Files integrating experimental data

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Introduction

- The thermodynamic assessment of a system provides a mathematical descripiton of the Gibbs energy of all the phases of that system.
- It follows several steps:
  - the critical assessment of all the experimental and theoretical knowledge on the system under consideration,
  - the definition of models able to reproduce this knowledge,
  - the assessment of the parameters of the models.
- These steps correspond roughly to the use of three modules of the Thermo-Calc package
  - `EDIT_EXPERIMENTS`,
  - `GES`,
  - `PARROT`.
- The present contribution foccusses on the edition of the `POP` files defining the experimental values handled by the module `EDIT_EXPERIMENTS`.
- The structure of the `exp` files that allow to compare experimental data to calculated behaviours will also be introduced.

What are POP files?

- They are files containing experimental information to be fitted during the optimisation process.
- They are included a PAR workspace where the optimisation will be processed after the definition of the phases with the COMPILE_EXPERIMENTS of the PARROT module..
- They consist of commands of the EDIT_EXPERIMENTS module.
- The information they generate in the PAR workspace is generally modified during the optimisation procedure.
- They can be generated by the MAKE_POP_FILE command of the EDIt_EXPERIMENTS module.
- It is worth keeping updated by edition POP because files automatically generated may need some human editing to be re-used by the software and loose some comment lines.

EDIT_EXPERIMENTS

- The module EDIT_EXPERIMENTS is a module related to the module PARROT like POST is related to POLY_3. It is the command EDIT_EXPERIMENTS that allows to go to this module.
- Most of the commands available in this module are those of the POLY_3. They allow to define an equilibrium, like in POLY_3.
- Specific commands are related to optimisation procedure.
  They are used to
  - define and process many different equilibria,
  - define experimental values to fit and their uncertainty,
  - handle weights.

  Some are not available in the interactive mode but only in POP files.

EDIT_EXPERIMENTS commands

ADVANCED_OPTIONS
BACK
CHANGE_STATUS
COMMENT
COMPUTE_ALL_EQUILIBRIA
COMPUTE_EQUILIBRIUM
CREATE_NEW_EQUILIBRIUM
DEFINE_COMPONENTS
DELETE_SYMBOL
ENTER_SYMBOL
EVALUATE_FUNCTIONS
EXIT
EXPERIMENT
EXPORT
FLUSH_BUFFER
GRAPHICS_PLOT
HELP
IMPORT
INFORMATION
LABEL_DATA
LIST_ALL_EQUILIBRIA
LIST_CONDITIONS
LIST_EQUILIBRIUM
LIST_STATUS
LIST_SYMBOLS
MAKE_POP_FILE
READ_WORKSPACES
REINITIATE_MODULE
RESTORE_ALL_WEIGHTS
SAVE_WORKSPACES
SELECT_EQUILIBRIUM
SET_ALL_START_VALUES
SET_ALTERNATE_CONDITION
SET_CONDITION
SET_NUMERICAL_LIMITS
SET_REFERENCE_STATE
SET_START_CONSTITUTION
SET_START_VALUE
SET_WEIGHT
SHOW_VALUE
STORE_ALL_WEIGHTS
TABLE_HEAD
TRANSFER_START_VALUES

EDIT_EXPERIMENTS commands

ADVANCED_OPTIONS	GRAPHICS_PLOT	SELECT_EQUILIBRIUM
BACK	HELP	SET_ALL_START_VALUES
CHANGE_STATUS	IMPORT	SET_ALTERNATE_CONDITION
COMMENT	INFORMATION	SET_CONDITION
COMPUTE_ALL_EQUILIBRIA	LABEL_DATA	SET_NUMERICAL_LIMITS
COMPUTE_EQUILIBRIUM	LIST_ALL_EQUILIBRIA	SET_REFERENCE_STATE
CREATE_NEW_EQUILIBRIUM	LIST_CONDITIONS	SET_START_CONSTITUTION
DEFINE_COMPONENTS	LIST_EQUILIBRIUM	SET_START_VALUE
DELETE_SYMBOL	LIST_STATUS	SET_WEIGHT
ENTER_SYMBOL	LIST_SYMBOLS	SHOW_VALUE
EVALUATE_FUNCTIONS	MAKE_POP_FILE	STORE_ALL_WEIGHTS
EXIT	READ_WORKSPACES	TABLE_HEAD
EXPERIMENT	REINITIATE_MODULE	TRANSFER_START_VALUES
EXPORT	RESTORE_ALL_WEIGHTS	
FLUSH_BUFFER	SAVE_WORKSPACES	

Commands available of all modules

EDIT_EXPERIMENTS commands

ADVANCED_OPTIONS
BACK
CHANGE_STATUS
COMMENT
COMPUTE_ALL_EQUILIBRIA
COMPUTE_EQUILIBRIUM
CREATE_NEW_EQUILIBRIUM
DEFINE_COMPONENTS
DELETE_SYMBOL
ENTER_SYMBOL
EVALUATE_FUNCTIONS
EXIT
EXPERIMENT
EXPORT
FLUSH_BUFFER
GRAPHICS_PLOT
HELP
IMPORT
INFORMATION
LABEL_DATA
LIST_ALL_EQUILIBRIA
LIST_CONDITIONS
LIST_EQUILIBRIUM
LIST_STATUS
LIST_SYMBOLS
MAKE_POP_FILE
READ_WORKSPACES
REINITIATE_MODULE
RESTORE_ALL_WEIGHTS
SAVE_WORKSPACES
SELECT_EQUILIBRIUM
SET_ALL_START_VALUES
SET_ALTERNATE_CONDITION
SET_CONDITION
SET_NUMERICAL_LIMITS
SET_REFERENCE_STATE
SET_START_CONSTITUTION
SET_START_VALUE
SET_WEIGHT
SHOW_VALUE
STORE_ALL_WEIGHTS
TABLE_HEAD
TRANSFER_START_VALUES

Commands identical to POLY_3 commands

EDIT_EXPERIMENTS commands

ADVANCED_OPTIONS
BACK
CHANGE_STATUS
COMMENT
COMPUTE_ALL_EQUILIBRIA
COMPUTE_EQUILIBRIUM
CREATE_NEW_EQUILIBRIUM
DEFINE_COMPONENTS
DELETE_SYMBOL
ENTER_SYMBOL
EVALUATE_FUNCTIONS
EXIT
EXPERIMENT
EXPORT
FLUSH_BUFFER
GRAPHICS_PLOT
HELP
IMPORT
INFORMATION
LABEL_DATA
LIST_ALL_EQUILIBRIA
LIST_CONDITIONS
LIST_EQUILIBRIUM
LIST_STATUS
LIST_SYMBOLS
MAKE_POP_FILE
READ_WORKSPACES
REINITIATE_MODULE
RESTORE_ALL_WEIGHTS
SAVE_WORKSPACES
SELECT_EQUILIBRIUM
SET_ALL_START_VALUES
SET_ALTERNATE_CONDITION
SET_CONDITION
SET_NUMERICAL_LIMITS
SET_REFERENCE_STATE
SET_START_CONSTITUTION
SET_START_VALUE
SET_WEIGHT
SHOW_VALUE
STORE_ALL_WEIGHTS
TABLE_HEAD
TRANSFER_START_VALUES

Specific commands.

