CompuTherm
FOR MATERIALS DESIGN

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Pandat 软件
第一期优化培训教程

第五讲

2020年7月11日

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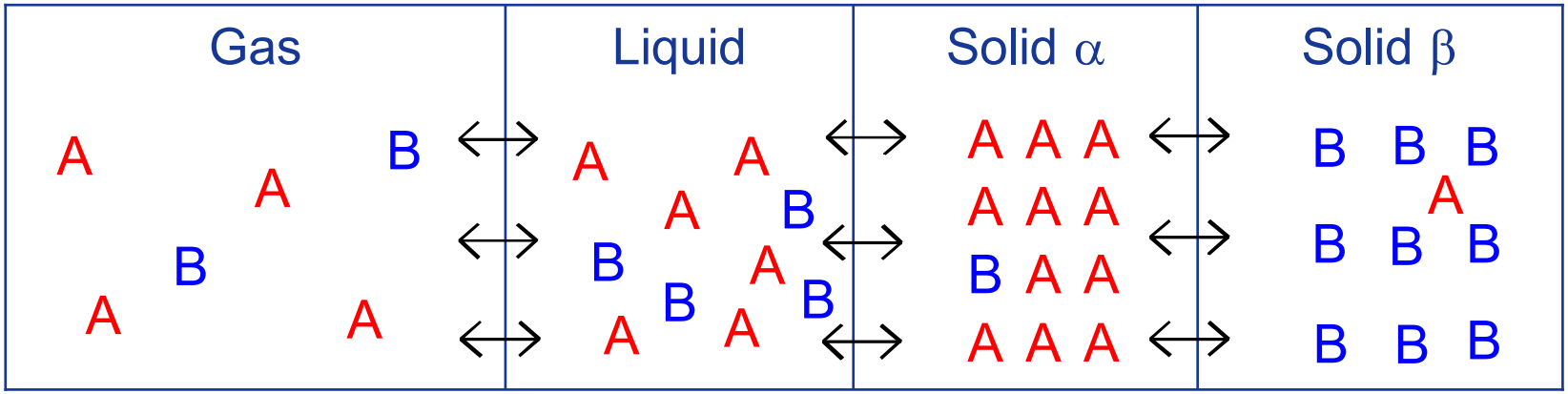
建立热力学描述(数据库)

平衡条件： $G = G(T, P, n_j)$ 在 $dT = dP = dn_j = 0$ 时，达到最小值。

使用单独的 G^{φ} 模型描述每一个相

建立Gibbs能函数 G^{φ} 的表达式



气相 $G^{\varphi}(T,P)$

$$G_m^{gas} = \sum_{i=1}^{s(gas)} y_i[G_i^{0,\varphi}(T) + RTln(y_i\frac{P}{P_0})]$$

i: 元素原子，气相分子, O2, O, O3, CO, CO2…

$G_i^{0,\varphi}(T)$ = A + BT + CT *ln*T + DT^2 + ET^3 + FT^{-1} + . . .

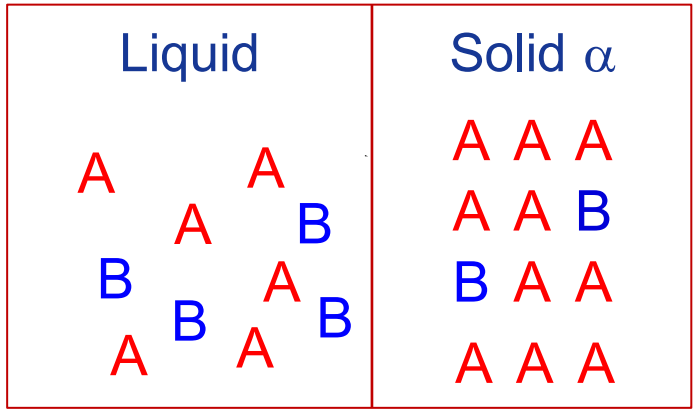
```
Function GHSERO 298.15  -3480.87-25.503038*T-11.1355*T*LN(T)-5.098875E-3*T**2
        +0.661845833E-6*T**3-38365*T**(-1); 1000 Y ……
Function GGAS_O1 298     +243206.529-42897.0876*T**(-1)-20.7513421*T
    -21.0155542*T*LN(T)+1.26870532E-04*T**2-1.23131285E-08*T**3; 2950 Y …
Function GGAS_O2 298    +2*GHSERO; 6000 N !

Phase Gas:G % 1 1 !
Constituent Gas :O,O2,O3 ...:!
 Parameter G(Gas,O;0) 298    +GGAS_O1 +RTLNP; 6000 N !
 Parameter G(Gas,O2;0) 298   +GGAS_O2 +RTLNP; 6000 N !
```

SGTE 数据库中只有O_2和N_2的 $G_i^{0,\varphi}(T)$。

NIST 数据库：ΔH; S_{298}, C_p **http://webbook.nist.gov/chemistry/**

溶液相模型(无序液相，置换固溶体)

$$G^{\varphi} = \underbrace{\boxed{\sum_i x_i \cdot G_i^{0,\varphi}}}_{{}^{\mathrm{ref}}G_m} + \underbrace{RT \sum_i x_i \ln x_i}_{{}^{\mathrm{conf}}G_m} + \boxed{G^{ex,\varphi}}$$



$$G^{ex,\varphi} = \sum_{i,j>i} x_i \cdot x_j \cdot \sum_{\nu} L_{i,j}^{\nu,\varphi} \cdot (x_i - x_j)^{\nu}$$

$G_i^{0,\varphi}$： i= A, B，endmember （Lattice stability）必须给出

$L_{i,j}^{\nu,\varphi}$: interaction parameters: 根据需要优化

纯元素(SGTE 数据)

https://www.sgte.net/en/free-pure-substance-database

目前版本: unary50.tdb: Updated 2 June 2009

Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) pp. 317-425

阅读这篇文章：数据格式介绍，数据的来源，各个参数的含义。

G-HSER 的形式：

$$G_i^{0,\varphi} = G_i^{\varphi}(T) - H_i^{SER} = A + BT + CT\,\ln T + DT^2 + ET^3 + FT^{-1} + \ldots$$

SER: 标准参考状态， $H_i^{SER} = 0$.
在Calphad领域，采用 P = 1 bar，T = 298.15 K, 时的稳定相结构.

H (T) = ? S (T) = ? Cp (T) = ?

$G_i^{0,\varphi}$ 包括 **稳定相** 和 **亚稳相**

锌 Zn: Liquid, Hcp, bcc, fcc, **Lattice Stabilities**

纯组元的吉布斯能[91Din]

Data for Zn in the form of G-HSER

$G_i^{0,\varphi} = G_i^{\varphi}(T) - H_i^{SER} = A + BT + CT\,ln T + DT^2 \ldots$

稳定相：基于实验数据

HCP_A3 (Zn non ideal)

-7285.787 + 118.470069 T - 23.701314 T ln(T) - 1.712034E-3 T^2 - 1.264963E-6 T^3 (298.15 < T < 692.68)

-11070.559 + 172.34566 T - 31.38 T ln(T) + 4.7051E26 T^{-9} (692.68 < T < 1700)

LIQUID

$G_i^{\varphi}(T)$

-128.574 + 108.177079 T - 23.701314 T ln(T) - 1.712034E-3 T^2 - 1.264963E-6 T^3 - 3.5896E-19 T^7 (298.15 < T < 692.68)

-3620.391 + 161.608594 T - 31.38 T ln(T) (692.68 < T < 1700)

稳定相：基于实验数据

BCC_A2

-4398.827 + 115.959669 T - 23.701314 T ln(T) - 1.712034E-3 T^2 - 1.264963E-6 T^3 (298.15 < T < 692.68)

-8183.599 + 169.83526 T - 31.38 T ln(T) + 4.7051E26 T^{-9} (692.68 <T< 1700)

FCC_A1

-4315 967 + 116.900389 T - 23.701314 T ln(T) - 1.712034E-3 T^2 - 1.264963E-6 T^3 (298.15 < T < 692.68)

