

# Introduction to the constrained equilibrium method

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# Motivation

- Most technical processes are not in equilibrium.
- Kinetic limitations impose constraints on the equilibrium.
- Simple methods can sometimes be very effective in describing constrained equilibria.



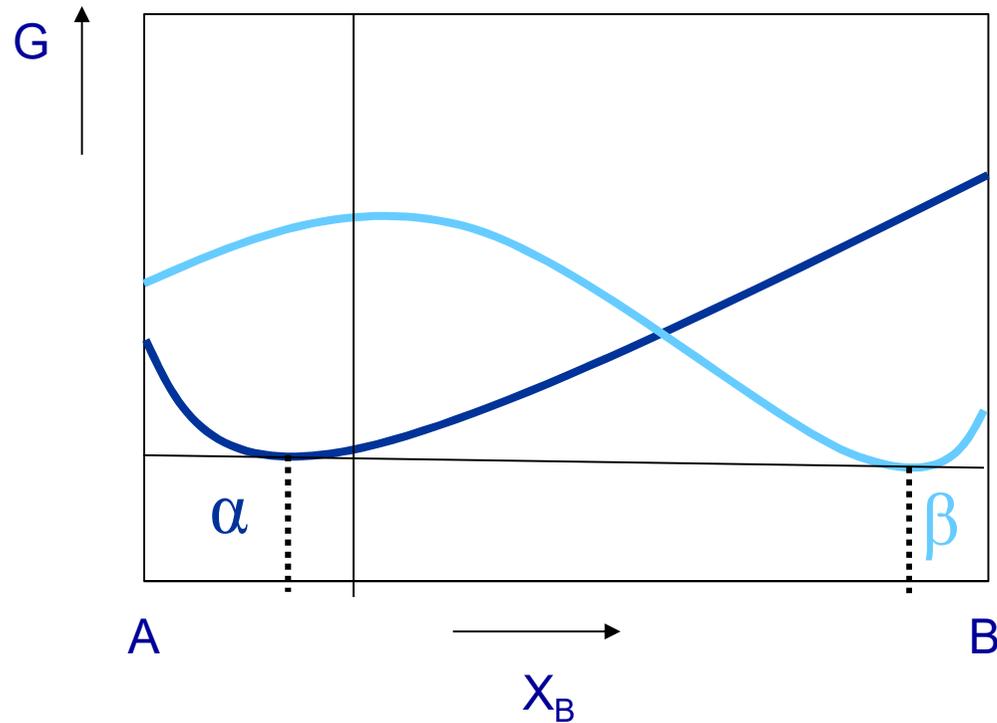
# Outline

- Dormant species
- Paraequilibrium calculations with and without diffusing elements
- Scheil cooling calculations
- Immaterial system components (for work terms and reaction rate constraints)



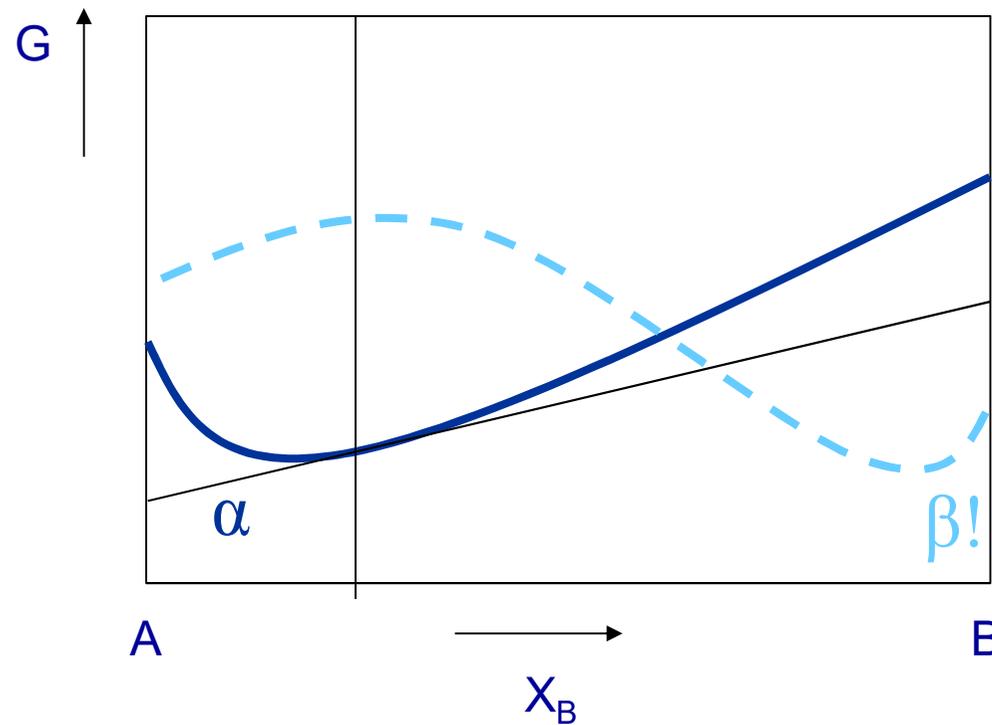
# Dormant species

- Dormant species may not form, but their thermodynamic properties are calculated.



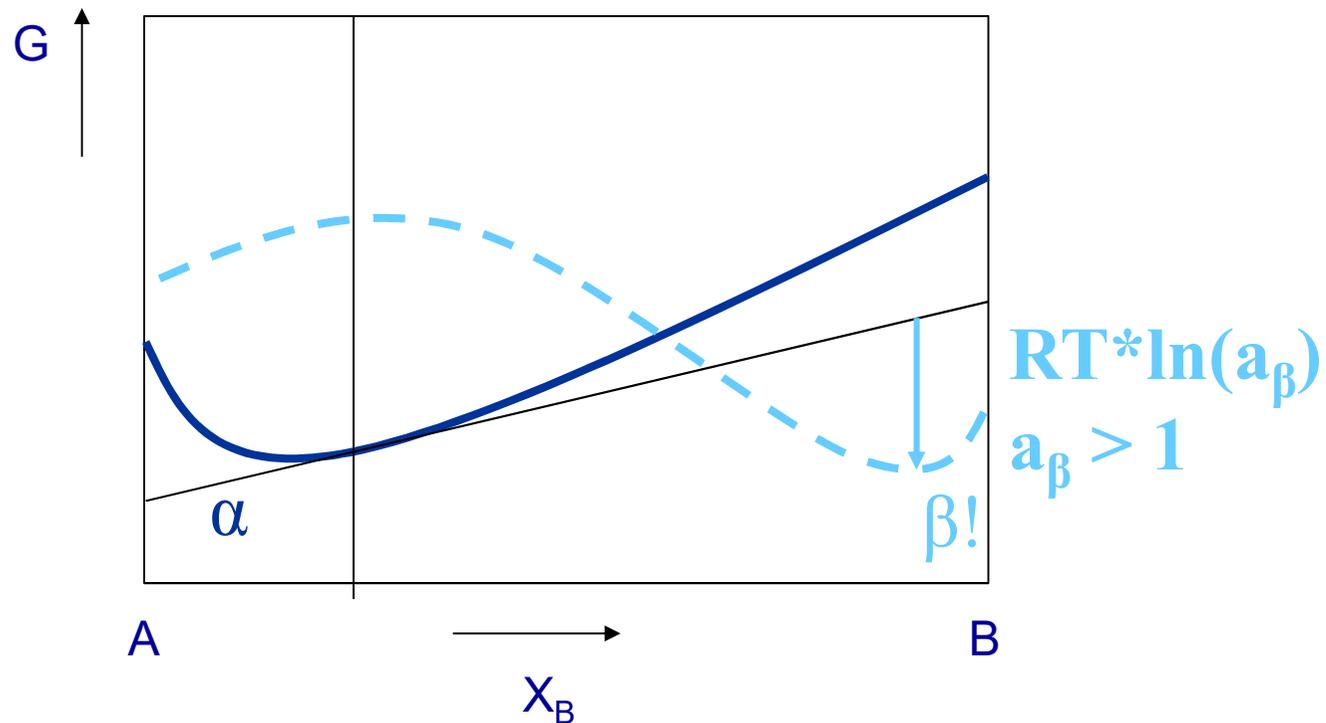
# Dormant species

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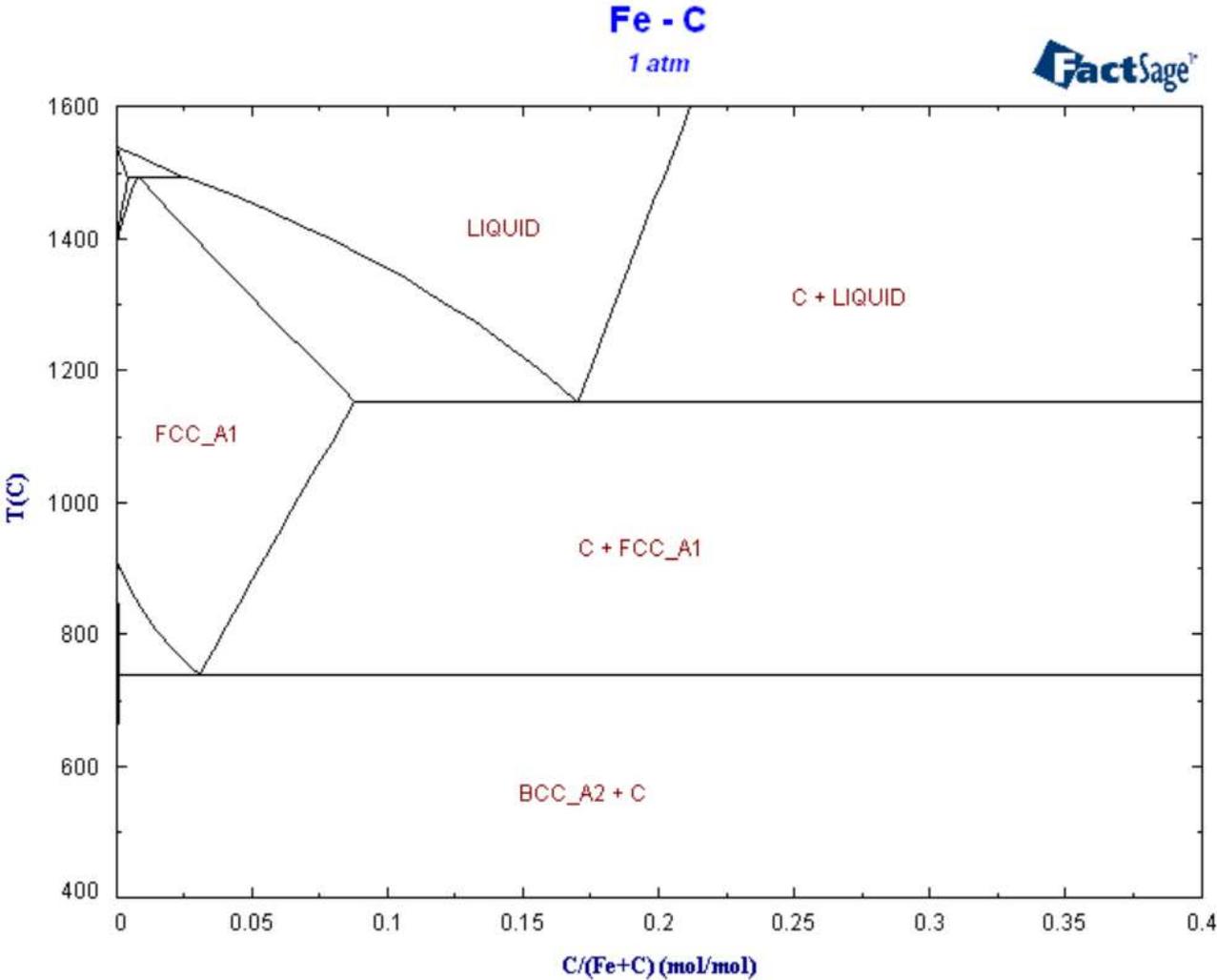


# Dormant species

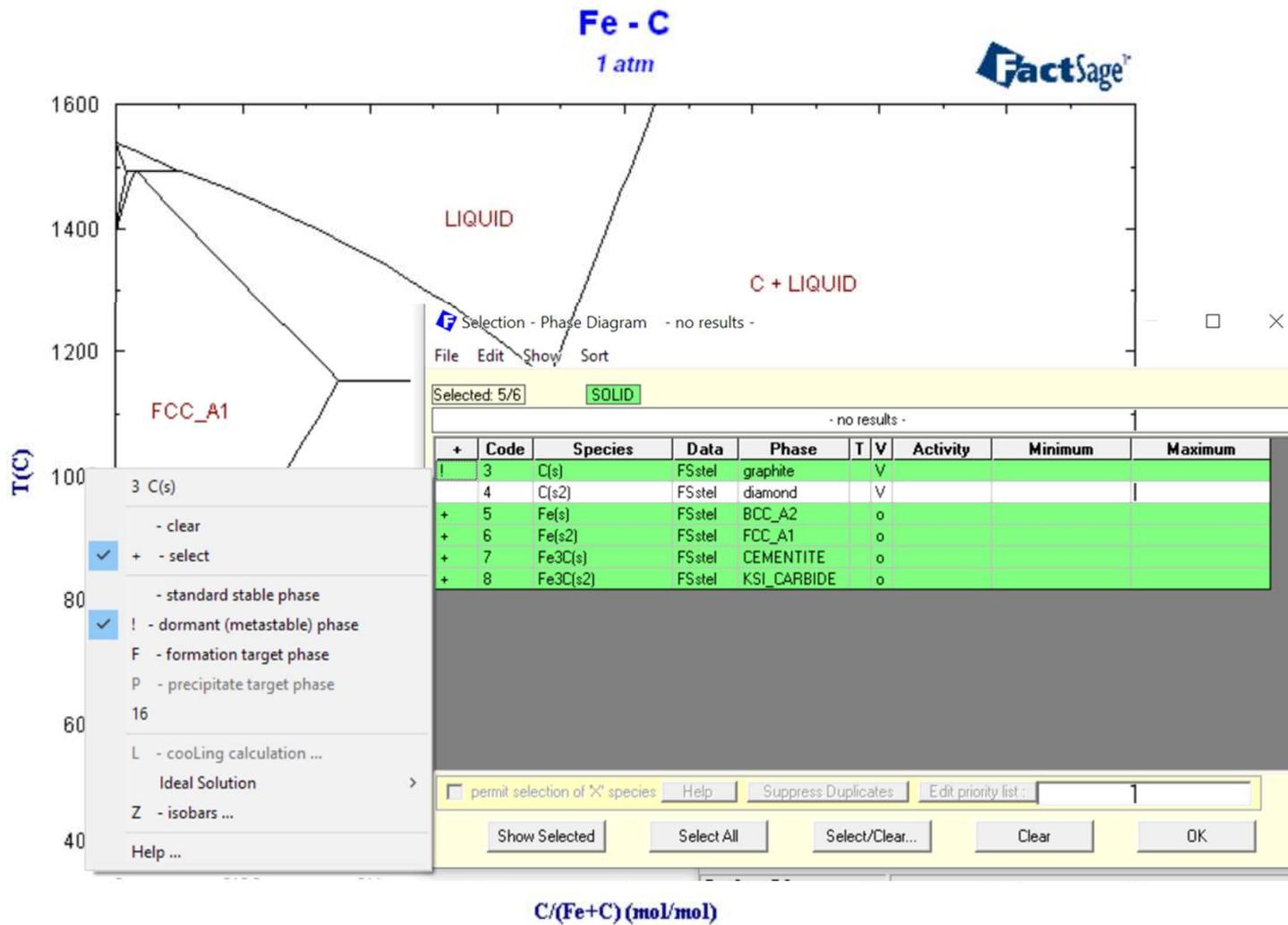
- Dormant species may not form, but their thermodynamic properties are calculated.