EDIT_EXPERIMENTS commands

ADVANCED_OPTIONS
BACK
CHANGE_STATUS
COMMENT
COMPUTE_ALL_EQUILIBRIA
COMPUTE_EQUILIBRIUM
CREATE_NEW_EQUILIBRIUM
DEFINE_COMPONENTS
DELETE_SYMBOL
ENTER_SYMBOL
EVALUATE_FUNCTIONS
EXIT
EXPERIMENT
EXPORT
FLUSH_BUFFER
GRAPHICS_PLOT
HELP
IMPORT
INFORMATION
LABEL_DATA
LIST_ALL_EQUILIBRIA
LIST_CONDITIONS
LIST_EQUILIBRIUM
LIST_STATUS
LIST_SYMBOLS
MAKE_POP_FILE
READ_WORKSPACES
REINITIATE_MODULE
RESTORE_ALL_WEIGHTS
SAVE_WORKSPACES
SELECT_EQUILIBRIUM
SET_ALL_START_VALUES
SET_ALTERNATE_CONDITION
SET_CONDITION
SET_NUMERICAL_LIMITS
SET_REFERENCE_STATE
SET_START_CONSTITUTION
SET_START_VALUE
SET_WEIGHT
SHOW_VALUE
STORE_ALL_WEIGHTS
TABLE_HEAD
TRANSFER_START_VALUES

Specific commands that will be introduced in this lecture.

Singular equilibrium

```
$.....................................................................
$                                                  Calo  1983 Sommer
$.....................................................................
CREATE_NEW_EQUILIBRIUM 350,1
CHANGE_STATUS PHASE LIQUID=ENT 1
SET_CONDITION P=P0 N=1 T=1120 X(CU)=0.075
SET_REFERENCE_STATE CU LIQUID * 1E5
SET_REFERENCE_STATE MG LIQUID * 1E5
 EXPERIMENT HMR=-1900:5%
 LABEL AL
 COMMENT                              Liq - Calo - SOMMER
 GRAPHICS 5 .075 -1900 MS200
```

POLY_3 commands

```
$.....................................................................
$                                                    Calo  1983 Sommer
$.....................................................................
CREATE_NEW_EQUILIBRIUM 350,1
CHANGE_STATUS PHASE LIQUID=ENT 1
SET_CONDITION P=PO N=1 T=1120 X(CU)=0.075
SET_REFERENCE_STATE CU LIQUID * 1E5
SET_REFERENCE_STATE MG LIQUID * 1E5
 EXPERIMENT HMR=-1900:5%
 LABEL AL
 COMMENT                              Liq - Calo - SOMMER
 GRAPHICS 5 .075 -1900 MS200
```

POLY_3 commands

```
$.....................................................................
$                                                  Calo  1983 Sommer
$.....................................................................
CREATE_NEW_EQUILIBRIUM 350,1
CHANGE_STATUS PH
SET_CONDITION P=
SET_REFERENCE_ST
SET_REFERENCE_ST
 EXPERIMENT HMR=
 LABEL AL
 COMMENT
 GRAPHICS 5 .075
```

The definition of each equilibrium begins with the CREATE_NEW_EQUILIBRIUM command.

It requires a first integer corresponding to the identifier of the equilibrium. This identifier can be used in the SELECT_EQUILIBRIUM later on.

The second required integer is an initialisation code

- $\rightsquigarrow$ 0 : components and phases suspended
- $\rightsquigarrow$ 1 : components entered and phases suspended
- $\rightsquigarrow$ 2 : components and phases entered

```
$.........................
$
$.........................
CREATE_NEW_EQUILIBRIUM 350,1
CHANGE_STATUS PHASE LIQUID=E
SET_CONDITION P=PO N=1 T=112
SET_REFERENCE_STATE CU LIQUI
SET_REFERENCE_STATE MG LIQUI
 EXPERIMENT HMR=-1900:5%
 LABEL AL
 COMMENT
 GRAPHICS 5 .075 -1900 MS200
```

The EXPERIMENT command defines the value of a quantity to be fitted as well as its uncertainty.

The uncertainty can be an absolute value or a relative percentage, as in this example.

Several EXPERIMENT commands can be given for an equilibrium, like the composition of several phases.

The EXPERIMENT command can be used with an inegality sign.

This command is optional. An equilibirum can be defined just to define a symbol.

```
$.....................
$
$.....................
CREATE_NEW_EQUILIBRIUM
CHANGE_STATUS PHASE LI
SET_CONDITION P=PO N=1
SET_REFERENCE_STATE CU
SET_REFERENCE_STATE MG
 EXPERIMENT HMR=-1900:
 LABEL AL
 COMMENT
 GRAPHICS 5 .075 -1900
```

LABEL is an optional command. Its use is recommanded to change easily the weight of all the equilibria having the same label.

The label is a string of maximum 4 characters, begining with an A.

It is displayed when selecting an equilibirum after the number of the selected equilibrium, on the first first line of the output of the LIST_EQUILIBRIUM and in the second column of the output when giving the COMPUTE_ALL_EQUILIBRIA

Only one label is attached to an equilibrium. If several LABEL commands are given, the last one superseeds the previous ones.

This command can be given interactively.

It is not used in the POP files generated by the MAKE_POP_FILE command.

```
$.....................................................................
$                                                  Calo  1983 Sommer
$.....................................................................
CREATE_NEW_EQUILIBRIUM 350,1
CHANGE_STATUS PHASE LIQUID=ENT 1
SET_CONDITION P=PO N=1 T=1120 X(CU)=0.075
SET_REFERENCE_STATE CU LIQUID * 1E5
SET_REFERENCE_STATE MG LIQUID * 1E5
 EXPERIMENT HMR=-1900:5%
 LABEL AL
 COMMENT                              Liq - Calo - SOMMER
 GRAI
```

COMMENT is an optional command that cannot be given interactively.

