The *Phase Diagram* module

- Use the ***Phase Diagram*** module to generate various types of phase diagrams for systems containing stoichiometric phases as well as solution phases, and any number of system components.
- The ***Phase Diagram*** module accesses the compound and solution databases.
- The **graphical output** of the ***Phase Diagram*** module is handled by the ***Figure*** module.

Table of contents

Section	**1**	Table of contents
Section	**2**	Opening the Phase Diagram Module
Section	**3**	The various windows of the Phase diagram module
Section	**4**	Calculation of the phase diagram and graphical output
Section	**5**	Predominance area diagram: **Cu-SO_2-O_2**
Section	**6**	Metal-metal-oxygen diagram: **Fe-Cr-O_2** (Data Search)
Section	**7**	Classical binary phase diagram: **Fe-Cr**

(continued)

Table of contents **(continued)**

Section 8	Metal-oxygen diagram: **$Fe-O_2$**
Section 9	Ternary isopleth diagram: **Fe-C-W, 5 wt% W**
Section 10	Quaternary predominance area diagram: **$Fe-Cr-S_2-O_2$**
Section 11	Quaternary isopleth diagram: **Fe-Cr-V-C, 1.5% Cr, 0.1% V**
Section 12	Ternary isothermal diagram: **$CaO-Al_2O_3-SiO_2$**
Section 13	Projections-Liquidus and First-Melting
Section 14	Reciprocal Salt Polythermal Liquidus Projection
Section 15	Paraequilibrium and Minimum Gibbs Energy Calculations
Section 16	Enthalpy-Composition (H-X) phase diagrams
Section 17	Plotting Isobars and Iso-activities
Section 18	Scheil-Gulliver Constituent Diagrams
Section 19	Aqueous phase diagrams

Table of contents **(continued)**

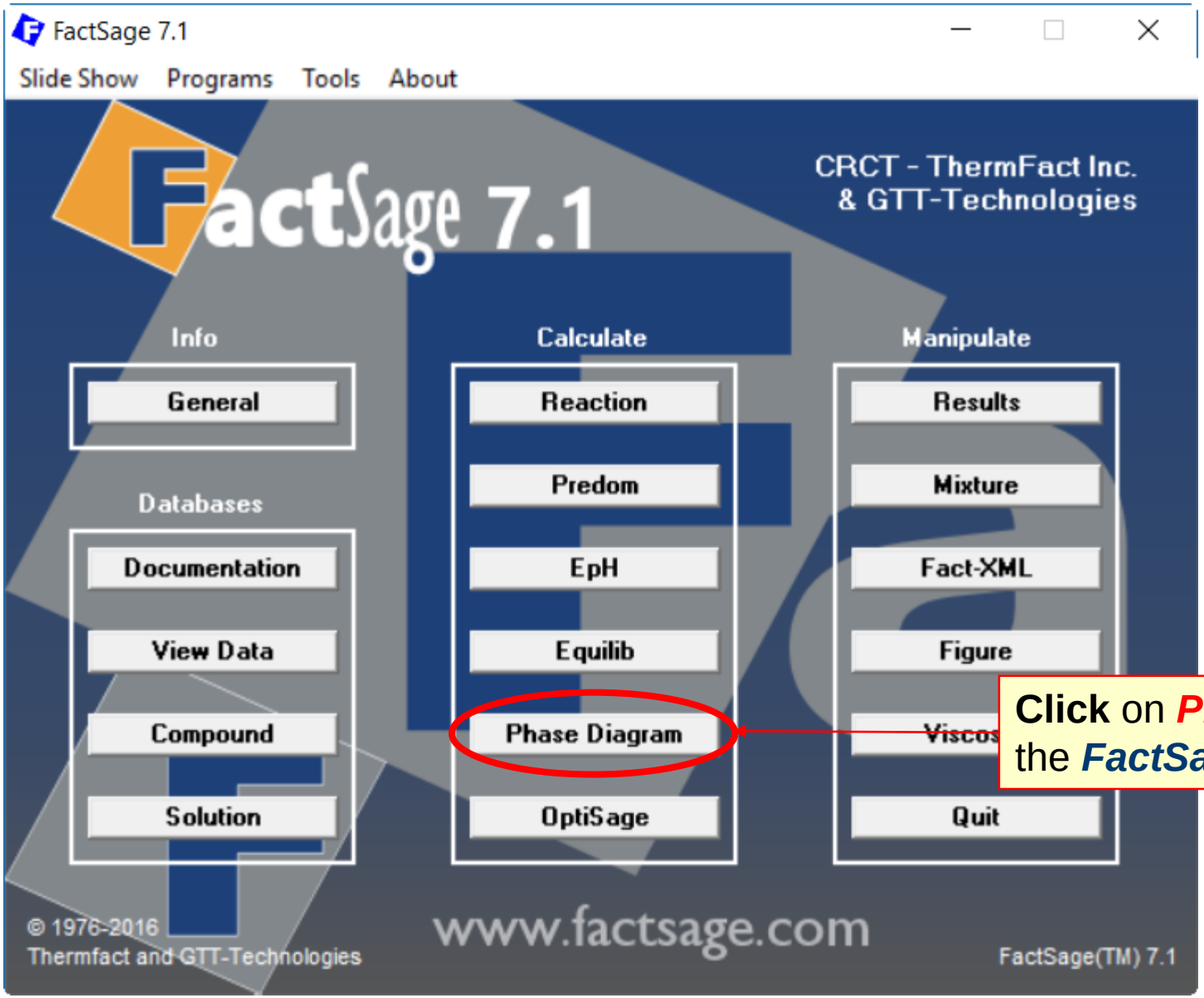
Appendix 1 Zero Phase Fraction (ZPF) Lines

Appendix 2 Generalized rules for the N-Component System

Appendix 3 Using the rules for classical cases: **MgO-CaO, Fe-Cr-S_2-O_2**

Appendix 4 Breaking the rules: **H_2O, Fe-Cr-C**

Initiating the *Phase Diagram* module



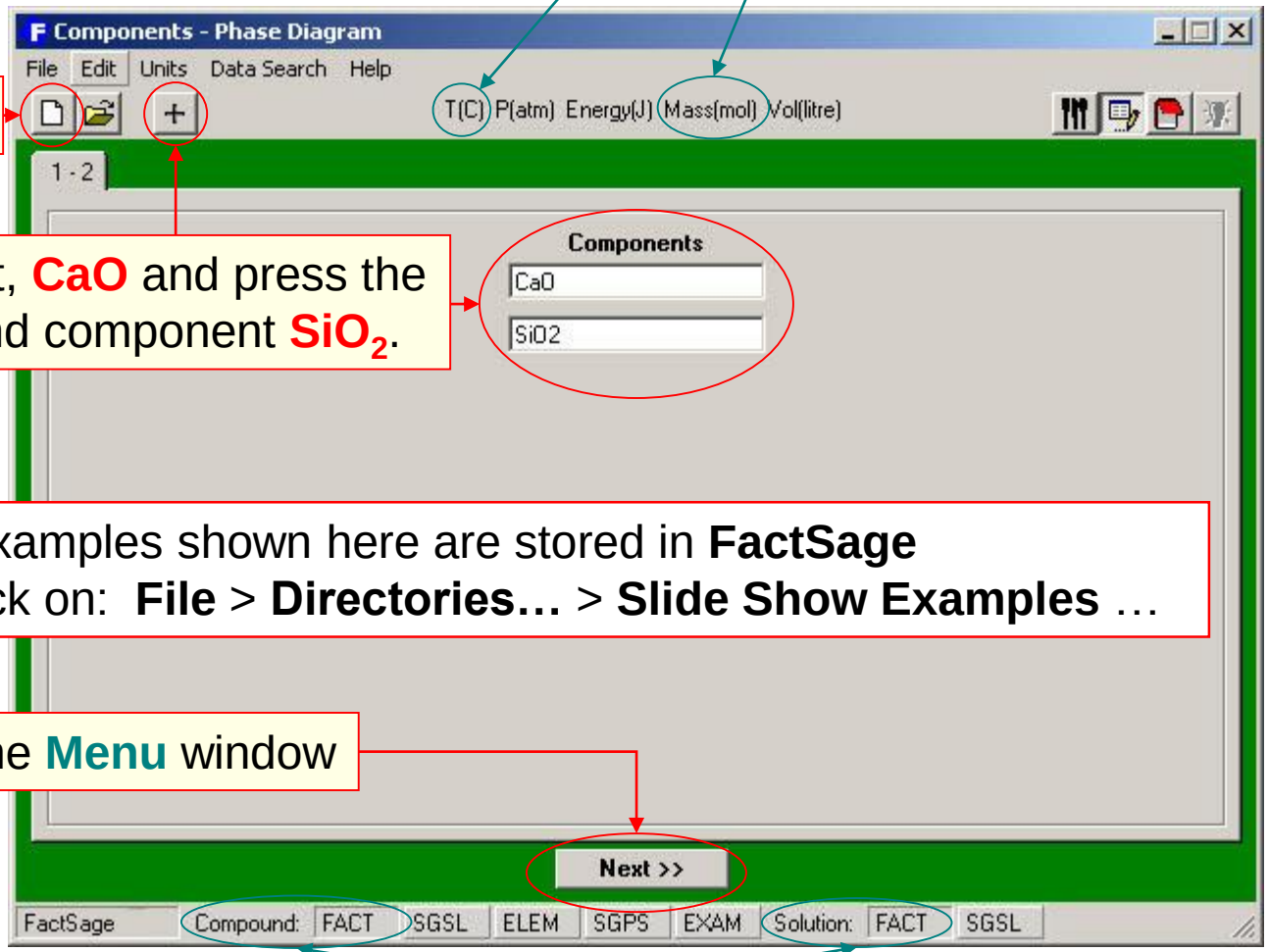
Click on ***Phase Diagram*** in the ***FactSage*** menu window

Components window – preparing a new *Phase Diagram*: CaO – SiO_2

Calculation of the CaO-SiO_2 binary phase diagram – T(C) vs. X(SiO_2)

1° Click on the **New** button

2° Enter the first component, **CaO** and press the **+** button to add the second component **SiO_2**.



All examples shown here are stored in **FactSage**
- click on: **File** > **Directories…** > **Slide Show Examples** …

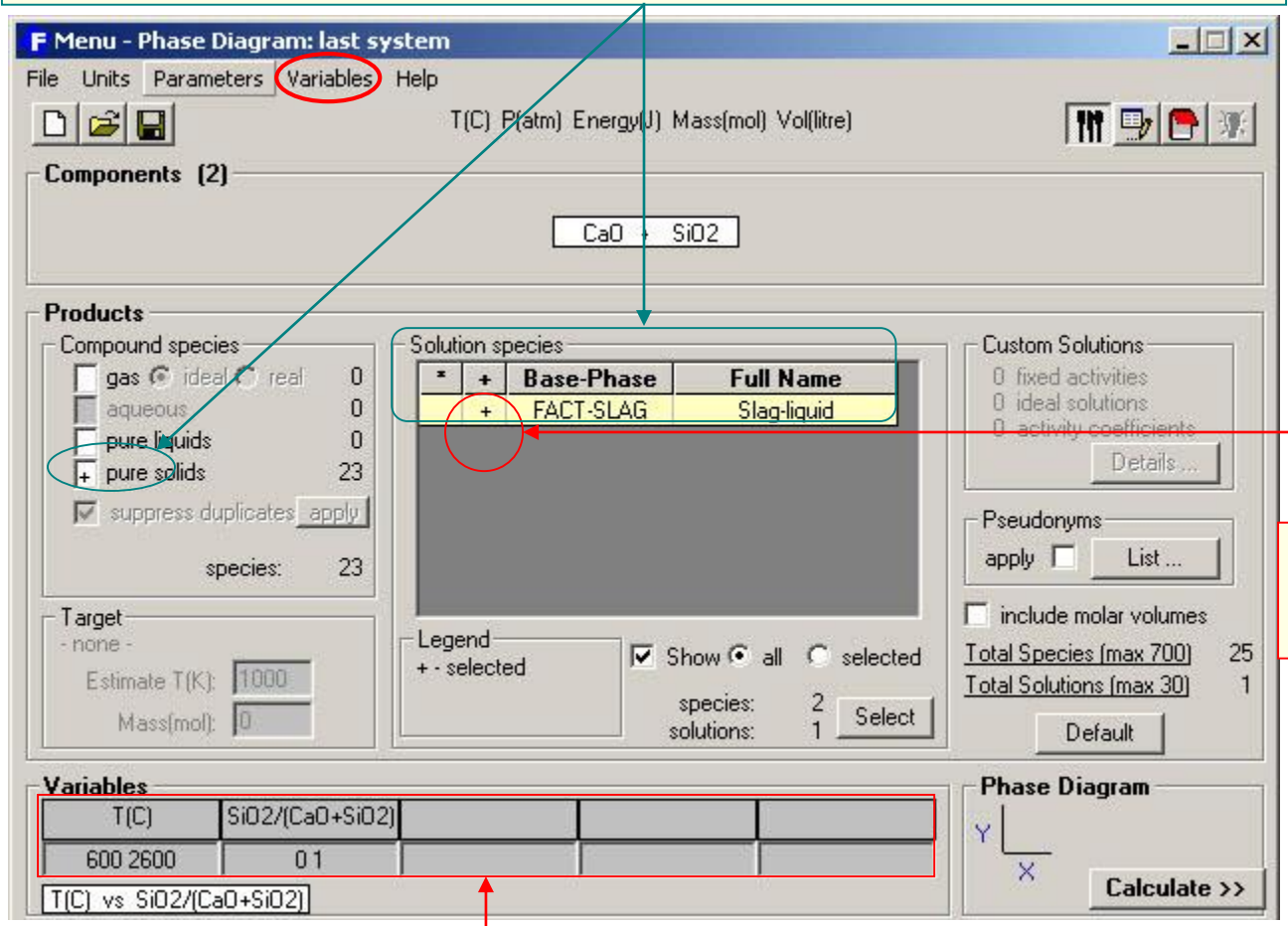
3° Press Next >> to go to the **Menu** window

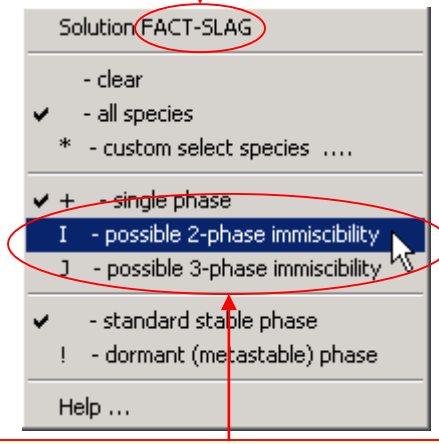
The ***FACT*** Compound and solution databases are selected.

Menu window – selection of the compound and solution species

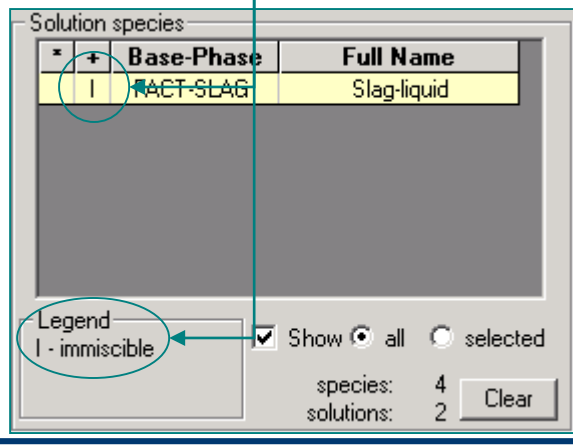
1° Select the products to be included in the calculation: pure solid compound species and the liquid slag phase.

2° Right-click to display the extended menu on **FACT-SLAG**.





3° Select the option possible 2-phase immiscibility



4° Click in the Variables' boxes to open the Variables window (or click on **Variables** in the menu bar).

Compound species selection - *FactSage 6.4*

In **FactSage 6.4** there is a new <u>default exclusion of species from compound species selection</u>

When two or more databases are connected, the same species may appear in more than one database. In such cases, a species should generally only be selected from one database. Otherwise conflicts will probably occur. In order to assist users in deciding which species to exclude, the FactSage developers have assigned priorities. When you initially click on "pure solids", "pure liquids", or "gas" you may now see that several species marked with an "X" have not been selected. That is, they have been excluded by default because of probable conflicts between databases. The FactSage developers suggest that these species not be selected for this particular calculation.

If you wish to select species marked with an "X" you must first click on 'permit selection of "X" species'. This will then override the default setting and permit you to select species as in FactSage 6.3. This will also activate the 'suppress duplicates' button and enable you to define a database priority list as in FactSage 6.3.

<u>IMPORTANT</u> : For many calculations, it may frequently be advisable or necessary to de-select other species in addition to those marked with an "X."

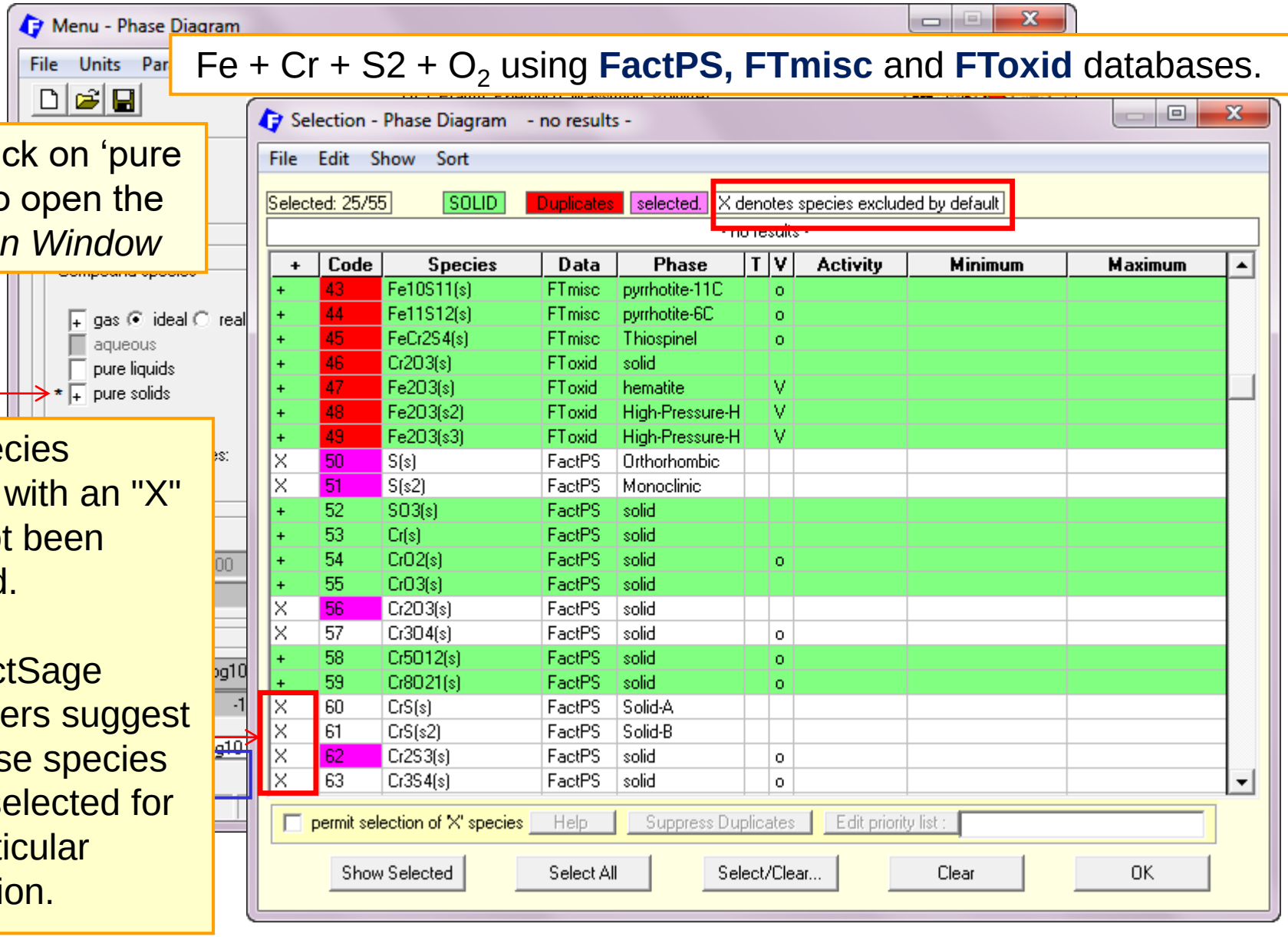
Compound species selection - *FactSage 6.4*

Fe + Cr + S2 + O_2 using **FactPS, FTmisc** and **FToxid** databases.

Right-click on 'pure solids' to open the *Selection Window*

The species marked with an "X" have not been selected.

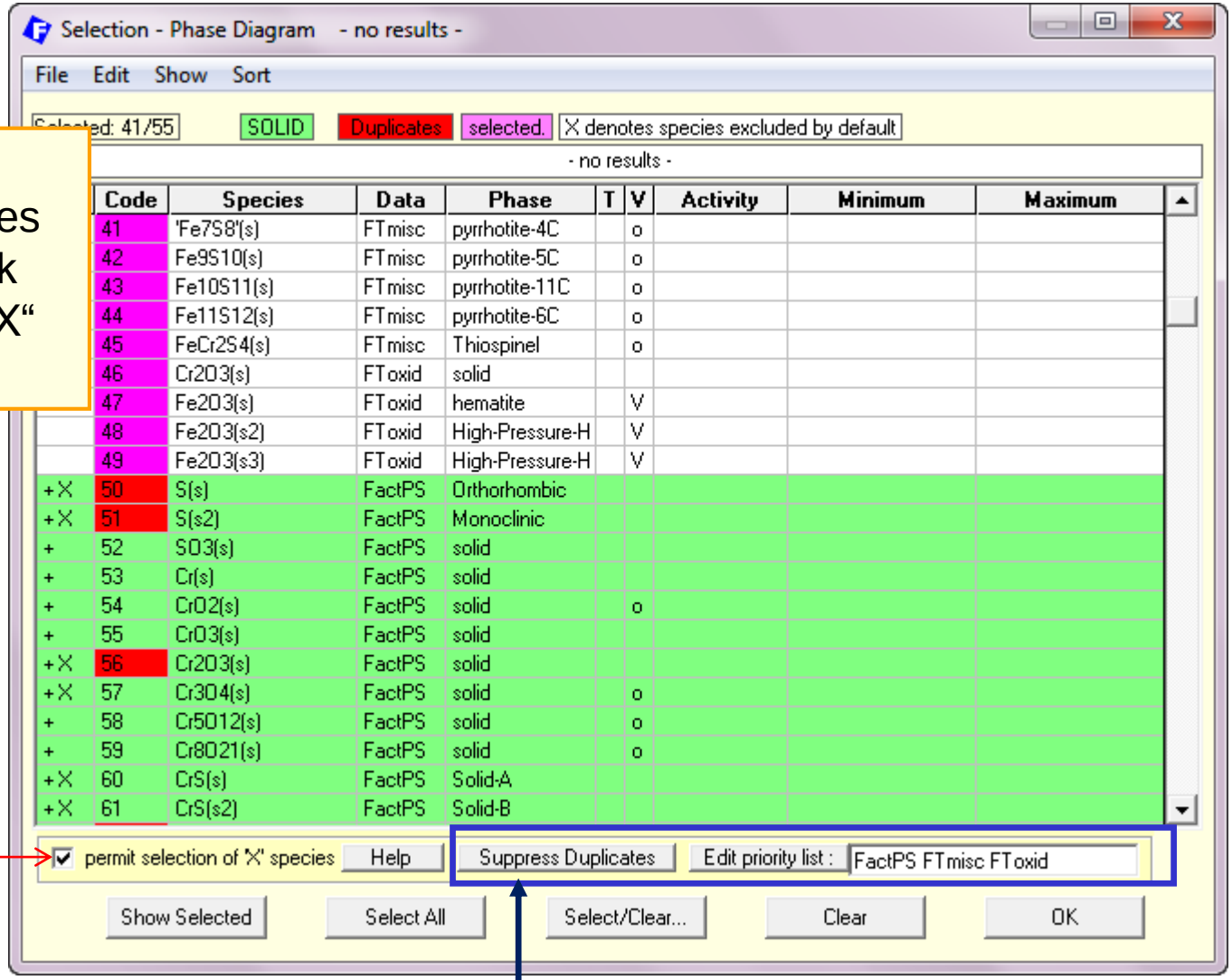
The FactSage developers suggest that these species not be selected for this particular calculation.



+	Code	Species	Data	Phase	T	V	Activity	Minimum	Maximum
+	43	Fe10S11(s)	FTmisc	pyrrhotite-11C		o			
+	44	Fe11S12(s)	FTmisc	pyrrhotite-6C		o			
+	45	FeCr2S4(s)	FTmisc	Thiospinel		o			
+	46	Cr2O3(s)	FToxid	solid					
+	47	Fe2O3(s)	FToxid	hematite		V			
+	48	Fe2O3(s2)	FToxid	High-Pressure-H		V			
+	49	Fe2O3(s3)	FToxid	High-Pressure-H		V			
X	50	S(s)	FactPS	Orthorhombic					
X	51	S(s2)	FactPS	Monoclinic					
+	52	SO3(s)	FactPS	solid					
+	53	Cr(s)	FactPS	solid					
+	54	CrO2(s)	FactPS	solid		o			
+	55	CrO3(s)	FactPS	solid					
X	56	Cr2O3(s)	FactPS	solid					
X	57	Cr3O4(s)	FactPS	solid		o			
+	58	Cr5O12(s)	FactPS	solid		o			
+	59	Cr8O21(s)	FactPS	solid		o			
X	60	CrS(s)	FactPS	Solid-A					
X	61	CrS(s2)	FactPS	Solid-B					
X	62	Cr2S3(s)	FactPS	solid		o			
X	63	Cr3S4(s)	FactPS	solid		o			

Compound species selection - *FactSage 6.4*

To override the default setting and select species marked with an "X“, click on 'permit selection of "X“ species'.



	Code	Species	Data	Phase	T	V	Activity	Minimum	Maximum
	41	'Fe7S8'(s)	FTmisc	pyrrhotite-4C		o			
	42	Fe9S10(s)	FTmisc	pyrrhotite-5C		o			
	43	Fe10S11(s)	FTmisc	pyrrhotite-11C		o			
	44	Fe11S12(s)	FTmisc	pyrrhotite-6C		o			
	45	FeCr2S4(s)	FTmisc	Thiospinel		o			
	46	Cr2O3(s)	FToxid	solid					
	47	Fe2O3(s)	FToxid	hematite		V			
	48	Fe2O3(s2)	FToxid	High-Pressure-H		V			
	49	Fe2O3(s3)	FToxid	High-Pressure-H		V			
+X	50	S(s)	FactPS	Orthorhombic					
+X	51	S(s2)	FactPS	Monoclinic					
+	52	SO3(s)	FactPS	solid					
+	53	Cr(s)	FactPS	solid					
+	54	CrO2(s)	FactPS	solid		o			
+	55	CrO3(s)	FactPS	solid					
+X	56	Cr2O3(s)	FactPS	solid					
+X	57	Cr3O4(s)	FactPS	solid		o			
+	58	Cr5O12(s)	FactPS	solid		o			
+	59	Cr8O21(s)	FactPS	solid		o			
+X	60	CrS(s)	FactPS	Solid-A					
+X	61	CrS(s2)	FactPS	Solid-B					

You can then also set a database priority list and ‘Suppress Duplicates’.

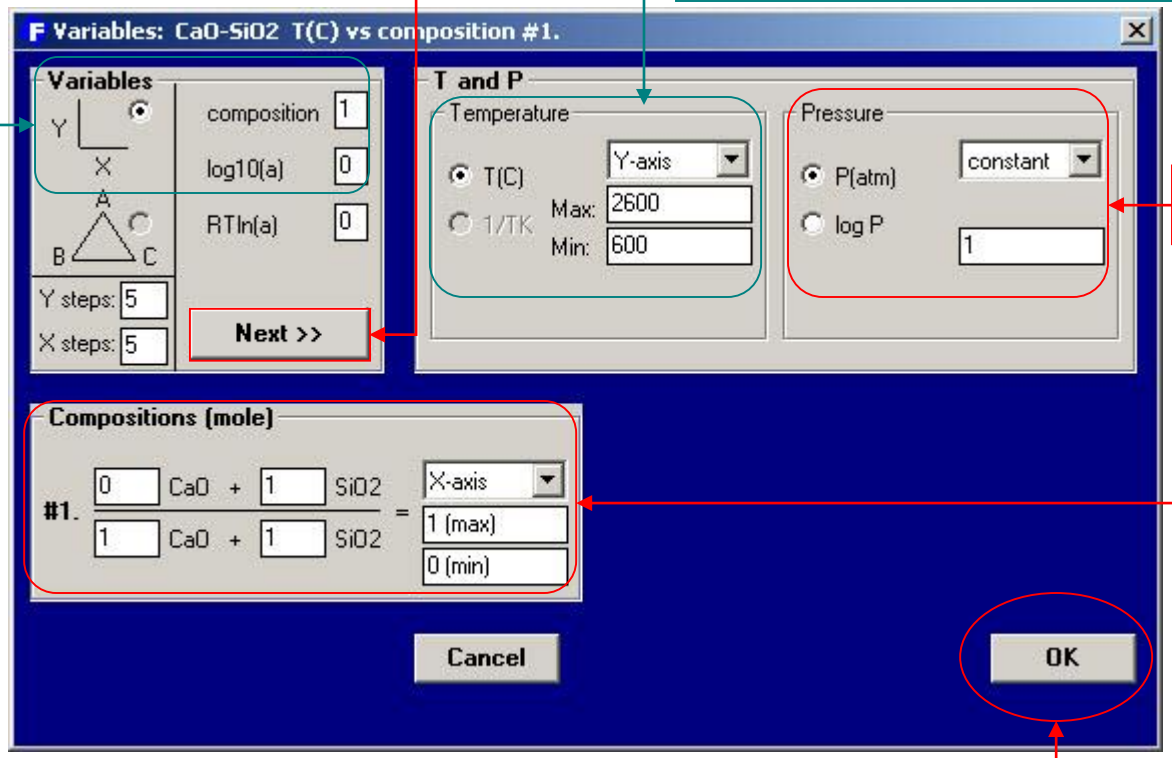
Variables window – defining the variables for the phase diagram

Calculation of the $CaO\text{-}SiO_2$ binary phase diagram – **T(C)** vs. **$X(SiO_2)$**

1° Select a X-Y (rectangular) graph and **one** composition variable: **$X(SiO_2)$**

2° Press Next >> to define the composition, temperature and pressure.

3° Set the **Temperature** as Y-axis and **enter** its limits.



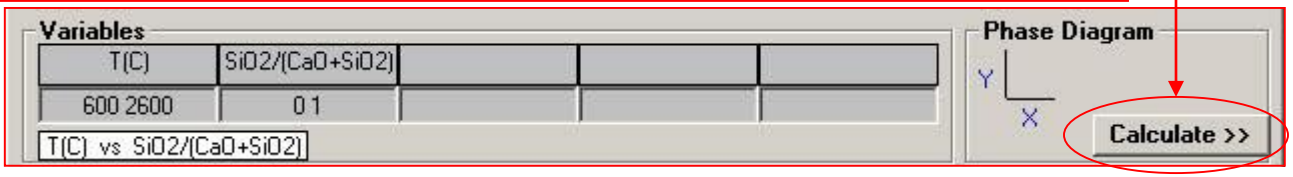
4° Set the **Pressure** at **1 atm**.

5° Set the **composition** [mole fraction **$X(SiO_2)$**] as X-axis and **enter** its limits.

6° Press OK to return to the **Menu** window.

Calculation of the phase diagram and graphical output

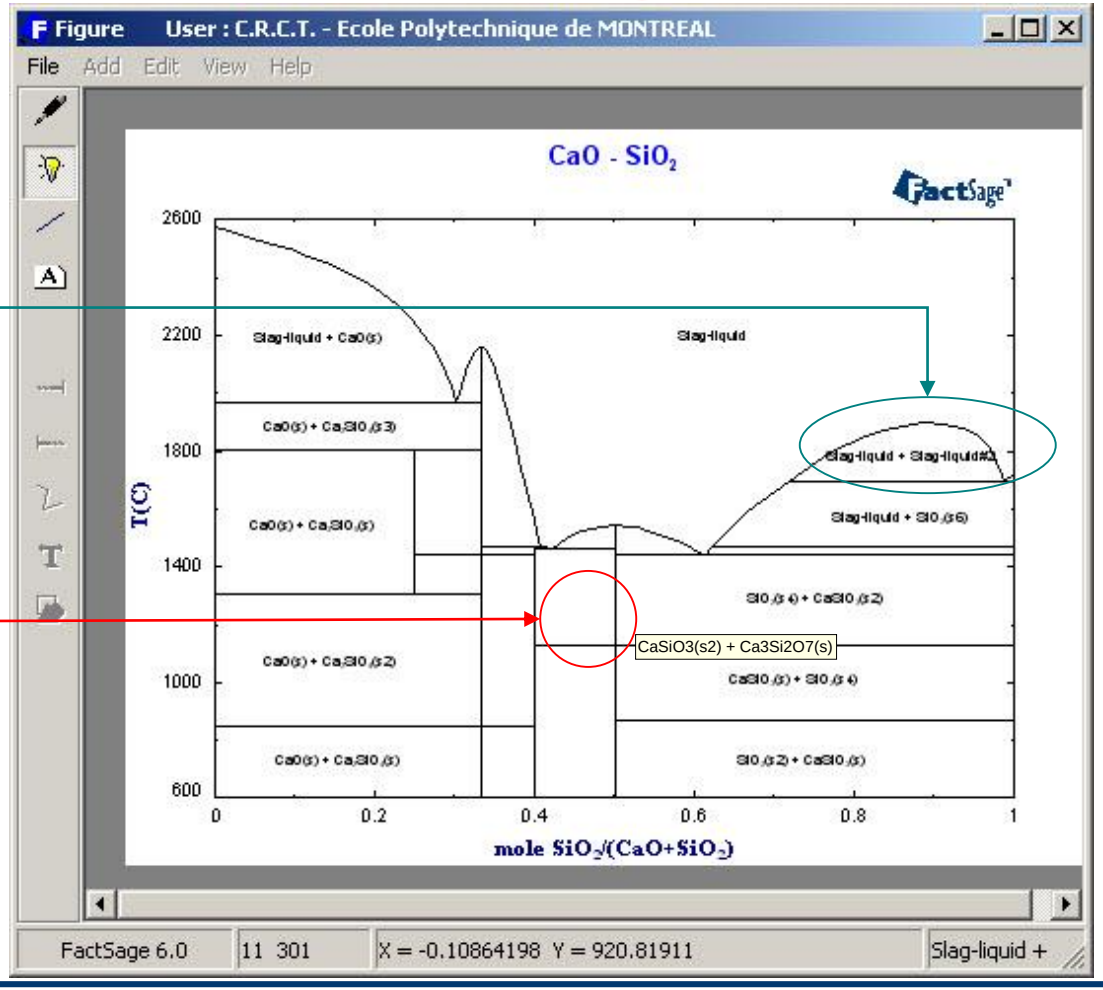
1° Press Calculate>> to calculate the phase diagram.



Note the effect of the **I** option: the miscibility gap is calculated.

2° You can point and click to label the phase diagram.

See the ***Figure*** slide show for more features of the ***Figure*** module.



A classical predominance area diagram

In the following two slides is shown how the ***Phase Diagram*** module is employed in order to generate the same type of diagram that can also be produced with the ***Predom*** module.

As an example the system is **Cu-SO_2-O_2**.

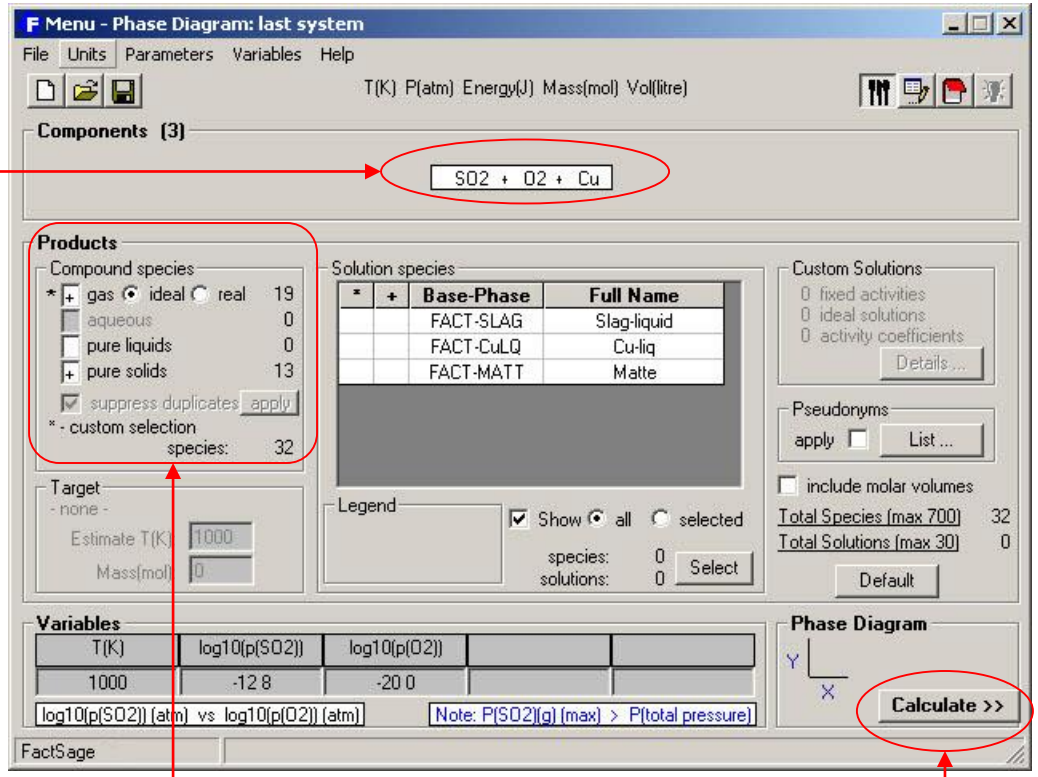
Note that SO_2 and O_2 are used as input in the Components window.

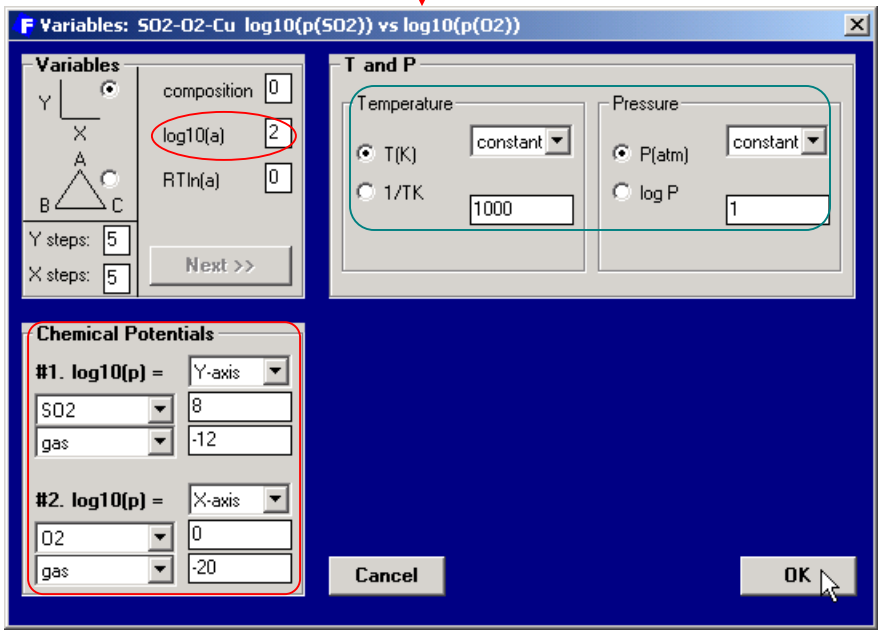
Predominance area diagram: Cu-SO_2-O_2

1° Entry of the components
(done in the **Components** window)

2° Definition of the variables:

- $\log_{10}(P_{SO_2})$, $\log_{10}(P_{O_2})$
- T = 1000K
- P = 1 atm



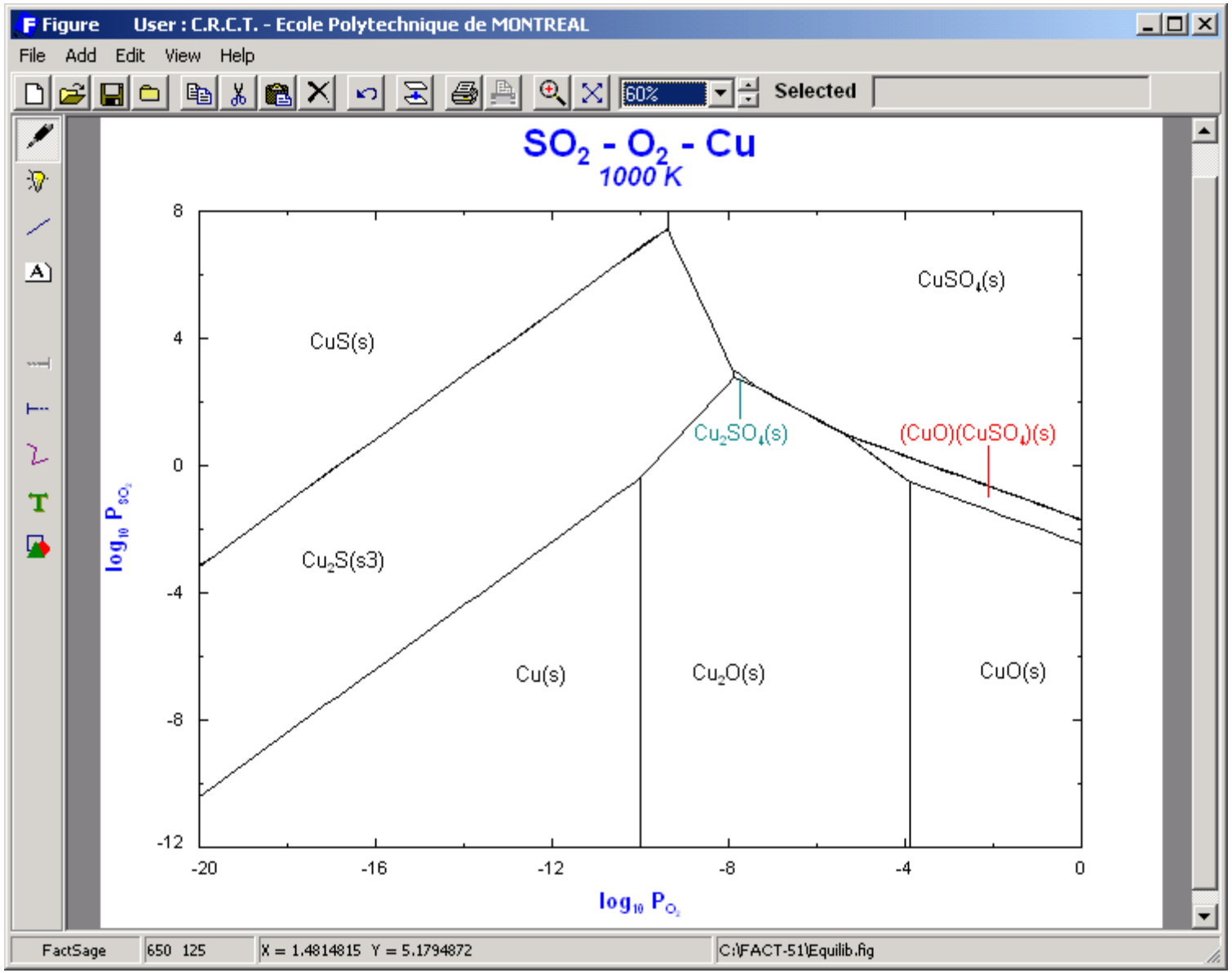


3° Selection of the products:

- gas ideal
- pure solids

4° Computation of the phase diagram

Predominance area diagram: Cu-SO_2-O_2 ; Graphical Output



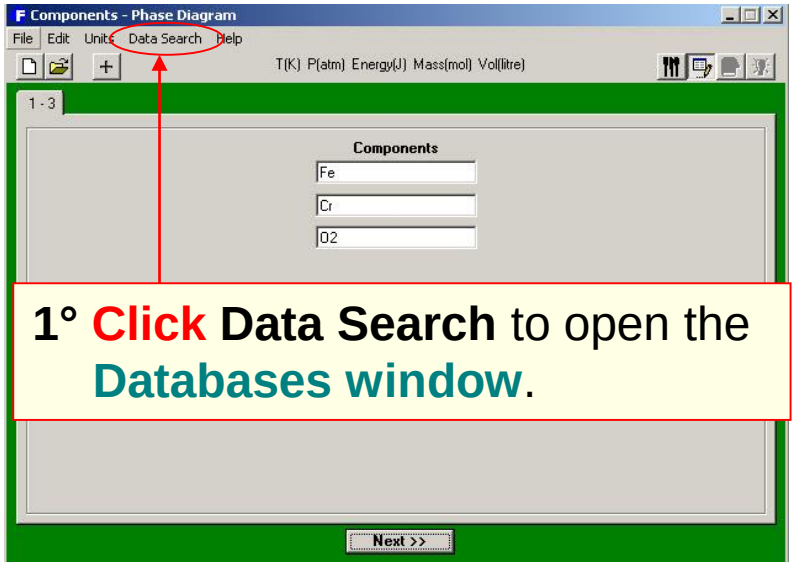
A two metal oxygen system – Fe-Cr-O_2

The following slides show how a phase diagram for an alloy system **Fe-Cr-O_2** with variable composition under a gas phase with variable oxygen potential (partial pressure) for constant temperature is prepared and generated.

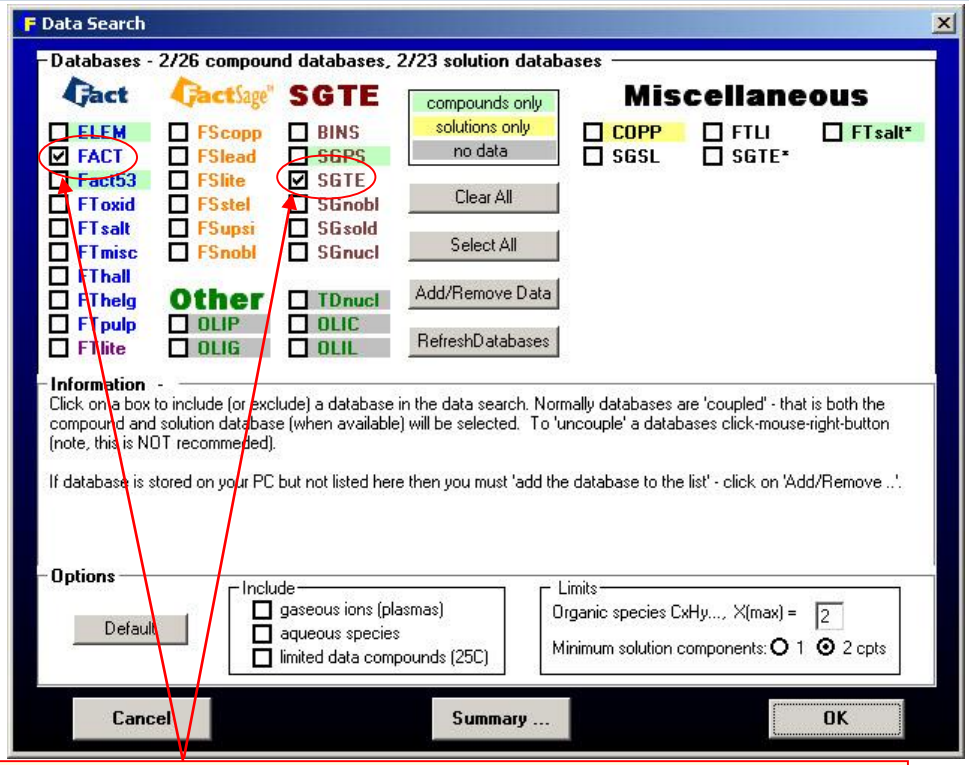
Note the use of the «metallic mole fraction» (Cr/(Cr+Fe)) on the x-axis and oxygen partial pressure log $P(O_2)$ on the y-axis.

This example combines FACT (for the oxides) with SGTE (for the alloy solid solutions) databases. It shows ``Data Search`` and how to select the databases.

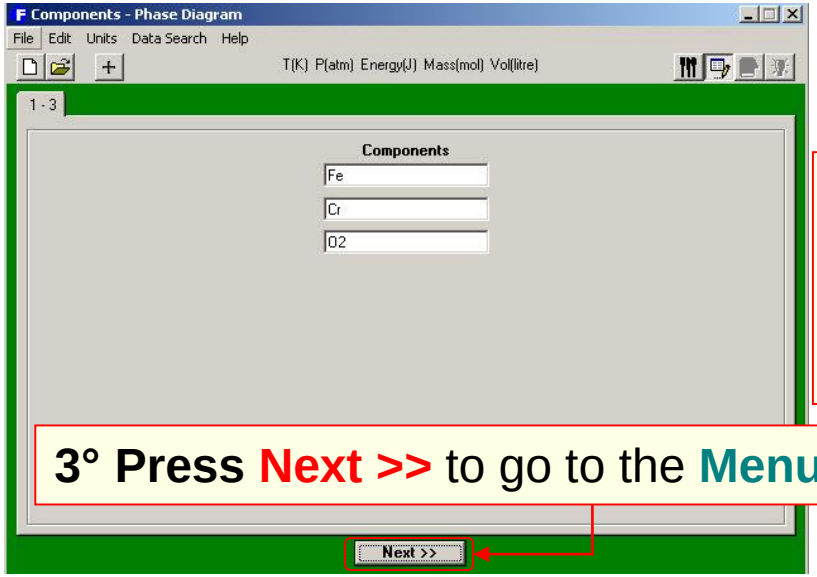
Fe-Cr-O_2 : selection of databases



1° **Click Data Search** to open the **Databases window**.



