User Guide to the Open Calphad software package version 1.0

VERY VERY PRELIMINARY

Bo Sundman, September 4, 2012

This is a first very preliminary version

1 Introduction

The Open Calphad software project aims to provide a hig quality software for thermodynamic calculations for inorganic systems i.e. gases. liquid, alloys with may different crystalline phases.

It also provides a framwork to store many different composition dependent properties of materials.

2 Some general features

The command monitor has a menu of command and each of these usually has submenus and finally some questions may be asked like phase names, a value or an expression. At any level the user should be able to type a ? and get some help, usually an extract from this manual, a menue or possible answers.

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 intitial letter. Some special symbols are also used:

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

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

- & are used in parameter identifiers to specify the constituent for the parameter.

2.2 Parameters

All data is organized on the base of 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 may 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" "reference"

These parts will now be explained in more detail.

2.2.1 Parameter Identifiers

The OC thermodynamic pacakage can handle any property that depend on composition using the composition models implemented. It is easy to extend the number of properties by declaring property identifiers in ths source code. The value of such identifiers can be obtained by the command "list symbol". 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 also.

The list here is tentative. Case should be used not to use the same symbol name for different things ...

- G, the Gibbs energy or an interaction parameter.

- TC, the critical temperature for ferro or antiferro magnetic ordering using the Inden model.

- BMAGN, the avarage Bohr magneton number using the Inden model.

- CTA, the Curie temperature for ferromagnetic ordering using a modified Inden model.

- NTA, the Neel temperature for antiferromagnetic ordering using a modified Inden model.

- IBM&C, 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, the Debye or Einstein temperature.

- MOBQ&C, the logarithm of the mobility of constituent C

- RHO, the electrical resistivity

- MAGS, the magnetic suseptibility

- GTT, the glas transition temperature

- VISC, the viscosity

- LPAX, the lattic parameter in X direction

- LPAY, the lattic parameter in Y direction

- LPAZ, the lattic parameter in Z direction

- LPTH, the deviation from cubic structure

- EC11A, the elastic constrant C11

- EC12A, the elastic constrant C12

- EC44A, the elastic constrant C44

2.3   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, ",". 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 describe the composition dependence of the property, without such parameter the property will vary liearly 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 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)

This would be the Gibbs energy of an Al1NI3 compound.

An interaction between vacancies and carbon in the austenite is

G(fcc,Fe:C,VA;0)

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

3 All commands

The commands in alphabetica order as listed with the ?

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

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.

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

3.1 Option

These should be possible to specify at each command. But they are not yet implemented.

- -OUTPUT *file name*

- -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.

5.1 Element

Not implemented yet.

5.2 Debye_Model

Not implemented yet.

5.3 Components

By default the elements are the components. Ths command can set any orthogonal set of species as components. The number of components cannot be changed.

Not implemented yet.

5.4 Constitution

The user can set a constitution of a phase before a calculation. This will be used as initial constitution for a calculation.

5.5 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 behaviour of the program.
- If global minimization is allowed or not.

- If gridpoints should be merged after global minimization (sometimes set for debugging).

- Forbid automatic creation or deletion of composition sets.

5.6   Parameter

The possible parameters are defined by the model of the phase. By specifying a parameter the user can change its expression. See the ENTER PARAMETER command.

5.7   Phase

Some of the properties of the phase can be amended by this command.

5.7.1   Magnetic_Contrib

A model for the magnetic contribution to the Gibbs energy can be set by this command.

5.7.2   Composition_Set

More composition sets of a phase can be created. 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. The composition set will always habe a suffix #digit where digiit is a number between 1 and 9. One cannot have more than 9 composition sets.

Composition sets can also be created automatically by the software. In such a case the composition set will have the suffix _AUTO,

In some cases it may be interesting to create metastable states inside miscibility gaps and one can prevent automatic creation of composition sets by AMEND GENERAL or for an individual phase by *SET PHASE BIT* phase *NO_AUTO_COMP_SET*

5.7.3   Default_Constit

The default constitution of a phase can be set. This will be used when the first calculation with the phase is made. Depending on the minimizing software used the initial consititution can be important to find the correct quilibrium if the phase has ordering or a miscibility gap.

5.7.4 Disordered_Fracs

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.

5.7.5 Glas_Transition

Not implemented yet.

5.7.6 Quit

Do not amend anything for the phase.

5.8 Quit

Do not amend anything.

5.9 Reference

The reference for a parameter can be amended.

