上海思响信息科技有限公司
地址：上海市浦东新区东方路428号235室
邮箱：yiwen.zhu@computherm.com
电话：13901652239

Pandat 软件

第一期优化培训教程

第三讲

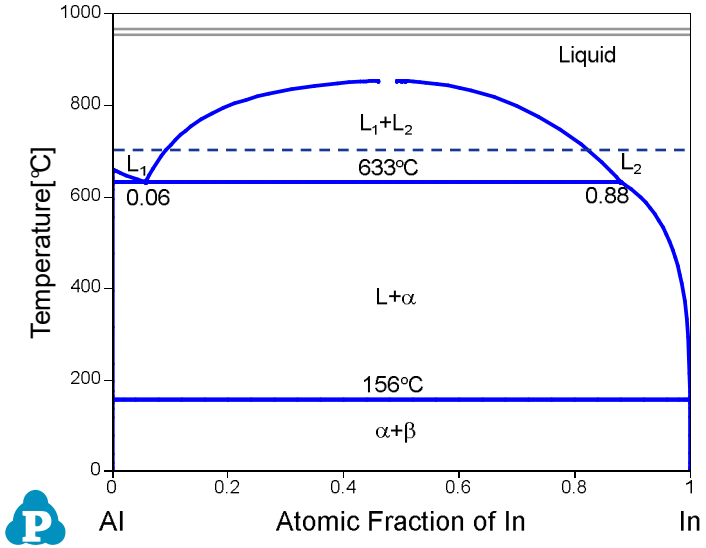
2020年7月4日

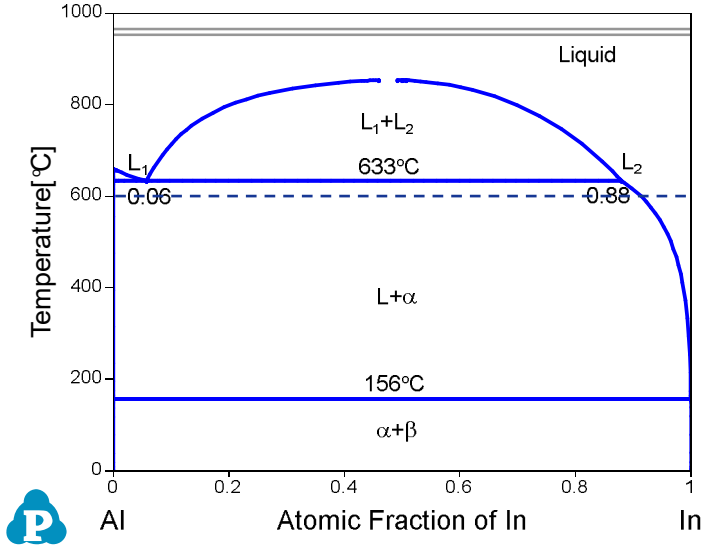
CompuTherm, LLC
8401 Greenway Blvd, Middleton, WI, USA
http://www.computherm.com

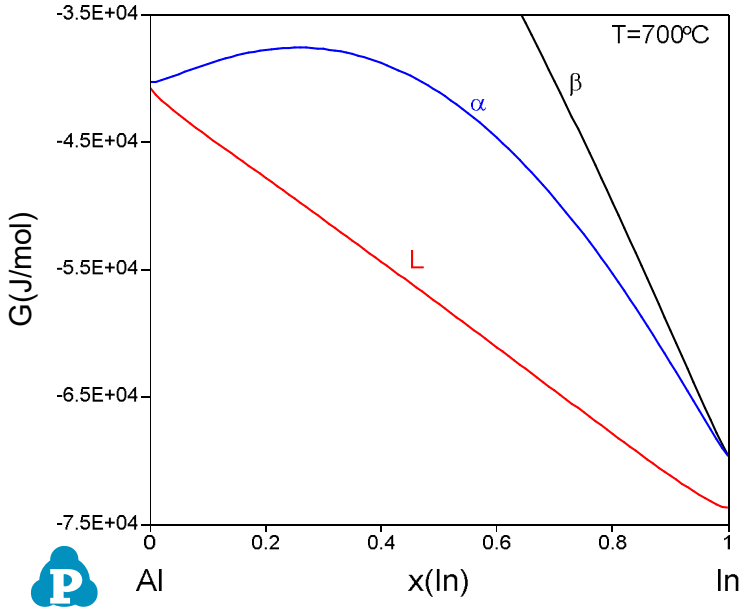
答 疑

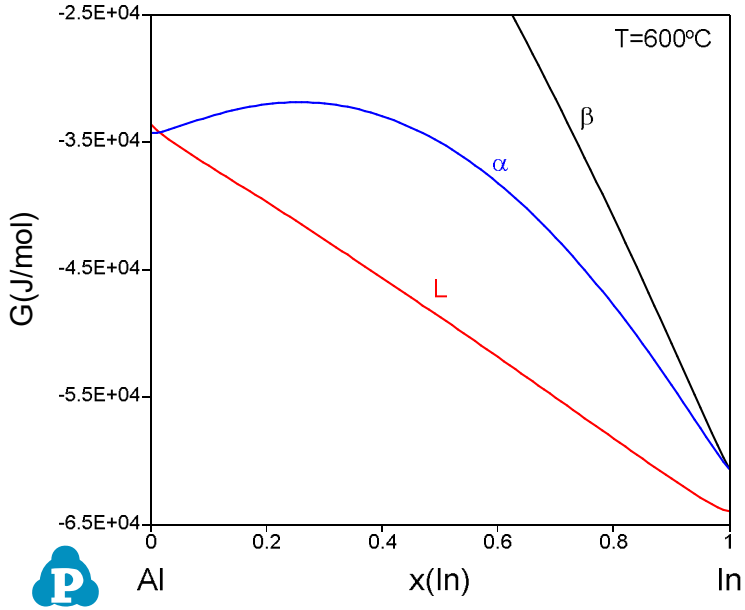
- 那个偏晶相图怎么计算，下次上课能展示一下吗?
- 下次上课时能否讲一下如何保存，调用和修改batch file?
- 能否讲一下如何进行high throughput计算
- 关于Pandat 的console module

偏晶相图vs吉布斯能

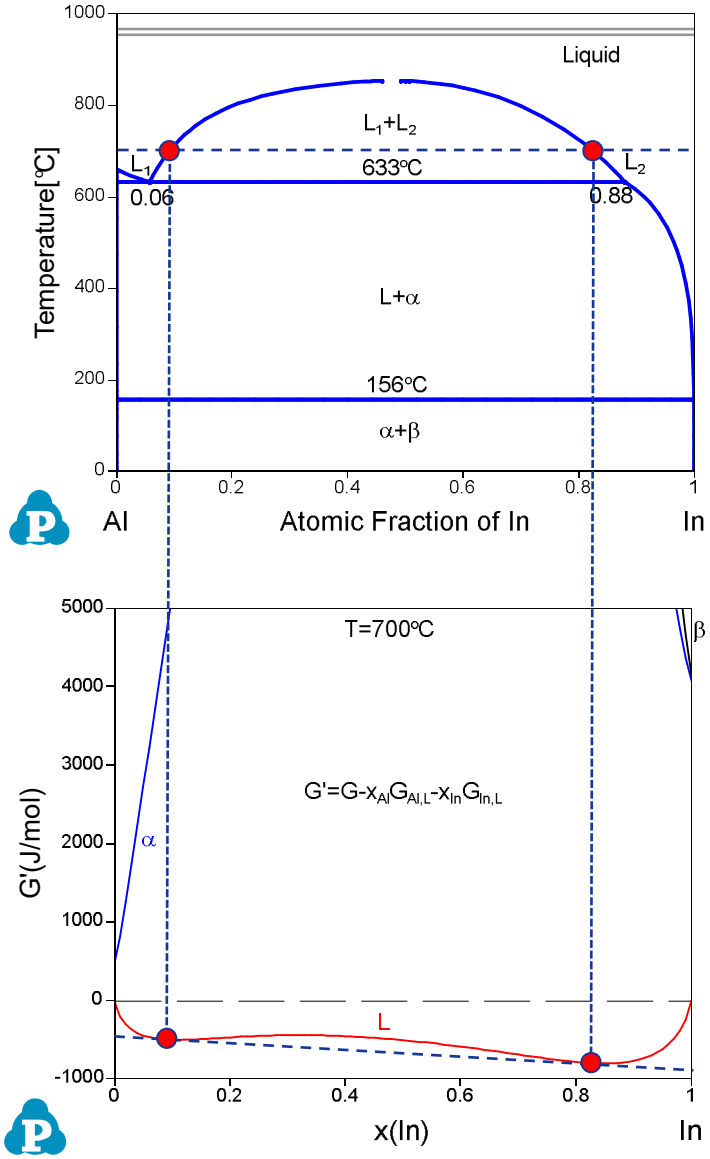

Liquid
L1+L2
L1
633°C
L2
0.06
0.88
L+α
156°C
α+β
Temperature[°C]
Al
Atomic Fraction of In
In

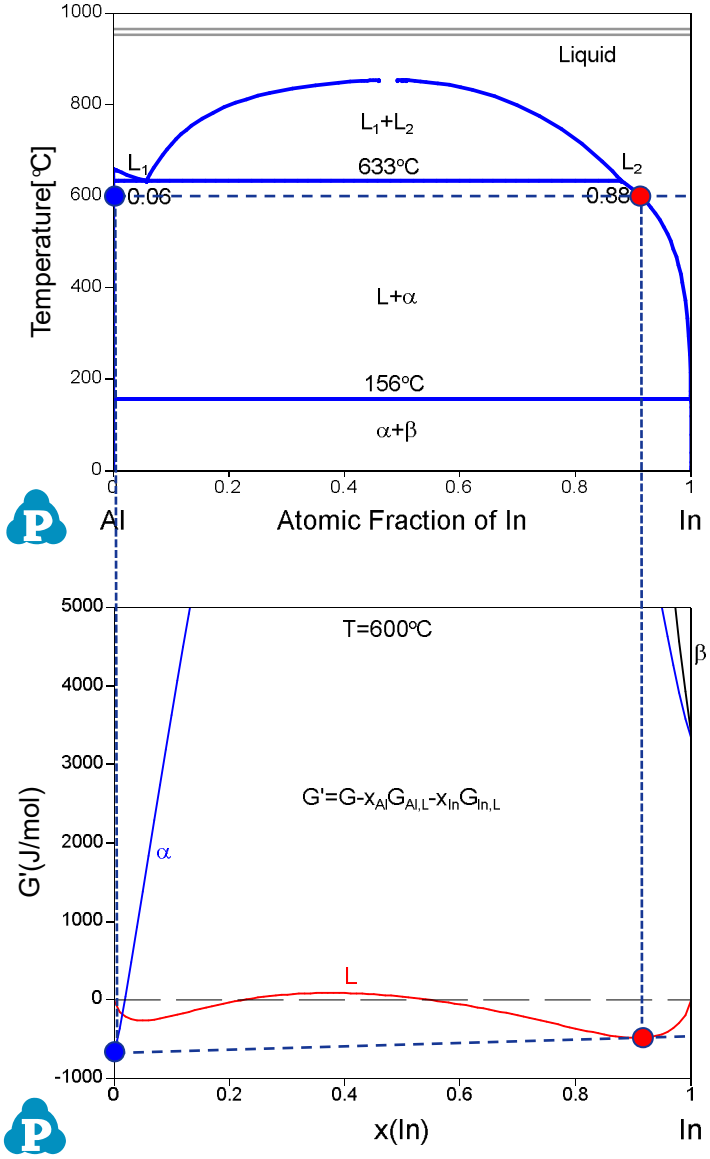

Liquid
L1+L2
L1
633°C
L2
0.06
0.88
L+α
156°C
α+β
Temperature[°C]
Al
Atomic Fraction of In
In


