Introduction to the constrained equilibrium method

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Motivation

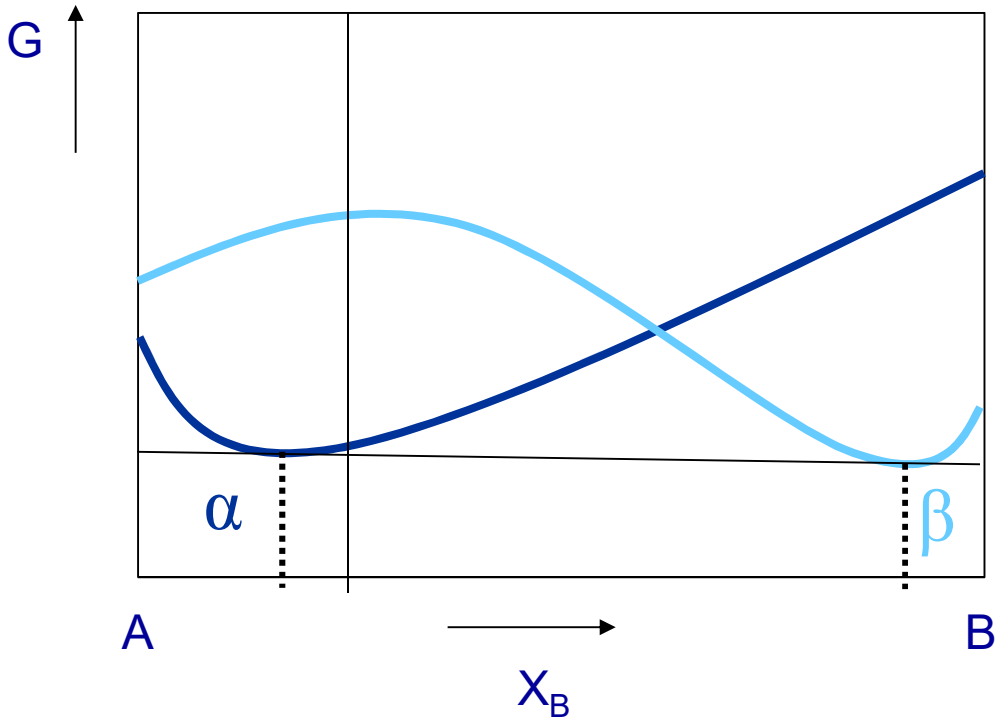
- Most technical processes are not in equilibrium.
- Kinetic limitations impose constraints on the equilibrium.
- Simple methods can sometimes be very effective in describing constrained equilibria.

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.



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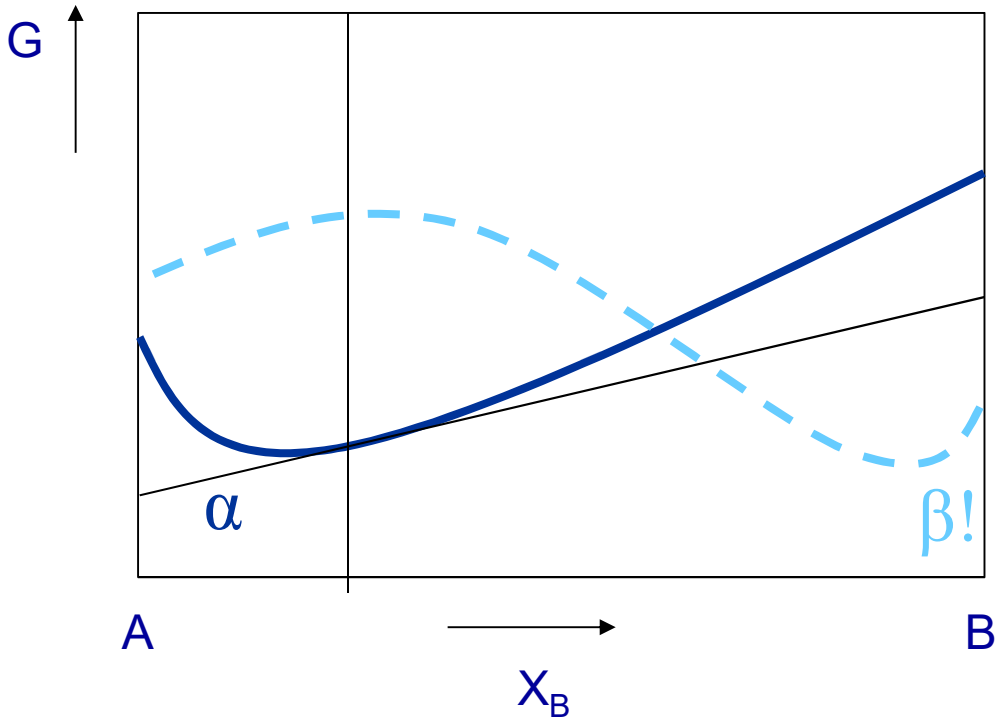

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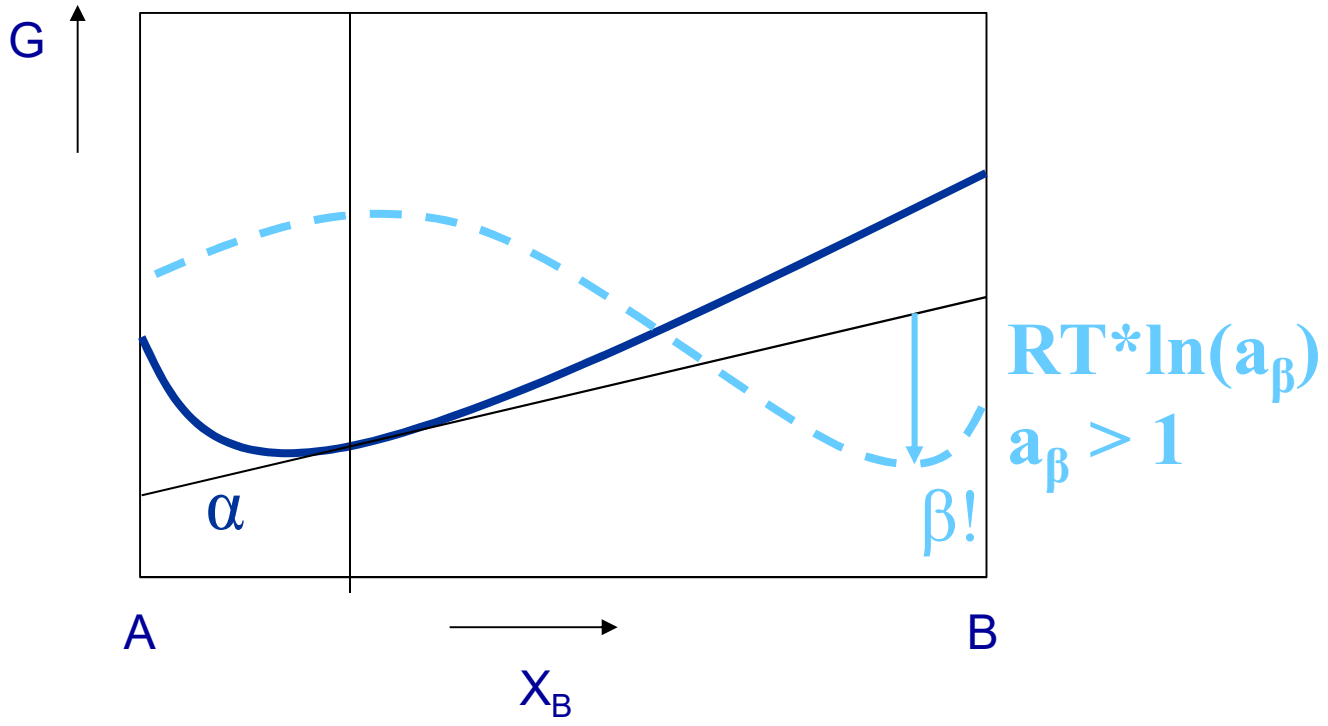

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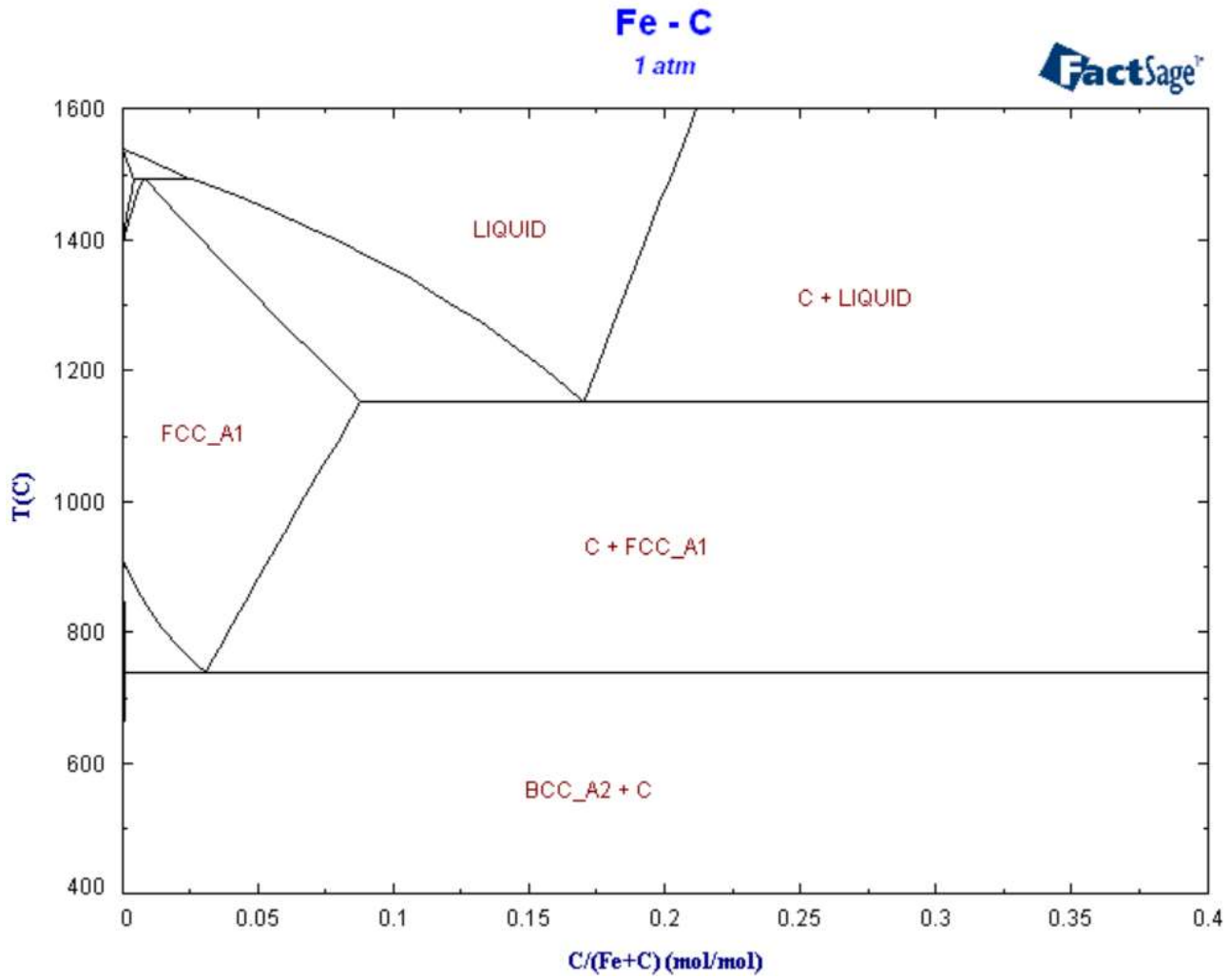

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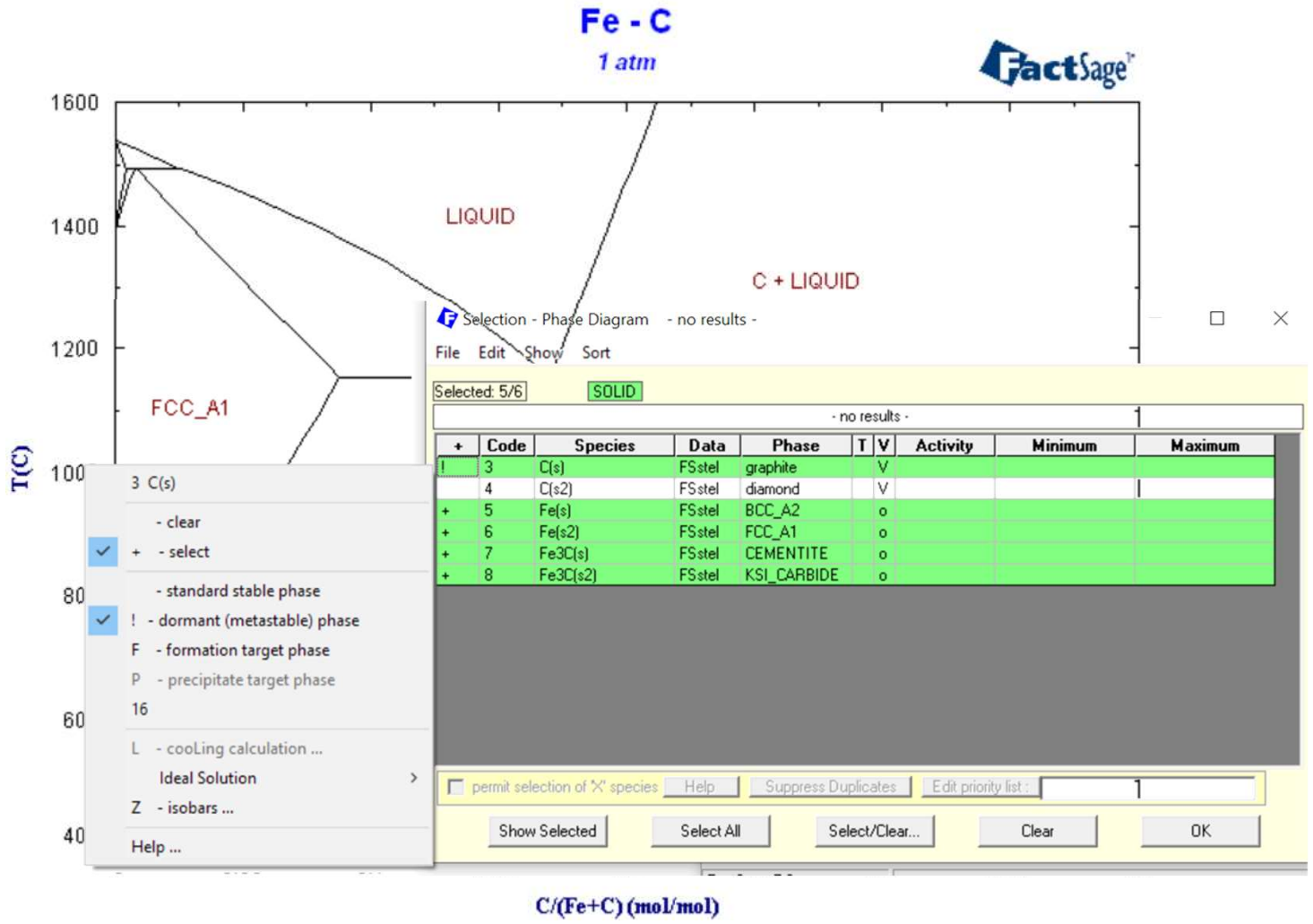
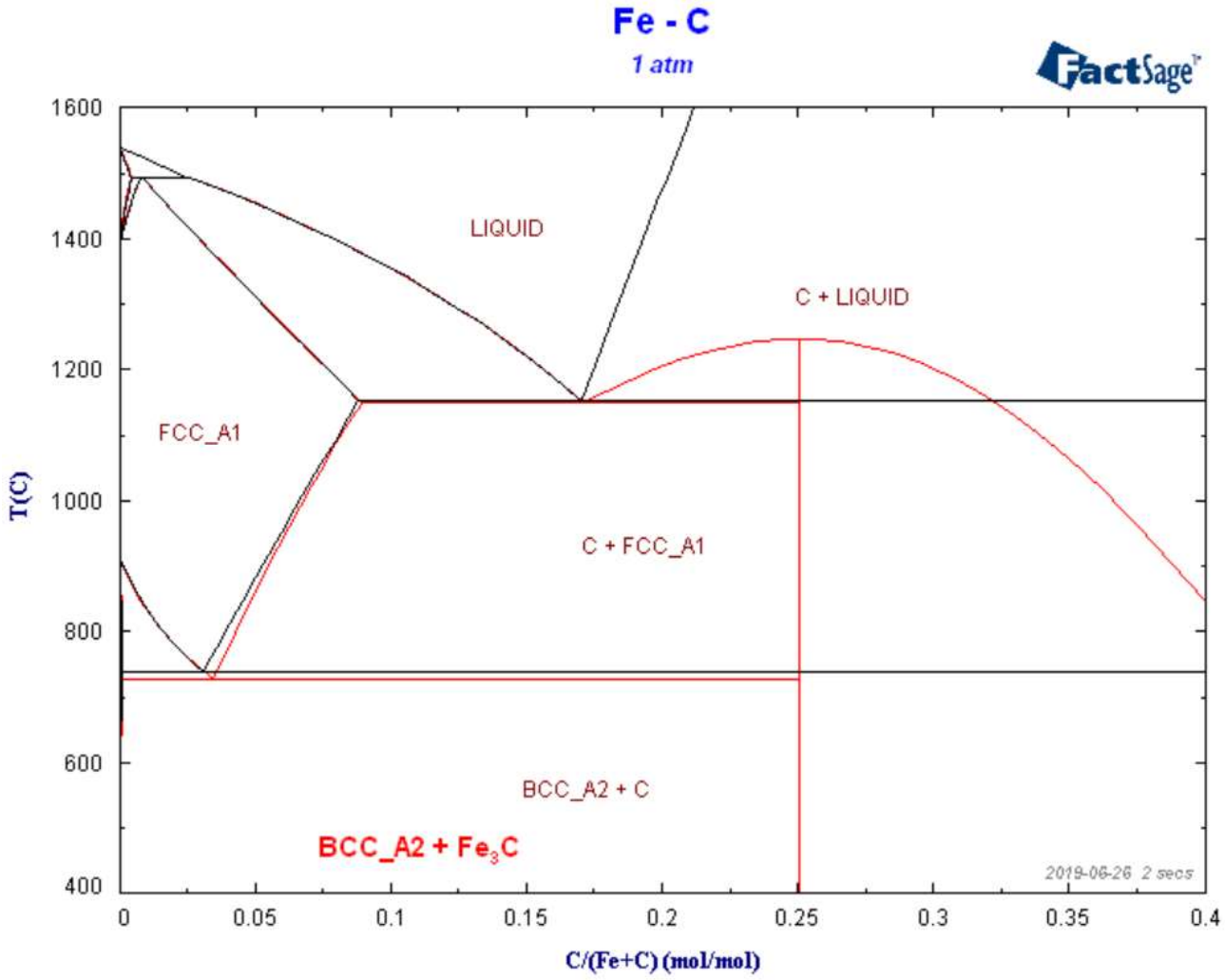
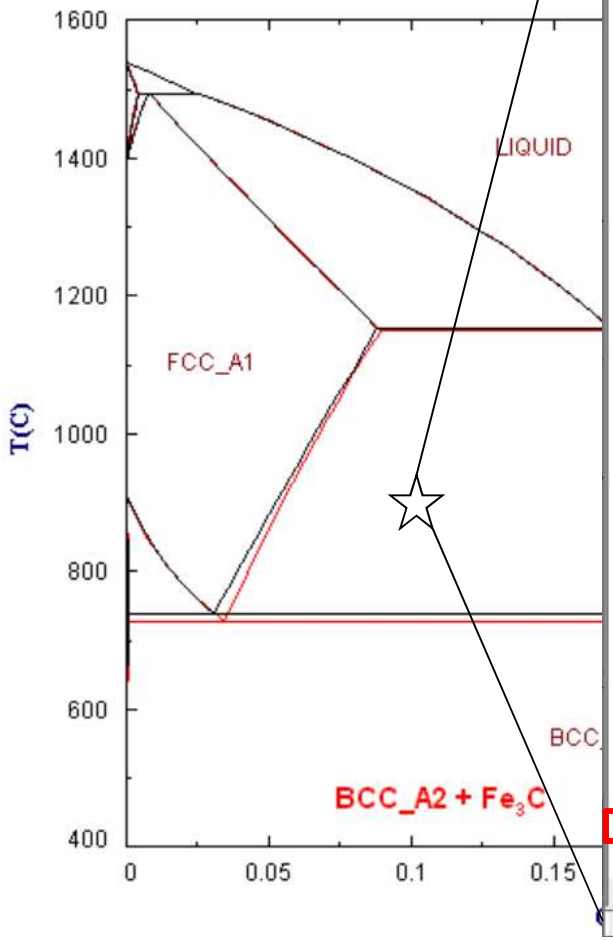