It defines a relatively short comment displayed when giving LIST_EQUILIBRIUM before output options and in the output when giving the COMPUTE_ALL_EQUILIBRIA

MAKE_POP_FILE will introduce these comments in POP files it generates.

```
$.....................................................................
$                                                    Calo  1983 Sommer
$.....................................................................
CREATE_NEW_EQUILIBRIUM 350,1
CHANGE_STATUS PHASE LIQUID=E
SET_CONDITION P=PO N=1 T=112
SET_REFERENCE_STATE CU LIQUI
SET_REFERENCE_STATE MG LIQUID * 1E5
 EXPERIMENT HMR=-1900:5%
 LABEL AL
 COMMENT                              Liq - Calo - SOMMER
 GRAI
```

Longer comments are often introduced in the POP file on lines beginning by $. These are not saved in the PAR workspace.

COMMENT is an optional command that cannot be given interactively.

It defines a relatively short comment displayed when giving LIST_EQUILIBRIUM before output options and in the output when giving the COMPUTE_ALL_EQUILIBRIA

MAKE_POP_FILE will introduce these comments in POP files it generates.

```
$.....................................................................
$                                                  Calo  1983 Sommer
$.....................................................................
CREATE_NEW_EQUILIBRIUM 350,1
CHANGE_STATUS_PHASE LIQUID-ENT 1
SET_C
SET_I
SET_I
 EXPI
 LABI
 COMMENT                                  Liq   Calo   Sommer
 GRAPHICS 5 .075 -1900 MS200
```

GRAPHICS is an optional command. It allows to define points in an exp file to be compared to calculated quantities. This file, named expfil.exp by default, is created when compiling the POP in the PARROT module. The information is then not stored in the PAR workspace.

```
$.....................................................................
$                                                    Calo  1983 Sommer
$.....................................................................
CREATE_NEW_EQUILIBRIUM 350,1
CHANGE_STATUS PHASE LIQUID=ENT 1
SET_C
SET_I
SET_I
 EXPI
 LABI
 COMMENT                                  Liq   Calo   Sommer
 GRAPHICS 5 .075 -1900 MS200
```

GRAPHICS is an optional command. It allows to define points in an exp file to be compared to calculated quantities. This file, named expfil.exp by default, is created when compiling the POP in the PARROT module. The information is then not stored in the PAR workspace.

The integer just after the GRAPHICS command corresponds to the DATASET in the exp file where the point will be introduced.

The next two numbers correspond to the coordinates of the point.

The last information correspond to the GOC (Graphical Operation Code).

Tables

- The definition of singular equilibria in EDIT_EXPERIMENT is, like in POLY_3, extremely flexible, allowing to compute any measured quantity.
- We have now introduced most of the specific commands of EDIT_EXPERIMENTS used in POP files:
  - CREATE_NEW_EQUILIBRIUM
  - EXPERIMENTS
  - LABEL
  - COMMENT
  - GRAPHICS
- Introducing single equilibria is tedious many experiments. The ability to use tables is another power of EDIT_EXPERIMENT, only available thanks to the use of POP files.

```
TABLE_HEAD  300
CREATE_NEW_EQUILIBRIUM @@,1
CHANGE_STATUS PHASE CUMG2,LAVES=ENT 1
SET_CONDITION P=P0 N=1 x(Mg)=.5 T=@2
SET_REFERENCE_STATE MG HCP * 1E5
SET_ALL_START_VALUES F
 EXPERIMENT MUR(MG)=@6:20%
 COMMENT                C15+CuMg2 - Mg PRESSURE - SMITH
 GRAPHICS 4 @2 @6 MS2
 LABEL @1
TABLE_VALUES
$       T/K  log p Mg (atm)  p Mg          a Mg     Mu Mg
   AC2 675   -6.4800         3.3113E-07    0.0786   -14276
   AC2 725   -5.6800         2.0893E-06    0.0839   -14937
   AC2 775   -4.9832         1.0394E-05    0.0889   -15597
   AC2 825   -4.3709         4.2569E-05    0.0935   -16258
   AC2 875   -3.8286         1.4840E-04    0.0977   -16918
TABLE_END
```

```
TABLE_HEAD  300
CREATE_NEW_EQUILIBRIUM @@,1
CHANGE_STATUS PHASE CUMG2,LA
SET_CONDITION P=PO N=1 x(Mg)
SET_REFERENCE_STATE MG HCP *
SET_ALL_START_VALUES F
 EXPERIMENT MUR(MG)=@6:20%
 COMMENT                 C15+C
 GRAPHICS 4 @2 @6 MS2
 LABEL @1
TABLE_VALUES
$       T/K  log p Mg (atm)
   AC2 675   -6.4800
   AC2 725   -5.6800
   AC2 775   -4.9832          1.0394E-05   0.0889   -15597
   AC2 825   -4.3709          4.2569E-05   0.0935   -16258
   AC2 875   -3.8286          1.4840E-04   0.0977   -16918
TABLE_END
```

A table begins by TABLE_HEAD followed by a integer corresponding to the identifier of the first equilibrium of the table. The identifier of the following equilibria will be automatically increment by 1.

At the compilation of the POP files, individual equilibrium are generated. The table structure is not stored in the PAR workspace. POP files writen by MAKE_POP_FILE don't have tables.

TABLE_HEAD cannot be run interactively.

```
TABLE_HEAD  300
CREATE_NEW_EQUILIBRIUM @@,1
CHANGE_STATUS PHASE CUMG2,LA
SET_CONDITION P=PO N=1 x(Mg)
SET_REFERENCE_STATE MG HCP *
SET_ALL_START_VALUES F
 EXPERIMENT MUR(MG)=@6:20%
 COMMENT                C15+CuMg2 - Mg PRESSURE - SMITH
 GRAPHICS 4 @2 @6 MS2
 LABEL @1
TABLE_VALUES
$       T/K  log p Mg (atm)  p Mg          a Mg     Mu Mg
   AC2 675    -6.4800        3.3113E-07    0.0786   -14276
   AC2 725    -5.6800        2.0893E-06    0.0839   -14937
   AC2 775    -4.9832        1.0394E-05    0.0889   -15597
   AC2 825    -4.3709        4.2569E-05    0.0935   -16258
   AC2 875    -3.8286        1.4840E-04    0.0977   -16918
TABLE_END
```

The identifier of the equilibrium being automatically generated, it is replaced by @@ in the CREATE_NEW_EQUILIBRIUM command.

```
TABLE_HEAD  300
CREATE_NEW_EQUILIBRIUM @@,1
CHANGE_STATUS PHASE CUMG2,LAVES=ENT 1
SET_CONDITION P=PO N=1 x(Mg)=.5 T=@2
SET_REFERENCE_STATE MG HCP * 1E5
SET_ALL_START_VALUES F
 EXPERIMENT MUR(MG)=@6:20%
 COMMENT                C15+CuMg2 - Mg PRESSURE - SMITH
 GRAPHICS 4 @2 @6 MS2
 LABEL @1
TABLE_VALUES
$       T/K  log p Mg (atm)  p Mg          a Mg     Mu Mg
   AC2 675    -6.4800        3.3113E-07    0.0786   -14276
   AC2 725    -5.6800        2.0893E-06    0.0839   -14937
   AC2 775    -4.9832        1.0394E-05    0.0889   -15597
   AC2 825    -4.3709        4.2569E-05    0.0935   -16258
   AC2 875    -3.8286        1.4840E-04    0.0977   -16918
TABLE_END
```