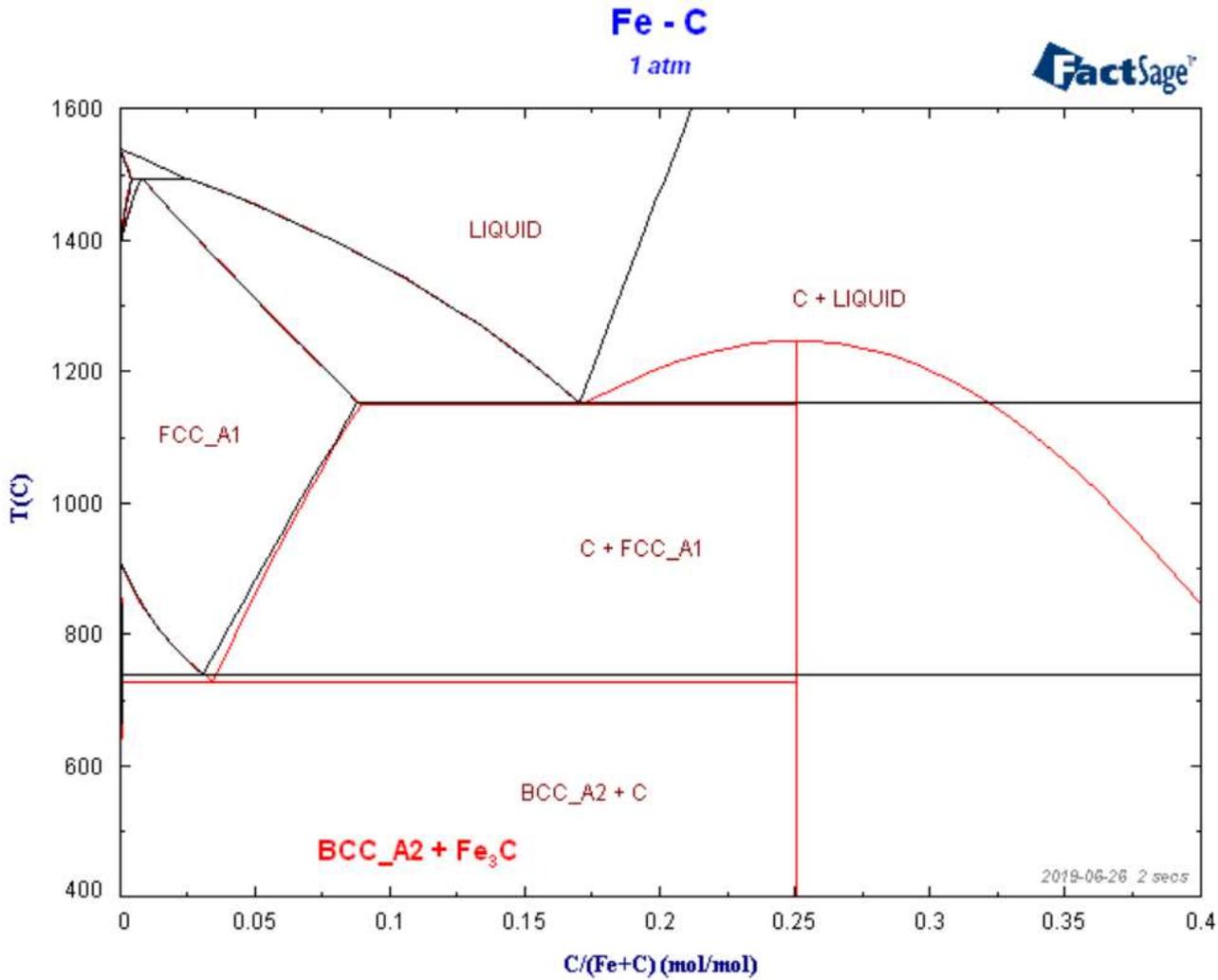
# Dormant species



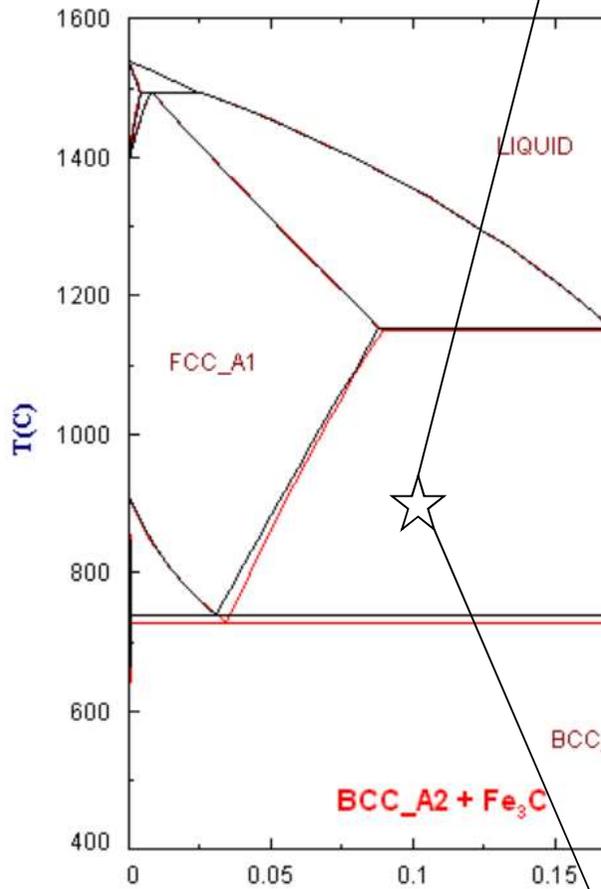
# Dormant species



# Dormant species



# Dormar



Phase Diagram Equilibrium

File Edit Format

1

T = 771.60 C  
P = 1 atm  
V = 0 dm3

STREAM CONSTITUENTS	AMOUNT/mol
Fe	8.8380E-01
C	1.1620E-01

C\_graphite(s), selected as a dormant (metastable) phase, has an activity > 1

PHASE: FCC_A1	EQUIL AMOUNT mol	MOLE FRACTION	ACTIVITY
Fe	5.8525E-01	9.5900E-01	9.5258E-01
FeC	2.5023E-02	4.1004E-02	1.0439E-03
TOTAL:	6.1027E-01	1.0000E+00	1.0000E+00

Site fraction of sublattice constituents:

Fe	1.0000	Stoichiometry = 1
-----		
Va	0.95900	Stoichiometry = 1
C	4.1004E-02	

System component	Amount/mol	Amount/gram	Mole fraction	Mass
Fe	0.61027	34.081	0.96061	0.
C	2.5023E-02	0.30055	3.9389E-02	8.

Neel temperature = -206.15 C  
Average magnetic moment/atom = 0.70000

PHASE: BCC_A2	mol	MOLE FRACTION	ACTIVITY
FeC3	0.0000E+00	4.9047E-04	1.4034E-20
Fe	0.0000E+00	9.9951E-01	9.7562E-01
TOTAL:	0.0000E+00	1.0000E+00	9.7706E-01

PHASE: LIQUID	mol	MOLE FRACTION	ACTIVITY
C	0.0000E+00	1.3535E-01	3.0832E-05
Fe	0.0000E+00	8.6465E-01	4.9728E-01
TOTAL:	0.0000E+00	1.0000E+00	6.8482E-01

mol	ACTIVITY
Fe3C CEMENTITE(s)	9.1177E-02
C_graphite(s)	! 0.0000E+00
Fe_BCC_A2(s)	0.0000E+00
Fe_FCC_A1(s)	0.0000E+00



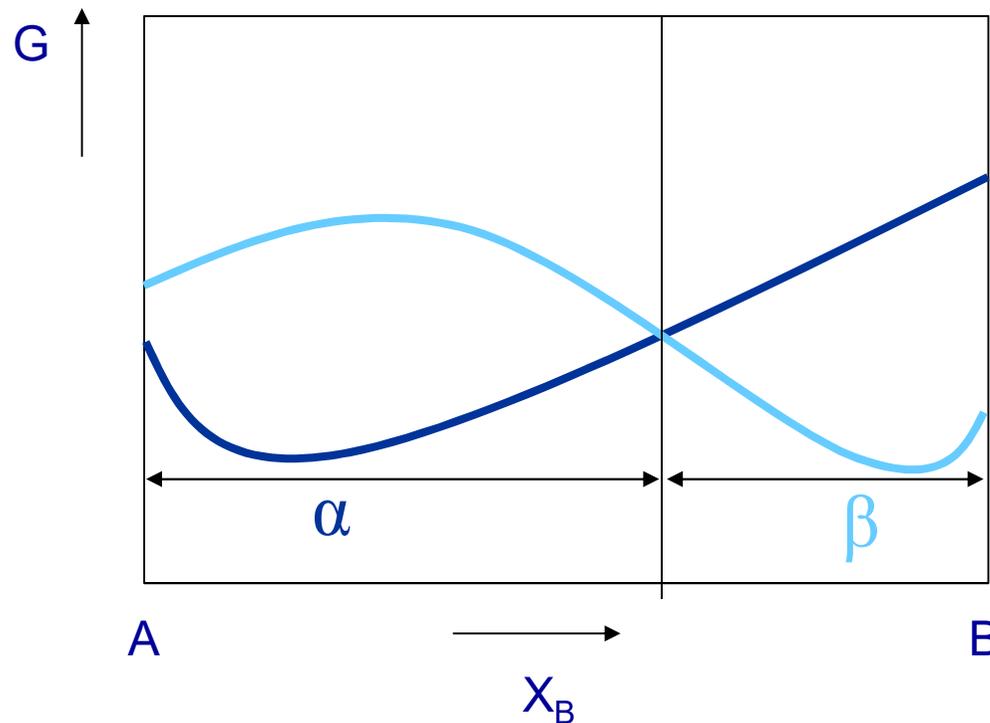
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- Dormant species
- Paraequilibrium calculations with and without diffusing elements
- Scheil cooling calculations
- Immaterial system components (for work terms and reaction rate constraints)



# Paraequilibrium (no diffusing elements)

- In paraequilibrium, the single phase with lowest Gibbs energy forms



# Paraequilibrium (no diffusing elements)

- In paraequilibrium, the single phase with lowest Gibbs energy forms

Phase Diagram - Menu: last system

File Units Parameters Variables Help

T(C) P(atm) Energy(J) Quantity(mol) Vol(litre)

Components (2)

Fe + C

Products

Compound species

gas  ideal  real 0

aqueous 0

pure liquids 0

pure solids  6

species: 6

Target

- none -

Estimate T(K): 1000

Solution phases

*	+	Base-Phase	Full Name
	+	FSstel-Liqu	LIQUID
	+	FSstel-FCC	FCC_A1
	+	FSstel-BCC	BCC_A2

Legend

+ - selected 3

Show  all  selected

species: 6

solutions: 3

Custom Solutions

0 fixed activities Details ...

0 ideal solutions

Pseudonyms

apply  Edit ...

Volume data

assume molar volumes of solids and liquids = 0

include molar volume data and physical properties data

paraequilibrium & Gmin edit

Virtual species: 1

Total Species (max 5000) 12

Total Solutions (max 200) 3

Total Phases (max 1500) 9

Variables

T(C)	C/(Fe+C)			
400 1600	0.4			

T(C) vs C/(Fe+C)