Dormant species



Dorma



Phase Diagram Equilibrium

File Edit Format

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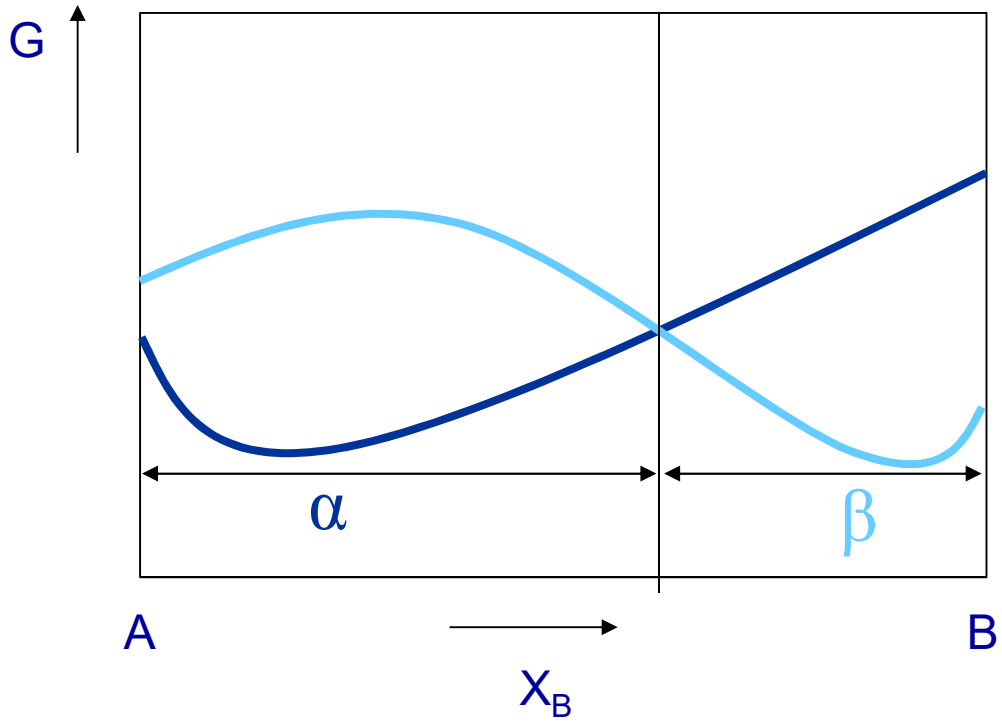
```
T = 771.60 C
P = 1 atm
V = 0 dm3

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

                                 EQUIL AMOUNT  MOLE FRACTION     ACTIVITY
PHASE: FCC_A1                        mol
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                    1.0000E+00
C_graphite(s)              !     0.0000E+00                    1.1762E+00
Fe_BCC_A2(s)                     0.0000E+00                    9.7562E-01
```

Outline

- 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



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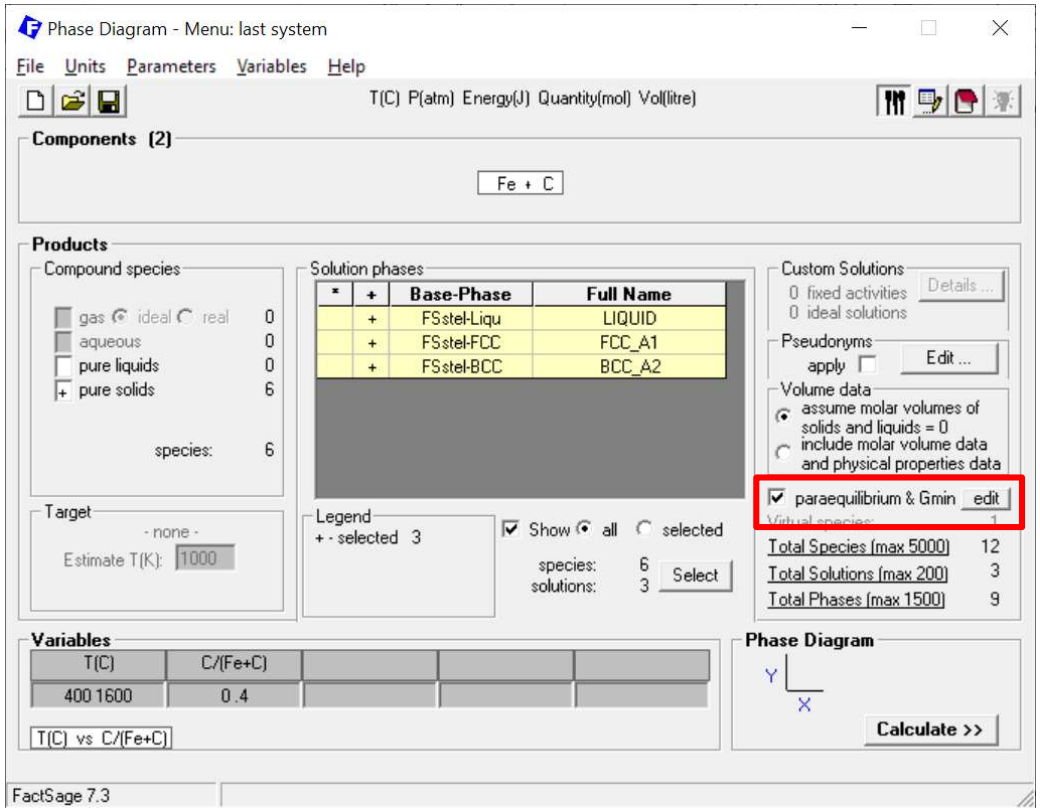
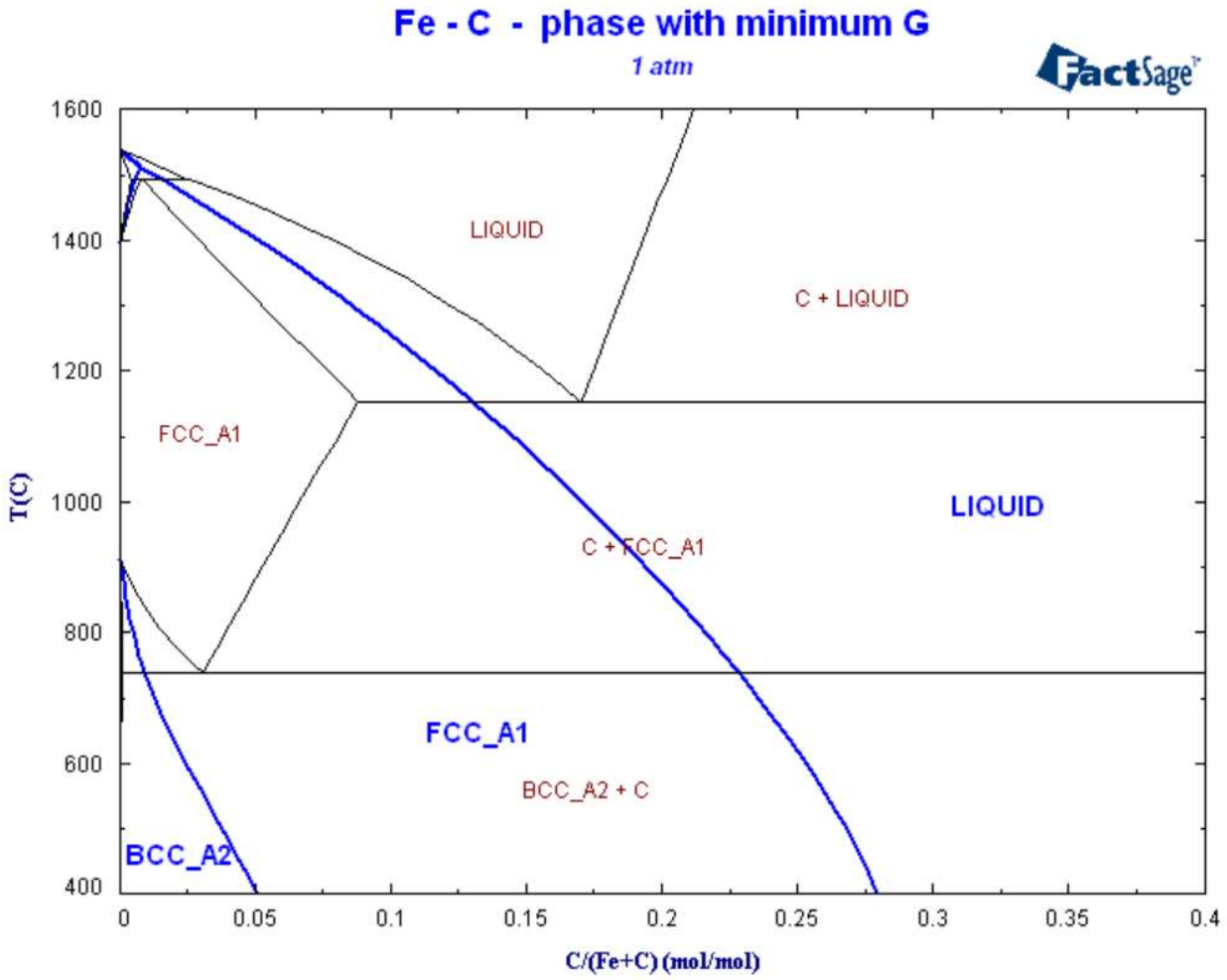
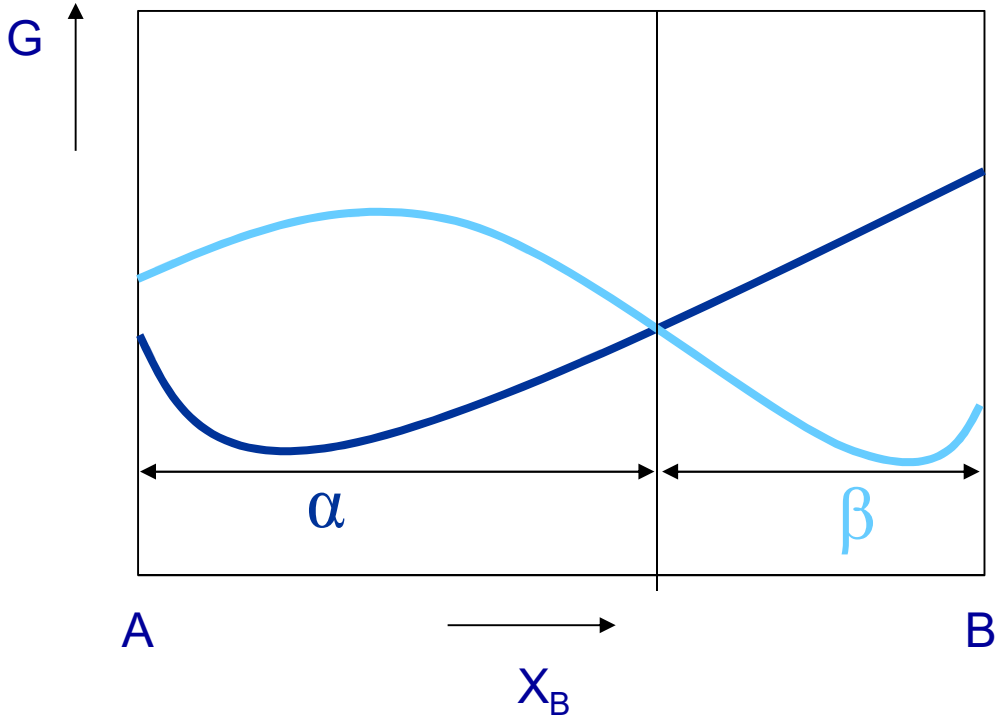


Paraequilibrium (no diffusing elements)