@2 corresponds to the content in the 2nd column.

```
TABLE_HEAD  300
CREATE_NEW_EQUILIBRIUM @@,1
CHANGE_STATUS PHASE CUMG2,LAVES=ENT 1
SET_CONDITION P=PO N=1 x(Mg)=.5 T=@2
SET_REFERENCE_STATE MG HCP * 1E5
SET_ALL_START_VALUES F
 EXPERIMENT MUR(MG)=@6:20%
 COMMENT                C15+CuMg2 - Mg PRESSURE - SMITH
 GRAPHICS 4 @2 @6 MS2
 LABEL @1
TABLE_VALUES
$       T/K  log p Mg (atm)  p Mg          a Mg     Mu Mg
   AC2 675    -6.4800        3.3113E-07    0.0786   -14276
   AC2 725    -5.6800        2.0893E-06    0.0839   -14937
   AC2 775    -4.9832        1.0394E-05    0.0889   -15597
   AC2 825    -4.3709        4.2569E-05    0.0935   -16258
   AC2 875    -3.8286        1.4840E-04    0.0977   -16918
TABLE_END
```

@6 corresponds to the content in the 6th column.

```
TABLE_HEAD  300
CREATE_NEW_EQUILIBRIUM @@,1
CHANGE_STATUS PHASE CUMG2,LAVES=ENT 1
SET_CONDITION P=PO N=1 x(Mg)=.5 T=@2
SET_REFERENCE_STATE MG HCP * 1E5
SET_ALL_START_VALUES F
 EXPERIMENT MUR(MG)=@6:20%
 COMMENT                C15+CuMg2 - Mg PRESSURE - SMITH
 GRAPHICS 4 @2 @6 MS2
 LABEL @1
TABLE_VALUES
$       T/K  log p Mg (atm)
   AC2 675   -6.4800
   AC2 725   -5.6800
   AC2 775   -4.9832
   AC2 825   -4.3709
   AC2 875   -3.8286
TABLE_END
```

@6 corresponds to the content in the 6th column.

@n can be used in any command of EDIT_EXPERIMENTS.
Errors may appear at the compilation if its type doesn't respect the expectation of the command (integer, phase, string, ...)

```
TABLE_HEAD  300
CREATE_NEW_EQUILIBRIUM @@,1
CHANGE_STATUS PHASE CUMG2,LAVES=ENT 1
SET_CONDITION P=PO N=1 x(Mg)=.5 T=@2
SET_REFERENCE_STATE MG HCP * 1E5
SET_ALL_START_VALUES F
 EXPERIMENT MUR(MG)=@6:20%
 COMMENT                C15+C
 GRAPHICS 4 @2 @6 MS2
 LABEL @1
TABLE_VALUES
$       T/K  log p Mg (atm)   p Mg          a Mg      Mu Mg
   AC2 675    -6.4800         3.3113E-07    0.0786    -14276
   AC2 725    -5.6800         2.0893E-06    0.0839    -14937
   AC2 775    -4.9832         1.0394E-05    0.0889    -15597
   AC2 825    -4.3709         4.2569E-05    0.0935    -16258
   AC2 875    -3.8286         1.4840E-04    0.0977    -16918
TABLE_END
```

The content of the table is introduced between TABLE_VALUES and TABLE_END.
Some columns can be useless.
Comments on the content of the columns are recommended.

POLY_3 commands

- The definition of equilibria and experimental quantities to be fitted in EDIT_EXPERIMENT should be done as close as possible to the actual experiment. POLY_3 commands usually seldom used maybe needed for that.
- The global minimisation is off by default in PAR workspaces and thus in EDIT_EXPERIMENT. It is recommended to keep it such unless very punctually. This requires a deeper knowledge of the commands handling starting values.

Starting values

As the global minimisation is turned off by default in PAR workspaces, computation fail more often. Some commands allow to start closer to the expected equilibrium and to converge more easily.

- SET_START_VALUE gives a starting value to a variable: T, P, NP(phase), y(phase,i). POP files generated by MAKE_POP_FILE use this command systematically for all unset variables.

Starting values

As the global minimisation is turned off by default in PAR workspaces, computation fail more often. Some commands allow to start closer to the expected equilibrium and to converge more easily.

- SET_START_VALUE gives a starting value to a variable: T, P, NP(phase), y(phase,i). POP files generated by MAKE_POP_FILE use this command systematically for all unset variables.

```
SET_START_VALUES T=990
SET_START_VALUES NP(LIQUID)=1
SET_START_VALUES Y(LIQUID,CU)=0.01
```

Starting values

As the global minimisation is turned off by default in PAR workspaces, computation fail more often. Some commands allow to start closer to the expected equilibrium and to converge more easily.

- SET_START_VALUE gives a starting value to a variable: T, P, NP(phase), y(phase,i). POP files generated by MAKE_POP_FILE use this command systematically for all unset variables.
- SET_START_CONSTITUTION gives a starting constitution to a phase.

Starting values

As the global minimisation is turned off by default in PAR workspaces, computation fail more often. Some commands allow to start closer to the expected equilibrium and to converge more easily.

- SET_START_VALUE gives a starting value to a variable: T, P, NP(phase), y(phase,i). POP files generated by MAKE_POP_FILE use this command systematically for all unset variables.
- SET_START_CONSTITUTION gives a starting constitution to a phase. After the phase name be given, a starting constitution can be entered in different formats.

Starting values

As the global minimisation is turned off by default in PAR workspaces, computation fail more often. Some commands allow to start closer to the expected equilibrium and to converge more easily.

- SET_START_VALUE gives a starting value to a variable: T, P, NP(phase), y(phase,i). POP files generated by MAKE_POP_FILE use this command systematically for all unset variables.
- SET_START_CONSTITUTION gives a starting constitution to a phase.

  ```
  SET_START_CONSTITUTION LIQUID NONE
  .99
  .01
  ```

  after NONE or nothing, individual starting values are given for each constituent of the phase on each sublattice.

Starting values

As the global minimisation is turned off by default in PAR workspaces, computation fail more often. Some commands allow to start closer to the expected equilibrium and to converge more easily.

- SET_START_VALUE gives a starting value to a variable: T, P, NP(phase), y(phase,i). POP files generated by MAKE_POP_FILE use this command systematically for all unset variables.
- SET_START_CONSTITUTION gives a starting constitution to a phase.

  ```
  SET_START_CONSTITUTION LIQUID CU
  ```

  Major constituent can be given on the line after phase name.
  This does not work for setting major constituent in different sublattices.