2° **Click** on a box to **include** or **exclude** a **database** from the data search. Here the **FACT** and **SGTE** compound and solution databases have been selected.



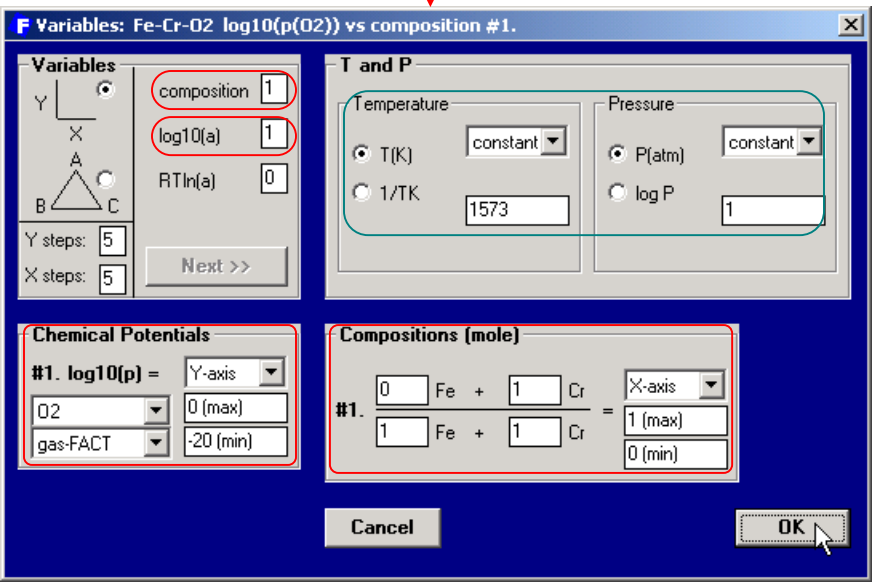
3° **Press Next >>** to go to the **Menu** window

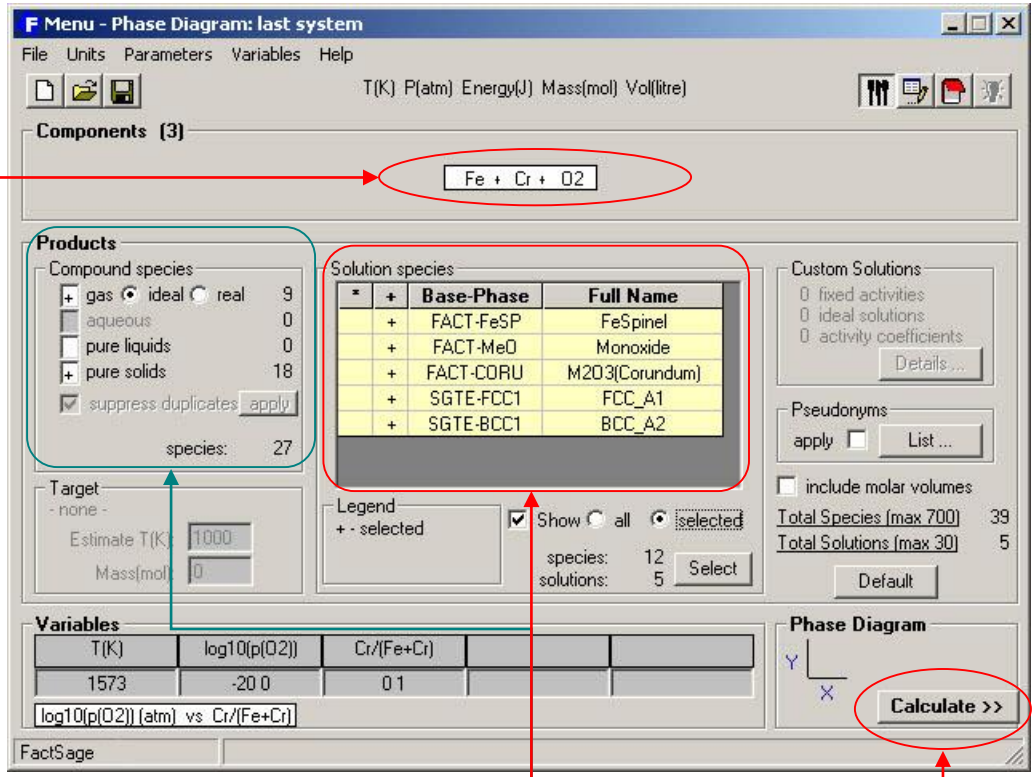
$Fe\text{-}Cr\text{-}O_2$: selection of variables and solution phases

1° Entry of the components
(done in the **Components** window)

2° Definition of the variables:

- **1 chemical potential: $P(O_2)$**
- **1 composition: X_{Cr}**
- **T = 1573K**
- **P = 1 atm**



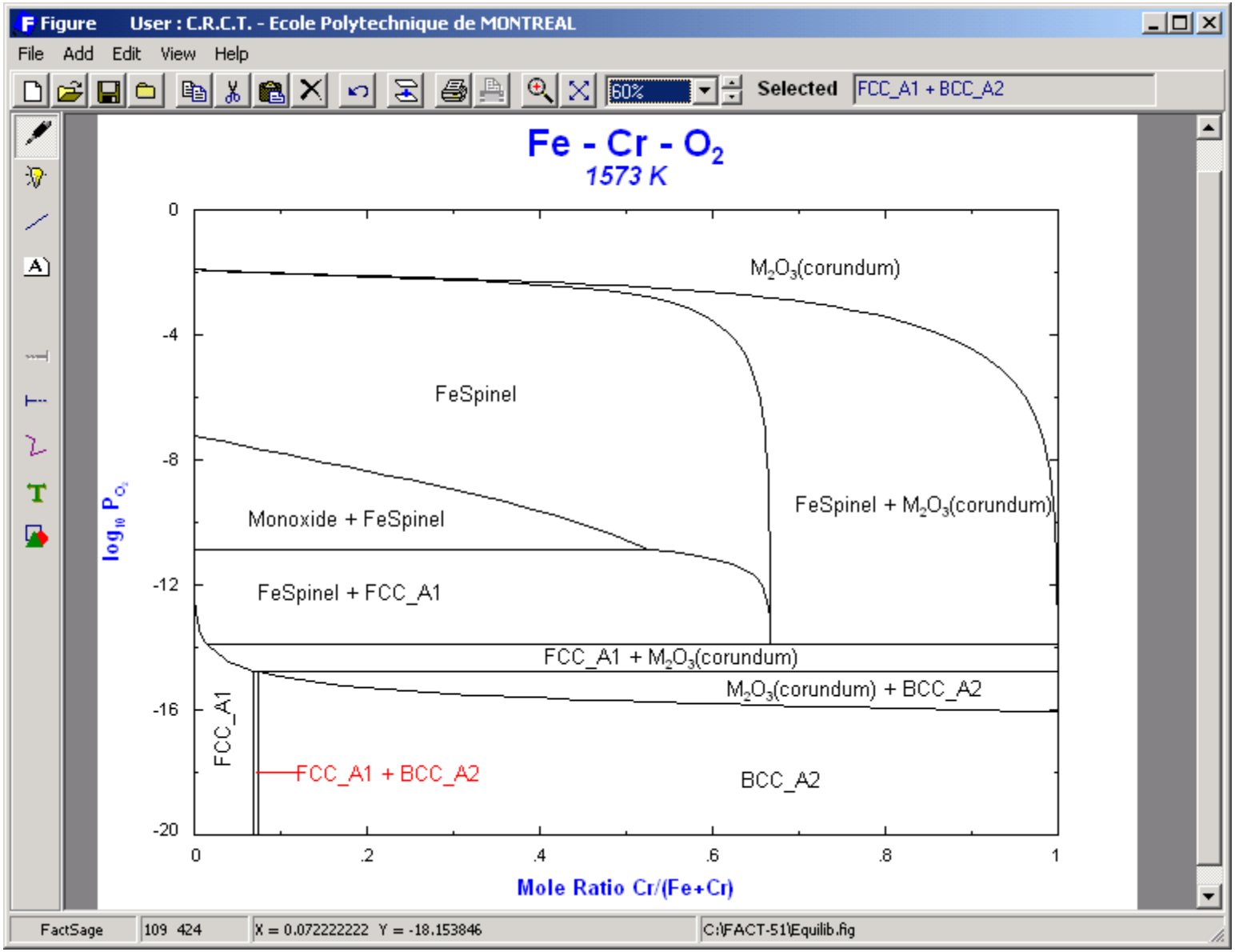


3° Selection of the products:

- **gas ideal**
- **pure solids**
- **5 solution phases**

4° Computation of the phase diagram

Fe-Cr-O_2 : graphical output



A classical temperature vs composition diagram

The following two slides show the preparation and generation of a labelled binary T vs X phase diagram.

Note: The labels are entered into the diagram interactively. Click on the «A» button (stable phases label mode) and then move the cursor through the diagram. Where the left mouse button is clicked a label will be inserted into the diagram.

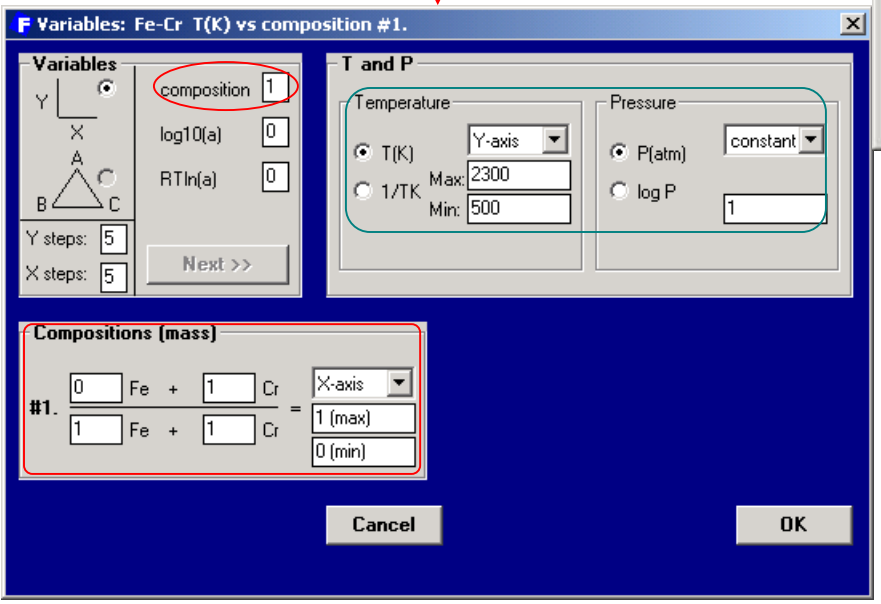
The **Fe-Cr system** is used in this example.

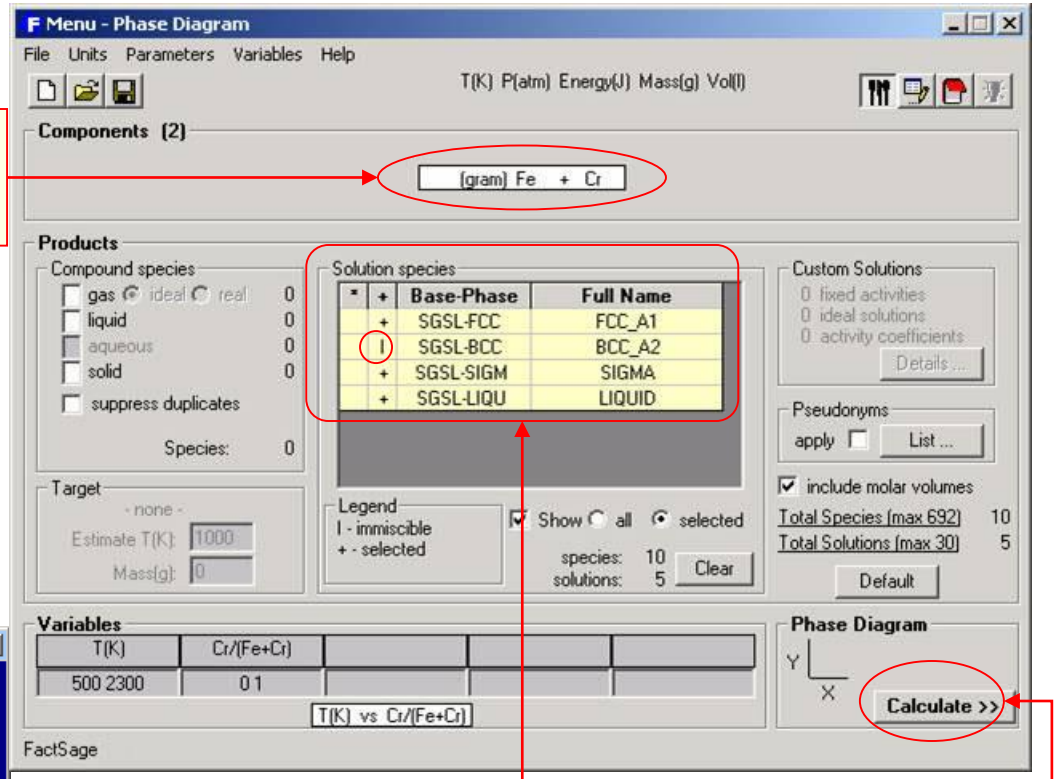
Fe-Cr binary phase diagram: input variables and solution species

1° **Entry** of the components
(done in the **Components** window)

2° **Definition** of the variables:

- **composition: $0 < Wt_{Cr} < 1$**
- **500K < T < 2300K**
- **P = 1 atm**





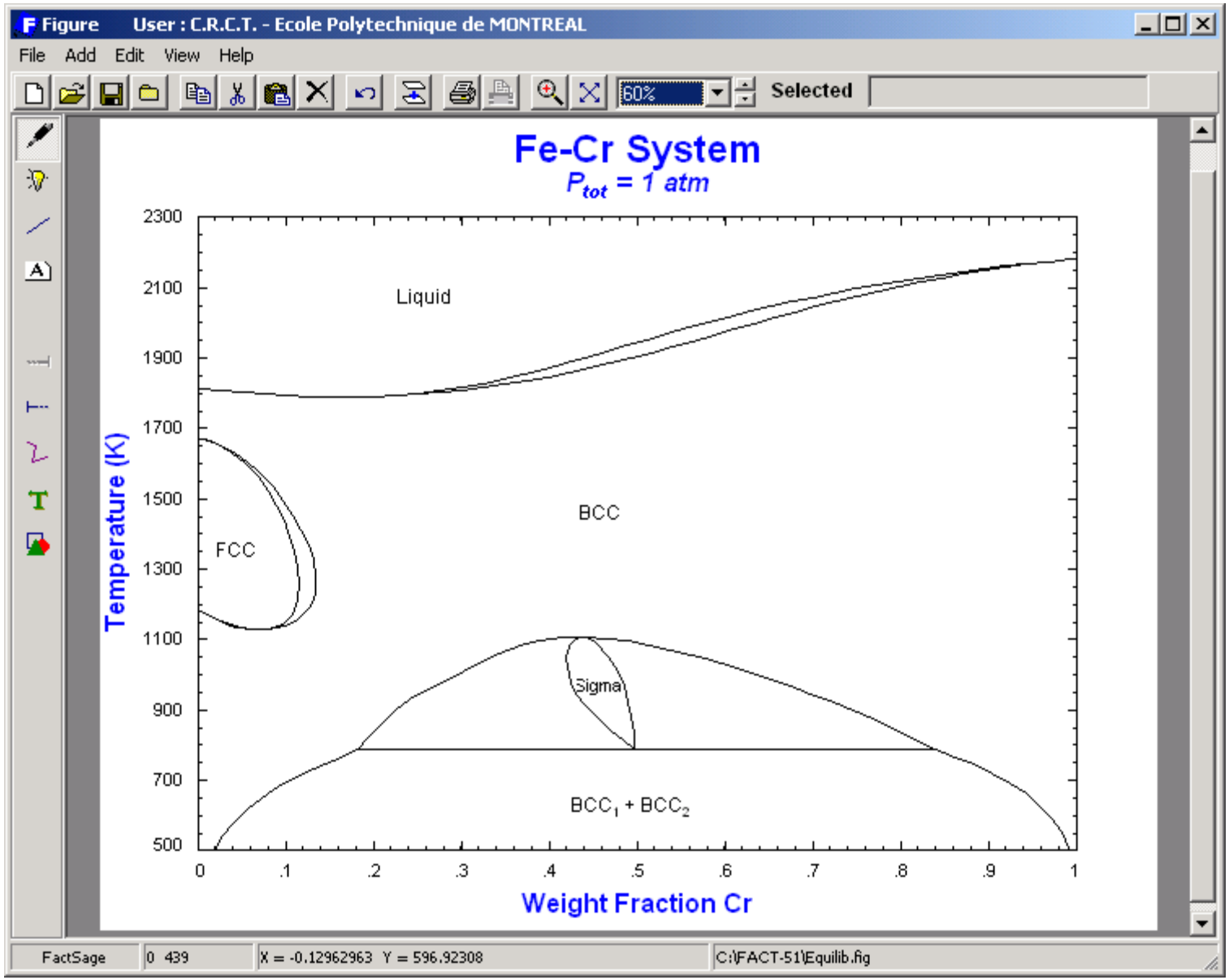
3° **Selection** of the products:

- **4 solid solution phases**
- **1 liquid solution phase**

Note the immiscibility for the BCC phase

4° **Computation** of the phase diagram

Fe-Cr binary phase diagram: graphical output



A two potential phase diagram

In the following two slides the preparation and generation of a phase diagram with two potential axes is shown.

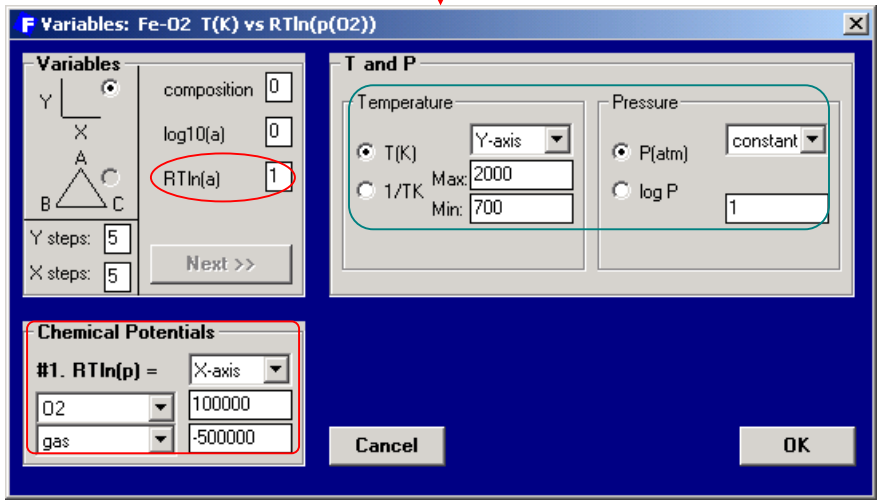
The chosen axes are temperature and one chemical potential in a binary system. Note the difference in the diagram topology that results from the choice of RT ln $P(O_2)$ rather than log $P(O_2)$.

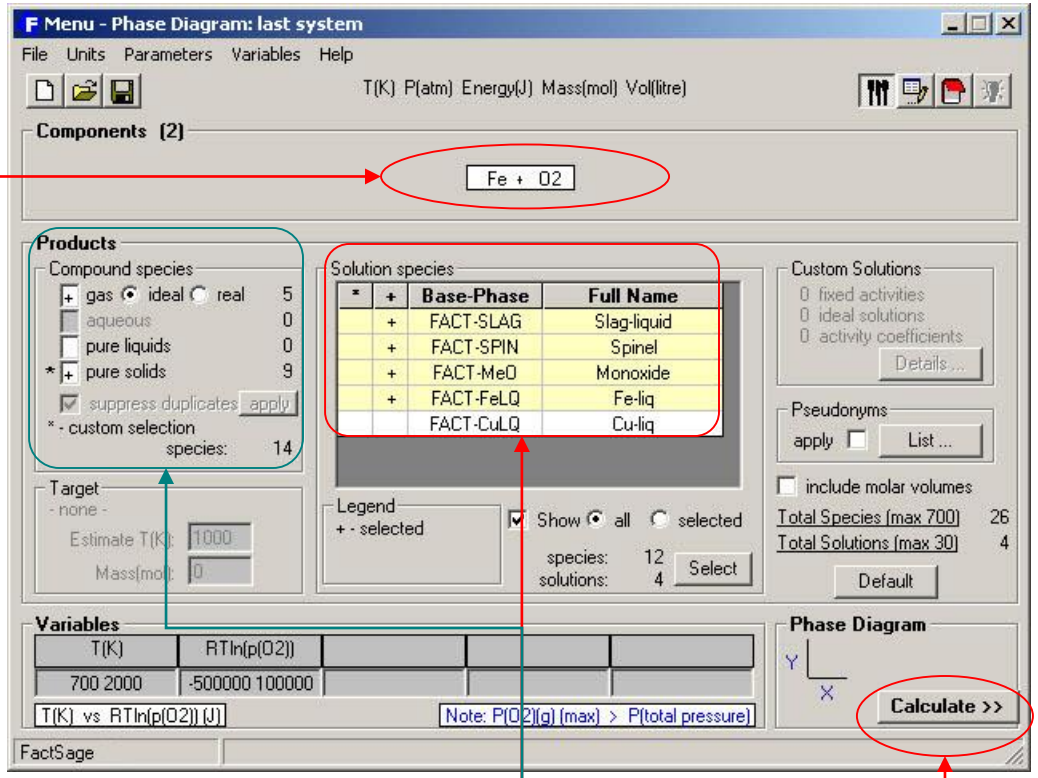
The **Fe-O_2** system is used as the example.

$Fe\text{-}O_2$ system: input

1° **Entry** of the components
(done in the **Components** window)

2° **Definition** of the variables:
- **1 chemical potential**
- **700K < T < 2000K**
- **P = 1 atm**

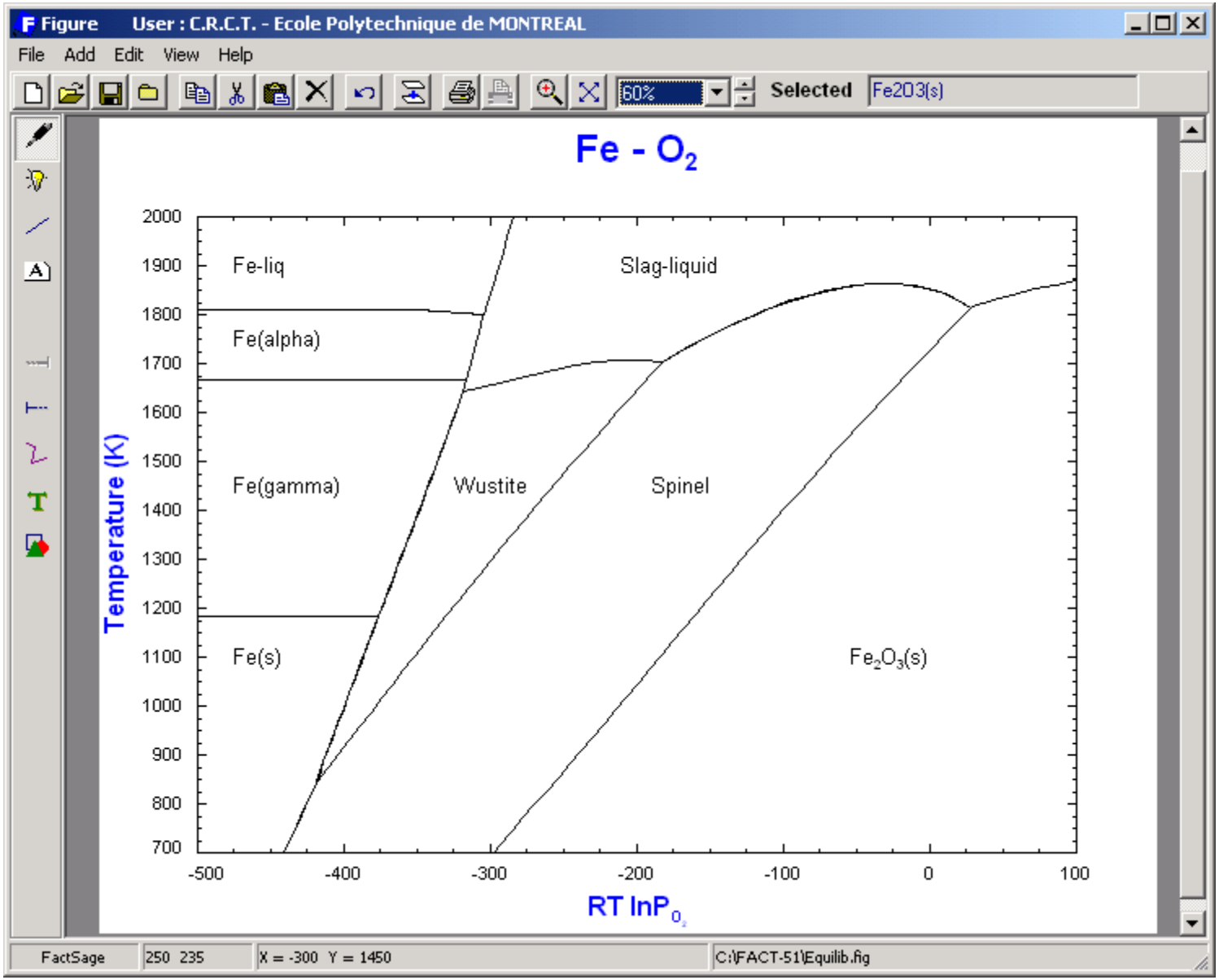




3° **Selection** of the products:
- **pure solids**
- **4 solution phases**

4° **Computation** of the phase diagram

$Fe\text{-}O_2$ system: graphical output



A ternary isopleth diagram

The following two slides show how a ternary isopleth diagram is prepared and generated.

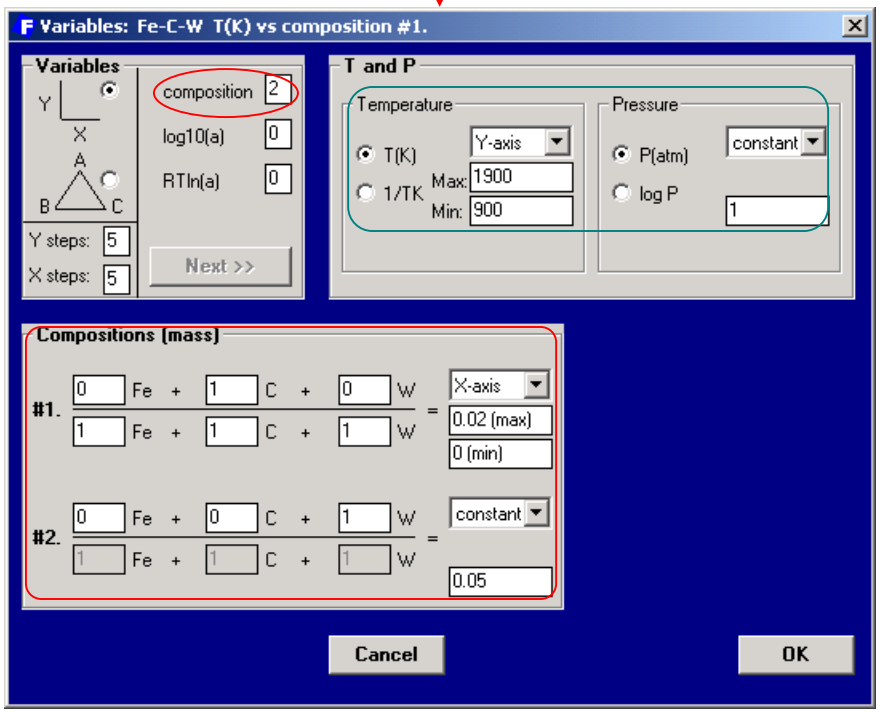
Temperature and one weight percent variable are used on the axes while the third compositional variable (here the wt% of the second metallic component) is kept constant.

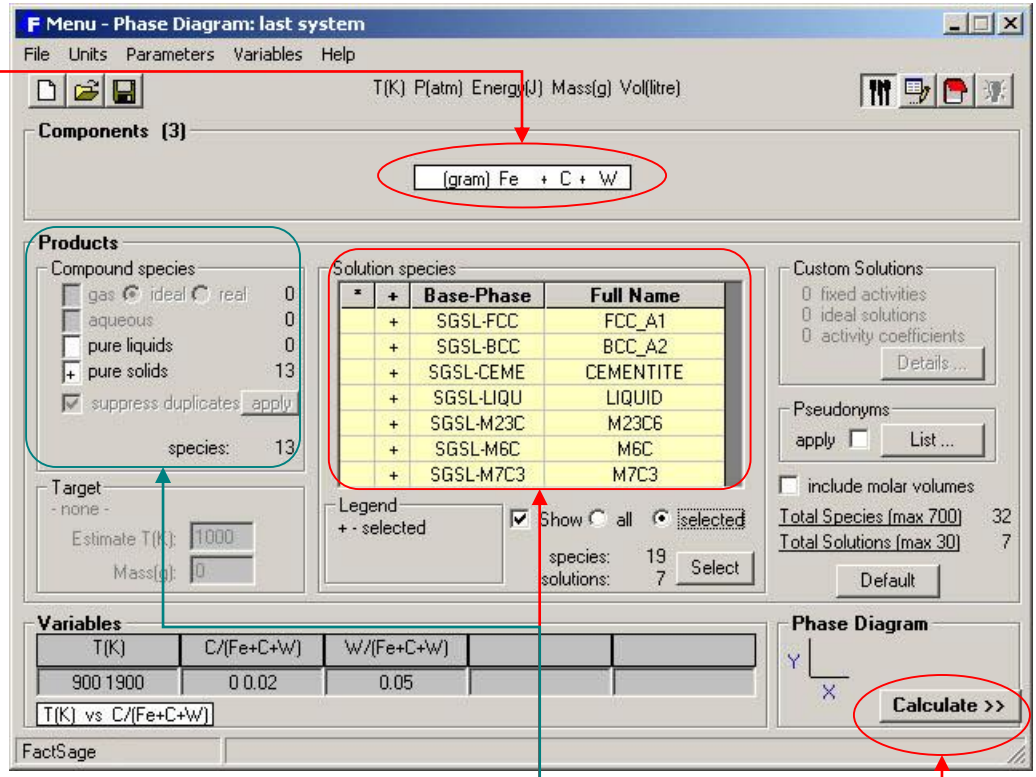
As an example the **Fe-W-C system** is used.

Fe-C-W system at 5 wt% W: input

1° **Entry** of the components
(done in the **Components** window)

2° **Definition** of the variables:
- **2 compositions (mass)**
- **900K < T < 1900K**
- **P = 1 atm**

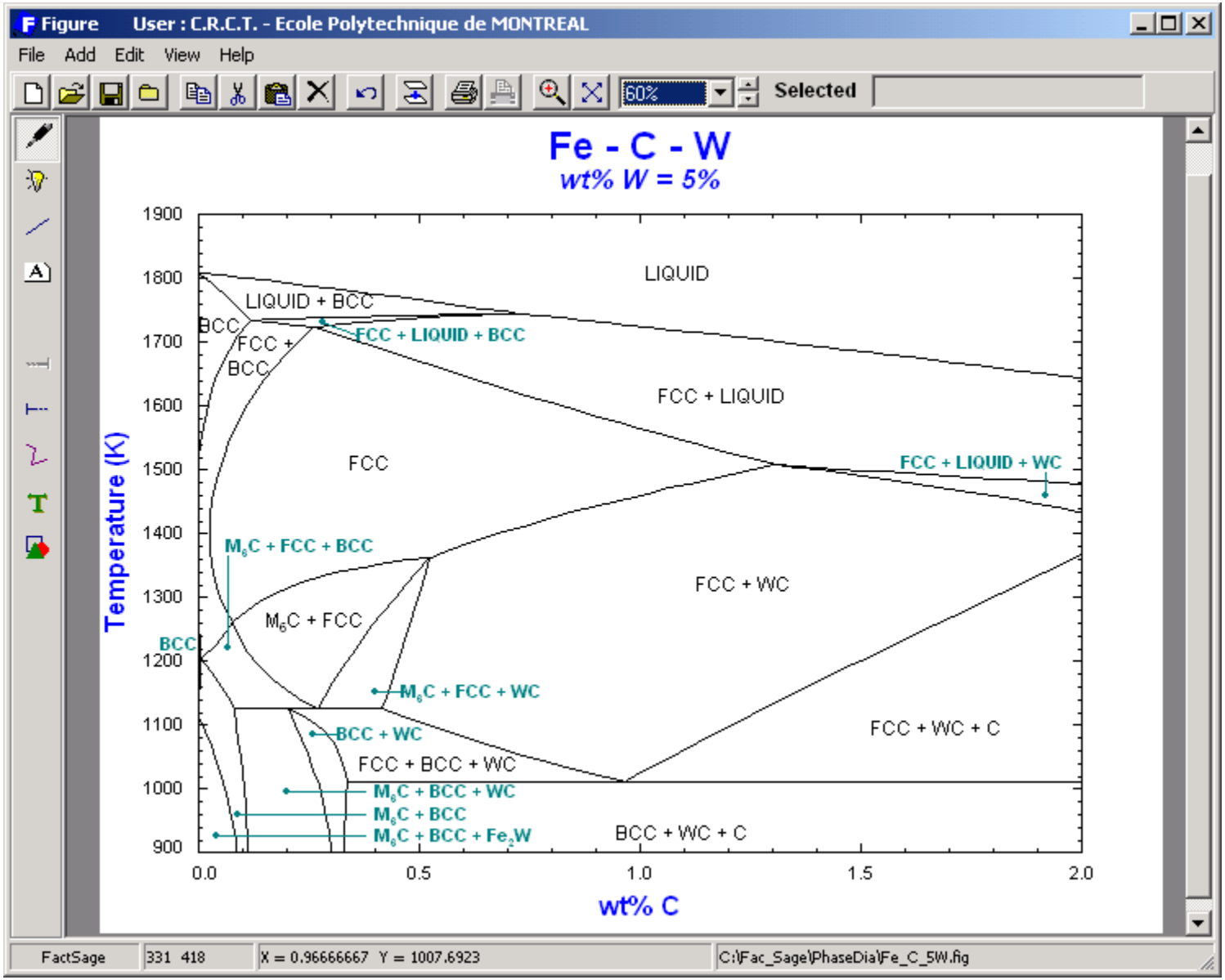




3° **Selection** of the products:
- **pure solids**
- **7 solution phases**

4° **Computation** of the phase diagram

Fe-C-W system at 5 wt% W: graphical output



A quaternary predominance area diagram

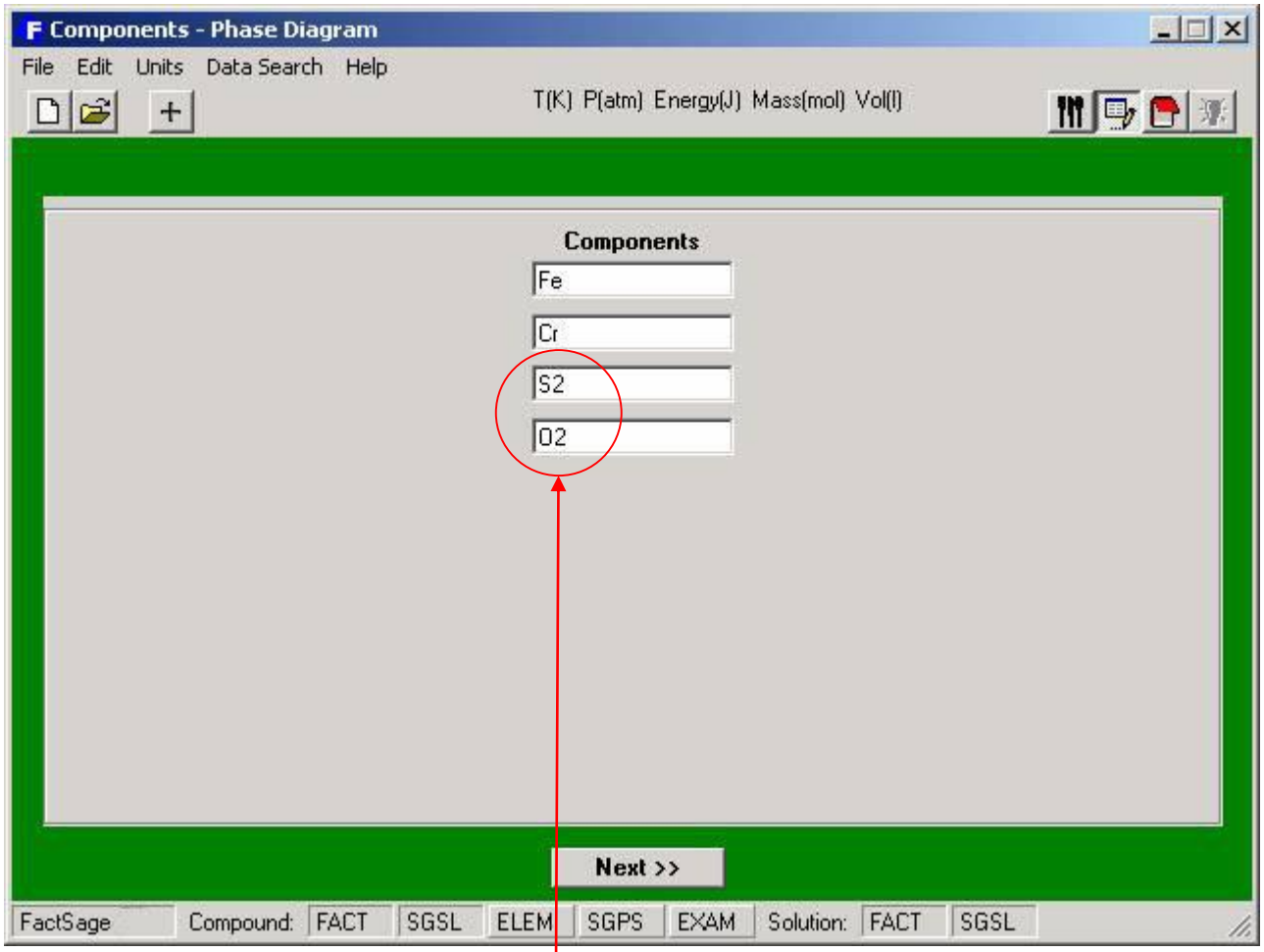
The following three slides show the preparation and calculation of a predominance area type phase diagram with two metal components and two gaseous components.

The partial pressures, i.e. chemical potentials, of the gaseous components are used as axes variables. Note the use of the species names O_2 and S_2 in the Components window. These are used to retrieve the data for the correct gas species from the database. Temperature and total pressure are kept constant.

Different from the Predom module the present diagram also shows the effect of solution phase formation (FCC, BCC, (Fe,Cr)S, Fe-spinel).

As an example the **Fe-Cr-S_2-O_2** system is used.

Predominance area diagram: Fe-Cr-S_2-O_2 System, solid solution input



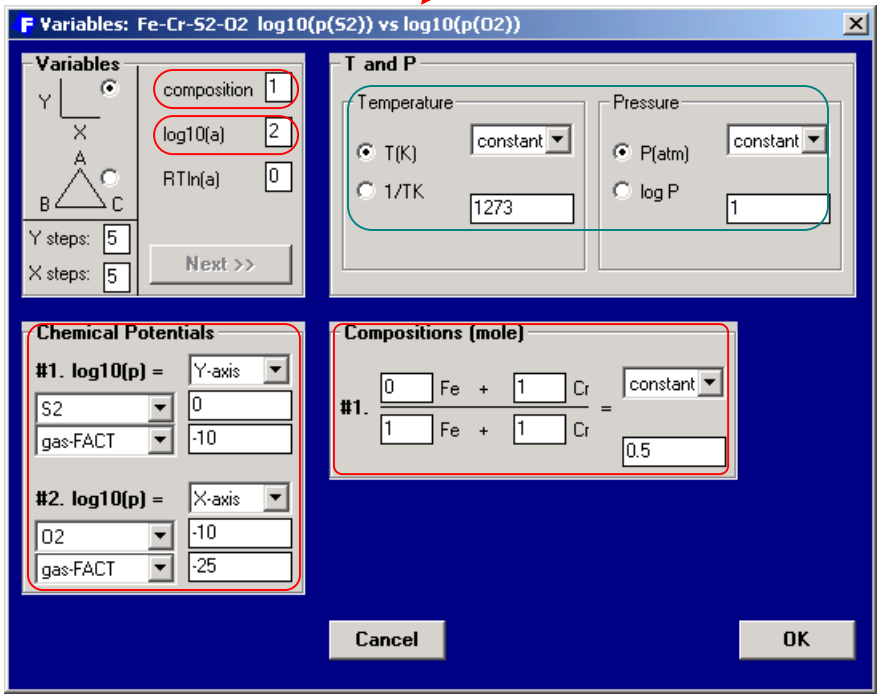
Note the chemical formula of the gas components.
These are used because log p_{O_2} and log p_{S_2} are going to be axes variables.

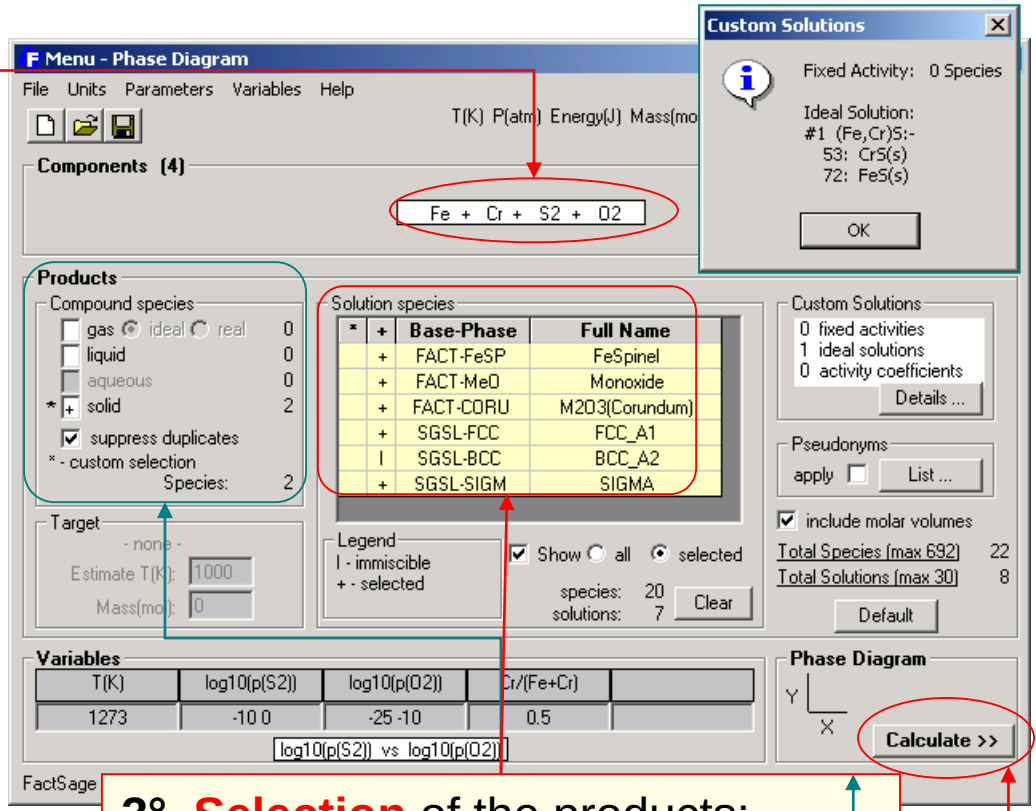
$Fe\text{-}Cr\text{-}S_2\text{-}O_2$ System, variable and solid solution input

1° Entry of the components
(done in the **Components** window)

2° Definition of the variables:

- **1 composition: X_{Cr}= 0.5**
- **2 chemical potentials: $P(O_2)$ and $P(S_2)$**
- **T = 1273K**
- **P = 1 atm**



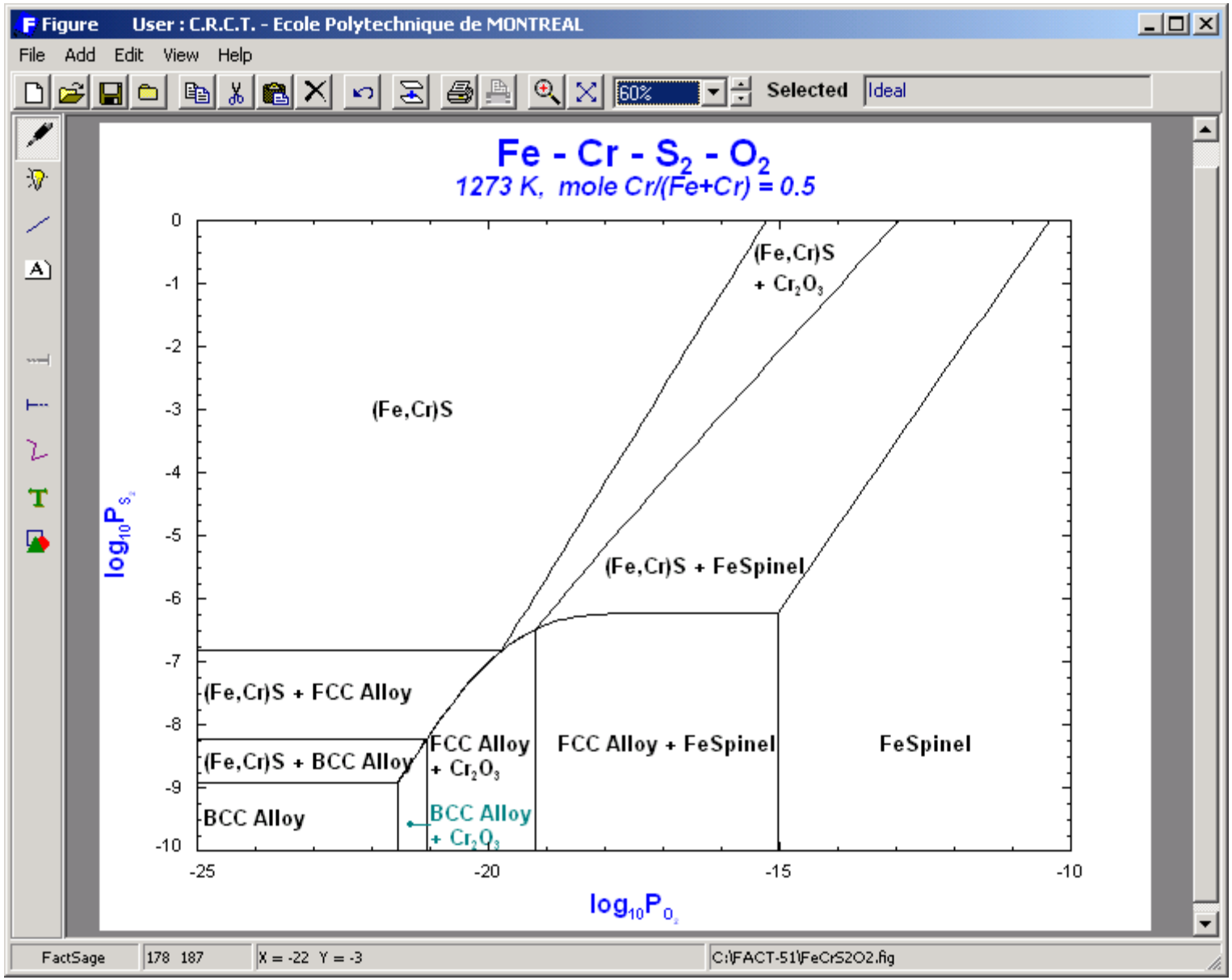


3° Selection of the products:

- **solid (custom selection:** an ideal solution**)**
- **6 solution phases** (including one with a possible miscibility gap)

4° Computation of the phase diagram

Predominance area diagram: Fe-Cr-S_2-O_2 System, graphical output



A quaternary isopleth diagram

The following three slides show how the calculation of a quaternary isopleth diagram is prepared and executed.