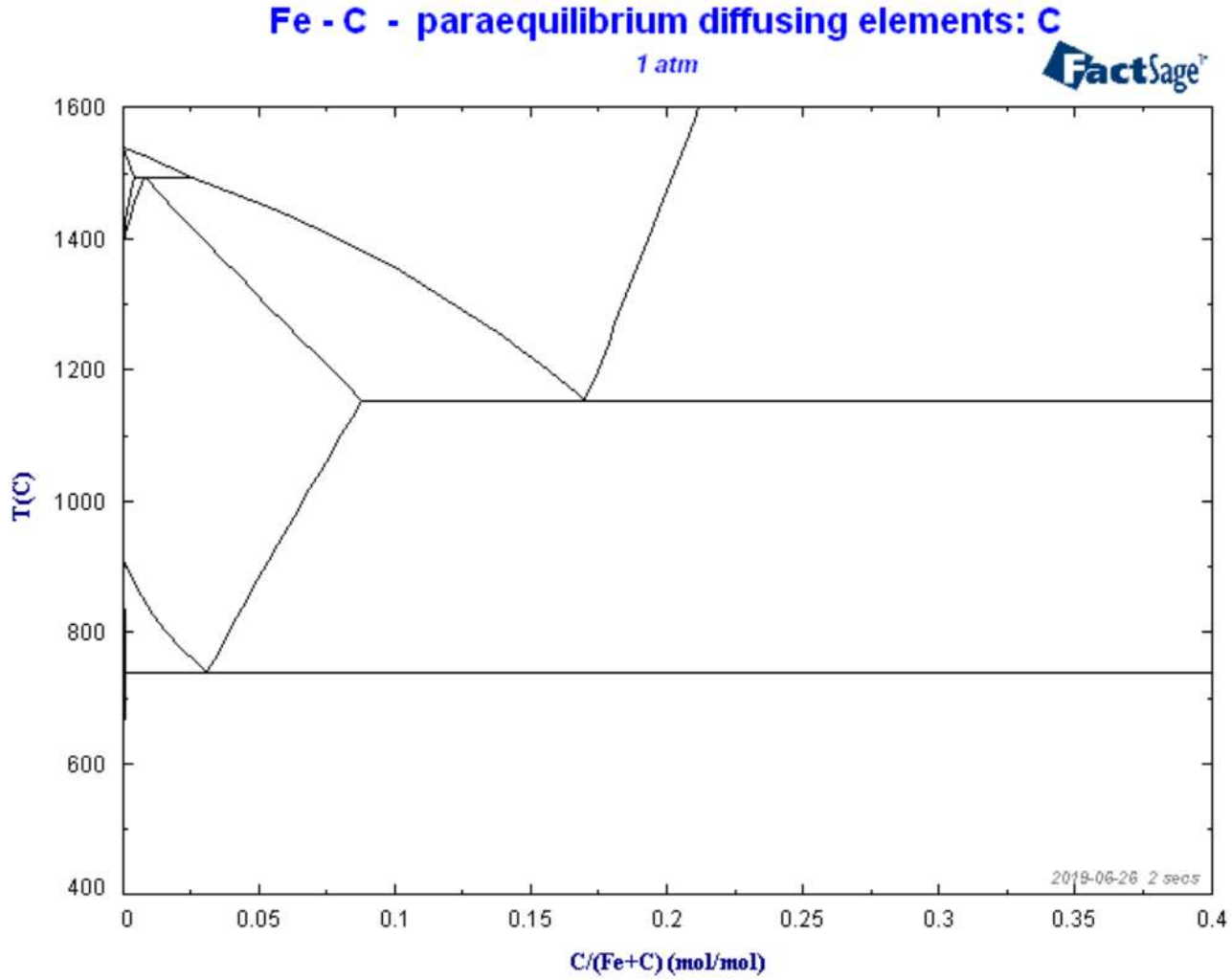


Paraequilibrium (diffusing elements)

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



Paraequilibrium (diffusing elements)



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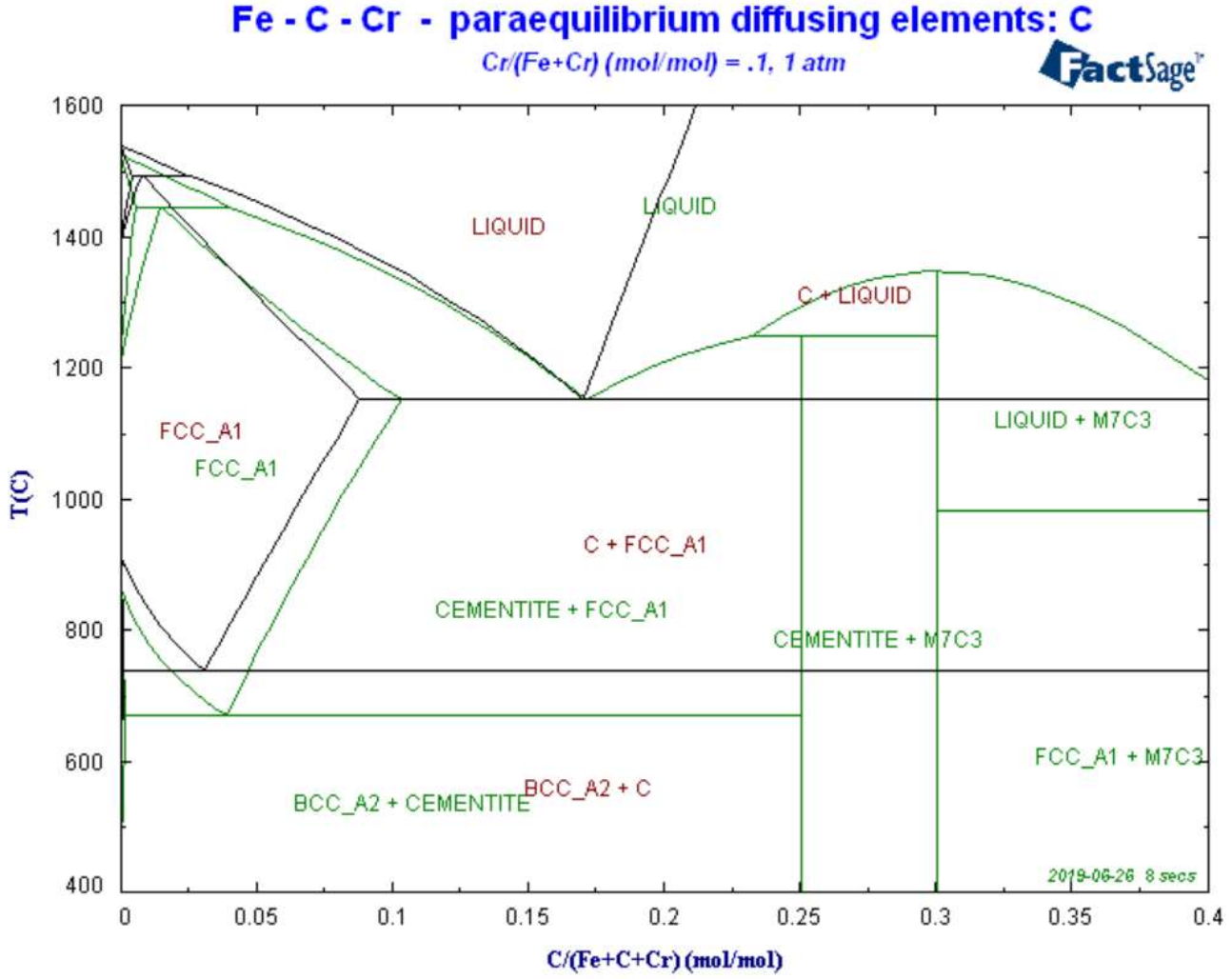

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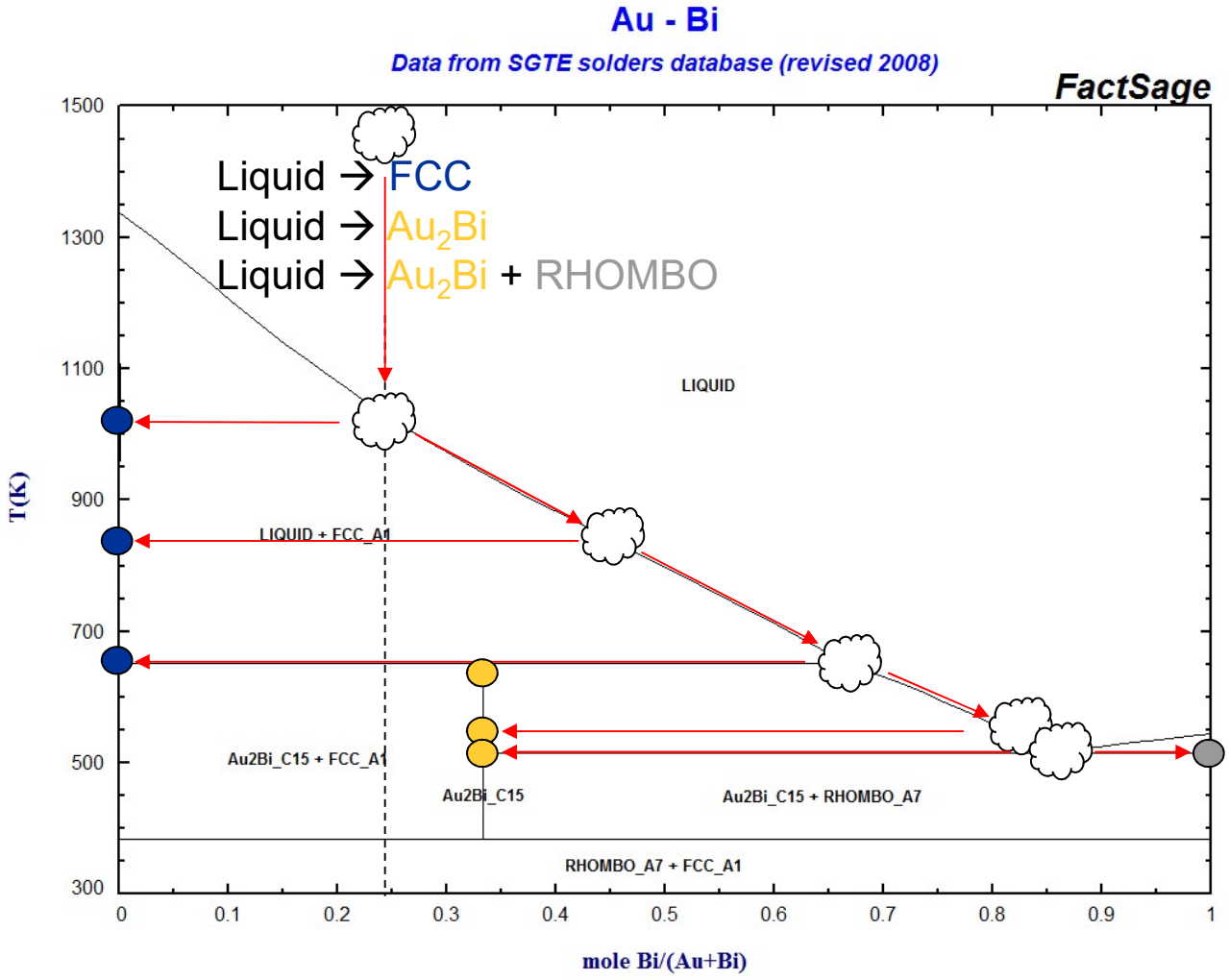
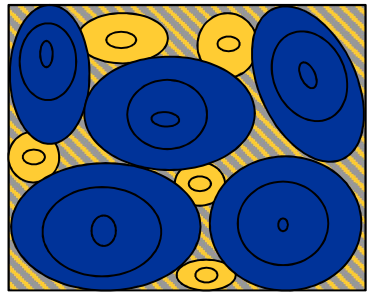
2 component Scheil cooling



microstructure:



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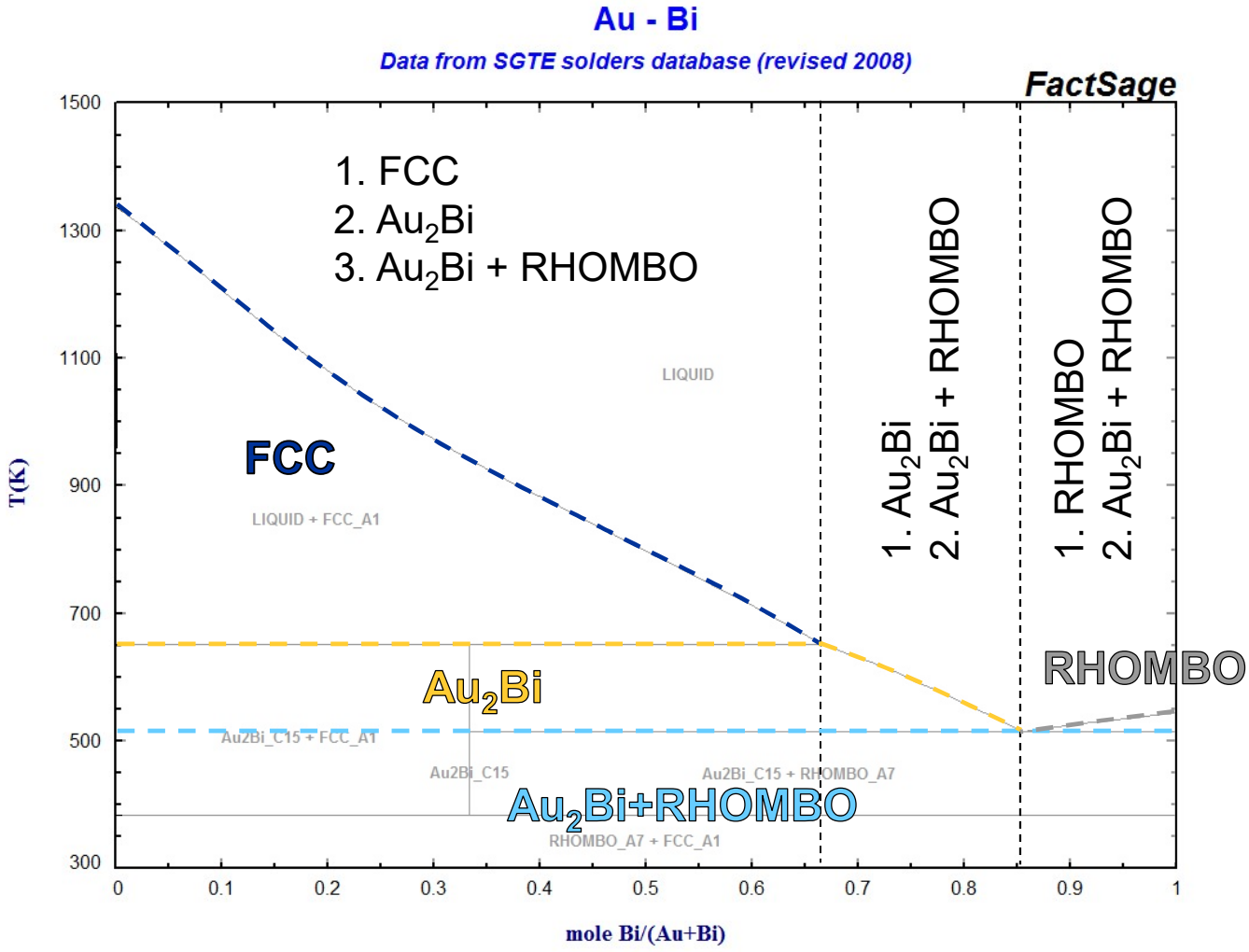
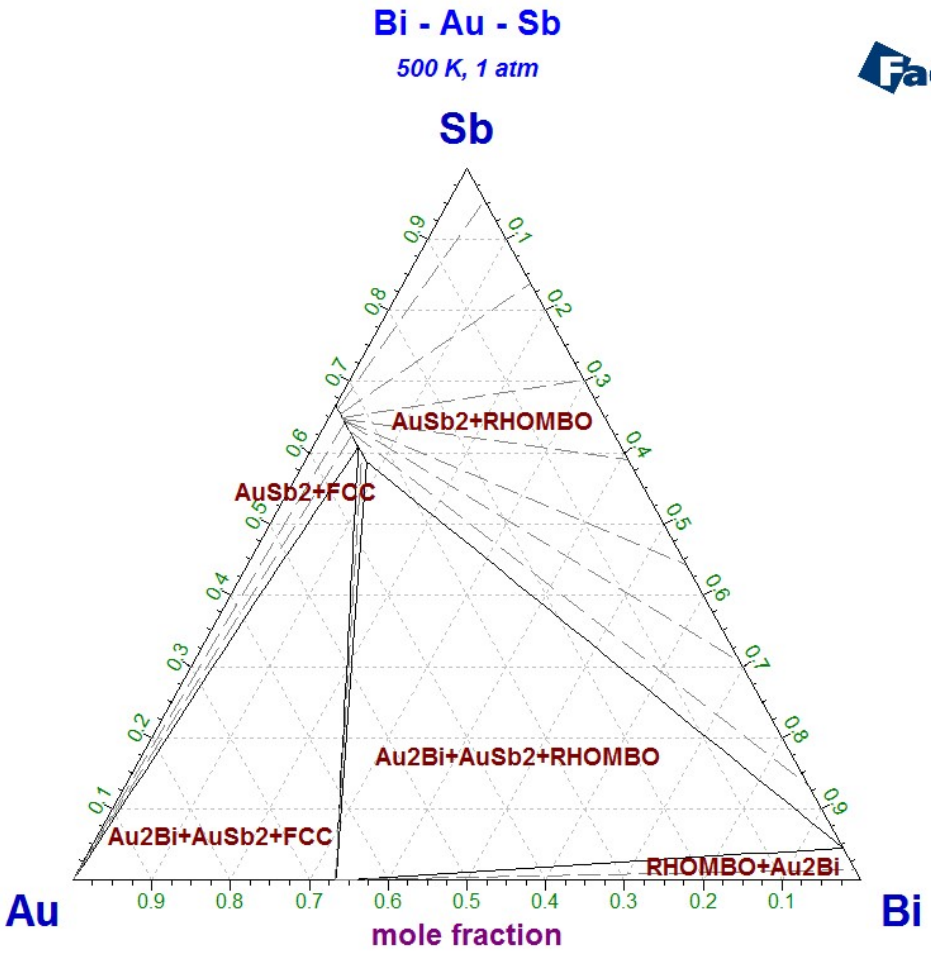
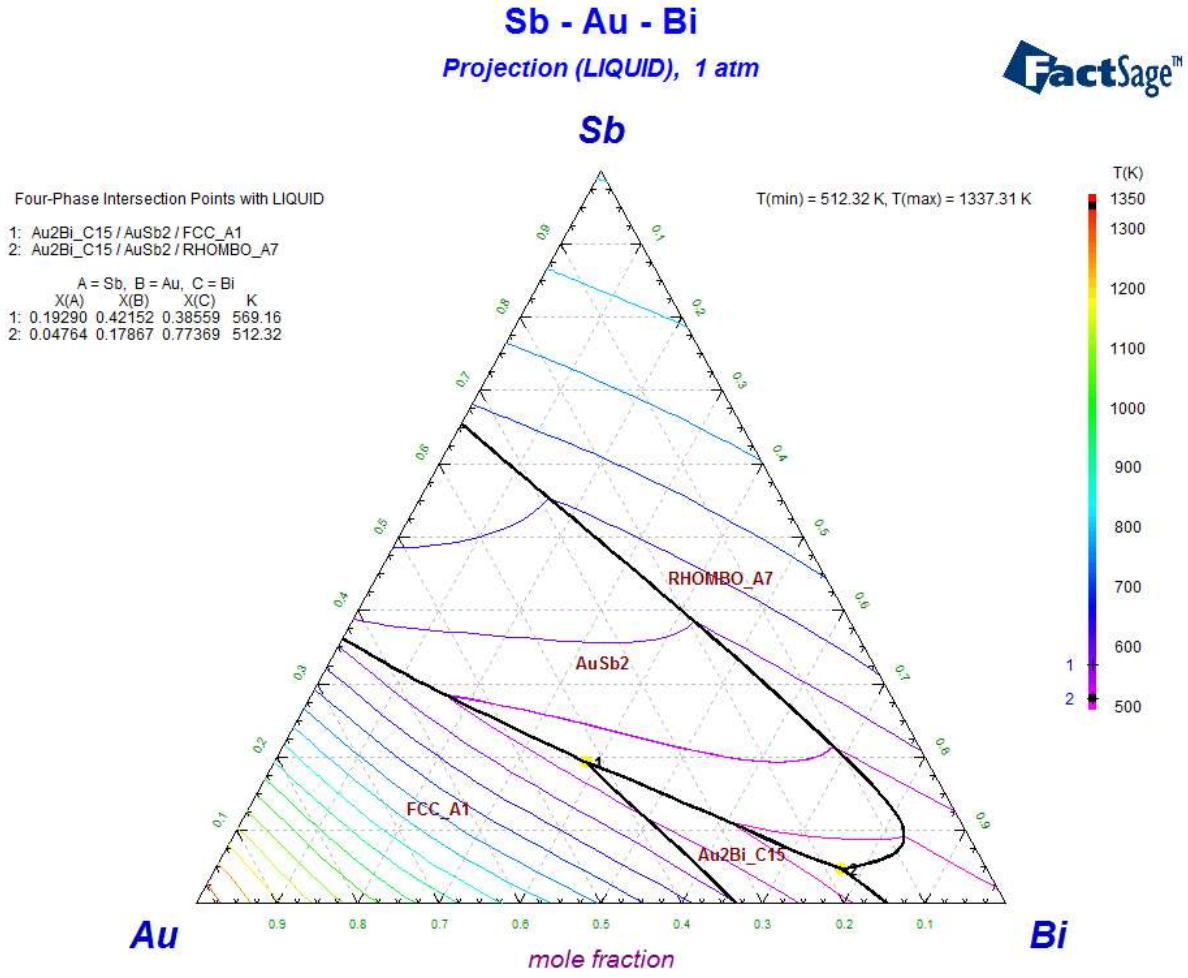


