPONENTS | EQUILIBRIUM | PHASE | TPFUN_SYMBOL |
| CONSTITUTION | GENERAL | QUIT | |

## 5.1 *amend* All optimizing coefficients

The values of the optimizing coefficients, see section 26.16 can be rescaled (start values set to current values) or recovered (current values set to previous start values).

## 5.2 *amend* Bibliography

The text for bibliographic reference identifier can be amended. The reference identifier is case insensitive.

## 5.3 *amend* Components

By default the elements are the components. This command can set any orthogonal set of species as components. The number of components cannot be changed by this command. The new components must exist as species and be orthogonal.

You must use components when setting conditions on amounts, mole fractions, chemical potentials or activities. Note that when you have other components than the elements you may have negative mole fractions and phase amounts.

## 5.4 *amend* Constitution

The program will ask for a phase name and the user can set the amount and constitution of the phase. This will be used as initial constitution for a calculation unless the grid minimizer is used.

## 5.5 *amend* $C_P$ model

The low temperature heat capacity model can be amended. Not implemented yet.

## 5.6 *amend* Element

The data for the element can be amended, not implemented yet.

## 5.7 *amend* Equilirium

Not sure what could be amended and anyway not implemented.

## 5.8 *amend* General

A number of user specific settings for defaults can be made:

- The name of the system.

- The level of the user (beginner, frequent user, expert). This may affect the behavior of the program (not implemented yet).

- If global minimization is allowed or not.

- If the grid minimizer is allowed to merge gridpoints in the same phase after global minimization.

- If the grid minimizer can automatic create composition sets is allowed or not.

- If redundant composition sets can be deleted automatically after an equilibrium calculaion.

Note that these and some other general feautures can be changed by the command **SET BIT GLOBAL**

## 5.9 *amend* Line

After a STEP or MAP command it is possible to give the command LIST LINE to list all calculated equilibria or AMEND LINE which allows the user to EXCLUDE lines or INCLUDE lines from the plotting.

## 5.10 *amend* Parameter

The possible parameters that can be amended depend on the model of the phase. By specifying a parameter the user can change its expression. This is not yet implemented you must use the command **ENTER PARAMETER** to change the parameter expression.

## 5.11 *amend* Phase *<phase>*

You must first specify the phase name and then you can amend some of the properties of the phase:

| | | | |
|---|---|---|---|
| AQUEUS_MODEL | DISORDERED_FRACS | FLORY_HUGG_MODEL | MAGNETIC_CONTRIB |
| BCC_PERMUTATIONS | ELASTIC_MODEL_1 | GADDITION | QUASICHEM_MODEL |
| COMPOSITION_SET | FCC_CVM_TETRAHDR | LIQUID_2_STATEML | QUIT |
| DEFAULT_CONSTIT | FCC_PERMUTATIONS | LOWT_CP_MODEL | |

### 5.11.1 *amend phase ...* Aqueous_model

A model with dilute configurational entropy. Not implemented yet.

### 5.11.2 *amend phase ...* BCC_permutations

This is intended for the 4 sublattice CEF model for BCC ordering. The BCC tetrahedron is asymmetric which makes it a bit more complicated than the FCC. There can be a 5th sublattice with interstitials.

With this model parameters with permutations has to be entered just once.

### 5.11.3 *amend phase ...* Composition set

Each phase has by default a single composition set. If the same phase can exist as stable (or metastable) with two or more compositions (miscibility gaps or order/disorder transformations) you may have to amend the phase by creating additional composition sets.

Composition sets can also be created automatically by the grid minimizer during an equilibrium calculation. In such a case the composition set will have the suffix _AUTO,

Composition sets of a phase can be created and deleted. Phases with miscibility gaps or which can exist with different chemical ordering like A2 and B2 must be treated as different composition sets. The user can specify a prefix and suffix for the composition set. Extra composition sets will always have a suffix #digit where digit is a number between 2 and 9. One cannot have more than 9 composition sets.

The composition set number is given after the phase name and preceded by a hash character #. In some cases phase tuples are used to identify a phase and a composition set by a single number.

In some cases it may be interesting to calculate metastable states inside miscibility gaps and one can prevent the automatic creation of composition sets by turning off the global minimazation using **AMEND GENERAL** or for an individual phase by **SET PHASE ... BIT NO_AUTO_COMP_SET**

### 5.11.4 *amend phase ...* Default Constitution

A default constitution of a phase can be set. This will be used for the first calculation with the phase and sometimes if there are convergence problems. NOTE that if you want to specify a

default constitution for the second or higher composition set of a phase you must specify the composition set with the phase name!

Depending on the minimizing software used the initial constitution can be important to find the correct equilibrium if the phase has ordering or a miscibility gap.

For each constituent you can specify a minimum > or maximum < fraction or give NONE if there are no default.

If a phase has miscibility gaps and the user has created composition sets with default constitutions the grid minimizer will try to select the composition set with a composition closest to the default for a stable phase.

To temporarily set a new constitution of a phase use the command **AMEND CONSTITU-TION** <phase> or **CALCULATE PHASE ...** .

### 5.11.5 *amend phase ...* Disordered fraction sets

For phases with several sublattices the Gibbs energy of the phase can be divided into two sets of fractions where the second or "disordered" set have only one or two sublattice and the fractions on these represent the sum of fraction on some or all of the first or "ordered" set of sublattices.

This is particularly important for phases with ordering like FCC, BCC and HCP and for intermediate phases like SIGMA, MU etc.

### 5.11.6 *amend phase ...* Elastic model 1

A contribution to the Gibbs energy due to elastic strain can be added. This also requires values of the elastic constants and lattice parameters, see section 2.4.1.

There is no code to calculate the elastic energy implemented yet.

### 5.11.7 *amend phase ...* FCC_CVM_tetradrn

This model is intended for the CVM tetrahedron model for FCC and HCP. Not implemented yet.

### 5.11.8 *amend phase ...* FCC_permutations

FCC_PERMUTATIONS is intended for the 4 sublattice CEF model for fcc ordering. Setting this bit means that only unique model parameters needs to be entered, the software will take care of all permutations. HCP permutations is also handled by this bit as they are identical in the 4 sublattice model. There can be a 5th interstitial sublattice.