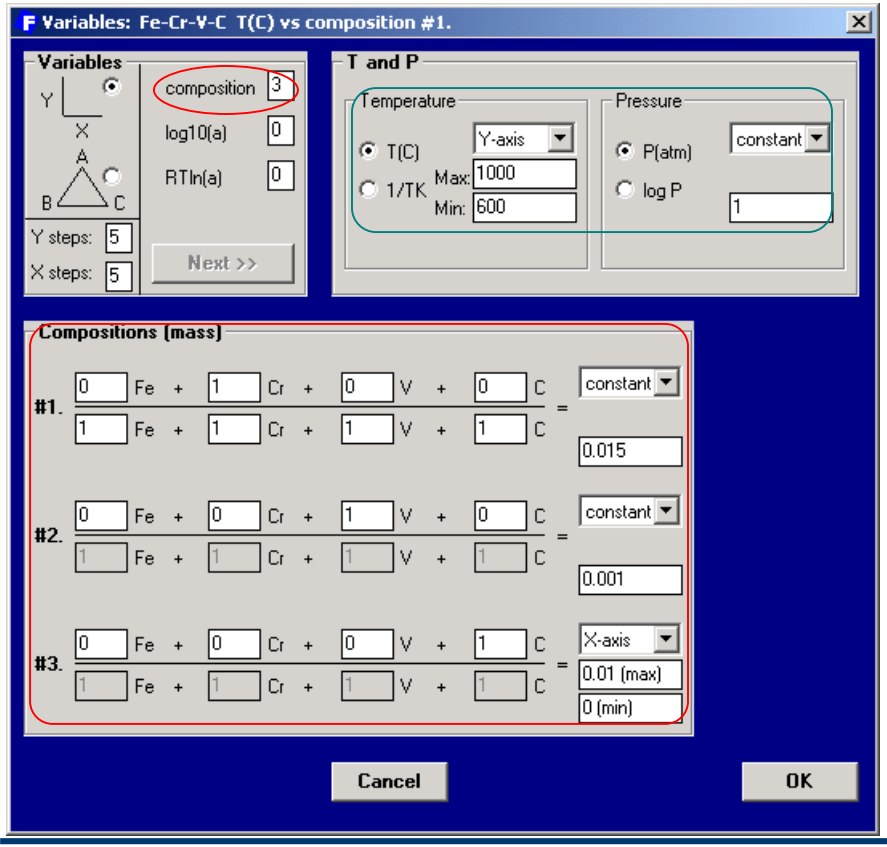
Furthermore, the use of the Point Calculation option is demonstrated. The resulting equilibrium table is shown and explained.

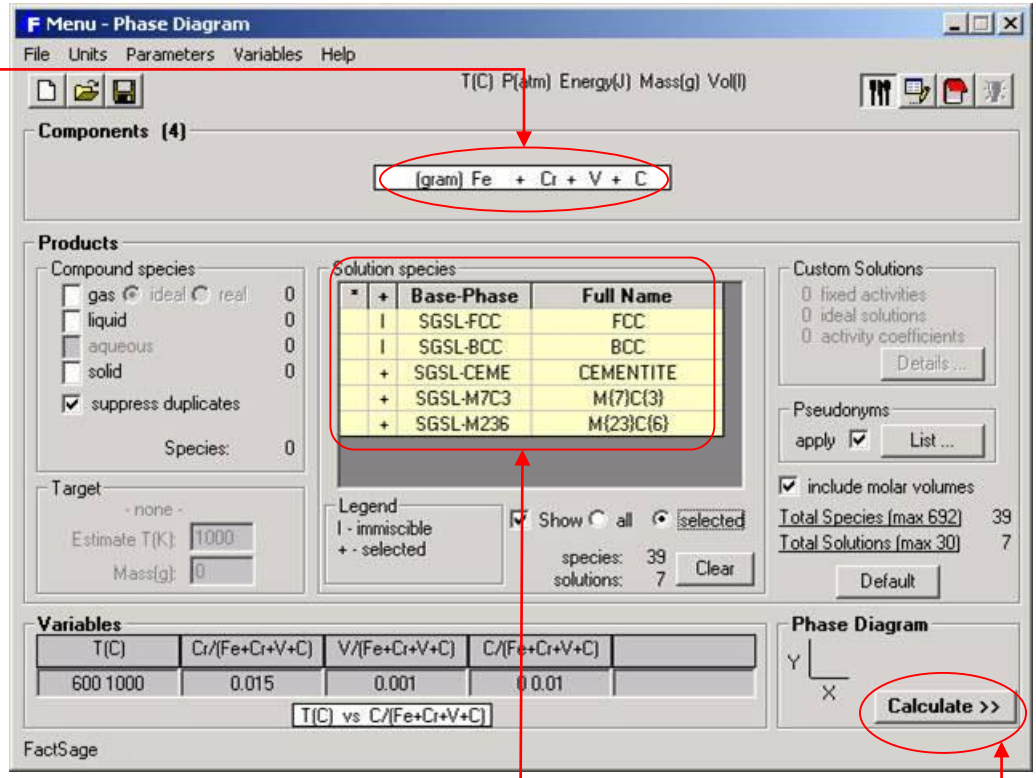
As an example the **Fe-Cr-V-C** system is used.

Fe-Cr-V-C system at 1.5 wt% Cr and 0.1 wt% V: input

1° Entry of the components
(done in the **Components** window)

2° Definition of the variables:
- **3 compositions (1 axis)**
- **600°C < T < 1000°C**
- **P = 1 atm**

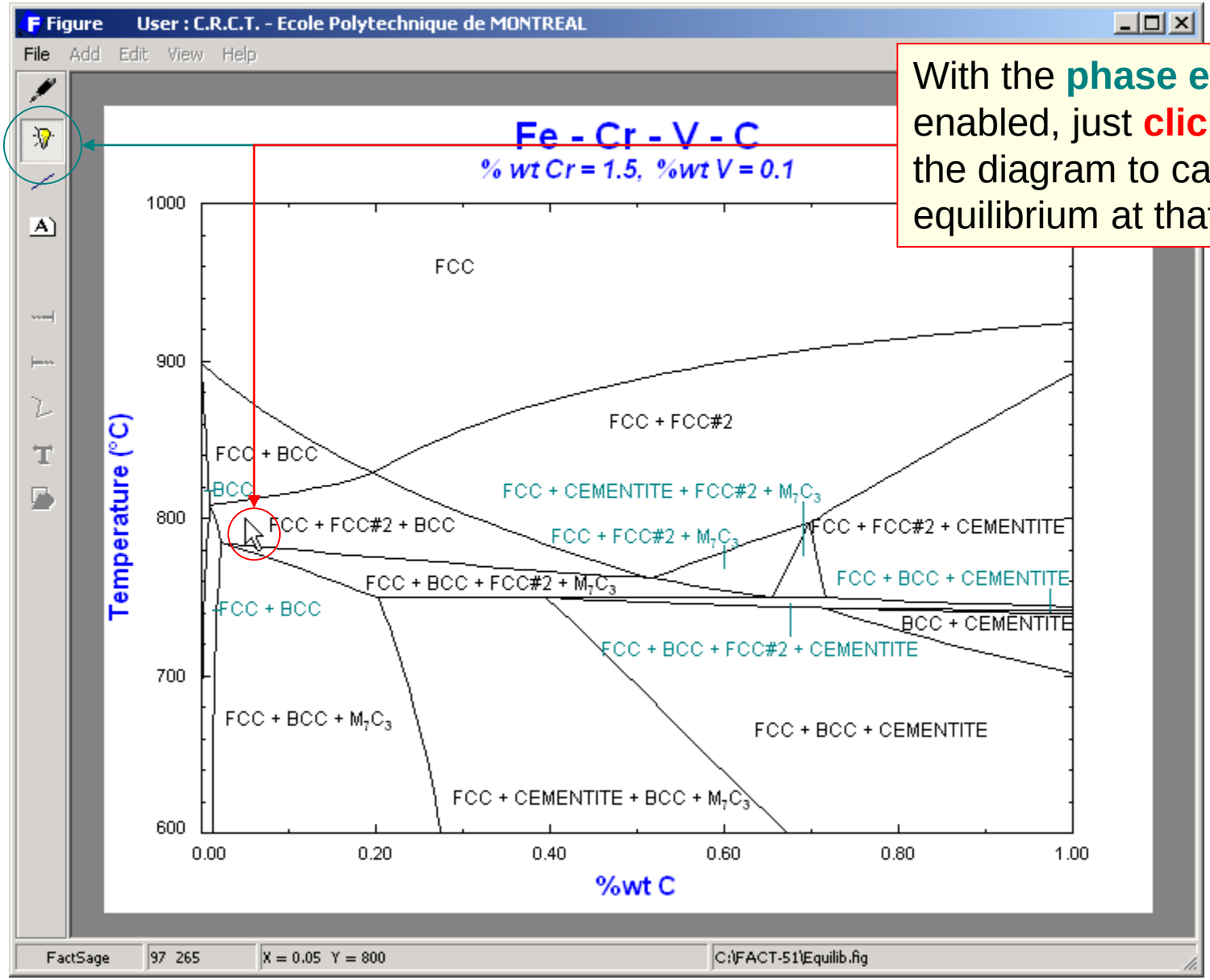




3° Selection of the products:
- **5 solid solutions** (including 2 with possible miscibility gaps)

4° Computation of the phase diagram

Fe-Cr-V-C system: graphical output



With the **phase equilibrium mode** enabled, just **click** at any point on the diagram to calculate the equilibrium at that point.

Fe-Cr-V-C system: phase equilibrium mode output

Output can be obtained in **FACT** or ***ChemSage*** format. See ***Equilib*** Slide Show.
Example is for FACT format.

Proportions and compositions of the **FCC** phase (Remember the miscibility gap).
NOTE: One of the FCC phases is metallic (FCC#1), the other is the $MeC_{(1-x)}$ carbide.

Proportion and composition of the **BCC** phase.

Show Results - page 1

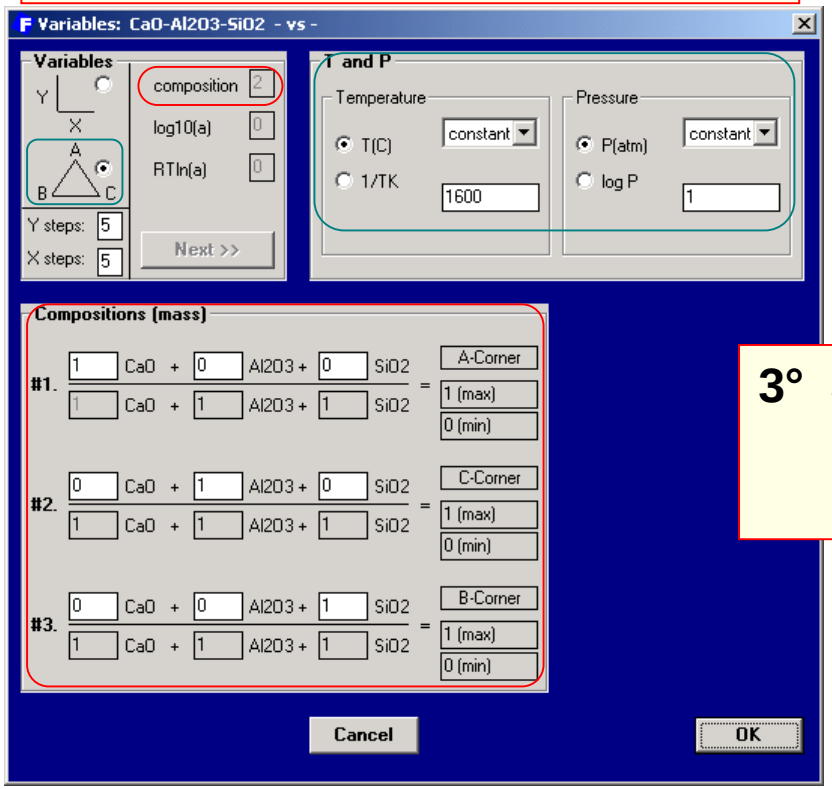
File Edit

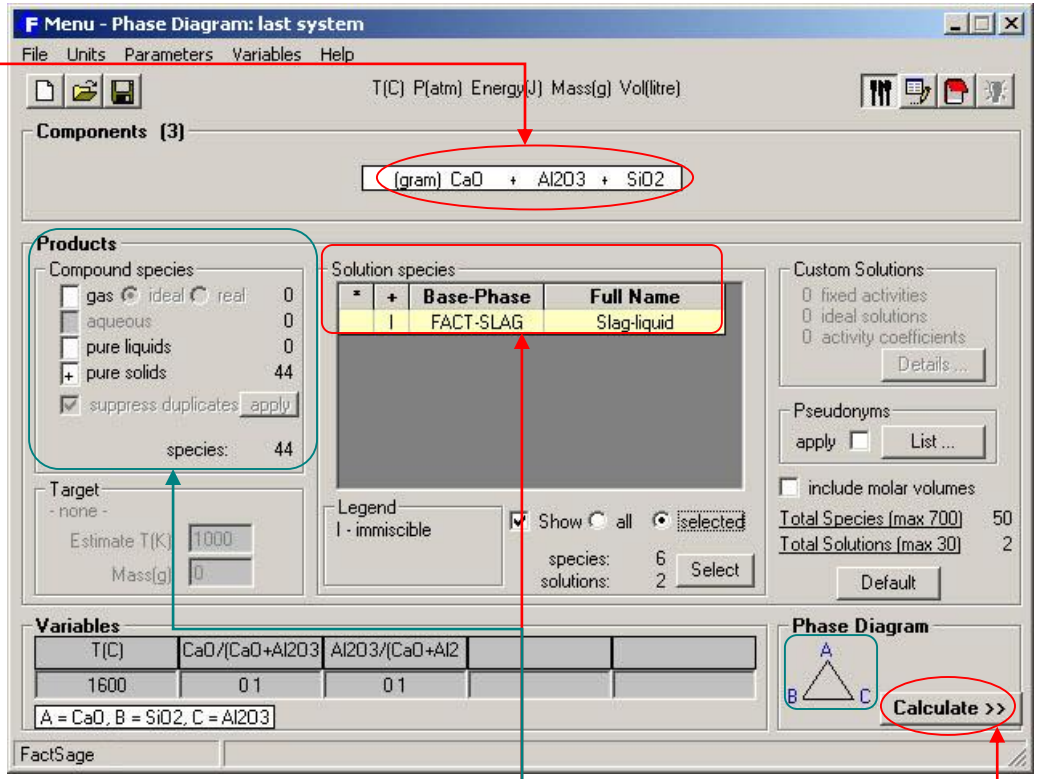
```
(gram)  Fe +  Cr +  V +  C =

   0.60411      gram  (  0.29060E-01 wt.% CrlCl                    SGSLo
                      +   1.6702     wt.% CrlVal                   SGSLo
                      +   1.6589     wt.% FelCl                    SGSLo
                      +   96.592     wt.% FelVal                   SGSLo
                      +  0.85663E-03 wt.% VlCl                     SGSLo
                      +  0.49042E-01 wt.% VlVal                    SGSLo)
                         (799.38 C, 1 atm, FCC#1)
                      Mole fraction of sublattice constituents in FCC#1:
                      Cr            0.18223E-01  Stoichiometry = 1.0000
                      Fe            0.98123
                      V             0.54617E-03
                      ------------------------
                      C             0.13938E-01  Stoichiometry = 1.0000
                      Va            0.98606

+  0.54488E-03 gram  (   7.4122     wt.% CrlCl                    SGSLo
                      +  0.68214     wt.% CrlVal                   SGSLo
                      +  0.33369     wt.% FelCl                    SGSLo
                      +  0.31112E-01 wt.% FelVal                   SGSLo
                      +   83.854     wt.% VlCl                     SGSLo
                      +   7.6872     wt.% VlVal                    SGSLo)
                         (799.38 C, 1 atm, FCC#2)
                      Mole fraction of sublattice constituents in FCC#2:
                      Cr            0.79714E-01  Stoichiometry = 1.0000
                      Fe            0.33850E-02
                      V             0.91690
                      ------------------------
                      C             0.89824      Stoichiometry = 1.0000
                      Va            0.10176

+  0.39535      gram  (  0.33016E-03 wt.% CrlC3                    SGSLo
                      +   1.1965     wt.% CrlVa3                   SGSLo
                      +  0.26466E-01 wt.% FelC3                    SGSLo
                      +   98.704     wt.% FelVa3                   SGSLo
                      +  0.20263E-04 wt.% VlC3                     SGSLo
                      +  0.72818E-01 wt.% VlVa3                    SGSLo)
                         (799.38 C, 1 atm, BCC#1)
                      Mole fraction of sublattice constituents in BCC#1:
                      Cr            0.12843E-01  Stoichiometry = 1.0000
                      Fe            0.98636
                      V             0.79775E-03
                      ------------------------
                      C             0.16295E-03  Stoichiometry = 3.0000
                      Va            0.99984

+  0.00000      gram  (  0.33016E-03 wt.% CrlC3                    SGSLo
```

$CaO-Al_2O_3-SiO_2$ ternary phase diagram: input

1° Entry of the components
(done in the **Components** window)

2° Definition of the variables:
- **2 compositions** (by default)
- **T = 1600°C**
- **P = 1 atm**
- **Gibbs triangle**

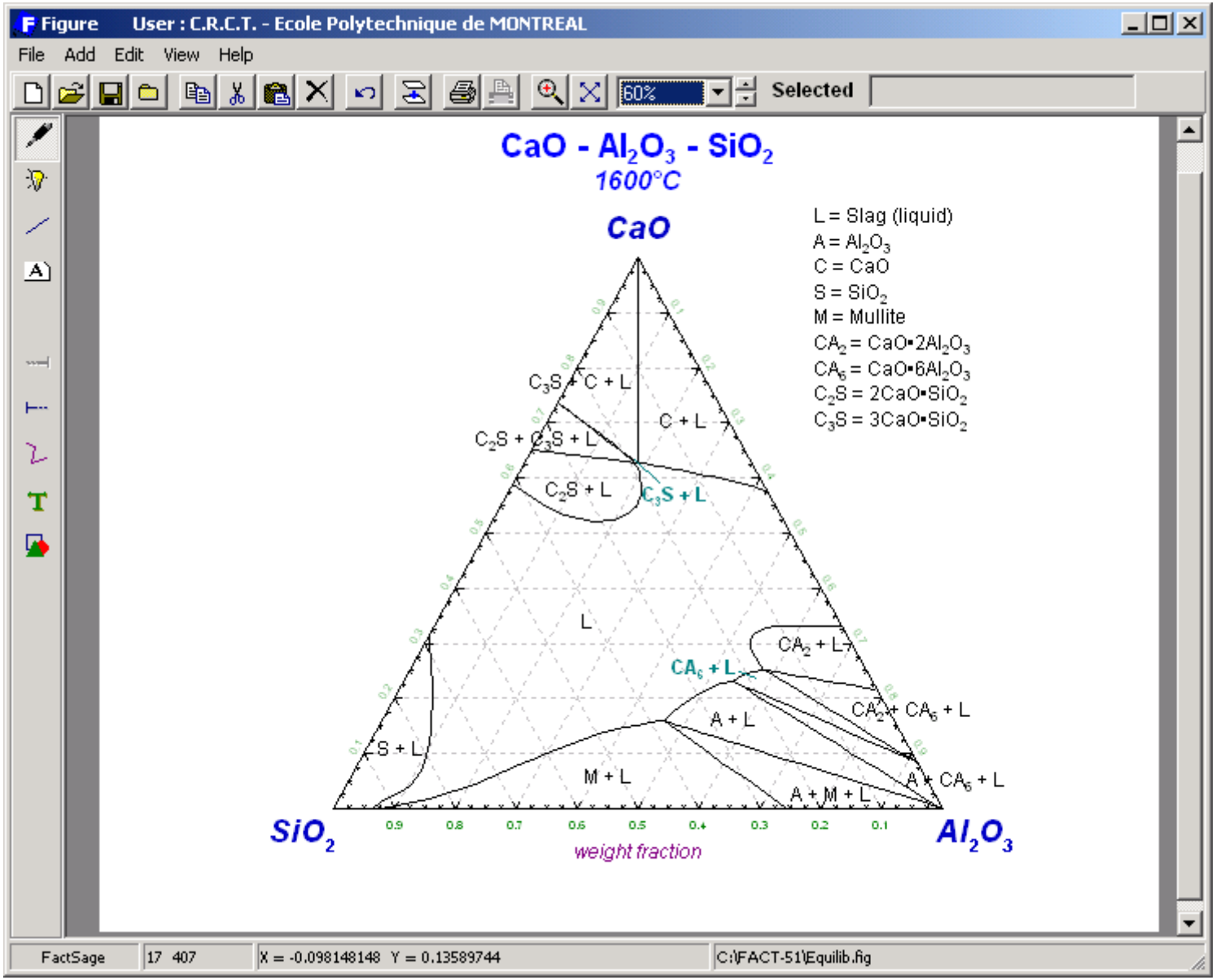




3° Selection of the products:
- **pure solids**
- **Immiscible solution phase (FACT-SLAG)**

4° Computation of the **Gibbs ternary phase diagram**

CaO-Al_2O_3-SiO_2 ternary phase diagram: graphical output

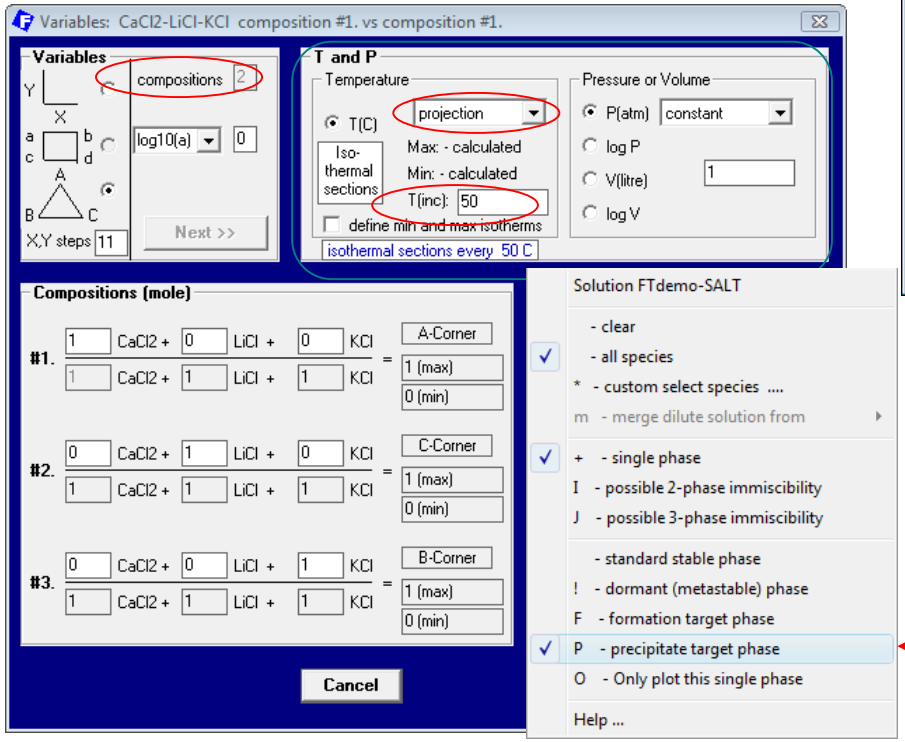


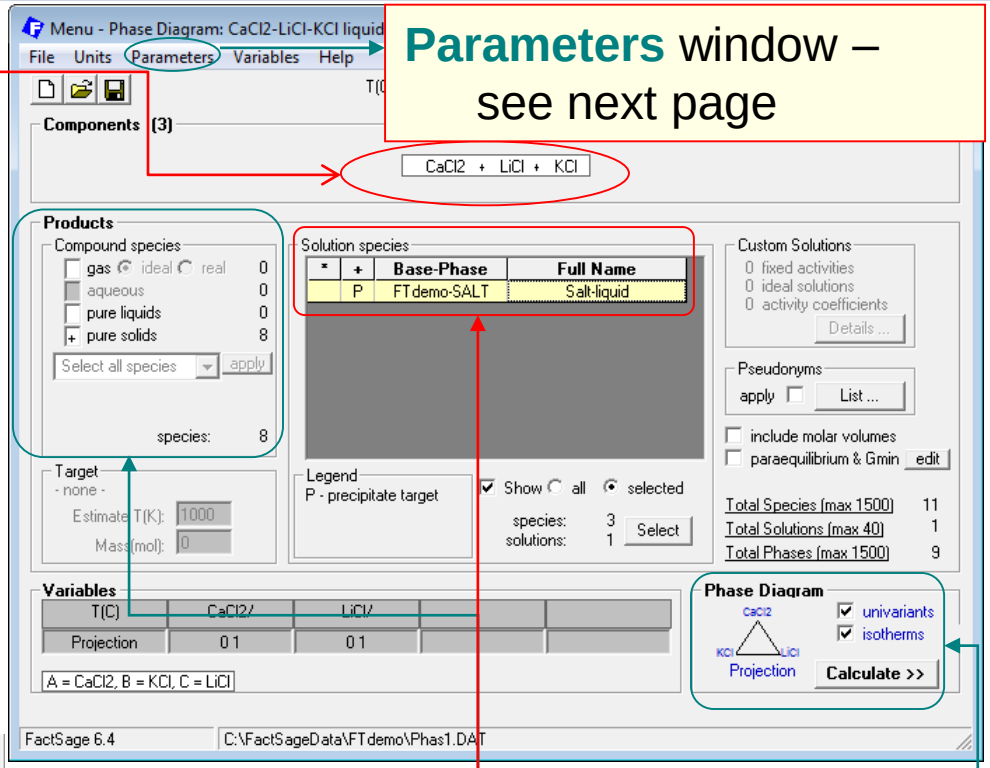
$CaCl_2$-LiCl-KCl polythermal liquidus projection

1° **Entry** of the components with **FTdemo** database selected

2° **Definition** of the variables:

- **2 compositions** (by default)
- **T = projection**
- **Step = 50 °C**
- **P = 1 atm**





Parameters window – see next page

3° **Selection** of the products:

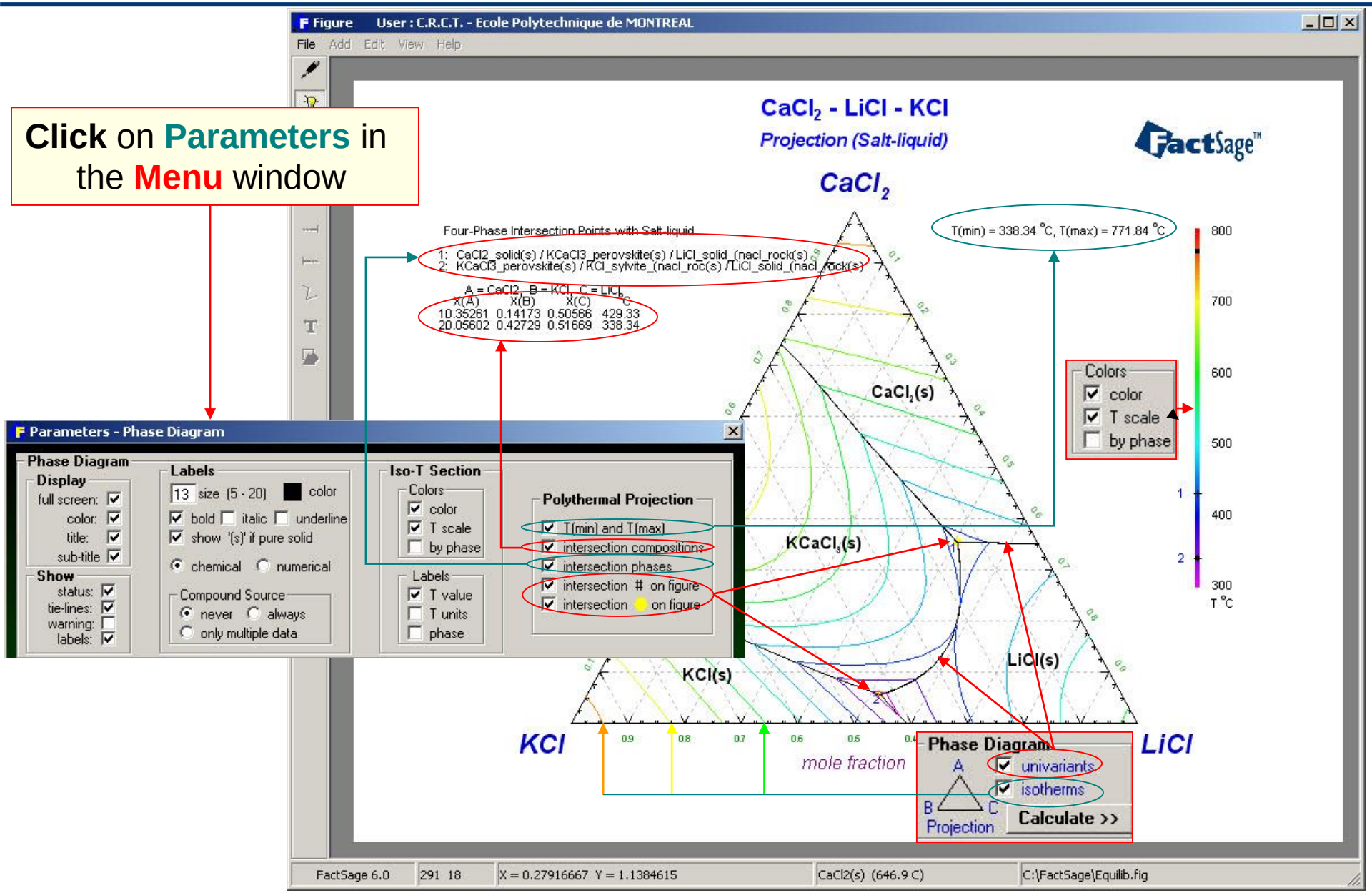
- **pure solids**
- **solution phase (FTdemo-SALT)**

option 'P' – Precipitation target

4° **Computation** of the univariant lines and liquidus isotherms

$CaCl_2$-LiCl-KCl polythermal liquidus projection : graphical output

Click on **Parameters** in the **Menu** window

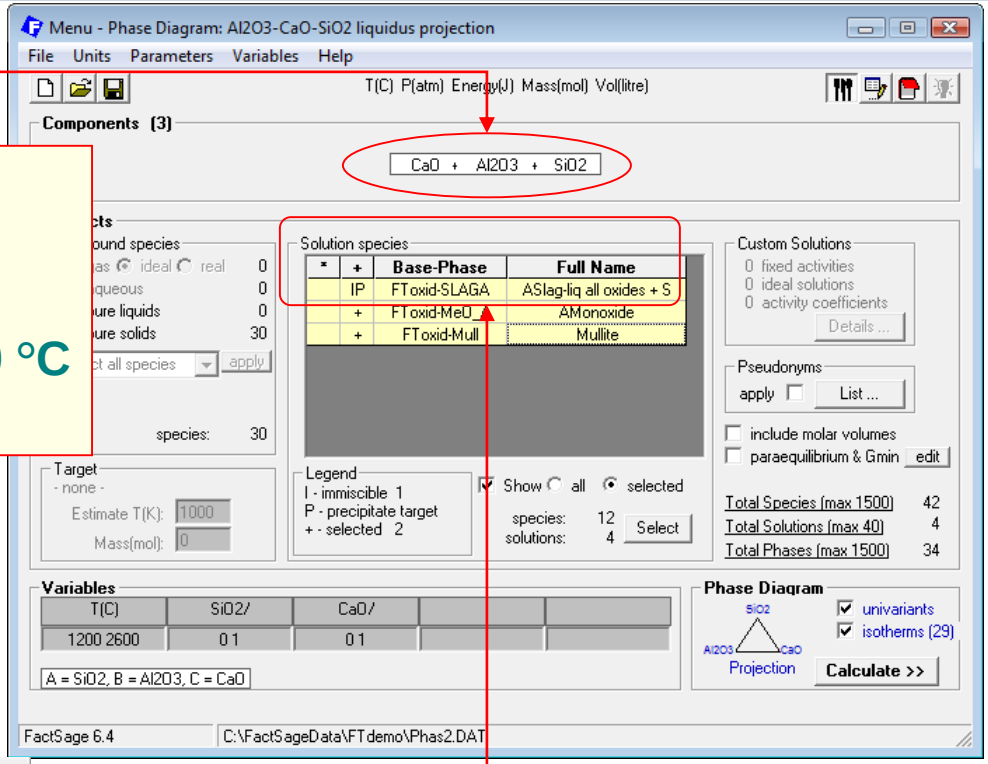


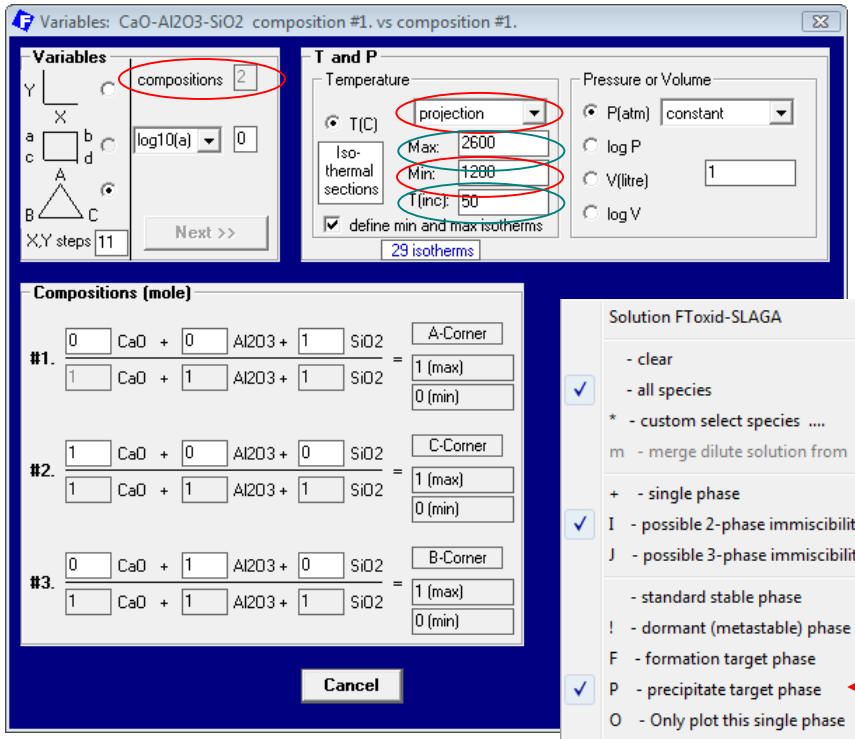
Al_2O_3-CaO-SiO_2 polythermal liquidus projection

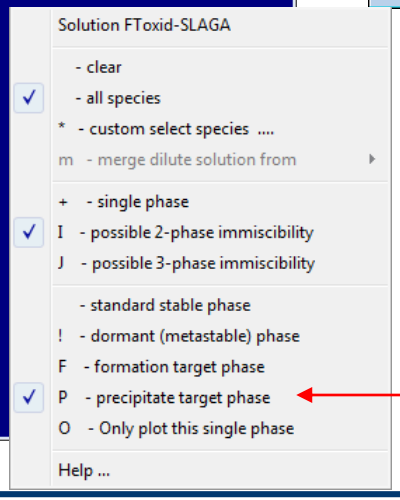
1° **Entry** of the components with **FToxid** database selected

2° **Definition** of the variables:

- **2 compositions** (by default)
- **T = projection**
- **Max = 2600, Min = 1200, Step = 50 °C**
- **P = 1 atm**







3° **Selection** of the products:

- **pure solids**
- **solution phases (FToxid-SLAGA) with option 'P' – Precipitation target**

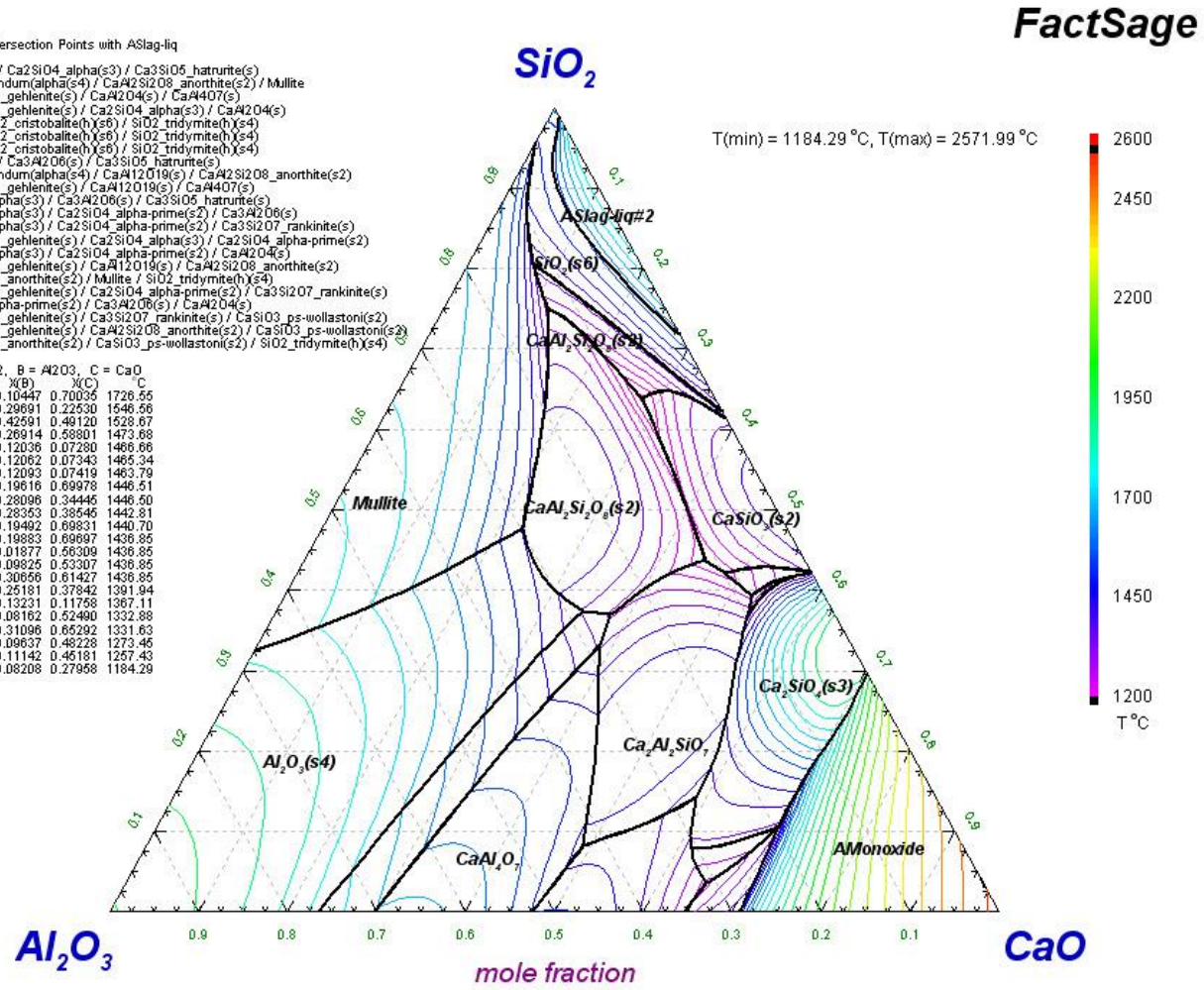
Al_2O_3-CaO-SiO_2 polythermal liquidus projection : graphical output

Four-Phase Intersection Points with ASlag-liq

1: AMonoxide / Ca2SiO4_alpha(s3) / Ca3SiO5_hatrurite(s)
2: Al2O3_corundum(alpha(s4) / CaAl2Si2O8_anorthite(s2) / Mullite
3: Ca2Al2SiO7_gehlenite(s) / CaAl2O4(s) / CaAl4O7(s)
4: Ca2Al2SiO7_gehlenite(s) / Ca2SiO4_alpha(s3) / CaAl2O4(s)
5: Mullite / SiO2_cristobalite(h)(s6) / SiO2_tridymite(h)(s4)
6: Mullite / SiO2_cristobalite(h)(s6) / SiO2_tridymite(h)(s4)
7: Mullite / SiO2_cristobalite(h)(s6) / SiO2_tridymite(h)(s4)
8: AMonoxide / Ca3Al2O6(s) / Ca3SiO5_hatrurite(s)
9: Al2O3_corundum(alpha(s4) / CaAl12O19(s) / CaAl2Si2O8_anorthite(s2)
10: Ca2Al2SiO7_gehlenite(s) / CaAl12O19(s) / CaAl4O7(s)
11: Ca2SiO4_alpha(s3) / Ca3Al2O6(s) / Ca3SiO5_hatrurite(s)
12: Ca2SiO4_alpha(s3) / Ca2SiO4_alpha-prime(s2) / Ca3Al2O6(s)
13: Ca2SiO4_alpha(s3) / Ca2SiO4_alpha-prime(s2) / Ca3Si2O7_rankinite(s)
14: Ca2Al2SiO7_gehlenite(s) / Ca2SiO4_alpha(s3) / Ca2SiO4_alpha-prime(s2)
15: Ca2SiO4_alpha(s3) / Ca2SiO4_alpha-prime(s2) / CaAl2O4(s)
16: Ca2Al2SiO7_gehlenite(s) / CaAl12O19(s) / CaAl2Si2O8_anorthite(s2)
17: CaAl2Si2O8_anorthite(s2) / Mullite / SiO2_tridymite(h)(s4)
18: Ca2Al2SiO7_gehlenite(s) / Ca2SiO4_alpha-prime(s2) / Ca3Si2O7_rankinite(s)
19: Ca2SiO4_alpha-prime(s2) / Ca3Al2O6(s) / CaAl2O4(s)
20: Ca2Al2SiO7_gehlenite(s) / Ca3Si2O7_rankinite(s) / CaSiO3_ps-wollastoni(s2)
21: Ca2Al2SiO7_gehlenite(s) / CaAl2Si2O8_anorthite(s2) / CaSiO3_ps-wollastoni(s2)
22: CaAl2Si2O8_anorthite(s2) / CaSiO3_ps-wollastoni(s2) / SiO2_tridymite(h)(s4)

A = SiO2, B = Al2O3, C = CaO

	X(A)	X(B)	X(C)	°C
1:	0.19519	0.10447	0.70035	1726.55
2:	0.47779	0.29691	0.22530	1546.56
3:	0.08289	0.42591	0.49120	1528.67
4:	0.14285	0.26914	0.58801	1473.68
5:	0.80684	0.12036	0.07280	1466.66
6:	0.80594	0.12062	0.07343	1465.34
7:	0.80489	0.12093	0.07419	1463.79
8:	0.10406	0.19616	0.69978	1446.51
9:	0.37459	0.28096	0.34445	1446.50
10:	0.33102	0.28353	0.38545	1442.81
11:	0.10677	0.19492	0.69831	1440.70
12:	0.10420	0.19883	0.69697	1436.85
13:	0.41814	0.01877	0.56309	1436.85
14:	0.36868	0.09825	0.53307	1436.85
15:	0.07917	0.30656	0.61427	1436.85
16:	0.36977	0.25181	0.37842	1391.94
17:	0.75011	0.13231	0.11758	1367.11
18:	0.39348	0.08162	0.52490	1332.88
19:	0.03612	0.31096	0.65292	1331.63
20:	0.42135	0.09637	0.48228	1273.46
21:	0.43677	0.11142	0.45181	1257.43
22:	0.63835	0.08208	0.27958	1184.29

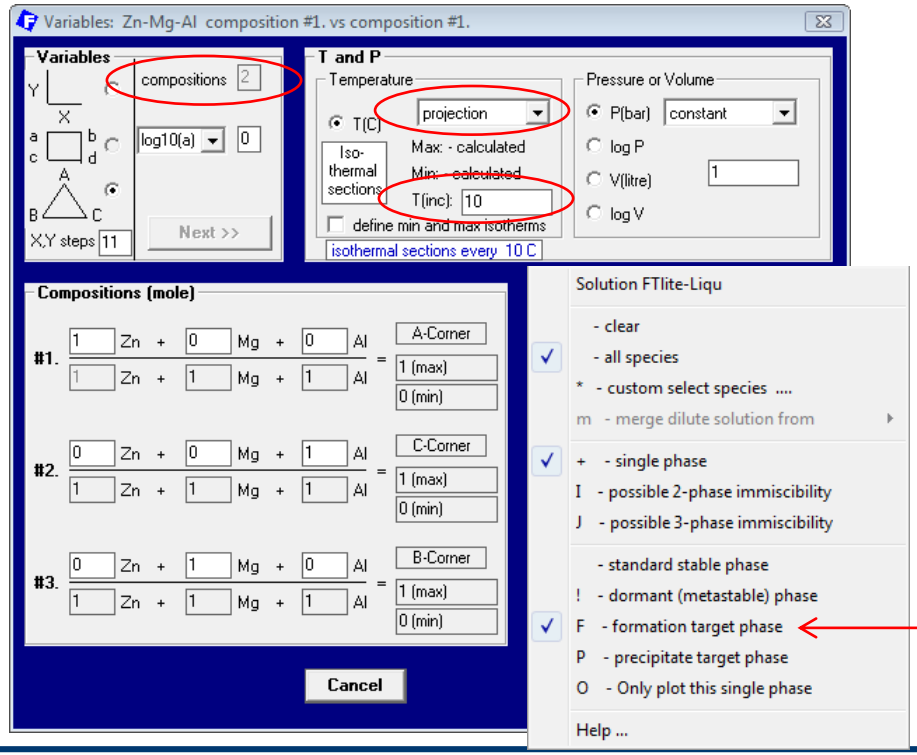


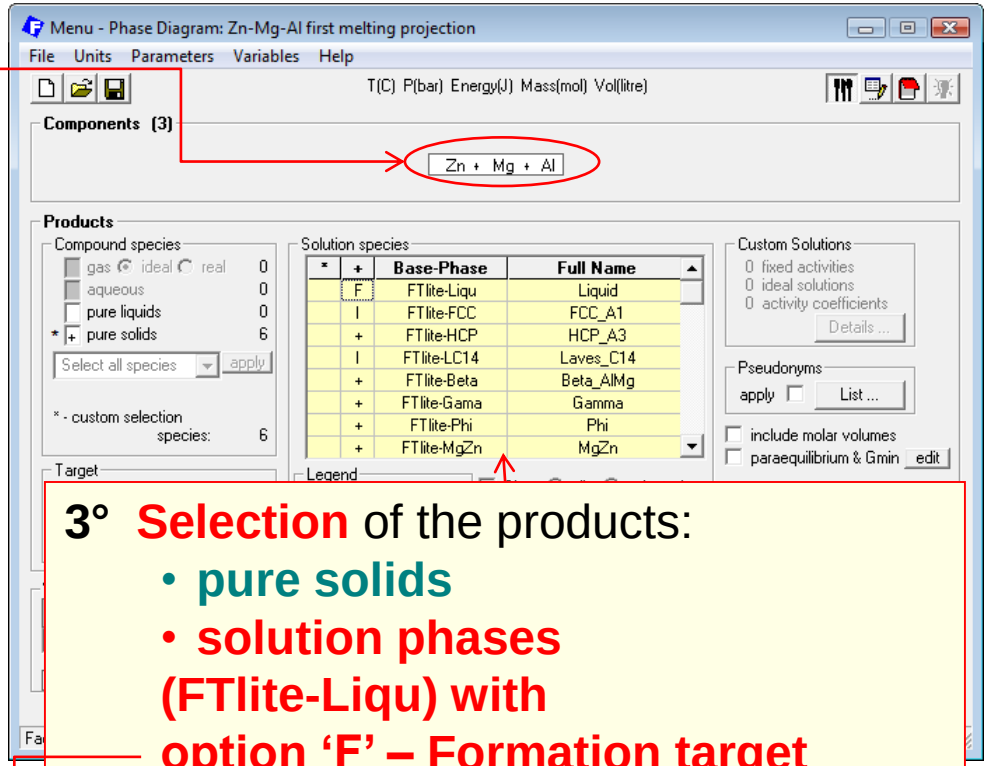
Zn-Mg-Al polythermal first melting (solidus) projection

1° Entry of the components with **FTlite** database selected

2° Definition of the variables:

- **2 compositions** (by default)
- **T = projection**
- **Step = 10 °C**
- **P = 1 atm**





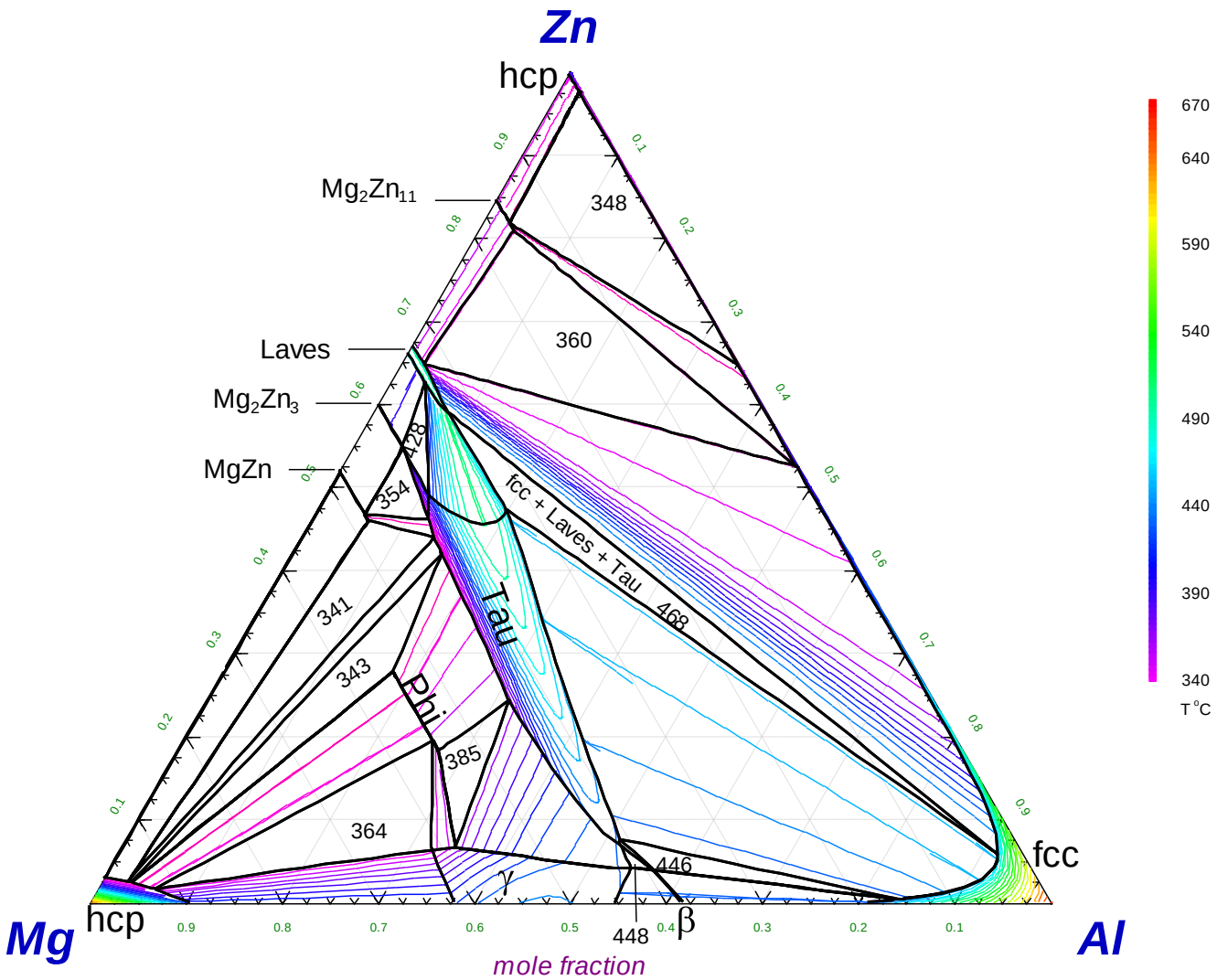
3° Selection of the products:

- **pure solids**
- **solution phases (FTlite-Liqu) with option 'F' – Formation target**

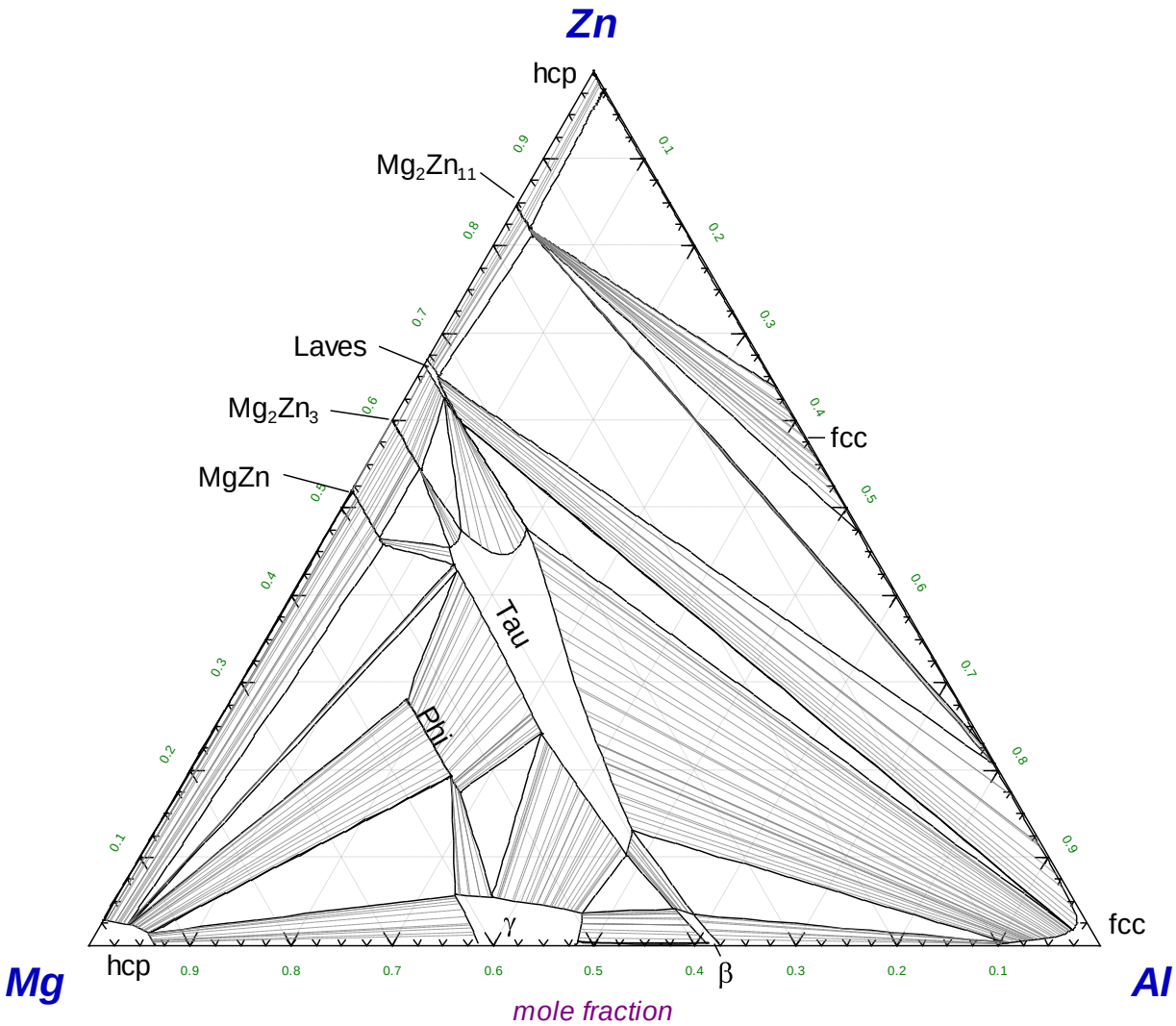
Note: The calculation of projections, particularly first melting sections, can be very time-consuming. Therefore, **I** and **J** options should not be used unless necessary.