3 components: What are the stable solid phases?

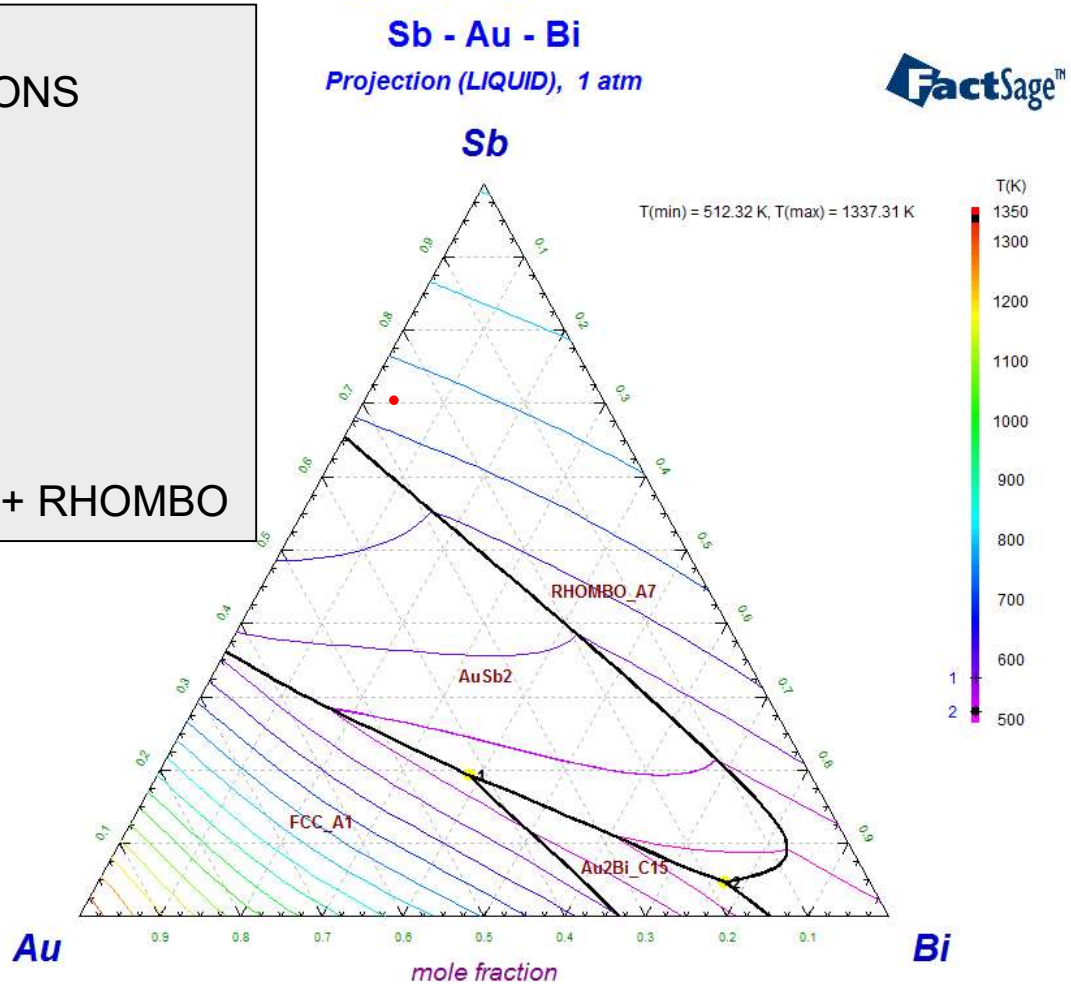


3 components: What is the first precipitating phase? → liquidus!



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 → AuSb2
538.48 to 512.32 K:
LIQ → Au2Bi + AuSb2
512.32 K (isothermal):
LIQ → Au2Bi + AuSb2 + RHOMBO



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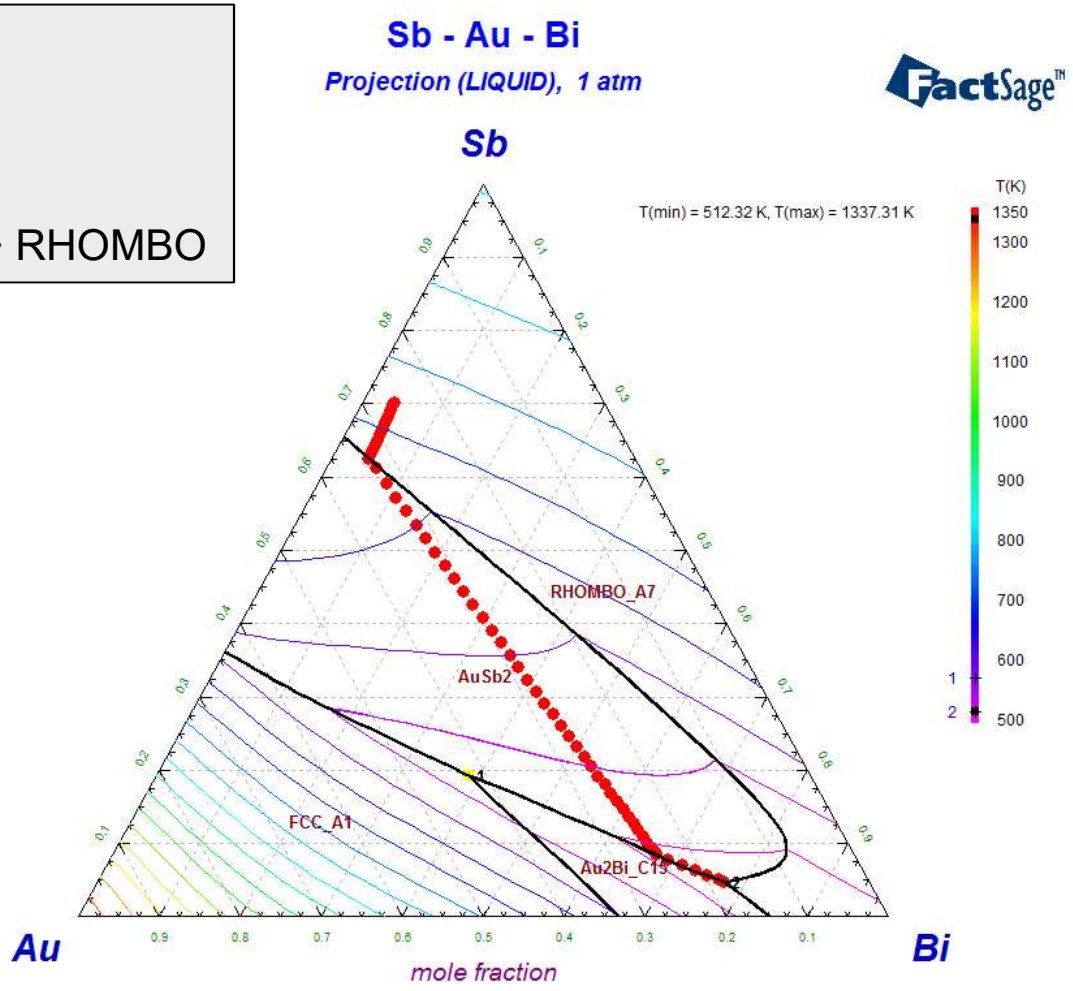

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LIQ → RHOMBO
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LIQ → Au2Bi + AuSb2
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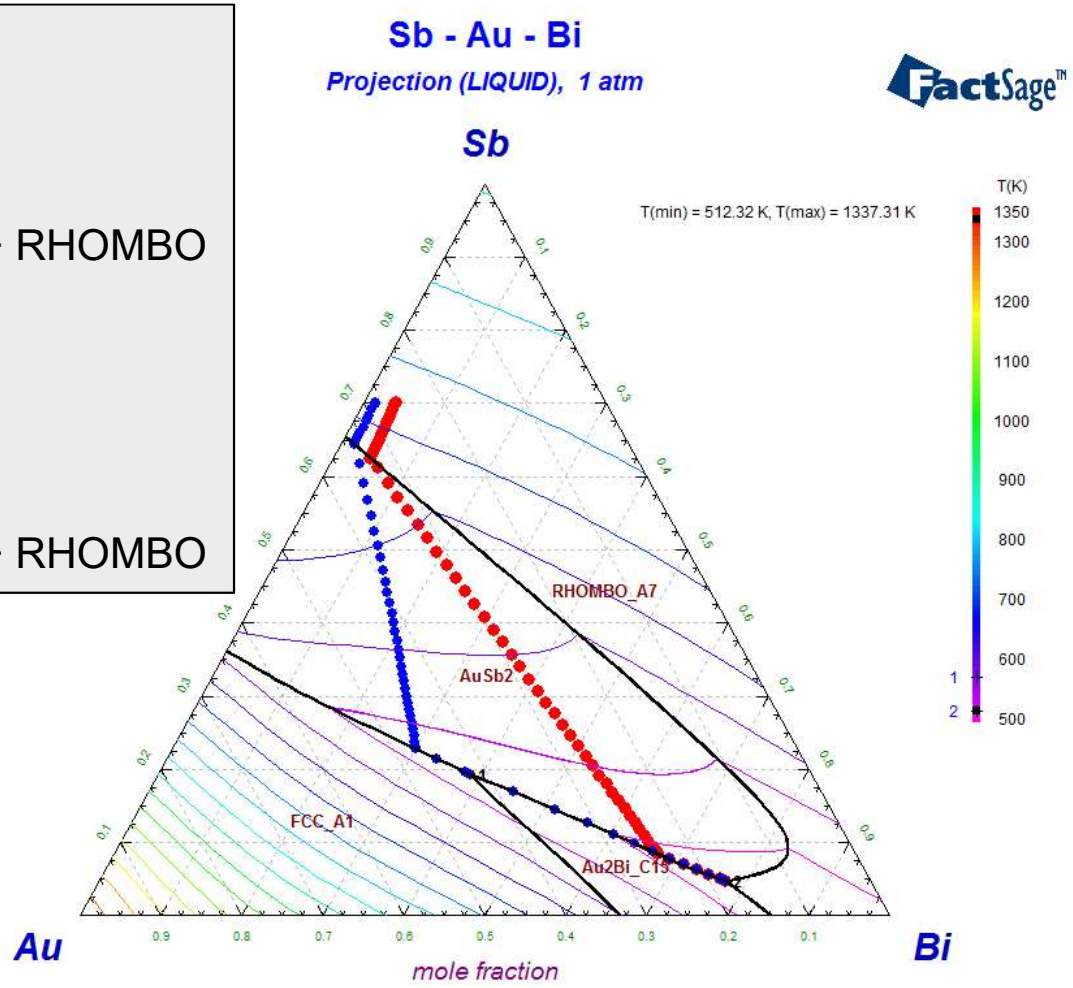
Sb70-Au28.5-Bi1.5
LIQ → RHOMBO
LIQ → AuSb2
LIQ → FCC + AuSb2
LIQ → Au2Bi + AuSb2
LIQ → Au2Bi + AuSb2 + RHOMBO



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Sb70-Au28.5-Bi1.5
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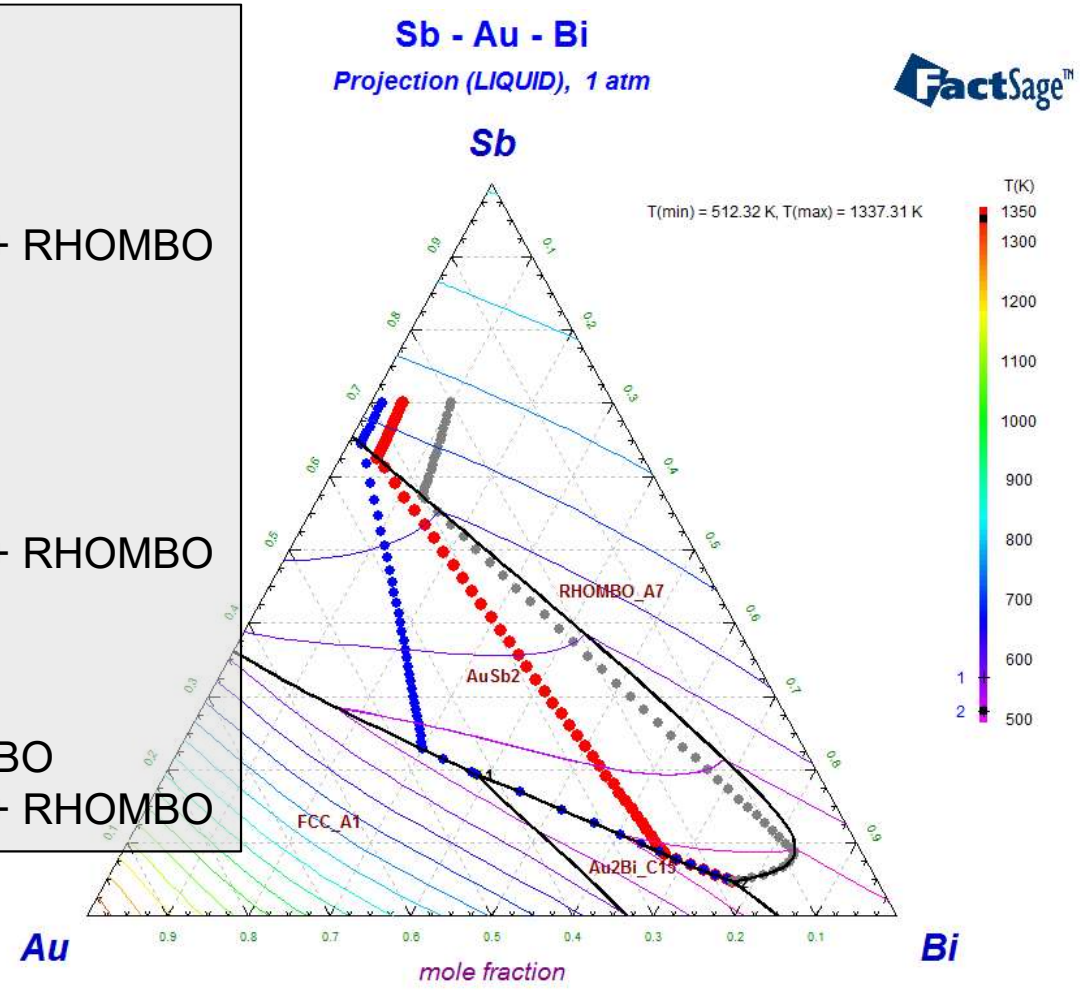
- LIQ → AuSb2
- LIQ → AuSb2 + FCC
- LIQ → AuSb2 + Au2Bi
- LIQ → AuSb2 + Au2Bi + RHOMBO