### 5.11.9  *amend phase ...* Flory_Huggins model

A model when the configurational entropy takes into account that the constituents have very different size. Not implemented yet.

### 5.11.10  *amend phase ...* Gaddition

The user can add a constant value of the Gibbs energy in Joule per formula unit to a phase. This is a simple way to implement a nucleation barrier.

### 5.11.11  *amend phase ...* Liquid_2_stateml

The two-state model for the hear capacity for the undercooled liquids can be added. It uses the model_parameter_ident bf G2 listed in section 2.4.1.

Not implemented yet.

### 5.11.12  *amend phase ...* Low temperature $C_P$ model

The Einstein and Debye model for heat capactities from 0 to 300 K will be implemented shortly.

### 5.11.13  *amend phase ...* Magnetic_Contrib

The Inden-Hillert and the modified Xiong-Inden model for the magnetic contribution to the Gibbs energy can be set by this command This depends on model parameters describing the Curie and Neel temperatures and the Bohr magneton number, as listed in model parameters identifiers 2.4.1, for the phase.

The Inden-Hillert model is decsribed in [07Luk] and the Xiong modified model requires separate values of the Curie and Neel Temperatures and individual Bohr magneton numbers of the constituents of the phase.

### 5.11.14  *amend phase ...* Quasichemical

There are several quasichemical models for the liquid that only describes the short range ordering (SRO). None of them are yet implemented.

### 5.11.15  *amend phase ...* Quit

Do not amend anything for the phase.

## 5.12  *amend* Quit

Do not amend anything (more).

## 5.13  *amend* Species *<species>*

Not implemented yet.

## 5.14  *amend* Symbol *<symbol>*

This command is a bit special. It is mainly used in assessments to specify that a particular symbol must not be evaluated except when specified explicity, or when calculating a specific equilibrium.

A symbol can refer to another symbol and thus all symbols are normally evaluated whenever the value of any symbol is requested. This is to ensure that all symbol values are consistent and refer to the same equilibrium. But in certain cases one wants to enter a symbol that is only evaluted when referenced explicity and this can be set with this command.

Another case when one wants to restrict when a symbol is evaluated is when one wants to compare the value of a thermodynamic property, like the enthalpy, in two equilibria. For example if one has experimental data on the heat difference for a compound at various $T$. In such a case the heat content at the reference $T$ can be stored in a symbol, which is then amended with this command and the equilibrium at which it should be evaluated is specified. In all other equilibria the value of this symbol will then refer to its value at the specified equilibrium. See also the documentation on the assessment procedure.

You cannot amend the expression for the symbol.

## 5.15  *amend* Tpfun_Symbol *<symbol>*

You can replace a TP function with a new expression.

# 6   Back

Return back from the command monitor to the application program. In the OC software itself it means terminate the program.

# 7 Calculate

Different things can be calculated. The normal thing to calculate is **equilibrium**, the other things are special.

| | | | |
|---|---|---|---|
| ALL_EQUILIBRIA | NO_GLOBAL | SYMBOL | WITH_CHECK_AFTER |
| EQUILIBRIUM | PHASE | TPFUN_SYMBOLS | |
| GLOBAL_GRIDMIN | QUIT | TRANSITION | |

## 7.1 *calculate* All equilibria

Intended for the assessment procedure. Calculates all equilibria with non-zero weight as set by the command **SET RANGE**. It can also be used for other purposes, for example testing the parallelization. The equilibria can be entered by the command **ENTER MANY_EQUILIB**.

## 7.2 *calculate* Equilibrium

The normal command to calculate the equilibrium of a system for the current set of conditions and phase status. You can calculate a metastable equilibrium if some phases that should be stable have been set dormant or suspended or if automatic creation of composition sets is not allowed. If conditions allow the grid minimizer is used to find start values unless the grid minimizer is explicitly turned of.

## 7.3 *calculate* Global_Gridmin

Calculate with the global grid minimizer without using this result as a start point for the general minimizer. Used to debug the grid minimizer.

## 7.4 *calculate* No_Global

Calculate the equilibrium without using a global grid minimizer to generate start constitutions. The current equilibrium is used as start point. Can be quicker when only small changes of conditions made since previous calculation and this is how equilibria is calculated during STEP and MAP. It means no check of new miscibility gaps.

## 7.5 *calculate* Phase *<phase>*

You must provide a phase name, the amount of the phase and if you should use the current constitution or enter a new.

The Gibbs energy of a phase and possible derivatives and some other things can be calculated. Mainly for debugging the implementation of models.

### 7.5.1 *calculate phase ...* Only_G

The Gibbs energy and all $T$ and $P$ derivatives calculated and listed for the specified phase for current $T, P$.

### 7.5.2 *calculate phase ...* G_and_dGdy

The Gibbs energy, all $T$ and $P$ derivatives and all first derivatives with respect to constituents for the specified phase for current $T, P$ are calculated and listed.

### 7.5.3 *calculate phase ...* All_Derivatives

The Gibbs energy, all $T$ and $P$ derivatives and all first and second derivatives with respect to constituents for the specified phase for current $T, P$ are calculated and listed.

### 7.5.4 *calculate phase ...* Constitution_Adjust

You will be asked to enter a new composition (note NOT the constitution and default is current) of the phase and this command will then calculate the Gibbs energy and all chemical potentials. For a phase with sublattices the constitution of the phase will be adjusted to have the minimum Gibbs energy for the given composition.

It is useful when one or more components are parts of several constituents, for example in a gas or for phases with order/disorder transitions, in particular when the corresponding subroutine is used in simulations.

### 7.5.5 *calculate phase ...* Diffusion_Coefficients

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

$$\frac{\partial^2 G}{\partial N_{\mathrm{A}} \partial N_{\mathrm{B}}}$$

for all components (see the documentation of the minimiser) and also all mobility values (if there are any).

## 7.6 *calculate* Quit

Do not calculate anything.

## 7.7  *calculate* Symbol

A state variable symbol or function is calculated using the results from the last equilibrium or grid minimizer calculation. It is used in particular for calculation of "dot derivatives" like $H.T$ for the heat capacity.

If a wildcard, "*", is given as name all symbols, except dot derivatives and symbols that must be specified explicity and those that should be calculated for another specified equilibria. See section 5.14.