-8100.739 + 170.77598 T - 31.38 T ln(T) + 4.7051E26 T^{-9} (692.68 < T < 1700)

Data relative to HCP_A3 (Zn non ideal)

$G_i^{0,\varphi} = G_i^{\varphi,Hcp}(T) - G_i^{0,hcp}$

$G_i^{\varphi}(T)$

LIQUID

7157.213 - 10.29299 T - 3.5896E-19 T^7 (298.75 < T < 692.68)

7450.168 - 10.737066 T - 4.7051E26 T^{-9} (692.68 < T < 1700)

BCC_A2

2886.96 - 2.5104 T (298.75 < *T* < *1700*)

FCC_A1

2969.82 - 1.56968 T (298.75 < *T* < *1700*)

[91Din] A.T. Dinsdale, SGTE data for pure elements, Calphad, 15 (1991) 317-425

TDB中G的绝对值与相对值

```
Function GHSERZN 298.15    （标准状态，对于Zn为Hcp结构） 即：  GHCPZN
     -7285.787+118.470069*T-23.701314*T*LN(T)-.001712034*T**2
    -1.264963E-06*T**3;        692.68 Y
    0.000870323-11070.559+172.34566*T-31.38*T*LN(T)
    +4.70514E+26*T**(-9);     1700 N !
```

Gibbs能函数G(T)可以分段，但是分段函数之间应该连续的，并且不仅**G(T)**要连续，**G’(T)**也要连续(对应为**S**)， **G”(T)**也要连续(对应于**Cp**)，**G”’(T)** 也应该要连续(对应**Cp’**)。 [2016Liang_Calphad_82.pdf]

绝对值表达式 （液相）

```
Function GLIQZN  298.15
     -128.574+ 108.177079*T-23.701314*T*LN(T)-.001712034*T**2
    -1.264963E-06*T**3-3.5896E-19*T**7; 692.68 Y
    -3620.391+161.608677*T-31.38*T*LN(T); 2900 N !
```

相对值表达式（液相）

```
Function GLIQZN       298.15
    +7157.213-10.29299*T-3.5896E-19*T**7+GHSERZN; 692.68 Y
    +7450.168-10.737066*T-4.7051E+26*T**(-9)+GHSERZN; 1700 N !
```

G值不连续

Database Name : D:_Work\7_TrainingClass\202005_Opitmi
Case Sensitive : Yes

Warning (5)

Line	State	Message
20-21	Function GBCCZR 298.15 -525.5386908+124.9457*T-25.60 09*T**3+25233*T**(-1)-7.6142894e-11*T**4; 2128 Y -30	G is discontinuous at T = 2128 K, G(T = 2128-)=-155398 J, G(T = 2128+)=-155540 J. dG = 142.638 J.
69-72	Function GGASO2Zr1 298.15 -4.1440146958E+5+3.150719 2*T**2+1.8576154371E-6*T**3+2.9451754856E+5*T**(- 6.447477978E+1*T*LN(T) +2.7376810723E-3*T**2-2.201	G is discontinuous at T = 1100 K, G(T = 1100-)=-720754 J, G(T = 1100+)=-720717 J. dG = -36.192 J.
73-82	Function GGASZr1 298.15 +5.7449191494E+5+8.2104149638E+1*T-3.8691110000E+1*T*LN(T) +1.1528460000E-2*T**2-1.6932550000E-6*T**3+2.7063880000E+5*T**(-1); 700 Y +5.8360536701E+5-1.8366020705E+1*T-2.4061060000E+1*T*LN(T) +1.7436410000E-3*T**2-5.9431233333E-7*T**3-7.4894750000E+5*T**(-1); 1300 Y +5.8145674711E+5+5.8145674711E+5*T-2.0463610000E+1*T*LN(T) -2.9610840000E-3*T**2+1.0839143333E-7*T**3+5.2635250000E+5*T**(-1); 2700 Y +6.1836012548E+5-1.5427834040E+2*T-6.6473430000E+0*T*LN(T) -4.6738955000E-3*T**2+1.0683358333E-7*T**3-1.5872340000E+7*T**(-1); 6600 Y +4.9187534554E+5+1.3950085082E+2*T-4.0688010000E+1*T*LN(T) -6.3835700000E-4*T**2+1.7912533333E-8*T**3+7.1496950000E+7*T**(-1); 10000 N !	G is discontinuous at T = 1300 K, G(T = 1300-)=336518 J, G(T = 1300+)=7.5628e+08 J. dG = -7.55944e+08 J.

G is discontinuous at T = 2128 K, G (T = 2128-)=-155398 J, G(T = 2128+)=-155540 J. dG = 142.638 J.

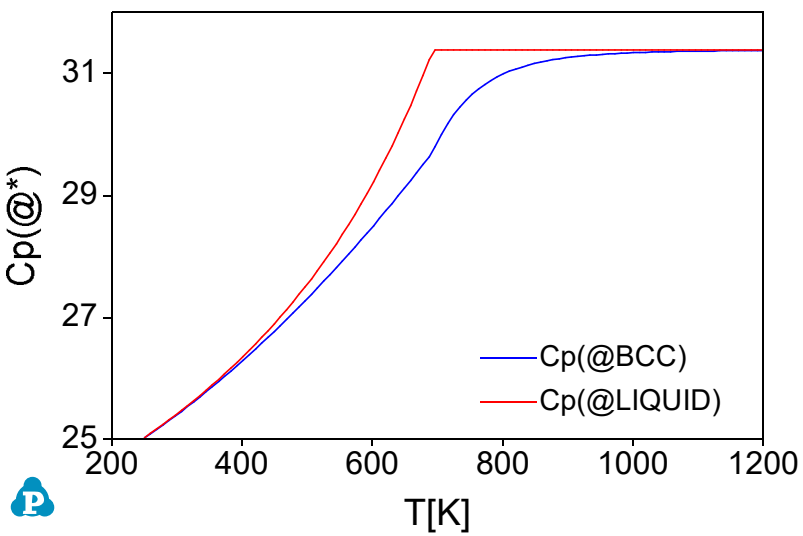
Pandat热力学性质计算练习（一）

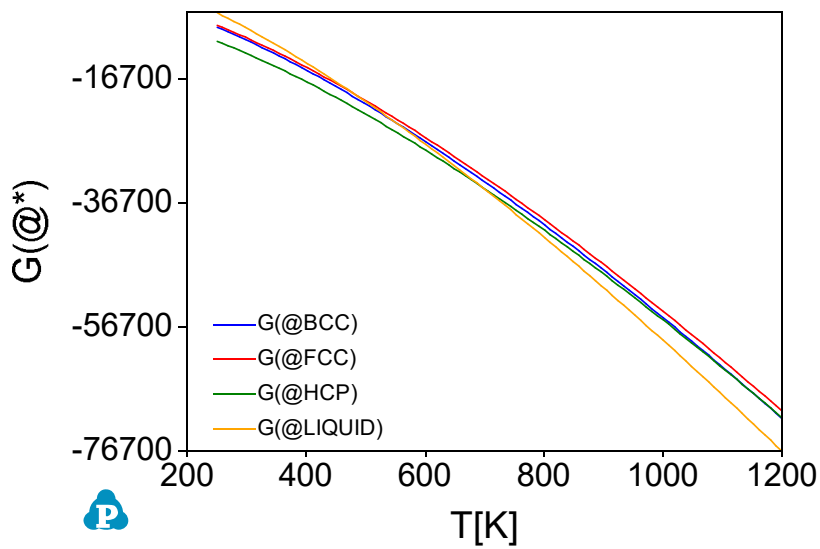
TDB文件: Zn.tdb

用Excel文件，以 Zn.tdb 中G函数为输入值，计算出不同结构(液相、Hcp、Bcc、Fcc)下 Zn的G, H, S 和Cp值。

然后将excel 计算的结果与Pandat计算结果对比。

计算组元的G, H, S, Cp 值





如果SGTE 数据库中没有$G_i^{0,\varphi}$

Mg-Si体系：

Si 是金刚石结构 (diamond). Mg在Si中有固溶度，采用置换型溶液模型，一个亚点阵。Diamond 相的亚点阵为(Mg, Si).