5.10 Species

Not implemented yet.

5.11 Symbol

Not implemented yet.

5.12 Tpfun_Symbol

Not implemented yet.

6 Back

Return back from the command monitor to the application program.

7 Calculate

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

7.1 All_Equilibria

Intended for the assessment procedure. Not implemented yet.

7.2 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.

7.3 Global_Gridmin

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

7.4 No_Global

Calculate the equilibrium with the current minimizer without using a global gid minimizer to generate start constitutions.

7.5 Phase

The Gibbs energy of a phase and possible derivatives are calculated. Mainly for debugging the implementation of models.

7.5.1 Only_G

The Gibbs energy and all T and P derivatives calculated and listed.

7.5.2 G_and_dGdy

The Gibbs energy, all T and P derivatives and all first derivatives with respect to constituents are calculated and listed.

7.5.3 All_Derivatives

The Gibbs energy, all T and P derivatives and all first and second derivatives with respect to constituents are calculated and listed.

7.6 Quit

Quit calculating.

7.7 Symbol

A state variable symbol is calculated using the results from the last equilibrium or grid minimizer calculation.

7.8 Tpfun_Symbols

A specific TPFUN symbol is calculated for current values of T and P.

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 Stop_on_Error

The program will stop at the command level after printing the error message if an error has occured when using macro file. This makes it easier to use macro files to find errors.

9　Delete

Not implemented yet and may never be, it is not so easy to allow deleting things when the data structure is so involved, it may be better to enter the data again without the thing that should be deleted.

10　Exit

Terminate the OC software.

11　Enter

In most cases data will be read from a database file. But it is possible to enter all thermodynamic data interactivly. 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.

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

At present the multicomponent CEF model is the only one implemented. This includes the gas phase, regular solutions with Redlich-Kister Muggianu model and phases with up to 10 sublattices and magnetic contributions.

11.1　Constitution

The constitution (fraction of all constituents) of a phase can be entered. This is a way to provide start values for a calculation or to calculate the Gibbs enegy for a specific phase at a specific constitution using **calculate phase**.

11.2　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.

11.3 Equilibrium

One can have several equilibria each with a unique set of conditions incuding phase status (dormant, suspended, fix or entered). 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.

11.4 Experiment

This is for assessment, not implemented yet.

11.5 Parameter

A parameter is definde 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 the constituent array.

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.

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

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.

One can store many different types of data in OC using the parameter identifier. A description of the identifiers currently implemeneted are given in the introduction. Here is a short list.

- G, the Gibbs energy or an interaction parameter

- TC, the critical temperature for ferro or antiferro magnetic ordering

- BMAGN, the avarage Bohr magneton number

- CTA, the Curie temperature for ferromagnetic ordering

- NTA, the Neel temperature for antiferromagnetic ordering

- IBM&C, the individual Bohr magneton number for constituent C

- THETA, the Debye or Einstein temperature

- MOBQ&C, the logarithm of the mobility of constituent C

- RHO, the electrical resistivity

- MAGS, the magnetic suseptibility

- GTT, the glas transition temperature

- VISC, the viscosity

- LPAX, the lattice parameter in X direction

- LPTH, the deviation from cubic structure

- EC11A, the elastic constrant C11

- EC12A, the elastic constrant C12

- EC44A, the elastic constrant C44

The actual list is given by LIST PARAMETER_ID.

11.6   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.

A phase can have 1 or more sublattices and the user must specify the number of sites on each. He must also specify the constituents on each sublattice. For some models, like the ionic liquid model, the number of sites may change with composition.

By default the model for a phase is assumed to be the Compound Energy Formalism (CEF). If any onther model should be used that is set by the **amend** or **set phase bit** commands.

11.7   Quit

Quit entering things.

11.8   Reference

Each parameter must have a reference. When entering a parameter a reference symbol is given and with this command one can give a full reference text for that symbol like a published paper or report.

11.9 Species

A species consists of a name and a stochiometric 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 c2h2cl1_trans c2h2cl2

- enter species c2h2cl1_cis c2h2cl2

- enter species h+ h1/- -1

Single letter element names must be followed by a stochiometric 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 name, not the stoichiometry, that is used when referring to the species elsewhere like as constituent.

11.10 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 K = X(LIQUID,CR)/X(BCC,CR);

where K is set to the partition of the Cr mole fractions between liquid and bcc.

It is intended to implement "dot" derivatives like CP=H.T which is the temperature derivative of the enthalpy for the given set of conditions in order to calculate heat capacities.