## 7.8  *calculate* Tpfun_Symbols

All or a specific TPFUN symbol are calculated for current values of $T$ and $P$.

## 7.9  *calculate* Transition

After calculating an equilibrium you can calculate directly when a phase will appear or disappear by releasing one of the conditions you have specified. Typically this is used to calculate the melting temperature of an alloy or a solubility limit.

You specify the phase name and the condition to be released. The program will set this phase as FIXED with zero amount and remove the condition you specified and calculate the equilibrium. The calculation may fail if the phase cannot be set stable with zero amount. If successful the removed condition will be set to the value calculated and the phase set stable with zero amount.

# 8  Debug

Several possibilities to trace calculations will be implemented in order to find errors. The only implemented feature is to stop the program whenever an error occurs. This is useful to find errors using macro files so the macro not just goes on doing other things.

## 8.1  *debug* Elasticity

Not implemented.

## 8.2  *debug* Free lists

Only for experts.

## 8.3 *debug* Stop_on_Error

The program will stop at the command level after printing the error message if an error has occurred when using macro file. This should make it easier to to find errors occurring when running macro files.

However, it is not implemented.

# 9 Delete

It is quite difficult to delete anything when the data structure is so involved. In many cases it may be better to enter the data again without the data that should be deleted. But there are a few things that must occationally be deleted.

| | | | |
|---|---|---|---|
| COMPOSITION_SET | EQUILIBRIUM | QUIT | STEP_MAP_RESULTS |
| ELEMENTS | PHASE | SPECIES | |

## 9.1 *delete* Composition set

The first composition set of a phase cannot be deleted. Otherwise there is usually no problem unless several equilibria are entered because the composition set must be deleted in all equilibria. Composition sets are created and deleted during normal equilibrium calculations to detect miscibility gaps.

## 9.2 *delete* Element

Dangerous and will probably never be implemented.

## 9.3 *delete* Equilibrium

Dangerous but sometimes necessary. Done automatically at a second STEP or MAP command if the user specifies to delete previous results.

## 9.4 *delete* Phase

Dangerous and will probably never be implemented.

## 9.5 *delete* Quit

Do not delete anything.

## 9.6 *delete* Species

Not implemented yet and will probably never be.

## 9.7 *delete* Step_Map_Results

This removes all equilibria and saved equilibria associated with STEP and MAP commands. It also deletes the axis.

# 10 Enter

In most cases data will be read from a database file. But it is possible to enter all thermodynamic data interactively. This should normally start by entering all elements, then all species (the elements will automatically also be species) and then the phases.

A species have a fixed stoichiometry and possibly a charge. The species are the constituents of the phases.

A phase can have sublattices and various additions like magnetic or elastic (the latter not implemented yet).

TPFUN symbols can be used to describe common parts of model parameters. See section 2.4.3 for an explation.

Each parameter of a phase is entered separately. One may use TPFUN symbols which are already entered.

At present the multicomponent CEF model and the ionic 2-sublattice liquid model are the only one implemented. The CEF model includes as special cases the gas phase, regular solutions with Redlich-Kister Muggianu model and phases with up to 9 sublattices and magnetic contributions.

The enter command is also used to enter equilibria for assessments and some other things.

The subcommands are:

| | | | |
|---|---|---|---|
| BIBLIOGRAPHY | EQUILIBRIUM | OPTIMIZE_COEFF | SPECIES |
| COMMENT | EXPERIMENT | PARAMETER | SYMBOL |
| CONSTITUTION | GNUPLOT_TERMINAL | PHASE | TPFUN_SYMBOL |
| COPY_OF_EQUILIB | MANY_EQUILIBRIA | PLOT_DATA | |
| ELEMENT | MATERIAL | QUIT | |

## 10.1 *enter* Bibliography

Each model parameter must have a bibliographic reference to ensure one can find the origin of its value. When entering a parameter a bibliographic reference symbol is given and with this command one can give a full reference text for that symbol like a published paper, a report or simply the reason for the value. The date and name of the responsible should also be given.

## 10.2 *enter* Comment

A line of comment text can be added to an equilibrium. It is particularly important when entering experimental data to give the reference to the data.

## 10.3 *enter* Constitution

The constitution (fraction of all constituents) of a phase can be entered. This is a way to provide start values for an equilibrium calculation (when not using grid minimizer). To calculate the Gibbs energy for a specific phase at a specific constitution use the command **CALCULATE PHASE**.

## 10.4 *enter* Copy of equilibrium

This command creates a copy of the current equilibrium with the same set of conditions and related data.

## 10.5 *enter* Element

The data for an element is entered. It consists of is symbol, name, reference state, mass, H298-H0 and S298. The latter two values are never used for any calculation.

## 10.6 *enter* Equilibrium

One can have several equilibria each with a unique set of conditions including phase status (dormant, suspended, fix or entered) but all with the same components and thermodynamic data. This is useful for compare different states, to simulate transformations and to assess model parameters as each experimental or theoretical information represented as an equilibrium.

All equilibria use the same thermodynamic data but they have an independent set of conditions and result data structure and they can be calculated in parallel.

## 10.7 *enter* Experiment

This is used for assessments, experimental data can be specified for an equilibrium. The experiment is a state variable or symbol which can be set equal to the experimental value followed by a colon, ":" and its uncertainty.

In some cases an experimental value can be an upper or lower limit. In such cases the ">" or "<" can be used. The value of the uncertainty will then be interpreted as a penalty factor if the calculated value is outside the specified limit.

## 10.8  *enter* GNUPLOT Terminal

For plotting OC generates a command file for the GNUPLOT [GNUPLOT] software. GNU-PLOT can be downloaded free for most OS but depending on your screen and other hardware you may prefer to specify your prefered set of terminals. On Windows the defaults are:

| 1 | SCREEN | > set terminal wxt size 900,600 |
| 2 | PS | > set terminal postscript color solid |
| 3 | PDF | > set terminal pdf color solid size 6,4 enhanced fontscale 0.45 |
| 4 | GIF | > set terminal gif |

The text after the > is written on the GNU command file. You can change these or add additional terminals. You can also change these in the source code (userif/mon6.F90 file) or use a macro file start.OCM file to set them.