T=700°C
α
β
L
G(J/mol)
Al
x(In)
In


T=600°C
β
α
L
G(J/mol)
Al
x(In)
In

偏晶相图vs吉布斯能


Liquid
L1+L2
633°C
L1
L2
0.06
0.88
L+α
156°C
α+β
Temperature[°C]
Al
Atomic Fraction of In
In
T=700°C
G'=G-xAlGAl,L-xInGIn,L
α
β
L
G'(J/mol)
x(In)

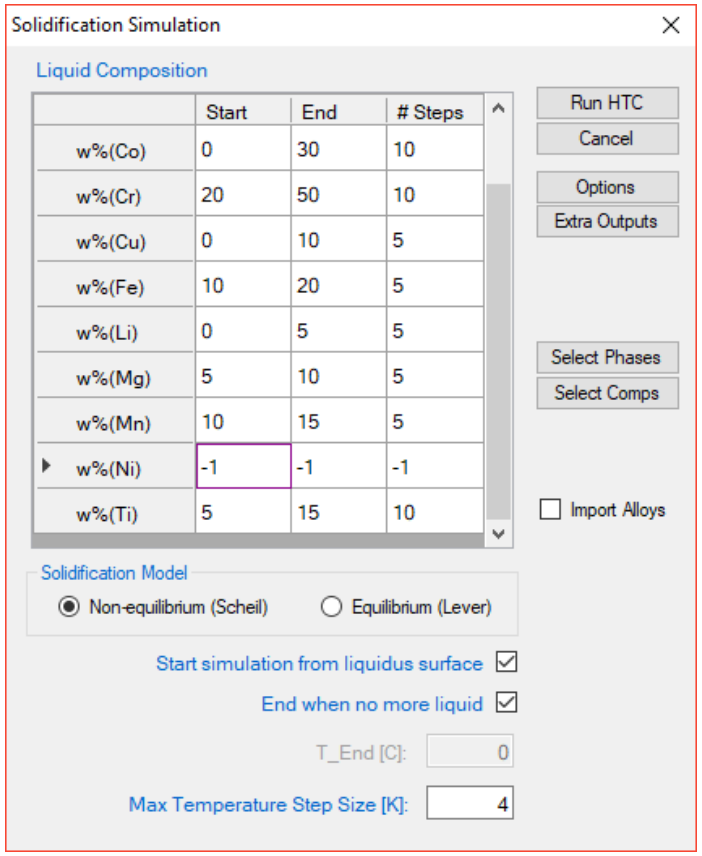

Liquid
L1+L2
633°C
L1
L2
0.06
0.88
L+α
156°C
α+β
Temperature[°C]
Al
Atomic Fraction of In
In
T=600°C
G'=G-xAlGAl,L-xInGIn,L
α
β
L
G'(J/mol)
x(In)

HTC 计算

- **高通量计算:** 在多维成分空间内，用户可以通过定义成分范围，来进行成千上万的计算。

- **计算结果的数据挖掘**： 通过对计算结果进行数据挖掘，确定满足用户定义的性能标准的合金成分范围。

目的: 加速新合金设计与研发



HTC 计算步骤

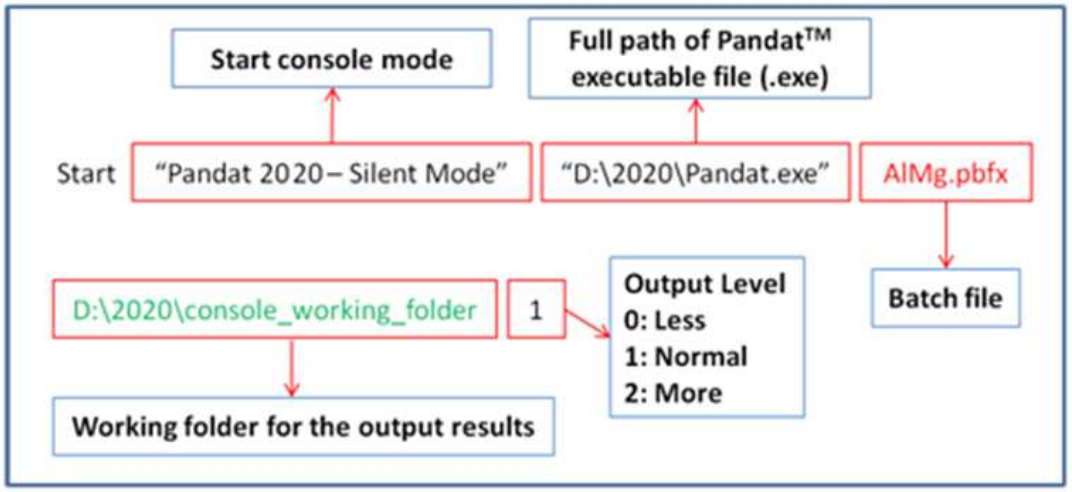
- 第一步: 用户定义成分
- 第二步: Pandat 进行所有成分的计算并且储存为一个工作空间。
- 第三步: 用户定义合金选择的标准条件
- 第四步: Pandat 在计算结果中进行数据挖掘，确定符合用户标准的合金成分。
- 第五步: Pandat 软件将数据挖掘结果显示为表格，并可利用表格数据绘制各种图形。

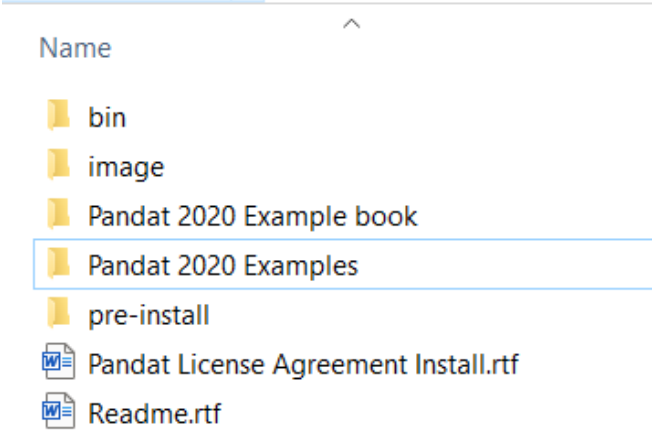
10 x 10 x 5 x 5 x 5 x 5 x 10 = 625000

Console 模块

C:\Program Files (x86)\CompuTherm LLC\Pandat 2020\Pandat 2020 Examples\ConsoleMode

Pandat Manual： Page 38



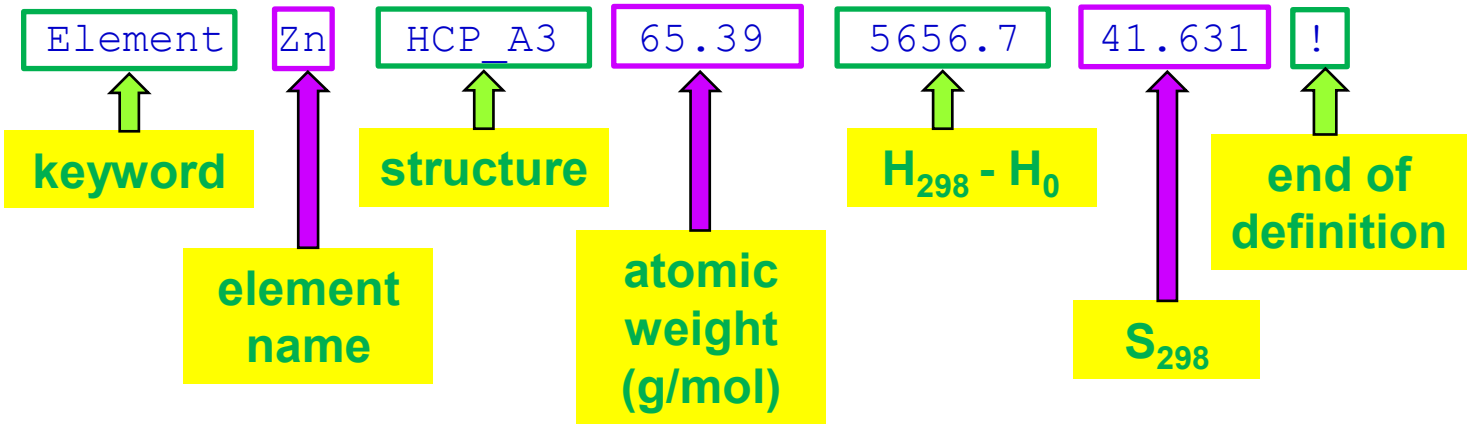


PanPy 模块: Pandat 与Python结合, 开源。
将在今年下半年的新版本中推出.

细说 TDB 文件

- Define Elements (and Spcies) in the system
- Define Functions (Gibbs energy functions at reference state)
- Define Phases (Sublattice Model, Site occupation, model parameters, Modification to normal state, such as Magnetic term, ordered part)

Element



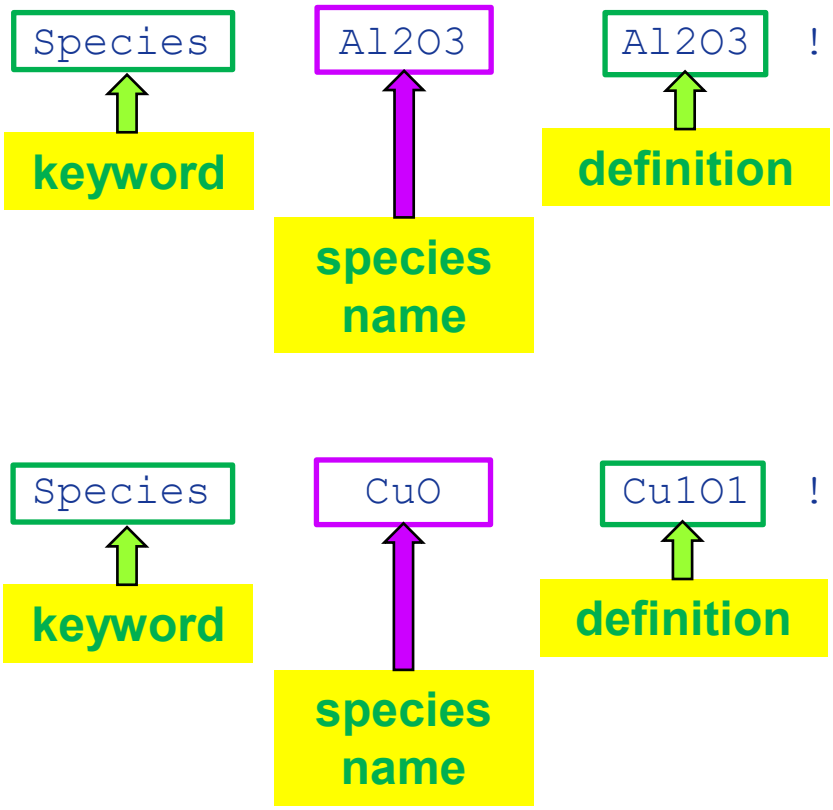

```
Element CaO  Halite 56.077  0  38.100 !
```