4° Computation of the univariant lines and liquidus isotherms

Zn-Mg-Al polythermal first melting (solidus) projection: graphical output

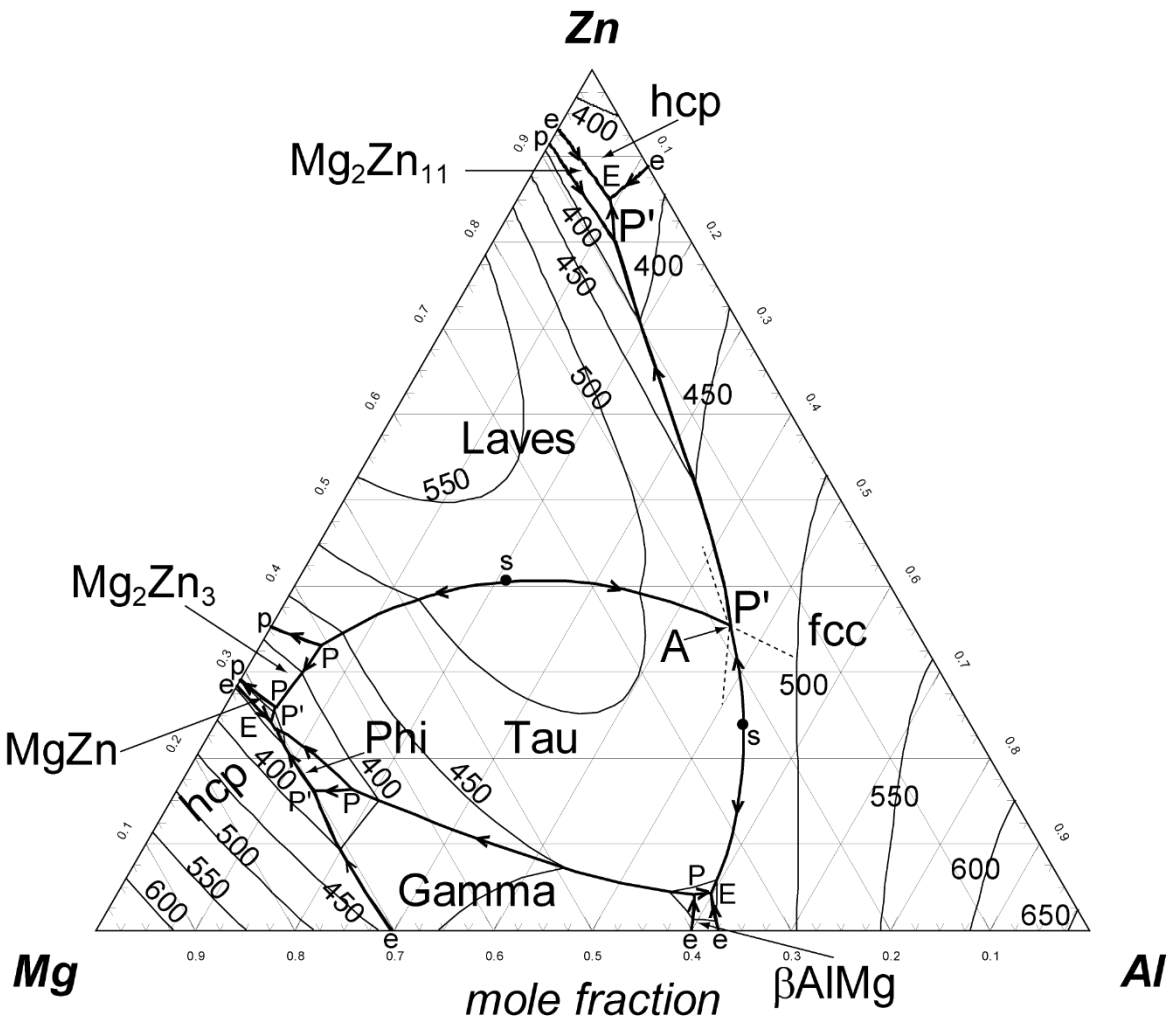


Zn-Mg-Al isothermal section at 330 °C



Note close similarity to the solidus projection of slide 13.6

Zn-Mg-Al liquidus projection



Each ternary invariant (P, E) point on the liquidus projection corresponds to a tie-triangle on the solidus projection of slide 13.6

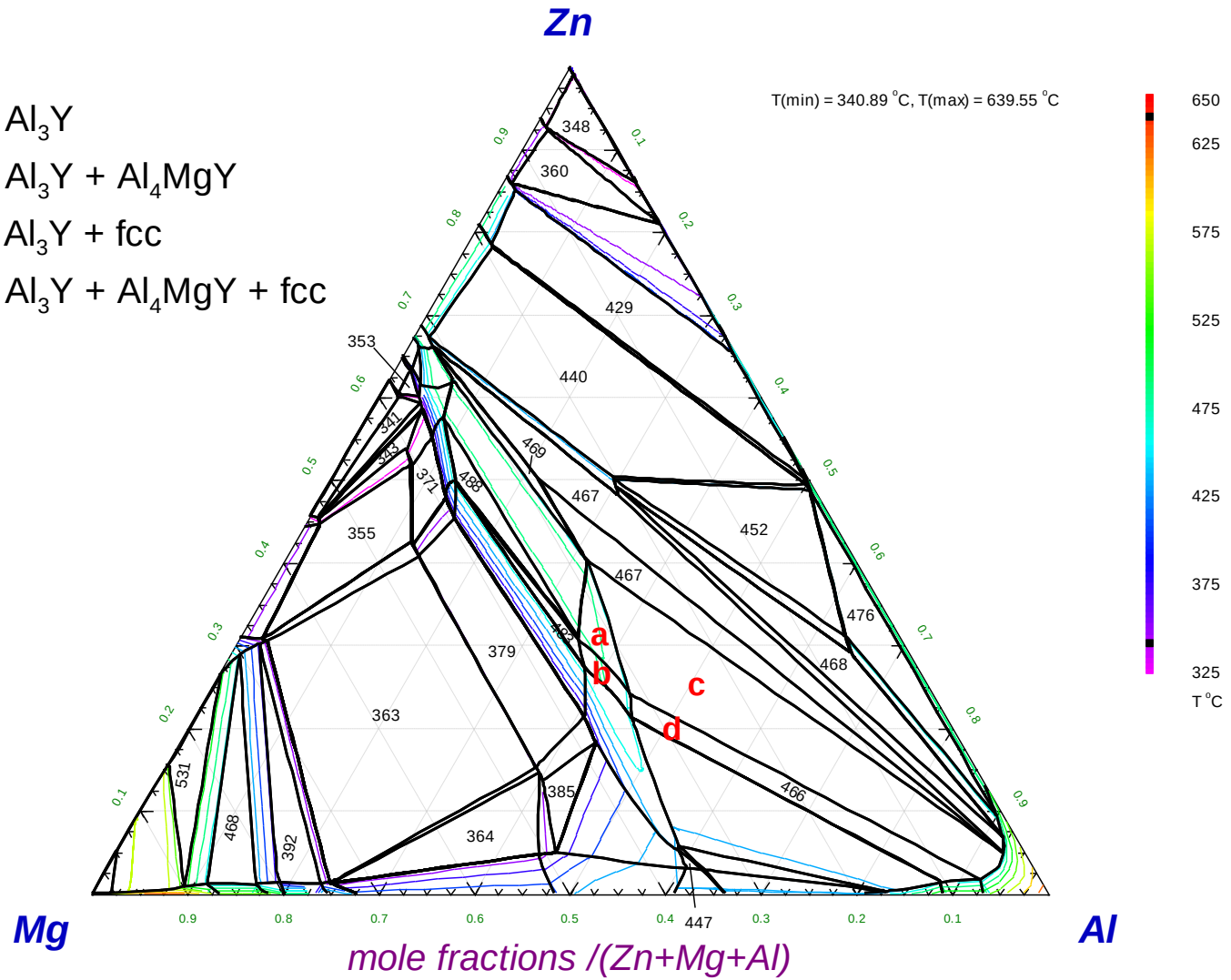
Zn-Mg-Al-Y First Melting (solidus) projection, mole fraction Yttrium = 0.05

a = Tau + Al_3Y

b = Tau + Al_3Y + Al_4MgY

c = Tau + Al_3Y + fcc

d = Tau + Al_3Y + Al_4MgY + fcc



When is a first melting projection not a solidus projection?

- In systems with catatectics or retrograde solubility, a liquid phase can re-solidify upon heating.

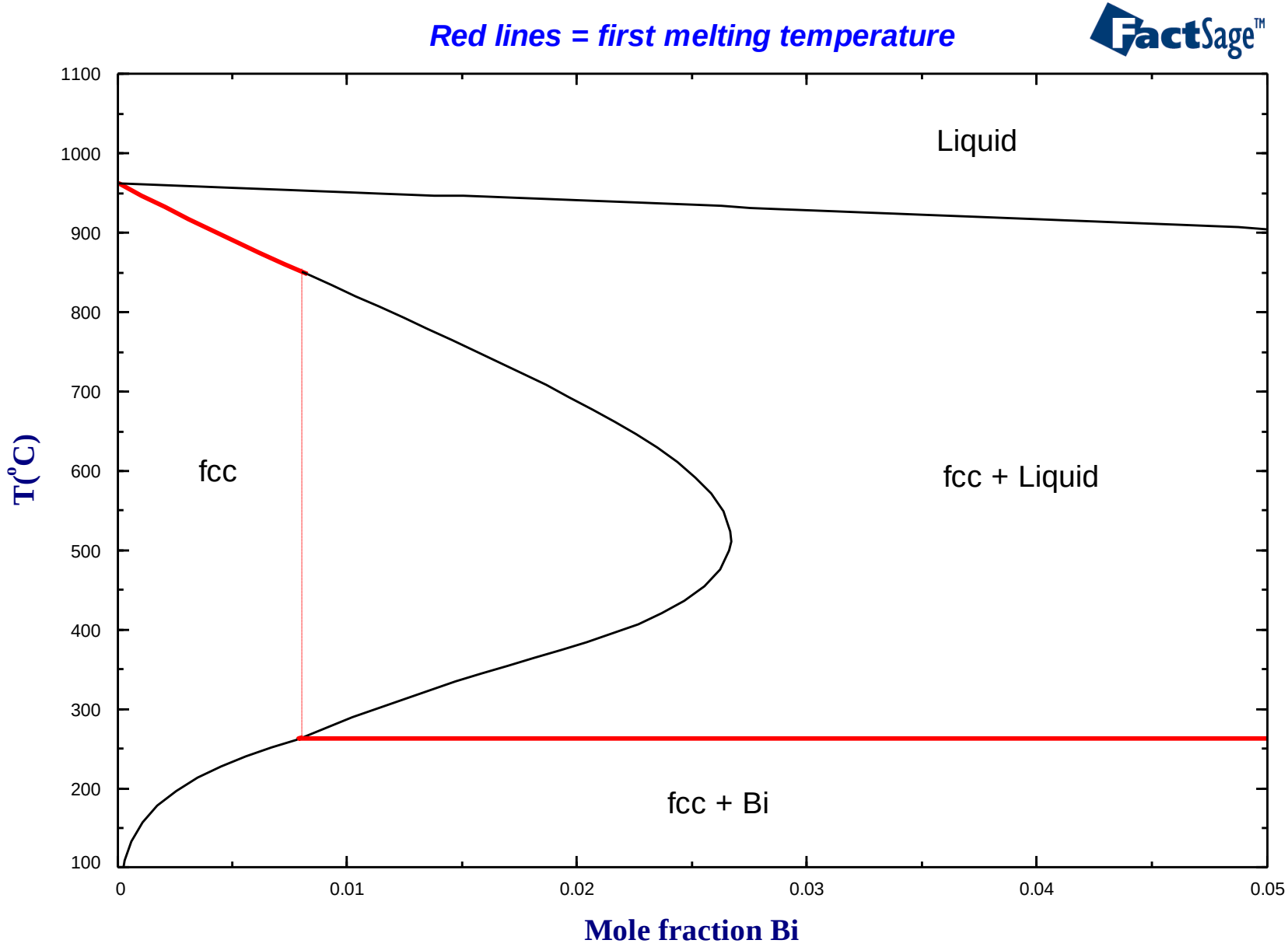
- In such systems, phase fields on a solidus projection can overlap.

- However, **“first melting temperature” projections** never overlap.

- If a system contains no catatectics or retrograde solubility (as is the case in the great majority of systems), the first melting temperature projection is identical to the solidus projection.

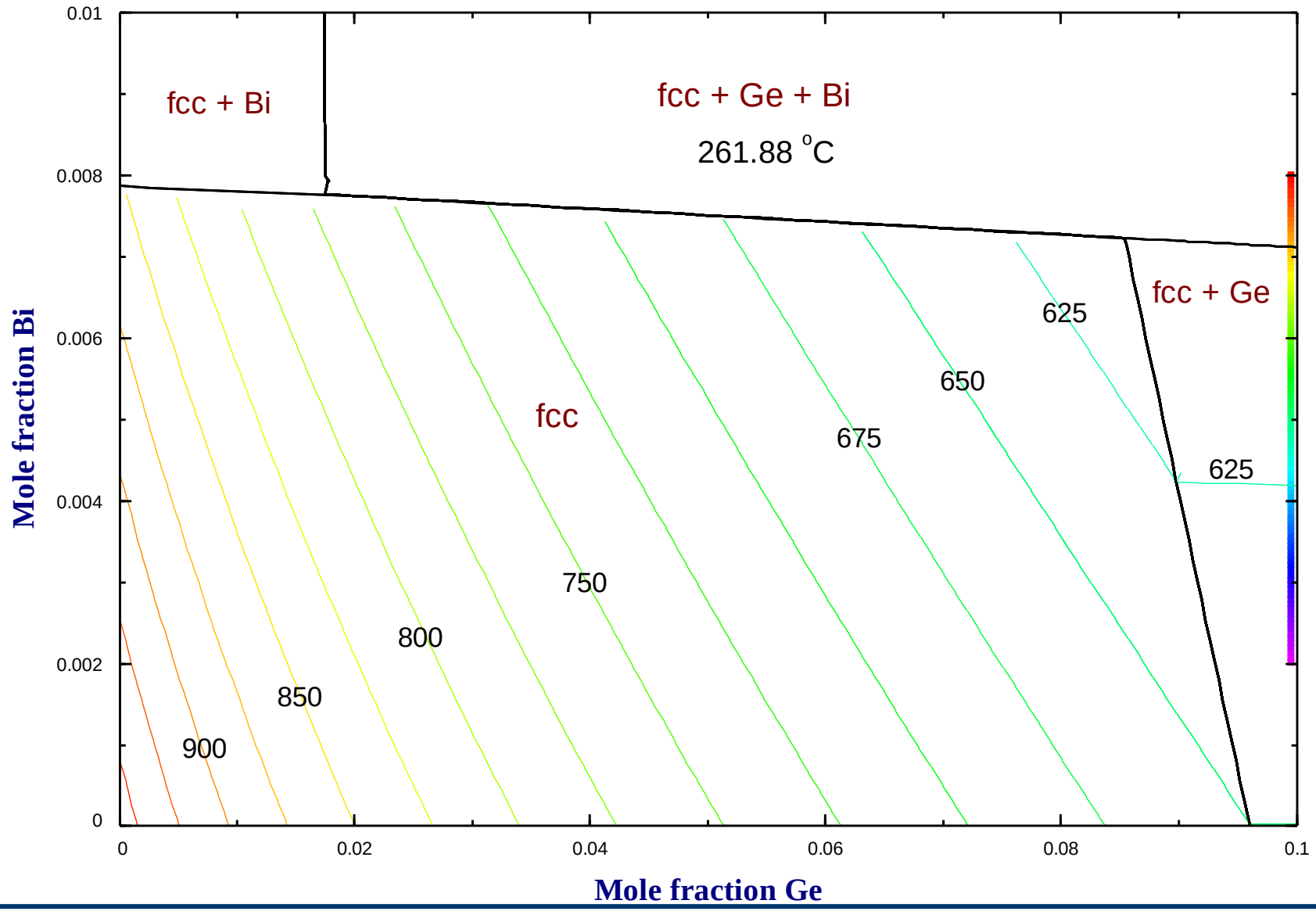
- In systems with catactectics or retrograde solubility the first melting projection will exhibit discontinuities in temperature (**and calculation times will usually be long**).

Ag-Bi, a system with retrograde solubility (SGTE database)

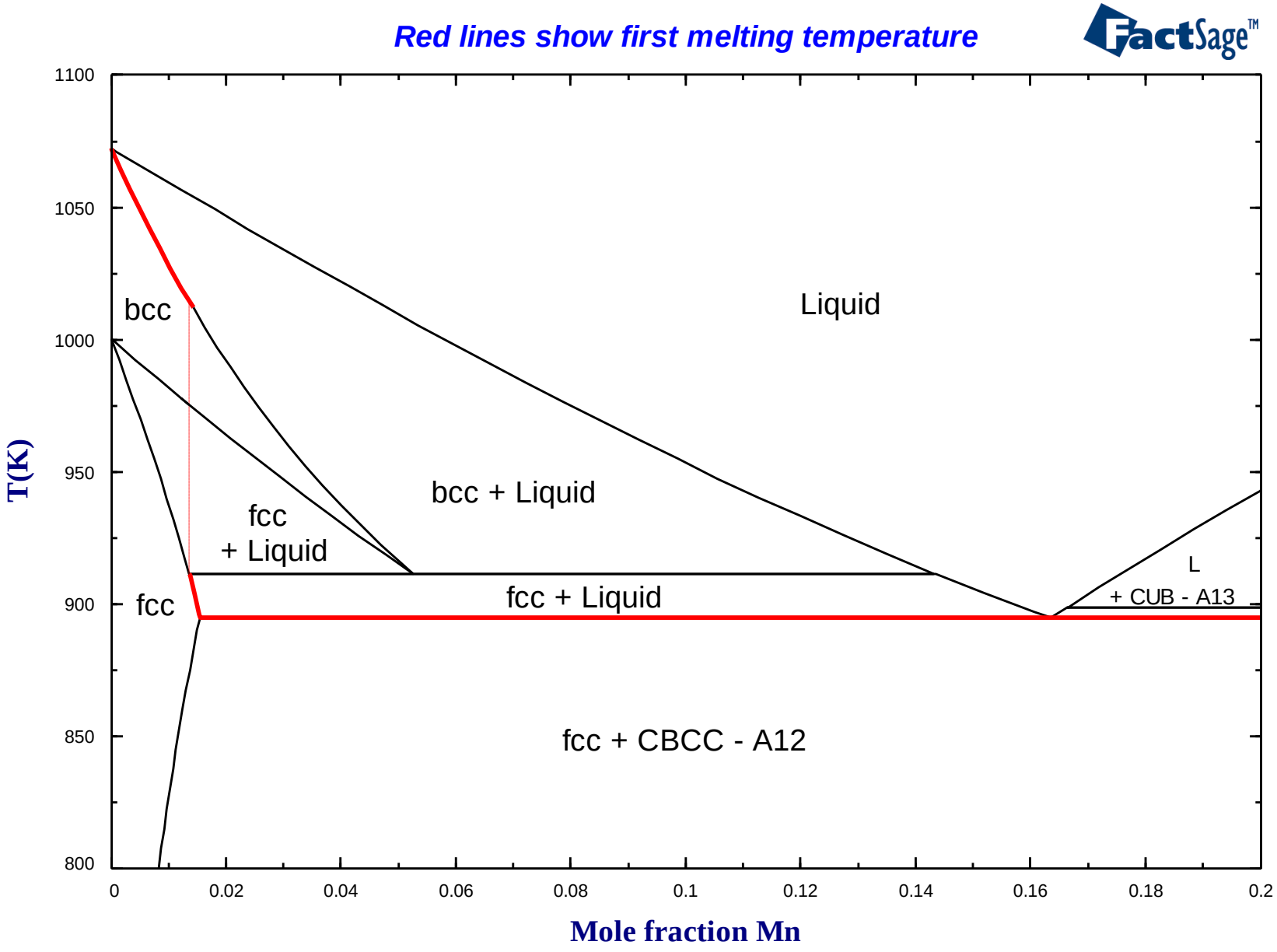


Ag-Bi-Ge, First Melting Projection (SGTE database)

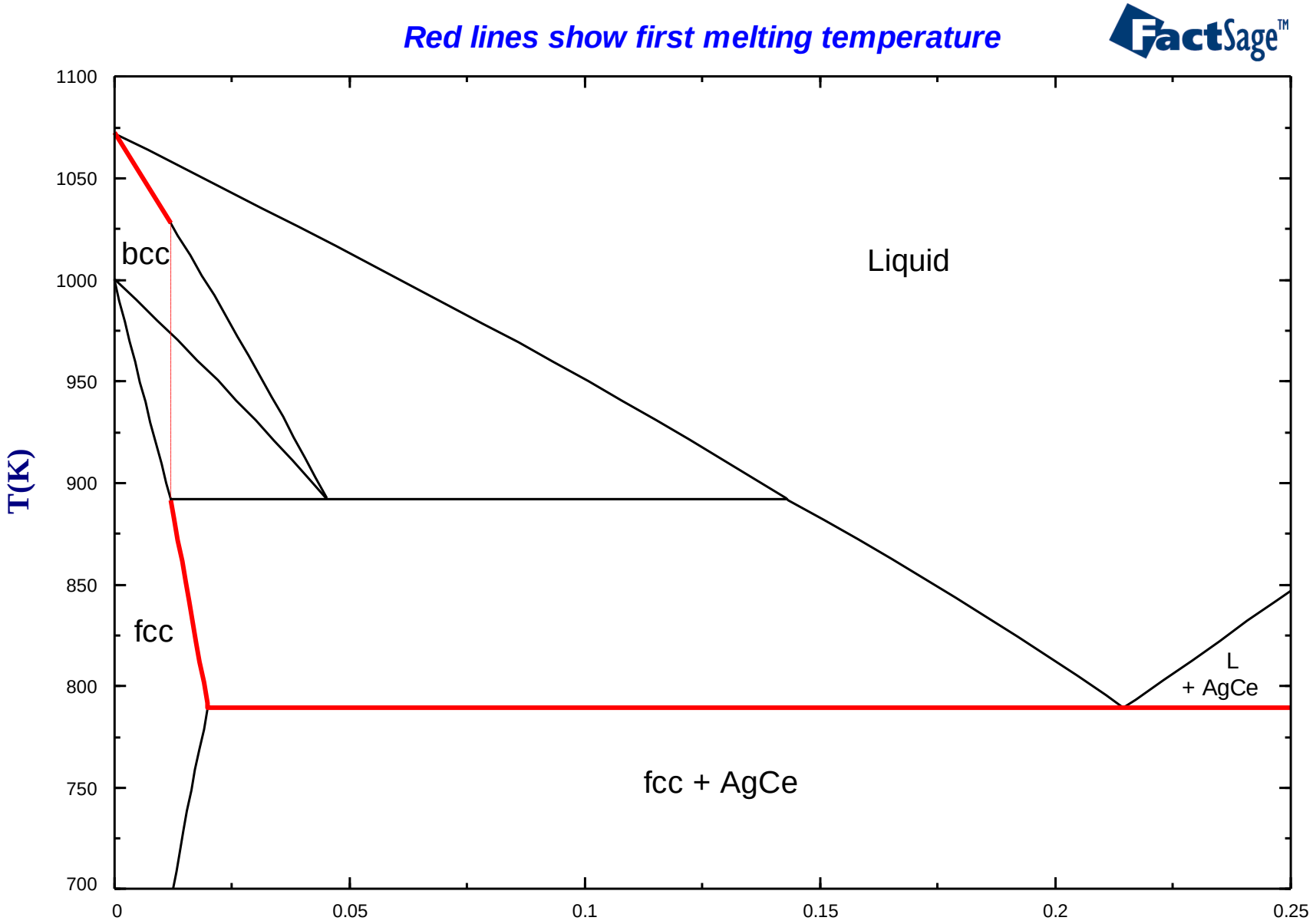
Note temperature discontinuities



Ce-Mn, a system with a catatectic (SGTE database)

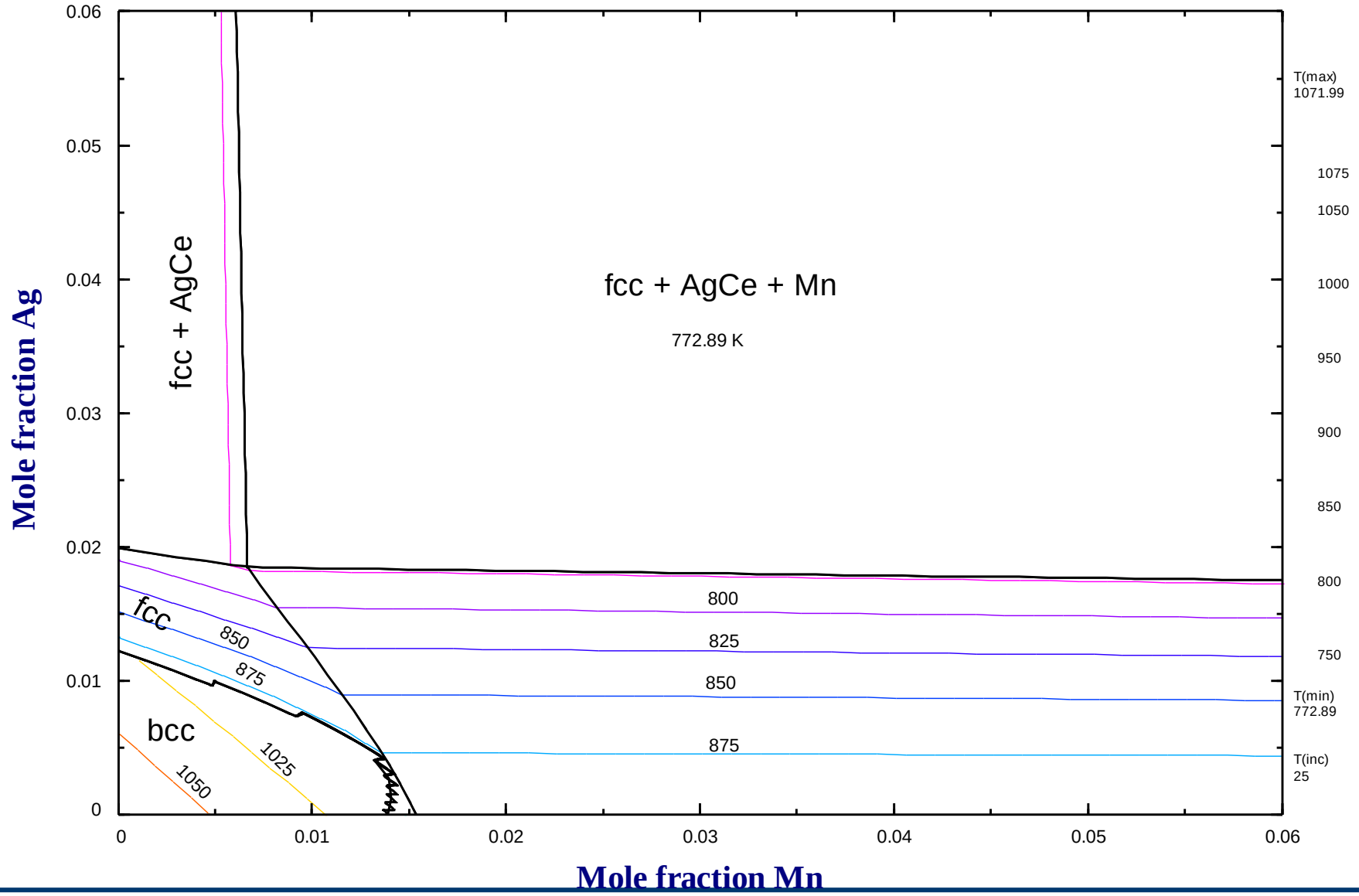


Ce-Ag, a system with a catatectic (SGTE database)

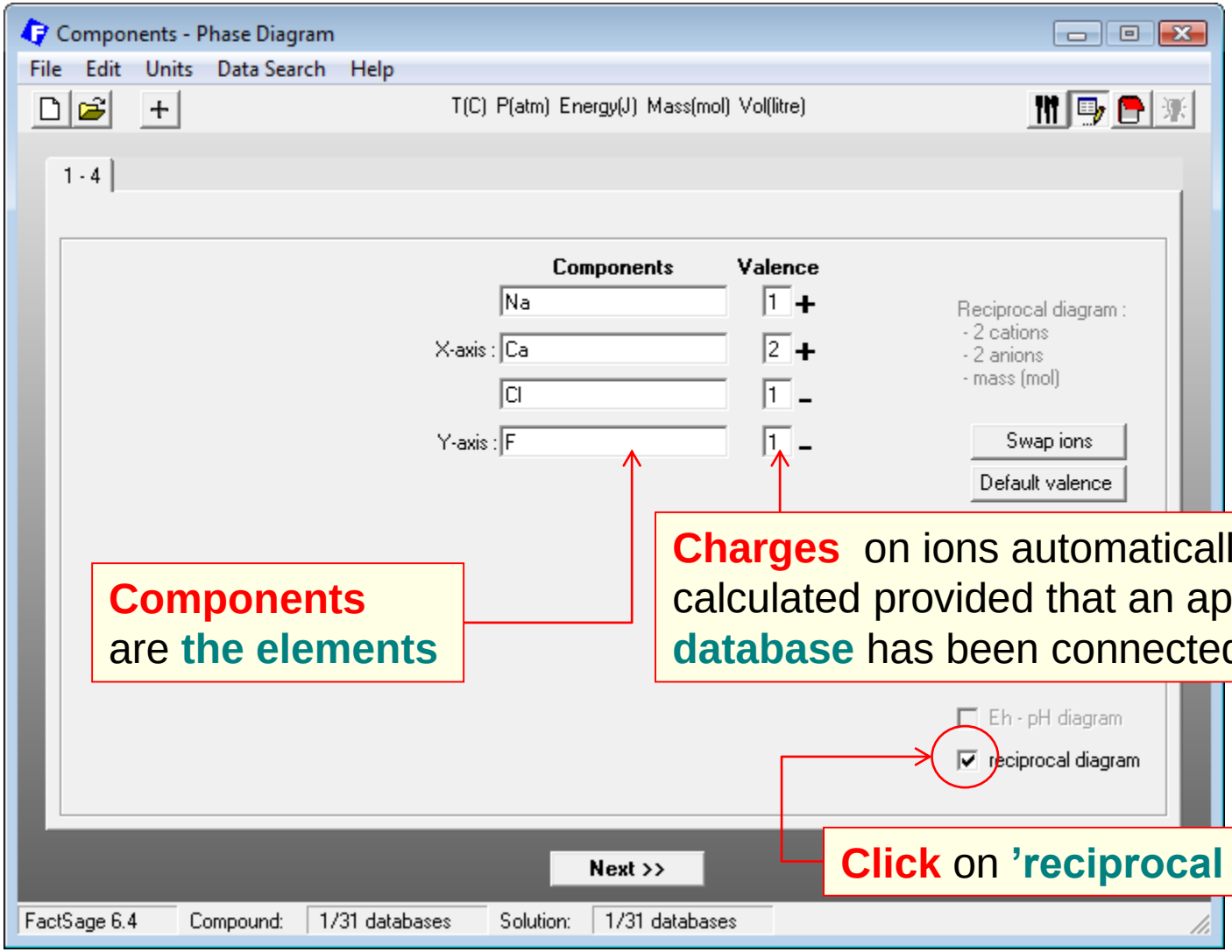


Ag-Mn-Ce, First Melting Projection (SGTE database)

Note temperature discontinuity between fcc and bcc fields



$CaCl_2$-NaF-CaF_2-NaCl ternary reciprocal salt polythermal liquidus projection



Components are **the elements**

Charges on ions automatically calculated provided that an appropriate **database** has been connected

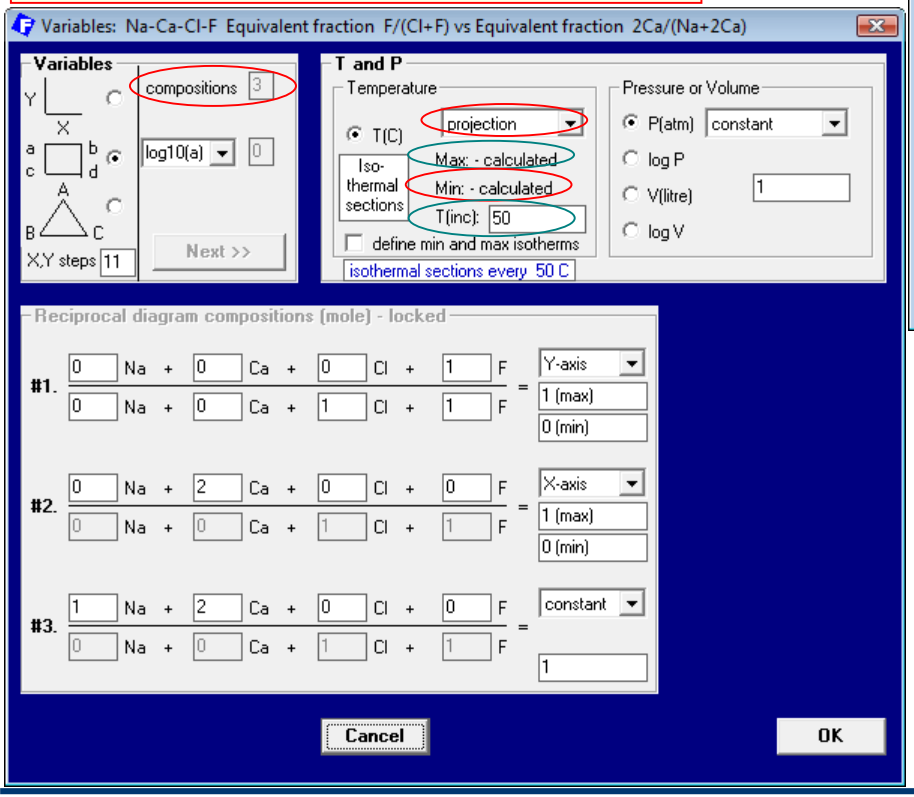
Click on **'reciprocal diagram'**

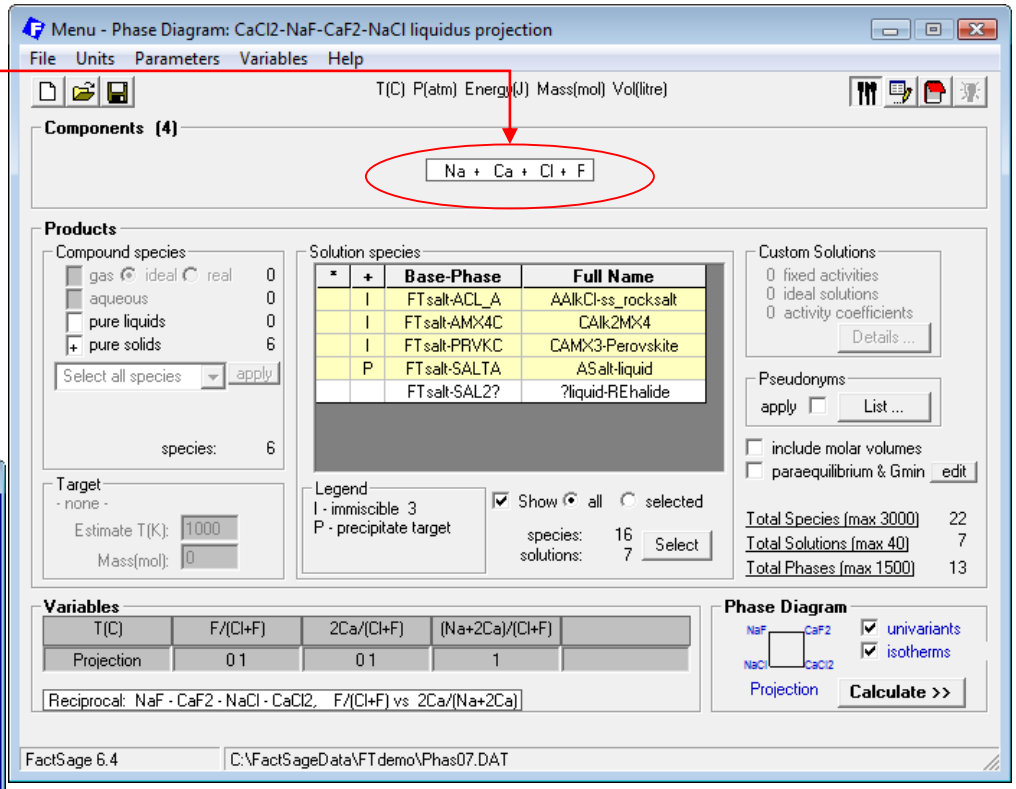
$CaCl_2$-NaF-CaF_2-NaCl ternary reciprocal salt polythermal liquidus projection

1° Entry of the components with **FTsalt** database selected

2° Definition of the variables:

- **3 compositions**
- **T = projection**
- **Step = 50 °C**
- **P = 1 atm**





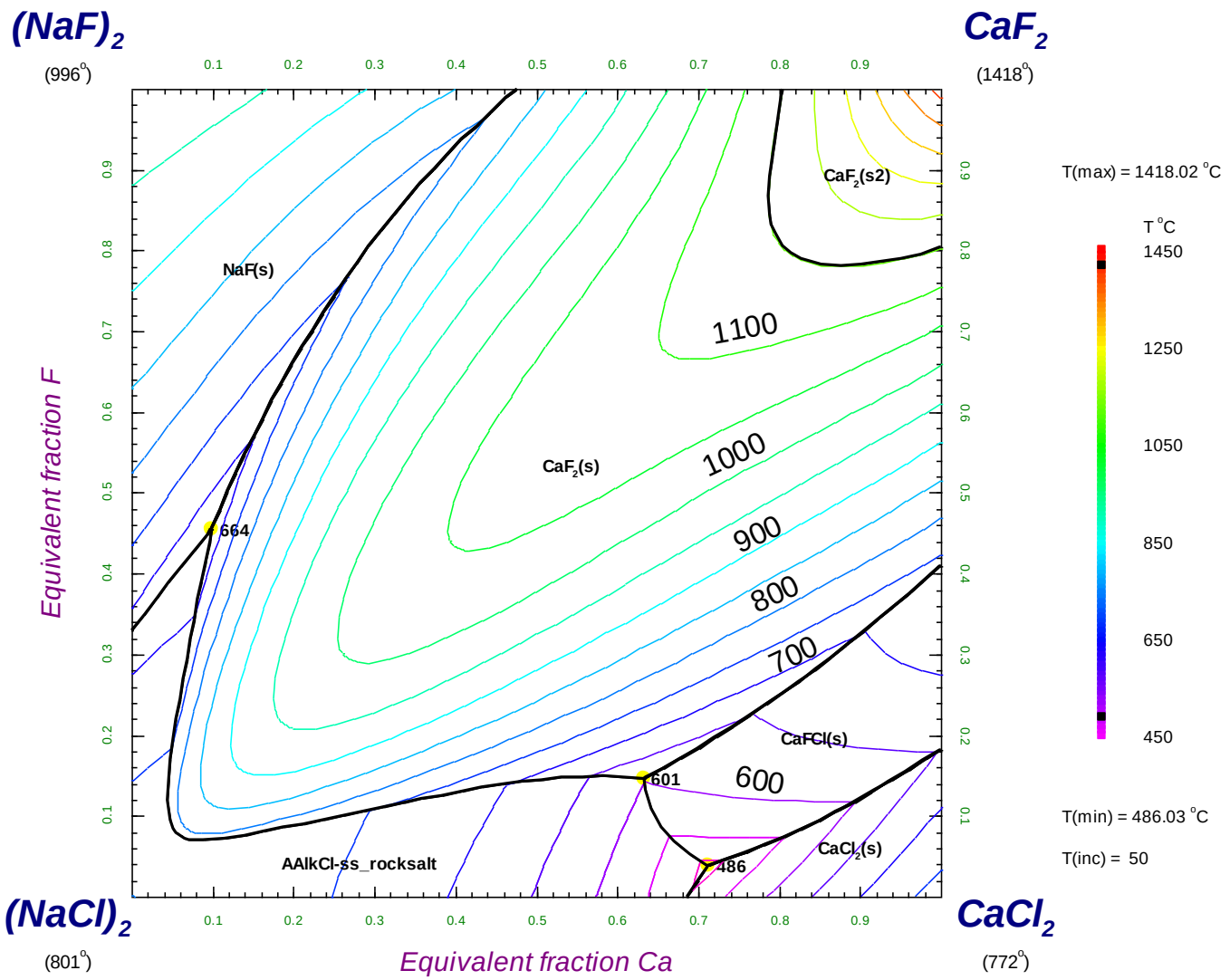
3° Selection of the products:

- **pure solids**
- **Immiscible solution phases**
- **FTsalt-SALTA with option 'P' – precipitate target**

$CaCl_2$-NaF-CaF_2-NaCl ternary reciprocal salt polythermal liquidus projection

Na - Ca - Cl - F

(Na[+] + 2Ca[2+]) = (Cl[-] + F[-]), 1 atm



$CaCl_2$-NaF-CaF_2-NaCl ternary reciprocal salt system

$CaCl_2$-NaF-CaF_2-NaCl is a reciprocal salt system because the chemistry can be defined by the following exchange reaction: $CaCl_2 + 2NaF = CaF_2 + 2NaCl$ and all phases are electroneutral. That is 2n(Ca[++]) + n(Na[+]) = n(F[-]) + n(Cl[-]) where n(i) = moles of ion i.

The components are Na, Ca, F, and Cl.