## 10.9  *enter* Many Equilibria

This command is intended for adding tables of experimental data of the same type. It can also be used for calculation of many equilibria using the **calculate all** command. The user first enters a TABLE HEAD giving the necessary phase status, conditions, experiments etc. In this "head" some values of text can be referred to columns in the following table using the "@" character followed by a digit 1 to 9, where the digit is the column number.

The prompt for input to the table head is "table head::"
In the examples below, taken from the parallel2.OCM macro file, user input is **in bold** and explanations *in italics*.

- By default all phases are suspended so the user must forst specify the phases with dormant, entered of fixed status (including amount) like
  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**

- Optional 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**
  The reference state for the component O will be gas at the current $T$ and 1 bar.

- Optional plot_data specifying a dataset number and coordinates to be plotted and a symbol. The coordinates can be table columns. Use the dataset numbers to have data of the same type together like enthalpies, phase diagram data etc.
  Table head: **plot 1 @1 @2 5**

- Optional comment
  Table head: **comment experimental data from Kubaschewski 1955**

- 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 referenced in the table head like:
Table row: **EQ1 1573 BCC 0.3 0.05 0.12 0.28**
Table row: **EQ2 1623 BCC 0.3 0.10 0.18 0.24**

The table is finished by an empty line or
Table row: **table_end**

## 10.10  *enter* Material

The user will be asked for a name of the material and possibly a database. Then he can give elements and their amount in mass percent or mole fraction. Finish with an empty line. Then he must specify the temperature and the program will automatically make a calculation at 1 bar. For example:

```
OC4:enter mat
Database:steel7
Elements: C , MO, V , CR, FE, SI,
Major element or material:fe
Input in mass percent? /Y/:
Input expected in mass percent

First alloying element:c
Mass percent: /1/:
Second alloying element:cr
Mass percent: /1/: 5
Third alloying element:mo
Mass percent: /1/: 8
```

```
Next alloying element:v
Mass percent: /1/:
Next alloying element:
 3E reading a TDB file
 3D em:  W%(C)=1  W%(CR)=5  W%(MO)=8  W%(V)=1   N=1
Temperature /1000/:
 3Y Constitution of metastable phases set
 3Y Composition set(s) created:           1
Gridmin:   18846 points   6.25E-02 s and      78 clockcycles, T= 1000.00
Phase change: its/add/remove:     5    0    21
Equilibrium calculation  19 its,   6.2500E-02 s and      94 clockcycles
```

The user can specify another composition of the same alloy with the same command or use other commands like **SET CONDITION** and **CALCULATE**

## 10.11  *enter* Optimizing coefficient

The TP symbols for the coefficients to be optimized are entered. They have the names A00 to A99. They are used in model parameters and can be varied by the optimization procedure to minimize the difference between the experimental data and the same property calculated from the models of the phases.

## 10.12  *enter* Parameter

A model parameter is defined by its identifier, the phase and constituent array. A parameter can be a constant or depend on T and P. The parameter will be multiplied with the fractions of the constituents given by its constituent array. See the documentation of the GTP model package or the book by Lukas et al[07Luk] for more information about thermodynamic models.

For example G(LIQUID,CR) is the Gibbs energy of liquid Cr relative to its reference state, normally the stable state of Cr at 298.15 K and 1 bar, and called an endmember.

For a gas molecule the parameter G(GAS,C1O2) is also an endmember and represent the Gibbs energy of the C1O2 molecule relative to the reference states of C (carbon) and O (oxygen).

For interaction parameters the components are separated by a comma "," like in G(LIQUID,CR,FE).

For phases with sublattices the constituents in each sublattice are separated by a semicolon, ":" and interacting constituents in the same sublattice by a comma, ",". For example

G(FCC,FE:C,VA) is the interaction between C (carbon) and VA (vacant interstitial sites) in the FCC phase.

The only binary excess model implemented in OC is the Redlish-Kister Muggianu

$$L_{A,B} = \sum_{\nu=0}^{n} {}^{\nu}L_{A,B}(y_A - y_B)^{\nu}$$

where the degree, $\nu$, of the interaction parameter is specified after a semicolon, L(phase,A,B;$\nu$).

For ternary parameters and for reciprocal parameters the Hillert model for composition dependence is implemented, see [07Luk].

One can store many different types of data in OC using the parameter identifier. A description of the identifiers currently implemented are explained in section 2.4.1

The current list can be obtained by the command **LIST MODEL_PARAM_ID**. All of them can be composition dependent. Some cannot depend on $T$ or $P$ or neither.

Many parameters of the parameters are available but the models to handle them are not yet implemented.

## 10.13   *enter* Phase

All thermodynamic data are connected to a phase as defined by its parameters, see **enter parameter**. A phase has a name with can contain letters, digits and the underscore character. It must start with a letter.

After the phase name you must specify a model. The model specfication is implemented in a rather rudimentary way. The only recognized models are

- IDEAL for a single lattice phase without interactions (like GAS)

- RKM for a substitutional phase with interactions (like metallic liquid)

- I2SL for the ionic liquid phase (2 sublattices with variable site ratios). If the phase name is IONIC_LIQUID this prompted as the default model.

- CQC means the "Corrected Quasichemical model" for liquids.

- CEF for any other phase with two or more sublattices

This list may be extended. Many other model features like magnetism, quasichemical etc is specified with the **AMEND PHASE** command, see section 5.11. The AMEND PHASE command is also used to specify disordered fraction set, low temperature CP model and many other things.

For most models OC will ask for the number of sublattices and a phase can have 1 to 9 sublattices and the user must for each specify the number of sites. For some models, like the ionic liquid model, the number of sites may change with the composition of the phase so the number specified is irrelevant. See the book by Lukas et al [07Luk] for more details on models.

For each sublattice the user must specify the constituents on the sublattice. A constituent that is not an element must already have been entered as a species, see section 10.16.

The **AMEND PHASE** command 5.11 is used for some additional model features like magnetism or permutations.

## 10.14  *enter* Plot_data

The user can add points to be plotted to a dataset 1 to 9. The dataset must already exist as a file opened by a command **ENTER MANY_EQUILIB**.

## 10.15  *enter* Quit

Quit entering things.