Sb70-Au20-Bi10
- LIQ → RHOMBO
- LIQ → AuSb2
- LIQ → AuSb2 + RHOMBO
- LIQ → AuSb2 + Au2Bi + RHOMBO



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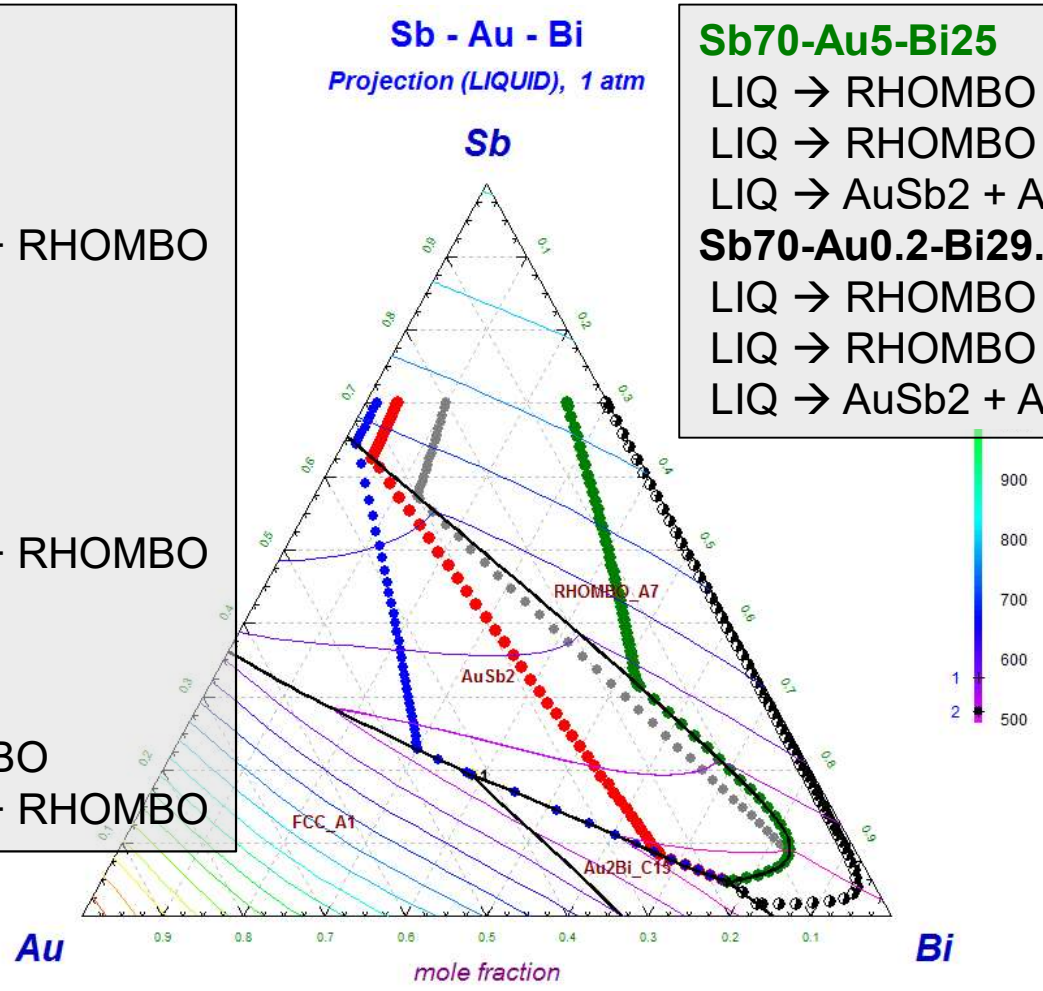

Sb70-Au5-Bi25
LIQ → RHOMBO
LIQ → RHOMBO + AuSb2
LIQ → AuSb2 + Au2Bi + RHOMBO

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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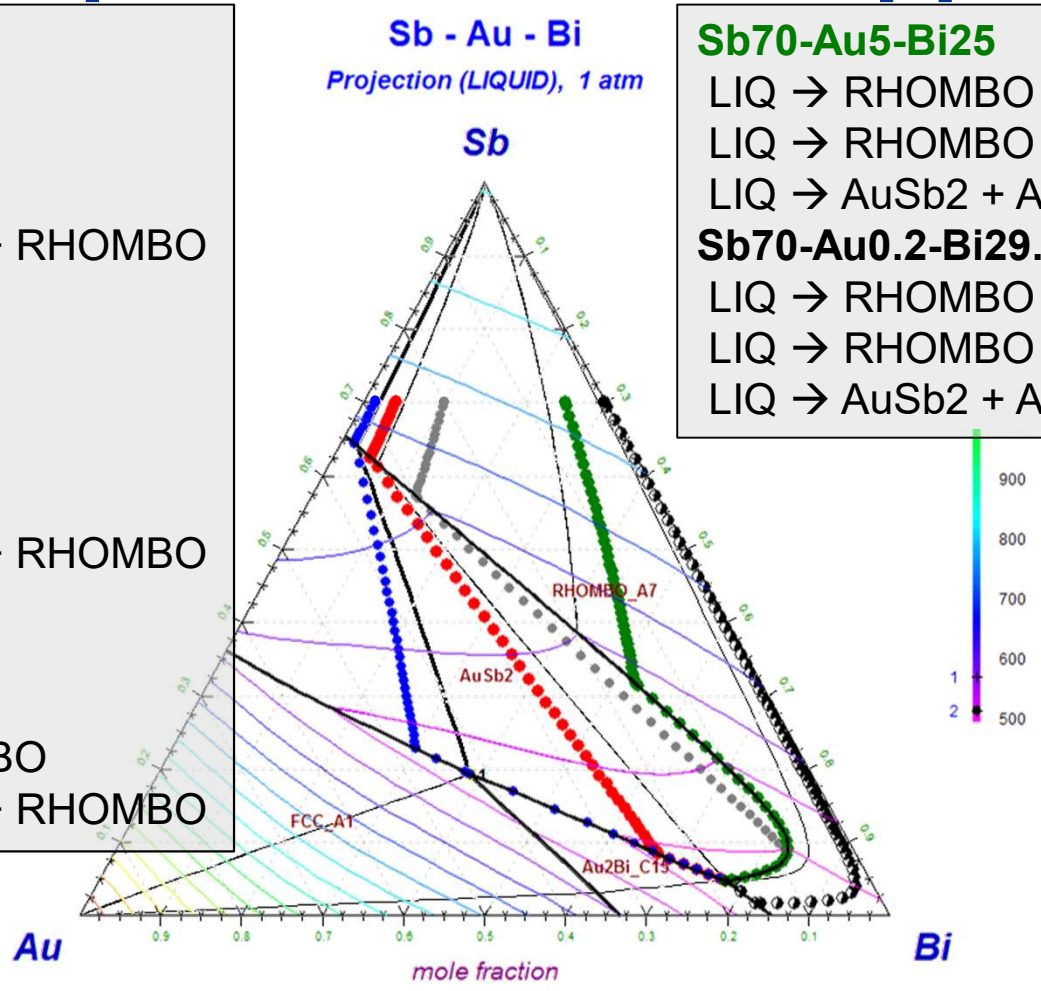

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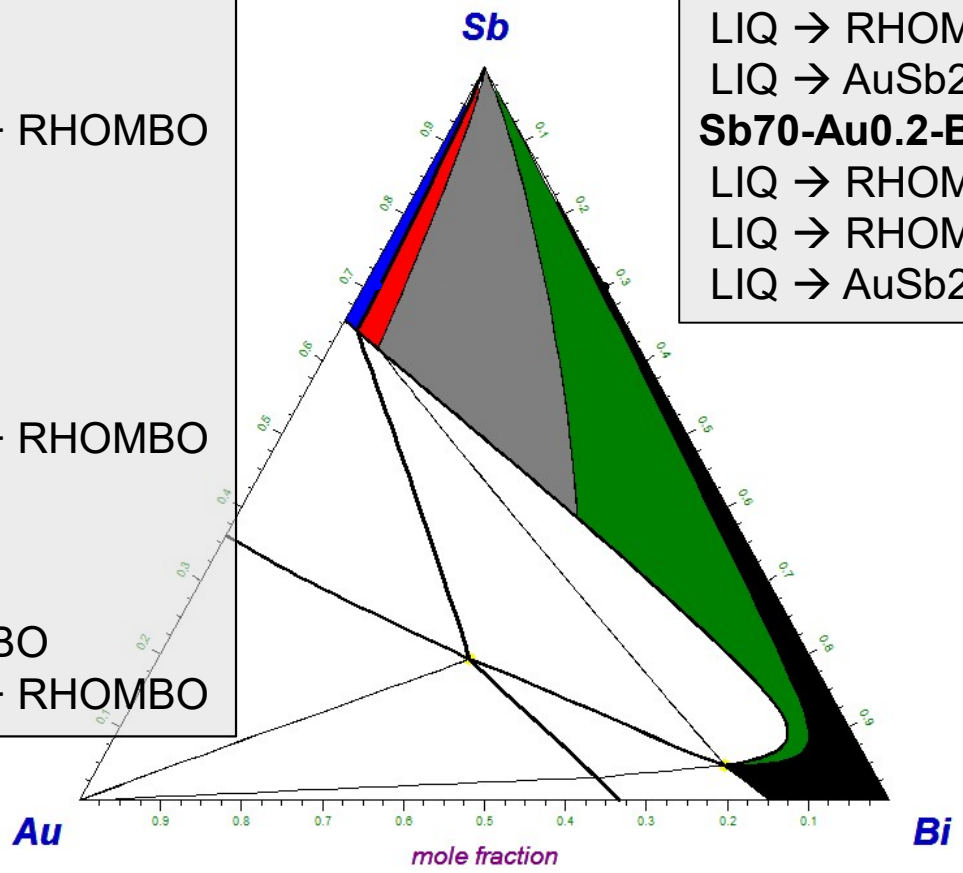

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Pertti Koukkari, *Introduction to constrained Gibbs energy methods in process and materials research*
www.vtt.fi/inf/pdf/technology/2014/T160.pdf
Risto Pajarre, Modelling of chemical processes and materials by free energy minimization www.vtt.fi/inf/pdf/science/2016/S141.pdf

Immaterial system components

- In a full equilibrium calculation, acetic acid would react to CO_2 + 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		
	EQUIL AMOUNT	MOLE FRACTION	FUGACITY
PHASE: gas_ideal	mol		bar
CH4	9.9933E-01	4.8786E-01	4.8786E-01
CO2	9.8402E-01	4.8038E-01	4.8038E-01
H2O	6.5053E-02	3.1758E-02	3.1758E-02
H2	3.9065E-06	1.9071E-06	1.9071E-06
C2H6	2.3499E-07	1.1472E-07	1.1472E-07
CO	5.6128E-10	2.7401E-10	2.7401E-10
TOTAL:	2.0484E+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

Moritz to Baben

Immaterial system components

- In a full equilibrium calculation, acetic acid would react to CO_2 + 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
PHASE: aqueous	mol		
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		1.0000E+00