Note

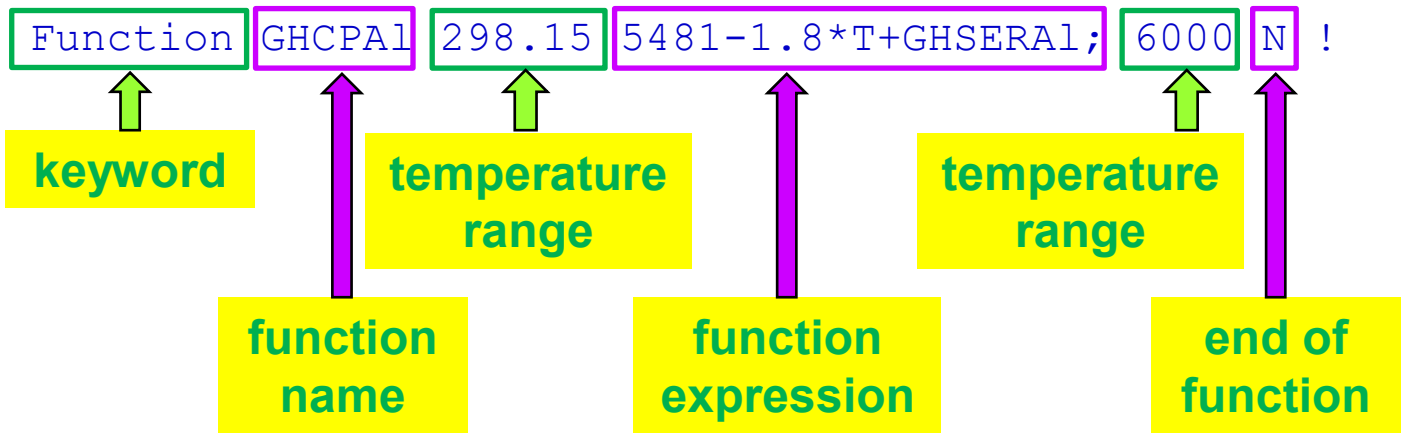
- Pandat has a built-in table of atomic weights of elements.
- If a compound (e.g., Al2O3) is defined as an element, its atomic weight has to be specified in the definition.
- Pandat does not use structure, H_{298} and S_{298} in current version.

CaMgO_TEST.tdb CaO-MgO_Test.tdb

Species

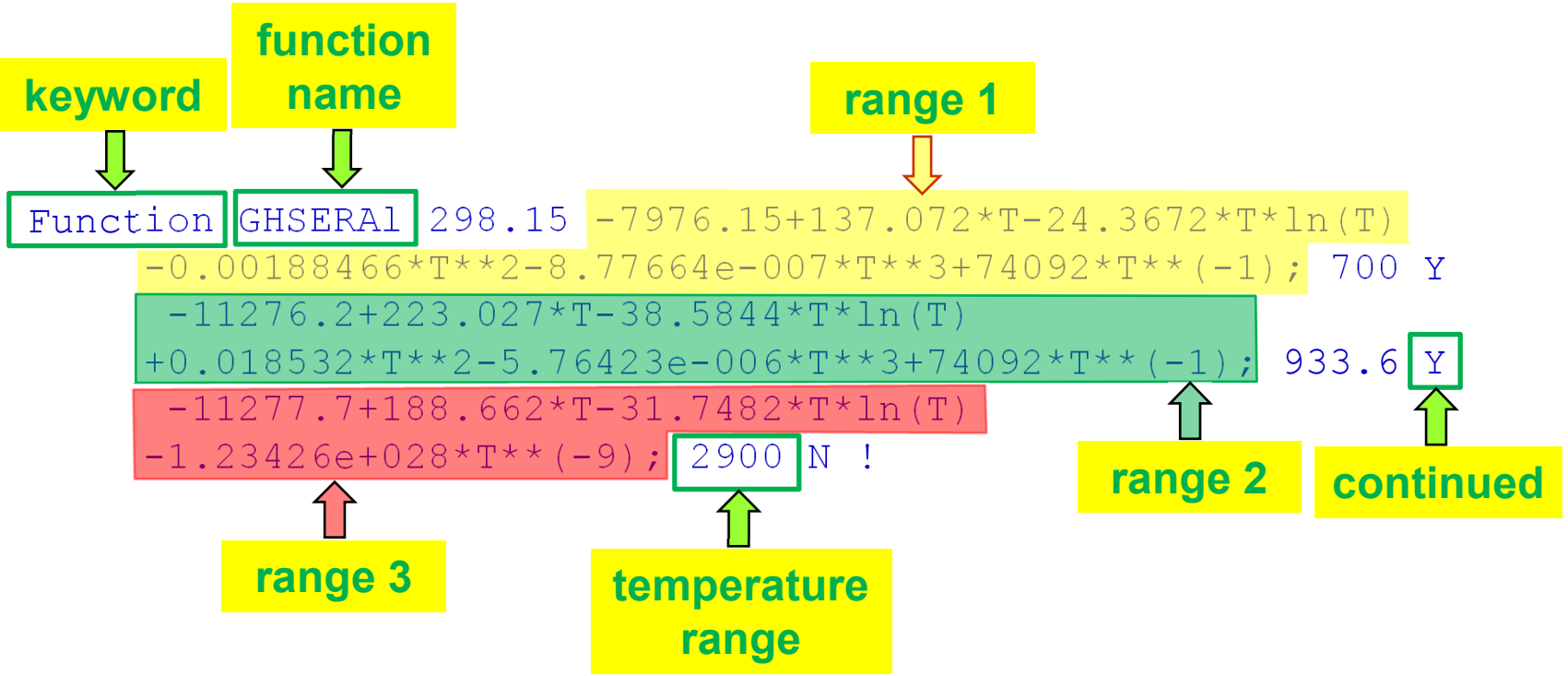

Species
keyword
Al2O3
species name
Al2O3 !
definition
Species
keyword
CuO
species name
Cu1O1 !
definition

Function



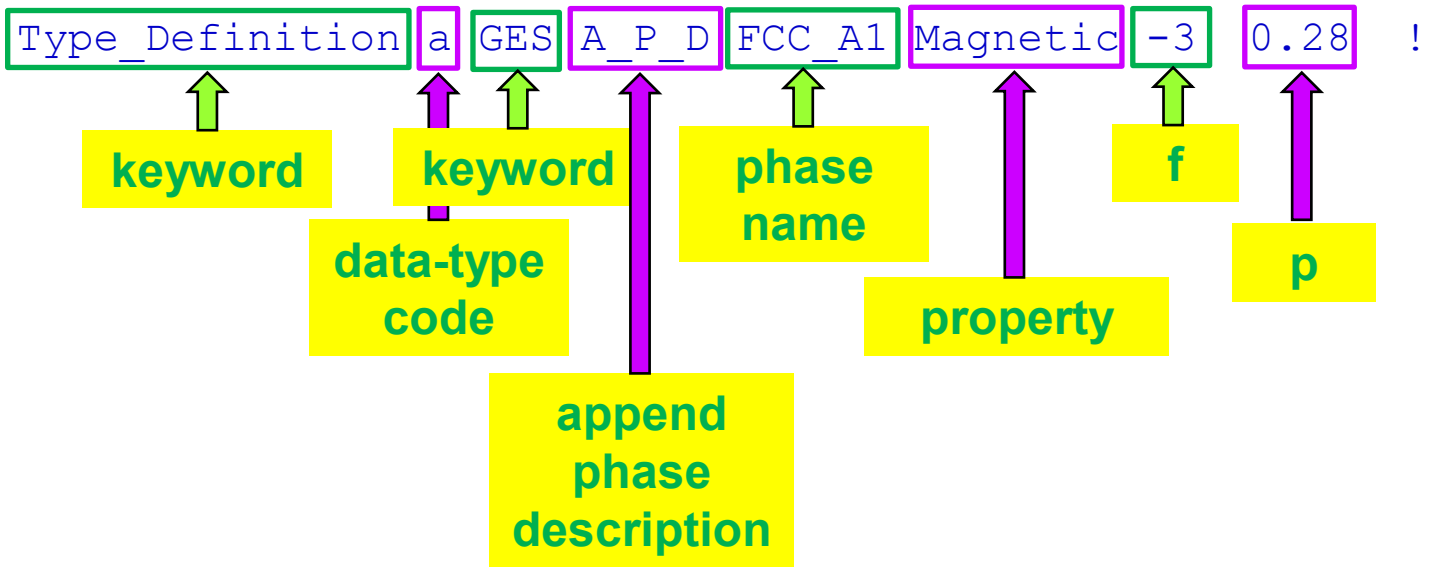
G_{Al}^{HCP} =5481-1.8T +$G_{Al}^{HSER}$$(J/mol)$ $(298.15K \leq T \leq 6000K)$

Function (multiple ranges)



G_{Al}^{HSER} = −7976.15+137.072 T−24.3672 T ln(T) −0.00188466 T^2−8.77664e−007 T^3
+74092 T^{-1}; (J/mol) $(298.15K \leq T \leq 700K)$
= −11276.2+223.027 T−38.5844 T ln(T) +0.018532 T^2−5.76423e−006∗T^3
+74092 T^{-1}; (J/mol) $(700K \leq T \leq 933.6K)$
= −11277.7+188.662 T−31.7482 T ln(T) −1.23426e+028 T^{-9}
(J/mol) $(933.6K \leq T \leq 2900K)$