## 10.16  *enter* Species

A species consists of a name and a stoichiometric formula. It can have a valence or charge. The name is often the stoichiometric formula but it does not have to be that. Examples:

- enter species water h2o

- enter species c2h2cl2_trans c2h2cl2

- enter species c2h2cl2_cis c2h2cl2

- enter species h+ h1/- -1

There can be a problem with ambiguity with a species name like h2o if there is also a species h2o2. In such cases use a final unity, i.e. h2o1.

Single letter element names must be followed by a stoichiometric factor unless it is the last element when 1 is assumed. Two-letter element names have by default the stoichiometric factor 1.

- enter species carbonmonoxide c1o1

- enter species cobaltoxide coo

- enter species carbondioxide c1o2

The species name is important as it is the name, not the stoichiometry, that is used when referring to the species elsewhere like as a phase constituent. It is of course convenient to choose a species name similar to its stoichiometric formula but as shown above, that is not always sufficient.

## 10.17 *enter* Symbol

The OC package has both "symbols" and "tpfun symbols", the latter has a very special syntax and can be used when entering parameters.

The symbols are designed to handle relations between state variables, one can define expressions like
**enter symbol KLBCR = X(LIQUID,CR)/X(BCC,CR);**
where KLBCR is set to the partition of the Cr mole fractions between liquid and bcc.

The symbols also include "dot derivatives" like $H.T$ which is the second derivative of the Gibbs energy with respect to the for the current system at the given set of conditions.

**enter symbol CP = H.T;**

If $T$ and $P$ are conditions and all other conditions are mass balance conditions CP is the heat capacity. It also takes account of the change of configurational entropy.

Currently $H.T$ is the only dot derivatives allowed but more will be added as soon as possible.


## 10.18 *enter* Tpfun_Symbol

This symbol is an expression depending on $T$ and $P$ that can be used when entering parameters. A TPfun can refer to another TPfun.

TPFUNs have a strict syntax because the software must be able to fast calculate first and second derivatives with respect to $T$ and $P$ during equilibrium calculations, see section 2.4.3.


# 11 Exit

Terminate the OC software in Swedish, Ha en bra dag.


# 12 Fin

Terminate the OC software in French, Au revoir.


# 13 Help

Can give a list if commands or subcommands or parts of this help text.

# 14 HPcalc

Start the reverse polish calculator.

# 15 Information

The intention is to provide the on-line user who does not like to read manuals with additional explanations but not implemented yet.

# 16 List

Many things can be listed. Output is normally on the screen unless it is redirected by the /output option.

| | | | |
|---|---|---|---|
| AXIS | ERROR_MESSAGE | PARAMETER | STATE_VARIABLES |
| BIBLIOGRAPHY | LINE_EQUILIBRIA | PHASE | SYMBOLS |
| CONDITIONS | MODEL_PARAM_ID | QUIT | TPFUN_SYMBOLS |
| DATA | MODEL_PARAM_VAL | RESULTS | |
| EQUILIBRIA | OPTIMIZATION | SHORT | |

## 16.1 *list* Axis

Lists the axis set by the user.

## 16.2 *list* Bibliography

List the bibliographic references for the data.

## 16.3 *list* Conditions

Lists the current set of conditions set by the user. If the degrees of freedoms are zero one can calculate an equilibrium.

## 16.4 *list* Data

Lists all thermodynamic data. The default is on SCREEN but you can also choose among the formats: LaTeX, MACRO, PDB and TDB.

The only formats implemented at present are SCREEN, PDB and TDB.

### 16.4.1  *list data* LaTeX

The thermodynamic data will be formatted according to LaTeX for later inclusion in publications. Not implemented.

### 16.4.2  *list data* Macro

The thermodynamic data will be written as a macro file that can later be read back into the OC software. Not implemented.

### 16.4.3  *list data* PDB

A "Portable phase related Data Format" similar to the TDB file format adapted for OC.

### 16.4.4  *list data* TDB

A variant of the TDB file format with Thermo-Calc flavor.

## 16.5  *list* Equilibria

Lists the equilibria entered (not any result ...).

## 16.6  *list* Error message

The message associated with an error code generated by OC can be listed

## 16.7  *list* Line equilibria

Lists the equilibria calculated during STEP or MAP commands. See also the command **AMEND LINE-EQUILIBRIA**.

## 16.8  *list* Model parameter identifiers

Lists the model parameter identifiers available in the current version of OC, see section 2.4.1.

## 16.9  *list* Model parameter value

The current value of a model parameter identifier can be listed. Note that the value is always phase dependent and may also depend on the composition set.

## 16.10    *list* optimization result

Lists results of an optimization, several sub-options will be implemented but currently there is a short version only.

## 16.11    *list* Parameter

List a specific parameter.

## 16.12    *list* Phase *<phase>*

You must first specify the phase name. Then you can specify if you want the phase CONSTI-TUTION, DATA or some MODEL information.

### 16.12.1    *list phase ...* Constitution

List the constitution of the phase.

### 16.12.2    *list phase ...* Data

List the model and model parameter expressions.

### 16.12.3    *list phase ...* Model

List some model data for example if there is a disordered fraction set.

## 16.13    *list* Quit

You did not really want to list anyting.

## 16.14    *list* Results

List the results of an equilibrium calculation. This is the most frequent list command. The listing will contain the current set of conditions, a table with global data, a table with component specific data and then a list of stable phases with amounts, compositions and possibly constitutions. It is possible to list also unstable phases.

There are 9 options for the formatting:

- 1 Output in mole fractions, phase constituents in value order (constituent with highest fraction first).

- 2 as 1 but include also the phase constitution (sublattices and their fractions) in value order.

- 3 as 1 with the phase composition in alphabetical order

- 4 Output in mass fractions, phase composition in value order.

- 5 as 4 with the phase composition in alphabetical order.

- 6 as 4 and also include the phase constitutions in value order.

- 7 Output all phases will with composition in mass fractions and in value order. Unstable phases will have a negative driving force.

- 8 Output all phases will with composition in mole fraction and constitution in alphabetic order. Unstable phases will have a negative driving force.

- 9 as 8 but in in value order.