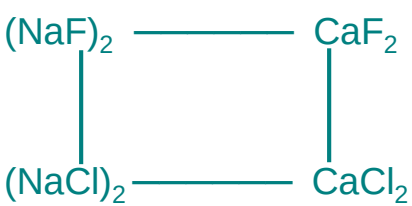
The Y-axis is the "equivalent fraction" F /(F + Cl): 0 to 1

The X-axis is the "equivalent fraction" 2Ca /(2Ca + Na): 0 to 1

where (2Ca + Na) = (F + Cl)

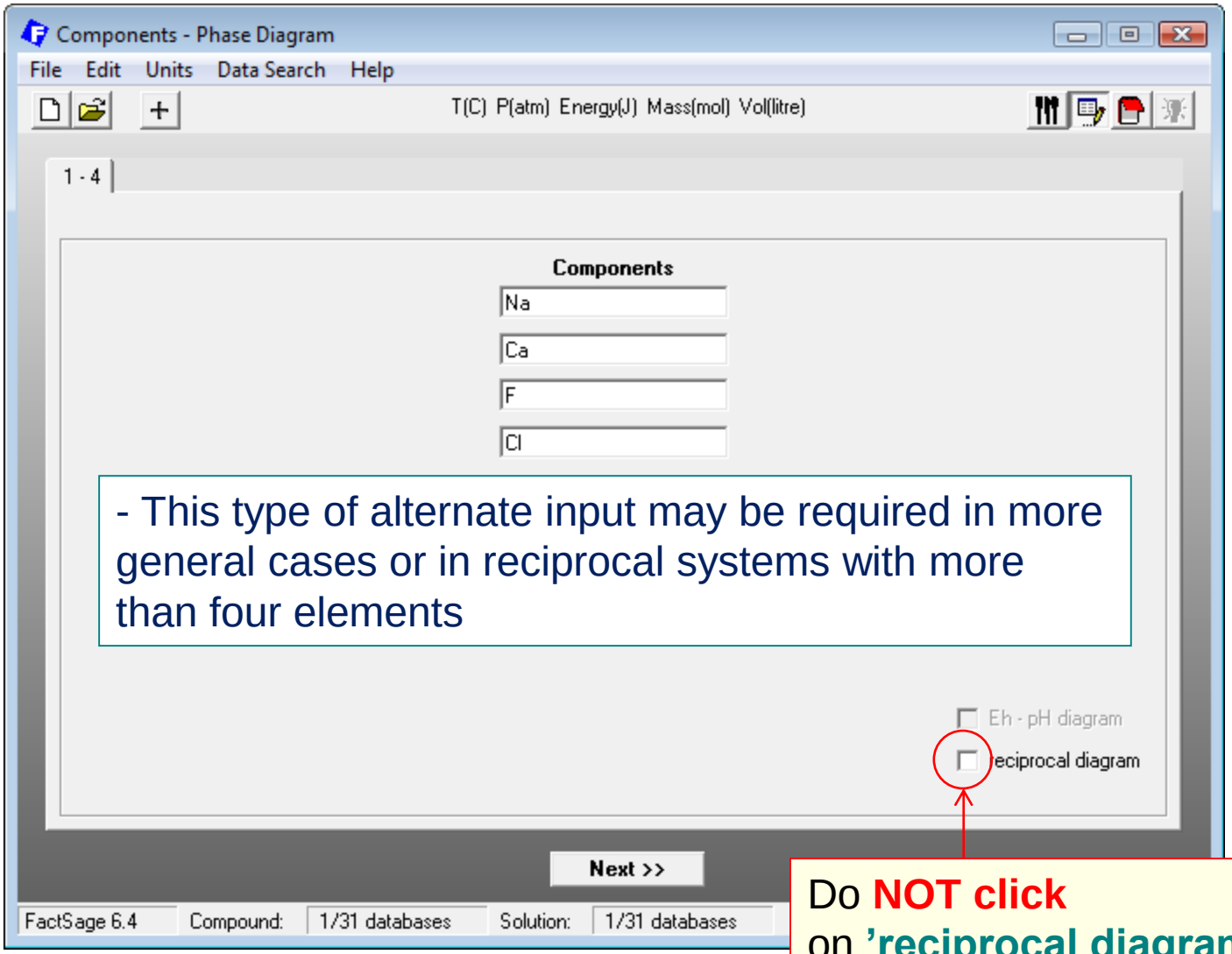
The diagram is not the $CaCl_2$-NaF-CaF_2-NaCl system but rather $CaCl_2$-$(NaF)_2$-CaF_2-$(NaCl)_2$

The corners and axes on the calculated diagram are:



$CaCl_2$-NaF-CaF_2-NaCl ternary reciprocal salt polythermal liquidus projection

- ALTERNATE INPUT/OUTPUT



- This type of alternate input may be required in more general cases or in reciprocal systems with more than four elements

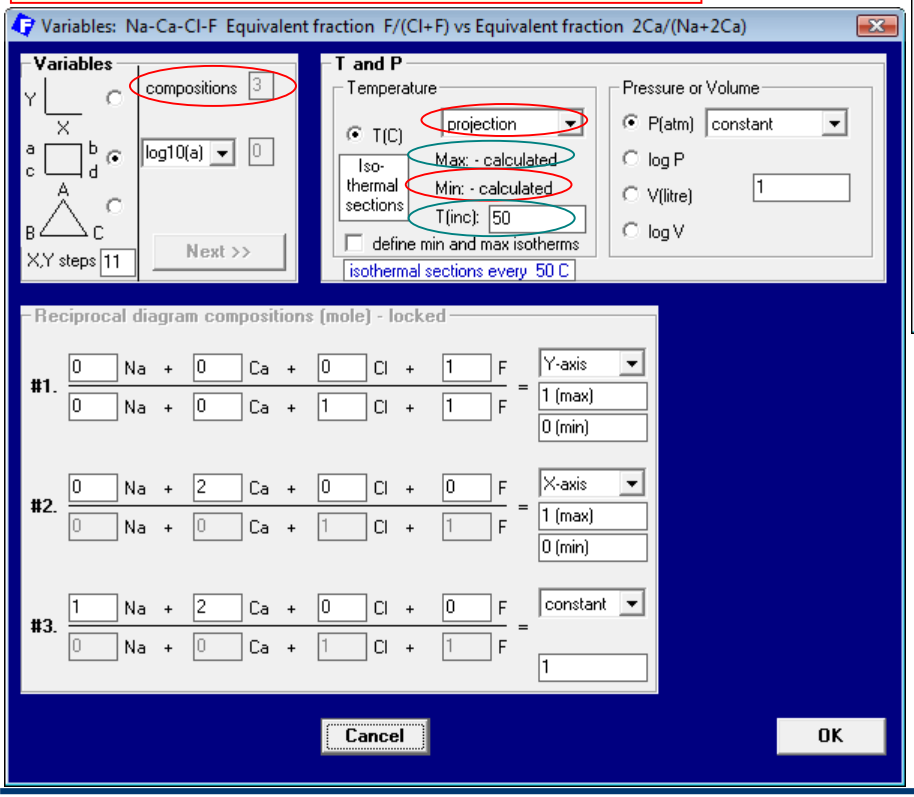
Do **NOT click** on **'reciprocal diagram'**

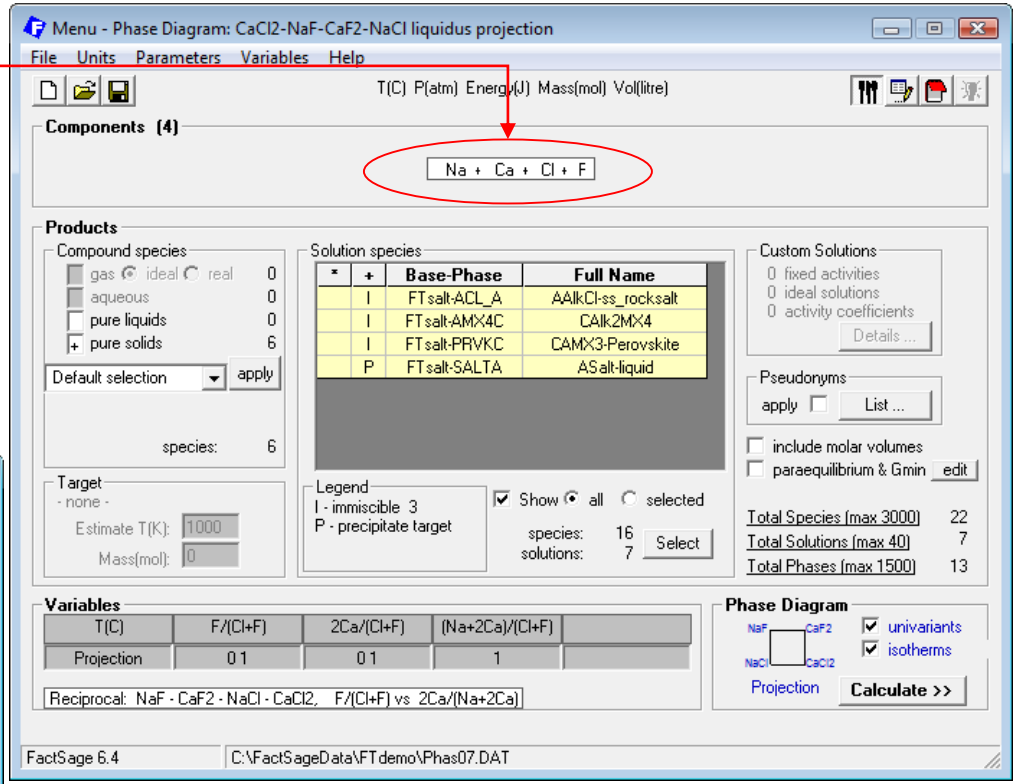
$CaCl_2$-NaF-CaF_2-NaCl ternary reciprocal salt polythermal liquidus projection

1° Entry of the components with **FTsalt** database selected

2° Definition of the variables:

- **3 compositions**
- **T = projection**
- **Step = 50 °C**
- **P = 1 atm**

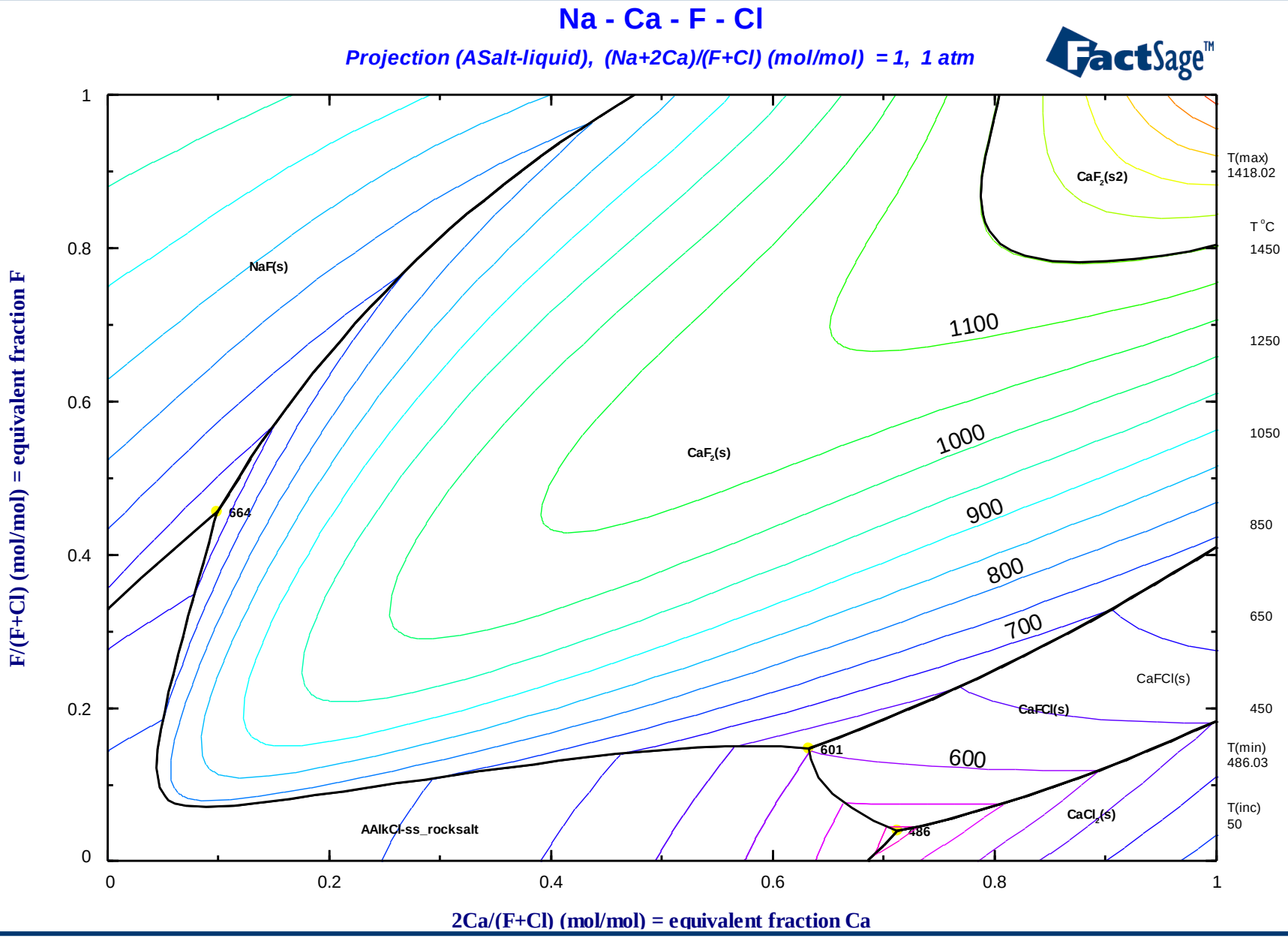




3° Selection of the products:

- **pure solids**
- **Immiscible solution phases**
- **FTsalt-SALTA with option 'P' – precipitate target**

$CaCl_2$-NaF-CaF_2-NaCl reciprocal salt polythermal liquidus projection- Alternate Output



Paraequilibrium and minimum Gibbs energy calculations

- In certain solid systems, some elements diffuse much faster than others. Hence, if an initially homogeneous single-phase system at high temperature is quenched rapidly and then held at a lower temperature, a temporary **paraequilibrium state** may result in which the rapidly diffusing elements have reached equilibrium, but the more slowly diffusing elements have remained essentially immobile.

- The best known, and most industrially important, example occurs when homogeneous austenite is quenched and annealed. Interstitial elements such as C and N are much more mobile than the metallic elements.

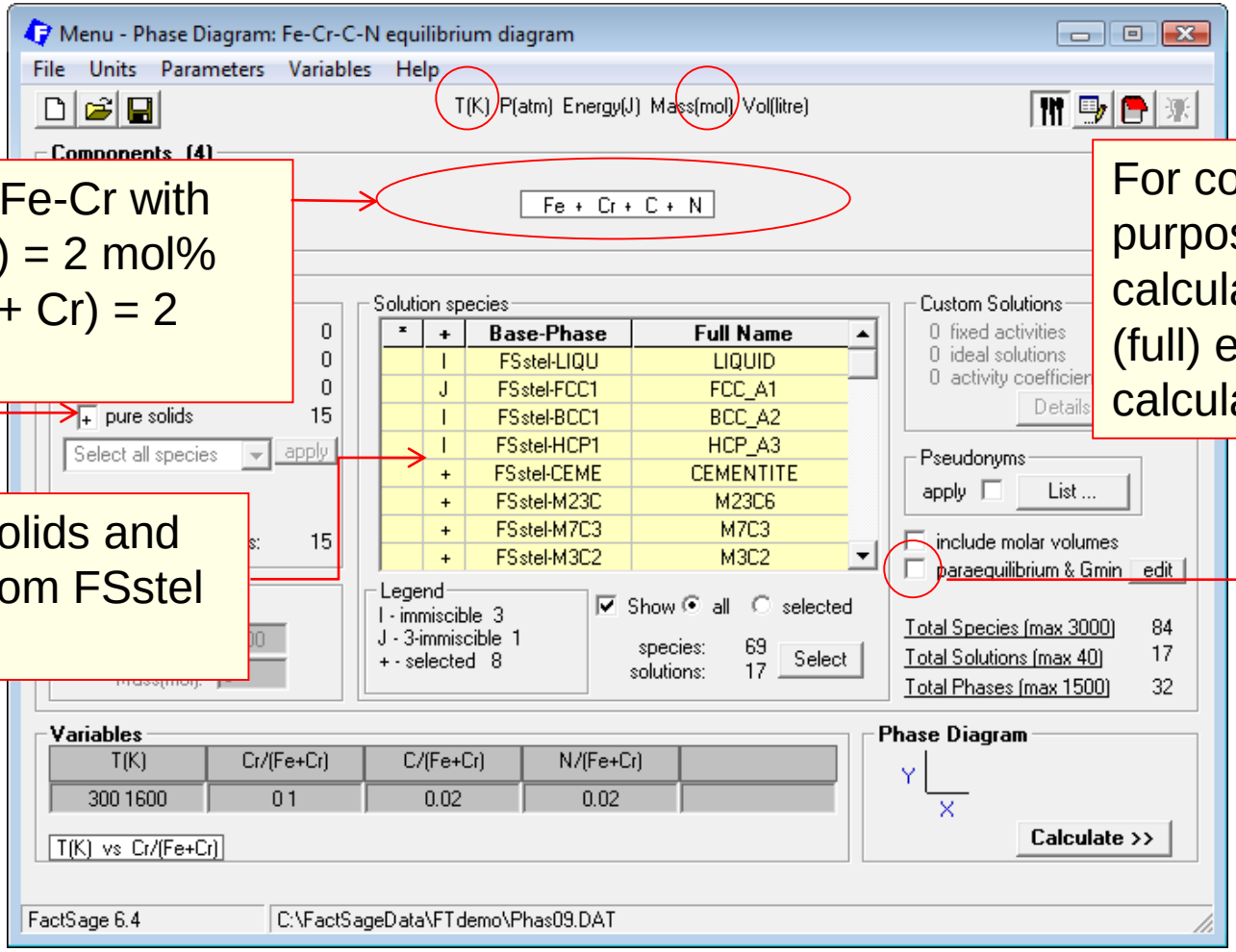
- At paraequilibrium, the ratios of the slowly diffusing elements in all phases are the same and are equal to their ratios in the initial single-phase alloy. The algorithm used to calculate paraequilibrium in FactSage is based upon this fact. That is, the algorithm minimizes the Gibbs energy of the system under this constraint.

- If a paraequilibrium calculation is performed specifying that no elements diffuse quickly, then the ratios of all elements are the same as in the initial homogeneous state. In other words, such a calculation will simply yield the single homogeneous phase with the minimum Gibbs energy at the temperature of the calculation. Such a calculation may be of practical interest in **physical vapour deposition** where deposition from the vapour phase is so rapid that phase separation cannot occur, resulting in a single-phase solid deposit.

- Paraequilibrium and minimum Gibbs energy conditions may also be calculated with the **Equilib Module**. See the **Advanced Equilib** slide show.

Paraequilibrium and minimum Gibbs energy calculations

Fe-Cr-C-N system



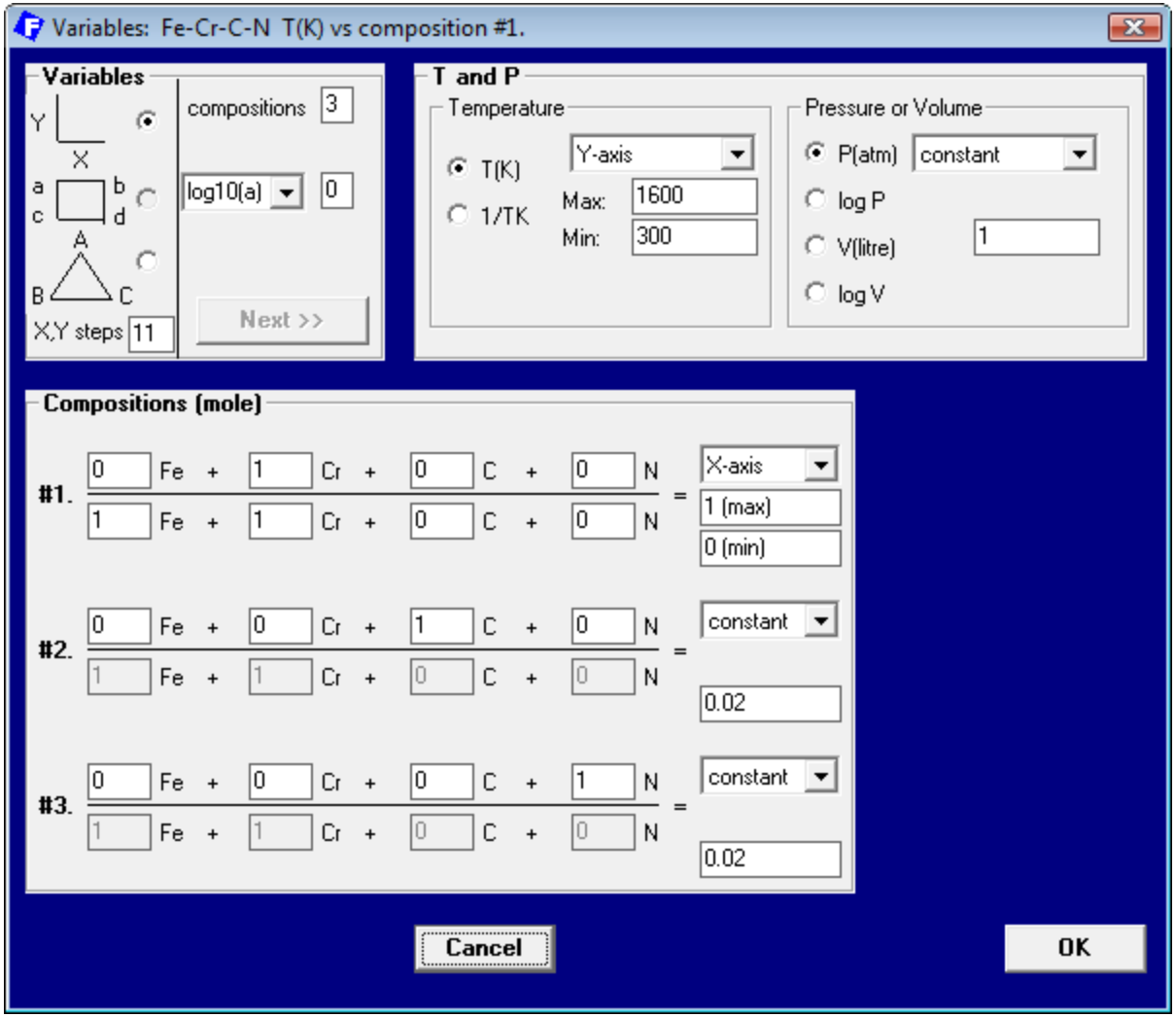
Equimolar Fe-Cr with C/(Fe + Cr) = 2 mol% and N/(Fe + Cr) = 2 mol%

Select all solids and solutions from FSstel database

For comparison purposes, our first calculation is a normal (full) equilibrium calculation

Paraequilibrium and minimum Gibbs energy calculations

Fe-Cr-C-N system



Molar ratios:

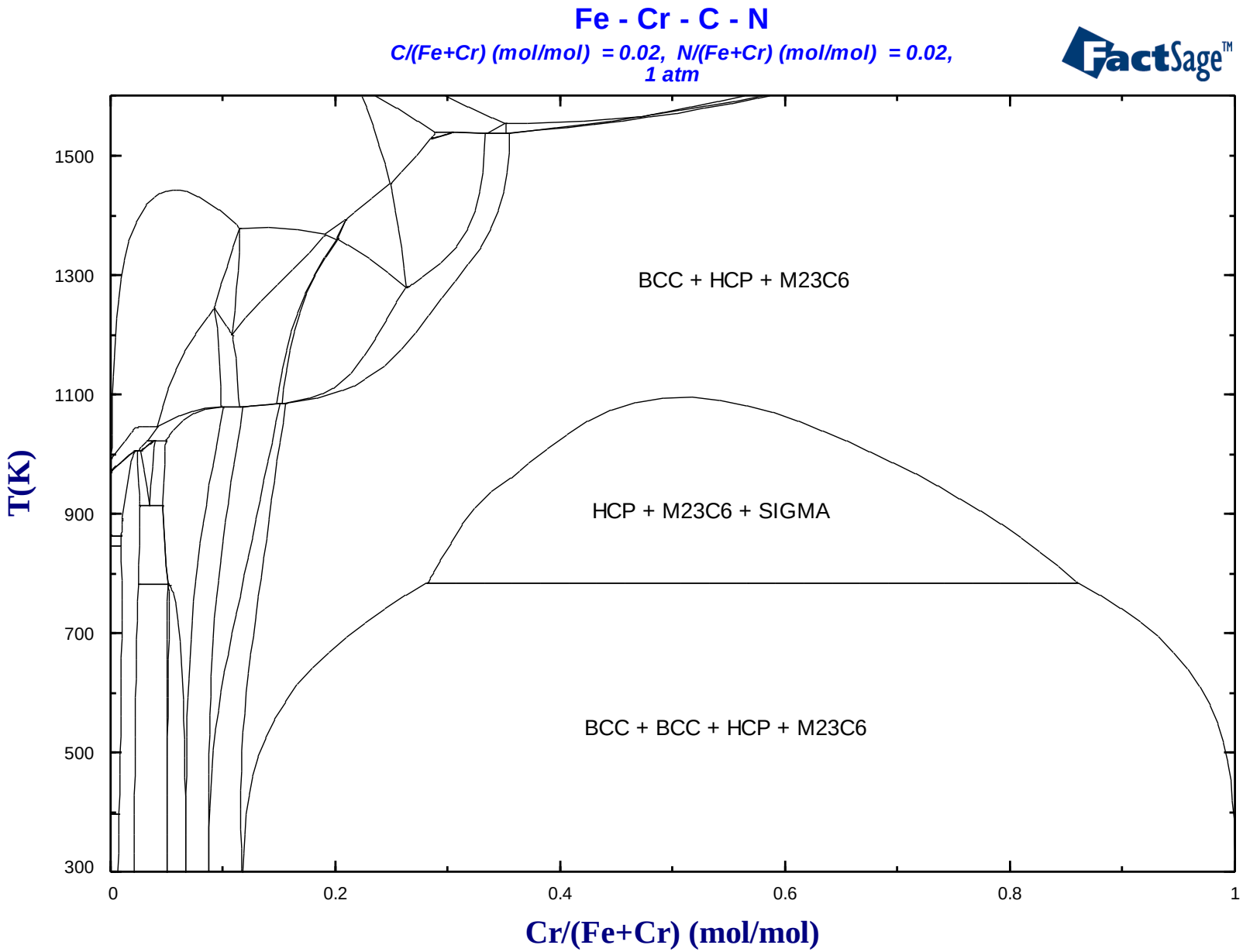
C/(Fe + Cr) = 0.02

N/(Fe + Cr) = 0.02

X-axis:

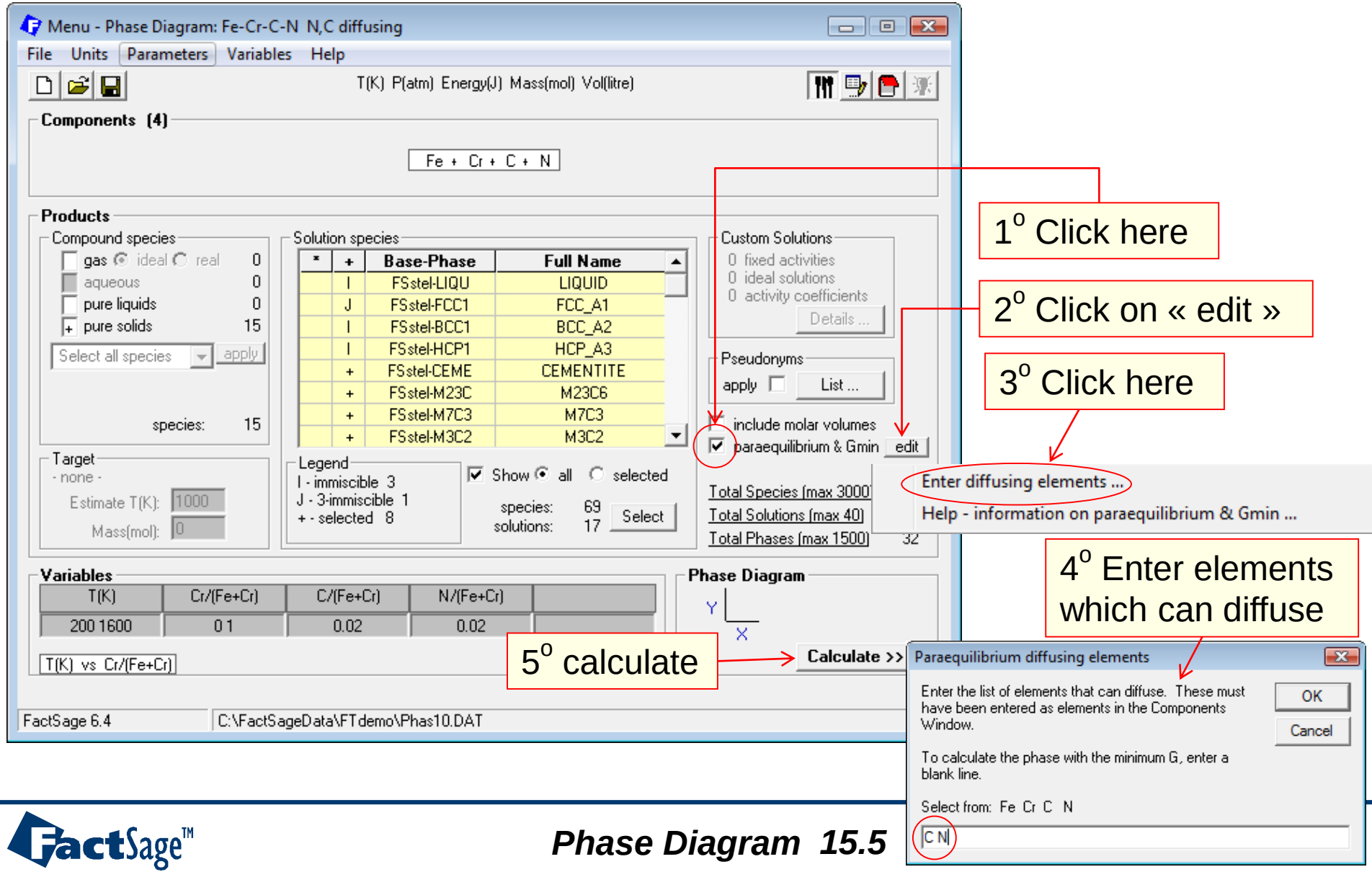
$0 \leq Cr/(Fe + Cr) \leq 1$

Output - Equilibrium phase diagram

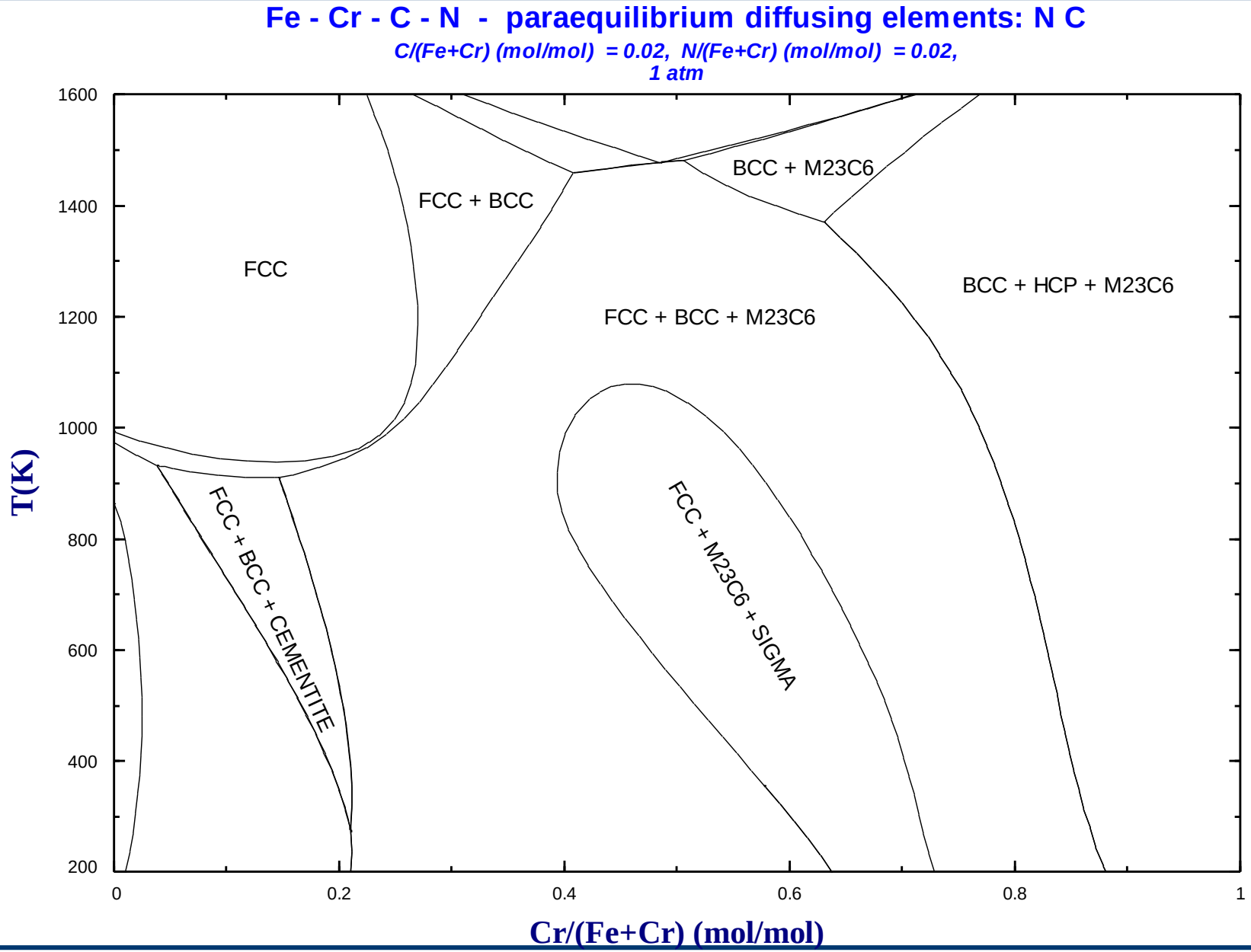


Paraequilibrium and minimum Gibbs energy calculations

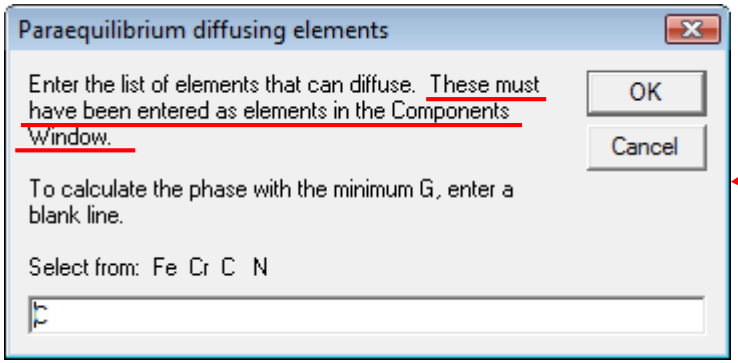
Fe-Cr-C-N system
when only C and N are permitted to diffuse



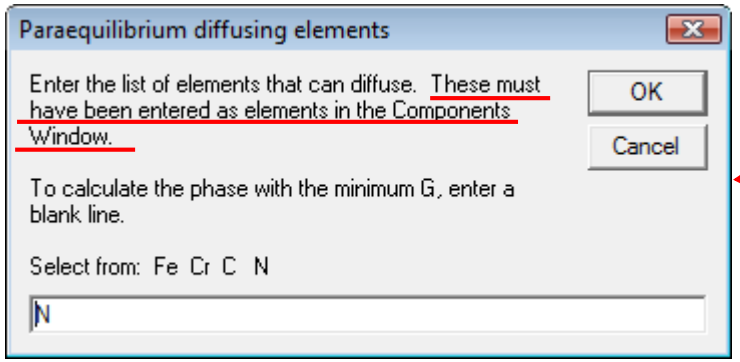
Output - Paraequilibrium phase diagram with only C and N diffusing



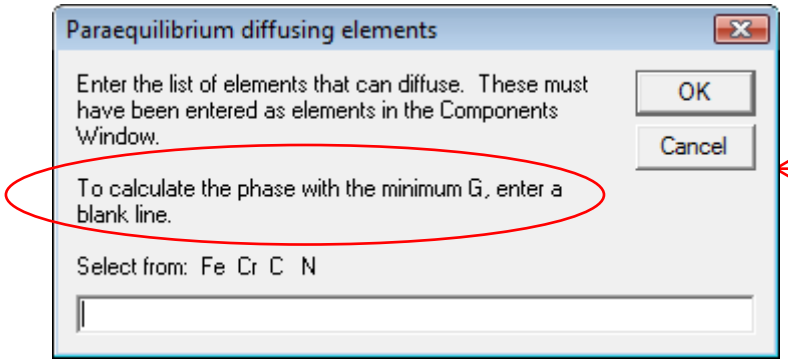
Paraequilibrium and minimum Gibbs energy calculations



Input when only C is permitted to diffuse

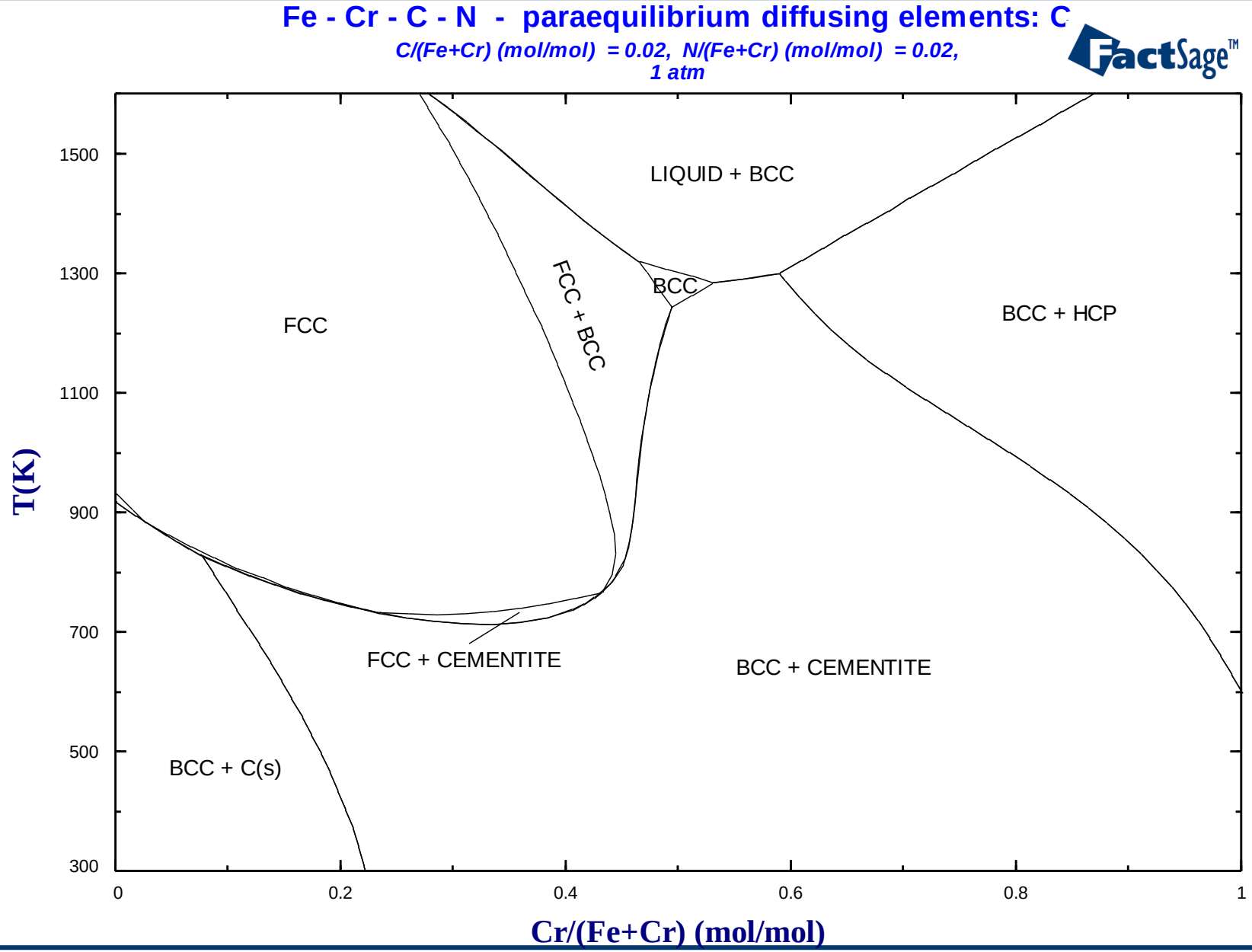


Input when only N is permitted to diffuse

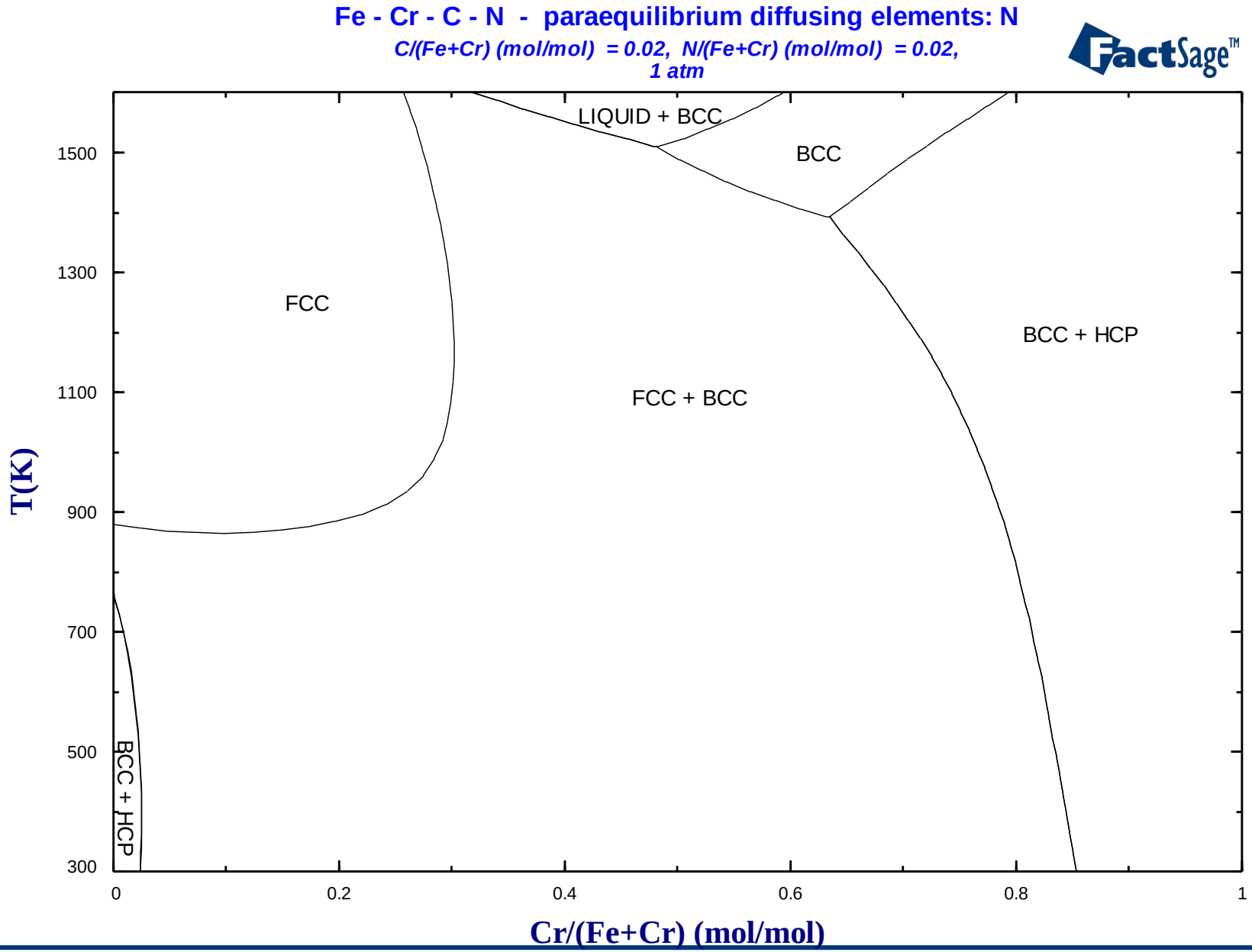


Input when no elements are permitted to diffuse (minimum Gibbs energy calculation). For this calculation, only elements must be entered in the Components Window

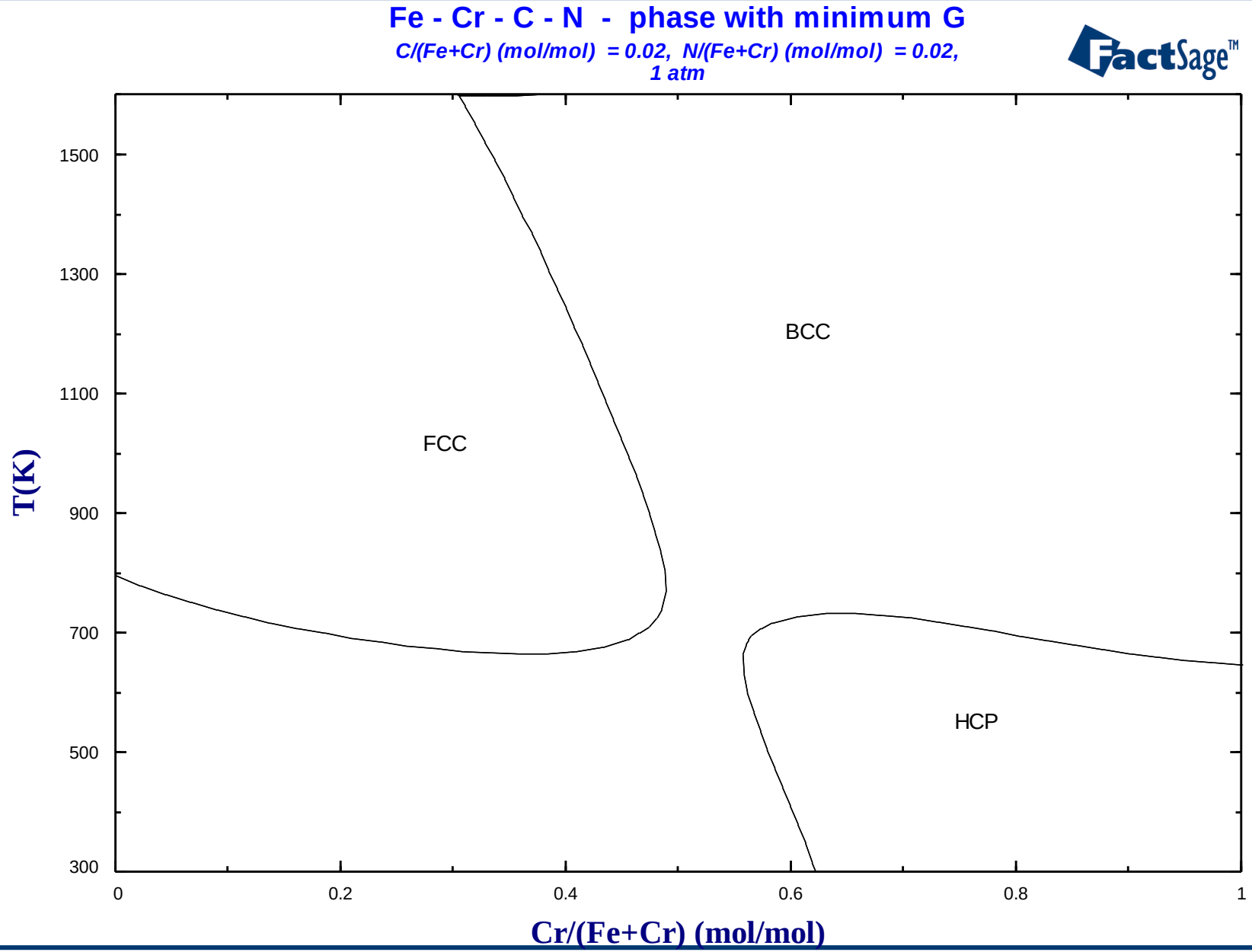
Output - Paraequilibrium phase diagram with only C diffusing



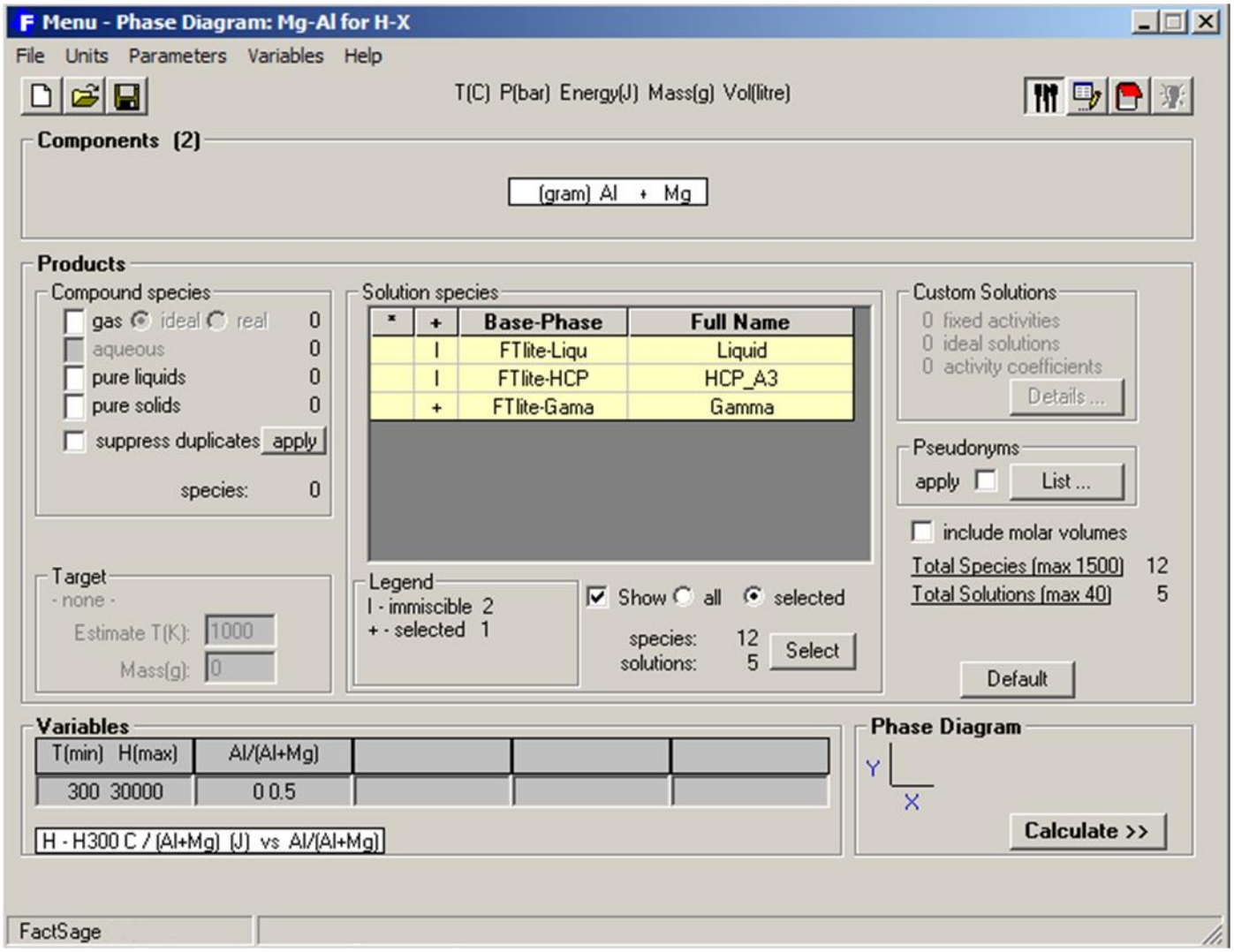
Output - Paraequilibrium phase diagram with only N diffusing