Starting values

As the global minimisation is turned off by default in PAR workspaces, computation fail more often. Some commands allow to start closer to the expected equilibrium and to converge more easily.

- SET_START_VALUE gives a starting value to a variable: T, P, NP(phase), y(phase,i). POP files generated by MAKE_POP_FILE use this command systematically for all unset variables.
- SET_START_CONSTITUTION gives a starting constitution to a phase.

  SET_START_CONSTITUTION LIQUID *

  * stands for a default constitution defined previously in GES with the AMEND_PHASE_DATA with option MAJOR_CONSTITUTENT.

Starting values

As the global minimisation is turned off by default in PAR workspaces, computation fail more often. Some commands allow to start closer to the expected equilibrium and to converge more easily.

- SET_START_VALUE gives a starting value to a variable: T, P, NP(phase), y(phase,i). POP files generated by MAKE_POP_FILE use this command systematically for all unset variables.
- SET_START_CONSTITUTION gives a starting constitution to a phase.
- SET_ALL_START_VALUES gives a starting values to all variables.

Starting values

As the global minimisation is turned off by default in PAR workspaces, computation fail more often. Some commands allow to start closer to the expected equilibrium and to converge more easily.

- SET_START_VALUE gives a starting value to a variable: T, P, NP(phase), y(phase,i). POP files generated by MAKE_POP_FILE use this command systematically for all unset variables.
- SET_START_CONSTITUTION gives a starting constitution to a phase.
- SET_ALL_START_VALUES gives a starting values to all variables.

  SET_ALL_START_VALUES N/Y

  Y gives automatic starting values for each entered,fixed or suspended phase. N, default answer, requires to enter starting values for each phase. Before entering Y/N, T or/and P are requested if they are not set.

Functions

Some thermodynamic properties require to be defined by the user, like the heat capacity, the heat increment, the melting enthalpy, the partial enthalpy,...

Functions

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`ENTER_SYMBOL FUNCTION CP=HM.T`
`HM.T` is the derivative of the molar enthalpy versus T;
it is the heat capacity in J/mol/T is P is set as condition

`ENTER_SYMBOL FUNCTION CPW=HW.T`
`HW.T` is the heat capacity in J/g/T if P set as condition

`ENTER_SYMBOL FUNCTION CPF=H.T`
`H.T` is the heat capacity for the number of component considered,
possibility a compound formula if *e.g.* `N(CU)=2,N(MG)=1`

Functions

Some thermodynamic properties require to be defined by the user, like the heat capacity, the heat increment, the melting enthalpy, the partial enthalpy,...

```
CREATE_NEW_EQUILIBRIUM 1,1
CHANGE_STATUS PHASE LAVES_C15=ENTERED 1
SET_CONDITION N(CU)=2 N(MG)=1 P=1E5 T=300
ENTER_SYMBOL VARIABLE H300=H;

CREATE_NEW_EQUILIBRIUM 2,1
CHANGE_STATUS PHASE LAVES_C15=ENTERED 1
SET_CONDITION N(CU)=2 N(MG)=1 P=1E5 T=1000
ENTER_SYMBOL FUNCTION DHCU2MG=H-H300;
```

DHCU2MG can be used in EXPERIMENT command to compare with experimental enthalpy increment for the compound formula at 1000K from 300K.

Functions

Some thermodynamic properties require to be defined by the user, like the heat capacity, the heat increment, the melting enthalpy, the partial enthalpy,...

Melting enthalpy requires two equilibria when the melting is not congruent.

```
CREATE_NEW_EQUILIBRIUM 1,1
CHANGE_STATUS PHASE LAVES_C15=ENTERED 1
CHANGE_STATUS PHASE LIQUID=FIX 0
COMMENT SOLIDUS
SET_CONDITION N=1 X(CU)=.3 P=1E5
ENTER_SYMBOL VARIABLE HSOL=H;

CREATE_NEW_EQUILIBRIUM 2,1
CHANGE_STATUS PHASE LAVES_C15=ENTERED 1
CHANGE_STATUS PHASE LIQUID=FIX 1
COMMENT LIQUIDUS
SET_CONDITION N=1 X(CU)=.3 P=1E5
ENTER_SYMBOL FUNCTION HFUS=H-HSOL;
```

Functions

Some thermodynamic properties require to be defined by the user, like the heat capacity, the heat increment, the melting enthalpy, the partial enthalpy,...

```
@@ Partial entropy is
ENTER_SYMBOL FUNCTION SMG=-MU(MG).T;
@@ Partial enthalpy is h = g + s*t
ENTER_SYMBOL FUNCTION HMG=MU(MG)+SMG*T;
```

SET_REFERENCE_STATE

When considering experimental thermodynamic quantities (enthalpies of formation, of mixing, activities, chemical potential, ...) , it is important to use the proper reference state for the components.

By default the reference state for a component is SER: its stable state at 298.15K, considered at 298.15K and10^5Pa. To change this reference :

`SET_REFERENCE_STATE` component phase T P

The phase should be described for the pure component.
T/P can be defined as the current temperature/pressure, entering `*`.

Taking into account the new reference state is then possible adding `R` to the thermodynamic variables (`HMR`, `ACR(i)`, `MUR(i)`, ...)

SET_REFERENCE_STATE

Mixing enthalpy in the liquid phase.

```
CHANGE_STATUS PHASE LIQUID=ENT 1
SET_CONDITION P=P0 N=1 T=1100 X(Mg)=.075
SET_REFERENCE_STATE CU LIQUID * 1E5
SET_REFERENCE_STATE MG LIQUID * 1E5
 EXPERIMENT HMR=-1900:5%
```

SET_REFERENCE_STATE

Mixing enthalpy in the liquid phase.

```
CHANGE_STATUS PHASE LIQUID=ENT 1
SET_CONDITION P=P0 N=1 T=1100 X(Mg)=.075
SET_REFERENCE_STATE CU LIQUID * 1E5
SET_REFERENCE_STATE MG LIQUID * 1E5
 EXPERIMENT HMR=-1900:5%
```

Using HM would have a different meaning. It would be the formation of the solution from the elements at room temperature. It can actually be the rough quantity measured. If it is given in the article, it is then better to fit this quantitty rather than postprocessed value.