Immaterial system components

- In a full equilibrium calculation, acetic acid would react to CO_2 + 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
PHASE: aqueous                  mol
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                      1.0000E+00
```

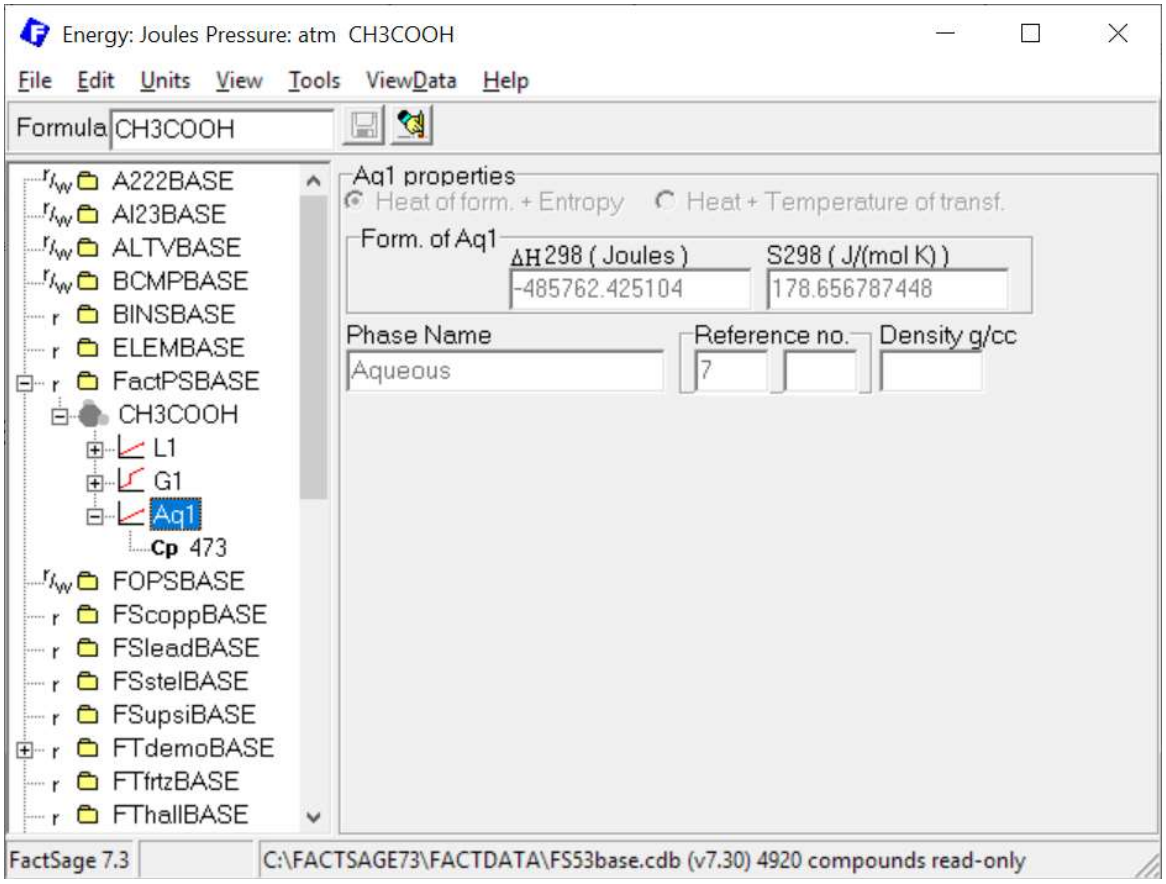
We need to introduce a real constraint CH_3COOH may ONLY dissociate!

Immaterial system components

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

Species	H	O	C	e(aq)	V
H2O	2	1	0	0	0
H[+]	1	0	0	-1	0
OH[-]	1	1	0	1	0
…					
CH3COO[-]	3	2	2	1	1
CH3COOH	4	2	2	0	1

Immaterial system components



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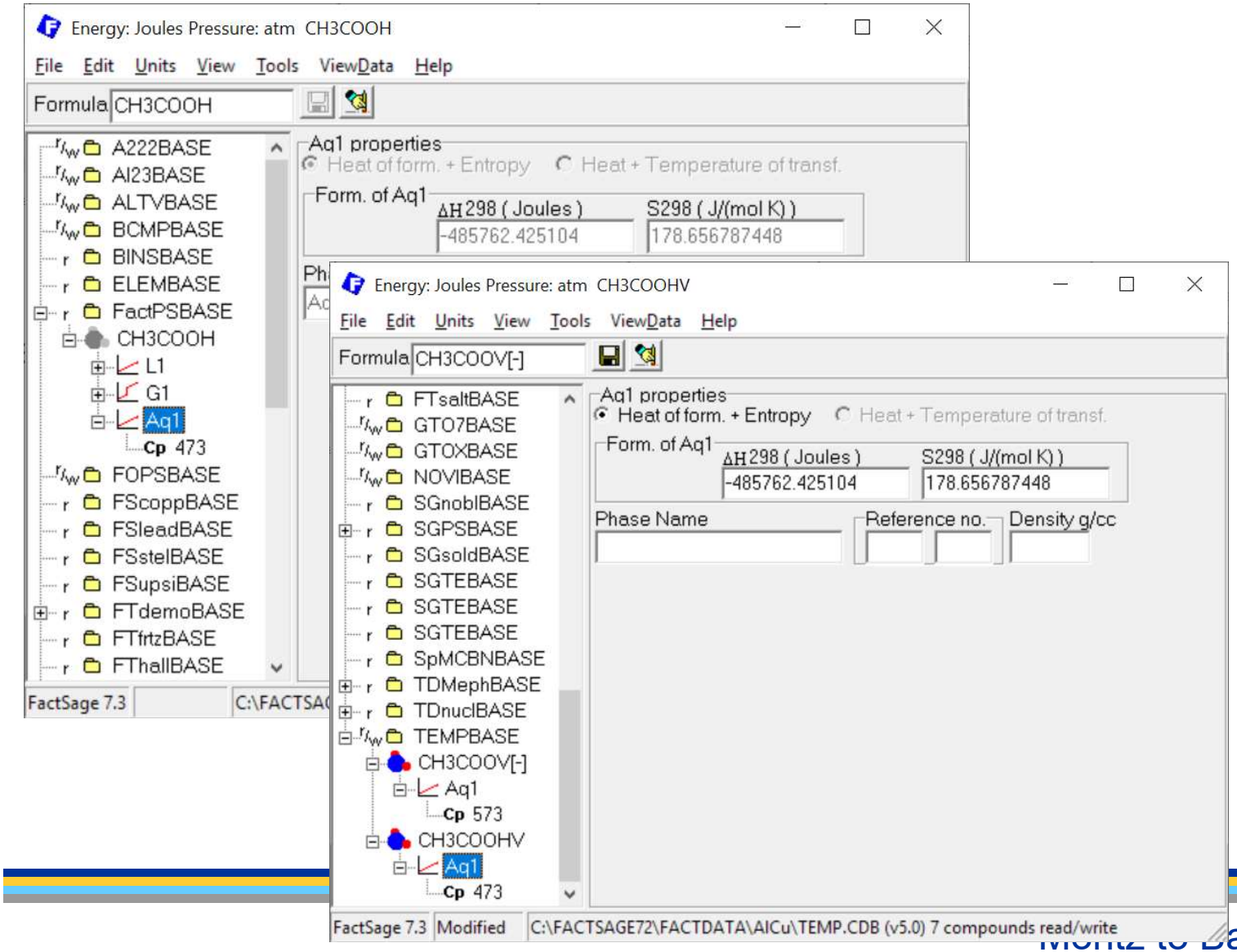
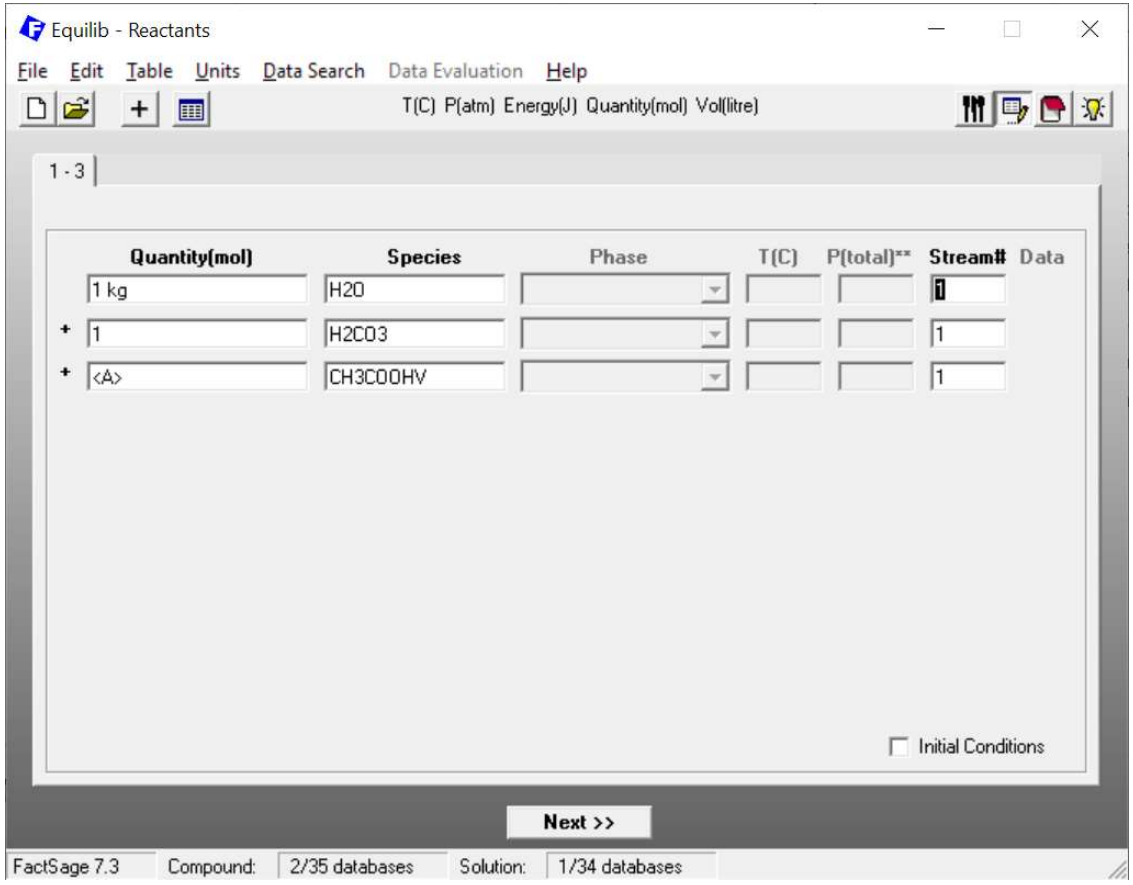


Example 1: Water + carbonic acid + acetic acid

$$H_2O + CO_{2(g)} \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2\,H^+ + CO_3^{2-}$$

$$CH_3COOH \leftrightarrow H^+ + CH_3COO^-$$



Example 1: Water + carbonic acid + acetic acid

$$H_2O + CO_{2(g)} \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2\,H^+ + CO_3^{2-}$$

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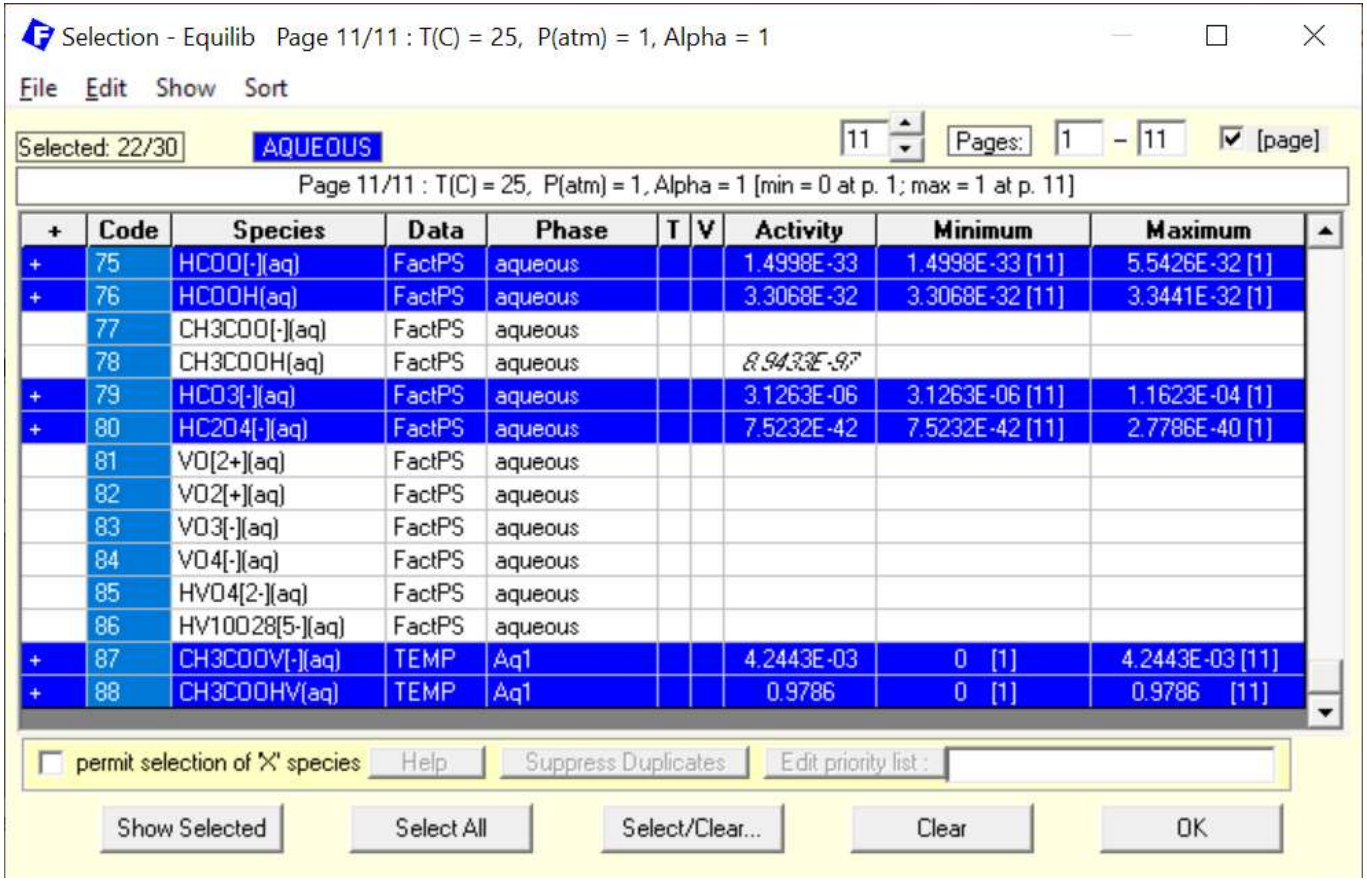
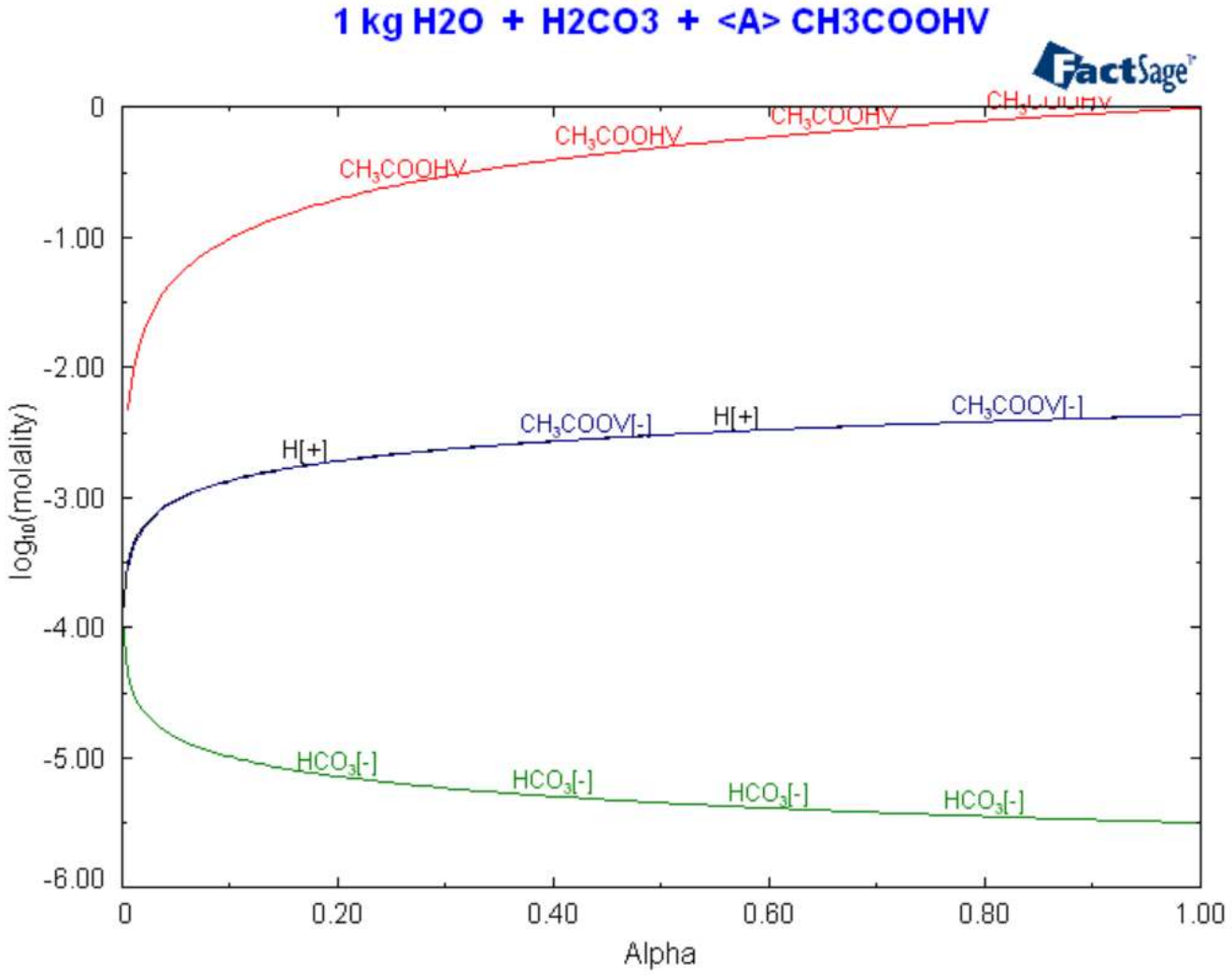


+	Code	Species	Data	Phase	T	V	Activity	Minimum	Maximum
+	75	HCOO[-](aq)	FactPS	aqueous			1.4998E-33	1.4998E-33 [11]	5.5426E-32 [1]
+	76	HCOOH(aq)	FactPS	aqueous			3.3068E-32	3.3068E-32 [11]	3.3441E-32 [1]
	77	CH3COO[-](aq)	FactPS	aqueous					
	78	CH3COOH(aq)	FactPS	aqueous			8.9433E-97		