SGTE 数据中有$G_{Si}^{0,\mathrm{Diamond}}$，但是没有 $G_{Mg}^{0,\mathrm{Diamond}}$，

Mg的稳定结构为Hcp，有$G_{Mg}^{0,Hcp}$

常用的估计方法：

$G_{Mg}^{0,\mathrm{Diamond}} = G_{Mg}^{0,Hcp} + 50000$;

$G_{Mg}^{0,\mathrm{Diamond}} = G_{Si}^{0,Hcp} + 30*T$;

结合第一原理计算

$G_{Mg}^{0,\mathrm{Diamond}} = G_{Mg}^{0,Hcp} + 74780$

http://oqmd.org/

https://materialsproject.org/

2016Liang_Calphad_82.pdf

$G^{ex,\varphi}$， Redich-Kister表达式

$$G^{ex,\varphi} = \sum_{i,j>i} x_i \cdot x_j \cdot \sum_{\nu} L_{i,j}^{\nu,\varphi} \cdot \left(x_i - x_j\right)^{\nu}$$

i，j 是组元， v是交互作用参数的级数 (order of interaction parameter)

二元 A-B 体系

$$G^{ex} = x_A \cdot x_B (L_{A,B}^{0} + L_{A,B}^{1} \cdot (x_A - x_B) + L_{A,B}^{2} \cdot (x_A - x_B)^2 + L_{A,B}^{3} \cdot (x_A - x_B)^3 \ldots)$$

其中：

$L_{A,B}^{i}$ $(i = 1,2,3) = a_i + b_i \cdot T$ 交互作用参数

$L_{A,B}^{i}$ 通常为温度的**线性关系**，

特殊情况是选用指数方程或LET方程[2016Lia]。

一般最高到3阶，即L^3，极少数到L^4.

[2016Lia] S.-M. Liang, P. Wang, R. Schmid-Fetzer, Inherently consistent temperature function for interaction parameters demonstrated for the Mg–Si assessment, Calphad, 54 (2016) 82-96.

两种液相模型

置换溶液模型(substitutional solution model)

$$G^{\varphi} = \sum_i x_i \cdot G_i^{0,\varphi} + RT \sum_i x_i \, ln \, x_i + G^{ex,\varphi}$$

Mg-Ca-O 体系:

Liquid: i = Mg, Ca, O

LIQOX: i = MgO, CaO

x_i是组元 i 的摩尔分数

CaMgO_TwoLiquid.tdb

CaO-MgO_LIQOX.tdb

缔合物模型(Associate model)

$$G^{\varphi} = \sum_i y_i \cdot G_i^{0,\varphi} + RT \sum_i y_i \, ln \, y_i + G^{ex,\varphi}$$

Mg-Ca-O 体系: i = Mg, MgO, Ca, CaO, O

y_i是组元 i 的点阵分数 $\neq$ 摩尔分数

CaMgO_ASSModel.tdb

CaO-MgO TDB 文件

```
Element          Ca                    Fcc     40.078      5736     41.588 !
Element          Mg                    Hcp     24.305      4998     32.671 !
Element           O        1/2_MOLE_O2(G)      15.999      4341     102.52 !
Species              CaO                   Ca1O1 !
Species              MgO                   Mg1O1 !
```

CaMgO_ASSModel.tdb

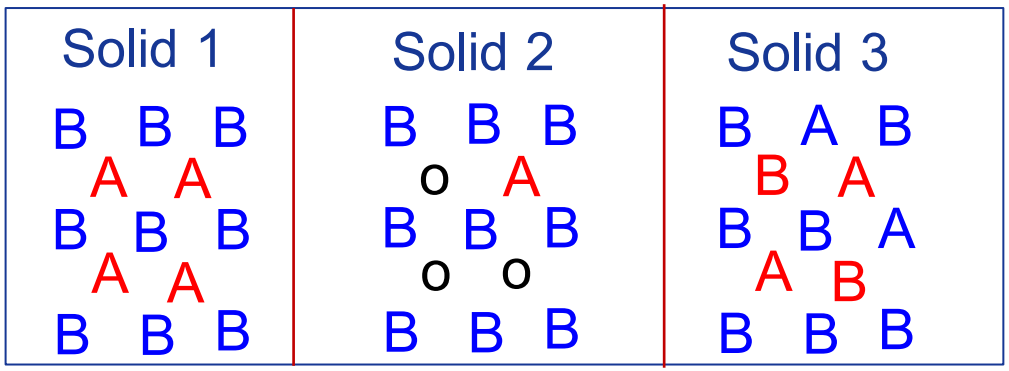
```
Phase Liquid:L % 1 1 !
Constituent Liquid:L :Ca,CaO,Mg,MgO,O:!
    Parameter G(Liquid,Ca;0) 298.15    +GLIQCA; 6000 N !
    Parameter G(Liquid,Mg;0) 298.15    +GLIQMG; 6000 N !
    Parameter G(Liquid,O;0) 298.15     +GLIQO; 6000 N !
    Parameter G(Liquid,CaO;0) 298.15   +GLIQCAO; 6000 N !
    Parameter G(Liquid,MgO;0) 298.15   +GLIQMGO; 6000 N !
    Parameter G(Liquid,Ca,Mg;0) 298.15    -32322.4+16.7211*T; 6000 N !
```

$G_i^{0,Liquid}$

$L_{Ca,Mg}^{0,Liquid}$

化合物能量模型(CEF 模型)

$$G^{\varphi} = \underbrace{\sum_{i,j} y_i^I \cdot y_j^{II} \cdot G_{i:j}^{0,\varphi}}_{^{\mathrm{ref}}G} + \underbrace{pRT \sum_i y_i^I \ln y_i^I + qRT \sum_j y_j^{II} \ln y_j^{II}}_{^{\mathrm{conf}}G} + G^{ex,\varphi}$$



$(A)_p(B)_q$ 计量化合物

$(A,Va)_p(B)_q$ 间隙固溶体

$(A,B)_p(A,B)_q$ 置换型多点阵固溶体

$G_{i:j}^{0,\varphi}$： i, j= A, B， endmember 必须给出

```
Parameter G(Cu2Mg_C15,Cu:Cu;0)
```

计量化合物模型

计量化合物 A_pC_q 作为体系金属间相

$(A)_p(C)_q$ 温度(T): $pA + qC = A_pC_q$ $G_{ApCq}(T) = G^{0,\varphi}_{A:C}$

$$\Delta G(T) = G_{A_pC_q}(T) - pG_A(T) - qG_C(T) = \Delta H - T\Delta S$$

$$\Longrightarrow G_{A_pC_q}(T) = \Delta H - T\Delta S + pG_A(T) + qG_B(T)$$ 浮动参考态

$$\boxed{G_{A_pC_q}(T)} = A + BT + \boxed{pG_A(T)} + \boxed{qG_B(T)}$$ 化学方应

$$C_p(A_pC_q) = pC_p(A) + qC_p(B)$$ **Neumann–Kopp rule**

计量化合物 A_pC_q是系统组元(component)

绝对参考态

$$G_{ApCq}(T) = A + BT + CT\,\ln T + DT^2 + ET^3 + FT^{-1} + \ldots$$

浮动参考态 vs 绝对参考态

Al_4Sr为例

浮动参考态 (Floating reference state)

$$G^{\mathrm{Al4Sr}}_{\mathrm{Al:Sr}}(T) = -26701 + 4.118\mathrm{T} + 0.8\, G^{0,fcc}_{Al}(T) + 0.2\, G^{0,fcc}_{Sr}(T)$$

```
Parameter G(Al4Sr, Al:Sr; 0)  298.15  -26701+4.118*T
                        +0.8*GFCCAL+0.2*GFCCSR; 6000 N !
```

-26701 J/mol-atoms = enthalpy of formation (T-independent)
-4.118J/mol-atoms K= entropy of formation(T-independent)

绝对参考态 (Absolute reference state)

常数

$$G^{\mathrm{Al4Sr}}_{\mathrm{Al:Sr}}(T) = a + bT + cT\ln(T) + dT2 + \cdots + 0.8\boxed{G^{0,fcc}_{Al}(298K)} + 0.2\boxed{G^{0,fcc}_{Sr}(298K)}$$

a, b ; determined from(but not equal to) enthalpy and entropy at 298.15K
c, d, … ; determined from experimental C_p of Al_4Sr

$G_{MxNy}(T) =$ A + BT + CT *ln*T + DT^2 + ET^3 + FT^{-1} + . . .