SET_REFERENCE_STATE

Formation energy of a compound

```
CHANGE_STATUS PHASE LAVES_C15=ENT 1
SET_CONDITION P=P0 T=298.15 N(Cu)=2 N(Mg)=1
SET_REFERENCE_STATE CU FCC_A1 * 1E5
SET_REFERENCE_STATE MG HCP_A3 * 1E5
 EXPERIMENT HMR=-11171.3:420
```

SET_REFERENCE_STATE

Formation energy of a compound

```
CHANGE_STATUS PHASE LAVES_C15=ENT 1
SET_CONDITION P=P0 T=298.15 N(Cu)=2 N(Mg)=1
SET_REFERENCE_STATE CU FCC_A1 * 1E5
SET_REFERENCE_STATE MG HCP_A3 * 1E5
 EXPERIMENT HMR=-11171.3:420
```

is actually identical to

```
CHANGE_STATUS PHASE LAVES_C15=ENT 1
SET_CONDITION P=P0 T=298.15 N(Cu)=2 N(Mg)=1
 EXPERIMENT HM=-11171.3:420
```

SET_REFERENCE_STATE

Formation energy of a compound

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```
CHANGE_STATUS PHASE LAVES_C15=ENT 1
SET_CONDITION P=P0 T=298.15 N(Cu)=2 N(Mg)=1
 EXPERIMENT HM=-11171.3:420
```

Note the way to define the ideal stoichiometry of a compound using `N(i)` rather than `X(i)`.

SET_REFERENCE_STATE

Chemical potentials

```
CHANGE_STATUS PHASE FCC,LAVES=FIX 1
SET_CONDITION P=P0 T=751
SET_REFERENCE_STATE MG HCP * 1E5
SET_ALL_START_VALUES F
 EXPERIMENT MUR(MG)=-30310:20%
```

SET_REFERENCE_STATE

Chemical potentials

```
CHANGE_STATUS PHASE FCC,LAVES=FIX 1
SET_CONDITION P=P0 T=751
SET_REFERENCE_STATE MG HCP * 1E5
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SET_ALL_START_VALUES F
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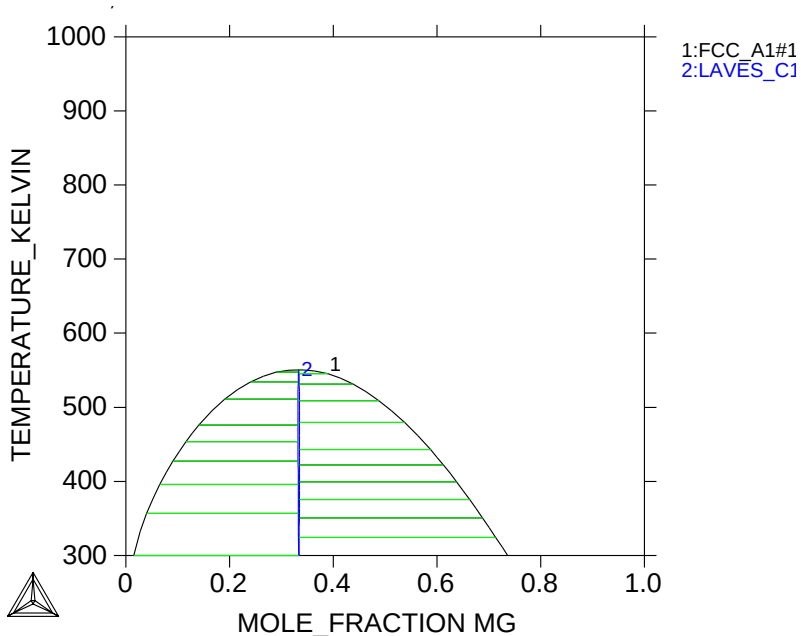
```

SET_REFERENCE_STATE



Chemical potentials

```
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SET_CONDITION P=P0 T=751
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```

when the phases are in equilibrium, at least metastably, at the considered temperature. If not, the 1st case cannot be computed

SET_REFERENCE_STATE

Chemical potentials

```
CHANGE_STATUS PHASE FCC,LAVES=FIX 1
SET_CONDITION P=P0 T=751
SET_REFERENCE_STATE MG HCP * 1E5
SET_ALL_START_VALUES F
 EXPERIMENT MUR(MG)=-30310:20%
```

Moreover this case can easily jump on the Mg side.

is identical to

```
CHANGE_STATUS PHASE FCC,LAVES=ENT 1
SET_CONDITION P=P0 T=751 X(Mg)=.2 N=1
SET_REFERENCE_STATE MG HCP * 1E5
SET_ALL_START_VALUES F
 EXPERIMENT MUR(MG)=-30310:20%
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Chemical potentials

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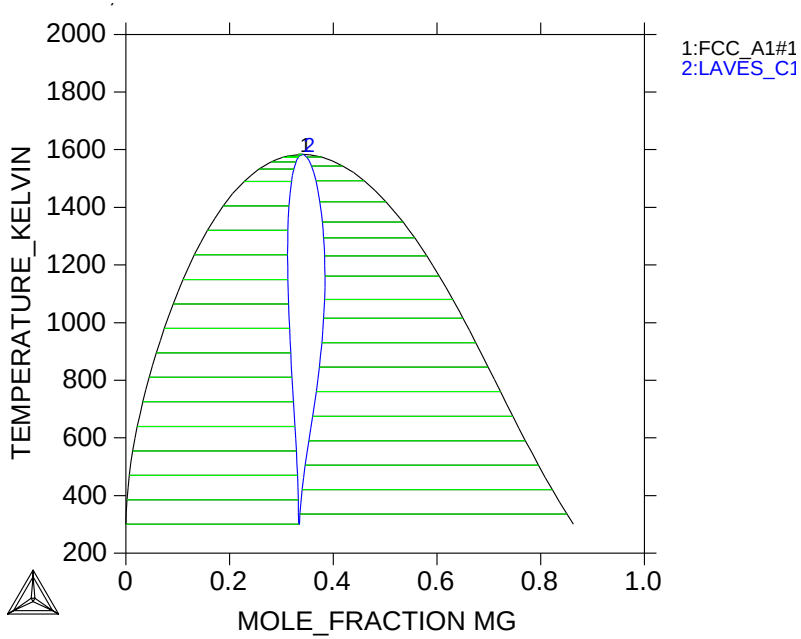
```