For each phase the name, status (S/D/E/F), moles (or mass), volume, number of formula units, atoms per formula units and driving force (in dimensionless units) is given on one line.

The moles of a phase is the number of formula unit multiplied with atoms per formula units. The gas phase and phases with interstitials and vacancies have a varying amount of moles of atoms per formula units. The composition of the phase can be in value order or alphabetical order.

## 16.15   *list* Short

There are 4 options: A/C/M/P

The A option lists a single line for each element, species and phase with some essential data.

The C option lists the components and their data.

The M option lists the models and constitution for all phases.

The P option lists one line for each stable phase and then one line for some of the remaining phases in decreasing order of stability.

## 16.16   *list* State_ Variables

Values of individual state variables like G, HM(LIQUID), X(LIQUID,CR) etc. can be listed. Terminate the command by an empty line. Note that the values of symbols and TP functions cannot be listed here, they are calculated by the CALCULATE SYMBOL or CALCULATE TP command.

The current values of parameter identifiers, see section 2.4.1 can be listed with the command, like TC(BCC) will give the calculated Curie temperature for BCC. A symbol like MQ&FE(FCC) will give the logarithm of the mobility of Fe in the FCC phase.

## 16.17  *list* Symbols

All state variable symbols listed but not their values, they are calculated by the CALCULATE SYMBOL command.

```
List of all state variable symbols
 No Special Name= expression ;
  1         R= 8.31451;
  2         RT= R*T;
  3         T_C= T-273.15;
  4      X  CP= HM.T;
```

In the "special" column the "X" means the symbol is calculated only when explicitly specified. There can also be a "C" indicating a numeric value that can be amended or a number indicating in which equilibrium the symbol is calculated. See section 5.14.

## 16.18  *list* Tpfun Symbols

All or some TPFUN expressions listed. By giving * all are listed, bu giving the g* all TP functions starting with G are listed.

Note that all parameters are also TP functions, they can be listed by giving "_*" as name. The abbreviation "_g*" will list the function for all parameters with identifiers starting with G.

To obtain the values of TP functions use the **calculate TP** command.

# 17  Macro

By specifying a file name commands will be read from that file. The default extension is OCM. A macro file can open another macro file (max 5 levels). When a macro file finish with SET INTERACTIVE the calling macro file will continue or the user can continue interactively.

A macro file name can be given on the same line as the program and the program will drictly start reading from this file.

# 18  Map

For phase diagram calculations. One must first set two axis with state variables also set as conditions.

If one gives several MAP commands one can choose to erase or keep the previous results.

During mapping each calculated equilibria is saved and different kinds of calculated state variables can be used for plotting.

# 19 New

To remove all data so a new system can be entered. It is fragile.

# 20 Optimize

The model parameters selected by SET VARIABLE_COEFF will be varied to obtain the best least square fit the experimental data provided.

Before this command the user must have entered the thermodynamic descriptions of the phases with model parameters depending on optimizing coefficients and the experimental data. He must also set the range and weights of the experiments and which coefficents to vary.

The user provides a maximum number of iterations allowed.

Developing better assessment software is one of the main aspects of the OC software. There will be more options to this command soon.

# 21 Plot

Plot the result from a STEP or MAP calculation. A simple interface to GNUPLOT [GNUPLOT] has been implemented in OC. This generates a command file which is later plotted using GNU-PLOT.

In OC you must first specify the state variable on the horizontal (x-axis) and vertical (y-axis) axis. Then you can give several of the options below, finish with RENDER or QUIT.

If you plot the same calculation several times the plot options you set (scaling, text, etc) will be kept unless you change the state variables to be plotted on the axis. If you do that these options will be reset to default values.

Default plotfile is "ocgnu.plt". This is the command file which will be executed by GNUPLOT. If GNUPLOT is correctly installed OC will start GNUPLOT and generate the graphics output when you RENDER the plot.

GNUPLOT is a very powerful graphics software, only a few of these are available by OC. The gnuplot command file generated by OC can be edited to exploit additional facilities in GNUPLOT.

You can APPEND a GNUPLOT command file generated by OC, or manually edited, in a new plot.

| | | | |
|---|---|---|---|
| APPEND | LOGSCALE | RATIOS_XY | TIE_LINES |
| AXIS_LABELS | OUTPUT_FILE | RENDER | TITLE |
| GIBBS_TRIANGLE | POSITION_OF_KEYS | SCALE_RANGES | |
| GRAPHICS_FORMAT | QUIT | TEXT | |

## 21.1 *plot xaxis yaxis* Append

A GNUPLOT file prevously generated by OC or edited manually can be specified to be overlayed on the current plot.

## 21.2 *plot xaxis yaxis* Axis_Labels

The user specifies for the X or Y axis the text written on the axis.

## 21.3 *plot xaxis yaxis* Gibbs triangle

A trial implementation is available which can generate equiaxial triangular isothermal diagrams.

## 21.4 *plot xaxis yaxis* Graphics format

The GNUPLOT terminals entered in section 10.8 can be used. For other formats than SCREEN one can also specify an output file which will be generated in the specified format.

## 21.5 *plot xaxis yaxis* Logscale

The user can set logarithimic scale on X or Y axis (or both).

## 21.6 *plot xaxis yaxis* Output file

By default plotting will generate a ocgnu.plt file for GNUPLOT. You can specify other name here. If you plot on other terminals than SCREEN there will be an additional file with extension ".ps" for Postscript, ".pdf" for Adobe PDF or ".gif" for GIF format.

## 21.7 *plot xaxis yaxis* Position of keys

The identification (labels) of the curves in the plot can be positioned with this command. See the GNUPLOT manual [GNUPLOT] for information.

## 21.8 *plot xaxis yaxis* Quit

No plot generated.

## 21.9  *plot xaxis yaxis* Render

Finally plot.

## 21.10  *plot xaxis yaxis* Scale_Range

The user specifies for the X or Y axis the minimum and maximum range. The default scaling range can be restored.

## 21.11  *plot xaxis yaxis* Text

The user must give two coordinates, an angle and a text to be plotted. For phase diagram there is an option to generate the text by calculating the stable set of phases at the specified coordinates. It is possible to modify the position, angle and the text.