Phase Diagram

Y

X

Calculate >>

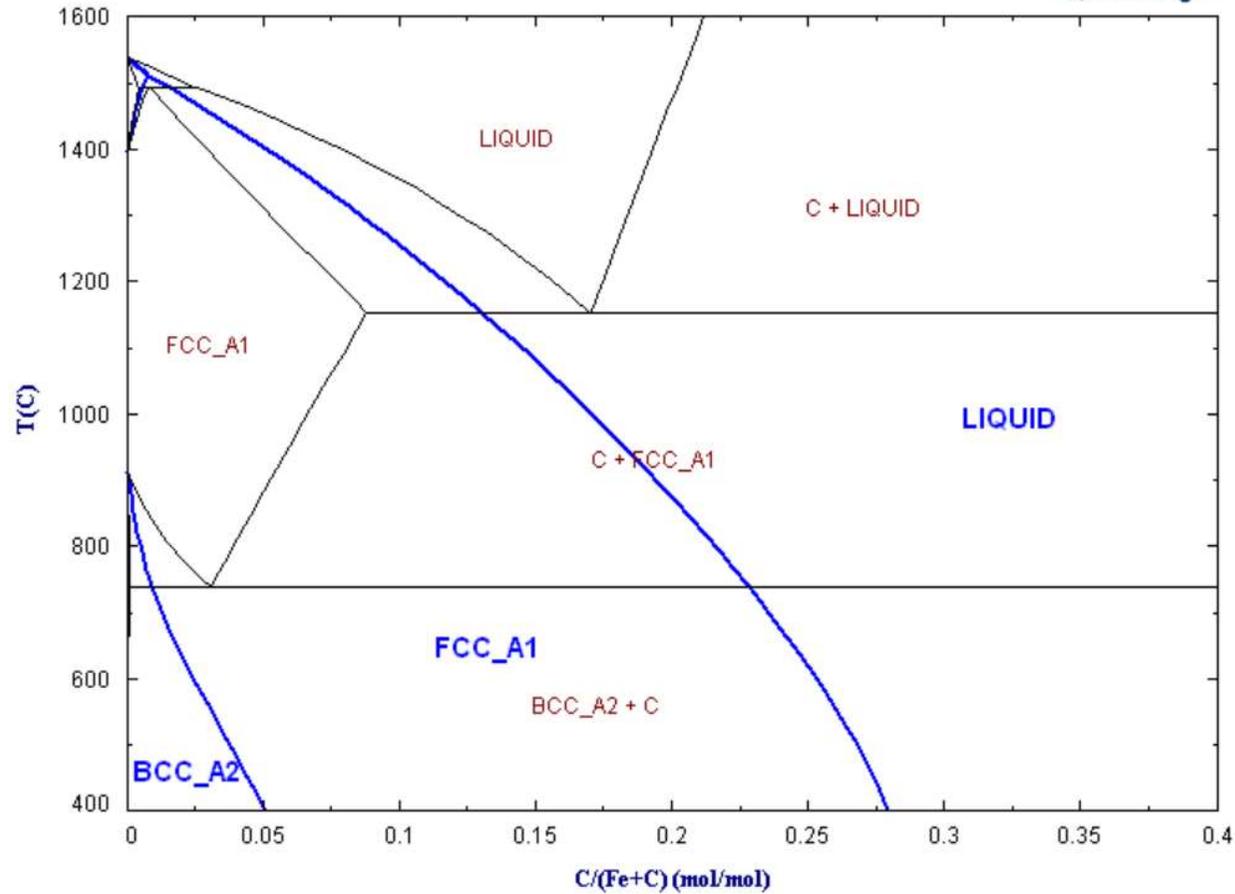
FactSage 7.3



# Paraequilibrium (no diffusing elements)

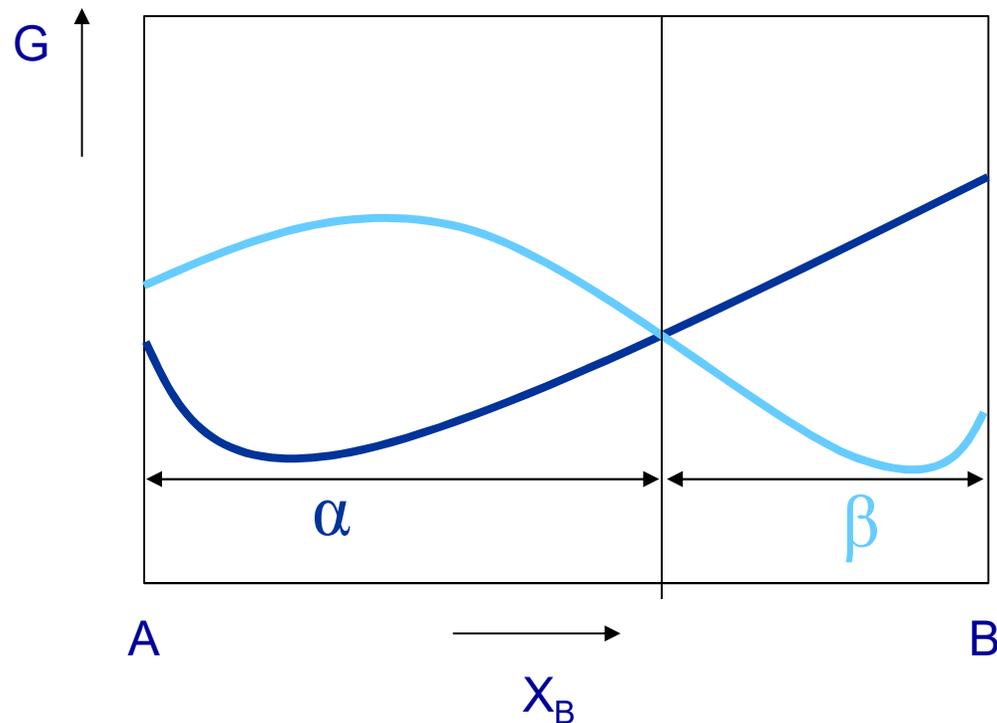
Fe - C - phase with minimum G

1 atm



# Paraequilibrium (diffusing elements)

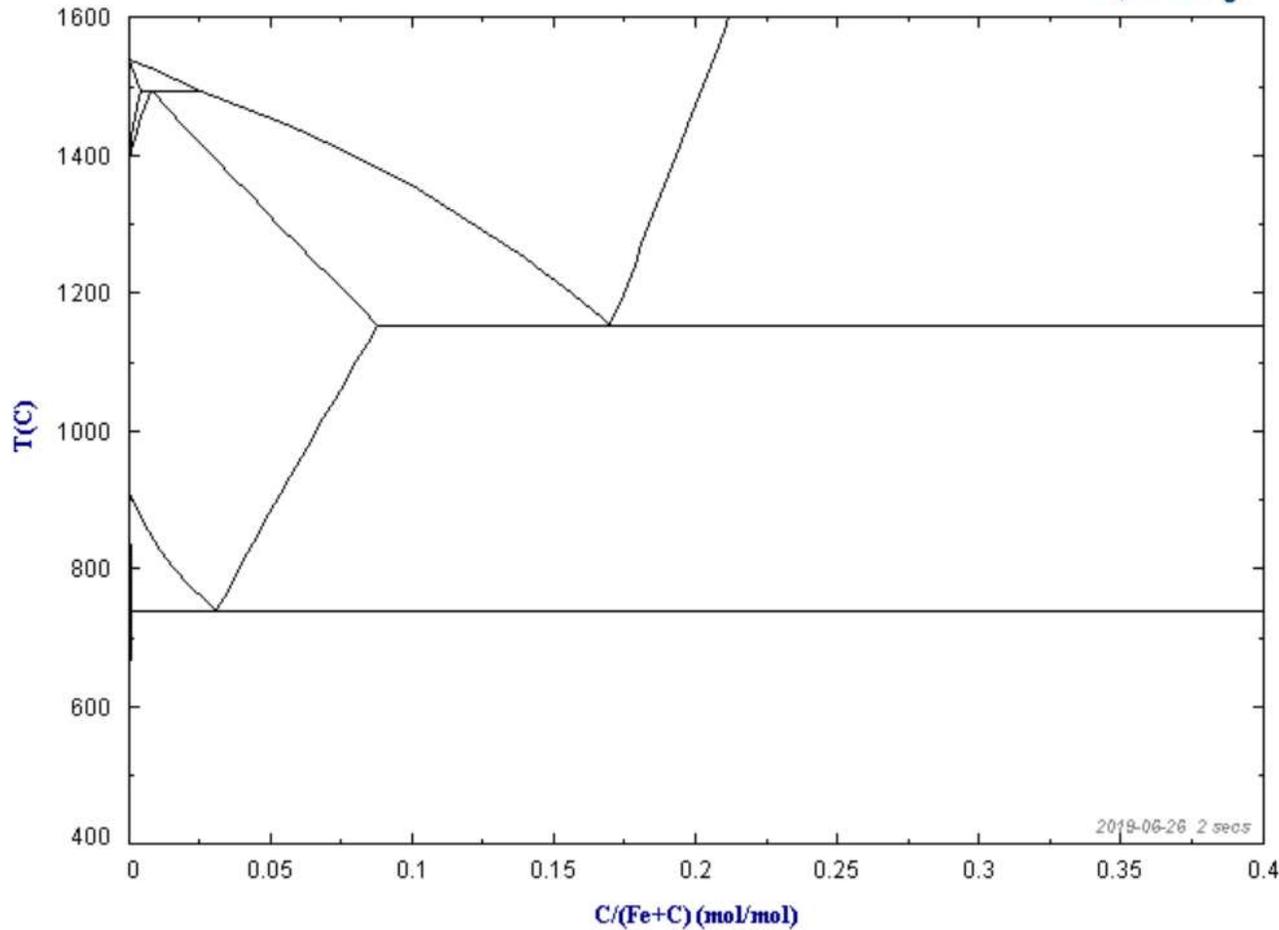
- One element (or more) allowed to partition
- Usually used for C or N



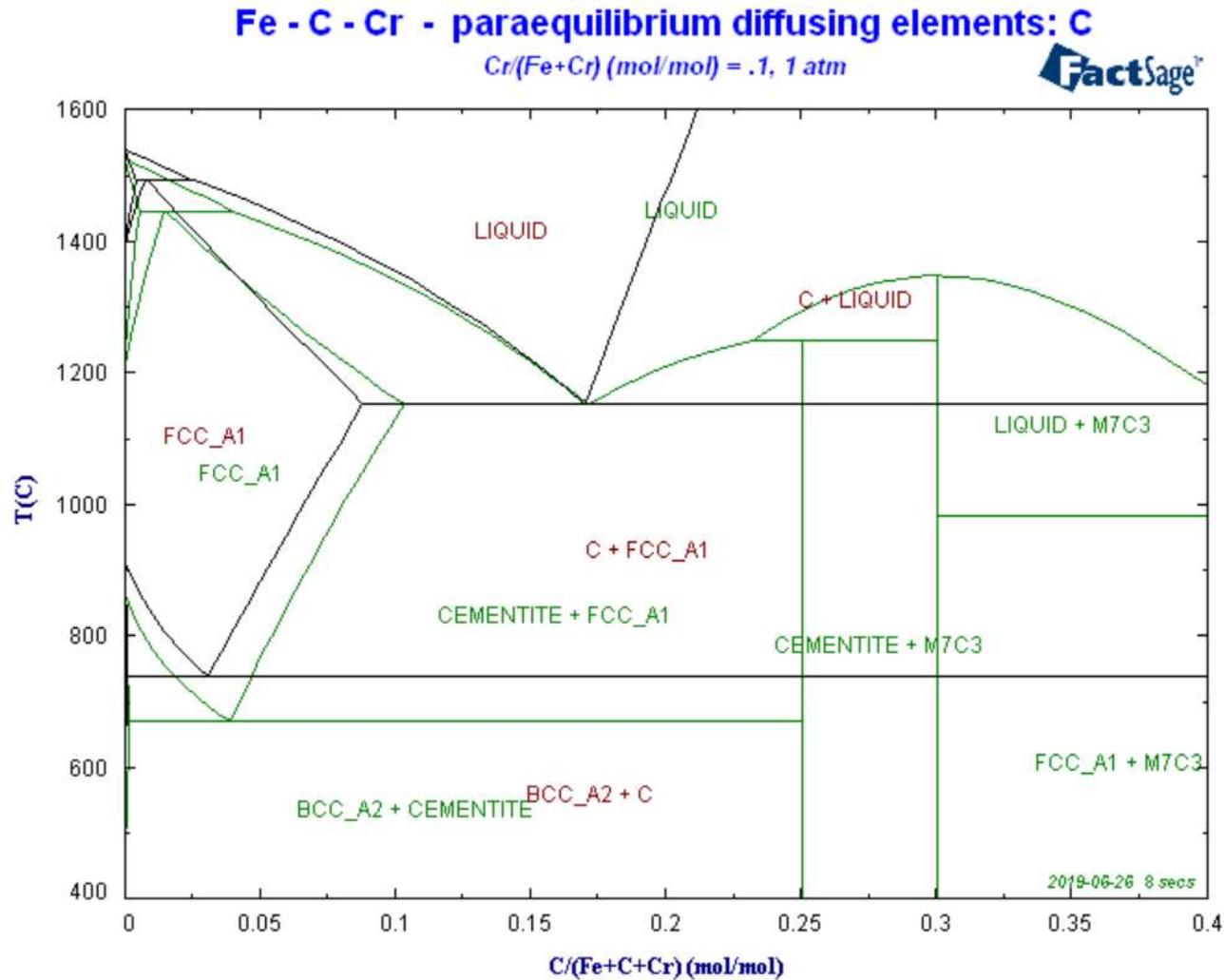
# Paraequilibrium (diffusing elements)

Fe - C - paraequilibrium diffusing elements: C

1 atm



# Paraequilibrium (diffusing elements)



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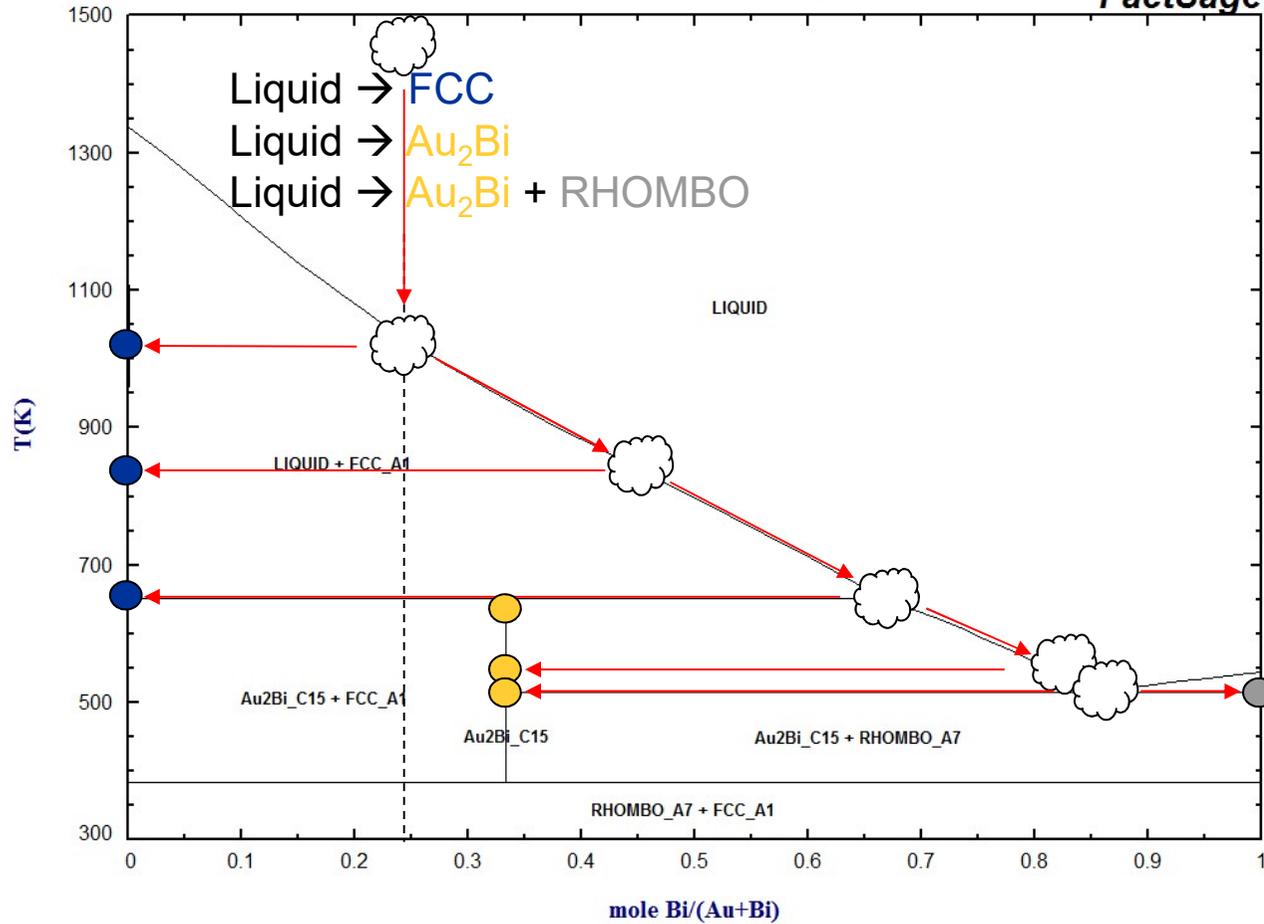


# 2 component Scheil cooling

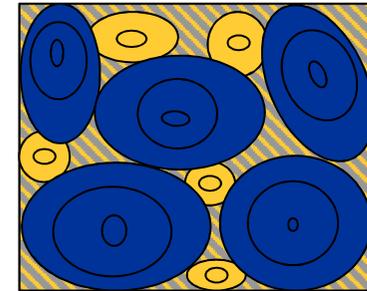
Au - Bi

Data from SGTE solders database (revised 2008)

FactSage



microstructure:

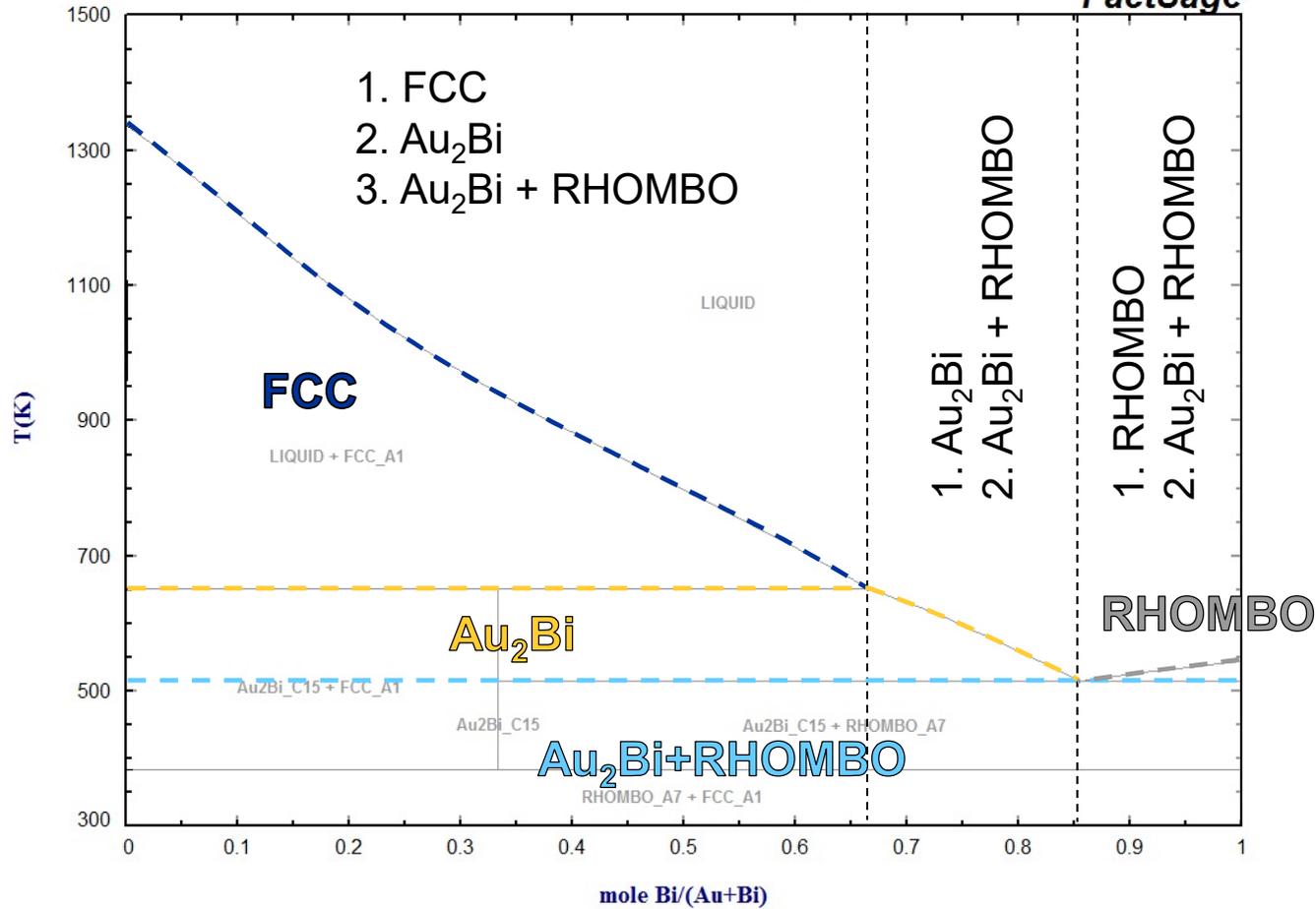


# 2 component Scheil cooling

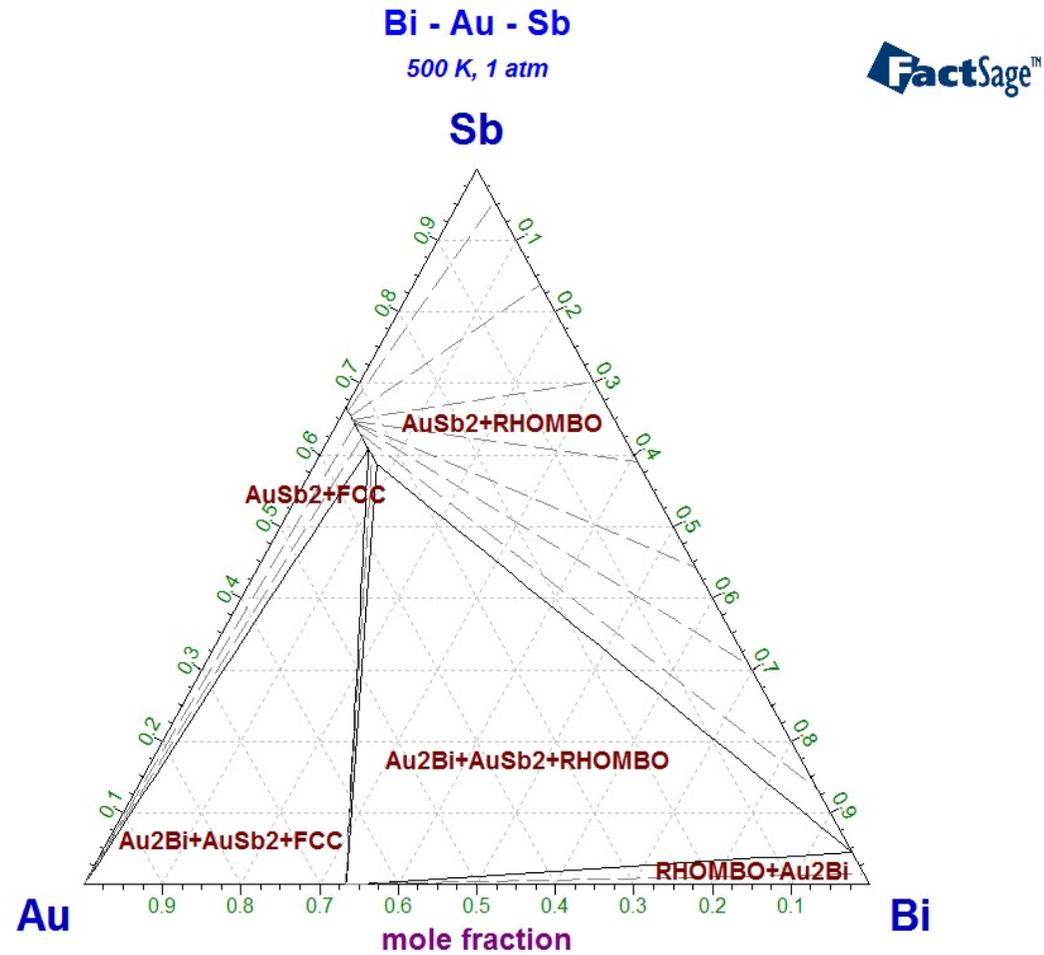
Au - Bi

Data from SGTE solders database (revised 2008)