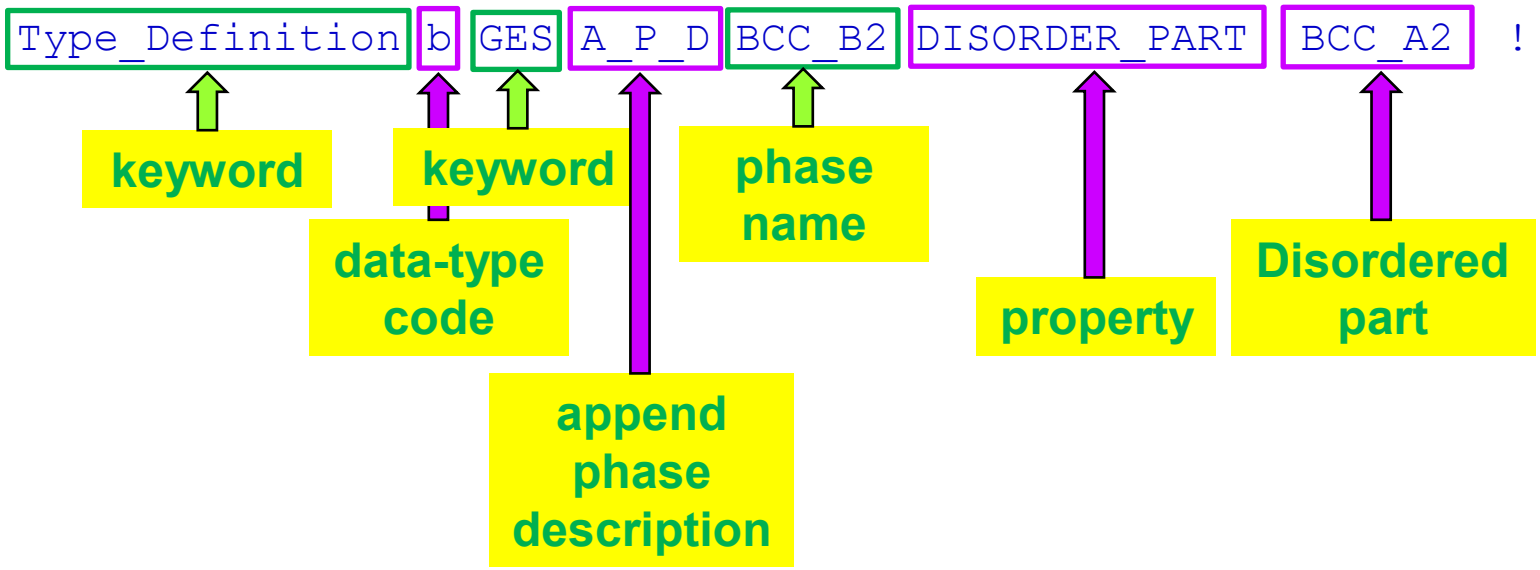
Type Definition



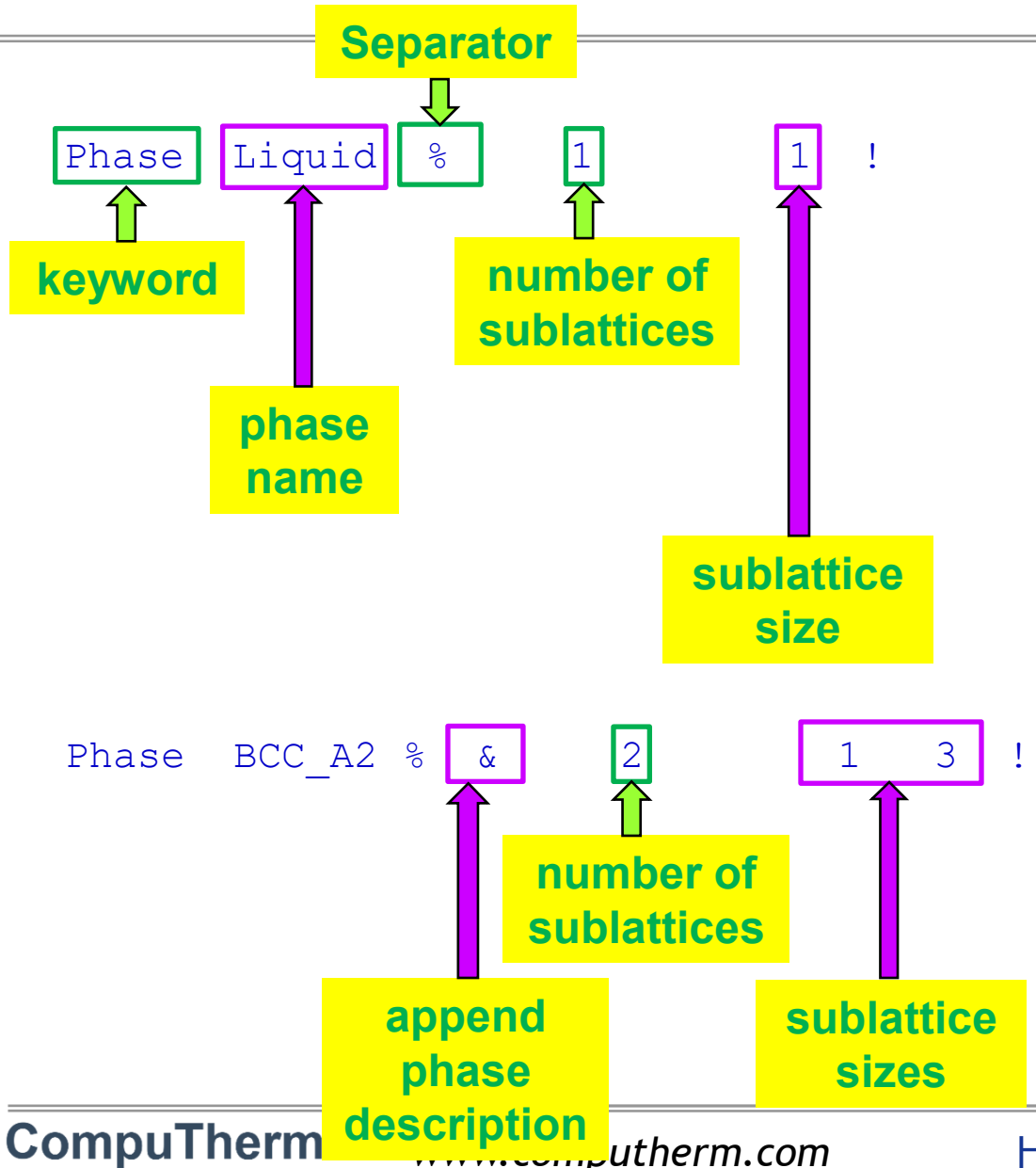
f : antiferromagnetic factor: **-1** for Bcc; **-3** for Fcc and Hcp

p : the fraction of the magnetic enthalpy absorbed above the critical temperature, depends on the structure
p = 0.40 (Bcc)
p = 0.28 (Fcc, Hcp…)

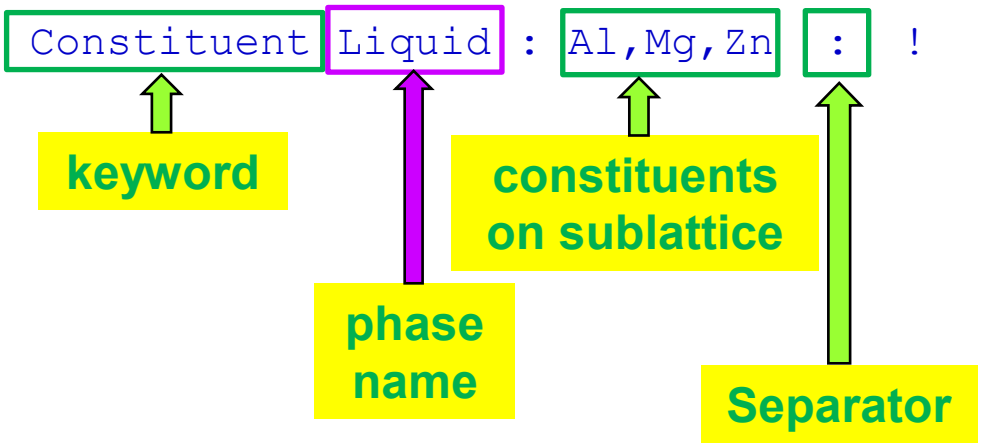
Type Definition

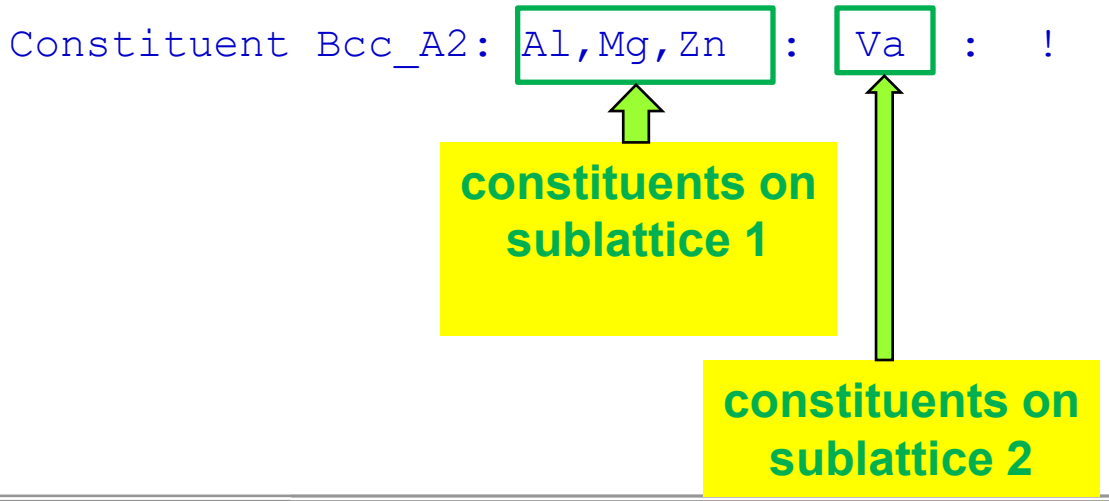


Phase


Separator
Phase
Liquid
%
1
1
!
keyword
phase name
number of sublattices
sublattice size
Phase BCC_A2 % &
2
1 3
!
number of sublattices
append phase description
sublattice sizes

Constituent





Parameter

```
Phase Liquid % 1 1 !
Constituent Liquid :Al,Mg,Zn:!
Parameter G (Liquid,Al;0) 298.15 +GLIQAl; 3000 N !
```

keyword

type

Phase name

power index of interaction

constituent

function

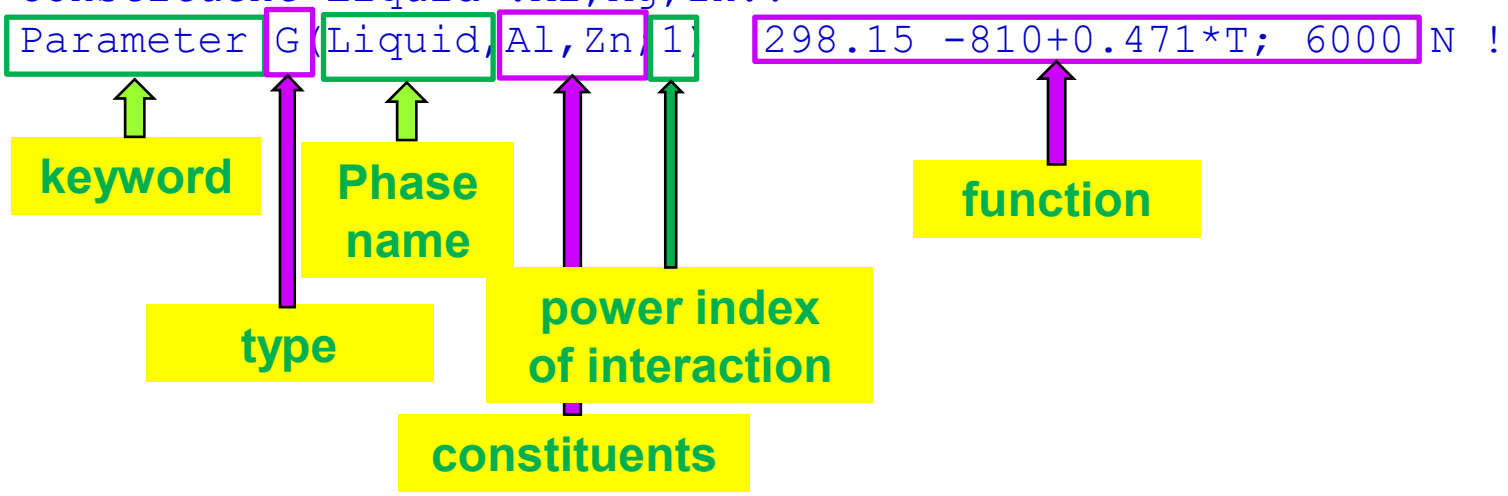
$x_{Al}\ G_{Al}^{Liquid,0}$

where

$$G_{Al}^{Liquid,0} = \texttt{GLIQAl} \quad (J/mol) \quad (298.15K \leq T \leq 3000K)$$