+	79	HCO3[-](aq)	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]

Example 1: Water + carbonic acid + acetic acid



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:

  $x_{rutile} = 1 - (1 - kt)^3$ with $k = A\, exp\left(-{}^{E_A}/_{RT}\right)$

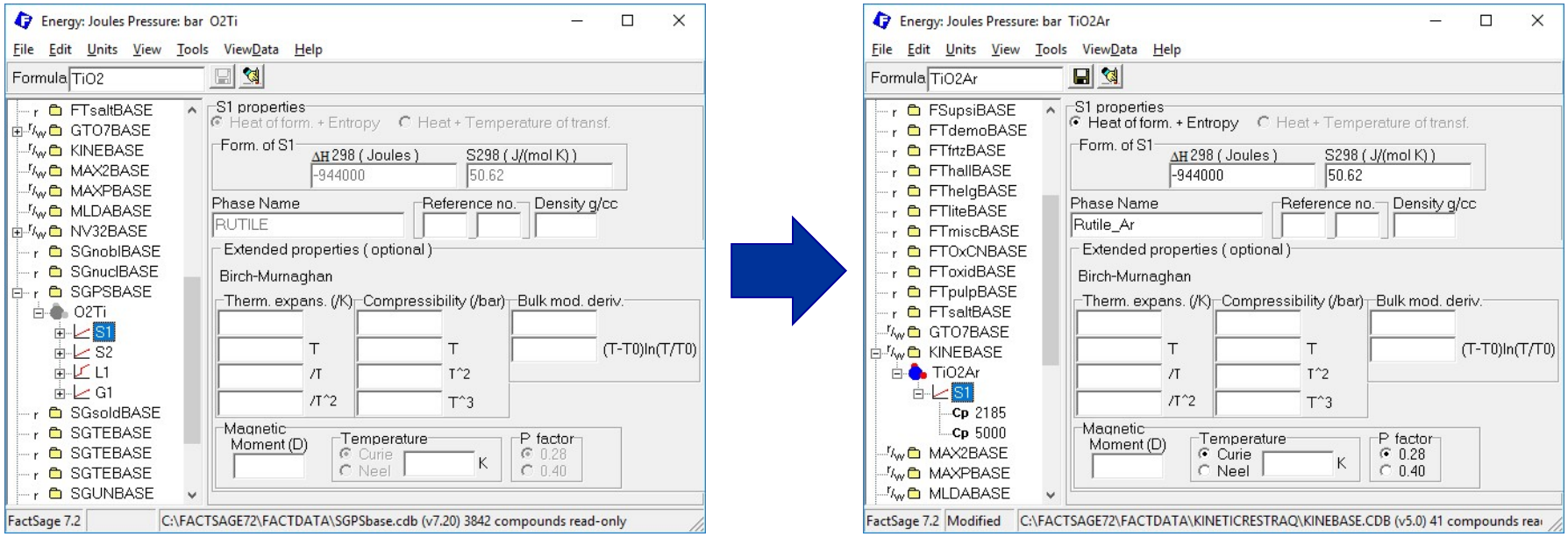
- The stoichiometric matrix is adjusted as follows:

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.



Example 2: Anatase → Rutile conversion

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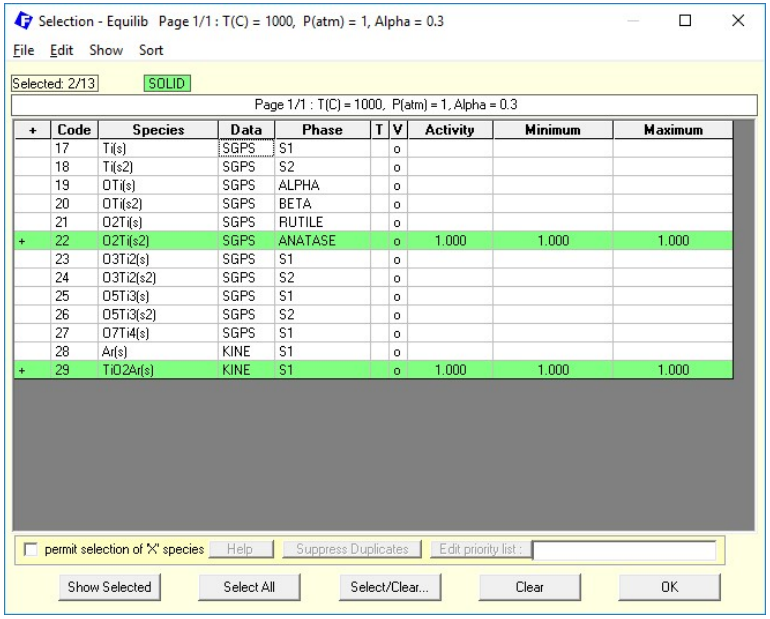

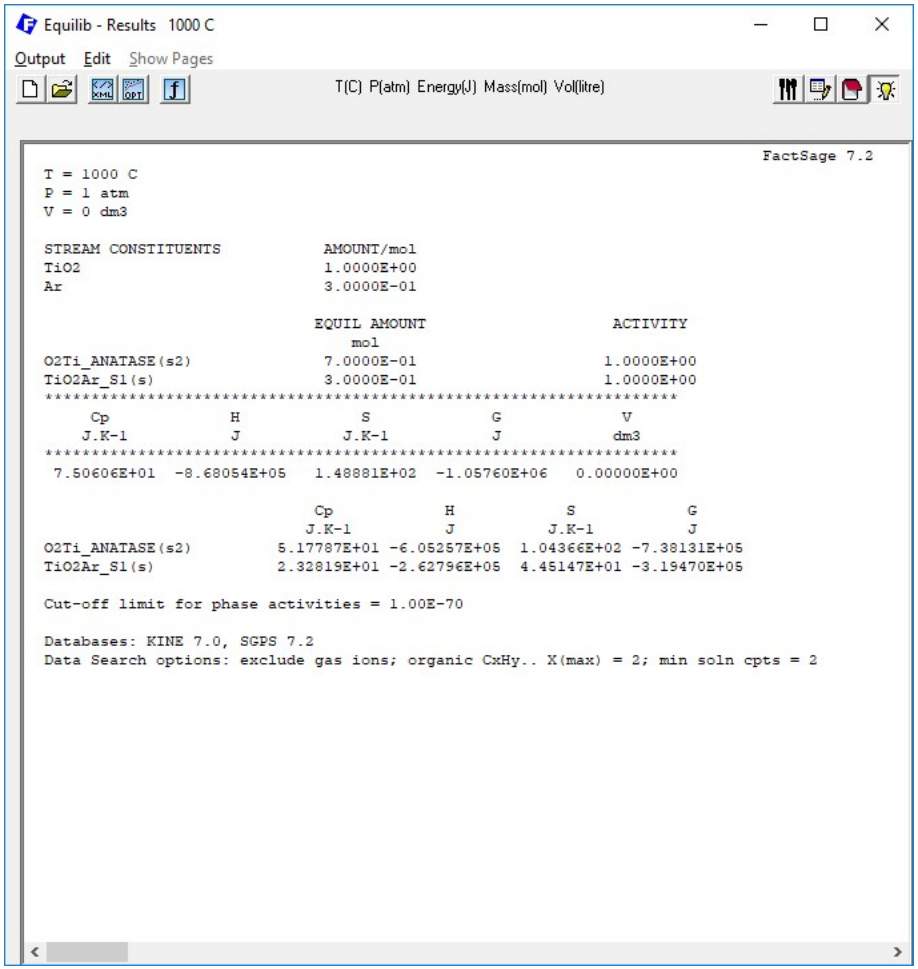

Immaterial system components

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	$\sum_{k=1}^{N_F} V_k n_k^F = V_F$	$\frac{V_k}{V_0}$	$\pi_F = \frac{\partial G}{\partial b_{(V_F)}} = \Pi \overline{V}_F$	Osmotic systems, fibers and membranes
EOR-controlled complex systems	$\sum_{k=1}^{N} a_{kr} n_k = b_{(r_i)}$	υ_{kr}	$\pi_{(r_i)} = \frac{\partial G}{\partial b_{(r_i)}} = \frac{\partial G}{\partial \xi_i} = -A ff_i$	Reactive systems Partial and 'super' equilibria

Para-equilibrium systems	$u_k = \frac{n_k}{\sum_M n_M} = const.$	$\frac{n_{Fe}}{n_M} a_{k,M} - a_{k,Fe}$	$\frac{\partial G}{\partial \xi} = \sum_{M^*} a_{k,M^*} \left(\frac{\partial G}{\partial b_{M^*}} \right) = \sum_{M^*} a_{k,M^*} \pi_{M^*}$	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
Electro-chemical (Donnan) multi-phase systems	$\sum_{k=1}^{N_\alpha} z_k n_k^\alpha = Q^\alpha$	z_k	$\pi_{(q^\alpha)} = \frac{\partial G}{\partial b_{(q^\alpha)}} = F \Delta \varphi^\alpha$	Electrochemi-cal membrane systems, Pulp suspensions