Output - Minimum Gibbs energy diagram (no elements diffusing)

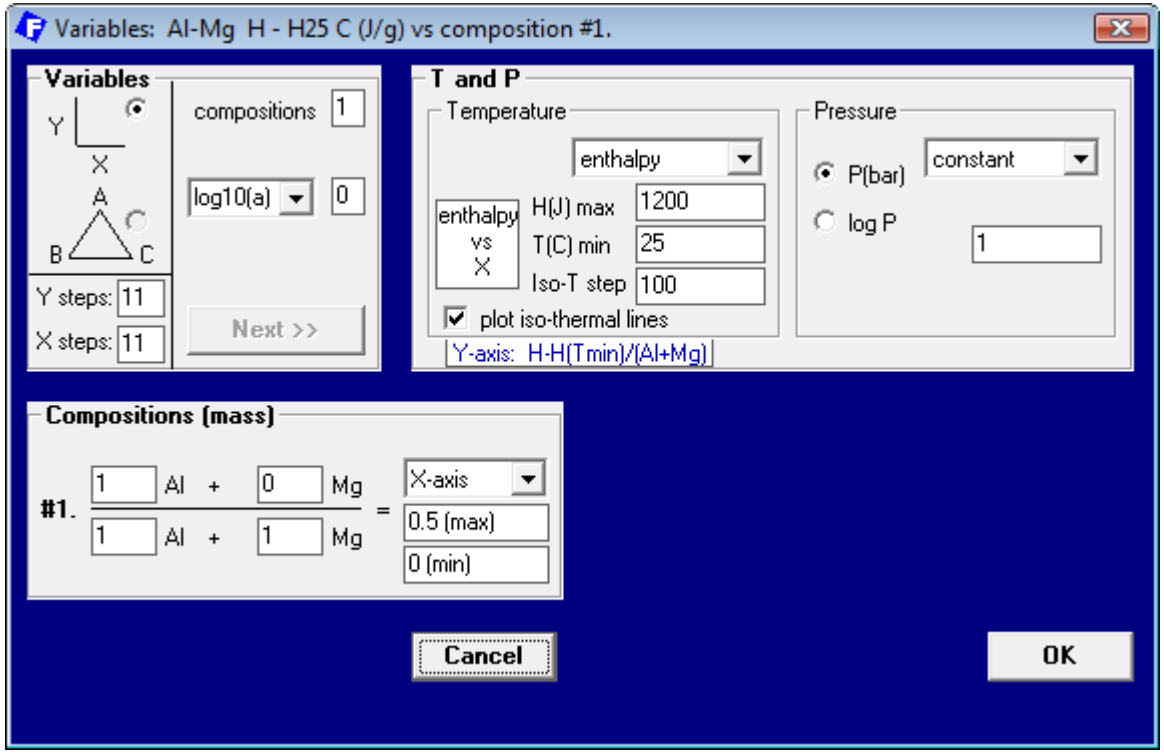


Enthalpy-Composition (H-X) phase diagrams



Selecting variables for H-X diagram

y-axis will be enthalpy difference **(H_T - $H_{25°C}$)**

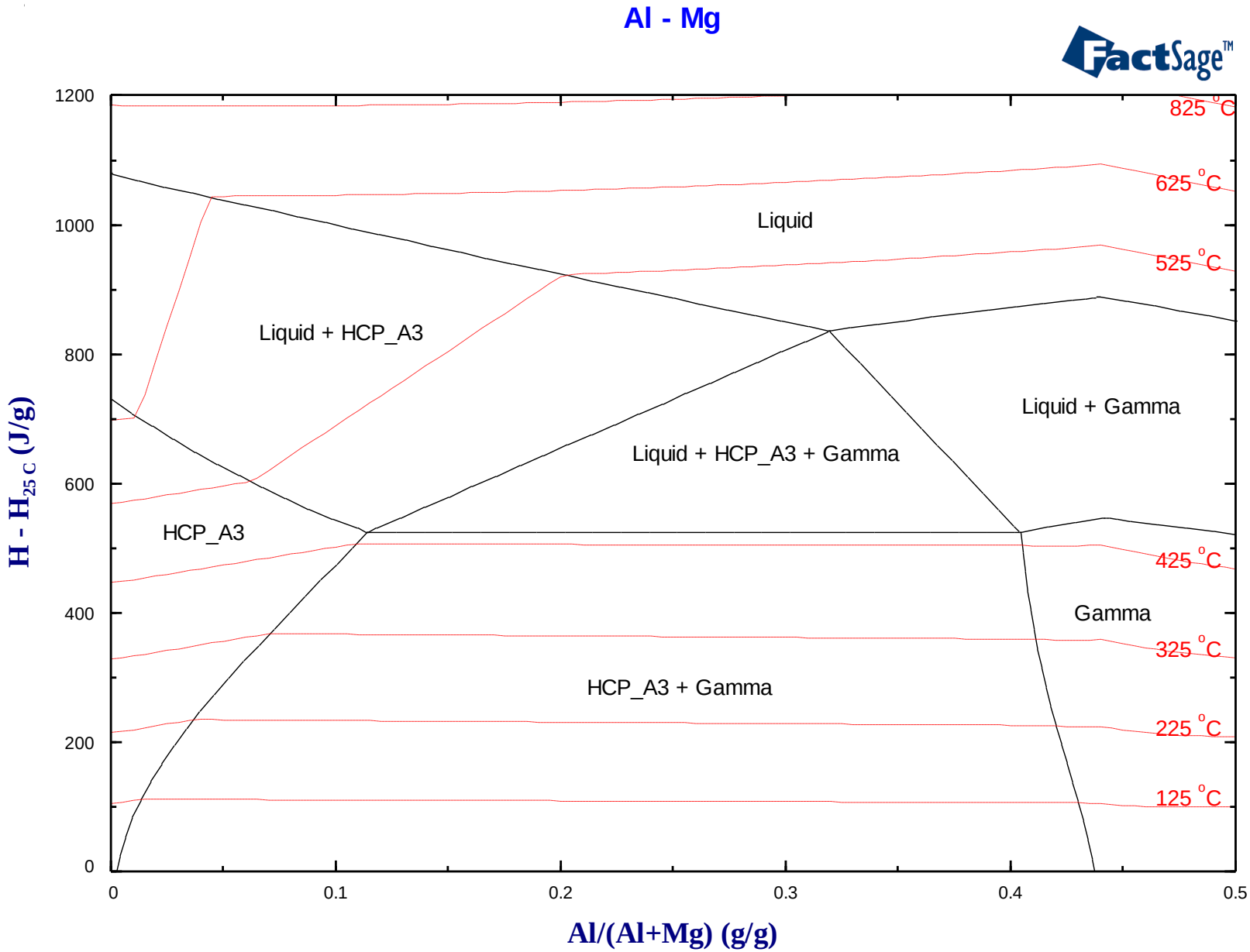


Isotherms plotted every **100°C**

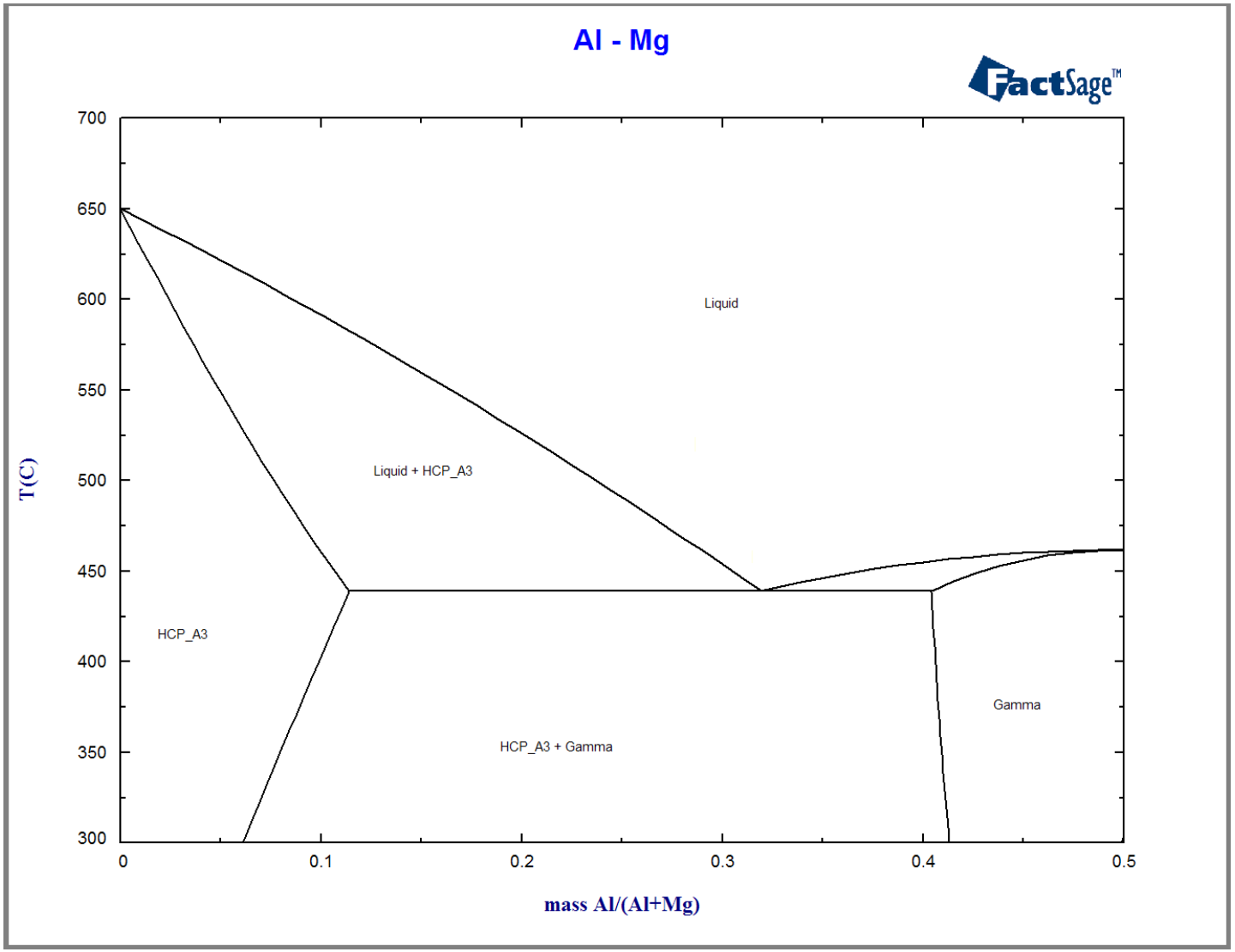
Maximum of **y-axis** will be **1200** Joules

x-axis plotted for **$0 \leq x \leq 0.5$**

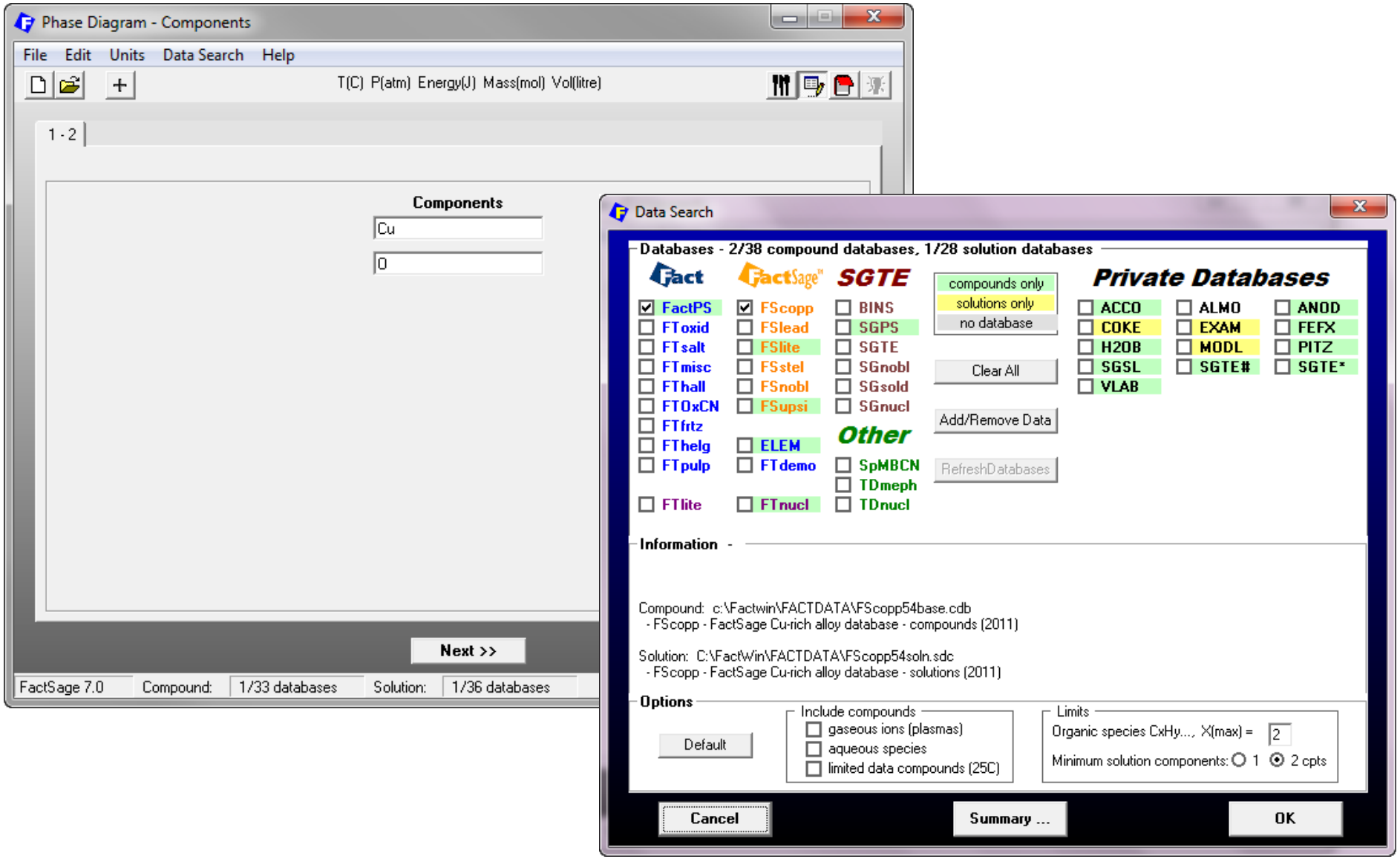
Calculated H-X diagram for Mg-Al system



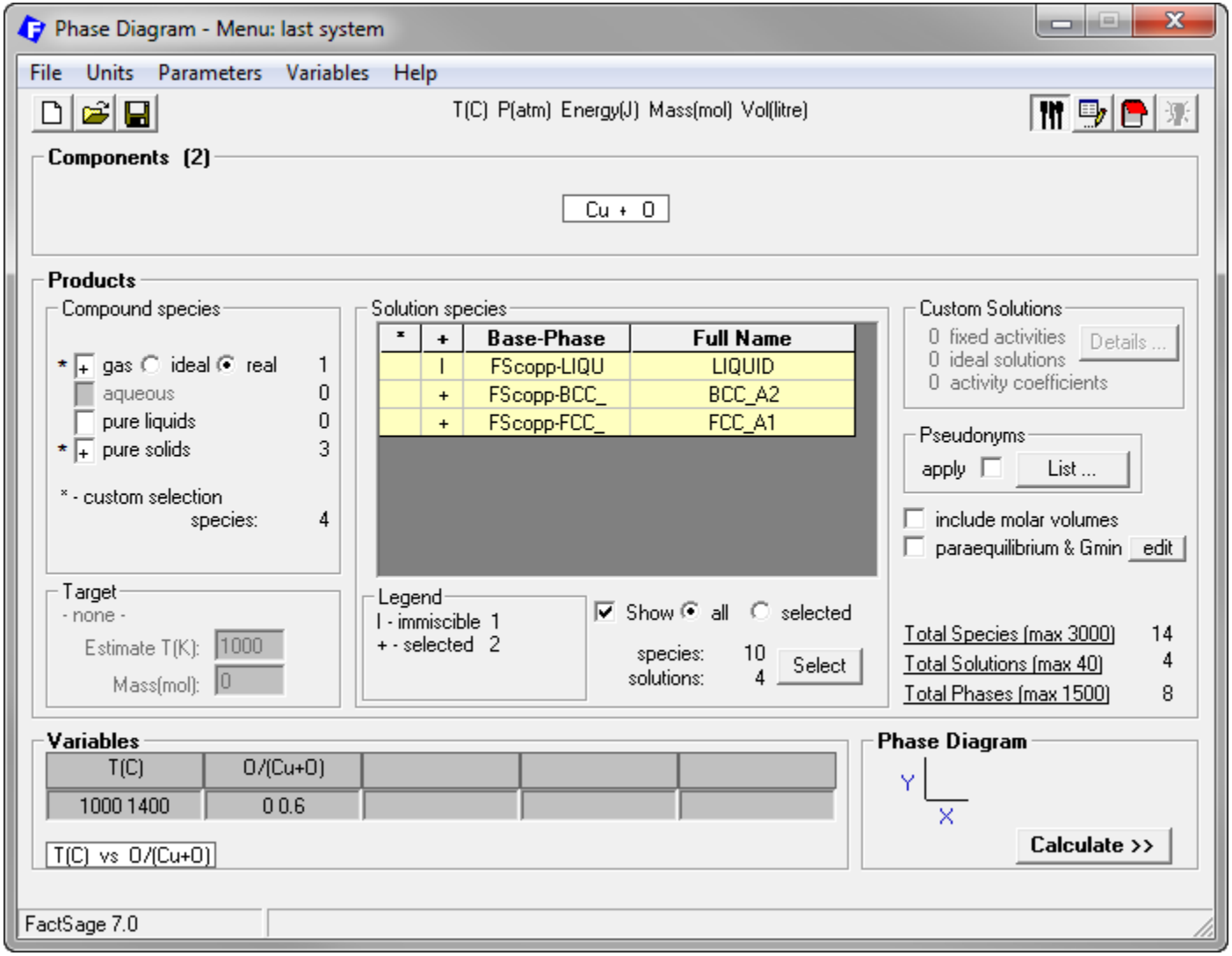
Compare to T-X diagram for Mg-Al



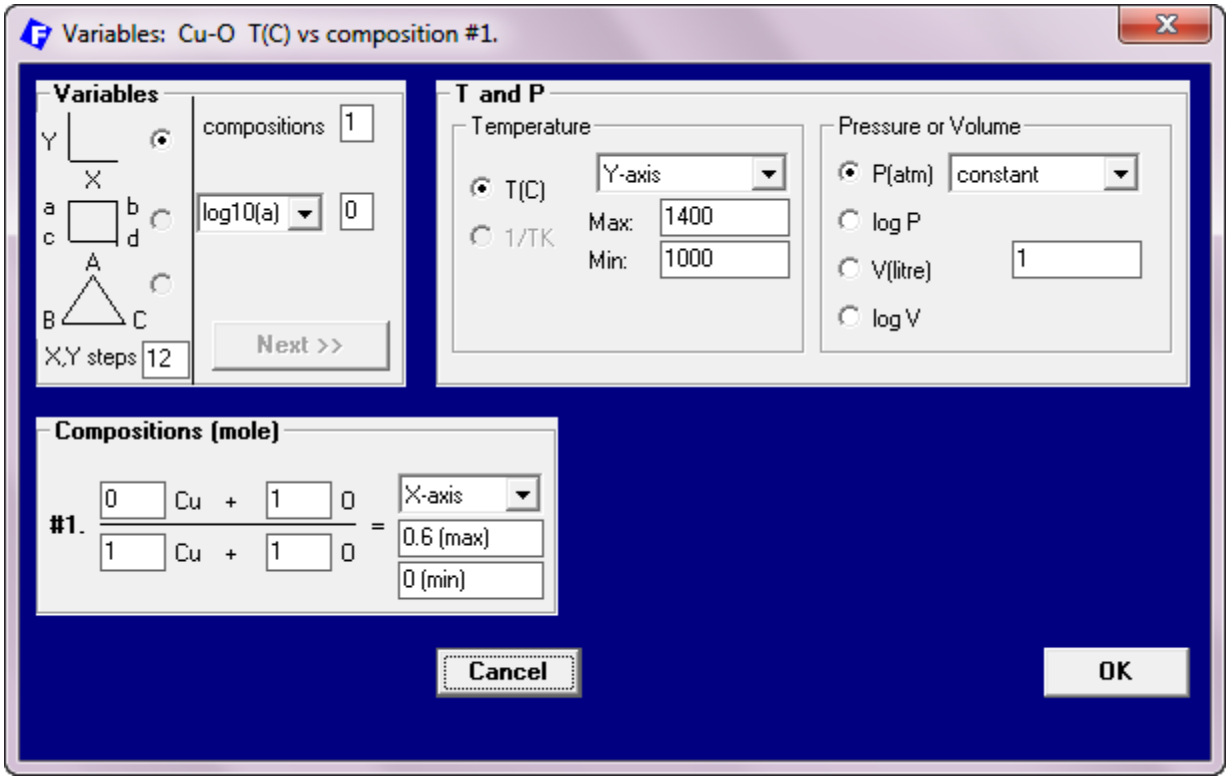
Isobars and Iso-activities - Cu-O – Components and Data Search



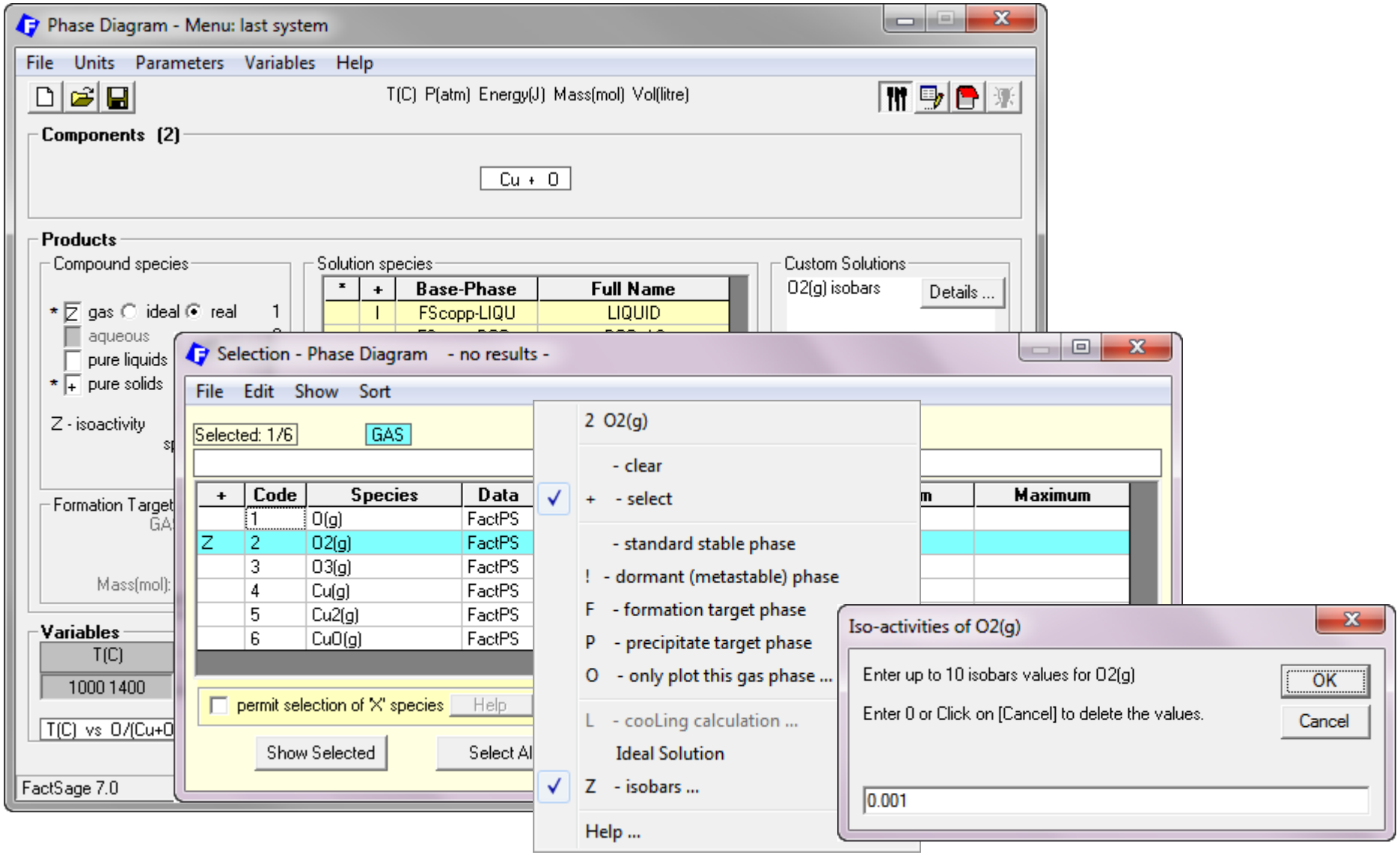
Isobars and Iso-activities - Cu-O – Menu Window



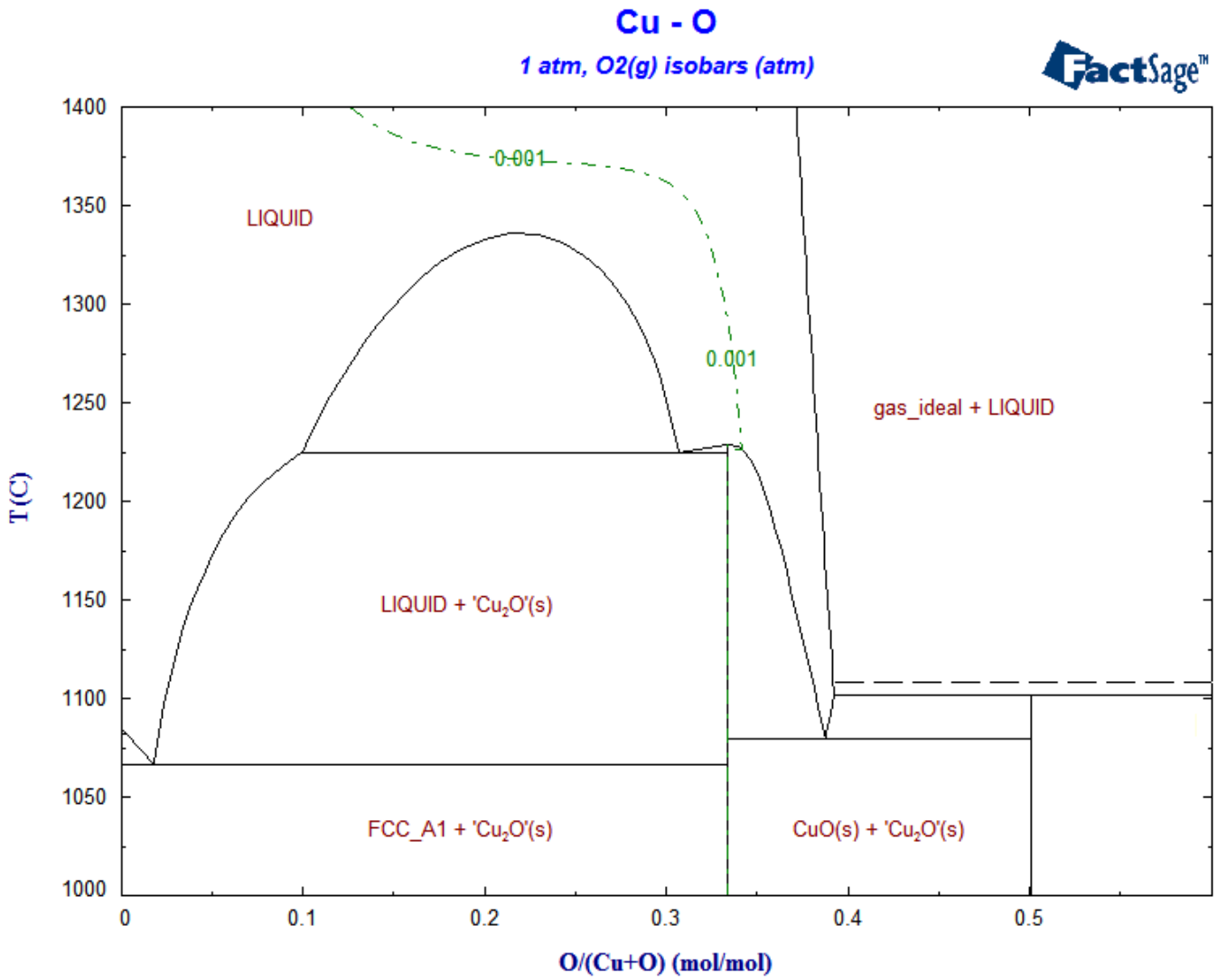
Isobars and Iso-activities - Cu-O – Variables Window



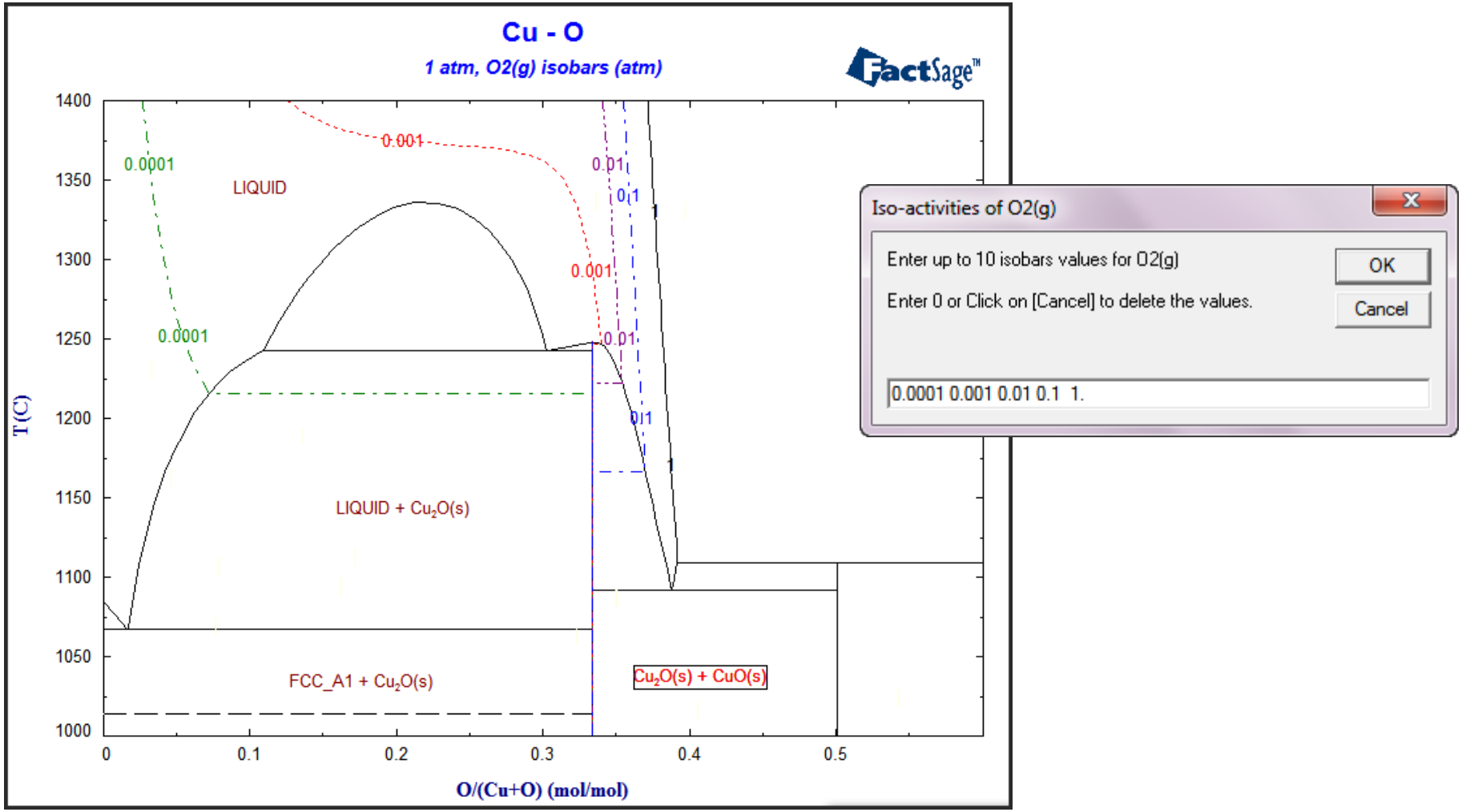
Isobars and Iso-activities - Gas Species Selection Window, option Z



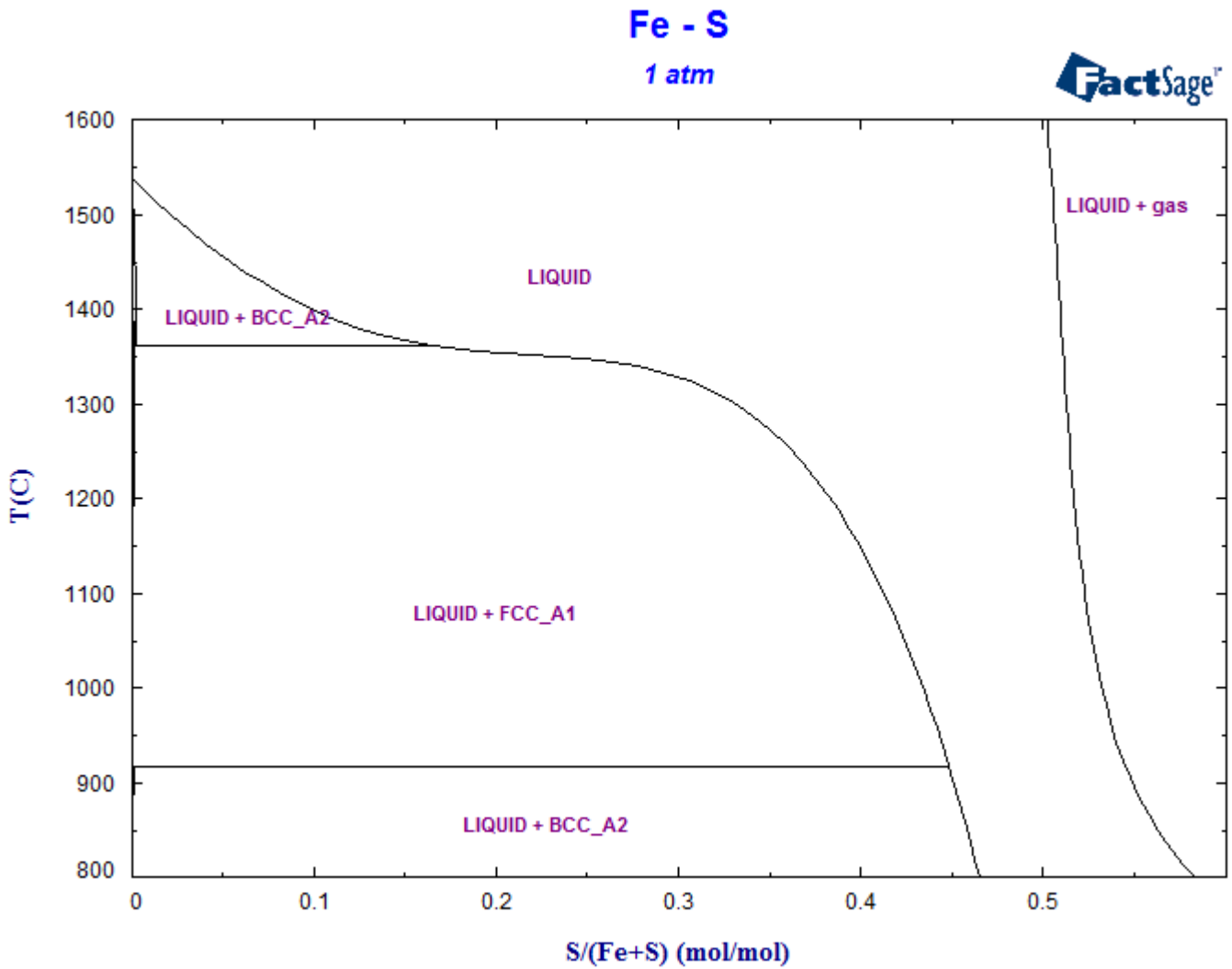
Isobars and Iso-activities - Phase Diagram – $P(O_2)$ 0.0001 atm isobar



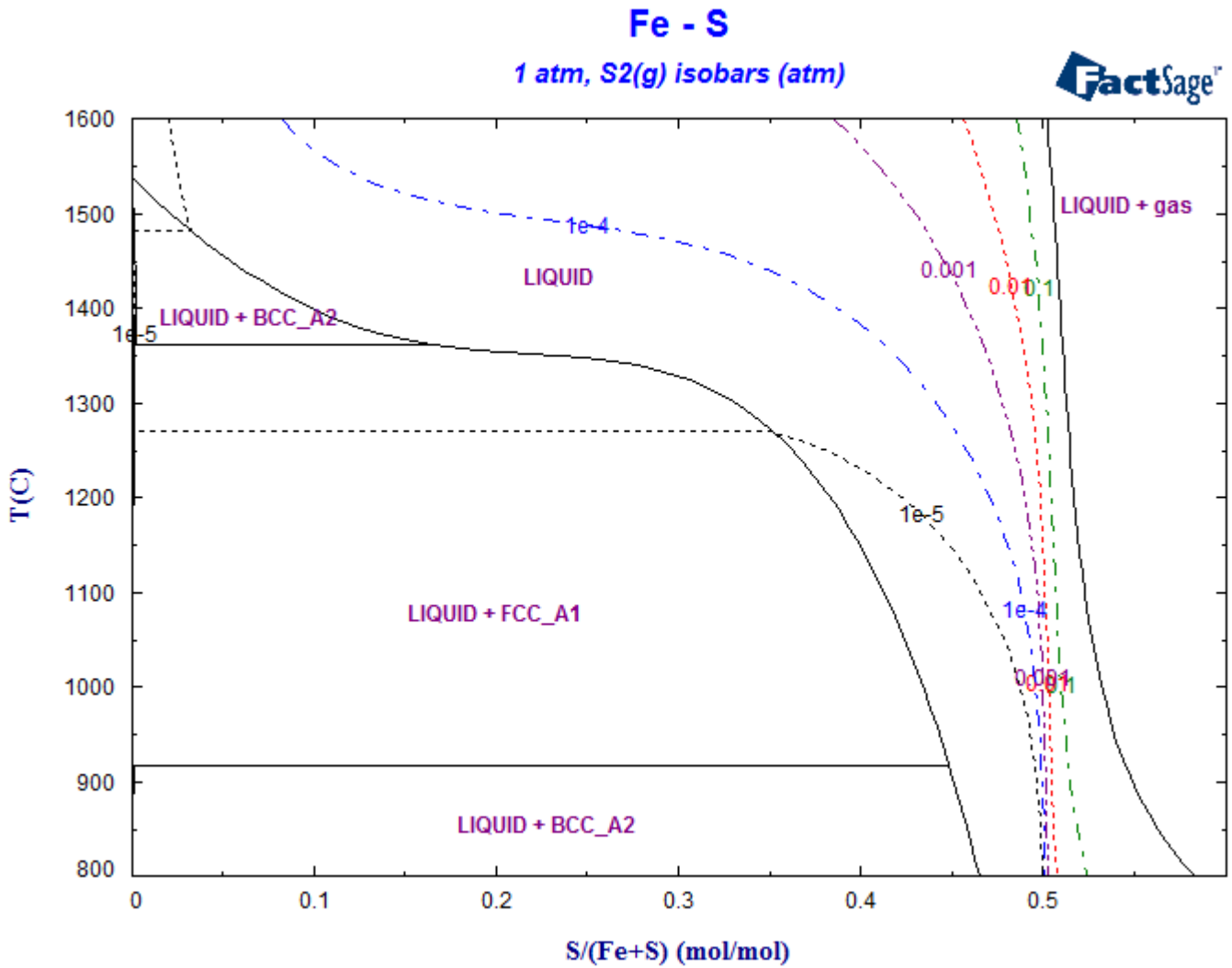
Isobars and Iso-activities - Cu-O Phase Diagram – O_2(g) isobars



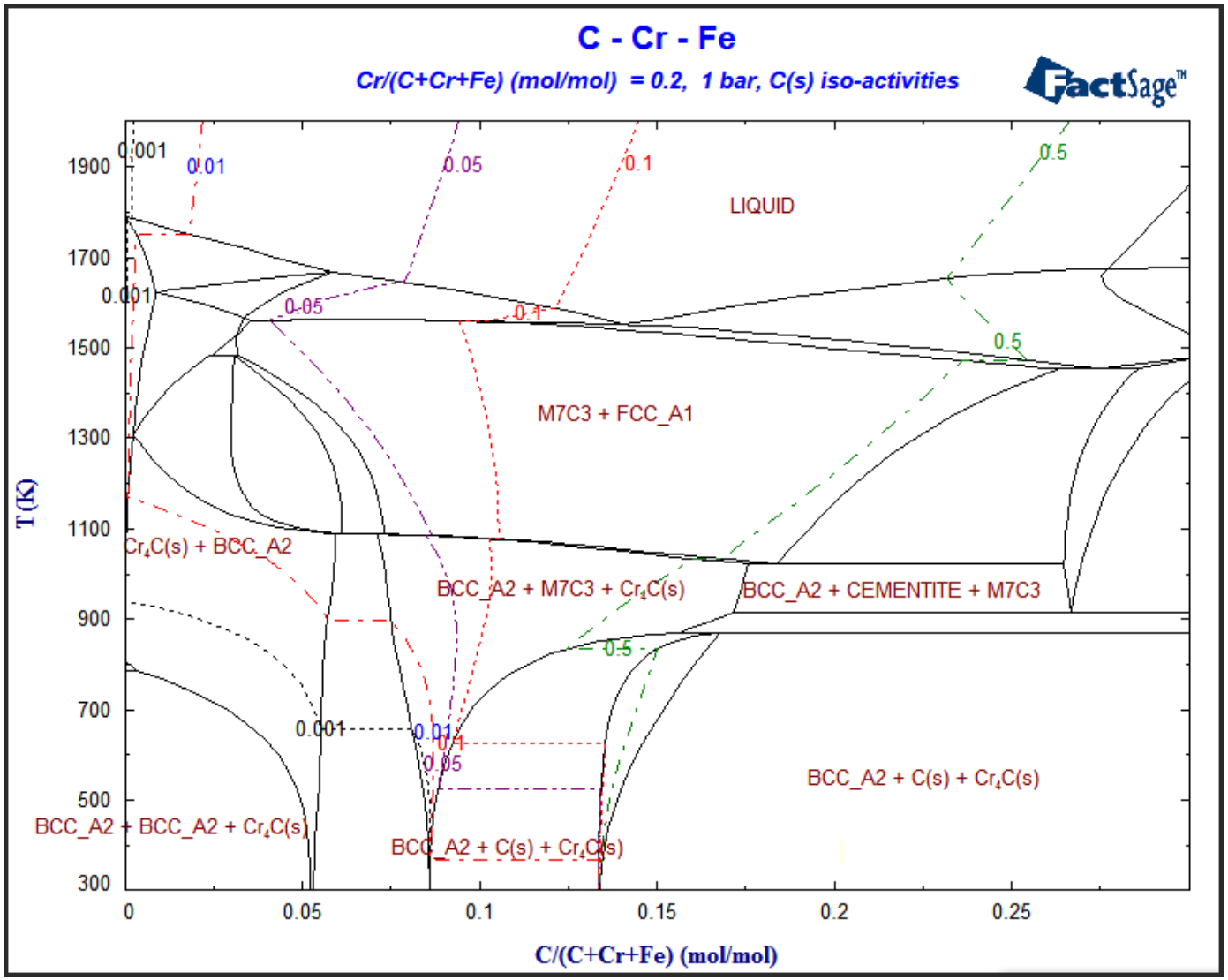
Isobars and Iso-activities - Fe-S Phase Diagram



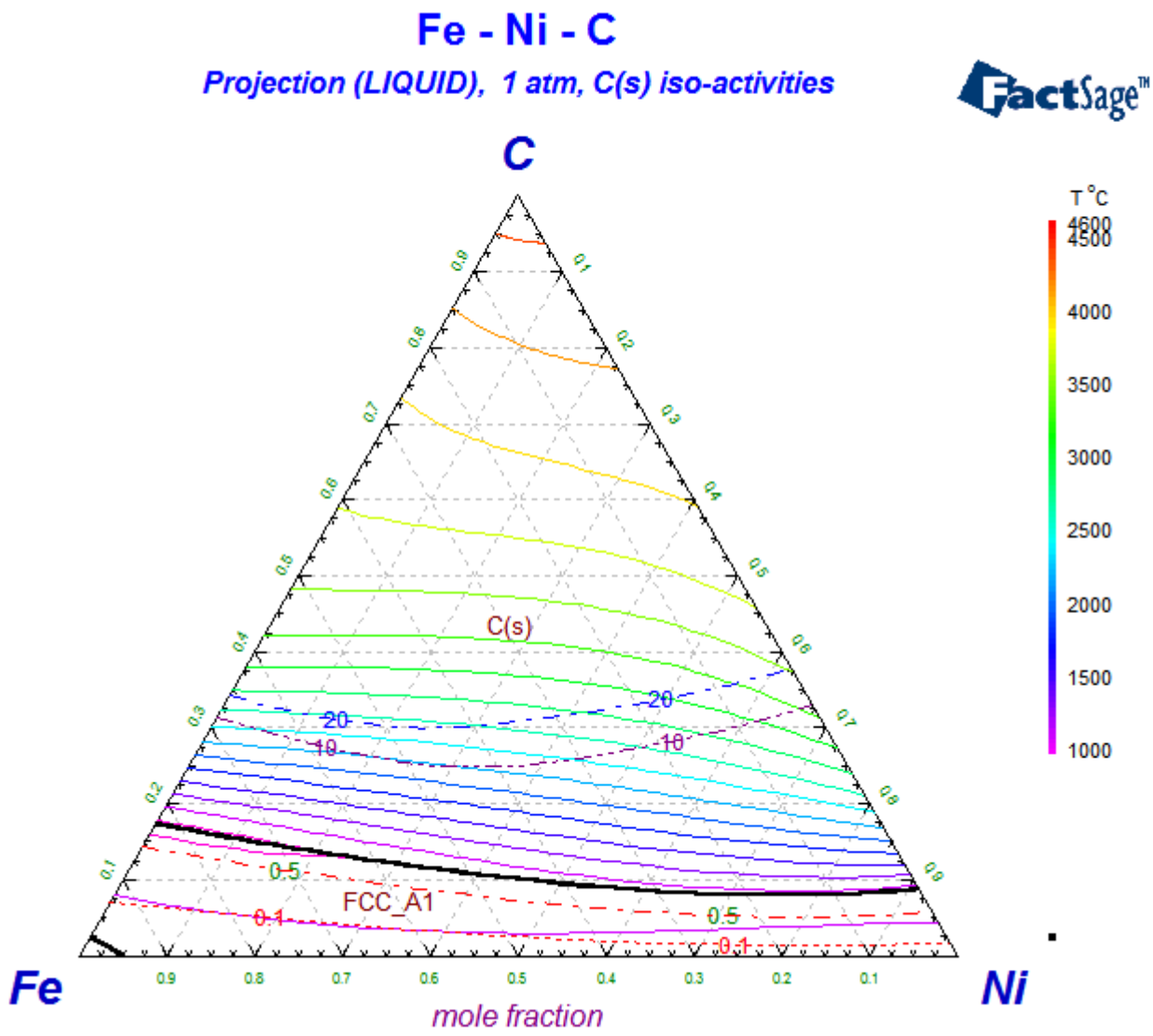
Isobars and Iso-activities - Fe-S Phase Diagram – $S_2(g)$ isobars