FactSage



# 3 components: What are the stable solid phases?



# 3 components: What is the first precipitating phase? → liquidus!

Sb - Au - Bi  
Projection (LIQUID), 1 atm

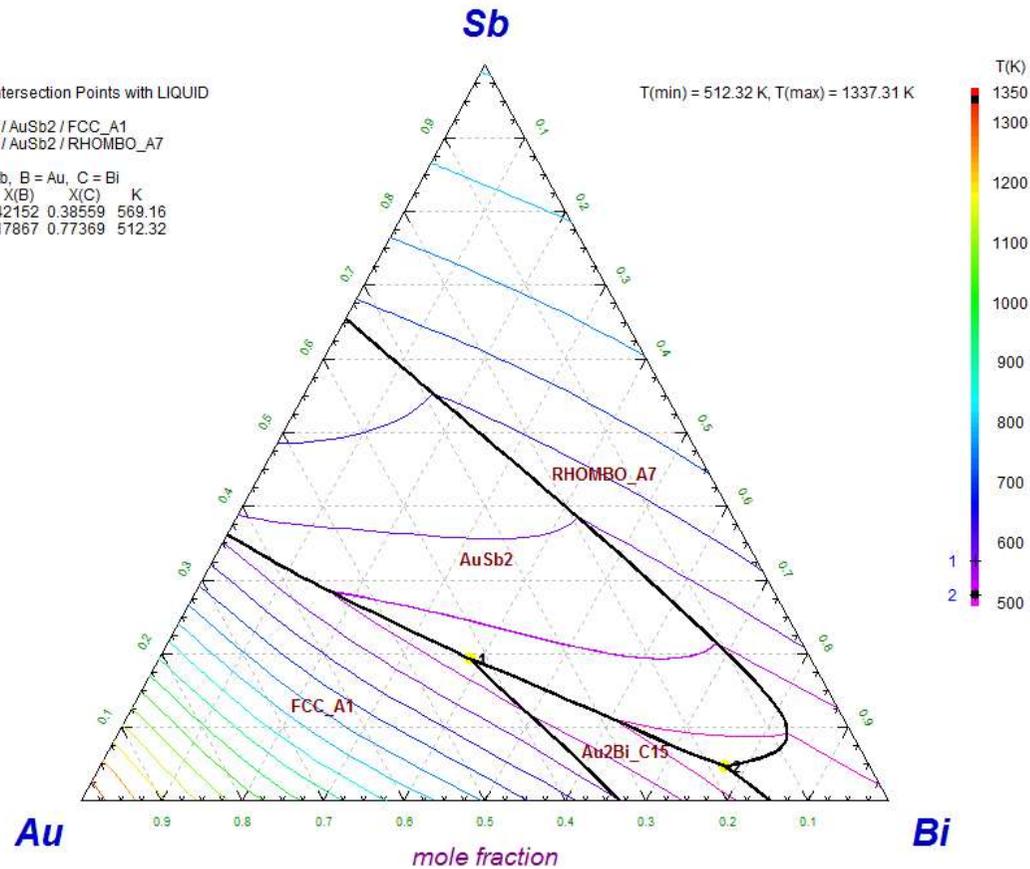


Four-Phase Intersection Points with LIQUID

- 1: Au2Bi\_C15 / AuSb2 / FCC\_A1
- 2: Au2Bi\_C15 / AuSb2 / RHOMBO\_A7

	A = Sb	B = Au	C = Bi	K
1:	0.19290	0.42152	0.38559	569.16
2:	0.04764	0.17867	0.77369	512.32

T(min) = 512.32 K, T(max) = 1337.31 K



# 3 components: Scheil cooling

## Sb70-Au26-Bi4

### SUMMARY OF REACTIONS

770.86 to 723.46 K:

LIQ → RHOMBO

723.46 to 538.48 K:

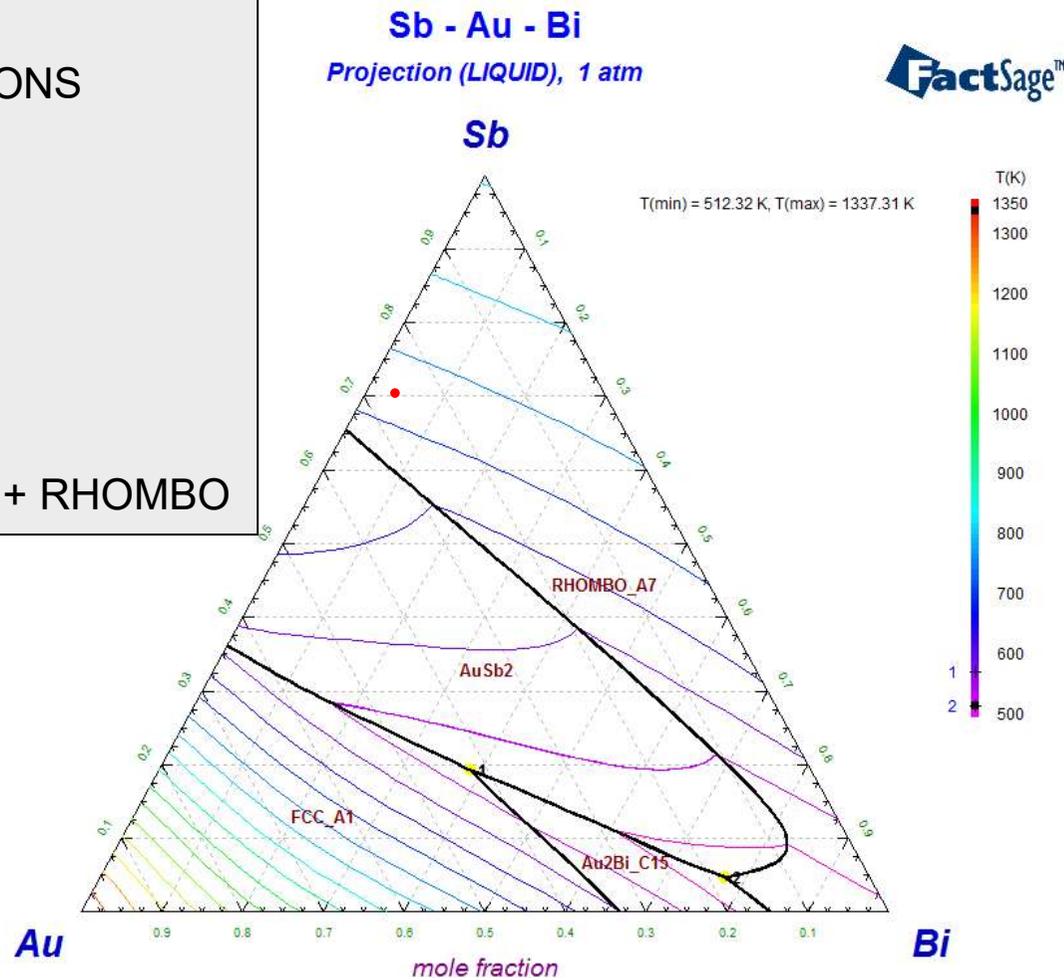
LIQ → AuSb<sub>2</sub>

538.48 to 512.32 K:

LIQ → Au<sub>2</sub>Bi + AuSb<sub>2</sub>

512.32 K (isothermal):

LIQ → Au<sub>2</sub>Bi + AuSb<sub>2</sub> + RHOMBO



# 3 components: Scheil cooling

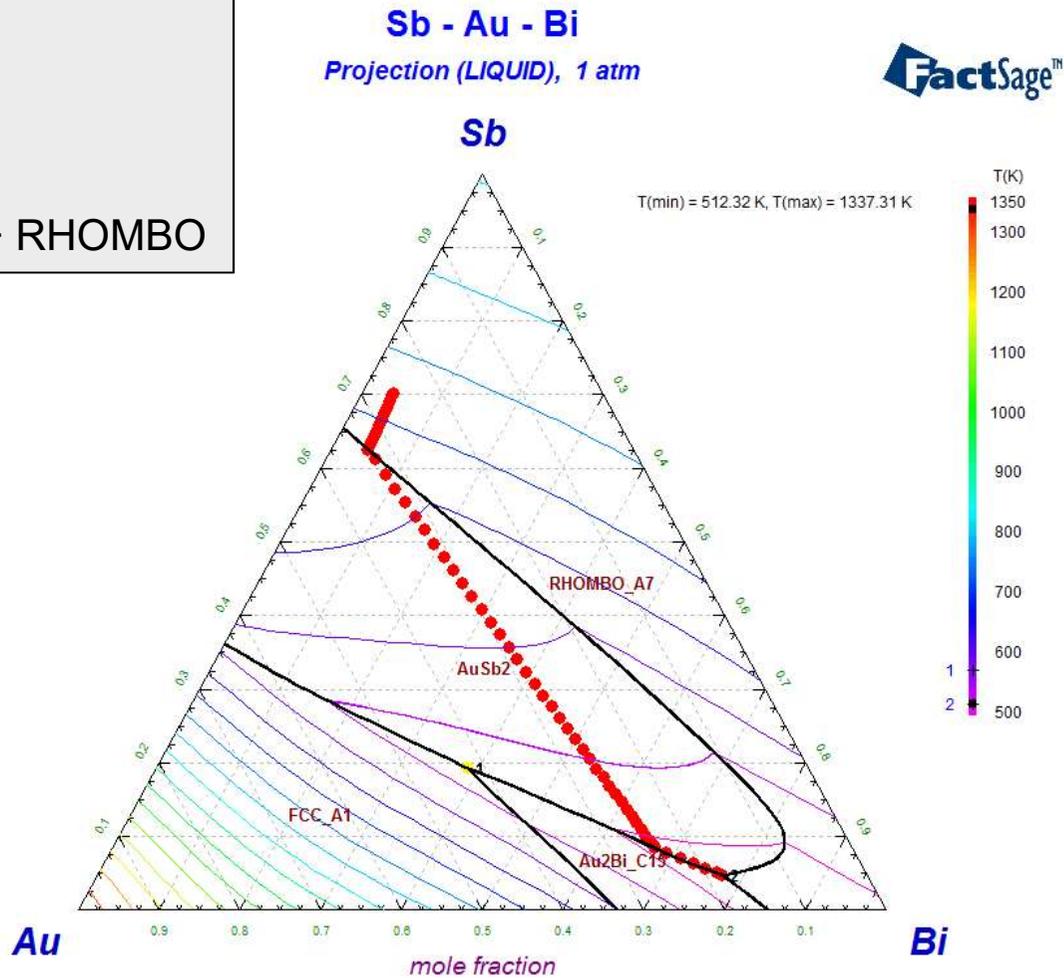
## Sb70-Au26-Bi4

LIQ → RHOMBO

LIQ → AuSb<sub>2</sub>

LIQ → Au<sub>2</sub>Bi + AuSb<sub>2</sub>

LIQ → Au<sub>2</sub>Bi + AuSb<sub>2</sub> + RHOMBO



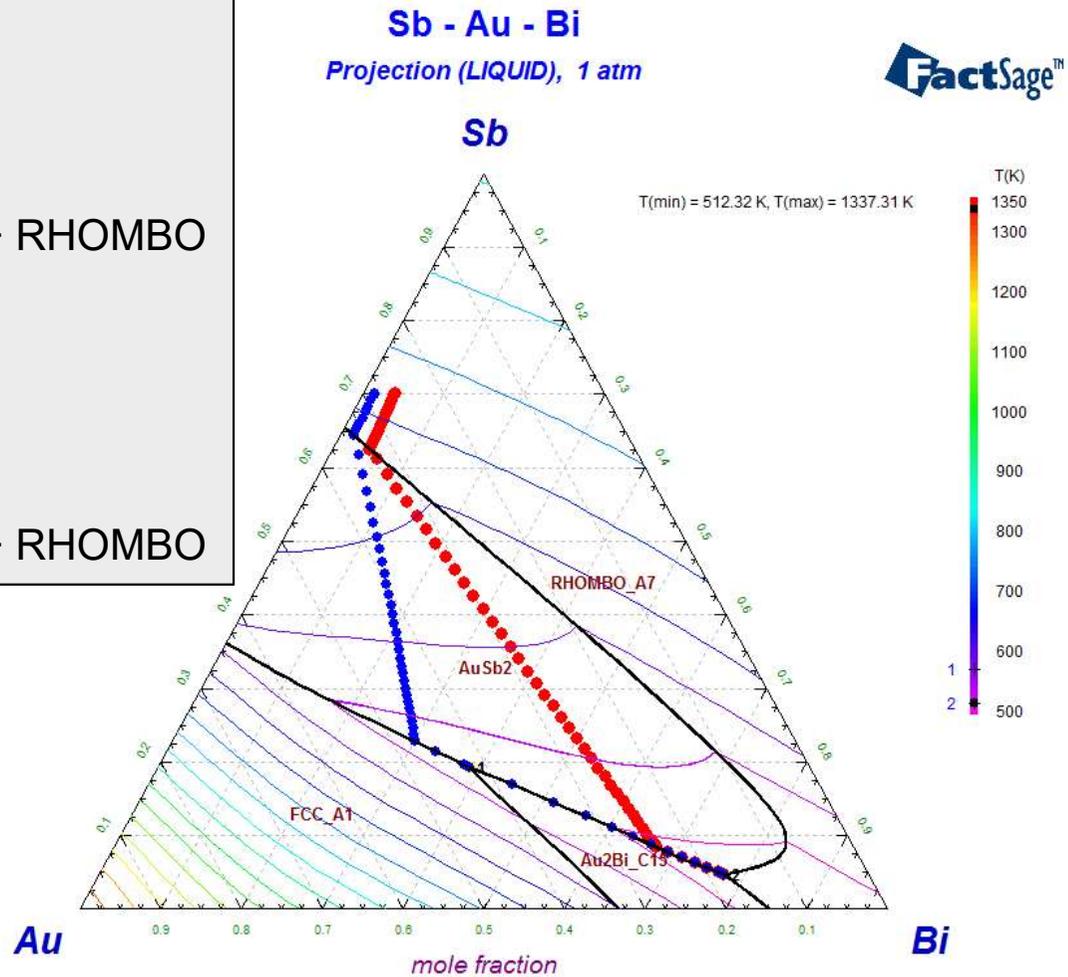
# 3 components: Scheil cooling

## Sb70-Au26-Bi4

- LIQ → RHOMBO
- LIQ → AuSb<sub>2</sub>
- LIQ → Au<sub>2</sub>Bi + AuSb<sub>2</sub>
- LIQ → Au<sub>2</sub>Bi + AuSb<sub>2</sub> + RHOMBO