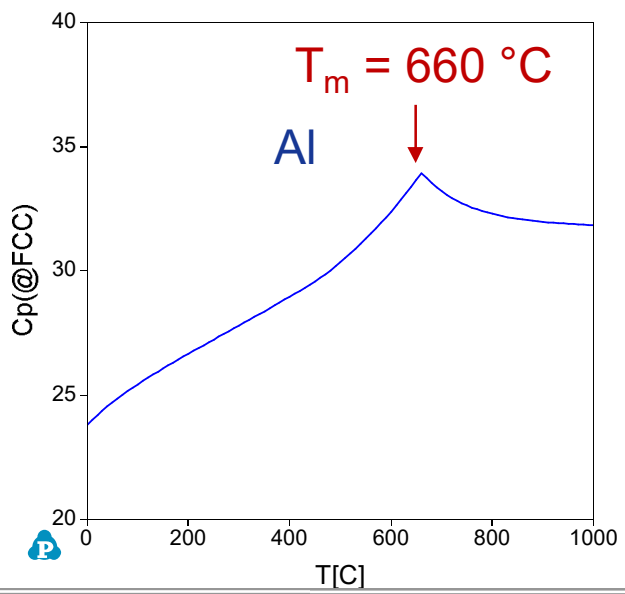
```
Parameter G(Al4Sr,Al:Sr;0)  298.15 -177788+535.06*T
                -94.4169*T*LN(T)-0.0534*T**2+6.93E-06*T**3;
```

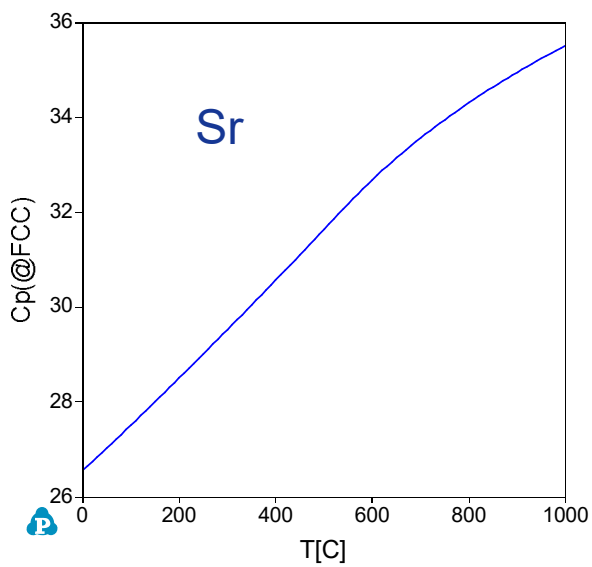
S.-M. Liang, et al., Key experiments and thermodynamic revision of the binary Al–Sr system, J. Alloys Compd., 610 (2014) 443-450.

浮动参考态

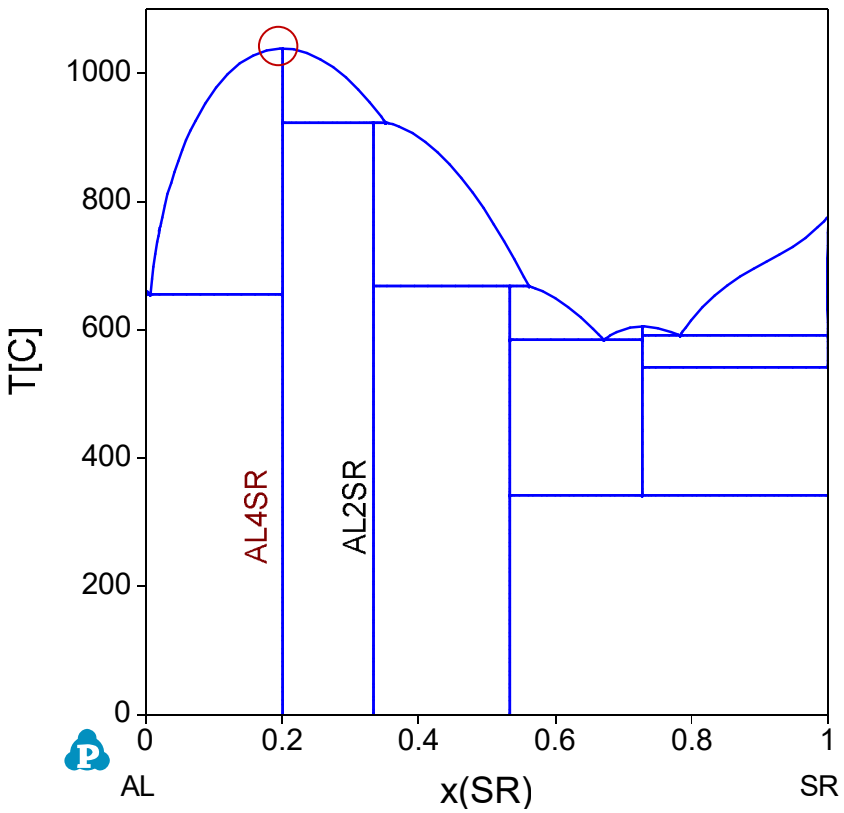
```
Function GHSERAL 298.14  -7976.15+137.093038*T-24.3671976*T*ln(T)-
0.001884662*T**2-8.77664e-007*T**3+74092*T**(-1); 700 Y
-11276.24+223.048446*T-38.5844296*T*ln(T)+0.018531982*T**2-5.764227e-
006*T**3+74092*T**(-1); 933.47 Y
-11278.378+188.684153*T-31.748192*T*ln(T)-1.230524e+028*T**(-9); 2900 N !
Function GHSERSR 298.14  -7532.367+107.183879*T-23.905*T*ln(T)
-0.00461225*T**2-1.67477e-007*T**3-2055*T**(-1); 820 Y
-13380.102+153.196104*T-30.0905432*T*ln(T)
-0.003251266*T**2+1.84189e-007*T**3+850134*T**(-1); 3000 N !
```

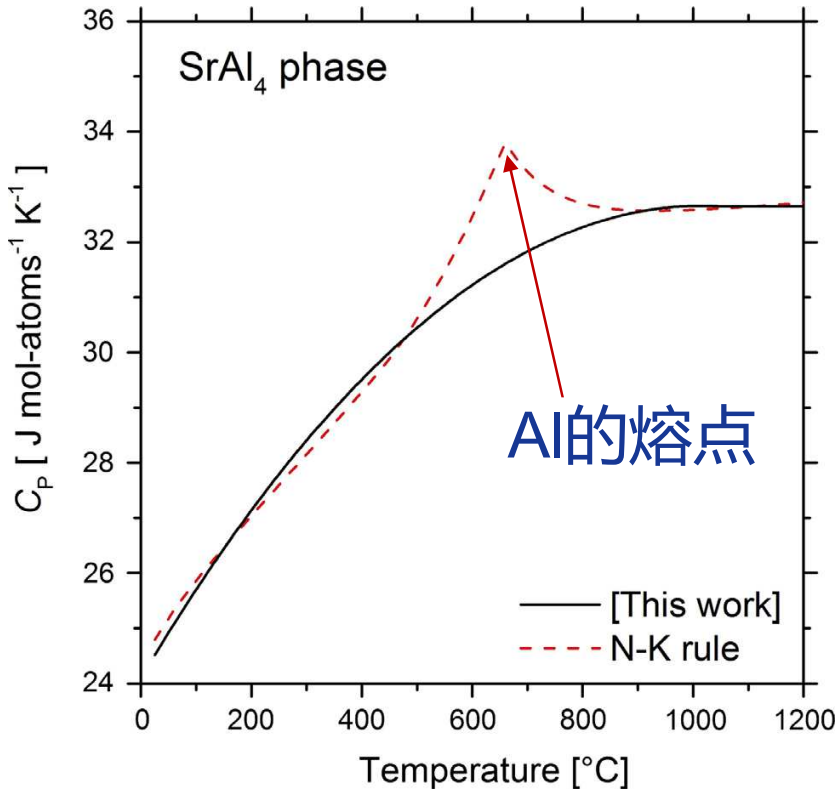
```
G(Al4Sr, Al:Sr; 0) = -26701+4.118*T+0.8*GFCCAL+0.2*GFCCSR
```