Parameter

```
Phase Liquid % 1 1 !
Constituent Liquid :Al,Mg,Zn:!
Parameter G(Liquid,Al,Zn,1) 298.15 -810+0.471*T; 6000 N !
```



$$x_{Al}x_{Zn}(x_{Al}-x_{Zn})^1 \; L_{Al,Zn}^{Liquid,1}$$

where

$$L_{Al,Zn}^{Liquid,1} = \texttt{-810+0.471*T} \; (J/mol) \quad (298.15K \leq T \leq 6000K)$$

Parameter

```
Parameter G(Liquid,Al,Mg,Zn;0)  298.15 -4094.48; 6000 N !
Parameter G(Liquid,Al,Mg,Zn;1)  298.15 -39973.7; 6000 N !
Parameter G(Liquid,Al,Mg,Zn;2)  298.15 -11337.5; 6000 N !
```

$$x_{Al}x_{Mg}x_{Zn}\left(x_{Al}L^{Liquid,0}_{Al,Mg,Zn}+x_{Mg}L^{Liquid,1}_{Al,Mg,Zn}+x_{Zn}L^{Liquid,2}_{Al,Mg,Zn}\right)$$

where

$$L^{Liquid,0}_{Al,Mg,Zn} = \text{-}4094.48 \quad (J/mol) \quad (298.15K \le T \le 6000K)$$
$$L^{Liquid,1}_{Al,Mg,Zn} = \text{-}39973.7 \quad (J/mol) \quad (298.15K \le T \le 6000K)$$
$$L^{Liquid,2}_{Al,Mg,Zn} = \text{-}11337.5 \quad (J/mol) \quad (298.15K \le T \le 6000K)$$

Parameter

```
Phase BCC_A2 %c 1 1 !
Constituent BCC_A2 :Al,Mg,Zn:!
Parameter G(BCC_A2,Al;0)  298.15 +GBCCAl; 6000 N !
Parameter G(BCC_A2,Mg;0)  298.15 +3100-2.1*T+GHSERMg; 6000 N !
Parameter G(BCC_A2,Zn;0)  298.15 +GBCCZn; 6000 N !
Parameter G(BCC_A2,Al,Zn;0)  298.15 +20000; 6000 N !
```

$$G^{BCC\_A2} = x_{Al}G_{Al}^{BCC\_A2,0} + x_{Mg}G_{Mg}^{BCC\_A2,0} + x_{Zn}G_{Zn}^{BCC\_A2,0} + \mathrm{RT}(x_{Al}lnx_{Al} + x_{Mg}lnx_{Mg} + x_{Zn}lnx_{Zn}) + x_{Al}x_{Zn}L_{Al,Zn}^{BCC\_A2,0}$$

where

$G_{Al}^{BCC\_A2,0}$ = GBCCAl (J/mol) $(298.15K \le T \le 6000K)$

$G_{Mg}^{BCC\_A2,0}$ = 3100-2.1*T+GHSERMg (J/mol) $(298.15K \le T \le 6000K)$

$G_{Zn}^{BCC\_A2,0}$ = GBCCZn (J/mol) $(298.15K \le T \le 6000K)$

$L_{Al,Zn}^{BCC\_A2,0}$ = 20000 (J/mol) $(298.15K \le T \le 6000K)$

Parameter

```
Phase SIGMA % 2 0.66667 0.33333 !
Constituent SIGMA : Al,Zn : Mg : !
Parameter G(SIGMA,Al:Mg;0)  298.15 +20133.7+6.3946*T
   +0.66667*GLIQAl+0.33333*GLIQMg; +3000 N !
Parameter G(SIGMA,Zn:Mg;0)  298.15 -19389.7+13.644*T
   +0.66667*GLIQZn+0.33333*GLIQMg; 3000 N !
Parameter G(SIGMA,Al,Zn:Mg;0)  298.15 -26000; 3000 N !
Parameter G(SIGMA,Al,Zn:Mg;1)  298.15 +9335.47; 3000 N !
```

$$G^{\sigma} = y_{Al}^{1}y_{Mg}^{2}G_{Al:Mg}^{\sigma,0} + y_{Zn}^{1}y_{Mg}^{2}G_{Zn:Mg}^{\sigma,0}$$
$$+\mathrm{RT}[a^{1}(y_{Al}^{1}lny_{Al}^{1} + y_{Zn}^{1}lny_{Zn}^{1}) + a^{2}(y_{Mg}^{2}lny_{Mg}^{2})]$$
$$+y_{Al}^{1}y_{Zn}^{1}y_{Mg}^{2}L_{Al,Zn:Mg}^{\sigma,0} + y_{Al}^{1}y_{Zn}^{1}y_{Mg}^{2}(y_{Al}^{1}-y_{Zn}^{1})L_{Al,Zn:Mg}^{\sigma,1}$$

where

$G_{Al:Mg}^{\sigma,0}$ = 20133.7+6.3946*T +0.66667*GLIQAl+0.33333*GLIQMg

$G_{Zn:Mg}^{\sigma,0}$ = -19389.7+13.644*T +0.66667*GLIQZn+0.33333*GLIQMg

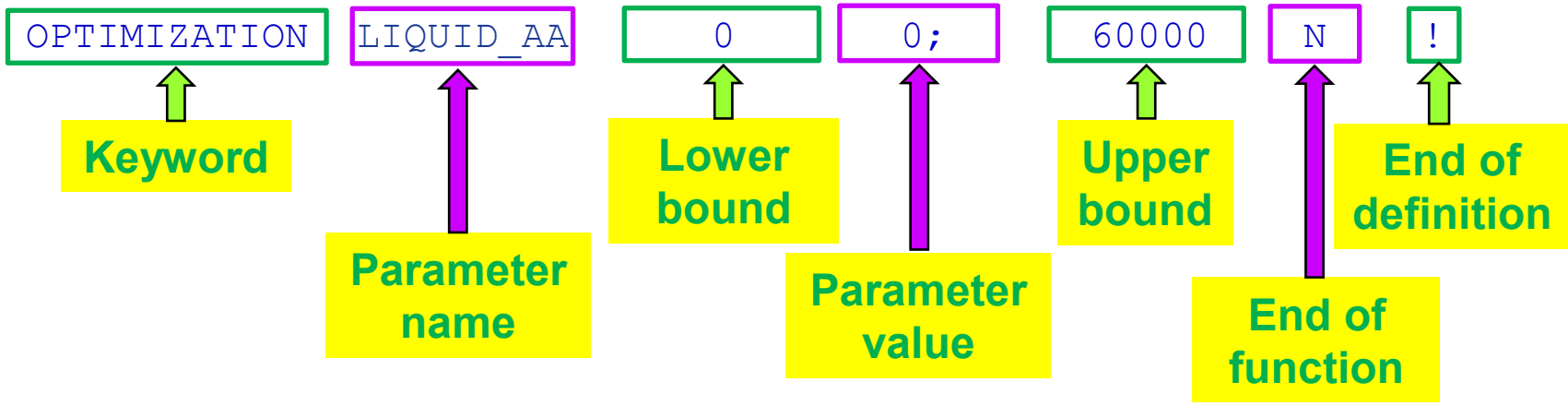
$L_{Al,Zn:Mg}^{\sigma,0}$ = -26000

$L_{Al,Zn:Mg}^{\sigma,1}$ = 9335.47

a^{1} = 0.66667

a^{2} = 0.33333

Parameter to be optimized



Note

- Parameters to be optimized are defined in the TDB file.
- Good start values for parameters are needed for efficient optimization.
- The lower bound and upper bound need to be selected carefully.

优化前的准备

- 理论信息 (Theoretical information)
- 实验数据 (Experimental data)
- 估算数据 (Estimated data)
- 类似体系 (Assessments of similar system)

实验数据

- 晶体结构

  根据晶体结构选择合适的模型

- 物理性质(磁性，摩尔体积)
- 热力学性质数据

  液相: 比热，混合焓，活度，蒸汽压 等

  固相: 比热，形成焓，电动势，分解压 等

- 相平衡数据: 实验相图

  相图边界，相区等。

热力学数据

- 量热数据(Calorimetric data): **Enthalpy** of mixing, ~ of formation, ~ of transformation
- 电动势(EMF), Knudsen cell data: 化学势，活度
- 相分压(partial pressure)： 活度
- DSC: 比热， **Enthalpy** of transformation （相变热，相变焓）

相平衡数据

- DTA/DSC: start/end temperatures of transformations
- Microscope(OM,SEM, TEM): phase identification, determining phase amounts
- EPMA（EDX）: phase identification, phase compositions (tie-lines)
- XRD: phase identification, lattice parameters.
- Neutron diffraction: site occupancies

估计数据与第一原理计算数据

Miedema 模型

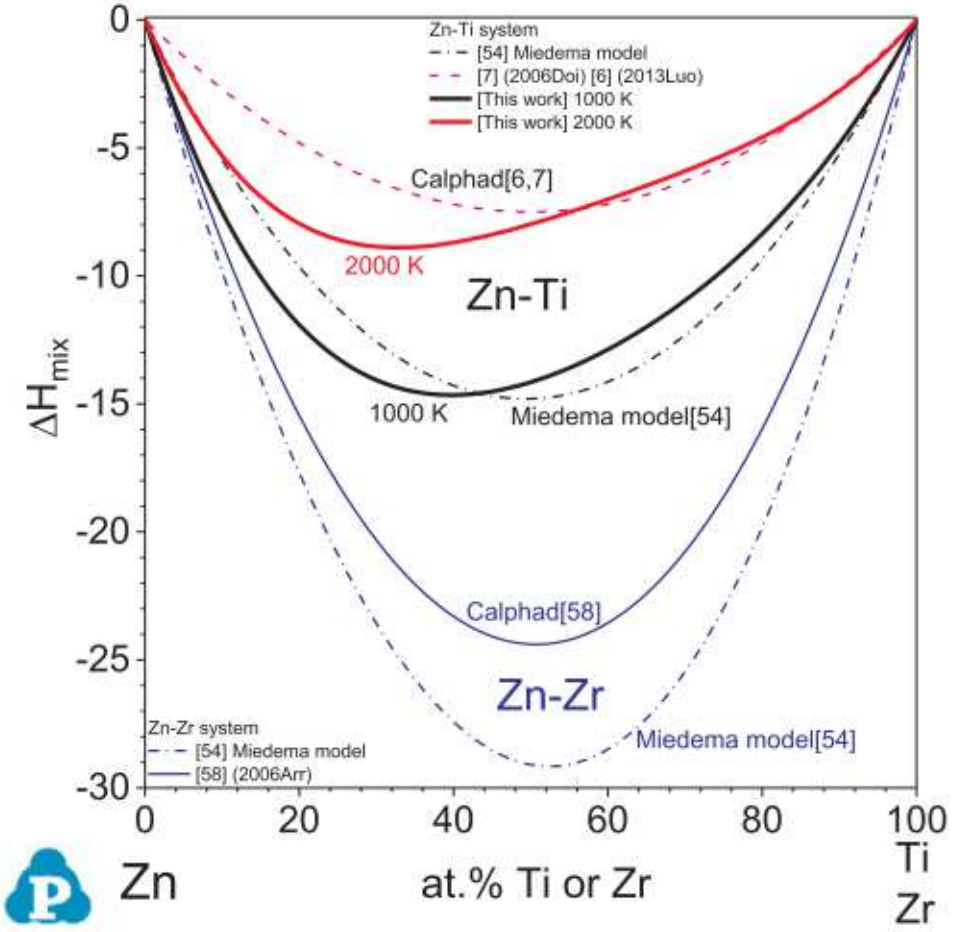
Enthalpy of mixing

第一原理计算

Enthalpy of formation at 0 K
https://materialsproject.org/
http://oqmd.org/

Cp

相似合金体系



S.-M. Liang, R. Schmid-Fetzer, Evaluation of Calphad Approach and Empirical Rules on the Phase Stability of Multi-principal Element Alloys, J. Phase Equilib. Diffus., 38 (2017) 369-381.