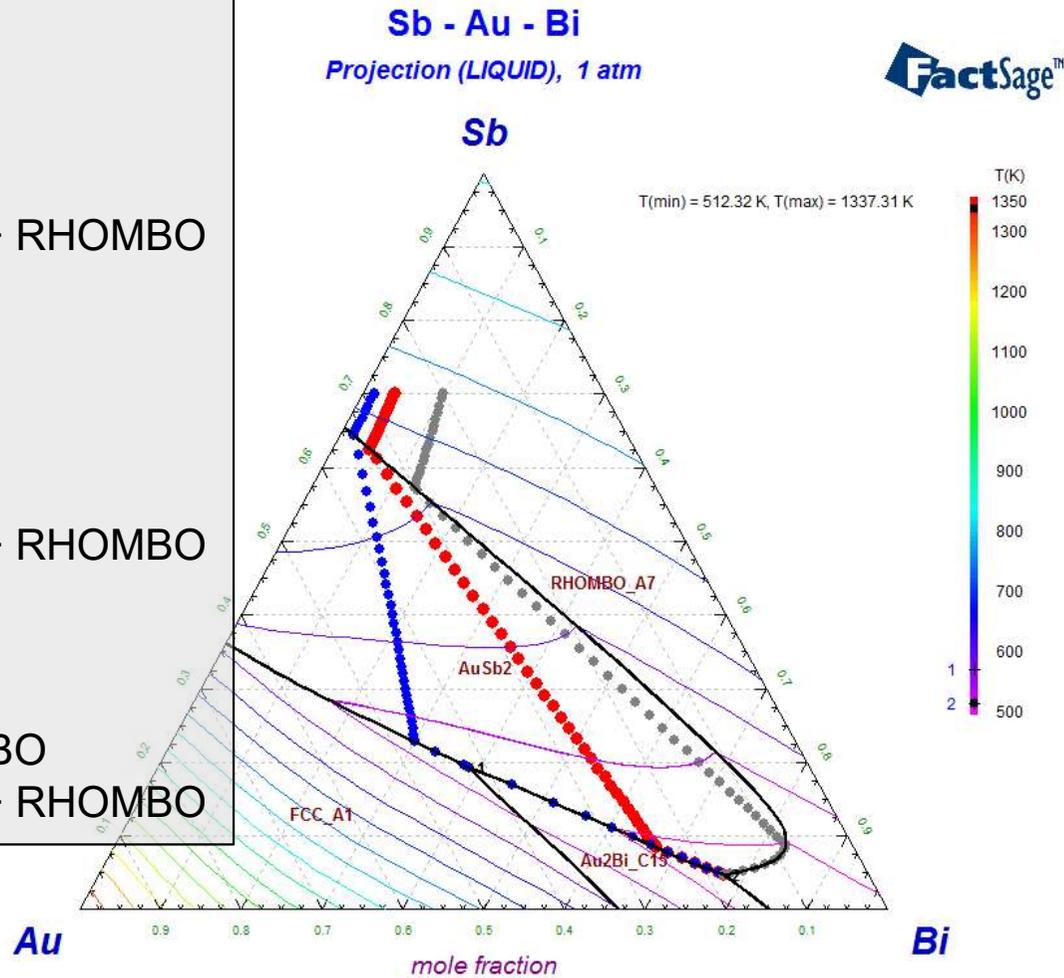
## Sb70-Au28.5-Bi1.5

- LIQ → RHOMBO
- LIQ → AuSb<sub>2</sub>
- LIQ → FCC + AuSb<sub>2</sub>
- LIQ → Au<sub>2</sub>Bi + AuSb<sub>2</sub>
- LIQ → Au<sub>2</sub>Bi + AuSb<sub>2</sub> + RHOMBO



# 3 components: Scheil cooling

- Sb70-Au26-Bi4**
  - LIQ → RHOMBO
  - LIQ → AuSb2
  - LIQ → AuSb2 + Au2Bi
  - LIQ → AuSb2 + Au2Bi + RHOMBO
- Sb70-Au28.5-Bi1.5**
  - LIQ → RHOMBO
  - LIQ → AuSb2
  - LIQ → AuSb2 + FCC
  - LIQ → AuSb2 + Au2Bi
  - LIQ → AuSb2 + Au2Bi + RHOMBO
- Sb70-Au20-Bi10**
  - LIQ → RHOMBO
  - LIQ → AuSb2
  - LIQ → AuSb2 + RHOMBO
  - LIQ → AuSb2 + Au2Bi + RHOMBO



# 3 components: Scheil cooling

## Sb70-Au26-Bi4

- LIQ → RHOMBO
- LIQ → AuSb2
- LIQ → AuSb2 + Au2Bi
- LIQ → AuSb2 + Au2Bi + RHOMBO

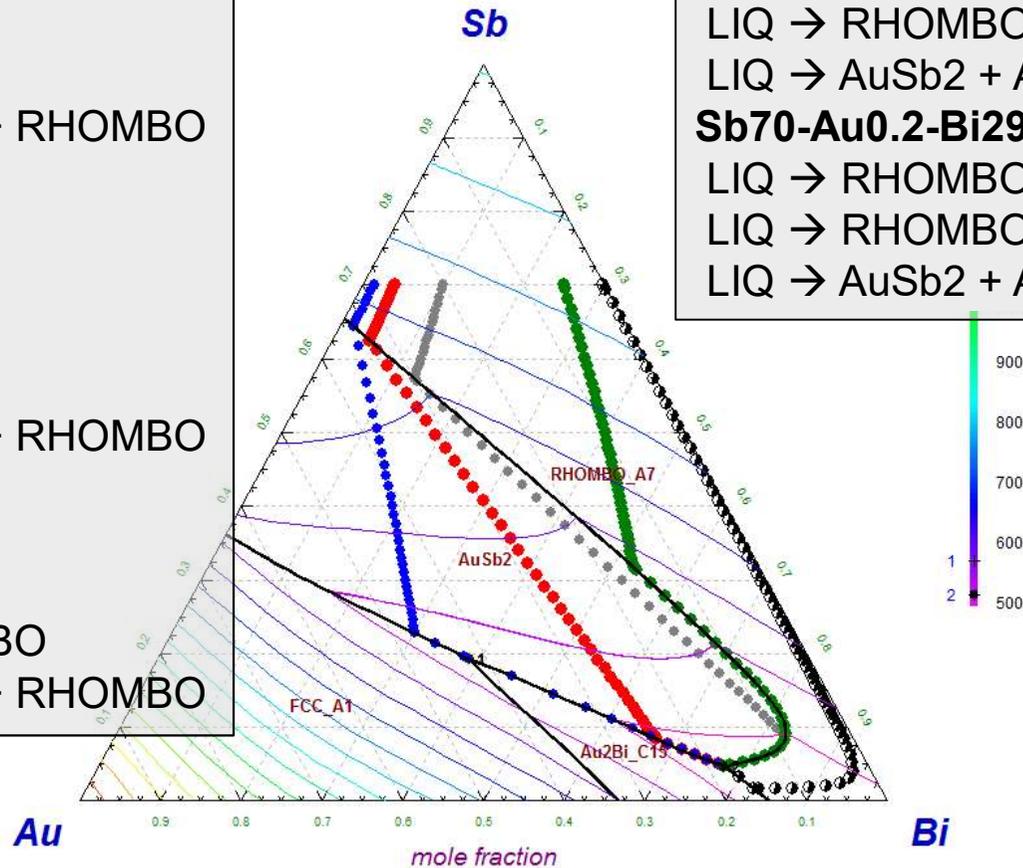
## Sb70-Au28.5-Bi1.5

- LIQ → RHOMBO
- LIQ → AuSb2
- LIQ → AuSb2 + FCC
- LIQ → AuSb2 + Au2Bi
- LIQ → AuSb2 + Au2Bi + RHOMBO

## Sb70-Au20-Bi10

- LIQ → RHOMBO
- LIQ → AuSb2
- LIQ → AuSb2 + RHOMBO
- LIQ → AuSb2 + Au2Bi + RHOMBO

Sb - Au - Bi  
Projection (LIQUID), 1 atm



## Sb70-Au5-Bi25

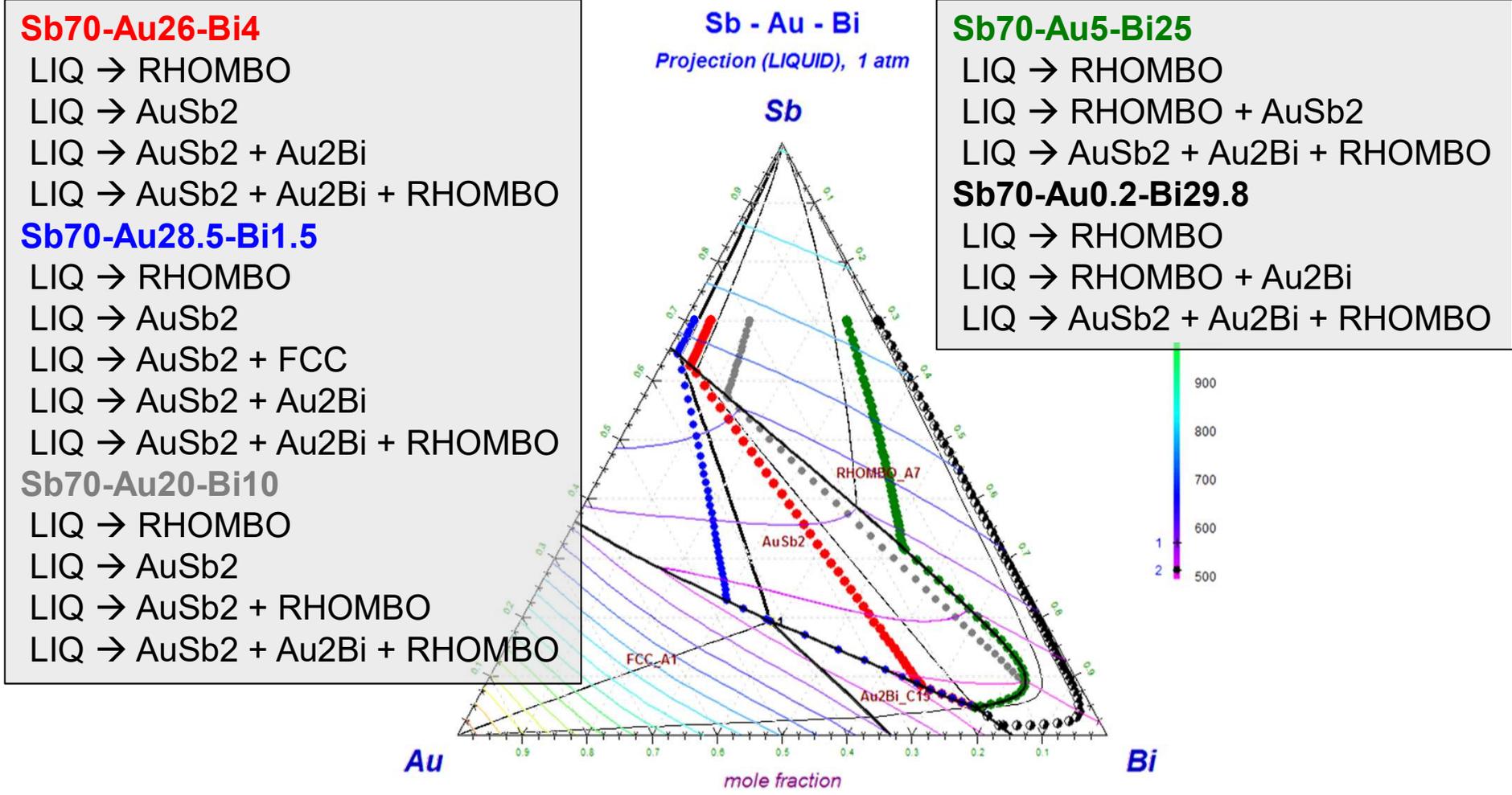
- LIQ → RHOMBO
- LIQ → RHOMBO + AuSb2
- LIQ → AuSb2 + Au2Bi + RHOMBO

## Sb70-Au0.2-Bi29.8

- LIQ → RHOMBO
- LIQ → RHOMBO + Au2Bi
- LIQ → AuSb2 + Au2Bi + RHOMBO



# Since FactSage7.1: 3-component Scheil mapping



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## Sb70-Au26-Bi4

- LIQ → RHOMBO
- LIQ → AuSb2
- LIQ → AuSb2 + Au2Bi
- LIQ → AuSb2 + Au2Bi + RHOMBO

## Sb70-Au28.5-Bi1.5

- LIQ → RHOMBO
- LIQ → AuSb2
- LIQ → AuSb2 + FCC
- LIQ → AuSb2 + Au2Bi
- LIQ → AuSb2 + Au2Bi + RHOMBO

## Sb70-Au20-Bi10

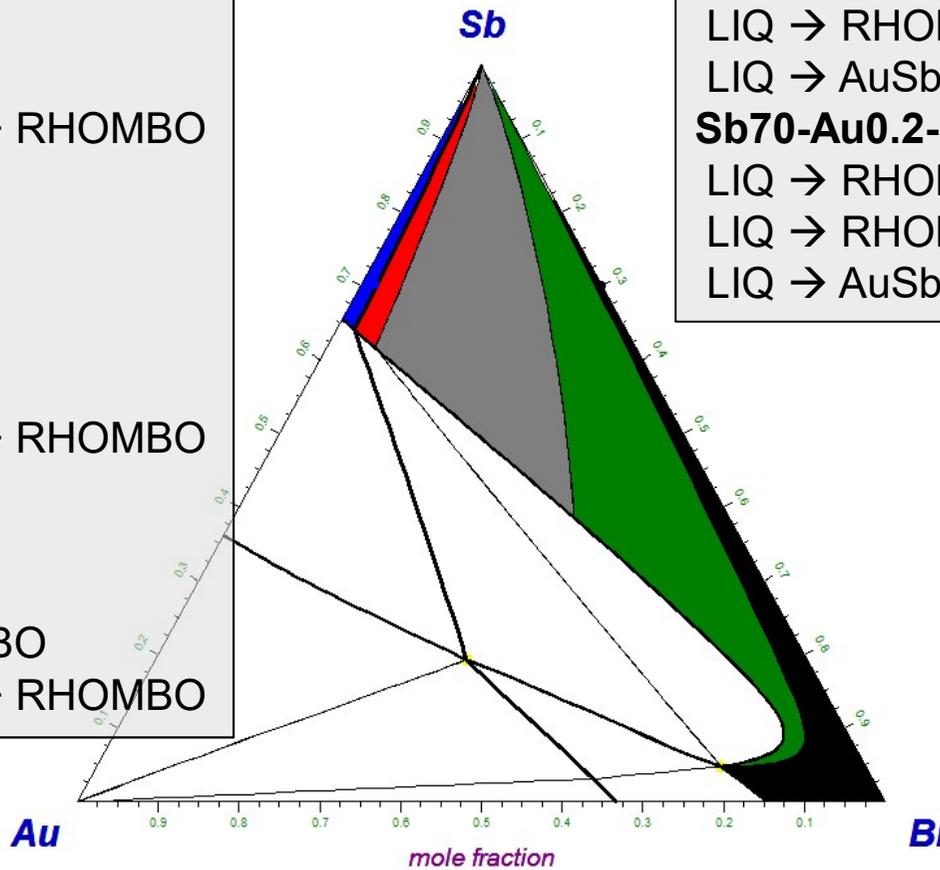
- LIQ → RHOMBO
- LIQ → AuSb2
- LIQ → AuSb2 + RHOMBO
- LIQ → AuSb2 + Au2Bi + RHOMBO

## Sb70-Au5-Bi25

- LIQ → RHOMBO
- LIQ → RHOMBO + AuSb2
- LIQ → AuSb2 + Au2Bi + RHOMBO

## Sb70-Au0.2-Bi29.8

- LIQ → RHOMBO
- LIQ → RHOMBO + Au2Bi
- LIQ → AuSb2 + Au2Bi + RHOMBO



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- Dormant species
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Pertti Koukkari, *Introduction to constrained Gibbs energy methods in process and materials research*

[www.vtt.fi/inf/pdf/technology/2014/T160.pdf](http://www.vtt.fi/inf/pdf/technology/2014/T160.pdf)

Risto Pajarre, *Modelling of chemical processes and materials by free energy minimization*

[www.vtt.fi/inf/pdf/science/2016/S141.pdf](http://www.vtt.fi/inf/pdf/science/2016/S141.pdf)



# Immaterial system components

- In a full equilibrium calculation, acetic acid would react to  $\text{CO}_2 + \text{CH}_4$ :
- However, acetic acid does not decompose spontaneously at room temperature.

```

T = 25 C
P = 1 bar
V = 50.779 dm3

```

STREAM CONSTITUENTS	AMOUNT/mol			
CH3COOH	1.0000E+00			
H2O	5.5508E+01			
PHASE: gas ideal		EQUIL AMOUNT	MOLE FRACTION	FUGACITY
		mol		bar
CH4	9.9933E-01	4.8786E-01	4.8786E-01	4.8786E-01
CO2	9.8402E-01	4.8038E-01	4.8038E-01	4.8038E-01
H2O	6.5053E-02	3.1758E-02	3.1758E-02	3.1758E-02
H2	3.9065E-06	1.9071E-06	1.9071E-06	1.9071E-06
C2H6	2.3499E-07	1.1472E-07	1.1472E-07	1.1472E-07
CO	5.6128E-10	2.7401E-10	2.7401E-10	2.7401E-10
TOTAL:	2.0484E+00	1.0000E+00	1.0000E+00	1.0000E+00
System component		Amount/mol	Amount/gram	Mole fraction
O	2.0331	32.528	0.24965	
C	1.9834	23.821	0.24354	
H	4.1274	4.1602	0.50681	
PHASE: aqueous		mol	MOLALITY	ACTIVITY
H2O_liquid	5.5443E+01	5.5508E+01	9.9970E-01	
H[+]	8.1229E-05	8.1325E-05	8.1325E-05	
H2	1.5955E-09	1.5974E-09	1.5974E-09	
CH4	6.6978E-04	6.7057E-04	6.7057E-04	
C2H2	5.2788E-40	5.2850E-40	5.2850E-40	
C2H4	6.1309E-22	6.1381E-22	6.1381E-22	
C2H6	1.9969E-10	1.9992E-10	1.9992E-10	
CH3COO[-]	1.5757E-10	1.5776E-10	1.5776E-10	
CH3COOH	6.9564E-10	6.9646E-10	6.9646E-10	