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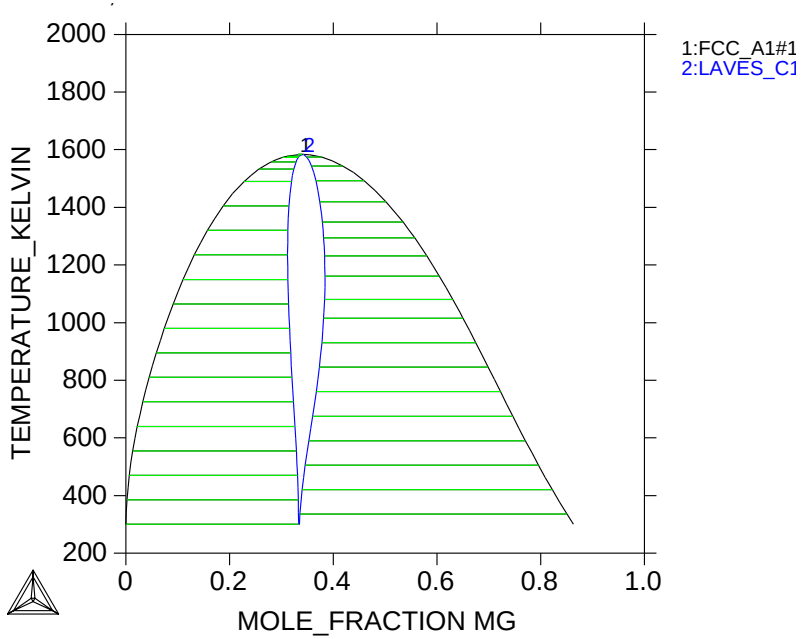
 EXPERIMENT MUR(MG)=-30310:20%
```



when the phases are in equilibrium, at least metastably, at the considered temperature. If not, the 1st case cannot be computed

Setting composition yields more robust equilibria than fixing phases.

POP file

- POP are needed to run a proper optimisation.
- It is not mandatory to introduce all the experimental available in a system in this file, in particular if some sets of data are disregarded for some reason or if the information is redundant.
- It is recommended comparing all experimental information with the computed values with the final description. This can be done using exp files.

What are exp files?

- The exp files are used by the POST module in order to plot calculated and experimental points data.
- The commands APPEND_EXPERIMENTAL_DATA allows to represent the content of such a file together with results of calculations performed in the current POLY_3 workspace.
- The commands QUICK_EXPERIMENTAL_PLOT allows to represent only the content of such a file.
- exp files containing calculated results can be generated by the MAKE_EXPERIMENTAL_DATA command.

What are exp files?

- The `exp` files are used by the `POST` module in order to plot calculated and experimental points data.
- When they correspond to experimental points, the files are usually edited manually. They can also have been generated when compiling a `POP` file where the `GRAPHICS` command has been used.
- Edition of automatically generated files allow to get nicer figures (colors, different type of lines, labels).
- The use of `exp` file during an optimisation is not mandatory but highly recommended.

exp files structure

- An `exp` file is consituted of two parts:
  - the `PROLOG` section and
  - the `DATASET` section.
- The `PROLOG` provides general information on the diagram: axis scale, text, lenght, diagram type, title, ...
- The `DATASET` provides tables of points and how to treat them (symbols, lines, colors, ...)
- It can contain several `PROLOG` and several `DATASET`, identified by integers.

exp files structure

- An exp file is consituted of two parts:
  - the PROLOG section and
  - the DATASET section.
- The PROLOG provides general information on the diagram: axis scale, text, lenght, diagram type, title, ...
- The DATASET provides tables of points and how to treat them (symbols, lines, colors, ...)
- It can contain several PROLOG and several DATASET, identified by integers.
- To use an exp file in POST with APPEND_EXPERIMENTAL_DATA or QUICK_EXPERIMENTAL_PLOT, an integer has to be given for the PROLOG number and one or several for the DATASET number.
- Several exp files can be considered if they are all given on the same line. PROLOG and DATASET numbers are then requested for each file. Only the last PROLOG will then be taken into account but all the DATASET indicated.

PROLOG

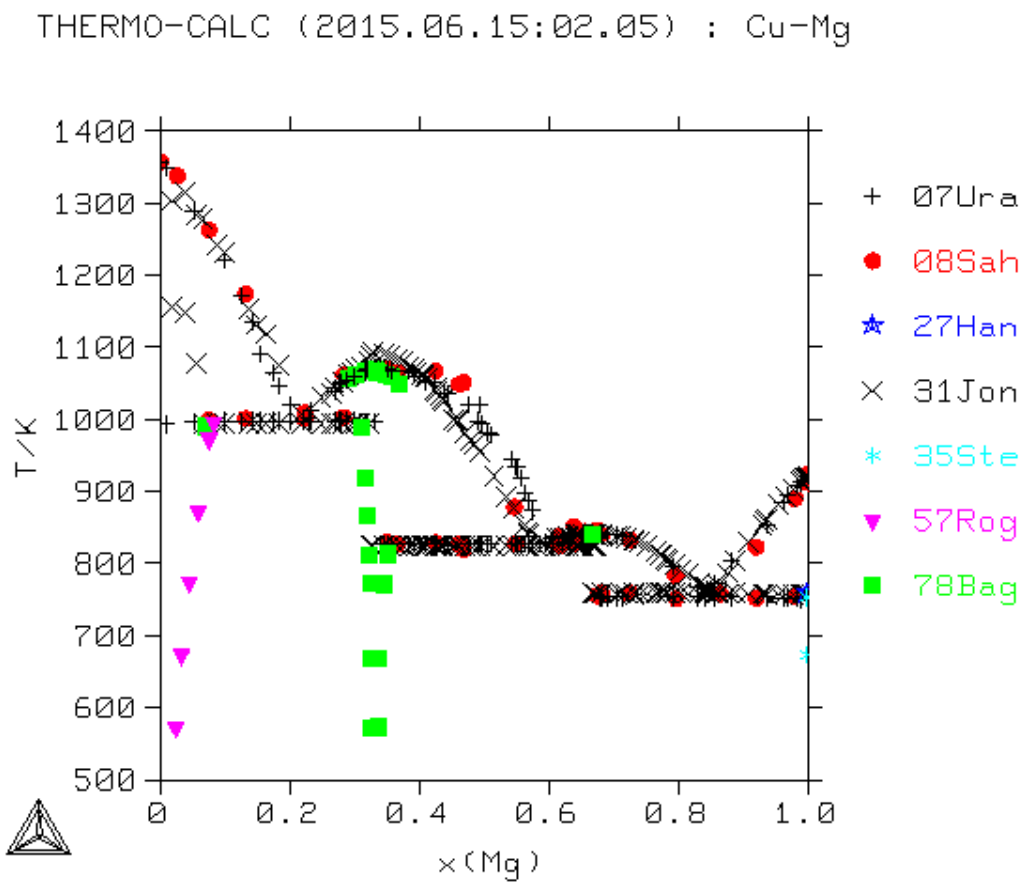
```
PROLOG 1 Phase diagram
 XSCALE 0.0 1.0
 YSCALE 500 1400
 XTYPE LINEAR
 YTYPE LINEAR
 XLENGTH 11.5
 YLENGTH 11.5
 TITLE Cu-Mg
 XTEXT x(Mg)
 YTEXT T/K
```

DATASET