数据的优先级别

实验数据 > 第一原理计算数据 > 估计数据

实验数据: 直接测定的实验数据，
而不是推导的实验数据

比如: 实验测得活度或者分压，推导出混合焓，
只能用活度来进行优化，而不能用它推导出的混合焓。

细说 pop 文件：实验数据文件

POP 文件: 储存用于优化的实验数据.

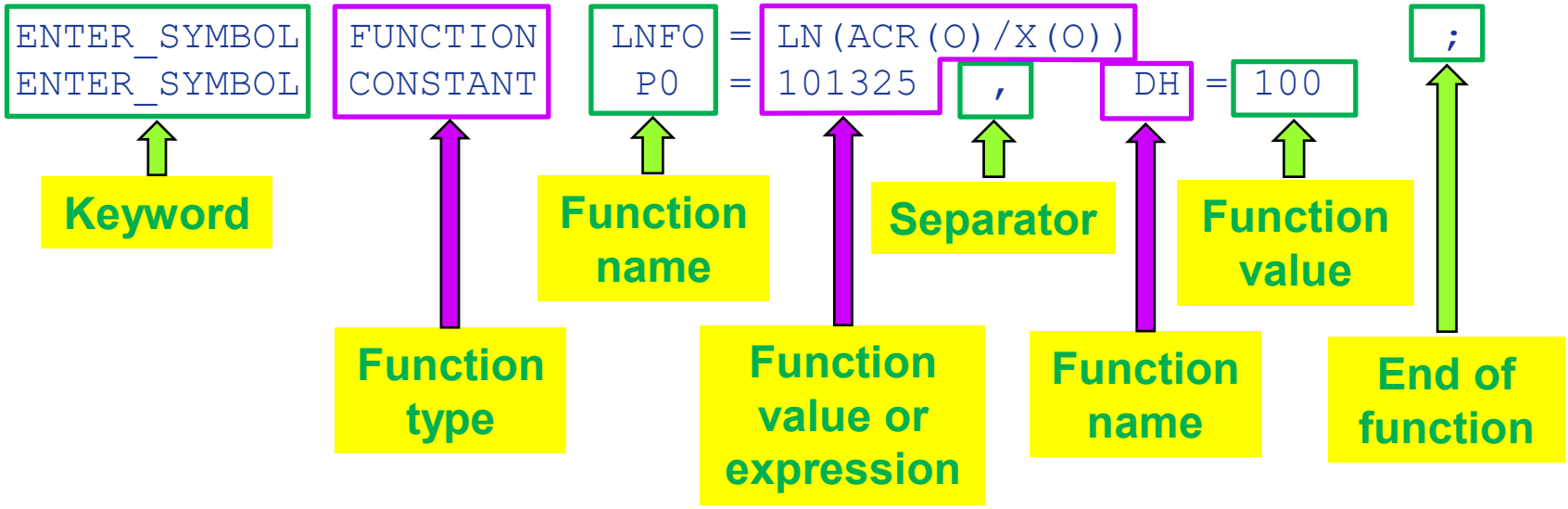
- 常用的关键词:
  CREATE_NEW_EQUILIBRIUM,
  SET_CONDITION,
  EXPERIMENT

- Syntax 与 Thermocalc 一致.

Keywords required by a typical equilibrium

```
CREATE_NEW_EQUILIBRIUM @@, 1

CHANGE_STATUS PHASE FCC_A1#1, FCC_A1#2 = FIX 1

SET_CONDITION P = P0, T = 500

EXPERIMENT X(FCC_A1#1, AL) = 0.2 : DX1, X(FCC_A1#2, AL) = 0.8 : DX1

SET_START_VALUE Y(FCC_A1#1,AL) = 0.2

SET_START_VALUE Y(FCC_A1#2,AL) = 0.8
```

Define constant/function in pop file



Note

- These constants/functions may be used in the following part.

Define a table in pop file

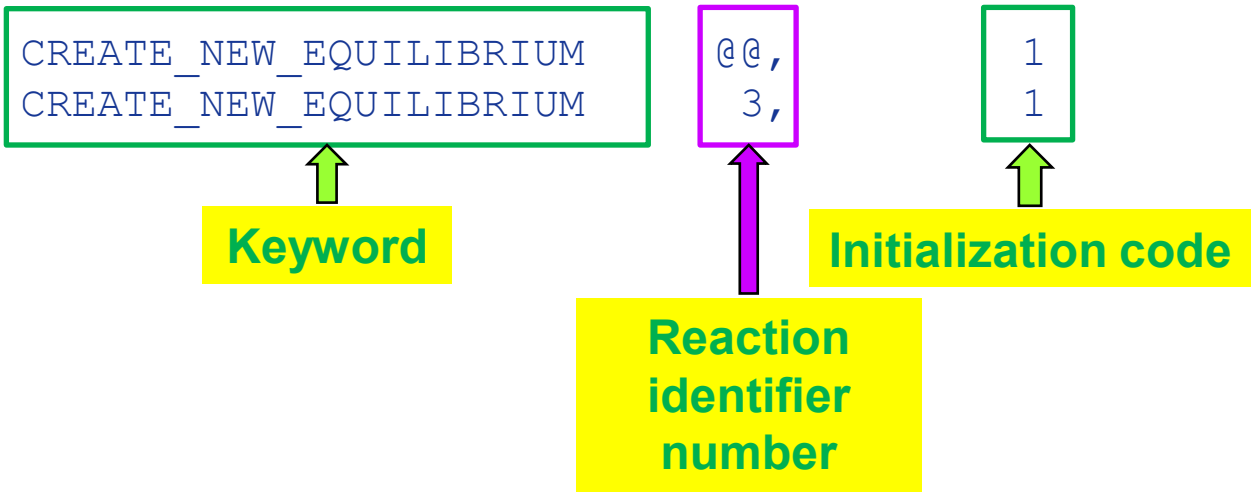
```
TABLE_HEAD
…
TABLE_VALUES
…
TABLE_END
```

Note

- Similar equilibria can be formulated as a table, such as two-phase equilibria at different temperatures in a binary system.

- Table values are listed as a matrix.
  - Each row represents the condition or properties for one equilibrium.
  - The columns are separated by space or tab, and expressed as @<column number>, i.e. @1, @2, @3 and so on.

Define an equilibrium in pop file

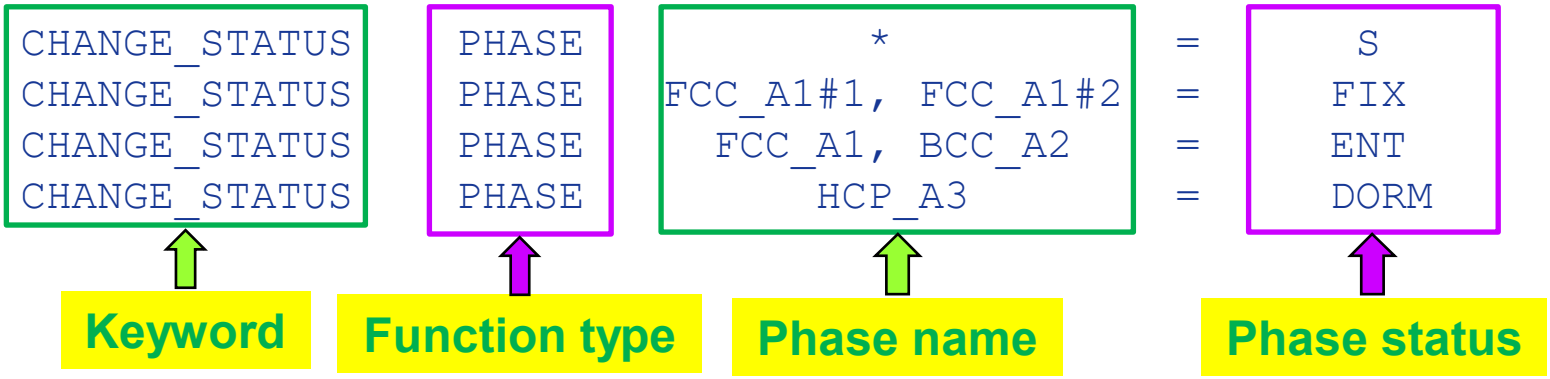


Note

- The reaction identifier number can be a natural number or "@@". "@@" means the number increased by 1 from the previous equilibrium.

- The initialization code can be 0, 1 or 2.
  - 1: all components are entered but all phases are suspended. it is appropriate in most cases.
  - 0: all components and phases are suspended.
  - 2: all components and phases are initially entered.

Define an equilibrium in pop file

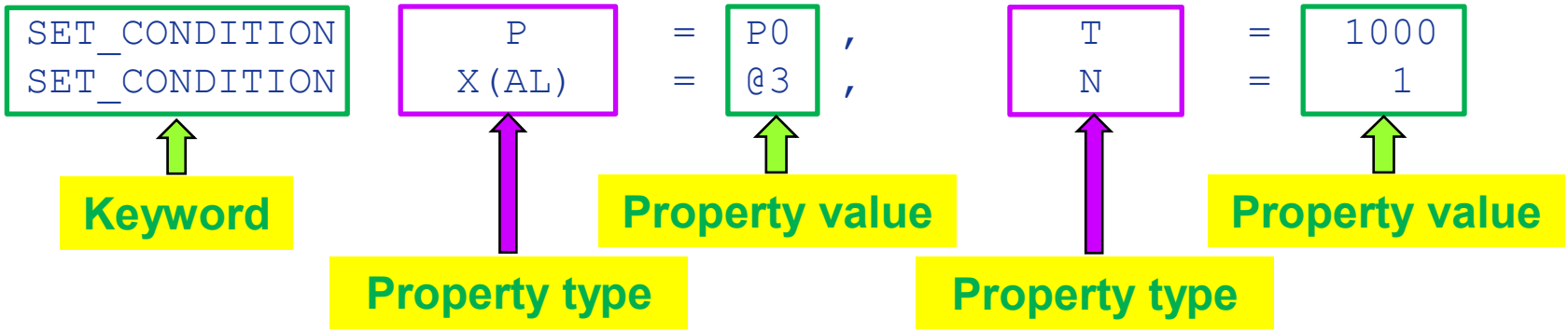


Note

- Phases name:
  - * means all the phases.
  - #1 and #2 postfixes are used for a phase with miscibility gap.