# Immaterial system components

- In a full equilibrium calculation, acetic acid would react to  $\text{CO}_2 + \text{CH}_4$ :
- However, acetic acid does not decompose spontaneously at room temperature.
- One option is to set the gas phase dormant:

```

T = 25 C
P = 1 atm
V = 0 dm3

```

STREAM CONSTITUENTS	AMOUNT/mol			
CH3COOH	1.0000E+00			
H2O	5.5508E+01			
		EQUIL AMOUNT	MOLALITY	ACTIVITY
		mol		
PHASE: aqueous				
H2O_liquid	5.5508E+01	5.5508E+01	9.6460E-01	
H[+]	6.3390E-04	6.3391E-04	6.3391E-04	
H2	3.4637E-09	3.4637E-09	3.4637E-09	
CH4	9.9957E-01	9.9958E-01	9.9958E-01	
C2H2	1.1519E-34	1.1519E-34	1.1519E-34	
C2H4	2.9008E-16	2.9009E-16	2.9009E-16	
C2H6	2.0487E-04	2.0487E-04	2.0487E-04	
CH3COO[-]	1.8940E-06	1.8940E-06	1.8940E-06	
CH3COOH	6.5176E-05	6.5177E-05	6.5177E-05	
HC03[-]	6.3200E-04	6.3201E-04	6.3201E-04	
HC204[-]	7.8563E-16	7.8564E-16	7.8564E-16	
TOTAL:	5.7508E+01		1.0000E+00	



# Immaterial system components

- In a full equilibrium calculation, acetic acid would react to  $\text{CO}_2 + \text{CH}_4$ :
- However, acetic acid does not decompose spontaneously at room temperature.
- ~~One option is to set the gas phase dormant:~~

```

T = 25 C
P = 1 atm
V = 0 dm3

STREAM CONSTITUENTS          AMOUNT/mol
CH3COOH                      1.0000E+00
H2O                          5.5508E+01

                                EQUIL AMOUNT      MOLALITY      ACTIVITY
                                mol
PHASE: aqueous
H2O_liquid                   5.5508E+01      5.5508E+01      9.6460E-01
H[+]                         6.3390E-04      6.3391E-04      6.3391E-04
H2                            3.4637E-09      3.4637E-09      3.4637E-09
CH4                           9.9957E-01      9.9958E-01      9.9958E-01
C2H2                         1.1519E-34      1.1519E-34      1.1519E-34
C2H4                         2.9008E-16      2.9009E-16      2.9009E-16
C2H6                         2.0487E-04      2.0487E-04      2.0487E-04
CH3COO[-]                    1.8940E-06      1.8940E-06      1.8940E-06
CH3COOH                      6.5176E-05      6.5177E-05      6.5177E-05
HCO3[-]                      6.3200E-04      6.3201E-04      6.3201E-04
HC2O4[-]                     7.8563E-16      7.8564E-16      7.8564E-16
TOTAL:                       5.7508E+01

```

We need to introduce a real constraint  $\text{CH}_3\text{COOH}$  may ONLY dissociate!



# Immaterial system components

- Therefore, the stoichiometric matrix of the aqueous solution species is adjusted:

Species	H	O	C	e(aq)	V
H <sub>2</sub> O	2	1	0	0	0
H[+]	1	0	0	-1	0
OH[-]	1	1	0	1	0
...					
CH <sub>3</sub> COO[-]	3	2	2	1	1
CH <sub>3</sub> COOH	4	2	2	0	1



# Immaterial system components

The screenshot displays the FactSage 7.3 software interface. The window title is "Energy: Joules Pressure: atm CH3COOH". The menu bar includes "File", "Edit", "Units", "View", "Tools", "ViewData", and "Help". The "Formula" field contains "CH3COOH".

The left sidebar shows a tree view of the database structure. Under "CH3COOH", the "Aq1" phase is selected and highlighted in blue. Other phases listed include "L1", "G1", and "Cp 473".

The main panel displays "Aq1 properties". The "Heat of form. + Entropy" radio button is selected. The "Form. of Aq1" section shows the following values:

$\Delta H_{298}$ (Joules)	$S_{298}$ (J/(mol K))
-485762.425104	178.656787448

The "Phase Name" is "Aqueous", the "Reference no." is "7", and the "Density g/cc" is empty.

The status bar at the bottom indicates "FactSage 7.3" and the file path "C:\FACTSAGE73\FACTDATA\F553base.cdb (v7.30) 4920 compounds read-only".



# Immaterial system components

The image displays two overlapping windows from the FactSage 7.3 software, illustrating immaterial system components.

**Top Window: CH3COOH**

- Formula: CH3COOH
- Aq1 properties:
  - Heat of form. + Entropy (selected)
  - Form. of Aq1:
 

$\Delta H_{298}$ (Joules)	S298 (J/(mol K))
-485762.425104	178.656787448

**Bottom Window: CH3COOV[-]**

- Formula: CH3COOV[-]
- Aq1 properties:
  - Heat of form. + Entropy (selected)
  - Form. of Aq1:
 

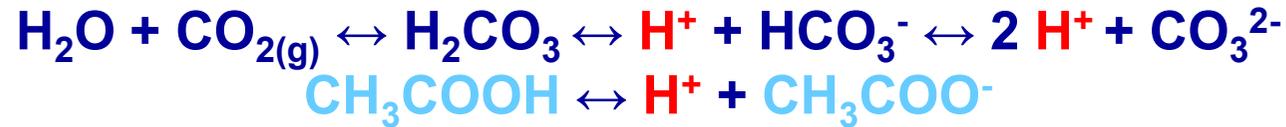
$\Delta H_{298}$ (Joules)	S298 (J/(mol K))
-485762.425104	178.656787448
  - Phase Name, Reference no., Density g/cc table:
 

Phase Name	Reference no.	Density g/cc

Both windows show a tree view of databases on the left. The top window's tree includes CH3COOH with sub-components L1, G1, and Aq1 (Cp 473). The bottom window's tree includes CH3COOV[-] with sub-components Aq1 (Cp 573) and CH3COOHV with sub-component Aq1 (Cp 473).



# Example 1: Water + carbonic acid + acetic acid



Equilib - Reactants

File Edit Table Units Data Search Data Evaluation Help

T(C) P(atm) Energy(J) Quantity(mol) Vol(litre)

1 - 3

Quantity(mol)	Species	Phase	T(C)	P(total)**	Stream#	Data
1 kg	H2O				1	
+ 1	H2CO3				1	
+ <A>	CH3COOH				1	

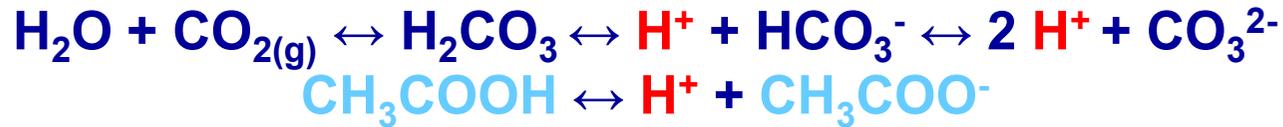
Initial Conditions

Next >>

FactSage 7.3 Compound: 2/35 databases Solution: 1/34 databases



# Example 1: Water + carbonic acid + acetic acid



Selection - Equilib Page 11/11 : T(C) = 25, P(atm) = 1, Alpha = 1

File Edit Show Sort

Selected: 22/30 **AQUEOUS** 11 Pages: 1 - 11 [page]

Page 11/11 : T(C) = 25, P(atm) = 1, Alpha = 1 [min = 0 at p. 1; max = 1 at p. 11]

+	Code	Species	Data	Phase	T	V	Activity	Minimum	Maximum
+	75	HCOO(-)(aq)	FactPS	aqueous			1.4998E-33	1.4998E-33 [11]	5.5426E-32 [1]
+	76	HCOOH(aq)	FactPS	aqueous			3.3068E-32	3.3068E-32 [11]	3.3441E-32 [1]
	77	CH3COO(-)(aq)	FactPS	aqueous					
	78	CH3COOH(aq)	FactPS	aqueous			8.9433E-97		
+	79	HCO3(-)(aq)	FactPS	aqueous			3.1263E-06	3.1263E-06 [11]	1.1623E-04 [1]
+	80	HC2O4(-)(aq)	FactPS	aqueous			7.5232E-42	7.5232E-42 [11]	2.7786E-40 [1]
	81	VO[2+](aq)	FactPS	aqueous					
	82	VO2[+](aq)	FactPS	aqueous					
	83	VO3(-)(aq)	FactPS	aqueous					
	84	VO4(-)(aq)	FactPS	aqueous					
	85	HVO4[2-](aq)	FactPS	aqueous					
	86	HV10O28[5-](aq)	FactPS	aqueous					
+	87	CH3COOV(-)(aq)	TEMP	Aq1			4.2443E-03	0 [1]	4.2443E-03 [11]
+	88	CH3COOHV(aq)	TEMP	Aq1			0.9786	0 [1]	0.9786 [11]

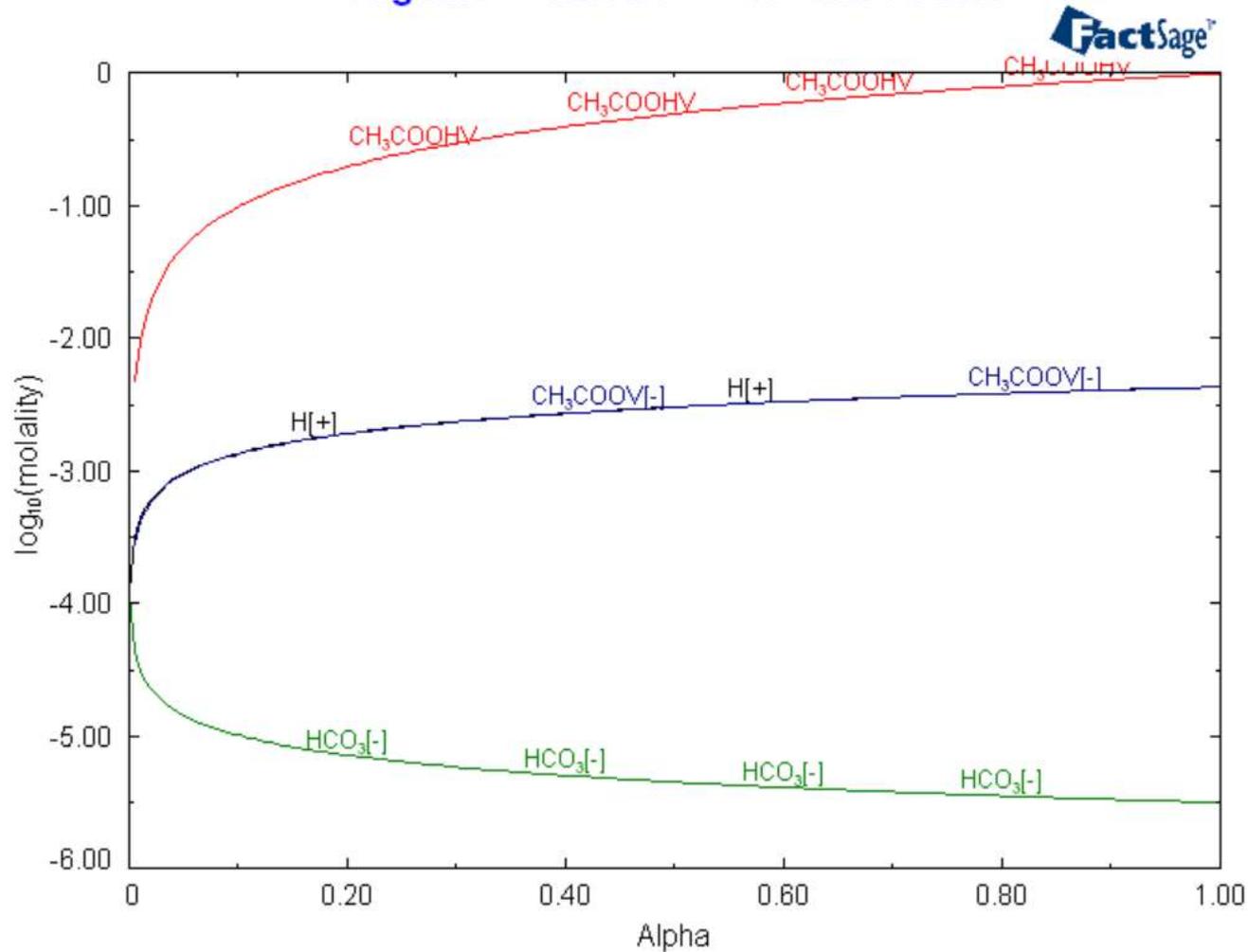
permit selection of 'X' species Help Suppress Duplicates Edit priority list:

Show Selected Select All Select/Clear... Clear OK



# Example 1: Water + carbonic acid + acetic acid

1 kg H<sub>2</sub>O + H<sub>2</sub>CO<sub>3</sub> + <A> CH<sub>3</sub>COOHV



## Example 2: Anatase → Rutile conversion

[Koukkari, Pajarre, Hack, SGTE Casebook Chapter IV.9]

- The growth of rutile is kinetically hindered and follows the growth law:

$$x_{rutile} = 1 - (1 - kt)^3 \quad \text{with} \quad k = A \exp\left(-\frac{E_A}{RT}\right)$$

- The stoichiometric matrix is adjusted as follows:

Species	Ti	O	Vi
Rutile	1	2	1
Anatase	1	2	0



# Example 2: Anatase → Rutile conversion

[Koukkari, Pajarre, Hack, SGTE Casebook Chapter IV.9]

- In FactSage, **Vi** cannot be entered. Therefore, **Ar** has been used.

Energy: Joules Pressure: bar O2Ti

Formula: TiO2

S1 properties  
 Heat of form. + Entropy  Heat + Temperature of transf.

Form. of S1  
 $\Delta H_{298}$  (Joules) S298 (J/(mol·K))  
 -944000 50.62

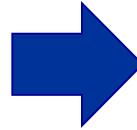
Phase Name Reference no. Density g/cc  
 RUTILE

Extended properties (optional)

Birch-Murnaghan  
 Therm. expans. (/K) Compressibility (/bar) Bulk mod. deriv.  
 T T (T-T0)ln(T/T0)  
 /T T^2  
 /T^2 T^3

Magnetic Moment (D) Temperature P factor  
 Curie  Neel K  0.28  0.40

FactSage 7.2 | C:\FACTSAGE72\FACTDATA\SGPSbase.cdb (v7.20) 3842 compounds read-only



Energy: Joules Pressure: bar TiO2Ar

Formula: TiO2Ar

S1 properties  
 Heat of form. + Entropy  Heat + Temperature of transf.