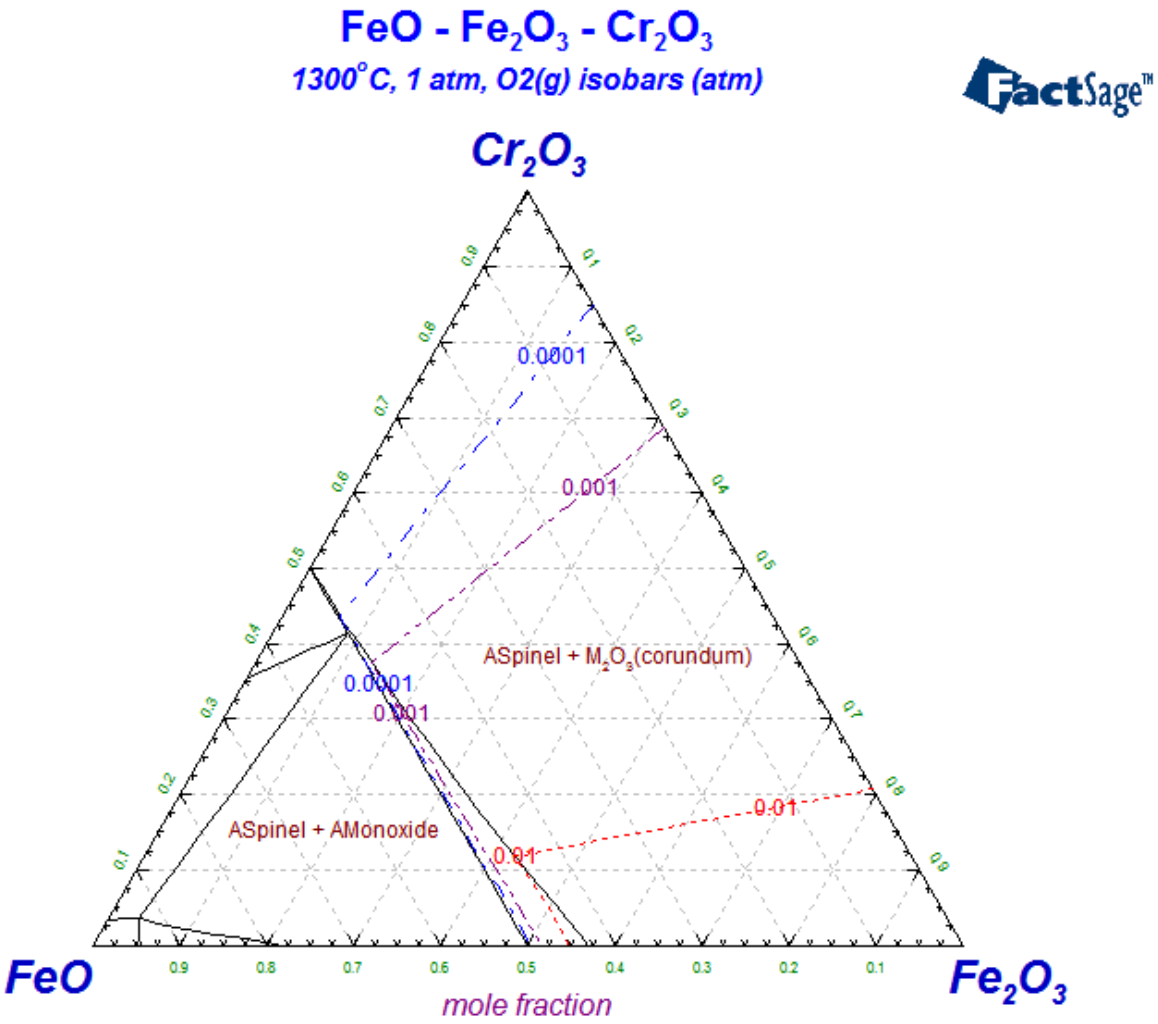
Isobars and Iso-activities - C-Cr-Fe Phase Diagram – C(s) iso-activities



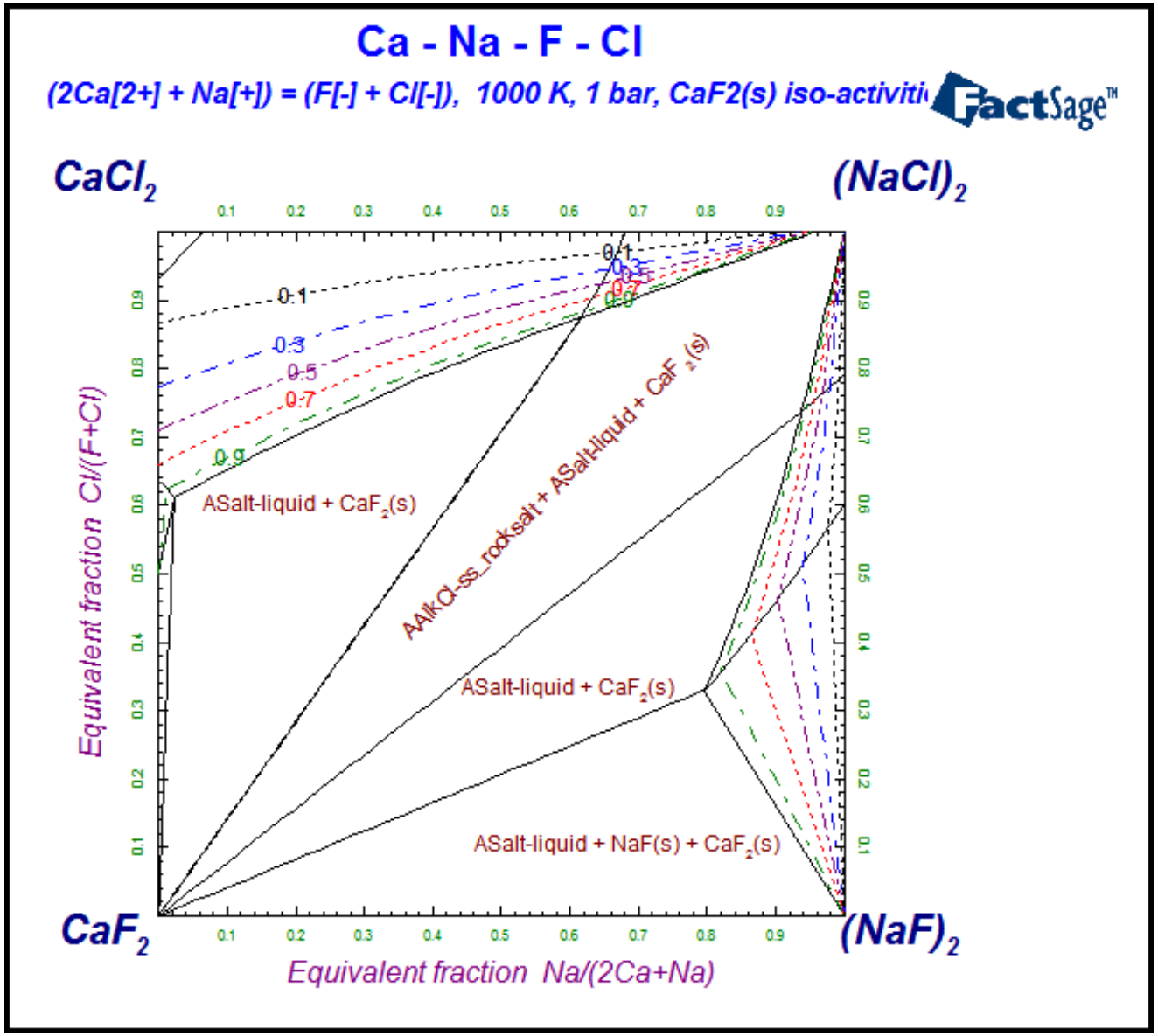
Isobars and Iso-activities - Polythermal Projection – C(s) iso-activities



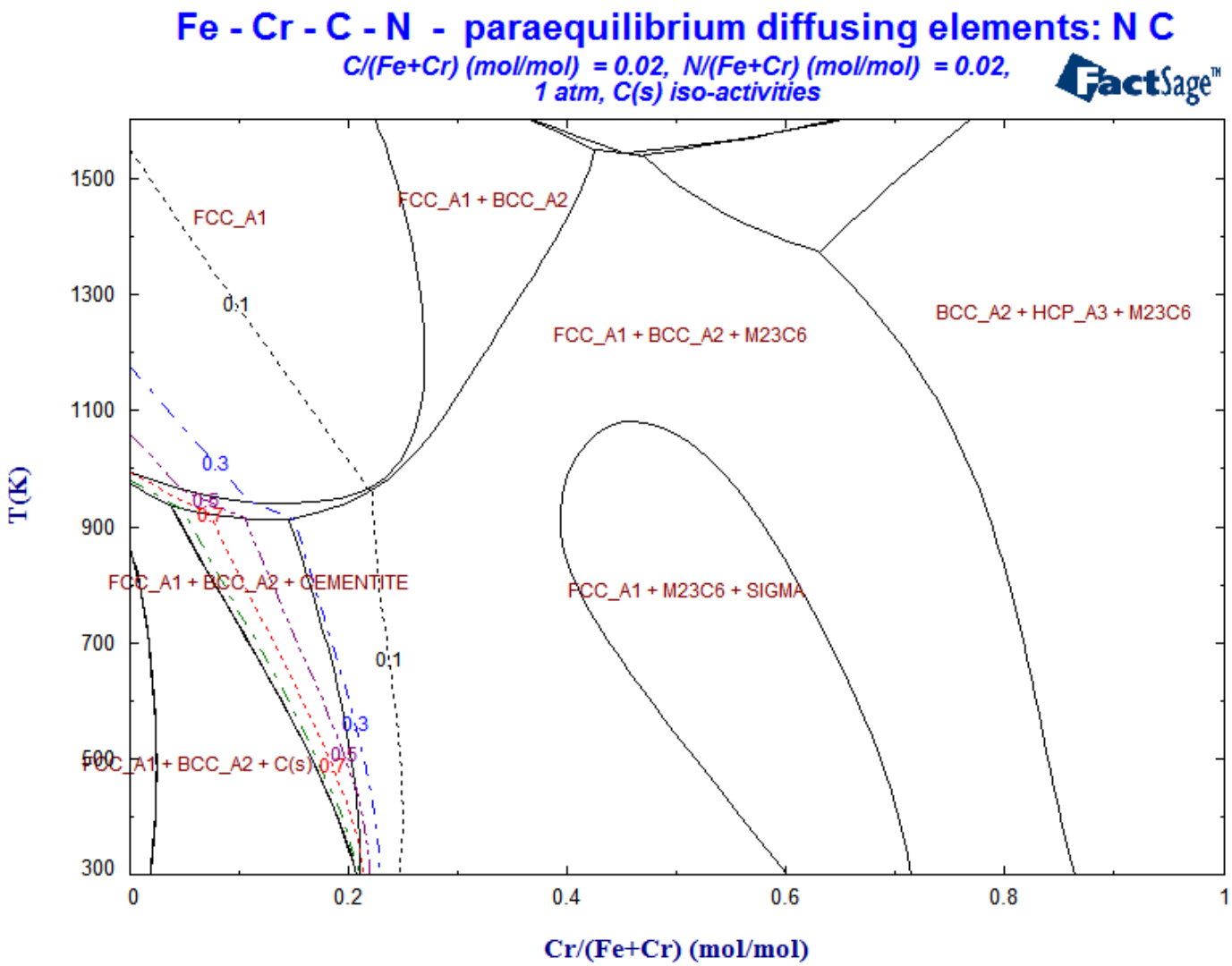
Isobars and Iso-activities - Isothermal $FeO-Fe_2O_3-Cr_2O_3$ Gibbs Section – $O_2(g)$ isobars



Isobars and Iso-activities - CaF_2(s) iso-activities in CaF_2-NaCl-$CaCl_2$-NaF at 1000 K



Isobars and Iso-activities - Fe-Cr-C-N Paraequilibrium – C(s) iso-activities



Scheil-Gulliver Constituent Diagrams

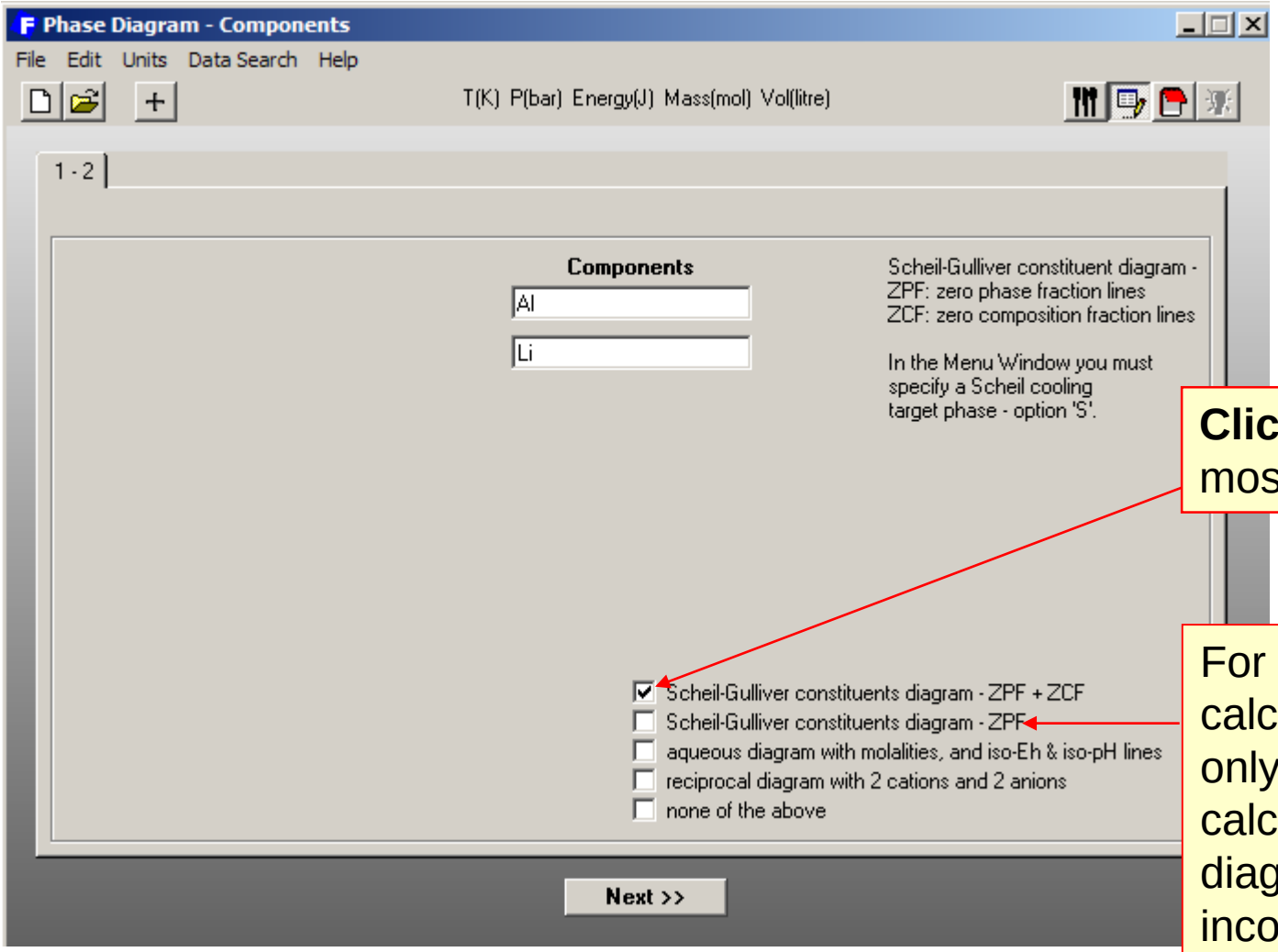
During cooling of an alloy from the liquid state at complete thermodynamic equilibrium, all solid solution phases remain homogeneous through internal diffusion and all peritectic reactions proceed to completion. Such conditions are generally approached only when the cooling rate is extremely slow. In practice, conditions often approach more closely to those of **Scheil-Gulliver** cooling in which solids, once precipitated, cease to react with the liquid or with each other, there is no diffusion in the solids, the liquid phase remains homogeneous, and the liquid and surfaces of the solid phases are in equilibrium.

With the **EQUILIB** module [see the **EQUILIB** Advanced Features Slide Show, Section 13] **Scheil-Gulliver** cooling can be simulated, but only at one composition at a time. By analogy with equilibrium phase diagrams which apply to equilibrium cooling, the present section shows how the **PHASE DIAGRAM** module can be used to calculate and plot **"Scheil-Gulliver constituent diagrams"** which permit one to visualize the course of **Scheil-Gulliver** solidification as temperature and composition are varied.

A **Scheil-Gulliver constituent diagram** shows the *microstructural constituents* which are formed as the system is cooled under **Scheil-Gulliver** conditions from temperatures above the liquidus. The fields on a **Scheil-Gulliver constituent diagram** are labelled not with the names of phases but with the names of the *microstructural constituents* which may be stoichiometric compounds, inhomogeneous solutions, or eutectic constituents. Hence, **Scheil-Gulliver** diagrams are more properly called **"constituent diagrams"** rather than phase diagrams.

An article describing the theory, calculation and applications of **Scheil-Gulliver** constituent diagrams can be found by going to the main **FactSage** menu and clicking on Slide Shows. Then click on "Article – Scheil-Gulliver constituent diagrams" (pdf).

Scheil-Gulliver Constituent Diagram of the Binary Al-Li system



Click here in most cases.

For large systems, calculations will be faster if only **ZPF** lines are calculated. However, the diagram will then be incomplete.

If the **gas phase** is selected it will be assumed to always remain in **equilibrium** with the liquid.

A **Scheil** target phase must be selected. This will almost always be the liquid solution. (Left click, then select **S**).

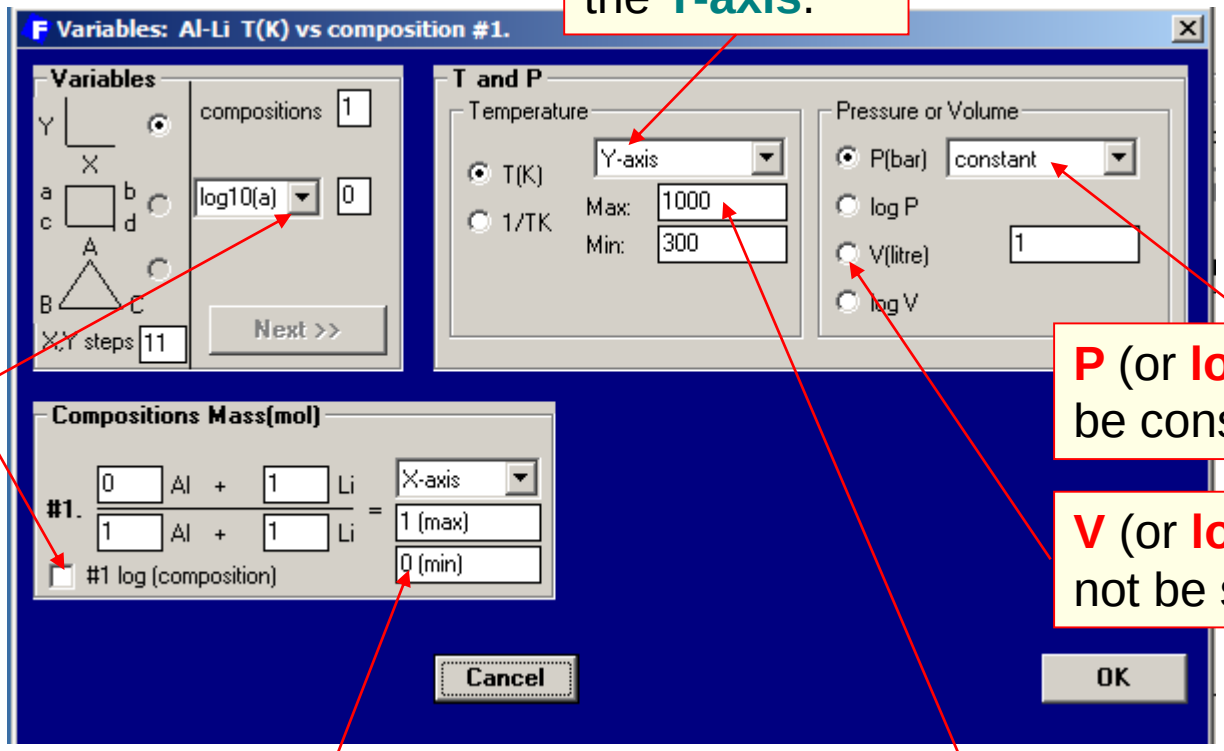
Scheil-Gulliver diagrams involve a relatively large amount of computer time. If you know that the **I** or **J** options (possible 2- or 3-phase immiscibility) are not required, it is best not to select them.

See Slide Show on **Equilib Advanced Features**, Section 13. A smaller step gives a more precise diagram, but the calculation time will increase.

Choice of variables for a Y-X binary **Scheil-Gulliver constituent diagram**

Such a diagram can only be a **T-Composition** diagram at constant **P**

T can only be the **Y-axis**.



Cannot be selected.

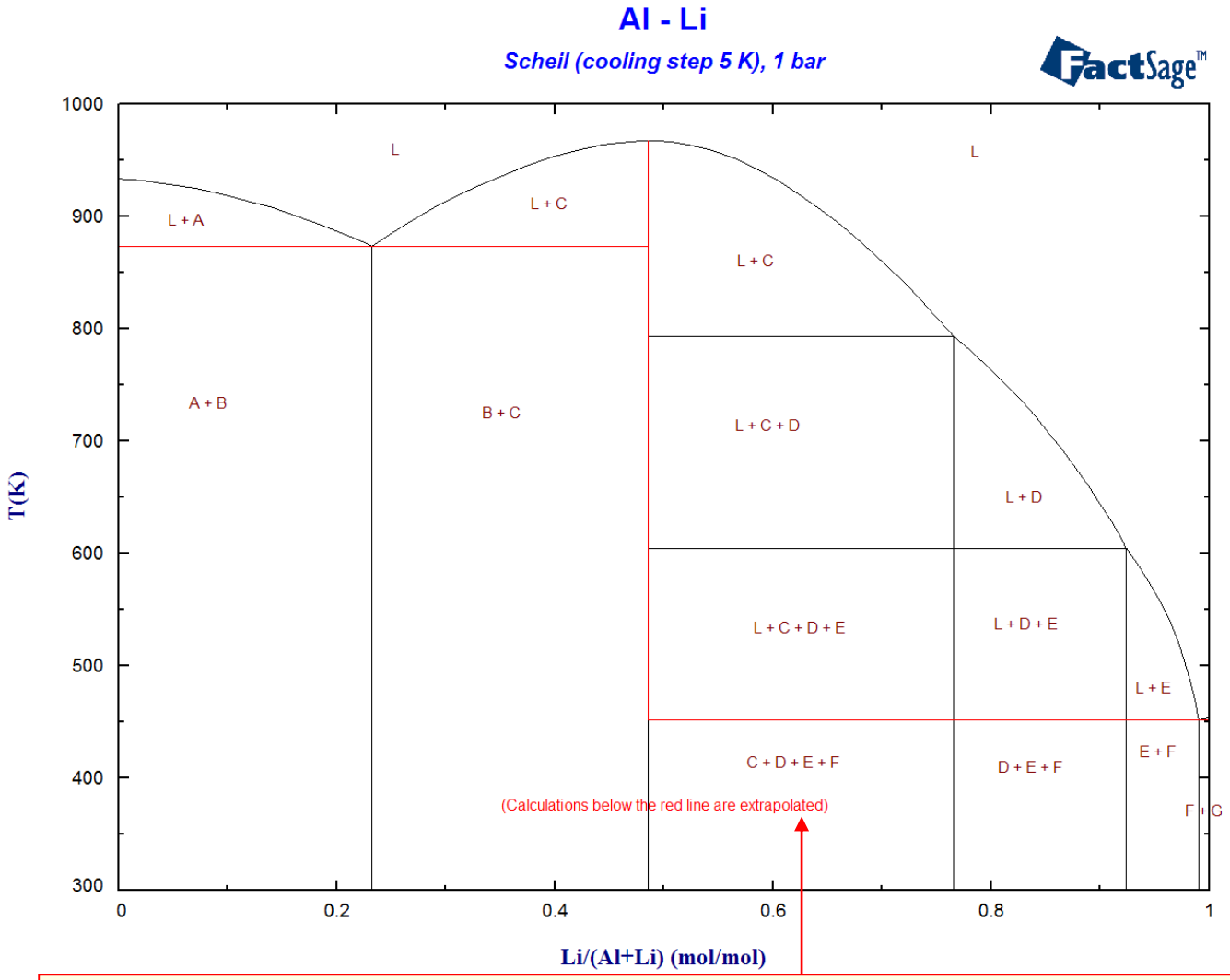
P (or **log P**) must be constant.

V (or **log V**) can not be selected.

The **X-axis** can only be composition.

The **maximum temperature** should be above the maximum liquidus temperature on the diagram.

Calculated **Scheil-Gulliver constituent diagram** of the **Al-Li** system

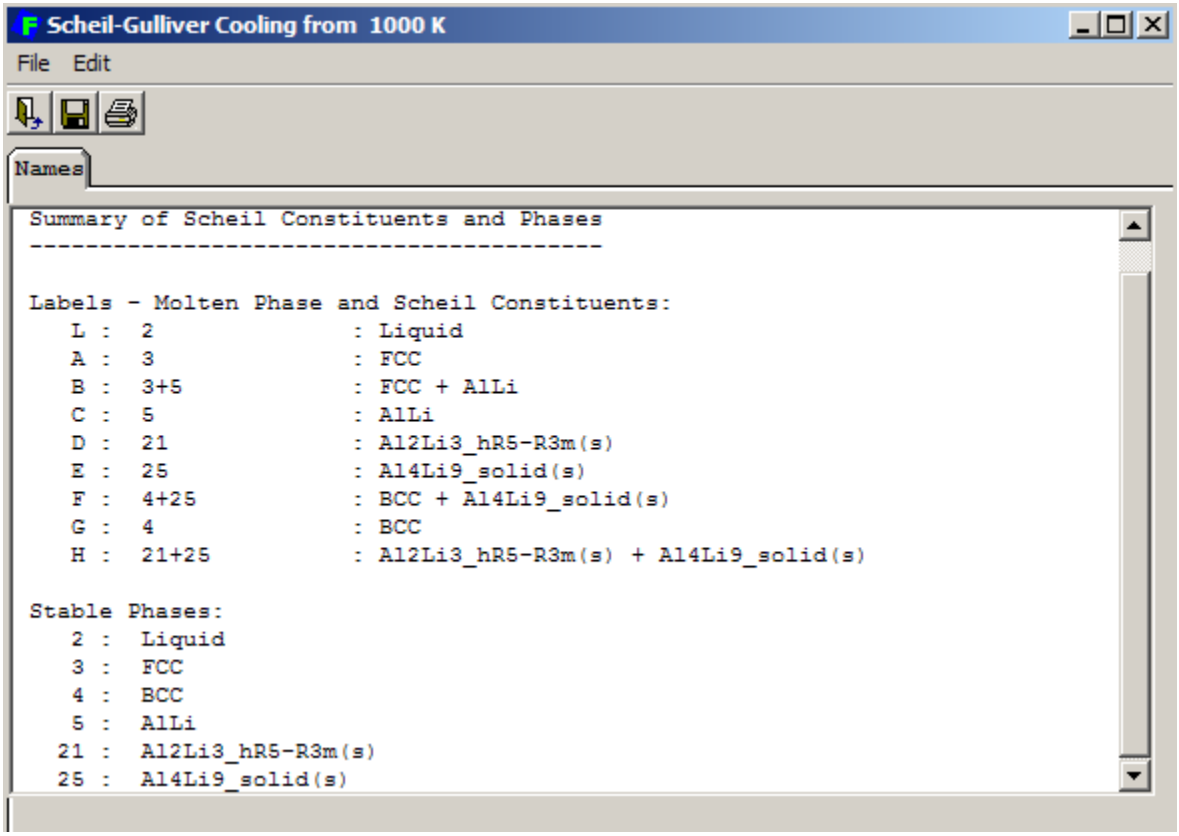


The **microstructural constituents** in each field are labelled by pointing and clicking in the same way as for equilibrium phase diagrams.

Below the red line, the **liquid phase** has disappeared. At **lower temperatures** it is assumed no further reactions occur (such as eutectoid, peritectoid, phase separation, massive, martensitic and spinodal decomposition reactions.)

Identification of stable **microstructural constituents** and phases

This table is automatically displayed along with the calculated diagram

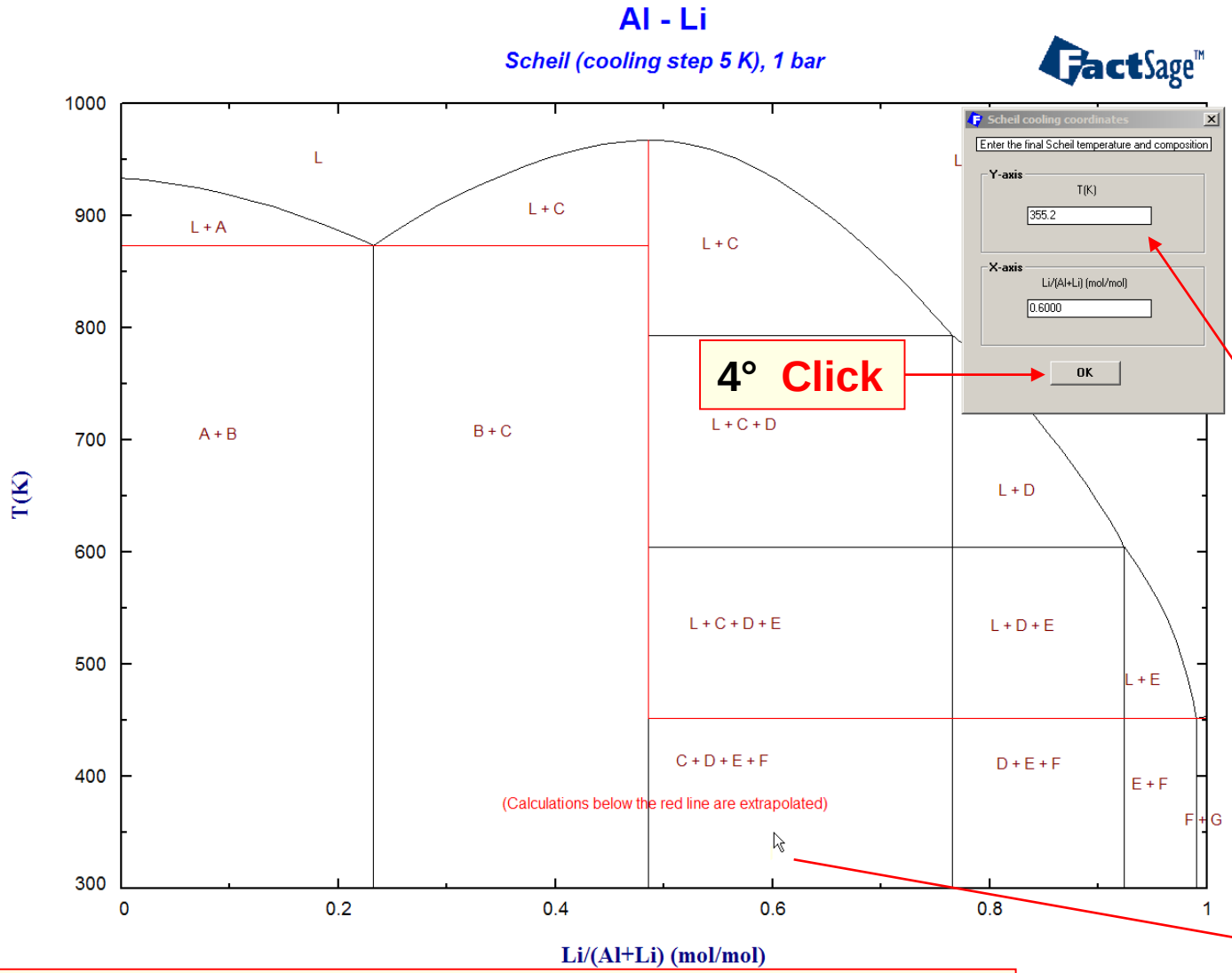



```
Summary of Scheil Constituents and Phases
-----------------------------------------

Labels - Molten Phase and Scheil Constituents:
   L :  2              : Liquid
   A :  3              : FCC
   B :  3+5            : FCC + AlLi
   C :  5              : AlLi
   D :  21             : Al2Li3_hR5-R3m(s)
   E :  25             : Al4Li9_solid(s)
   F :  4+25           : BCC + Al4Li9_solid(s)
   G :  4              : BCC
   H :  21+25          : Al2Li3_hR5-R3m(s) + Al4Li9_solid(s)

Stable Phases:
   2 :  Liquid
   3 :  FCC
   4 :  BCC
   5 :  AlLi
  21 :  Al2Li3_hR5-R3m(s)
  25 :  Al4Li9_solid(s)
```

For example, constituent **F** is a eutectic consisting of the phases (**BCC + Al_4Li_9**) while **A** is a primary **FCC** constituent.

Calculating details of **Scheil-Gulliver** cooling

At a selected composition from the liquidus down to a selected final temperature



3° Table showing **coordinates of the point** is generated. This table may be edited. (For example, you could change the final **T** to 298 K).

2° **Place** cursor at a selected composition and final temperature and **click**.

1° **Select** phase equilibrium mode (see Slide 11.2).

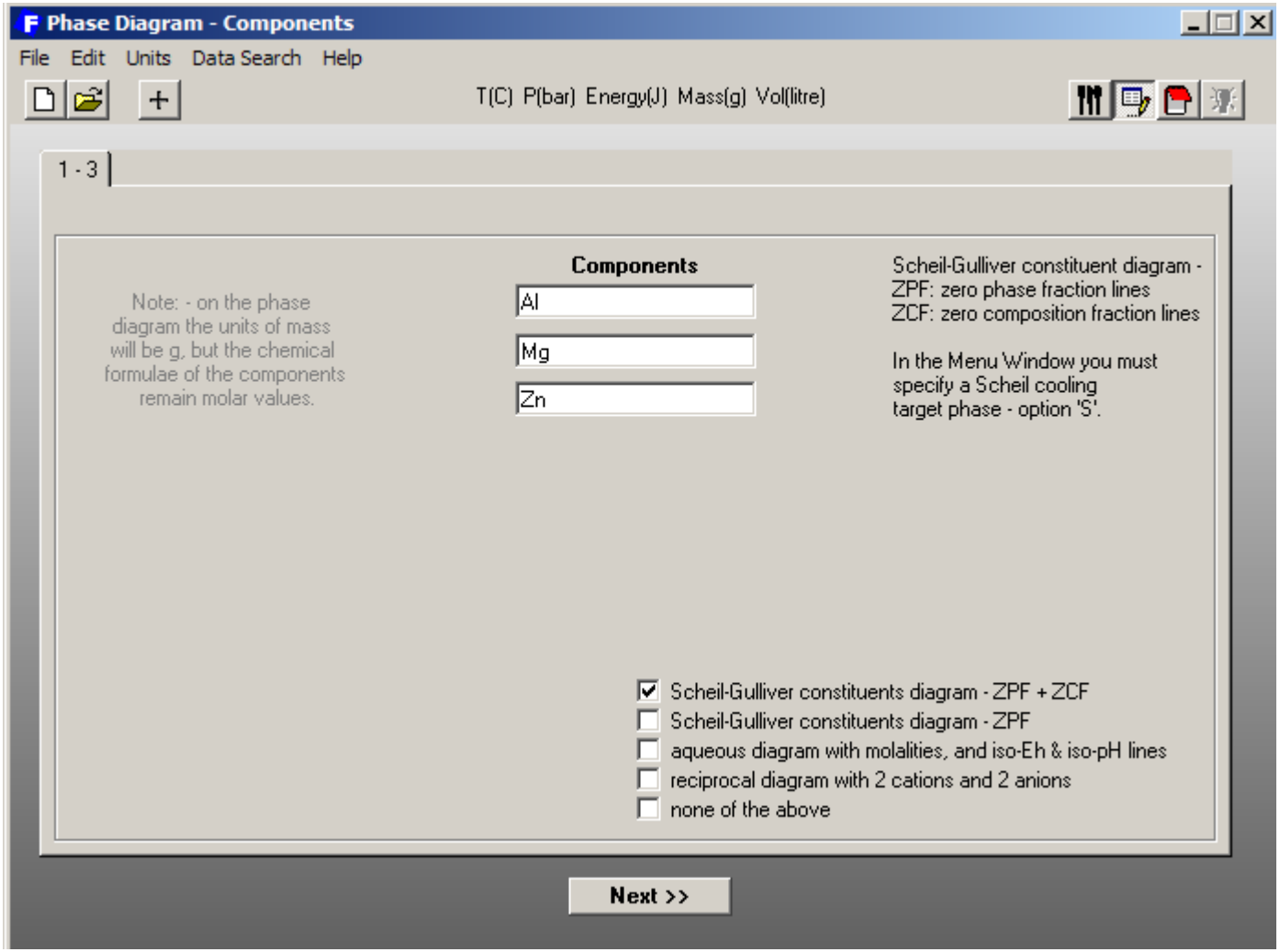
Output showing details of Scheil Gulliver cooling

At the selected composition (mole fraction of **Li = 0.6000**) from above the liquidus down to the selected temperature

```
T(K) = 355.2,  Li/(Al+Li) (mol/mol)  = 0.6
==========================================

 SCHEIL-GULLIVER COOLING

 COMPONENTS:
 Al                          AMOUNT/mol =  4.0000E-01
 Li                          AMOUNT/mol =  6.0000E-01

 CONSTITUENTS AND PHASES AT 452.05 K
 (temperature of final disappearance of Liquid)

 CONS. PHASE                   TOTAL AMT/g.atom TOTAL AMT/gram
   1   1 AlLi                     7.4406E-01      1.1979E+01

   2   1 Al2Li3_hR5-R3m(s)        1.2502E-01      1.8699E+00

   3   1 Al4Li9_solid(s)          2.9032E-02      3.8053E-01

   4   1 BCC                      1.0092E-01      7.1494E-01
   4   2 Al4Li9_solid(s)          9.7120E-04      1.2730E-02

 SUMMARY OF REACTIONS

 Cooling
 935 to 934.53 K        (DELTA H = -1.4469E+01 J)
 Liquid cooling

 Constituent 1
 934.53 to 793.01 K     (DELTA H = -1.2631E+04 J)
 Liquid -> AlLi

 Constituent 2
 793.01 to 604.35 K     (DELTA H = -2.8923E+03 J)
 Liquid -> Al2Li3_hR5-R3m(s)

 Constituent 3
 604.35 to 452.05 K     (DELTA H =  2.9943E+03 J)
 Liquid -> Al4Li9_solid(s)

 Constituent 4
 452.05 K (isothermal)  (DELTA H = -3.1854E+02 J)
```

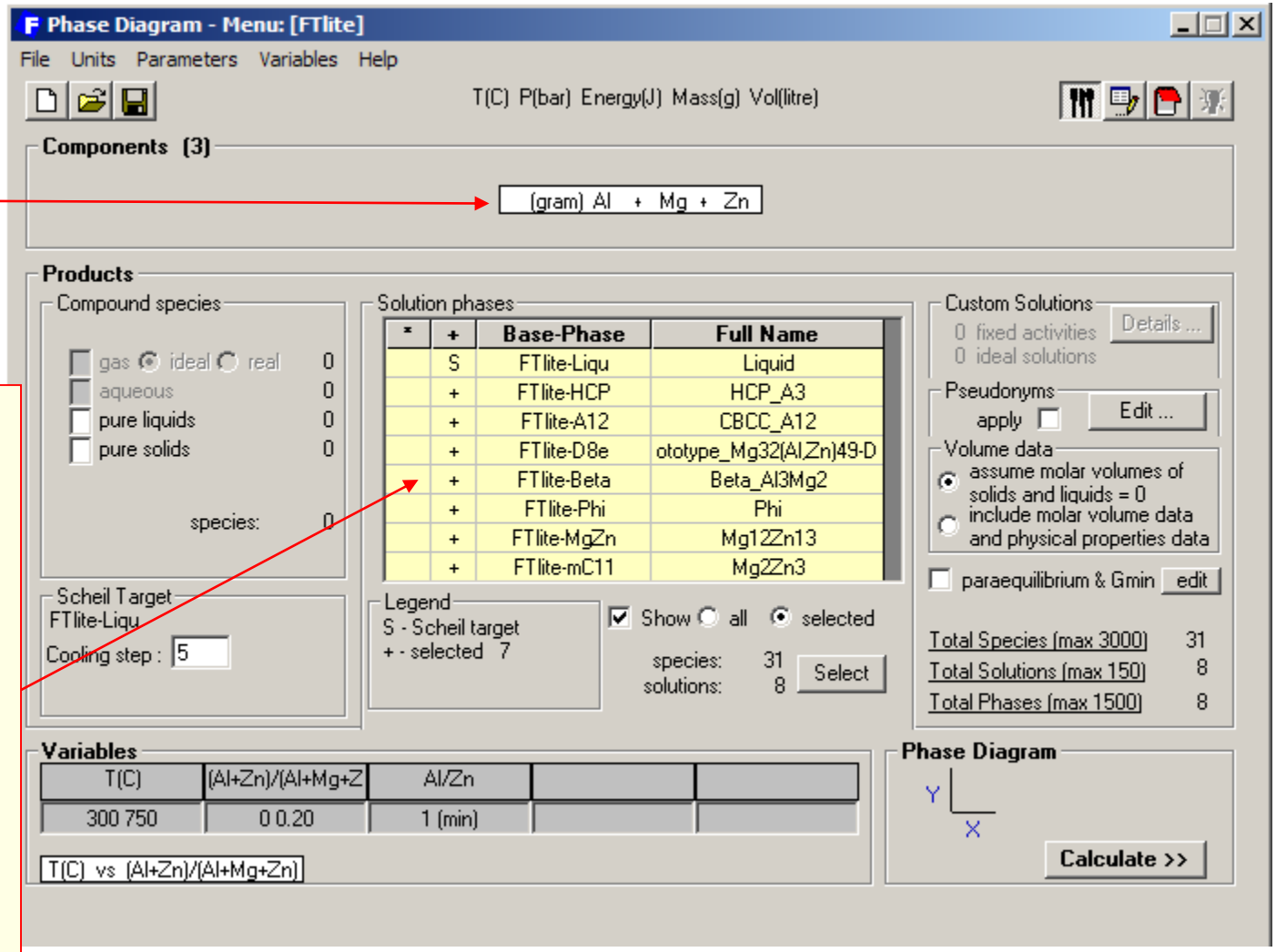
This is the same **output** as in generated by the **Equilib** module (See Slide show for **Equilibrium Module Advanced Features**, section 13).

Scheil-Gulliver constituent diagram



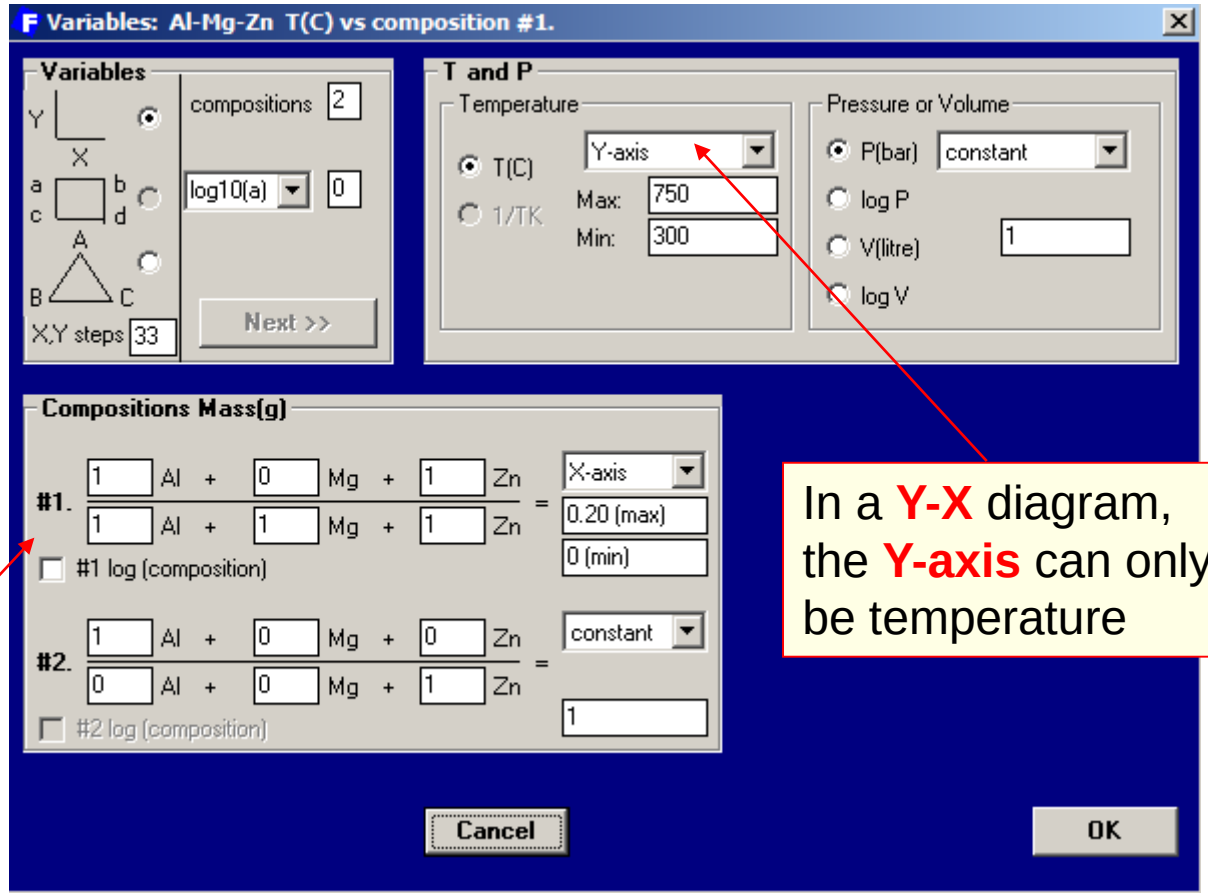
Mass units of grams were selected in this example.

Scheil-Gulliver diagrams involve a relatively large amount of computer time. If you know that the **I** or **J** options (possible 2- or 3-phase immiscibility) are not required, it is best not to select them.



Variables to calculate a diagram of T versus weight fraction of Zn

At constant weight ratio **Al/Zn = 1.0** in the Mg-rich corner of the **Mg-Al-Zn** system

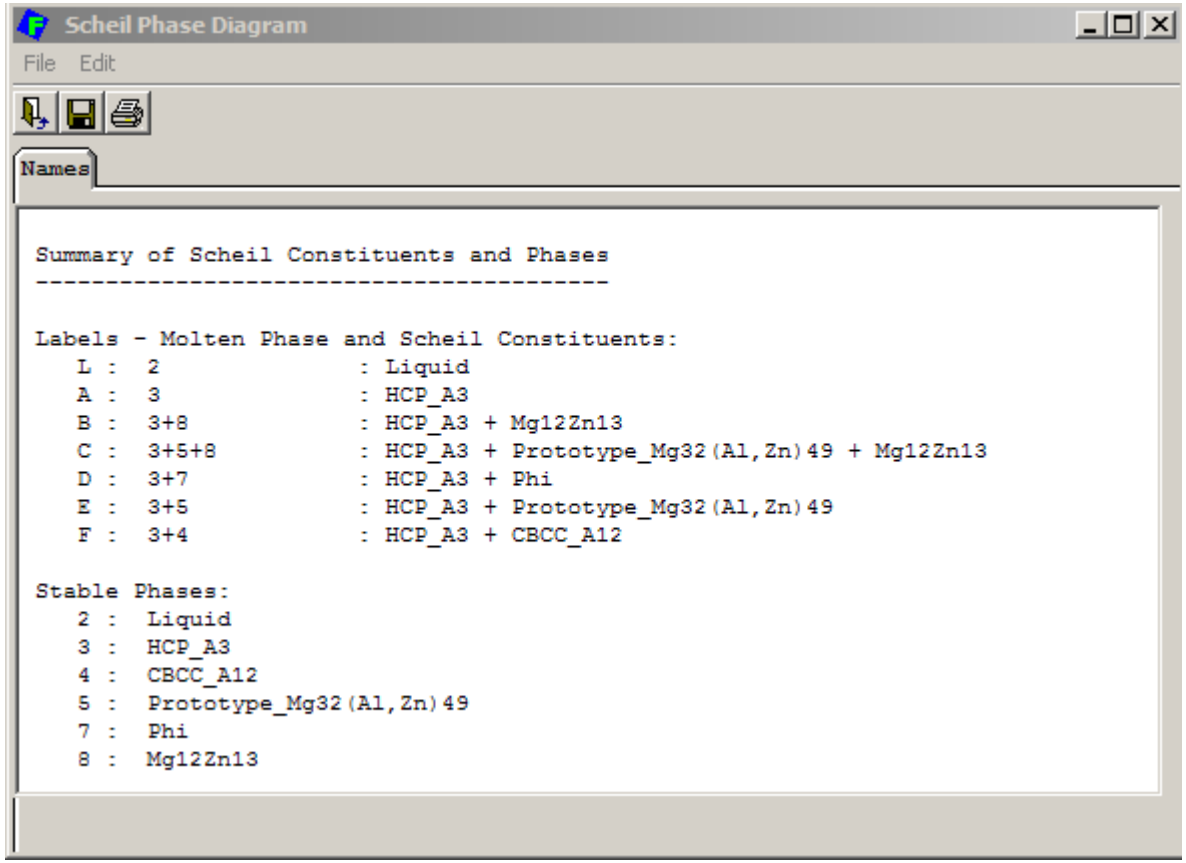


In a **Y-X** diagram the **X-axis** can only be composition

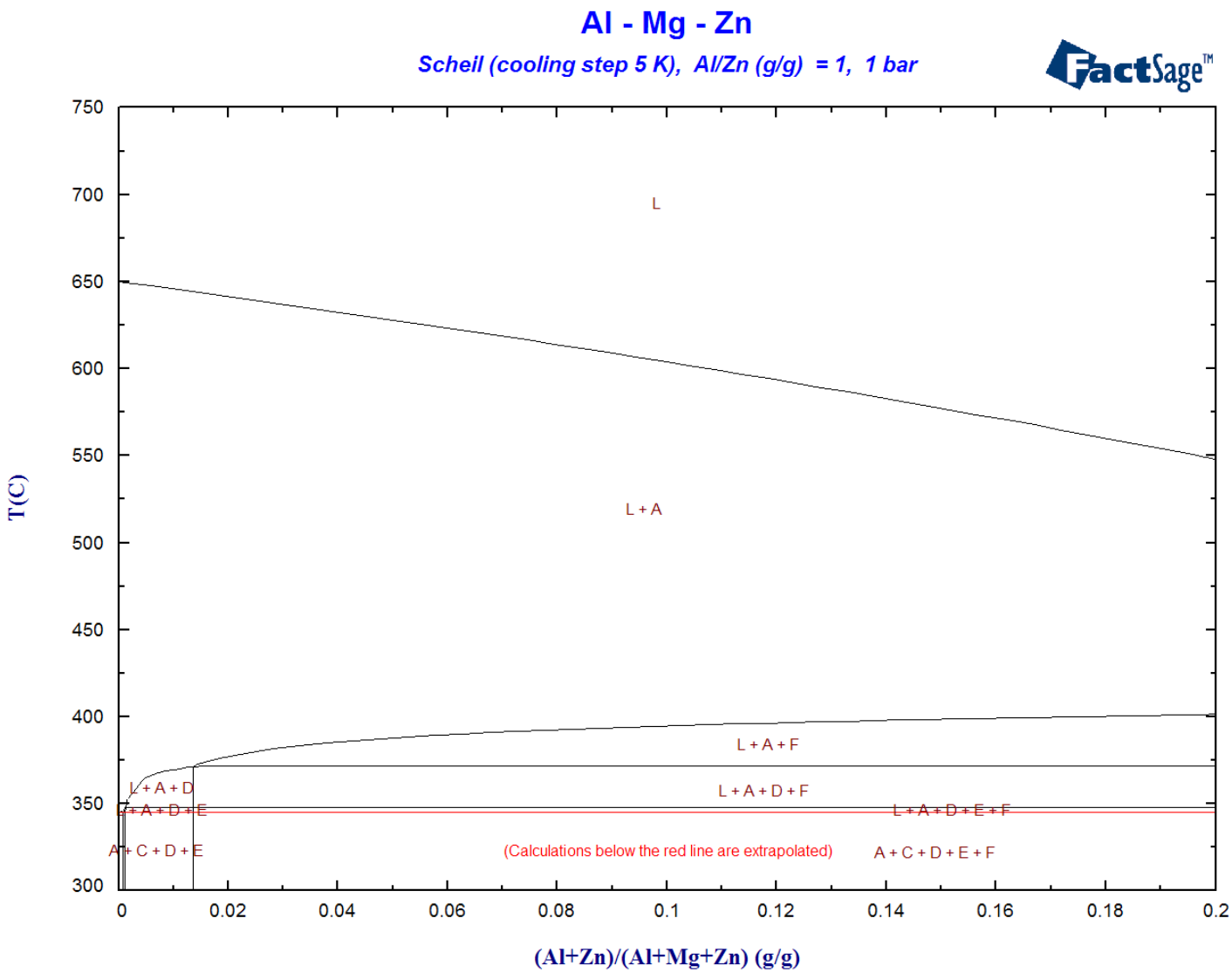
In a **Y-X** diagram, the **Y-axis** can only be temperature

In this ternary system a **constant must be specified**. In this example this constant is a composition. It is also permissible to select **$\log a_i$ (or $\log P_i$)** as a constant.