- Phase status:
  - S : phase suspended, not considered in the equilibrium.
  - FIX: phase used as fixed, must involves in the equilibrium.
  - ENT: phase used as entered, involves in the equilibrium.
  - DORM: phase used as dormant, not involves in the equilibrium, used to calculate the driving force for this phase.

Define an equilibrium in pop file

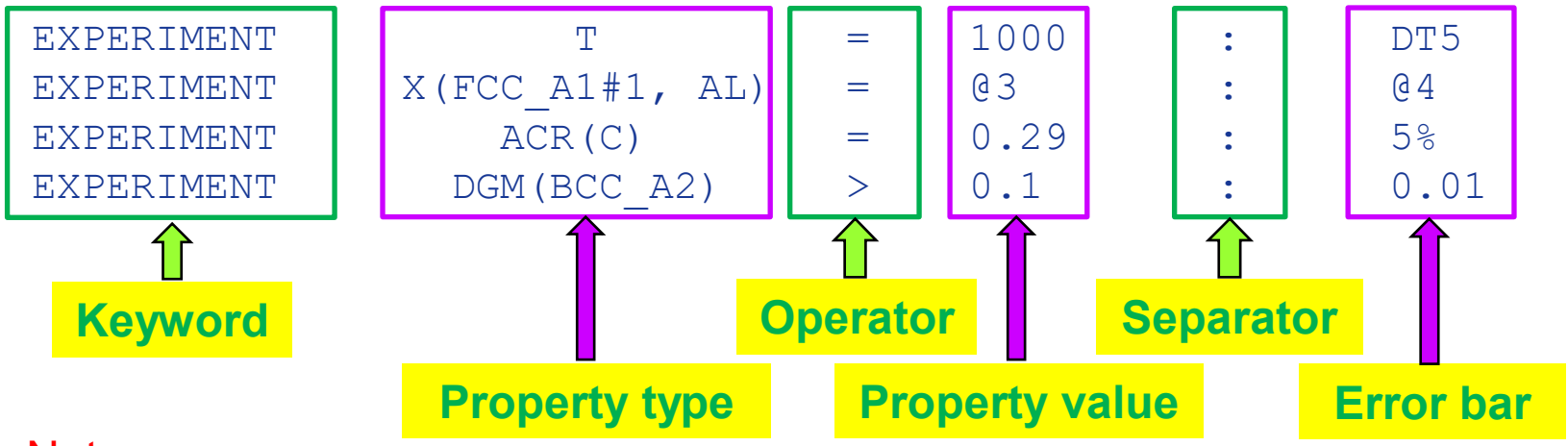


Note

- Keyword SET_CONDITION is used to input the given condition about an equilibrium, such as pressure (in Pa), temperature (in K) and alloy compositions (in atomic/weight fraction).

- The property value can be a real number, a defined constant, or the values of a specific column in a table.

Define an equilibrium in pop file



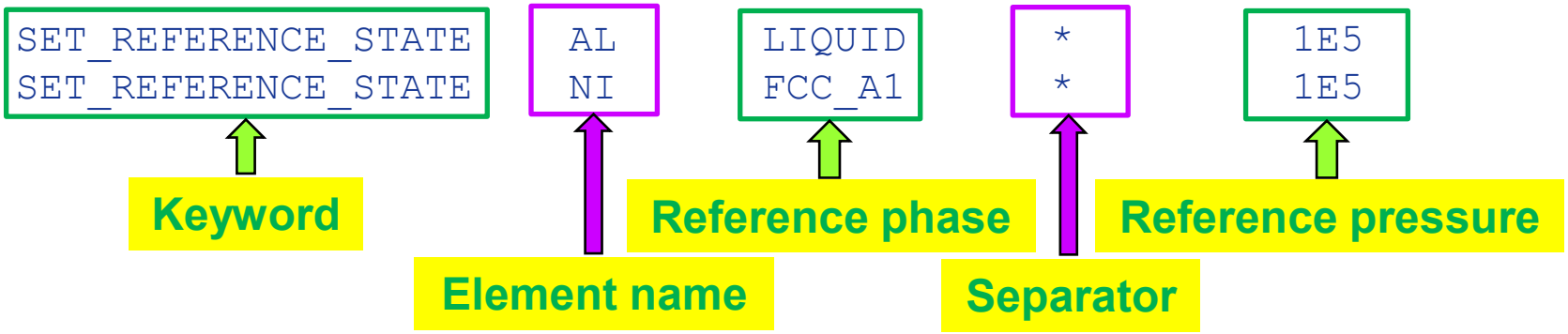
Note

- Keyword EXPERIMENT is only used in pop file for fine-tune. It is used to input all the information about an equilibrium under given conditions, such as temperature (in K), phase compositions, activity and other properties.

- The property value can be a real number, a defined constant, or the values of a specific column in a table.

- The error bar can be a real number, a defined constant, the values of a specific column in a table, or a relevant percentage of the property value.

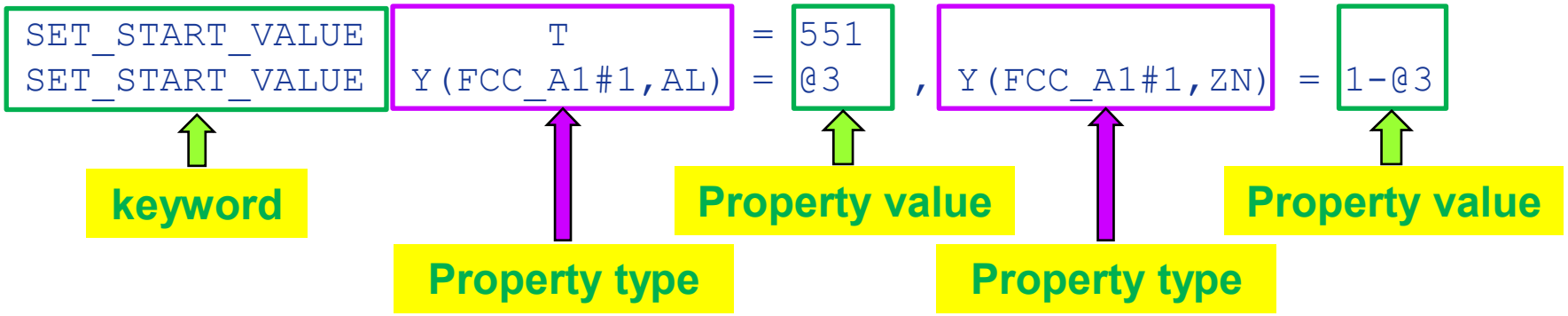
Set reference state for an element



Note

- Keyword SET_REFERENCE_STATE is used to set the element reference state when calculating relative properties, such as enthalpy, activity.

Set start values

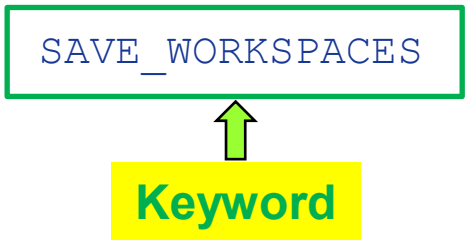


Note

- Keyword SET_START_VALUE is used to give some good starting point for the optimizer to calculate the equilibrium locally.

- The property value can be a real number, a defined constant, the values of a specific column in a table, or even an expression.

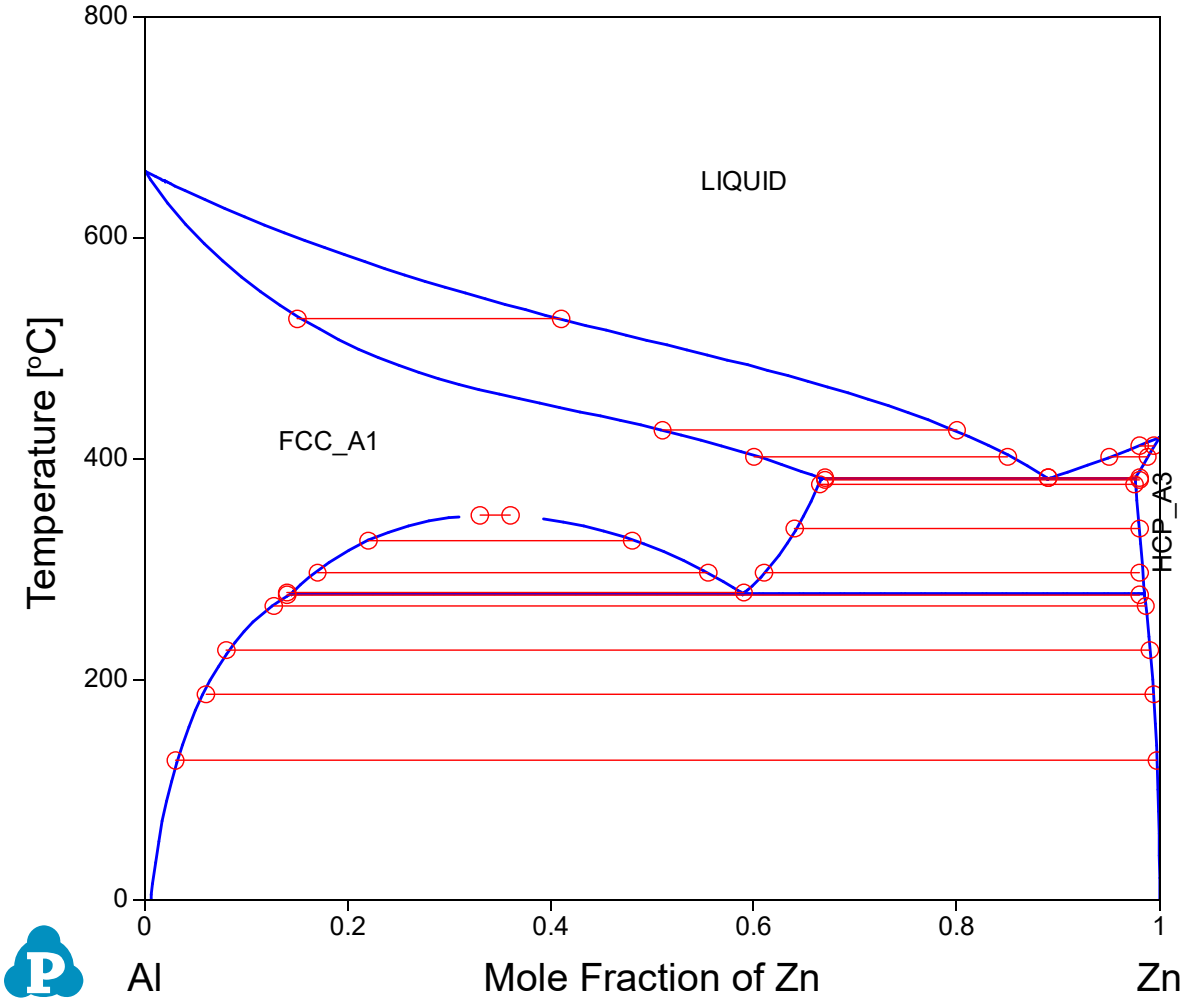
End of the pop file



Note

- Keyword SAVE_WORKSPACES is required for the end of inputting equilibria into the pop file.