Form. of S1  
 $\Delta H_{298}$  (Joules) S298 (J/(mol·K))  
 -944000 50.62

Phase Name Reference no. Density g/cc  
 Rutile\_Ar

Extended properties (optional)

Birch-Murnaghan  
 Therm. expans. (/K) Compressibility (/bar) Bulk mod. deriv.  
 T T (T-T0)ln(T/T0)  
 /T T^2  
 /T^2 T^3

Magnetic Moment (D) Temperature P factor  
 Curie  Neel K  0.28  0.40

FactSage 7.2 | Modified | C:\FACTSAGE72\FACTDATA\KINETICRETRAQ\KINEBASE.CDB (v5.0) 41 compounds rea



# Example 2: Anatase → Rutile conversion

[Koukkari, Pajarre, Hack, SGTE Casebook Chapter IV.9]

Selection - Equilib Page 1/1: T(C) = 1000, P(atm) = 1, Alpha = 0.3

File Edit Show Sort

Selected: 2/13 SOLID

Page 1/1: T(C) = 1000, P(atm) = 1, Alpha = 0.3

+	Code	Species	Data	Phase	T	V	Activity	Minimum	Maximum
17	Ti(s)		SGPS	S1		o			
18	Ti(s2)		SGPS	S2		o			
19	OTi(s)		SGPS	ALPHA		o			
20	OTi(s2)		SGPS	BETA		o			
21	O2T(s)		SGPS	RUTILE		o			
+	22	O2T(s2)	SGPS	ANATASE		o	1.000	1.000	1.000
23	O3T2(s)		SGPS	S1		o			
24	O3T2(s2)		SGPS	S2		o			
25	O5T3(s)		SGPS	S1		o			
26	O5T3(s2)		SGPS	S2		o			
27	O7T4(s)		SGPS	S1		o			
28	Ar(s)		KINE	S1		o			
+	29	TiO2Ar(s)	KINE	S1		o	1.000	1.000	1.000

permit selection of \* species Help Suppress Duplicates Edit priority list:

Show Selected Select All Select/Clear... Clear OK

Equilib - Results 1000 C

Output Edit Show Pages

T(C) P(atm) Energy(J) Mass(mol) Vol(litre)

FactSage 7.2

T = 1000 C  
P = 1 atm  
V = 0 dm3

STREAM CONSTITUENTS

STREAM CONSTITUENTS	AMOUNT/mol
TiO2	1.0000E+00
Ar	3.0000E-01

EQUIL AMOUNT

EQUIL AMOUNT	ACTIVITY
mol	
O2Ti_ANATASE (s2)	7.0000E-01 1.0000E+00
TiO2Ar_S1 (s)	3.0000E-01 1.0000E+00

\*\*\*\*\*

Cp	H	S	G	V
J.K-1	J	J.K-1	J	dm3

\*\*\*\*\*

7.50606E+01	-8.68054E+05	1.48881E+02	-1.05760E+06	0.00000E+00
-------------	--------------	-------------	--------------	-------------

\*\*\*\*\*

Cp	H	S	G
J.K-1	J	J.K-1	J

\*\*\*\*\*

O2Ti_ANATASE (s2)	5.17787E+01	-6.05257E+05	1.04366E+02	-7.38131E+05
TiO2Ar_S1 (s)	2.32819E+01	-2.62796E+05	4.45147E+01	-3.19470E+05

Cut-off limit for phase activities = 1.00E-70

Databases: KINE 7.0, SGPS 7.2

Data Search options: exclude gas ions; organic CxHy.. X(max) = 2; min soln cpts = 2



# Immaterial system components

System	Constraint	Matrix element	Conjugate potential	Practical examples
Chemical equilibrium systems	$\sum_{k=1}^N a_{kj} n_k = b_j$	$a_{kj}$	$\pi_j = \frac{\partial G}{\partial b_j}$	Multiphase chemical equilibrium Phase diagrams
Systems with area constraints	$\sum_{k=1}^{N_s} A_k n_k^s = A$	$\frac{A_k}{A_0}$	$\pi_{area} = \frac{\partial G}{\partial b_{(area)}} = \sigma A_0$	Surface and interface systems, sorption phenomena
Systems with volume constraints	$\sum_{k=1}^{N_F} V_k n_k^F = V_F$	$\frac{V_k}{V_0}$	$\pi_F = \frac{\partial G}{\partial b_{(V_F)}} = \Pi \bar{V}_F$	Osmotic systems, fibers and membranes
EOR-controlled complex systems	$\sum_{k=1}^N a_{kr} n_k = b_{(r)}$	$v_{kr}$	$\pi_{(r)} = \frac{\partial G}{\partial b_{(r)}} = \frac{\partial G}{\partial \zeta_i} = -Aff_i$	Reactive systems Partial and 'super' equilibria

Para-equilibrium systems	$u_k = \frac{n_k}{\sum_M n_M} = const.$	$\frac{n_{Fk}}{n_M} a_{k,M} - a_{k,Fk}$	$\frac{\partial G}{\partial \zeta} = \sum_{M^*} a_{k,M^*} \left( \frac{\partial G}{\partial b_{M^*}} \right) = \sum_{M^*} a_{k,M^*} \pi_{M^*}$	Paraequilibria, co-precipitation
System with external magnetic field	$B = const.$	$\frac{\Delta_M \mu_i}{f(B) M_0}$	$\pi_M \equiv \frac{\partial G}{\partial b_M} = f(B) M_0$	Magnetic phase stability
Electrochemical (Donnan) multi-phase systems	$\sum_{k=1}^{N_a} z_k n_k^\alpha = Q^\alpha$	$z_k$	$\pi_{(q^\alpha)} = \frac{\partial G}{\partial b_{(q^\alpha)}} = F \Delta \varphi^\alpha$	Electrochemical membrane systems, Pulp suspensions
Constant contribution pH	$pH = const.$	$N_{H,k}$	$\pi_{H_a} \equiv RT \ln 10 pH_a$	Biochemical systems (pH = 7 at standard state)
Constant contribution ionic strength	$I = \frac{1}{2} \sum_k z_k^2 c_k = const.$	$z_k^2$	$\pi_I \equiv \frac{-\alpha RT \sqrt{I}}{1 + B \sqrt{I}} = \frac{RT}{z_k^2} \ln \gamma_k$	Biochemical systems with constant ionic strength

Pertti Koukkari, *Introduction to constrained Gibbs energy methods in process and materials research*

[www.vtt.fi/inf/pdf/technology/2014/T160.pdf](http://www.vtt.fi/inf/pdf/technology/2014/T160.pdf)



# Grain boundary partitioning

- Grain boundary density can be considered as constraint.
- Thus, grain boundaries can be treated as another phase associated with a virtual systems component.



# Grain boundary partitioning

ARTICLE **OPEN**

## A machine learning approach to model solute grain boundary segregation

Liam Huber<sup>1</sup>, Raheleh Hadian<sup>1</sup>, Blazej Grabowski<sup>1</sup> and Jörg Neugebauer<sup>1</sup>

Even minute amounts of one solute atom per one million bulk atoms may give rise to qualitative changes in the mechanical response and fracture resistance of modern structural materials. These changes are commonly related to enrichment by several orders of magnitude of the solutes at structural defects in the host lattice. The underlying concept—segregation—is thus fundamental in materials science. To include it in modern strategies of materials design, accurate and realistic computational modelling tools are necessary. However, the enormous number of defect configurations as well as sites solutes can occupy requires models which rely on severe approximations. In the present study we combine a high-throughput study containing more than 1 million data points with machine learning to derive a computationally highly efficient framework which opens the opportunity to model this important mechanism on a routine basis.

*npj Computational Materials* (2018)4:64; doi:10.1038/s41524-018-0122-7

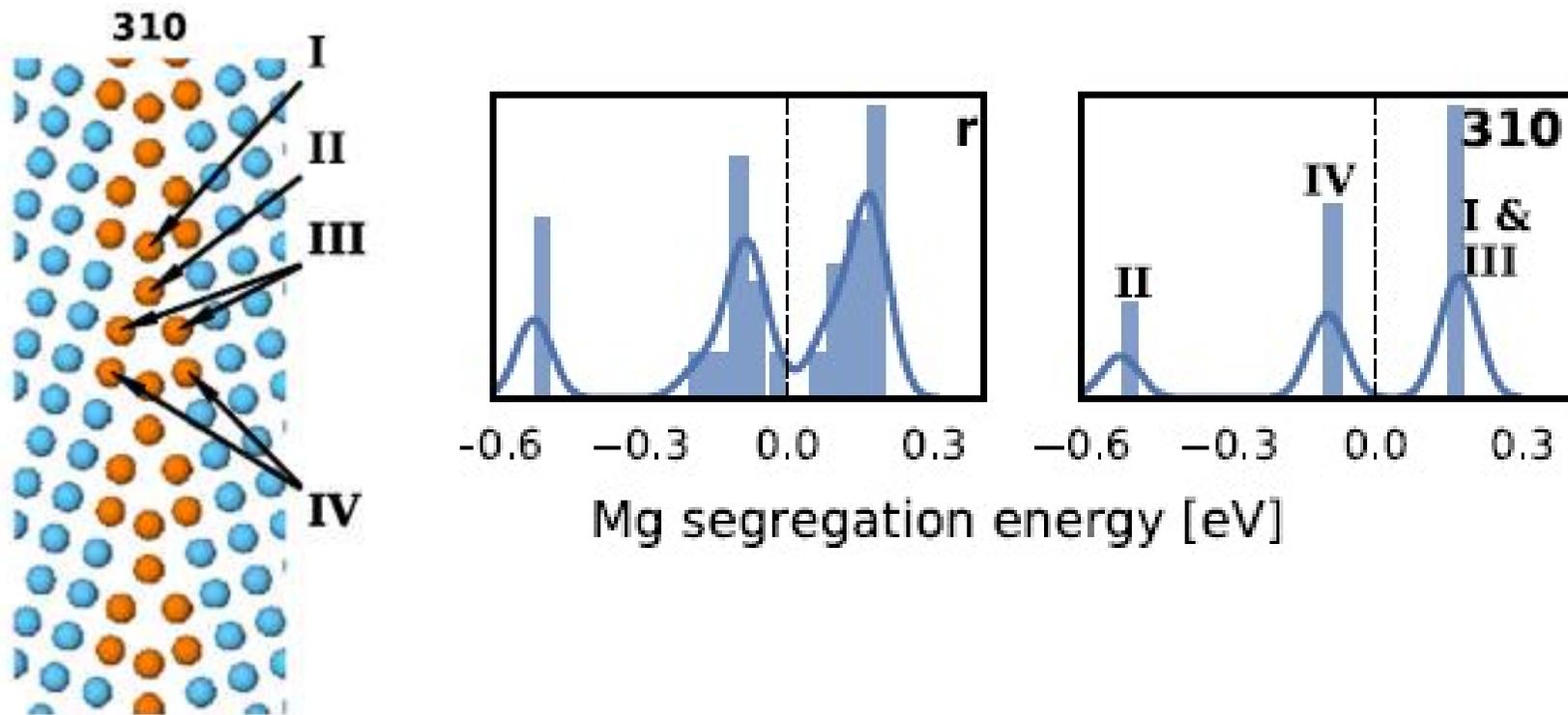


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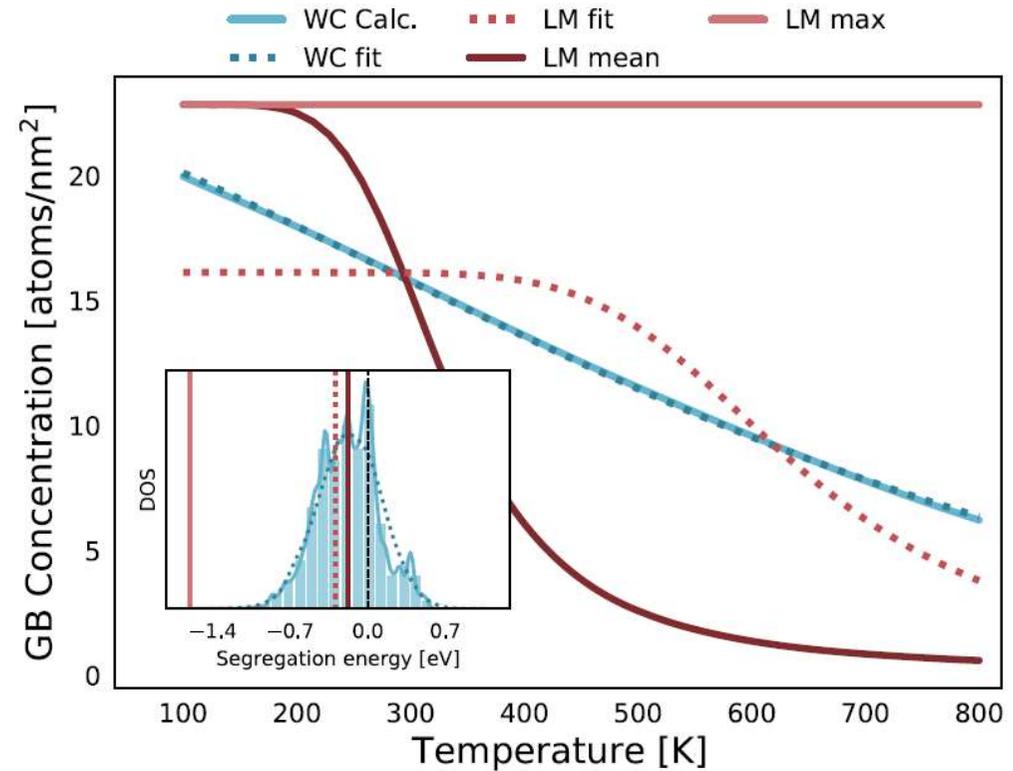
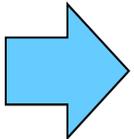
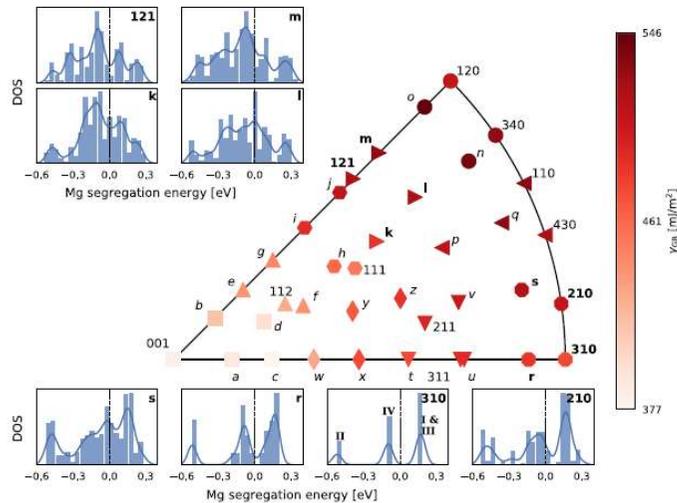


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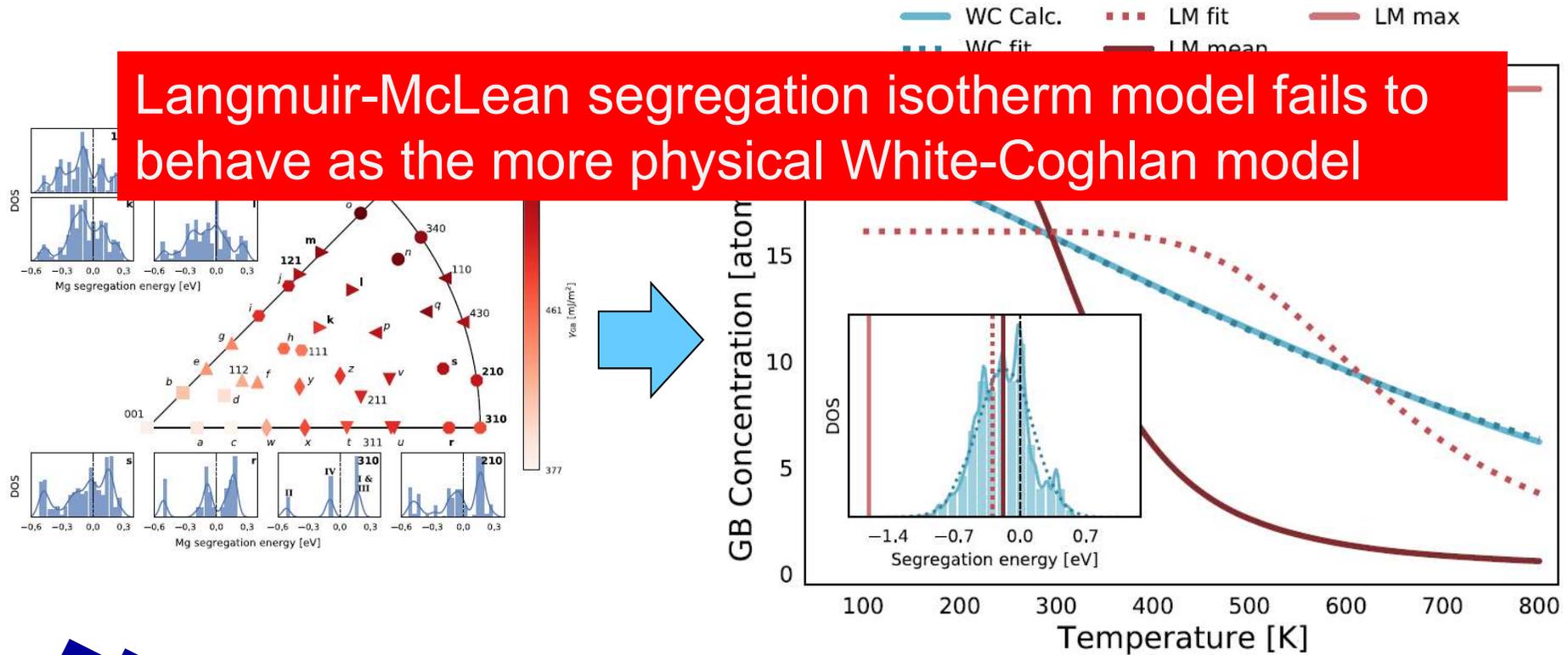
# Grain boundary partitioning

ARTICLE OPEN

A machine learning approach to model solute grain boundary segregation

Liam Huber<sup>1</sup>, Raheleh Hadian<sup>1</sup>, Blazej Grabowski<sup>1</sup> and Jörg Neugebauer<sup>1</sup>

Langmuir-McLean segregation isotherm model fails to behave as the more physical White-Coghlan model