## 21.12  *plot xaxis yaxis* Tie-line

Tie-lines in isothermal sections can be plotted. 0 means no tie-lines, 1 means a tie-line between every calculated equilibria and so on.

## 21.13  *plot xaxis yaxis* Title

Title on top of the figure. The conditions will always be there also.

# 22  Quit

Terminate the OC software in English, have a nice day.

# 23  Read

It is possible to read a (non-encrypted) TDB file but it should be not too different from what is normally generated by the LIST_DATA command in TC.

    DIRECT   PDB   UNFORMATTED
    QUIT     TDB

## 23.1  *read* Direct

In the future it will be possible to save results on a random access (DIRECT) file.

## 23.2  *read* Quit

You did not really want to read anything.

## 23.3  *read* PDB

A PDB file (with extension PDB) should be specified. The file should be un the Portrable phase dependent Data Base format.

## 23.4  *read* TDB

A TDB file (with extension TDB) should be specified. The TDB file must not deviate very much from the standard output from Thermo-Calc.

## 23.5  *read* Unformatted

For use to read a file created with a SAVE UNFORMATTED command. It will not always work as the data structure is not fixed.

# 24  Save

There are several forms of save, three forms write a text file that can be read and modified with a normal editor. Two forms are unformatted, either on a sequential file or a direct (random access) file.

```
DIRECT   SOLGAS   UNFORMATTED
QUIT     TDB      PDB
```

## 24.1  *save* Direct

It will eventually be possible to save the result of STEP and MAP commands on a random access file for later processing.

## 24.2  *save* Quit

You did not want to save anything

## 24.3  *save* PDB

Saves current set of model parameters and functions on a file in the Portable phase dependant Data Base format.

## 24.4  *save* TDB

Saves current set of model parameters and functions on a file in TDB format. Same as the command **list data tdb**.

## 24.5  *save* SOLGAS

Saves current set of model parameters and functions on a file in a format that can be read by the FactSage software. Not yet implemented.

## 24.6  *save* Unformatted

The intention is that one will be able to save the current status of the calculations on a file and then resume the calculations by reading this file. Not implemented yet.

# 25  Select

There are a few things that can be selected, most important which equilibrium the following commands will operate on.

## 25.1  *select* Equilibrium

As the user can enter several equilibria with different conditions this command allows him to select the current eqilibria.

## 25.2  *select* Graphics

Only GNUPLOT citegnuplot available.

## 25.3  *select* Language

Only English implemented.

## 25.4  *select* Minimizer

Only Hillert's algorithm implemented in matsmin [15Sun2] available.

## 25.5  *select* Optimizer

The LMDIF [LMDIF] least square fitting software is the only one implemented.

# 26  Set

Many things can be set. Things to be "set" and "amended" sometimes overlap.

| | | | |
|---|---|---|---|
| ADVANCED | FIXED_COEFF | OPTIMIZING_COND | STATUS |
| AS_START_EQUILIB | INPUT_AMOUNTS | PHASE | T_AND_P |
| AXIS | INTERACTIVE | QUIT | UNITS |
| BIT | LEVEL | RANGE_EXP_EQUIL | VARIABLE_COEFF |
| CONDITION | LOG_FILE | REFERENCE_STATE | VERBOSE |
| ECHO | NUMERIC_OPTIONS | SCALED_COEFF | WEIGHT |

## 26.1  *set* Advanced

A few options implemented

### 26.1.1  *set advanced* dense grid onoff

This toggles the grid minimizer to use/not use a denser grid (about 10 times more gridpoints) when generating start values for the interactive minimizer. It can be useful when the normal grid is too coarse to detect some miscibility gaps or order/disorder transitions. It takes about 10 times longer to calculate.

### 26.1.2  *set advanced* equilibrium transfer

This is only for experts who know what they are doing.

### 26.1.3  *set advanced* quit

You did not want to set anything advanced.

## 26.2   *set* As start equilibrium

The current equilibrium will be copied to the list of start equilibria for STEP and MAP commands.

## 26.3   *set* Axis

A condition can be set as an axis variable with a low and high limit and a maximum increment. With 2 or more axis one will calculate a phase diagram, i.e. lines where the set of stable phases changes.

  With one axis one calculates the set of stable phases and their properties while changing the axis variable.

## 26.4   *set* Bit

Many records have status words where the bits are used to signify different things. An advanced user can set these bits for the global, equilibrium and phase records, but only if you know what it means.

- 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

- 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

## 26.5   *set* Condition

A condition is a value assigned to a state variable or an expression of state variables. By setting the status of a phase to fix one has also set a condition.

Two cases of expressions can be used as conditions, for example a relation between mole fraction like
**set condition x(liq,o)-x(c1_mo2,o)=0**
means that the oxygen content in liquid and c1_mo2 phases should be the same. That is useful to calculate the congruent melting of c1_mo2.

Another case is if the total anount if some components has a relation, for example:
**set condition n(u)+n(zr)=1**
means that the total number of moles of the components U and Zr should be unity.

## 26.6   *set* Echo

This is useful command in macro files or when demonstrating the program.

## 26.7   *set* Fixed coefficient

An optimizing coefficient is assigned a fixed value.

## 26.8   *set* Input Amounts

This allows the user to specify a system by giving a redundant amount of various species in the system. The software will transform this to conditions on the amounts of the components.

## 26.9 *set* Interactive

The last command on a macro file. Gives command back to the keyboard of the user, or to the calling macro file. Without this the program will just terminate when the macro is finished.

## 26.10 *set* Level

I am no longer sure what this should do and if it is needed ...

## 26.11 *set* Log_File

A useful command to save all interactive input while running OC. The log file can easily be transformed to a macro file. All bug reports should be accompanied by a log file which reproduces the bug.

## 26.12 *set* Numeric_Options

The default number of iterations and accuracy can be specified. Default values are 500 and $10^{-6}$.

## 26.13 *set* Optimizing conditions

A few variables used to guide the optimization of model parameters can be set.

## 26.14 *set* Phase

You must specify a phase name. Some phase specific things can be set, also for the model.

### 26.14.1 *set phase ...* Amount

One can specify the amount of the phase which is used as initial value for an equilibrium calculation.