```
DATASET 10 Phase diagram
ATTRIBUTE CENTER
CLIP OF
  color 2
  1.1 .8 MANS200' 08Sah
CLIP ON
BLOCK X=C1/100; Y=C2+273.15; GOC=C3,MAWS200
$ from table in original paper Sahmen
$ at% T/C     liquidus
  0   1084
  2.6 1065
  7.5  990
 13.2  901
.....
BLOCKEND
```

DATASET

```
DATASET 10 Phase diagram
ATTRIBUTE CENTER
CLIP OF
  color 2
  1.1 .8 MANS200' 08Sah
CLIP ON
BLOCK X=C1/100; Y=C2+273
$ from table in original
$ at% T/C     liquidus
  0    1084
  2.6  1065
  7.5   990
 13.2   901
.....
BLOCKEND
```



DATASET

The basic lines are constituted by X Y GOC
where GOC Graphical Operating Code is a combination of

- ⇝ `M` move / `D` draw
- ⇝ `A` absolute / `R` relative
- ⇝ `N` normalized / `W` world
- ⇝ `S#` symbol identified by integer `#`
- ⇝ `'` text

```
1.1 .8 MANS200' 08Sah
```

corresponds to

- ⇝ a symbol (`S`), solid circle (200)
- ⇝ at the coordinate `1.1 0.8`
- ⇝ normalized (`N`) to the axis
- ⇝ followed by the text `08Sah`

BLOCK

Advanced operations can be applied to a set of points inside a `BLOCK`

```
BLOCK X=C1/100; Y=C2+273.15; GOC=C3,MAWS200
```

The points in that `BLOCK` are displayed

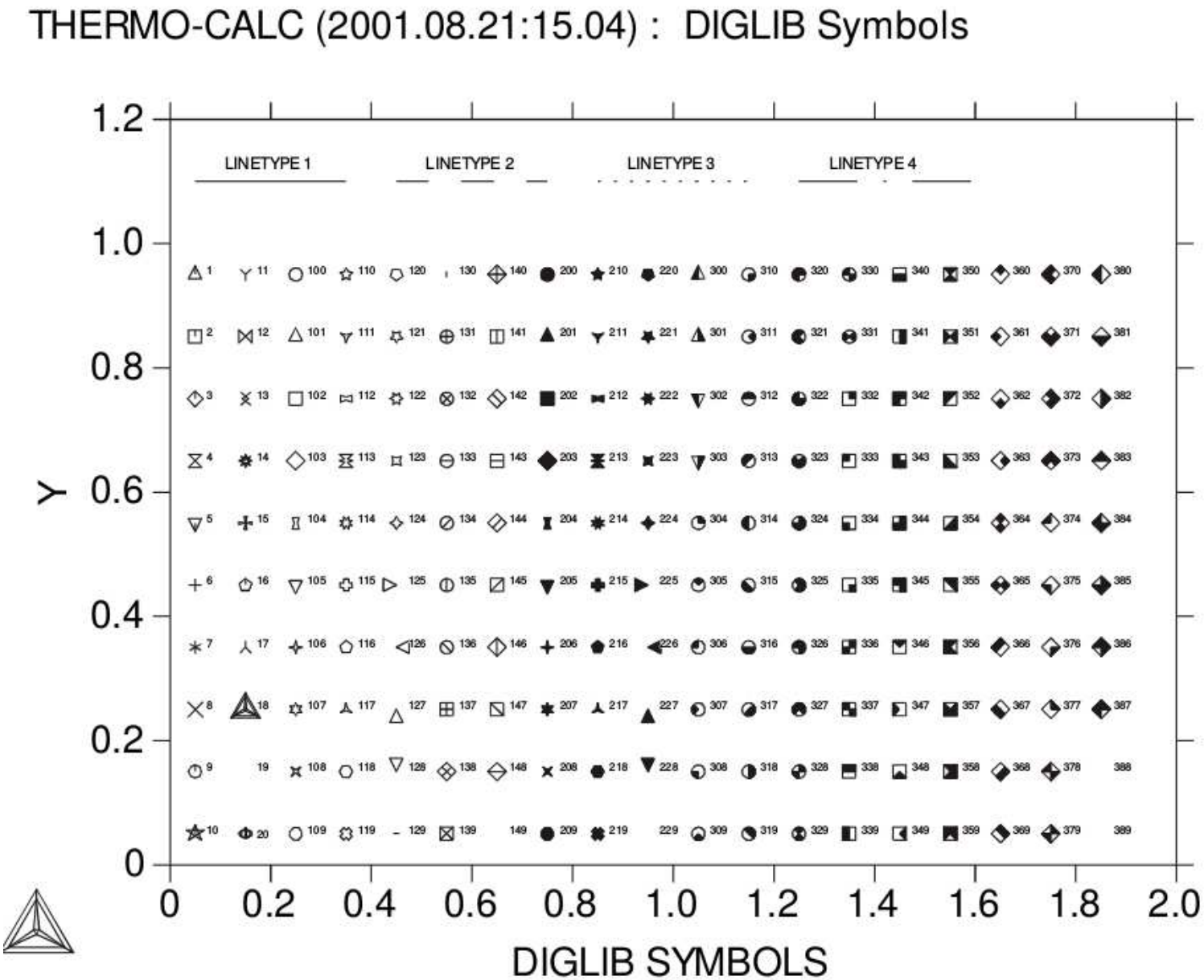
- ⇝ as symbols (`S`), solid circle (200)
- ⇝ at coordinates in the world space (`W`)
- ⇝ x coordinate beeing the value in the 1st column divided by 100
- ⇝ y coordinate beeing the value in the 2nd column + 273.15
- ⇝ change of the GOC for a point in 3rd column

DATASET

A few more features of interest

- `$` at the beginning of a line: comments
- `CLIP OFF/ON` enables to write out of the axis
- `COLOR` change of the color
- `LINETYPE #` change of the line type
- `SYMBOLSIZE` change of the size of the symbols
- `CHARSIZE` change of the size of the texts
- `ATTRIBUTE CENTER` to center symbols/text

Symbols


THERMO-CALC (2001.08.21:15.04) : DIGLIB Symbols
LINETYPE 1
LINETYPE 2
LINETYPE 3
LINETYPE 4
Y
1.2
1.0
0.8
0.6
0.4
0.2
0
0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0
DIGLIB SYMBOLS

Colors

Color Code: Color Effect	Color Code: Color Effect
1: Black	16: Seagreen
2: Red	17: Olivedrab
3: Green	18: Sienna
4: Blue	19: Orange
5: Yellow	20: Coral
6: Magenta	21: UserDef
7: Cyan	22 = 1
8: Purple	23 = 1
9: Gold	24 = 1
10: Turquoise	25 = 1
11: Pink	26 = 1
12: Gray	27 = 1
13: Orangered	28 = 1
14: Moroon	29 = 1
15: Plum	30 = 1