浮动参考态 vs 绝对参考态





浮动参考态: 简单，意义明确。$\Delta G = A + B\,T$； A 对应形成焓，-B对应形成熵。

缺点： 稳定相的Cp于实际不符，产生假象。

参考状态在pop文件中表述

$ enthalpy of formation of Al4Sr phase

EXPERIMENT **HMR**(AL4SR): 3000

SET_REFERENCE_STATE AL FCC * 1E5
SET_REFERENCE_STATE SR FCC * 1E5

$\Delta_f H_{298}$
生成(形成)焓

HMR:
H means enthalpy.
M: mole of atoms. i.e. $Al_{0.8}Sr_{0.2}$
R: means set_reference_state 命令后设定的Reference state.
如果不写，默认为GHSER 的参考态。**HM** 即Al4Sr 相的 H_{298}-H_0 值。

$$G^{\mathrm{Al4Sr}}_{\mathrm{Al:Sr}}(T) = \mathrm{A} + \mathrm{B\,T} + 0.8\, G^{0,fcc}_{Al}(T) + 0.2\, G^{0,fcc}_{Sr}(T)$$

设定 HMR(AL4SR)= -29051:3000 ⇨ A = - 29051 ± 3000

实际上 $\Delta_f H_{298} = \Delta_f H_T$

参考状态在pop文件中表述

$ entropy of formation of Al4Sr phase

EXPERIMENT **SMR**(AL4SR)= **-** 4.2:1

SET_REFERENCE_STATE AL FCC * 1E5
SET_REFERENCE_STATE SR FCC * 1E5

SMR:
S means entropy.

$$G^{\mathrm{Al4Sr}}_{\mathrm{Al:Sr}}(T) = \mathrm{A} + \mathrm{B\,T} + 0.8\, G^{0,fcc}_{Al}(T) + 0.2\, G^{0,fcc}_{Sr}(T)$$

设定 SMR(AL4SR)= **-** 4.2:1 ⇨ B = 4.2 ± 1

$\Delta_f S_{298}$

生成(形成)熵

可能为负值
也可能为正值

$ absolute entropy at 298 K: Al4Sr phase

SET_CONDITION T=298.15

EXPERIMENT **SM**(AL4SR)= 25:2

~~SET_REFERENCE_STATE AL FCC * 1E5~~
~~SET_REFERENCE_STATE SR FCC * 1E5~~

S°_{298}

绝对熵

肯定是正值

间隙固溶体

$(A)_p(B,Va)_q$

$$G^{\varphi} = \sum_{i,j} y_i^I \cdot y_j^{II} \cdot G_{i:j}^{0,\varphi} + pRT \sum_i y_i^I \ln y_i^I + qRT \sum_j y_j^{II} \ln y_j^{II} + G^{ex,\varphi}$$

$$G_{ApBq}(T) = G_{A:B}^{0,\varphi}(T)$$ Endmember 必须给出

$$G_{ApVaq}(T) = G_{A:Va}^{0,\varphi}(T) = G_A^{0,\varphi}$$ Endmember (Lattice stability)

Fcc, Bcc, Hcp： 如果整个数据库中第二个亚点阵都没有任何间隙原子填充，即没有$G_{A:B}^{0,\varphi}(T)$，仅仅只是空位，$G_{A:Va}^{0,\varphi}(T)$。 此时两个亚点阵模型就可以简化为一个亚点阵模型。

多亚点阵置换型固溶体相

φ 相: $(A,B)_p(A,B)_q$

$$G^{\varphi} = \sum_{i,j} y_i^I \cdot y_j^{II} \cdot G_{i:j}^{0,\varphi} + pRT \sum_i y_i^I \ln y_i^I + qRT \sum_j y_j^{II} \ln y_j^{II} + G^{ex,\varphi}$$

^{ref}G

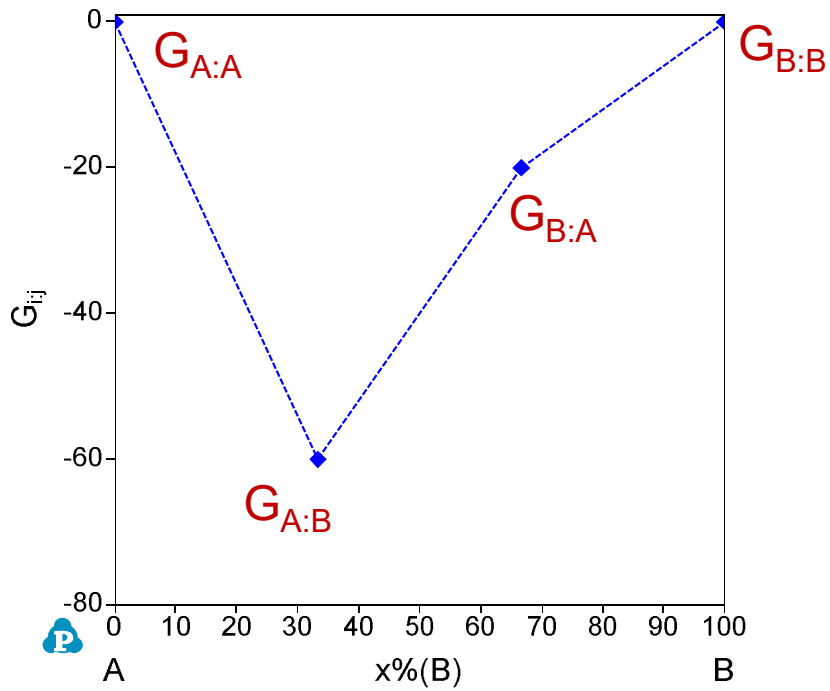
Endmember 值:

$G_{A:A}^{0,\varphi}$: φ相 全部为 A原子

$G_{B:B}^{0,\varphi}$: φ相 全部为 B原子

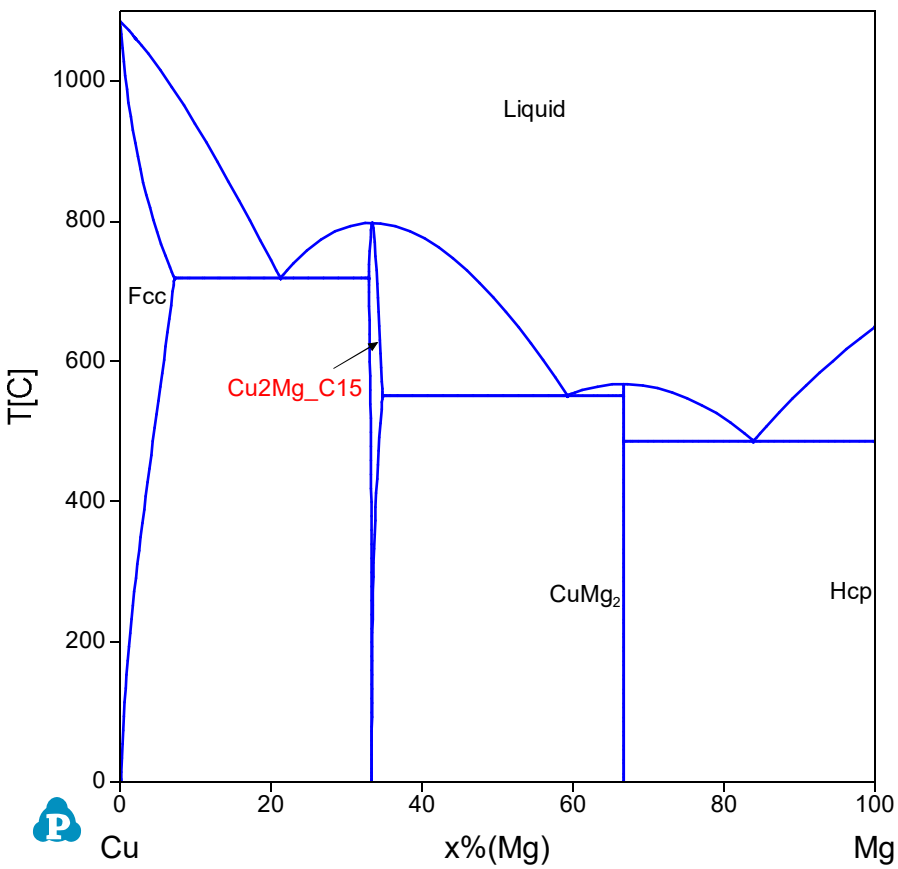
$G_{A:B}^{0,\varphi}$; φ相 为 A_pB_q

$G_{B:A}^{0,\varphi}$; φ相 为 B_pA_q



Endmember 值 确定了相的Gibbs能曲线的主要形状。

Cu-Mg 相图



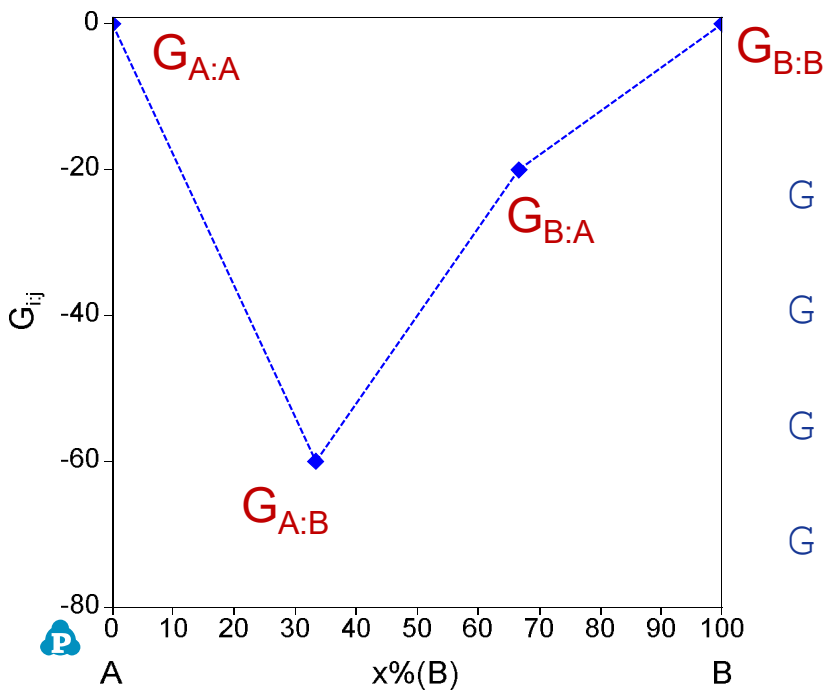
稳定相附件的endmember值，
有**Cp数据**： **采用绝对参考态。**
亚稳endmember值： 相对参考态。

Cu2Mg_C15:
(Cu, Mg)2(Cu,Mg)1

$G^{C15}_{Cu:Cu}$ = 21014.88+3*GHSERCU.
$G^{C15}_{Mg:Mg}$ = 27357.33+3*GHSERMG
$G^{C15}_{Cu:Mg}$ = -54690.99+364.73085*T
-69.276417*T*LN(T)
-5.1925E-4*T**2+143502*T**(-1)
$G^{C15}_{Mg:Cu}$ =+105000-
16.5*T+2*GHSERMG+GHSERCU

$G^{ex,\varphi}$

$$G^{ex,\varphi} = y_A^I y_B^I \cdot y_A^{II} \cdot \boxed{L^{\varphi}_{A,B:A}} + y_A^I y_B^I \cdot y_B^{II} \cdot \boxed{L^{\varphi}_{A,B:B}}$$
$$+ y_A^{II} y_B^{II} \cdot y_A^I \cdot \boxed{L^{\varphi}_{A:B,A}} + y_A^{II} y_B^{II} \cdot y_B^I \cdot \boxed{L^{\varphi}_{B:A,B}}$$



TDB 文件中逗号和冒号，分号的含义

`G(Cu2Mg_C15, Cu,Mg:Cu;0)` $L^{\varphi}_{Cu,Mg:Cu}$

`G(Cu2Mg_C15, Cu,Mg:Mg;0)` $L^{\varphi}_{Cu,Mg:Mg}$

`G(Cu2Mg_C15, Cu:Cu,Mg;0)` $L^{\varphi}_{Cu:Cu,Mg}$

`G(Cu2Mg_C15, Mg:Cu,Mg;0)` $L^{\varphi}_{Mg:Cu,Mg}$

Questions?