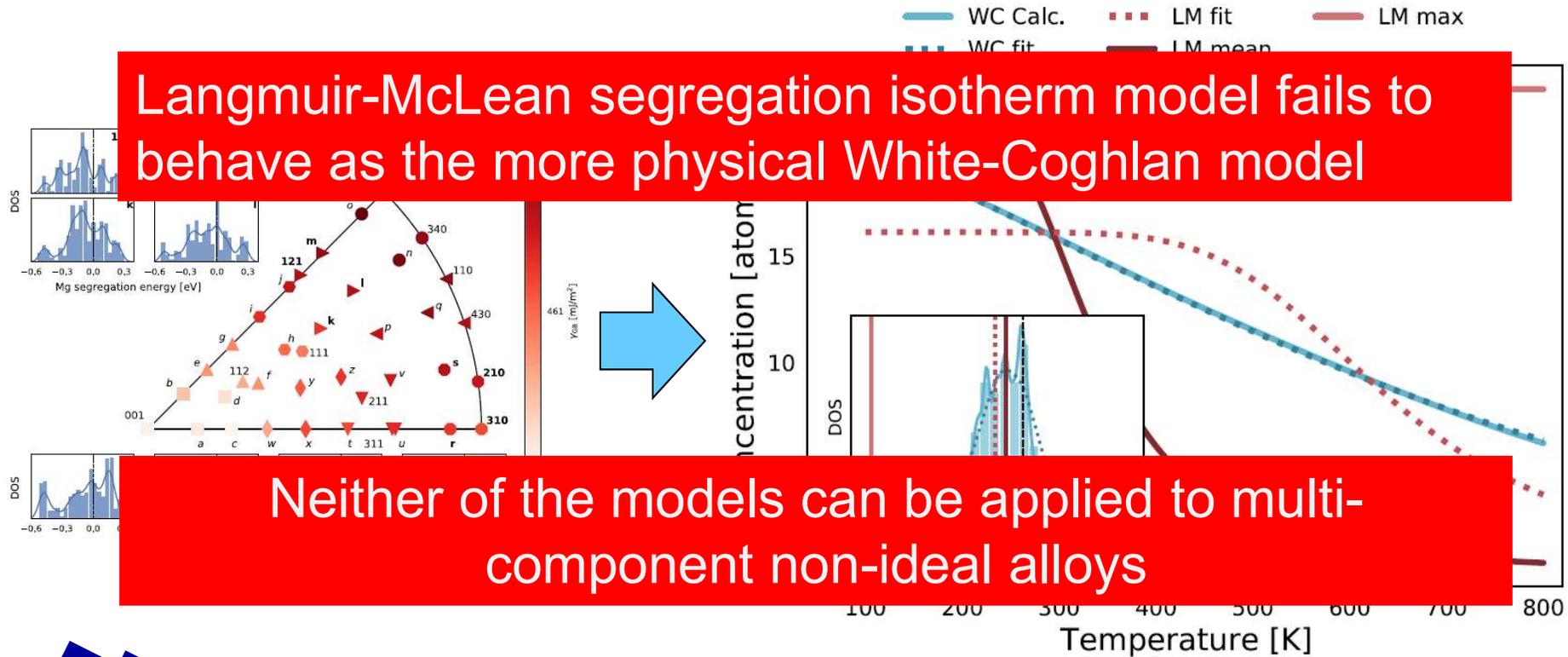


# Grain boundary partitioning

ARTICLE OPEN

## A machine learning approach to model solute grain boundary segregation

Liam Huber<sup>1</sup>, Raheleh Hadian<sup>1</sup>, Blazej Grabowski<sup>1</sup> and Jörg Neugebauer<sup>1</sup>

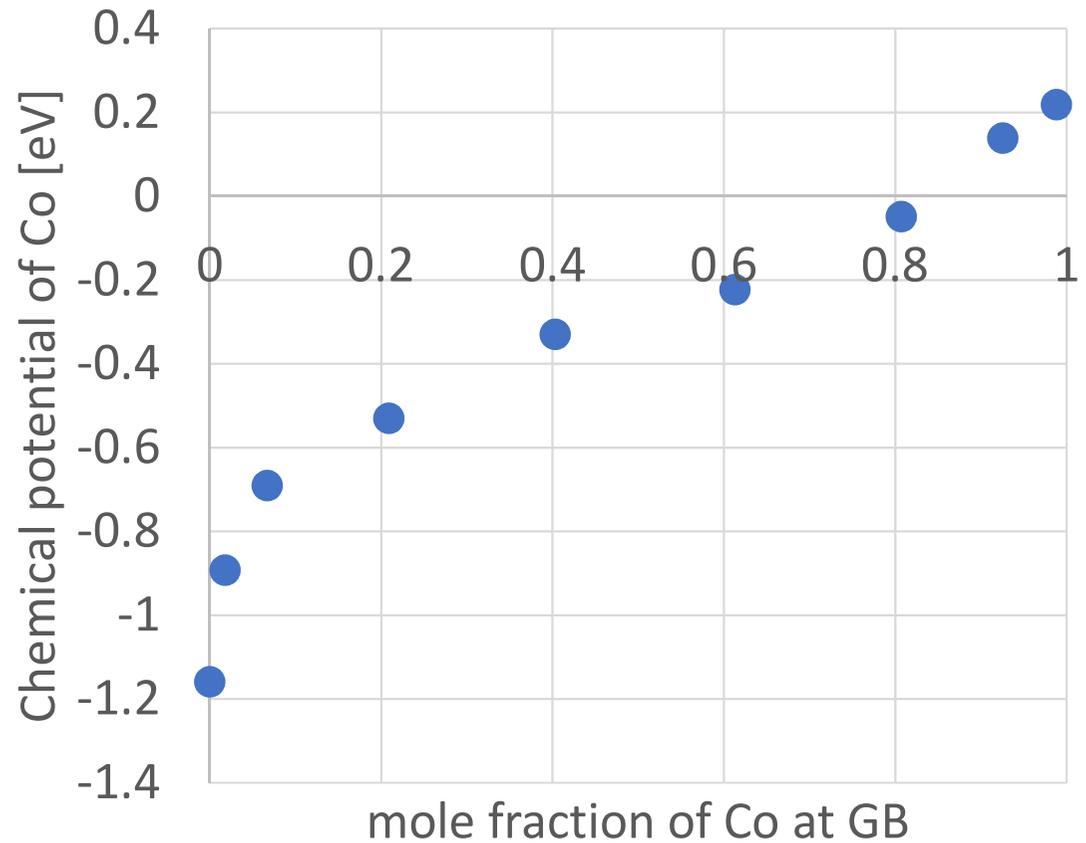
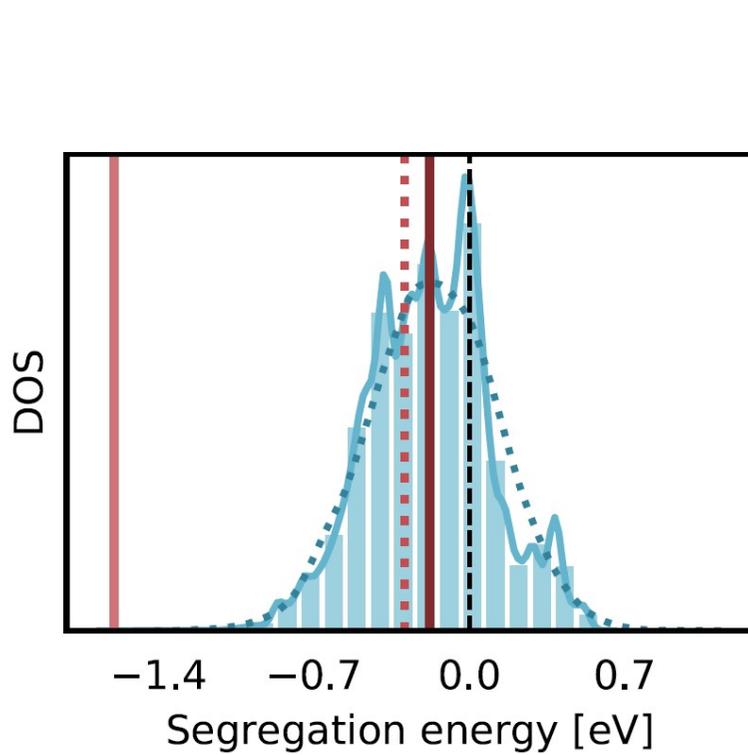


Langmuir-McLean segregation isotherm model fails to behave as the more physical White-Coghlan model

Neither of the models can be applied to multi-component non-ideal alloys



# Grain boundary partitioning



# Grain boundary partitioning

FactSage 7.3: Solution

File Edit Units Options Tools Help

Function Name  ACGBsoln.FCGB

Solution Name	Created	Last Modified	P factor
FCGB	2019.06.04	2019.06.04	<input checked="" type="radio"/> 0.28 <input type="radio"/> 0.40

Model Name  Compound Energy Formalism Lattices  2

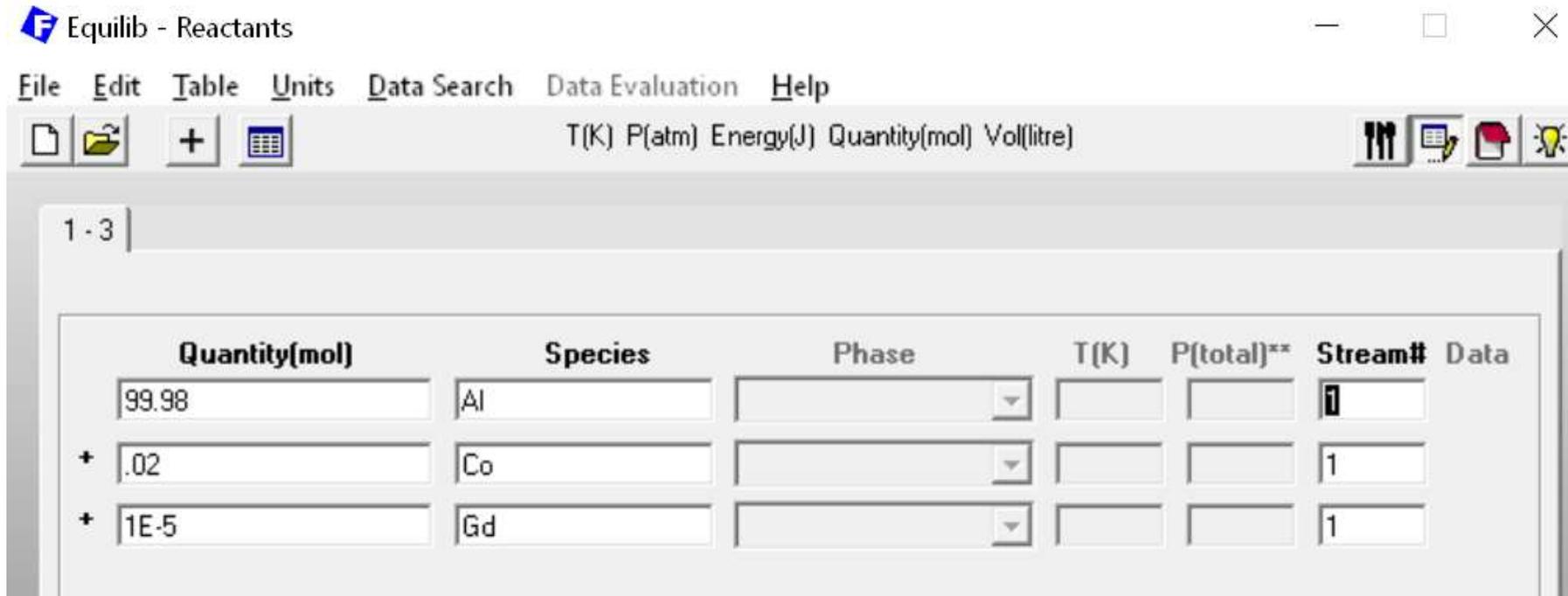
Solution description ...

GrainBoundary  
Original ChemSage file: C:\FactSage73\ChemSage\SGTE-AlCo.dat

- Solutions (2)
  - FCC\_ (12-2) (SUBL)
    - SubLattices
      - A (2)
        - Al
        - Co
      - B (1)
        - Va (A)
    - End Members (2)
      - (0) Al:Va
      - (1) Co:Va
    - Mixables (0)
    - Interactions (7)
  - FCGB (12-2) (SUBL)
    - SubLattices
      - A (2)
        - AIGB
        - CoGB
      - B (1)
        - Gd (A)
    - End Members (2)
      - (0) AIGB
      - (1) CoGB
    - Mixables (0)
    - Interactions (7)



# Grain boundary partitioning

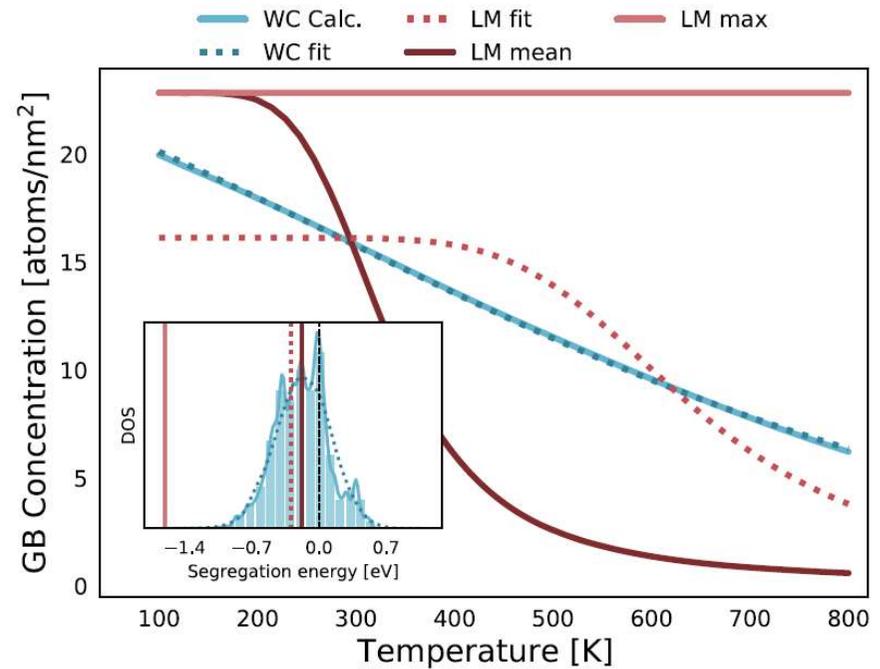
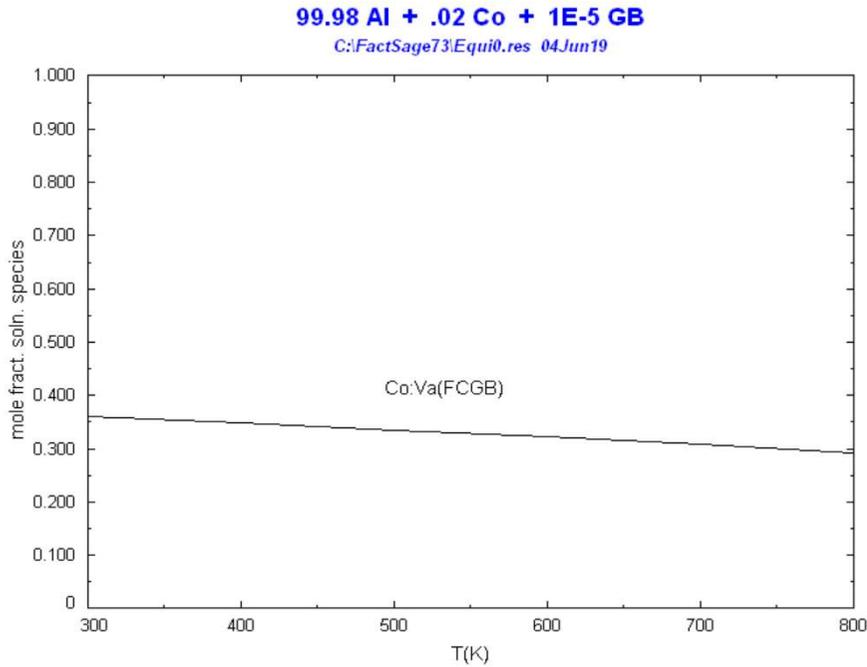


The screenshot shows the 'Equilib - Reactants' software window. The title bar includes the application name and standard window controls. The menu bar contains 'File', 'Edit', 'Table', 'Units', 'Data Search', 'Data Evaluation', and 'Help'. Below the menu bar is a toolbar with icons for file operations and a status bar displaying 'T(K) P(atm) Energy(J) Quantity(mol) Vol(litre)'. The main area shows a table with the following data:

Quantity(mol)	Species	Phase	T(K)	P(total)**	Stream#	Data
99.98	Al				1	
+ .02	Co				1	
+ 1E-5	Gd				1	



# Grain boundary partitioning



The behavior of the non-optimized FactSage model resembles the WC-model. The FactSage model can be applied to multi-component non-ideal alloys.



# Conclusion

- There are many ways how constraints can be considered semi-empirically in thermodynamic calculations.
- New routes and ideas will emerge!



**Thank you for your attention!**