Constant contribution pH	$pH = const.$	$N_{H,k}$	$\pi_{Ha} \equiv RT \ln 10 \, pH_a$	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

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[1], Raheleh Hadian[1], Blazej Grabowski[1] and Jörg Neugebauer[1]

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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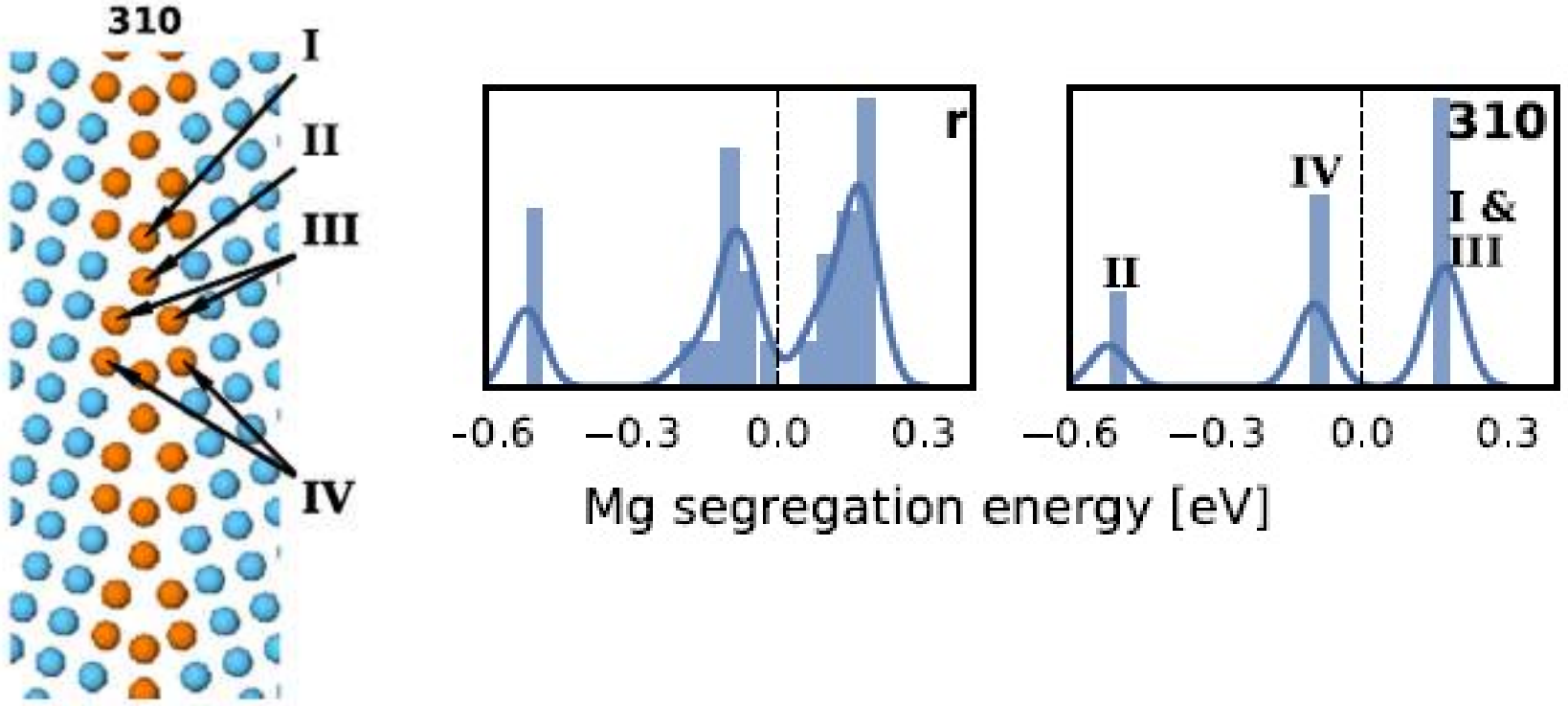

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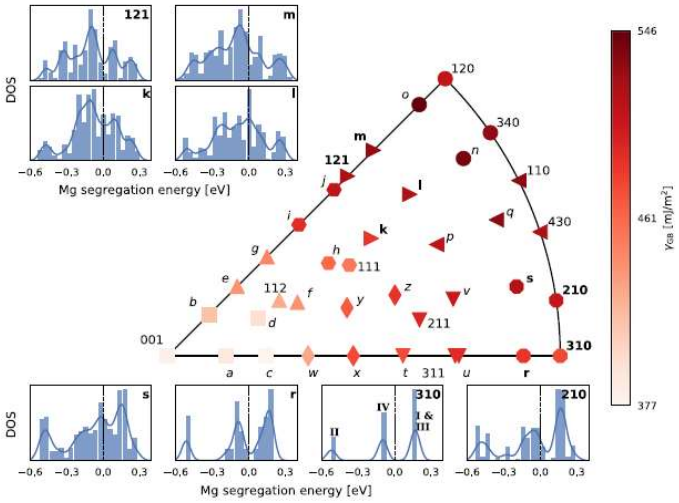

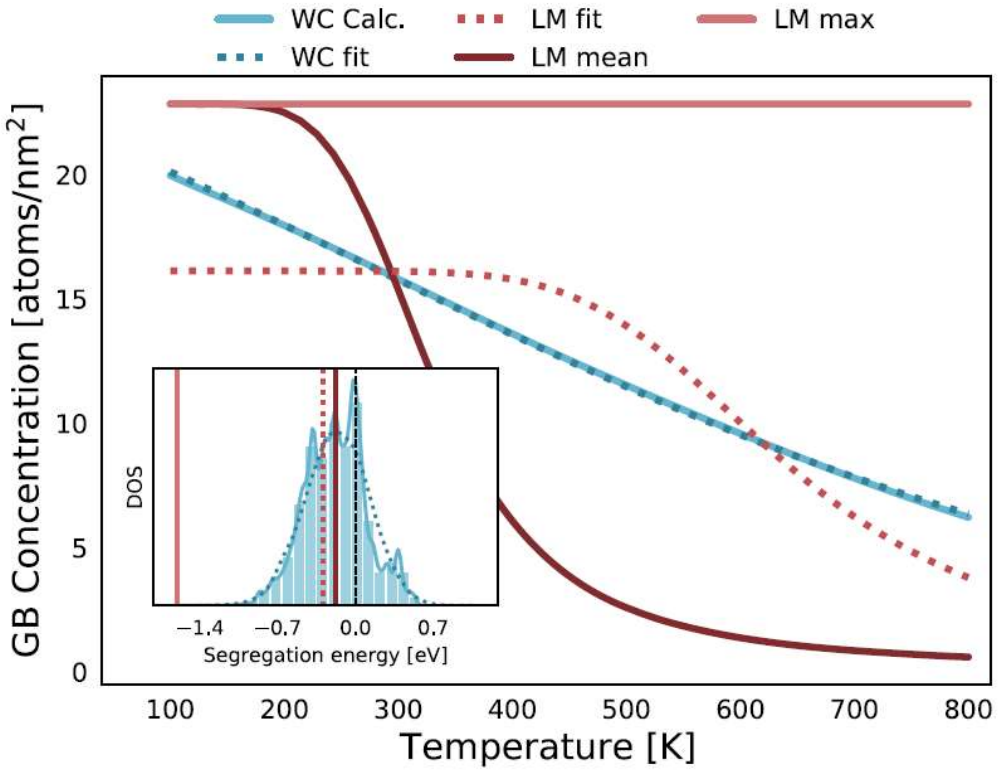

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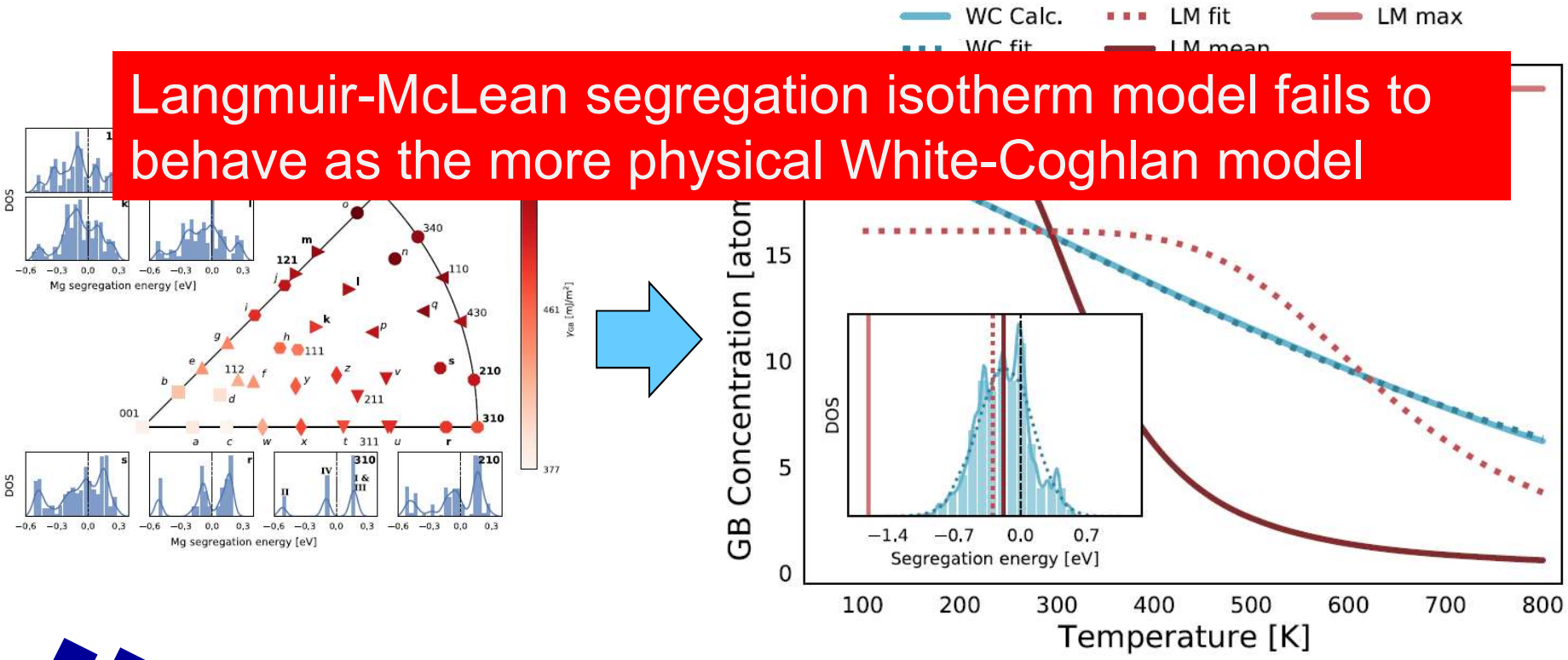
Langmuir-McLean segregation isotherm model fails to behave as the more physical White-Coghlan model



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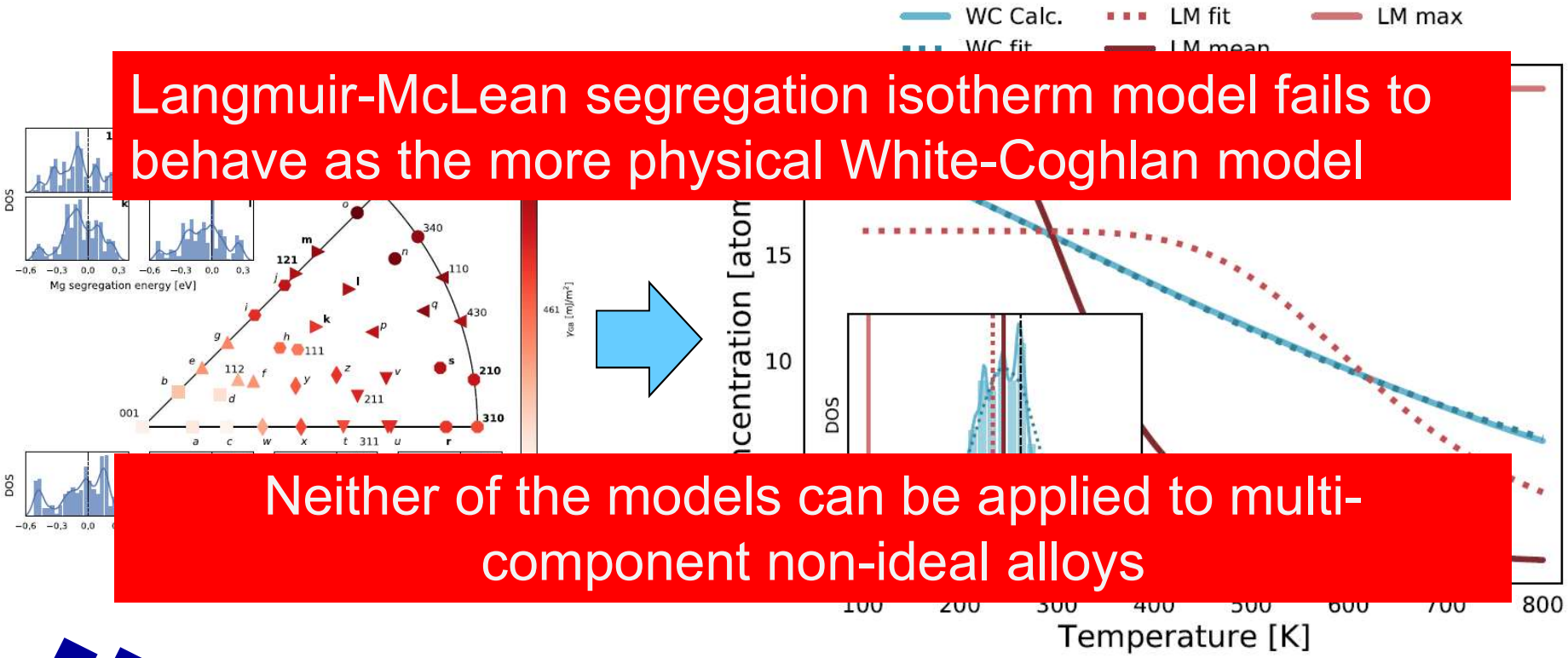
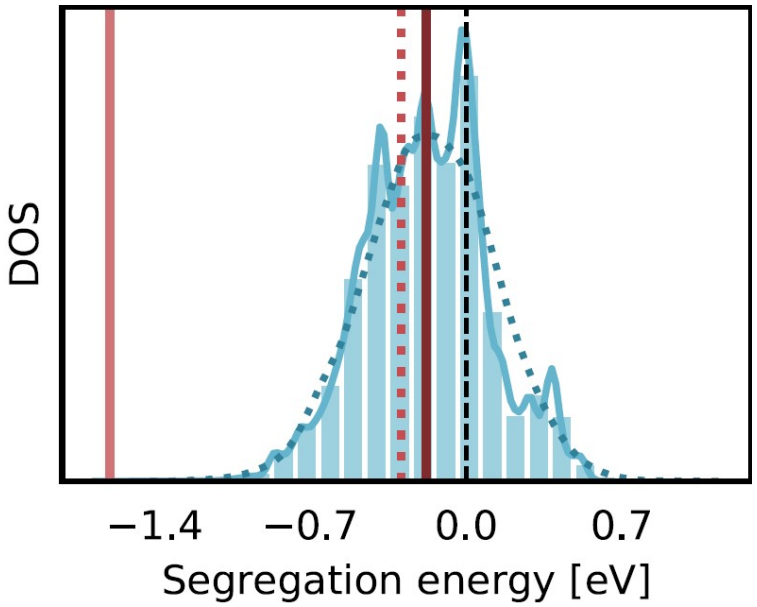
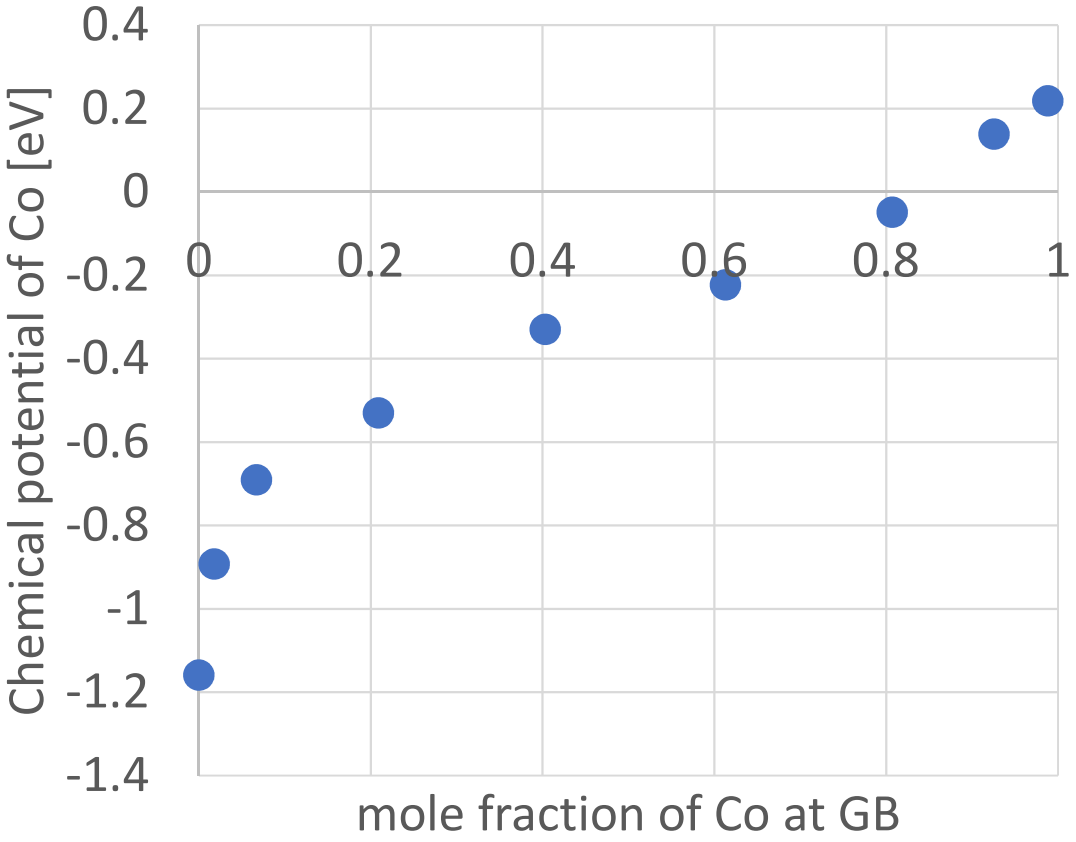


Grain boundary partitioning





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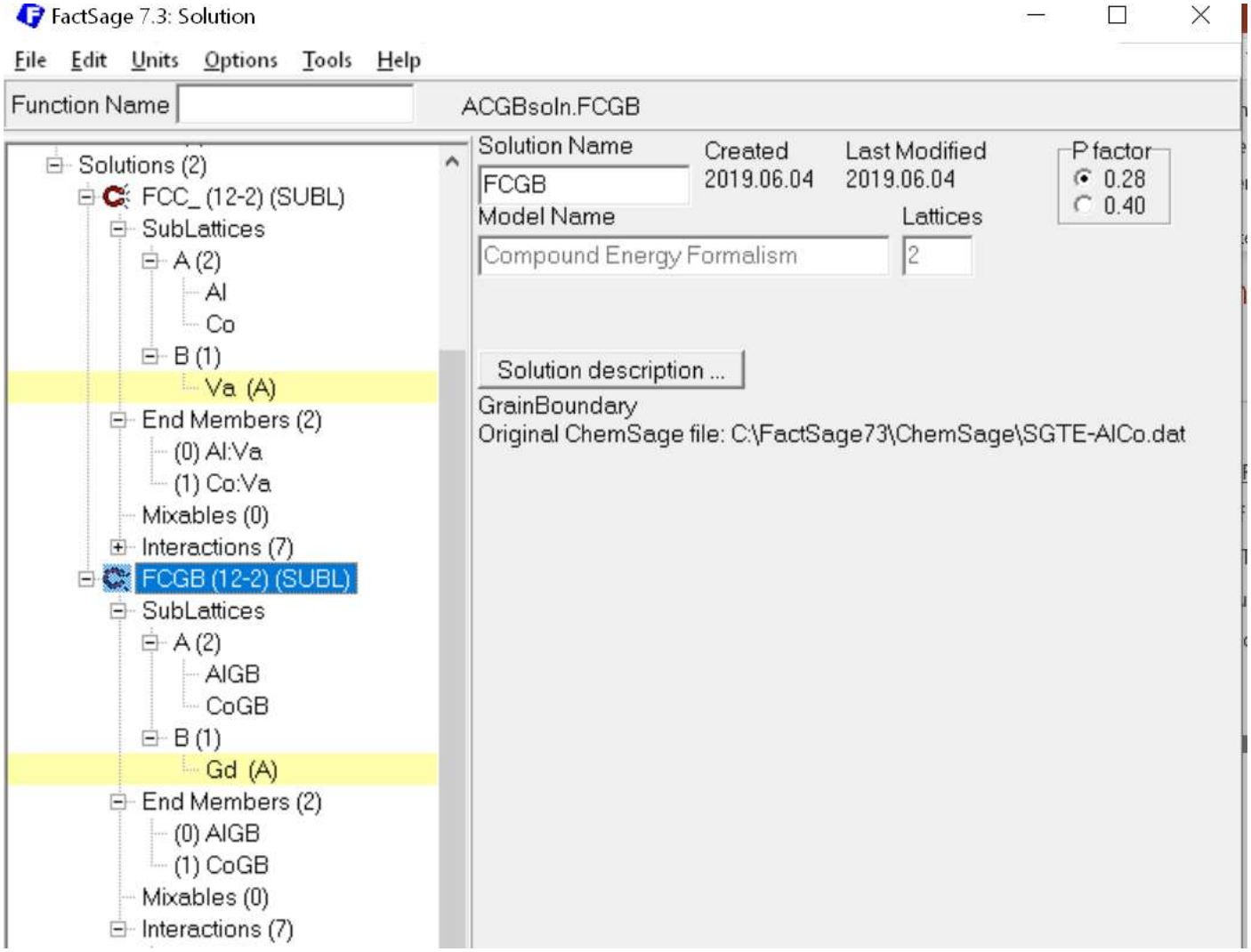
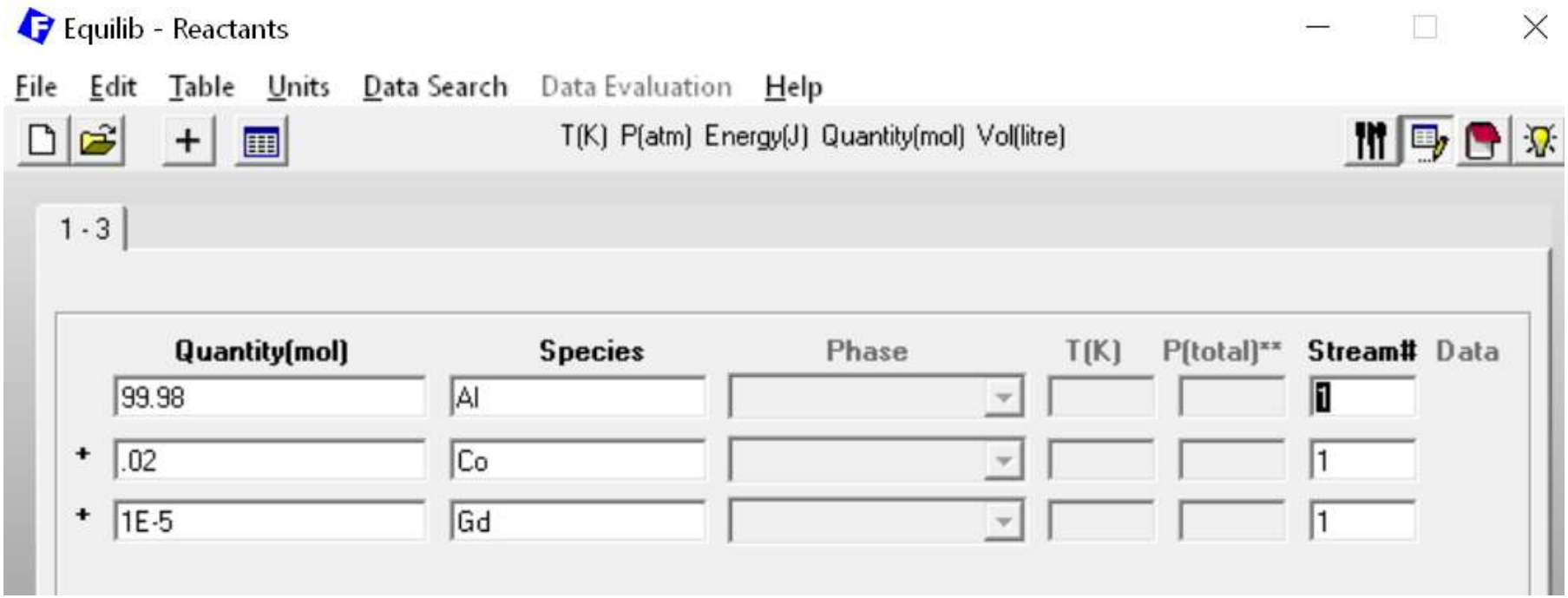


Grain boundary partitioning



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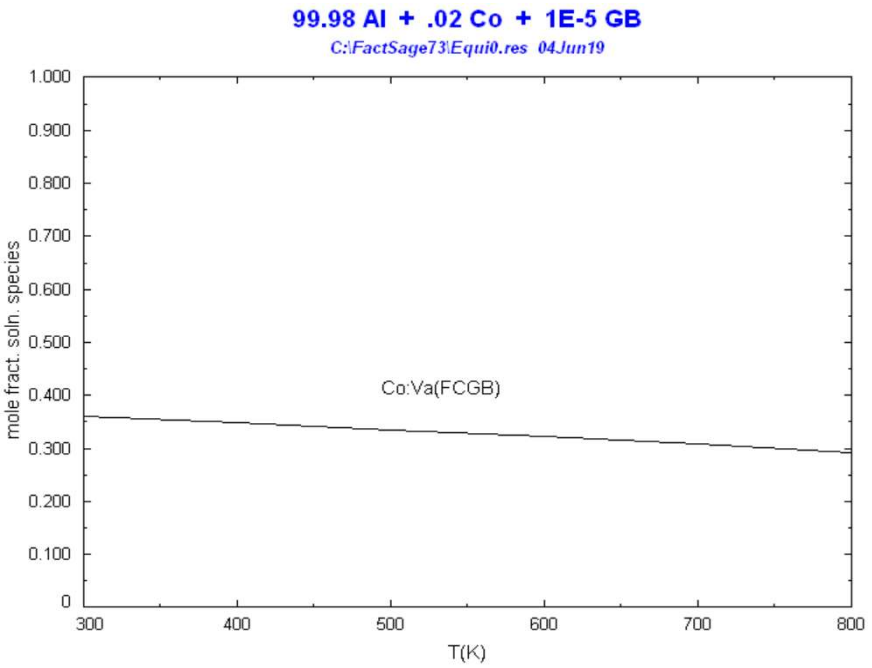

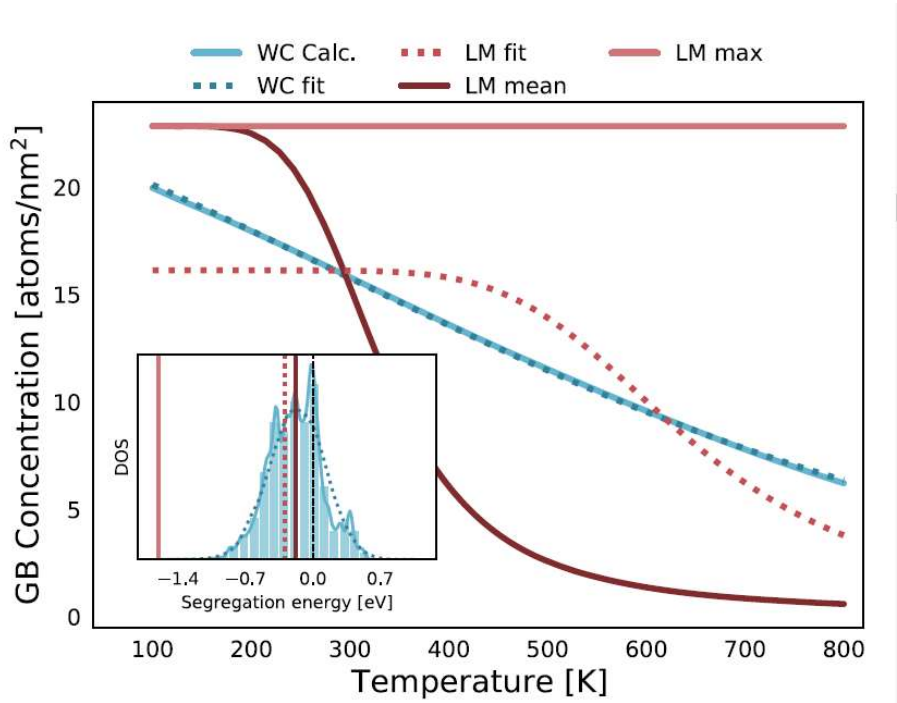

The behavior of the non-optimized FactSage model resembles the WC-model.
The FactSage model can be applied to multi-component non-ideal alloys.

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!