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

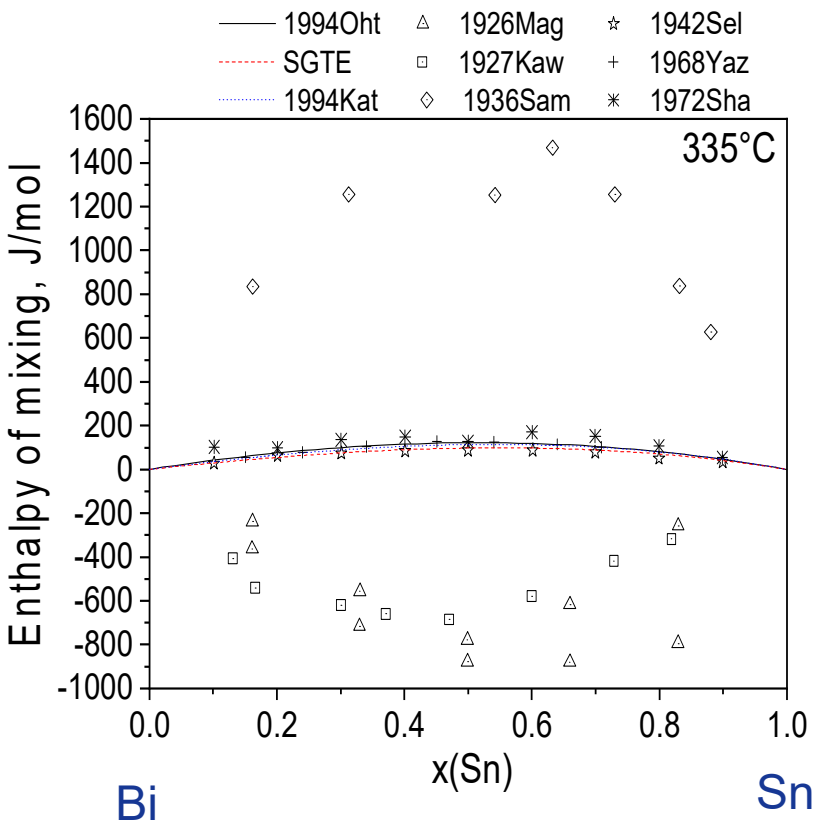
实验数据的处理过程

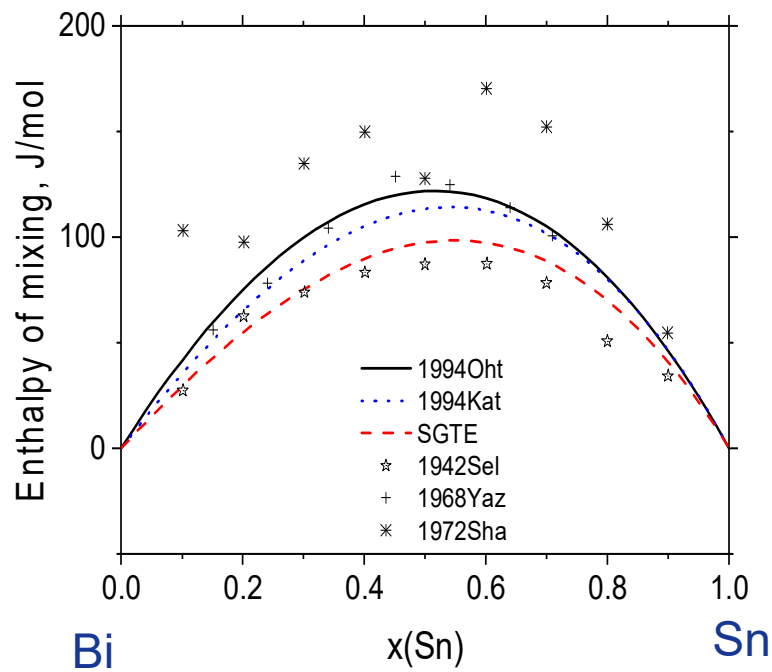
- 尽量收集全部数据

  综述性论文，
  JPED（H. Okamoto: 二元体系，V. Raghavan多元体系）
  MSI Euraka
  ASM Handbook

- 尽量查找原始文献
- 合理分析实验数据
- 建立POP文件

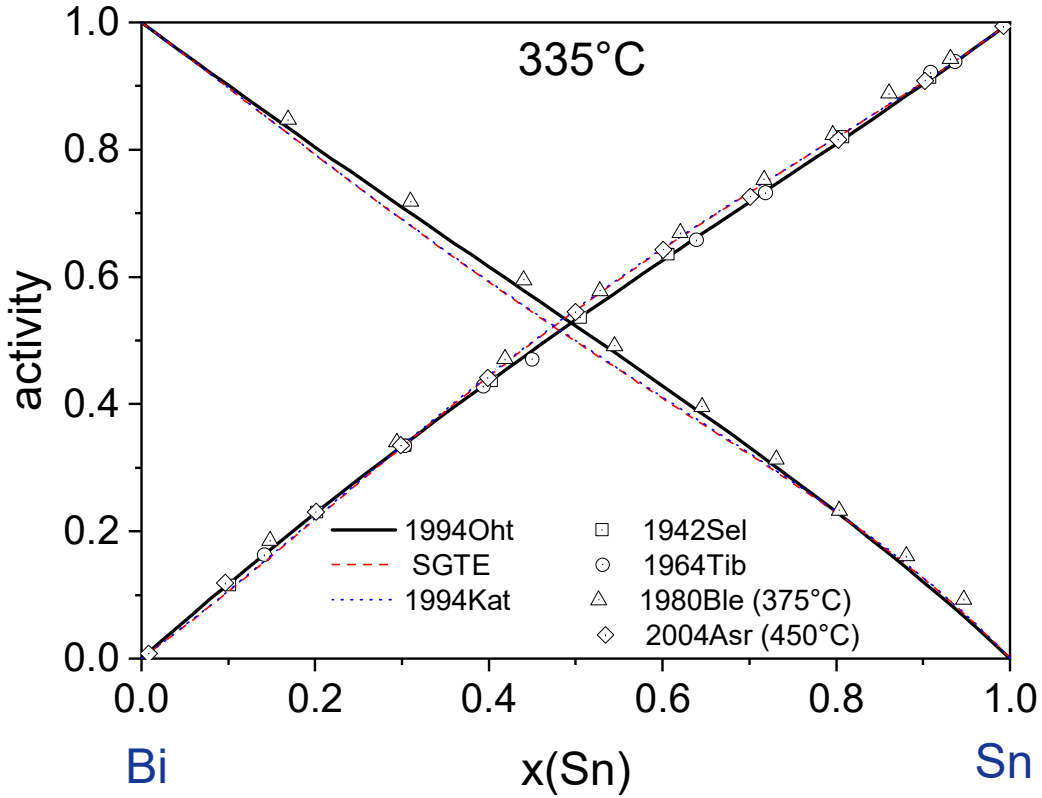
实验数据





有三组数据明显非常分散

实验数据



实验点是测量值

测量了活度 a_{Sn}

化学势 μ_{Sn}

Gibbs-Duhem

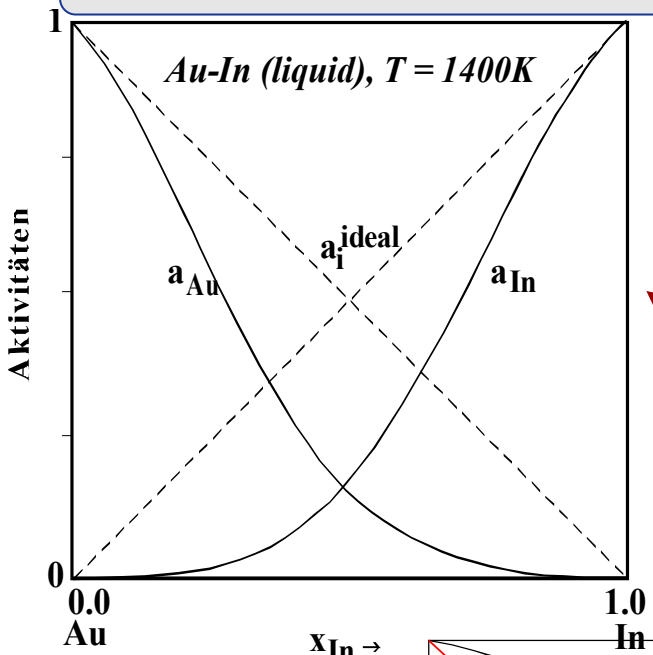
化学势 μ_{In}

G^{Liq}

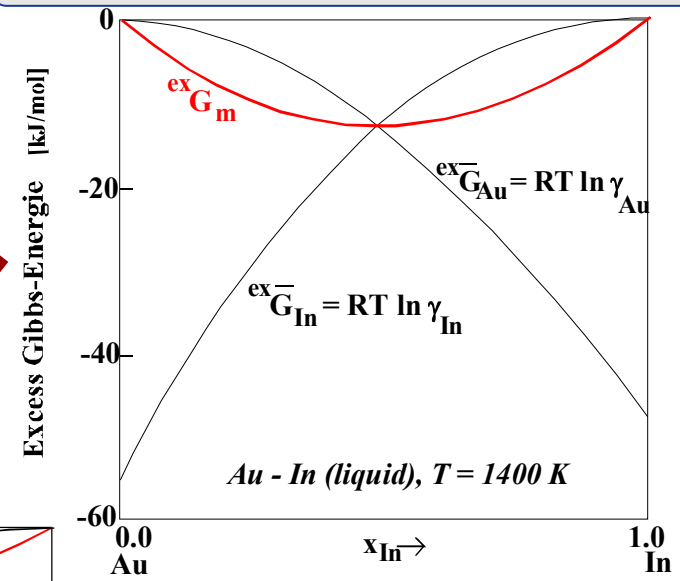
NOT CALPHAD SPIRIT

一致性 (Consistency)

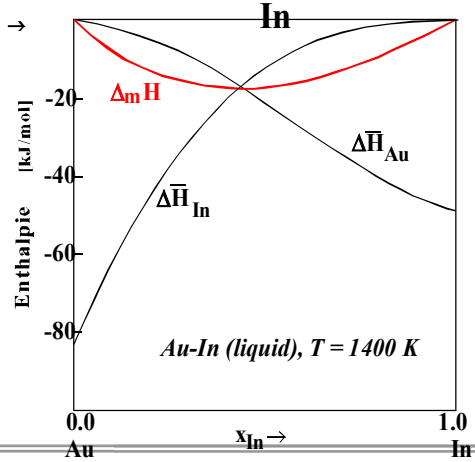
Never produce separate model for partial quantities!