### 26.14.2 *set phase ...* Bits

Some of the models and data storage depend on the bits of the phase. Note that most of them are set automatically by the software and changing them with this command may not have the expected effect. The bits are:

- EXTRA_DENSE_GRID makes it possible to have a larger number of gridpoints calculated for this phase by the gridminimizer.

- NO_AUTO_COMP_SET. This makes it possible to prevent that a specific phase has automatic composition set created during calculations.

- OUIT, do not set any more bits.

### 26.14.3   *set phase ...* Constitution

This is the same as **amend phase constitution**.

### 26.14.4   *set phase ...* Default_constitu

Same as **amend phase default_constit**.

### 26.14.5   *set phase ...* Quit

You did not want to set anything for the phase.

### 26.14.6   *set phase ...* Status

Use the SET STATUS PHASE command to set the status of several phases. The different status are explained there.

## 26.15   *set* Quit

You did not really want to set anything.

## 26.16   *set* Range of experimental equilibria

For an assessment several consquetive equilibria with experimental data must be entered. This command specifies the first and last of those equilibria. It possible to add more equilibria later one by one (not yet though).

The equilibria are assigned weight one by default. The weight can be changed with the SET WEIGHT command.

## 26.17   *set* Reference_State

By default the reference state for the components is SER (Stable Element Reference) which is the stable state of the element at 298.15 K and 1 bar. (NOTE: in principle SER is defined by the database but today almost all databases have SER as reference state.)

For each component (also for other components than the elements) one can specify a phase at a given temperature and pressure as reference state. The phase must exist for the component as pure. Instead of a fixed $T$ one can give a *, indicating current $T$, if one calculates at different values of $T$. Example:

**set reference O gas * 1e5**

Note that state variables like the chemical potential, MU(O), will refer to the user defined reference state. To obtain the value for the SER state one can use the suffix S, i.e. MUS(O) will give the chemical potential refered to SER.

NOTE also that the value of integral properties like Gibbs energy, $G$, enthalpy, $H$, etc. will always be given relative SER unless all components have the same phase as reference state. Thus in order to have the enthalpy of mixing of a phase all components must have that phase as reference state.

## 26.18   *set* Scaled coefficient

A coefficient for optimization can be specified with a start value, scaling factor and a minimum and maximum value. The *set* VARIABLE command sets the scaling factor equal to the start value and have no min or max values.

## 26.19   *set* Status

The status of elements, constituents, species or phases can be changed. Only phases are implemented.

### 26.19.1   *set status* Constituent

A constituent of a phase can be suspended. Not yet implemented.

### 26.19.2   *set status* Element

An element can be ENTERED or SUSPENDED. If an element is suspended all species with this element is automatically suspended. Not yet implemented.

### 26.19.3  *set status* Phase

A phase can have 4 status

- entered, this is the default. The phase will be stable if that would give the most stable state for the current conditions. The user can give a tentative amount.

- suspended, the phase will not be included in any calculations.

- dormant, the phase will be included in the calculations but will not be allowed to become stable even if that would give the most stable equilibrium. In such a case the phase will have a positive driving force.

- fixed means that it is a condition that the phase is stable with the specified amount. Note that for solution phases the composition is not known.

You can use a list of phase names or a wildcard for the phase name and the must give an equal sign, "=", before the new status. You can also use the special "*S" for all suspended phase, "*D" for all dormant phases.

Changing the phase status does not affect anything except the phase itself. For a single phase you can use SET PHASE ... STATUS <status>.

Setting a stable phase as dormant or suspended and calculate the equilibrium will give you a metastable equilibrium.

Setting a phase status as FIXED means it is a condition that this phase should be stable. Setting the liquid fix with the amount zero is a quick way to calculate the melting temperature of a system if there is no condition on the T.

### 26.19.4  *set status* Species

A species can be ENTERED or SUSPENDED. If a species is suspended all phases that have this as single constituent in a sublattice will be automatically suspended. Not yet implemented.

## 26.20  *set* T_and_P

Local values of T and P can be set. These are not conditions but are used for commands like **CALCULATE PHASE ...**.

## 26.21  *set* Units

For each property the unit can be specified like Kelvin, Farenheit or Celsius for temperature. Not implemented yet.

## 26.22  *set* Variable coefficient

A coefficient for optimization is assigned a start value.

## 26.23  *set* Verbose

Not implemented yet.

## 26.24  *set* Weight

Intended for assessments. A weight is zero or a positive value. Equilibria with weight zero will be ignored in an optimization.

You can specify the current equilibrium or give an abbreviation that will set the weight of all equilibria with a name for which the abbreviation fits.

# 27  Step

Requires that a single axis is set. If a second step command is given you have the choice of deleting or keeping the previous results.

## 27.1  *step* Conditional

A specified symbol is evaluated at each step. Can be used for Scheil-Gulliver solidification simulation when implemented.

## 27.2  *step* Normal

Calculates equilibria from the low axis limit to the high at each increment. The exact axis value for any phase changes is calculated.

## 27.3  *step* Quit

You did not want to *step*.

## 27.4  *step* Separate

Calculates each phase separately. It calculates equilibria for each phase separately. It can be used to calculate Gibbs energy curves.

# 28    Summary

That's all and I hope enough (when all is implemented). Have fun and report all errors or problems providing a macro file and the necessary data.

# References

[07Luk] H L Lukas, S G Fries and B Sundman, *Computational Thermodynamics, the CAL-PHAD method*, Cambridge Univ Press 2007.

[15Sun1] B Sundman, U R Kattner, M Palumbo and S G Fries, *OpenCalphad - a free thermodynamic software*, in Integrating Materials and Manufacturing Innovation, **4:1** (2015), open access

[15Sun2] B Sundman, X-L Liu and H Ohtani, *The implementation of an algorithm to calculate thermodynamic equilibria for multi-component systems with non-ideal phases in a free software*, Computational Materials Science, **101** (2015) 127-137

[16Sun] B Sundman, U R Kattner, C Sigli, M Stratmann, R Le Tellier, M Palumbo and S G Fries, *The OpenCalphad thermodynamic software interface*, Comp Mat Sci, **125** (2016) 188-196

[GNUPLOT] http://www.gnuplot.info/documentation.html

[LMDIF] https://www.math.utah.edu/software/minpack/minpack/lmdif.html