11.11 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.

12 Exit

Terminate the OC software in English.

13 Fin

Terminate the OC software in French.

14 Help

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

15 HPCALC

A reverse polish calculator.

16 Information

Not implemeneted yet.

17 List

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

17.1 Axis

Lists the axis set.

17.2 Conditions

Lists the conditions set.

17.3 Data

Lists all thermodynamic data.

17.4 Equilibria

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

17.5 Phase

List data for a phase

17.5.1 Data

List the model and thermodynamic data.

17.5.2 Constitution

List the constitution of the phase.

17.5.3 Model

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

17.6 Quit

You did not really want to list anyting.

17.7 References

List the references for data.

17.8 Results

List the results of an equilibrium calculation.

17.9   Short

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

17.10   State_Variables

Values of state variables like G, HM(LIQUID) etc. can be listed. Terminated by an empty line. Note that symbols cannot be listed here, they are calculated by the CALCULATE SYMBOL command.

17.11   Symbols

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

17.12   Tpfun_Symbols

All TPFUN symbols listed.

18   Macro

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

19   Map

For phase diagram calculations. Not implemented yet.

20   New

To remove all data so a new system can be entered. Not implemented.

21   Plot

Plot the result from a STEP or MAP calculation. A simple interface to gnuplot has been implemented for step calculations.

22   Quit

Terminate the OC software in Swedish.

23   Read

At present there is no SAVE command implemented in OC as it is difficult to do that before the datastructure is well defined.

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

23.1   Quit

Yuo did not really want to read anything.

23.2   TDB

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

23.3   Unformatted

For use when a SAVE command is implemeneted in OC.

24   Save

Not implemented yet.

25 Select

25.1 Equilibrium

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

25.2 Graphics

Not implemented yet.

25.3 Minimizer

There are two minimizers implemented, LUKAS and SUNDMAN_HILLERT and both have their limitations at present.

26 Set

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

26.1 Advanced

Not implemented yet

26.2 Axis

A condition can be set as an axis variable with a low and high limit and a maximum increement. 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.

26.3 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.

26.4 Echo

This is useful command in macro files.

26.5 Input_Amounts

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

26.6 Interactive

The usual end of 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.

26.7 Level

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

26.8 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.

26.9 Numeric_Options

Some numeric option can be set.

26.10 Phase

Some phase specific things can be set, also for the model.

26.10.1 AMOUNT

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

26.10.2 BITS

Some of the models and data storage depend on the bits of the phase. These are

- 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 handelled by this bit as they are identical in the 4 sublattice model.

- BCC_PERMUTATIONS is intended for the 4 sublattice CEF model for BCC ordering. The BCC tetrahedron is unsymmetric which makes it a bit more complicated. Not implemented yet.

- IONIC_LIQUID_MDL. By setting this bit the phase is treated with the 2 sublattice paritally ionic liquid model. It must have been entered with 2 sublattices and only cations in the first sublattice and only anions, vacancy and neutrals in the second.

- AQUEOUS_MODEL. Not implemented yet.

- QUASICHEMICAL. Is intended for the classical quasichemical model for crystalline phases. Not implemented yet.

- FCC_CVM_TETRADRN. Is intended for the CVM tetrahedron model. Not implemented yet.

- FACT_QUASICHEMCL. Is intended for one for the FACT modified quasichemical liquid models. Not implemented yet.

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

- ELASTIC_MODEL_A. This should specify the elastic model to be used. Not implemented yet.

26.10.3 CONSTITUTION

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

26.10.4 DEFAULT_CONSTITU

Same as **amend phase default_constit**.

26.10.5 STATUS

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.

26.11 Quit

You did not really want to set anything

26.12 Reference_State

For each component (also when not the elements) one should be able to specify a phase at a given temperature and pressure as reference state. The phase must exist for the pure component. Not implemented yet.

26.13 Status

26.14 Constituent

A constituent of a phase can be suspended. But not yet implemented.

26.15 Element

An element can be ENTERED or SUSPENDED. If an element is suspended all species with this element is automatically suspended.

26.16 Phase

A phase can have 4 status as described for the SET PHASE STATUS command above. Changing the pase status does not affect anything except the phase itself.

26.17   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 suspened.

26.18   Units

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

26.19   Weight

Intended for assessments. Not implemented yet.

27   Step

Requires that a single axis is set.

Calculates equilibria from the low axis limit to the high at each increment.

28   Summary

That's all.