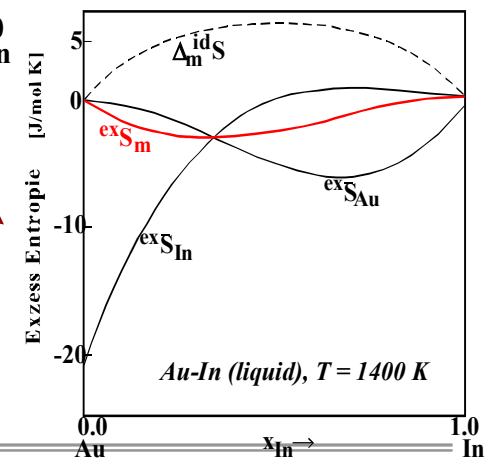


Derive a_i (T, x_i) from *integral* quantity, G^{ex}

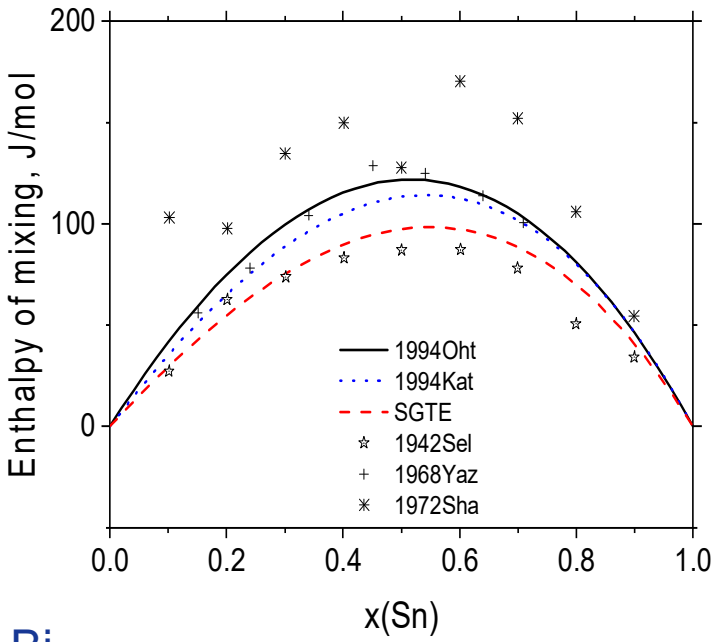


Forget about the Gibbs-Duhem integration method (not trivial in ternary...)

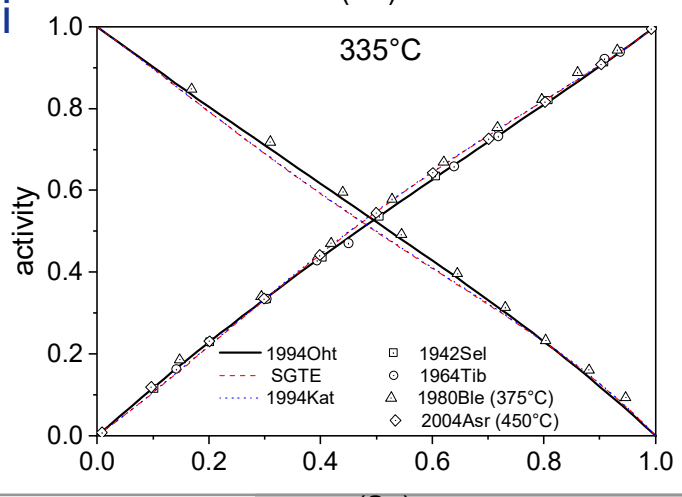




参考状态



Bi



Sn

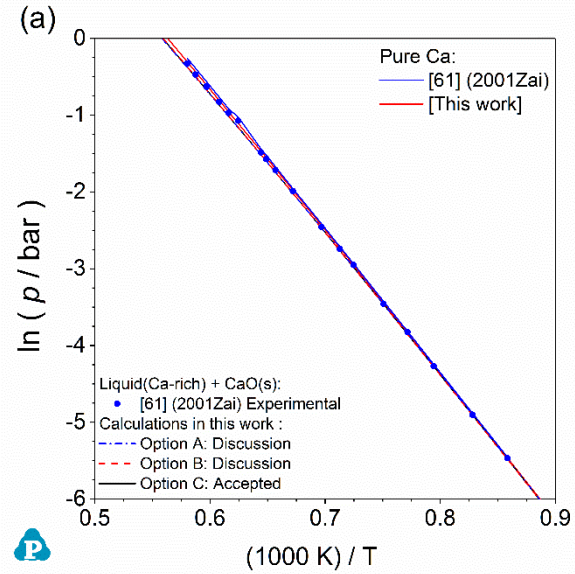
Enthalpy of mixing

液相是参考状态

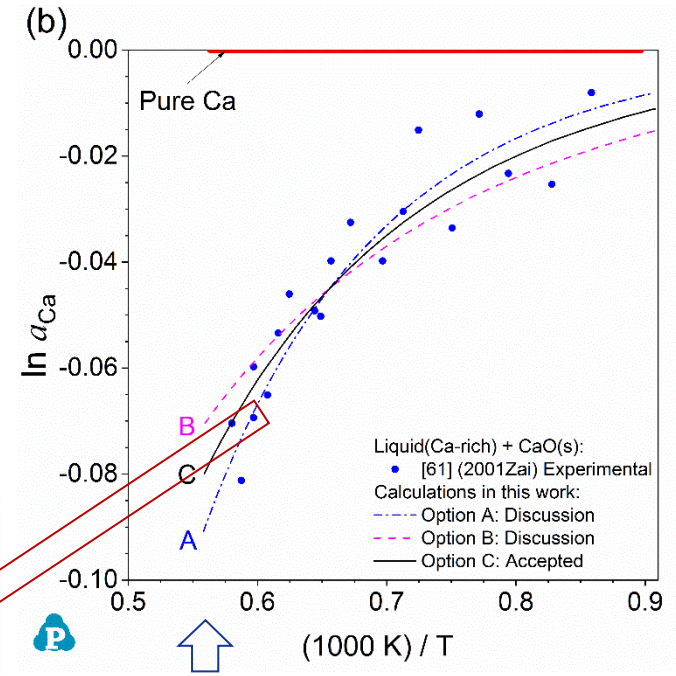
EXPERIMENT **HMR**(LIQUID): @2:DH
EXPERIMENT **ACR**(LIQUID): @3: DA

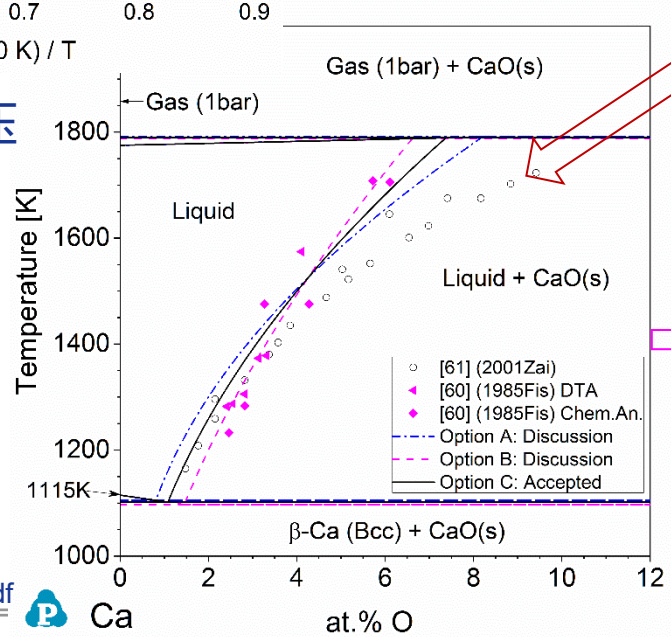
SET_REFERENCE_STATE BI LIQUID * 1E5
SET_REFERENCE_STATE SN LIQUID * 1E5

实验数据



Ca的分压





只用蓝色活度数据优化

L_0^{liquid} = -12500 + 10*T

只用粉色相图数据优化

L_0^{liquid} = -33850 + 24*T

上面两个参数的平均值

L_0^{liquid} = -23175 + 17*T

2018Liang_JEurCeramSoc_4768.pdf

Questions?