Al-Zn 相图实验数据:相边界



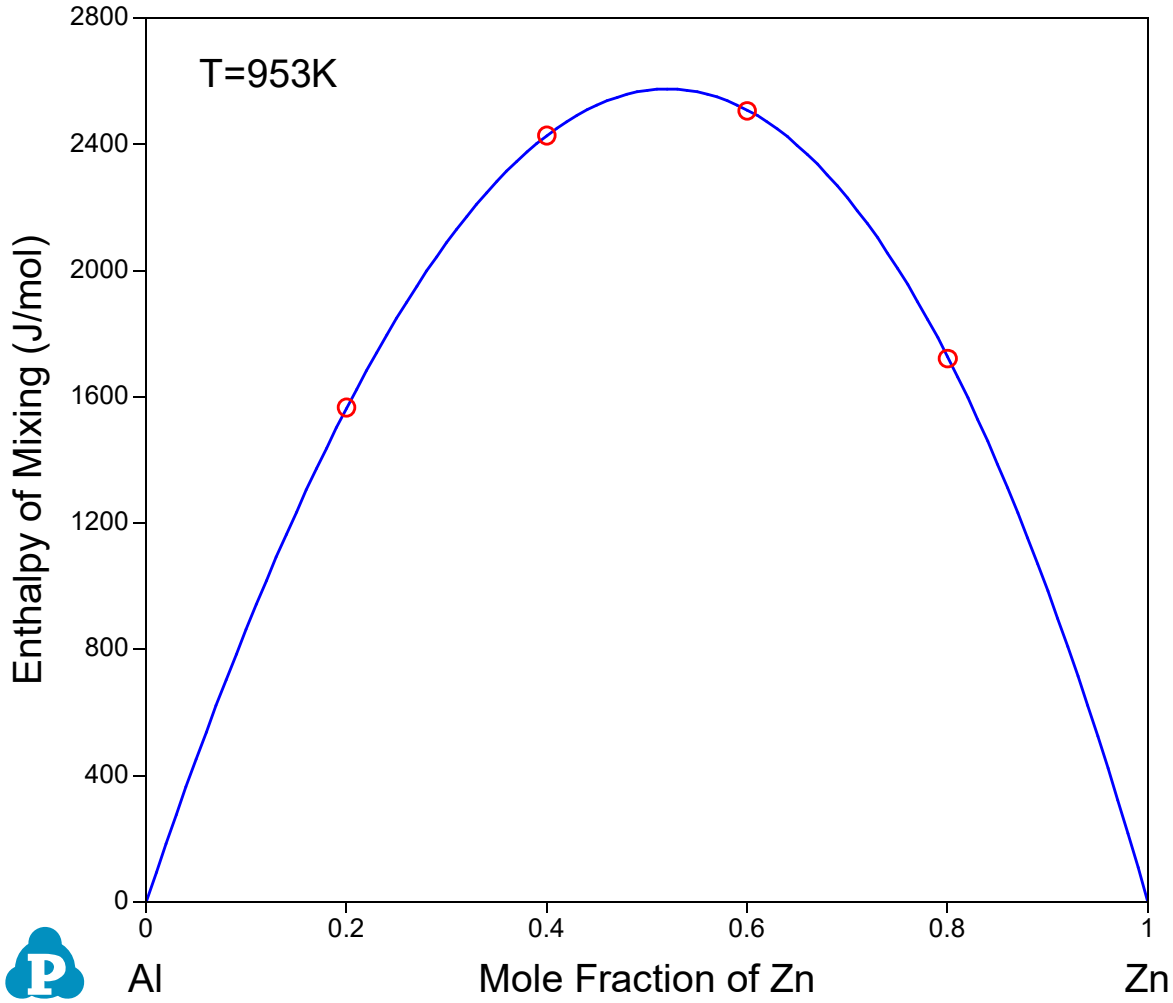
Two-phase equilibria example

```
$ Tieline between FCC_A1#1 and FCC_A1#2

TABLE_HEAD
CREATE_NEW_EQUILIBRIUM @@, 1
CHANGE_STATUS PHASE * = S
CHANGE_STATUS PHASE FCC_A1#1, FCC_A1#2 = FIX 1
SET_CONDITION P = P0, T = @1

EXPERIMENT X(FCC_A1#1, AL) = @3 : DX1, X(FCC_A1#2, AL) = @2 : DX1
SET_START_VALUE Y(FCC_A1#1,AL) = @3
SET_START_VALUE Y(FCC_A1#2,AL) = @2

TABLE_VALUES
$ LIST THE PHASE COMPOSITION IN EQUILIBRIUM
$ T[K]      X(FCC_A1#2, AL)    X(FCC_A1#1, AL)
 552                  0.86                    0.41
 570                  0.83                    0.445
 599                  0.78                    0.52
 622                  0.67                    0.64
TABLE_END
```

Three-phase equilibrium example

```
$ Invariant Reaction: LIQUID => FCC_A1 + HCP_A3

CREATE_NEW_EQUILIBRIUM @@, 1

CHANGE_STATUS PHASE LIQUID, FCC_A1, HCP_A3 = FIX 1

SET_CONDITION P = P0

EXPERIMENT T = 655 : DT2
EXPERIMENT X(LIQUID,ZN) = 0.89 : DX2
EXPERIMENT X(FCC_A1,ZN) = 0.667 : DX2
EXPERIMENT X(HCP_A3,ZN) = 0.977 : DX2

SET_START_VALUE T = 648
```

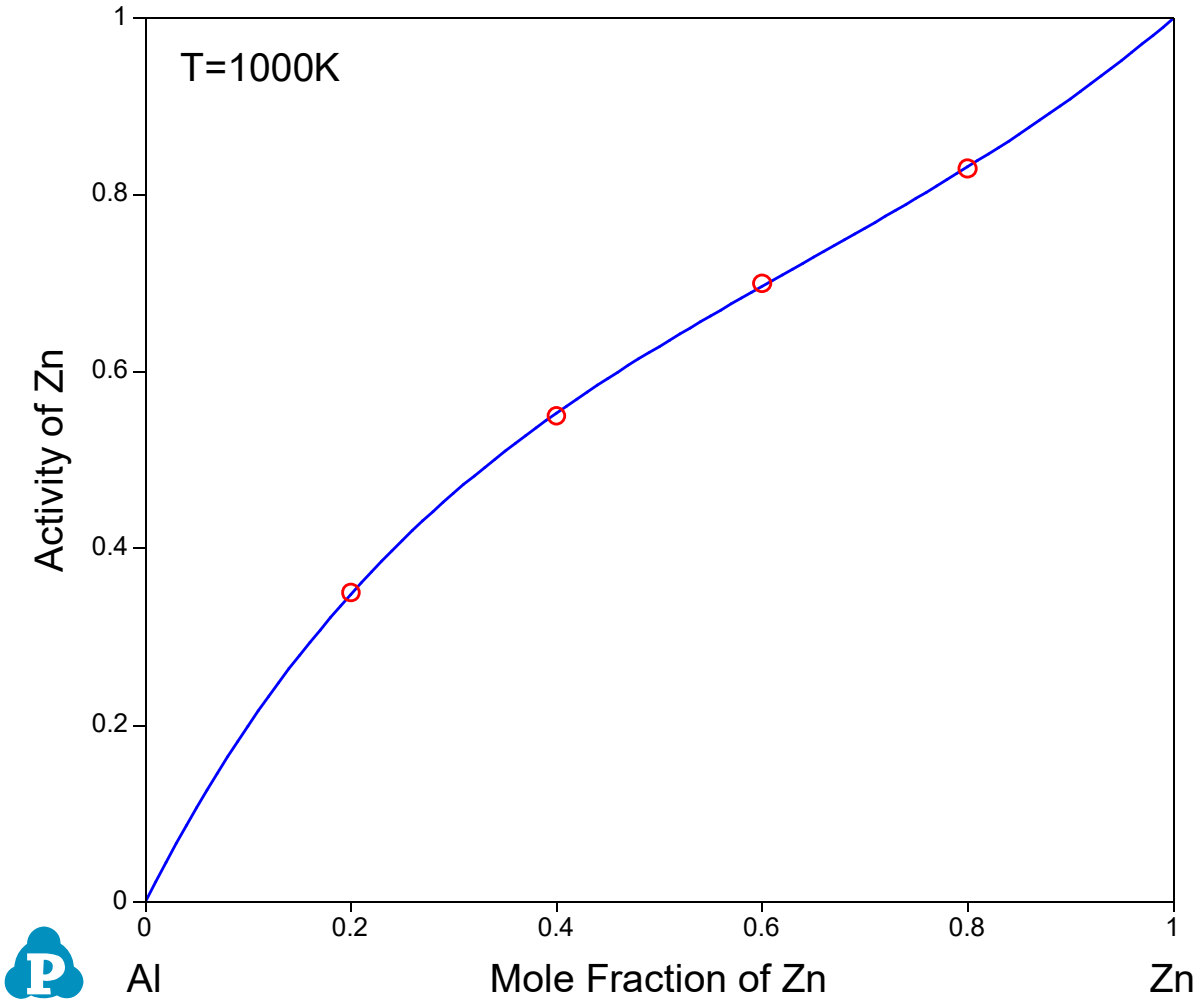
Al-Zn 相图实验数据:液相混合焓



Enthalpy of mixing example

```
$ Enthalpy of mixing for liquid phase at 953K

TABLE_HEAD
CREATE_NEW_EQUILIBRIUM @@,1
CHANGE_STATUS PHASE * = S
CHANGE_STATUS PHASE LIQUID = FIX 1
SET_CONDITION T = 953, P = P0, X(LIQUID,ZN) = @1

EXPERIMENT HMR(LIQUID) = @3 : @4

SET_REFERENCE_STATE AL LIQUID * 1E5
SET_REFERENCE_STATE ZN LIQUID * 1E5

TABLE_VALUES
$ X(ZN)   X(AL)     HMR              DH
0.2       0.8       1568             DH
0.4       0.6       2430             DH
0.6       0.4       2508             DH
0.8       0.2       1723             DH
TABLE_END
```

Al-Zn 相图实验数据:液相活度



Activity of a phase example

```
$ Activity of liquid phase at 1000K

TABLE_HEAD
CREATE_NEW_EQUILIBRIUM @@,1
CHANGE_STATUS PHASE *=S
CHANGE_STATUS PHASE LIQUID=FIX 1
SET_CONDITION T=1000, P = P0, X(LIQUID,ZN) = @1

EXPERIMENT ACR(ZN)= @3 : @4

SET_REFERENCE_STATE AL LIQUID * 1E5
SET_REFERENCE_STATE ZN LIQUID * 1E5

TABLE_VALUES
$ X(ZN)    X(AL)      ACR(ZN) D
0.2                   0.8     0.35              DX1
0.4                   0.6     0.55              DX1
0.6                   0.4     0.7               DX1
0.8                   0.2     0.83              DX1
TABLE_END
```