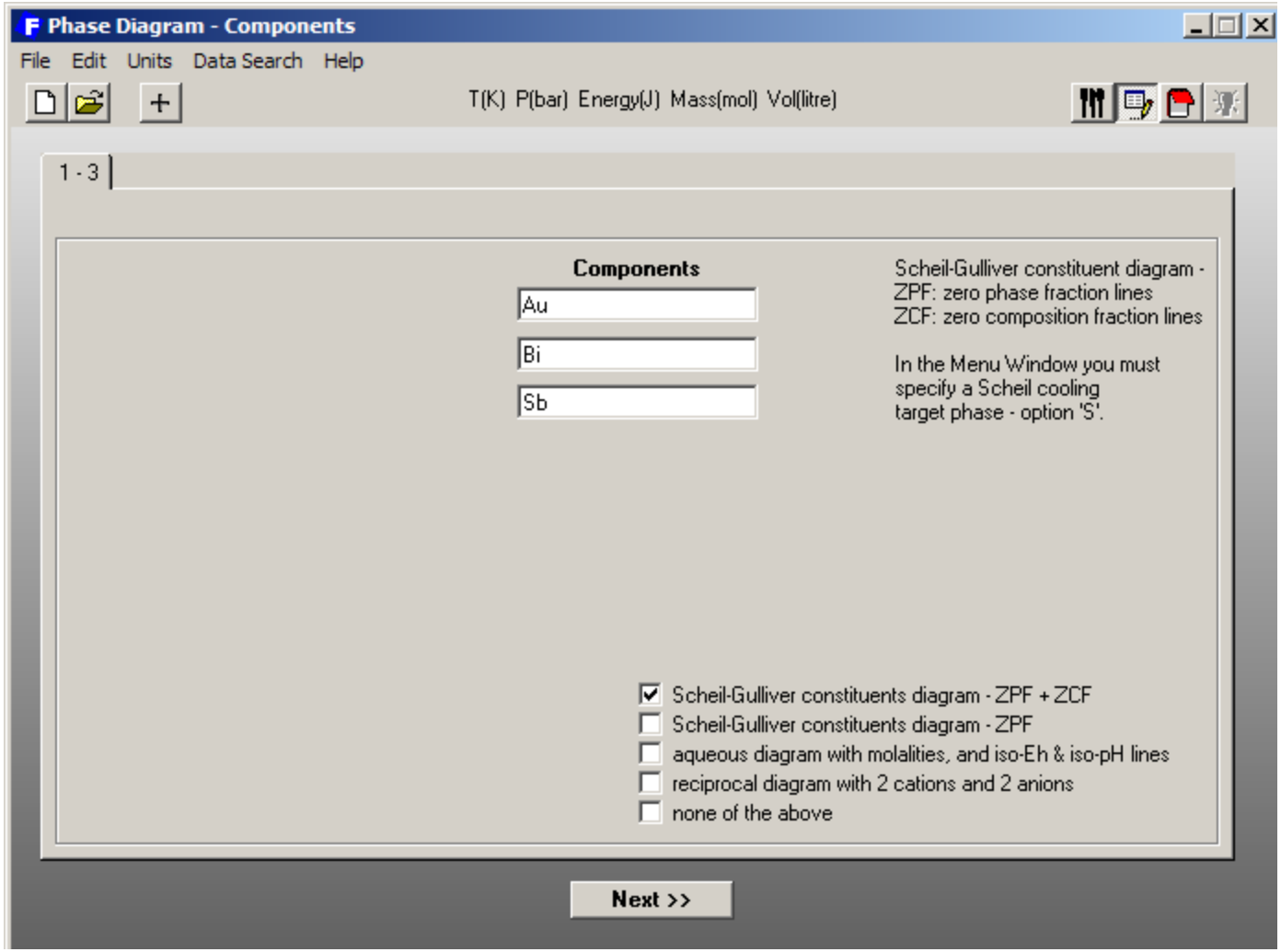
Table identifying the stable **miscrostructural constituents** and phases on the diagram. This table is automatically displayed along with the calculated diagram.



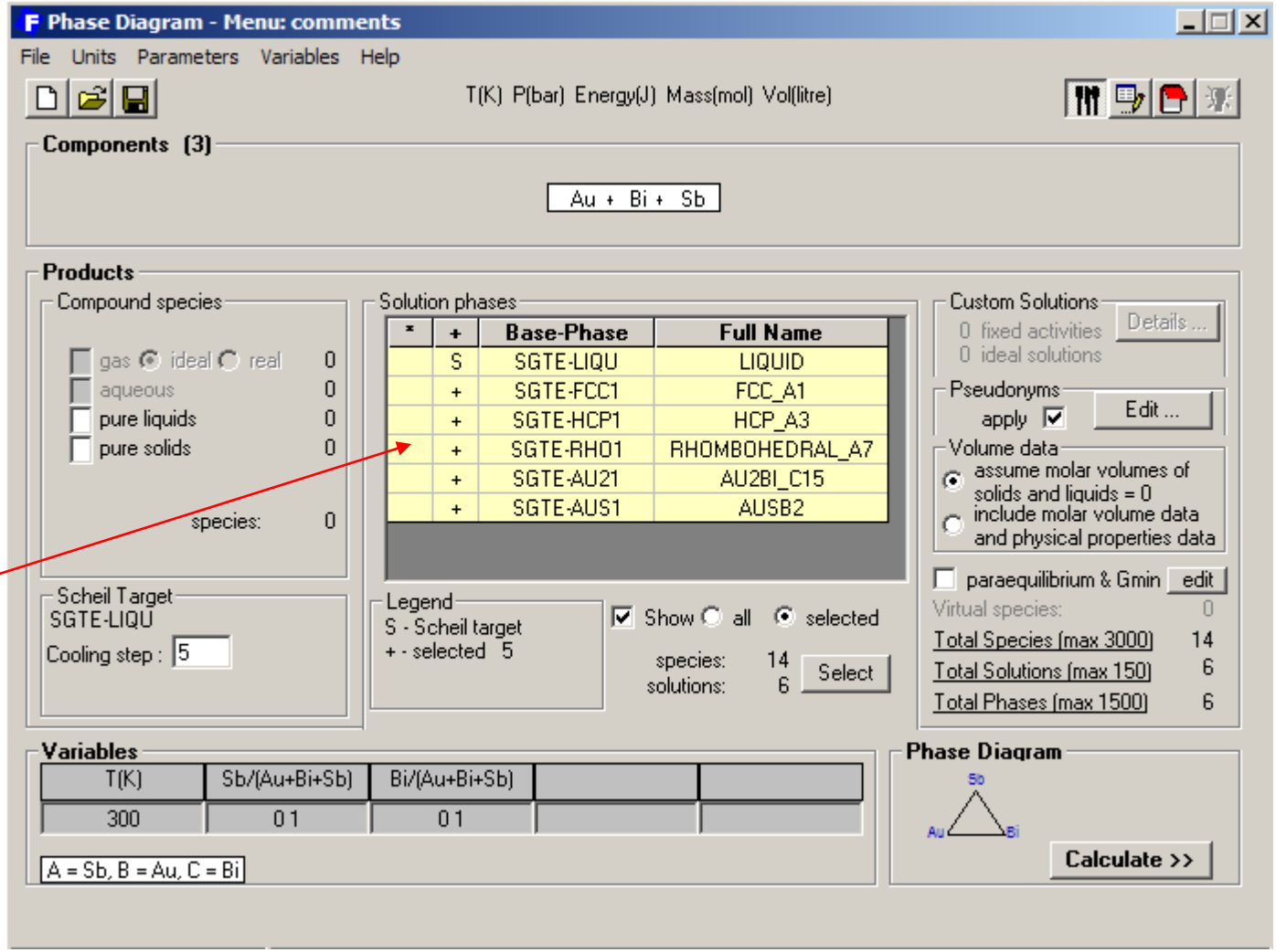
Calculated diagram with labelling



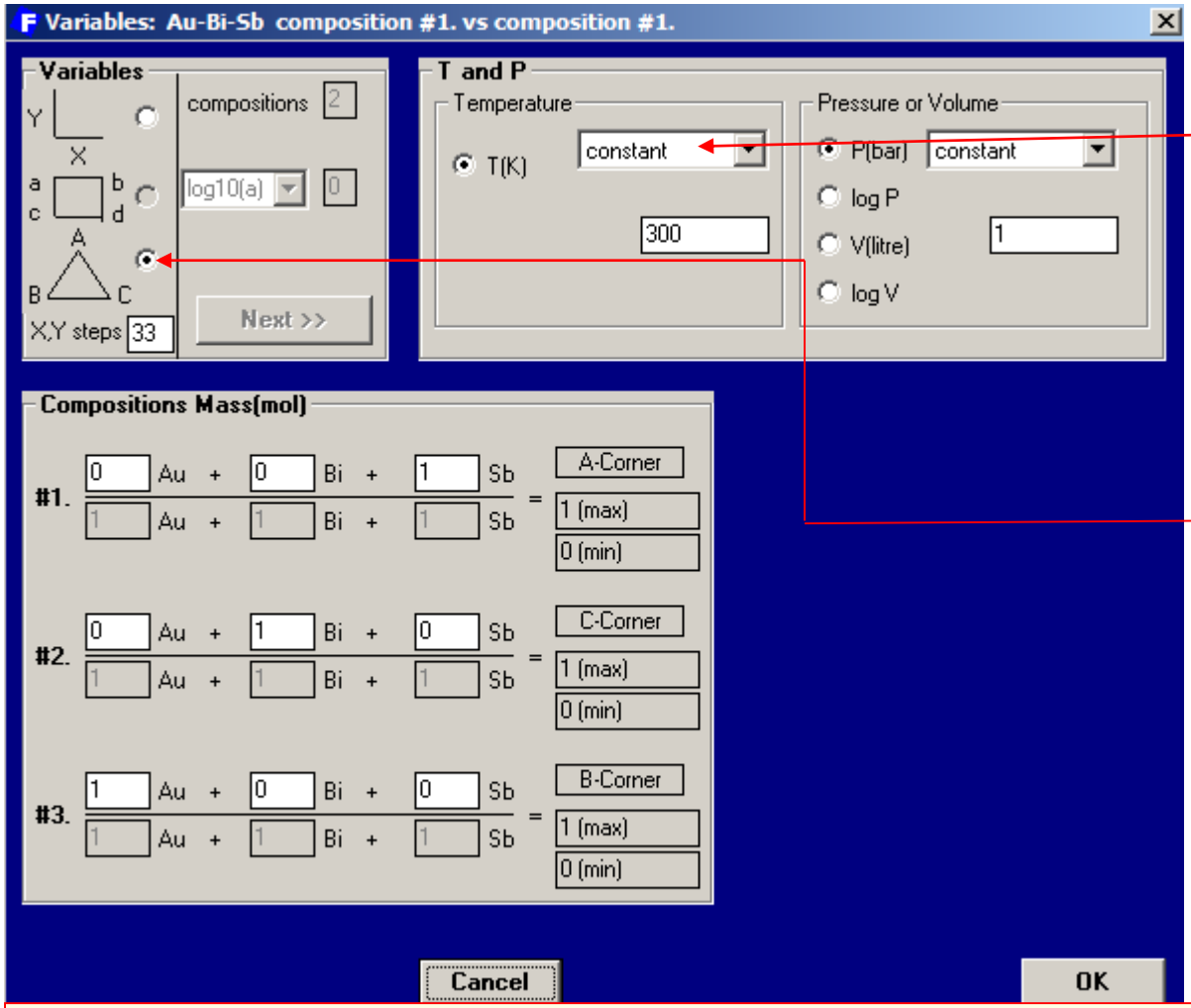
Calculation of an isothermal ternary Scheil-Gulliver constituent diagram



Scheil-Gulliver diagrams involve a relatively large amount of computer time. If you know that the **I** or **J** options (possible 2- or 3-phase immiscibility) are not required, it is best not to select them.



Variables to calculate an isothermal ternary Scheil-Gulliver constituent diagram



With triangular coordinates, **T** must be **constant**.

Isothermal **Scheil-Gulliver** diagrams can only be plotted on **triangular** coordinates.

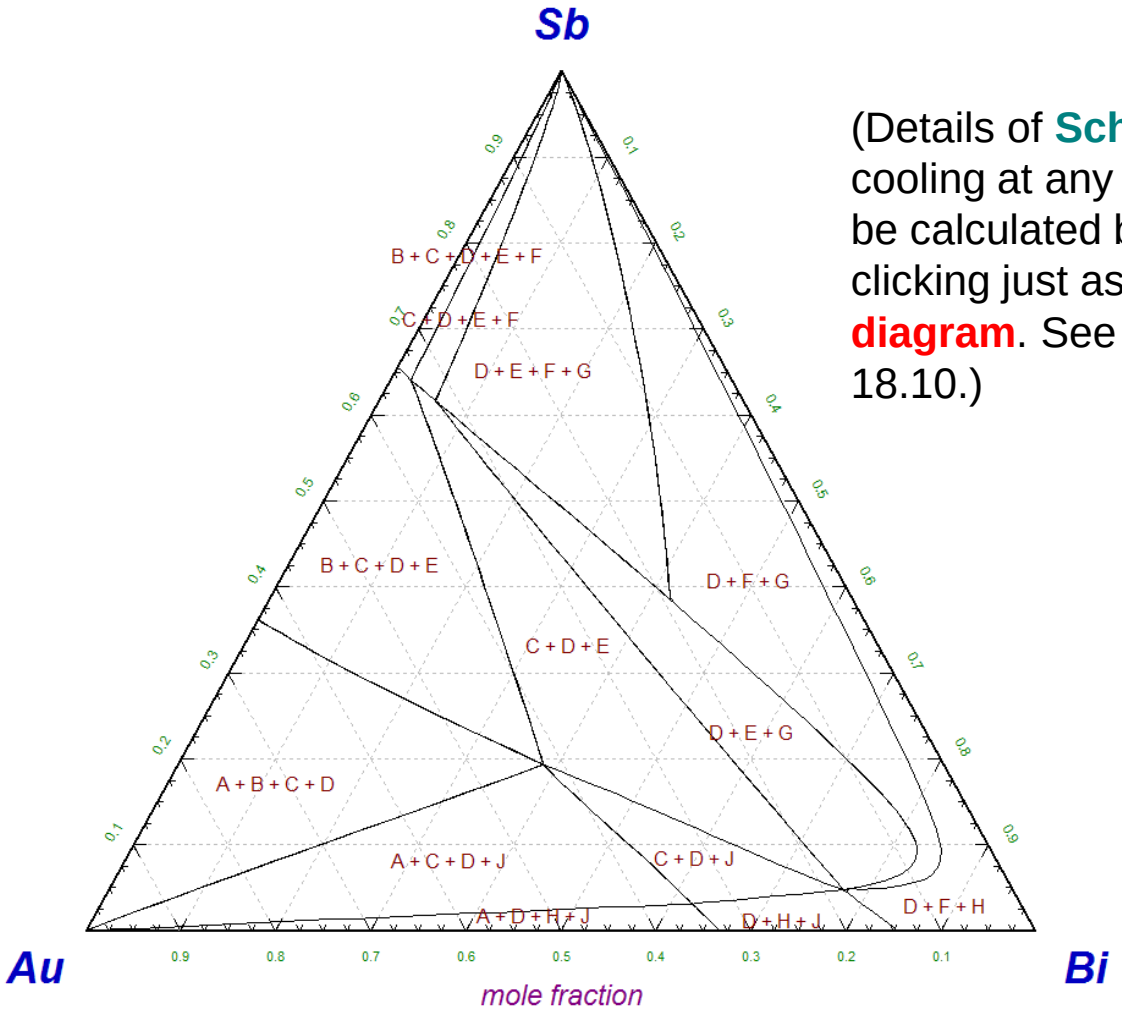
(With 4 or more components, compositions or **$\log a_i$ ($\log P_i$)** values may be constants.)

Note: Calculation times for isothermal **Scheil-Gulliver** diagrams are generally long. The calculation time may depend upon which component is chosen as component **A** at the **summit of the triangle**. (See also the suggestion on Slide 18.5).

Output with labelling of **microstructural constituents**.

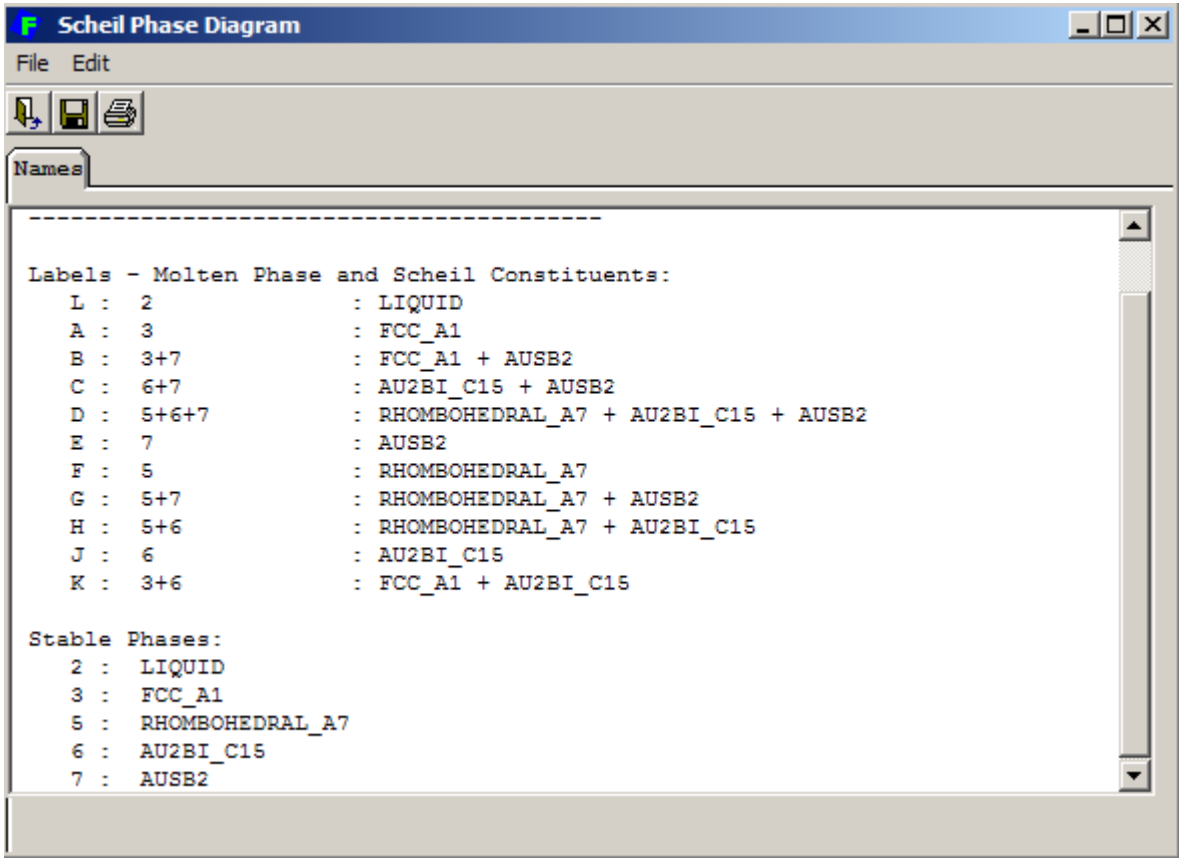
Au - Bi - Sb

Scheil (cooling step 5 K), 300 K, 1 bar



(Details of **Scheil-Gulliver** cooling at any composition can be calculated by pointing and clicking just as on a **Y-X diagram**. See Slides 18.9 and 18.10.)

Output identifying stable **microstructural constituents** and phases on the diagram
(Table automatically displayed along with the calculated diagram)



Aqueous Phase Diagrams

The **Phase Diagram** module treats aqueous solution phases like any other phase, and the full flexibility of the module can be exploited to calculate a wide variety of types of phase diagrams involving aqueous solutions.

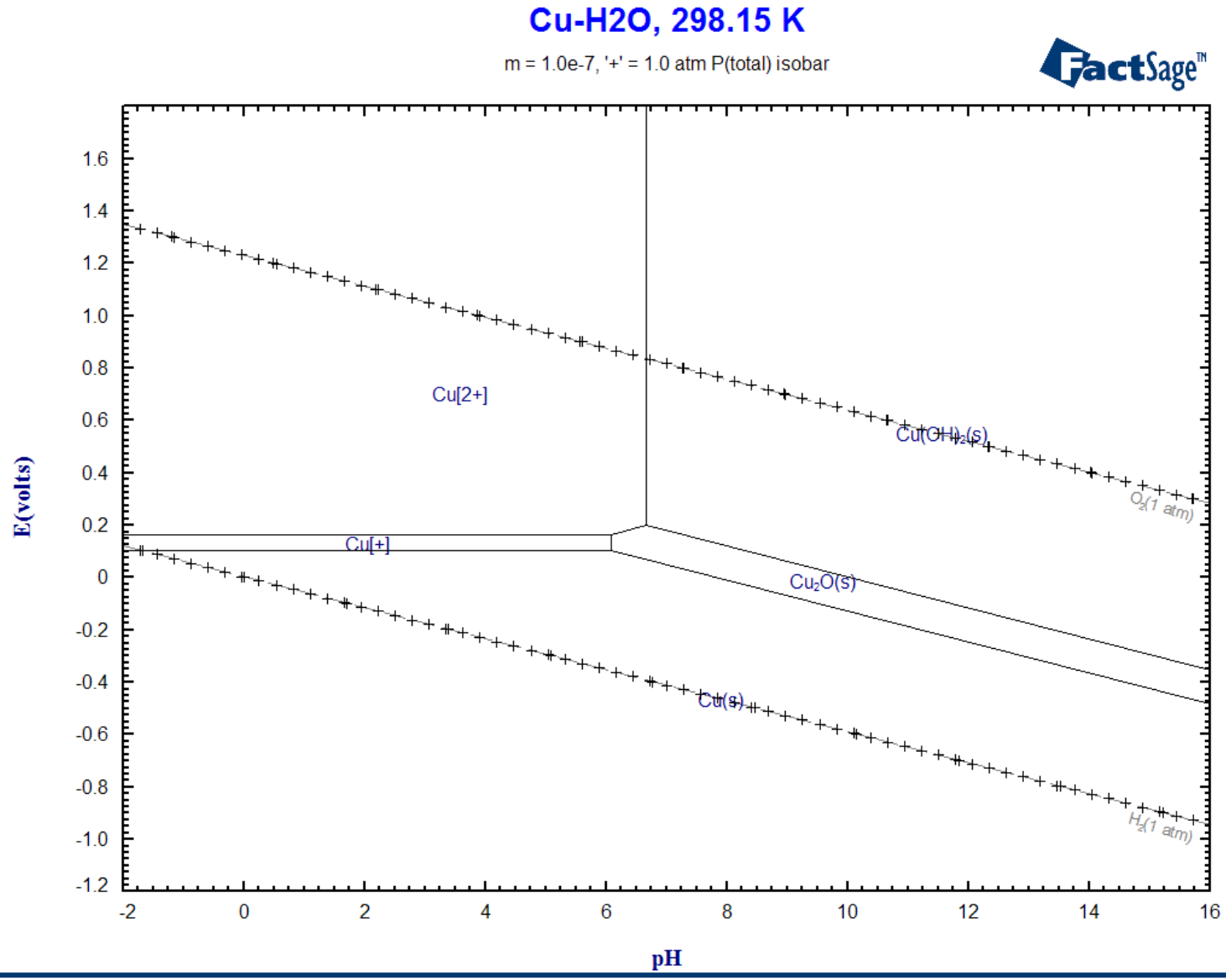
In FactSage 7.1 we have added the options of plotting **iso-Eh and iso-pH lines** and of entering compositions as molalities.

A classical **E-pH (Pourbaix) diagram** of the Cu-H_2O system when m(Cu) = 10^{-7} (where m = molality) is shown in Slide 19.2. This diagram was calculated with the FactSage **EpH module** (see EpH Slide Show). This is **not a true phase diagram**, but rather a **"predominance diagram"** showing the regions where various Cu-containing aqueous ions or solid compounds predominate. For example, the regions labelled Cu[2+] and Cu[+] taken together form the single-phase field where the aqueous solution is stable. The boundary between these two regions is not a phase boundary, but is the line separating the region in which Cu[2+] is predominant from the region where Cu[+] predominates.

Classical E-pH diagrams of this type generally do not take non-ideality of the aqueous solution into account. In the calculation of Slide 19.2, the aqueous phase is assumed to contain no anions (apart from those containing Cu, O and H). Hence, ionic interactions are not taken into account.

Classical **E-pH (Pourbaix) Diagram** of the Cu-H_2O system

$m_{Cu} = 10^{-7}$ calculated with the FactSage **EpH Module**



H_2O – O_2 – HCl – NaOH – Cu Phase Diagram with iso-Eh (volts) and iso-pH Lines

log $P(O_2)$ versus molar ratio NaOH/(HCl + NaOH) at constant molalities m(Cu) = 10^{-7} and (m(HCl) + m(NaOH)) = 0.1

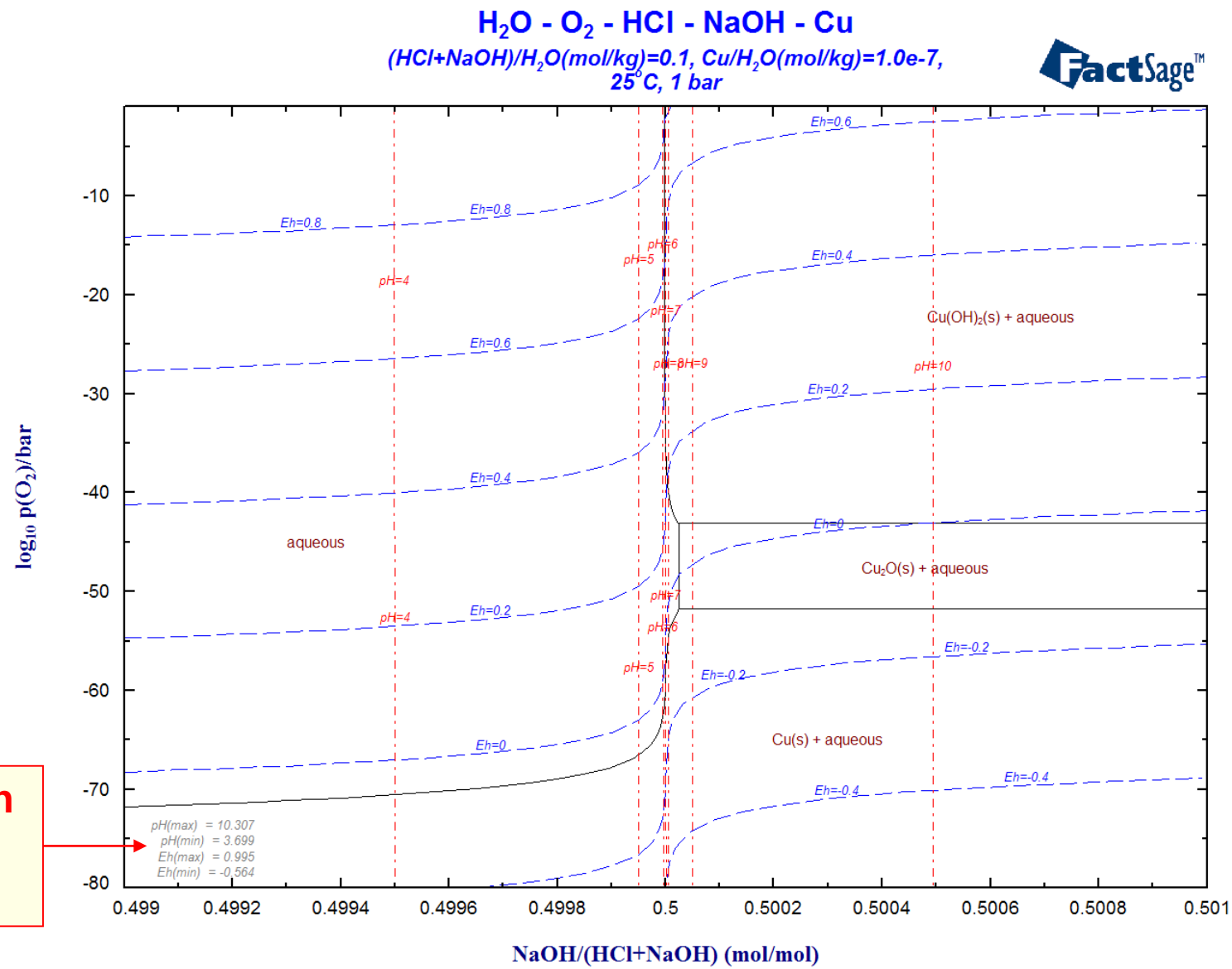
An **aqueous phase diagram calculated with the Phase Diagram module** is shown in Slide 19.4.
The y-axis is the **oxidation potential, log $P(O_2)$**, which is related to Eh as described on Slides 19.14 to 19.21.
The diagram is calculated at a constant **total overall** molality m(Cu) = 10^{-7} mol/kg H_2O and at a constant **total overall** molality (m(HCl) + m(NaOH)) = 0.1 mol/kg H_2O.
The x-axis is the **total overall** molar ratio NaOH/(HCl + NaOH).

The aqueous phase diagram (Slide 19.4) and the classical Pourbaix diagram (Slide 19.2) can be seen to have similar domains and topologies.

The diagram in Slide 19.4 can be considered to be that of a system of constant mass containing 1.0 kg H_2O, 10^{-7} mol Cu and 0.1 mol (HCl + NaOH). The region labelled simply as "Cu_2O" on the predominance diagram in Slide 19.2 is, on the true phase diagram of Slide 19.4, labelled as "Cu_2O + aqueous" because the aqueous phase is still present when Cu_2O precipitates. The total amount of Cu in the aqueous solution and the precipitated Cu_2O taken together is 10^{-7} moles. The molality of Cu in the aqueous phase is thus equal to 10^{-7} only in the single-phase aqueous field (see Slide 19.13). The boundary between the Cu[2+] and Cu[+] regions of Slide 19.2 does not appear on Slide 19.4 because this is all one single-phase region. (See, however, Slides 19.10 to 19.12.)

The input to calculate the aqueous phase diagram of Slide 19.4 is shown in Slides 19.5 to 19.9.

→ (H_2O – O_2 – HCl – NaOH – Cu Phase Diagram continued)

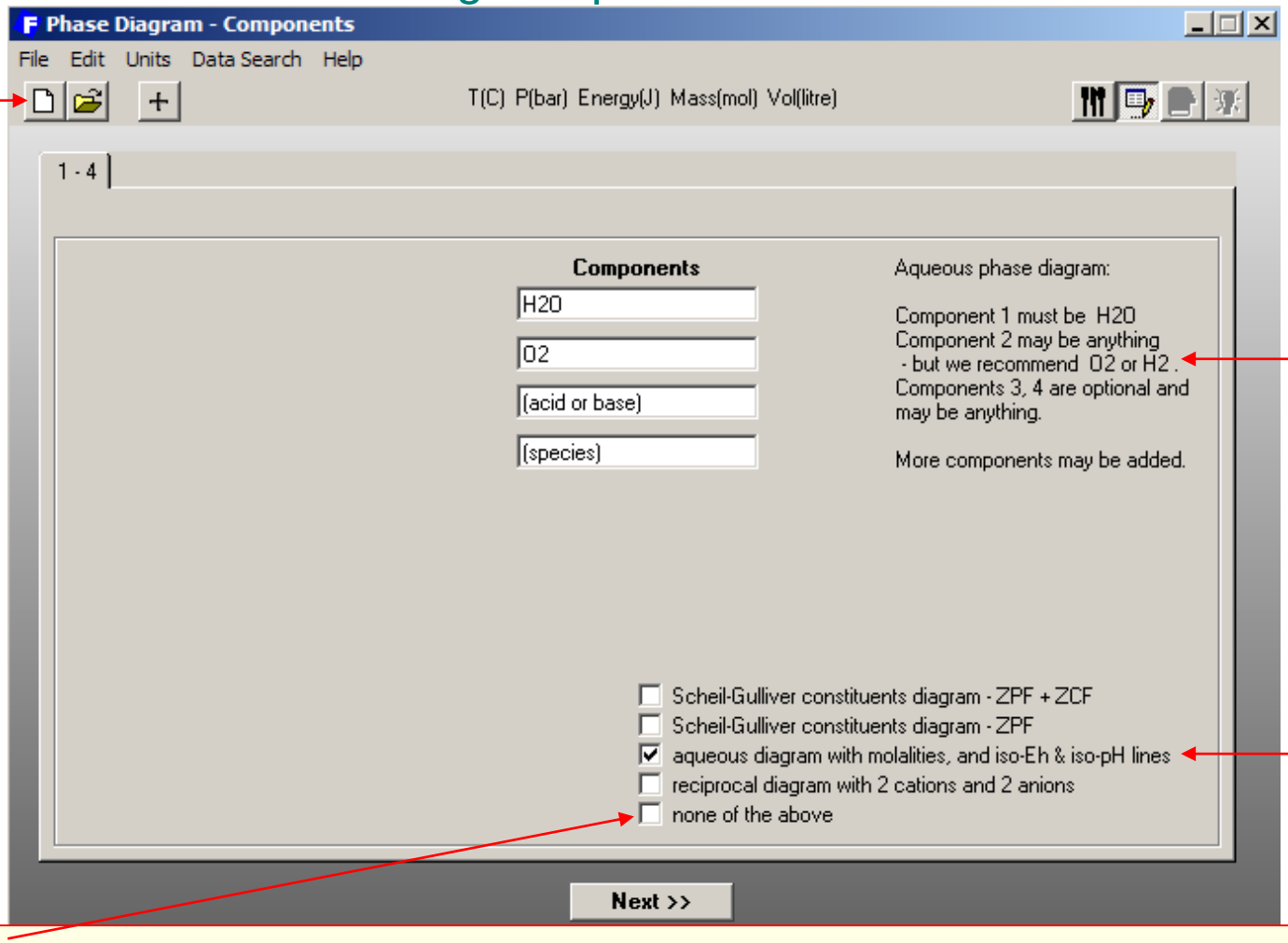


Max and min **Eh** and **pH** values on the diagram

Initiating the calculation of a phase diagram with an aqueous phase

With the options of plotting **iso-Eh** and **iso-pH** lines and entering compositions as molalities

1° Click.



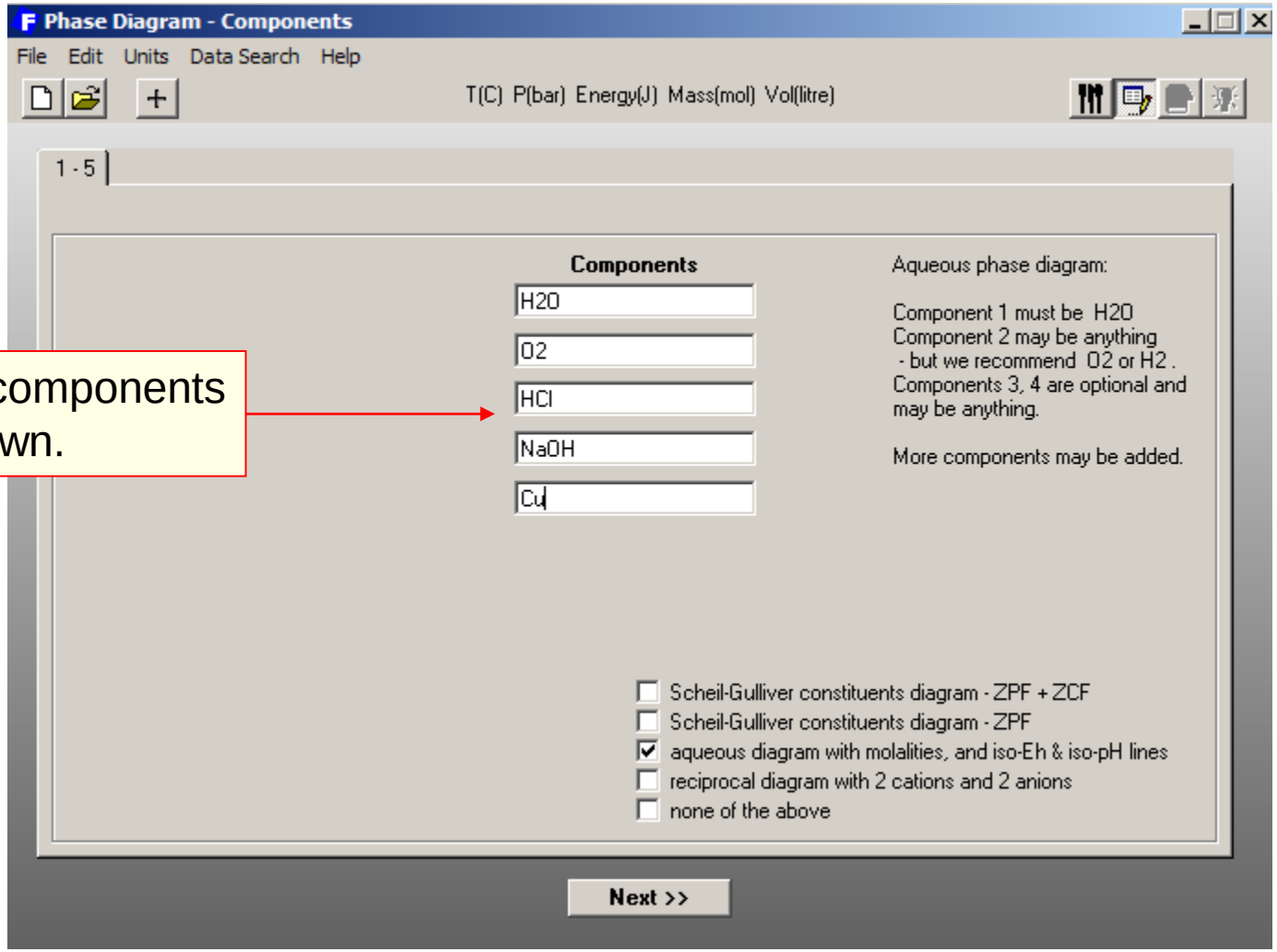
Please read this.

2° Click.

If you click **here** you can still calculate a phase diagram with an aqueous phase. You just will not have the option of plotting iso-Eh and iso-pH lines or of easily entering compositions as molalities.

Entry to generate H_2O – O_2 – HCl – NaOH – Cu aqueous phase diagram of Slide 19.4

Components window

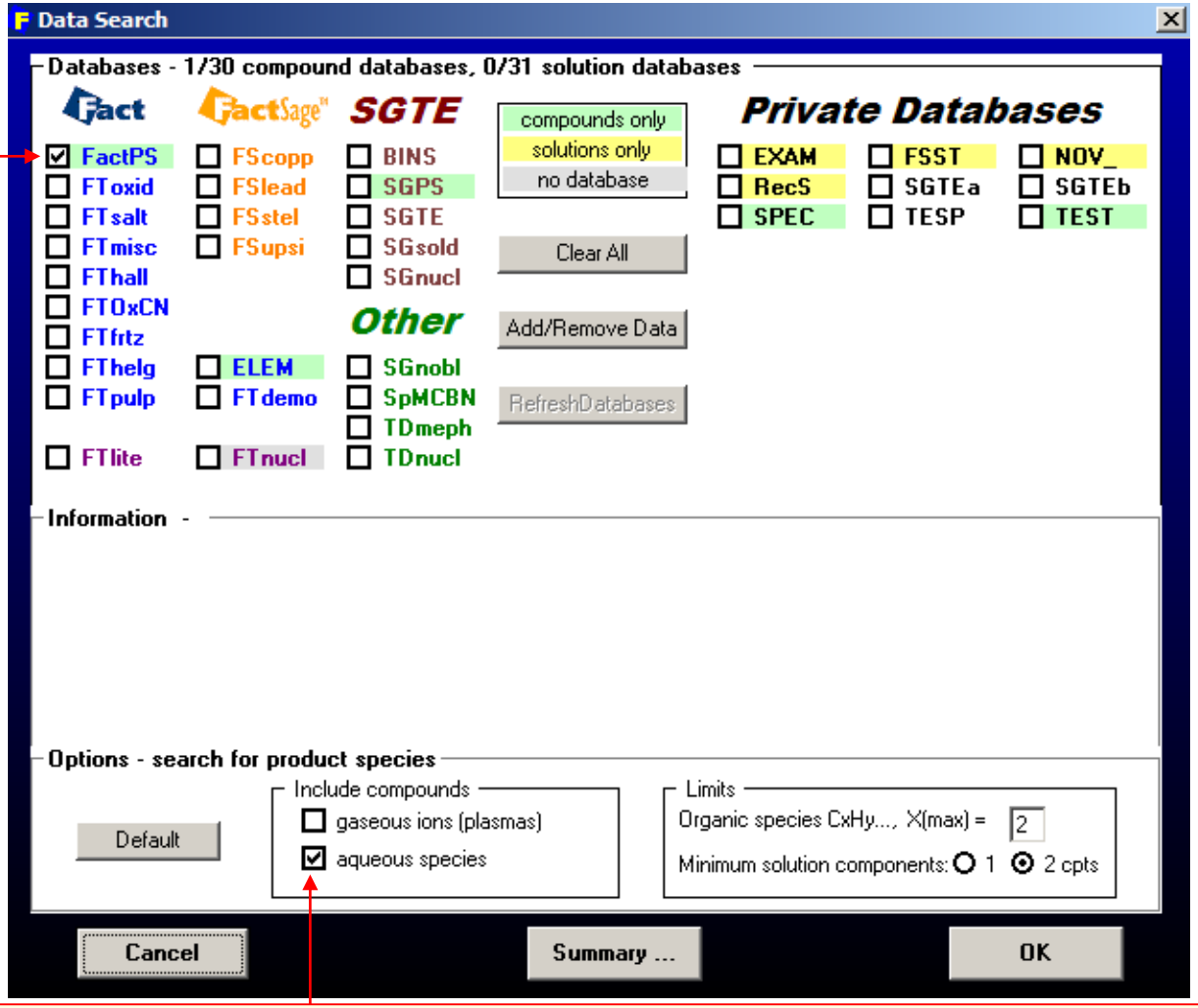


Enter components as shown.

→ (Entry continued from previous Slide – Data Search window)

The **FactPS** pure substances database is used for the aqueous solution in this example. (This database assumes an ideal dilute solution.)

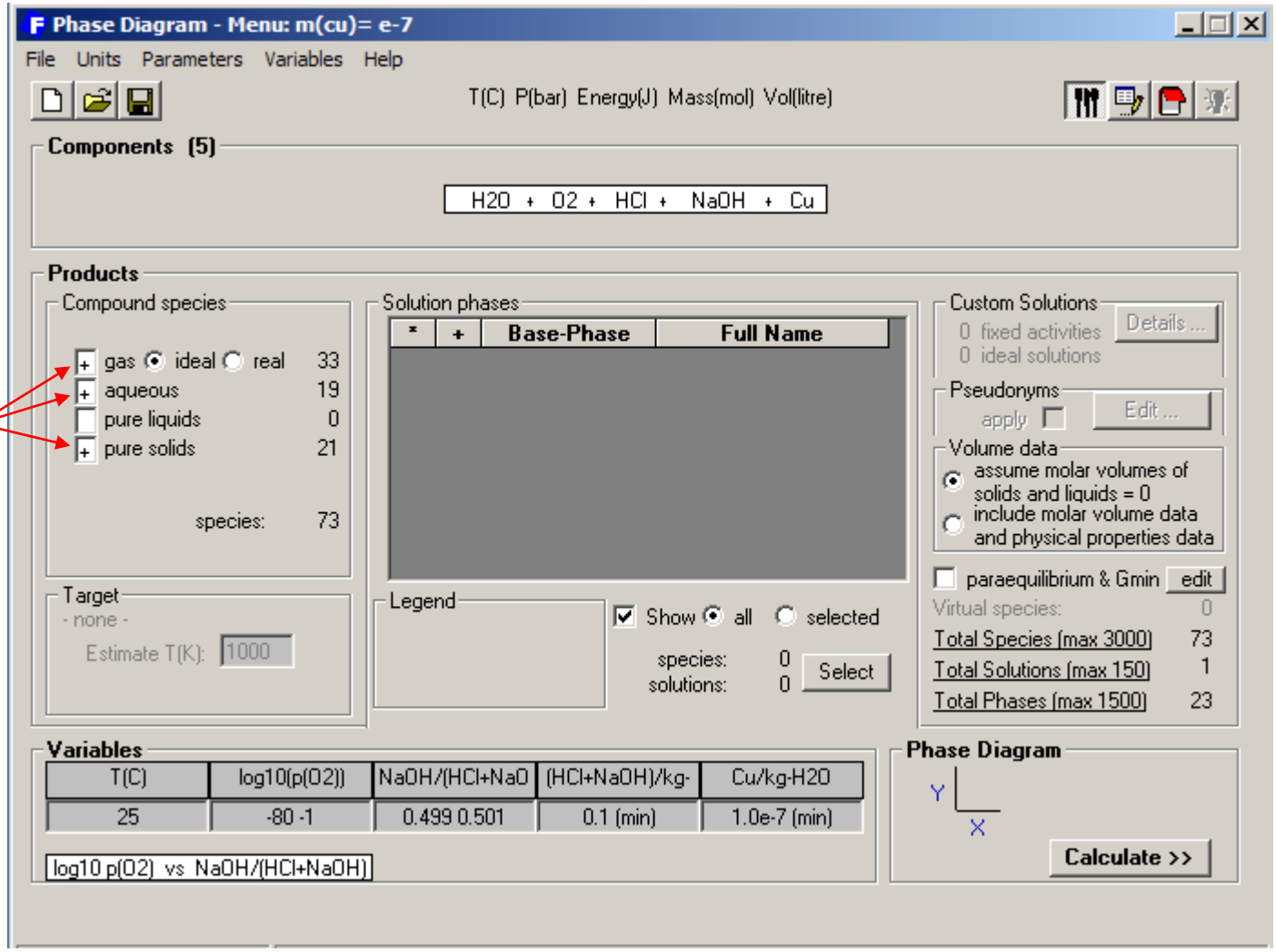
1° Click.



2° You must check this box in order for the **aqueous** solution to be active on the menu window.

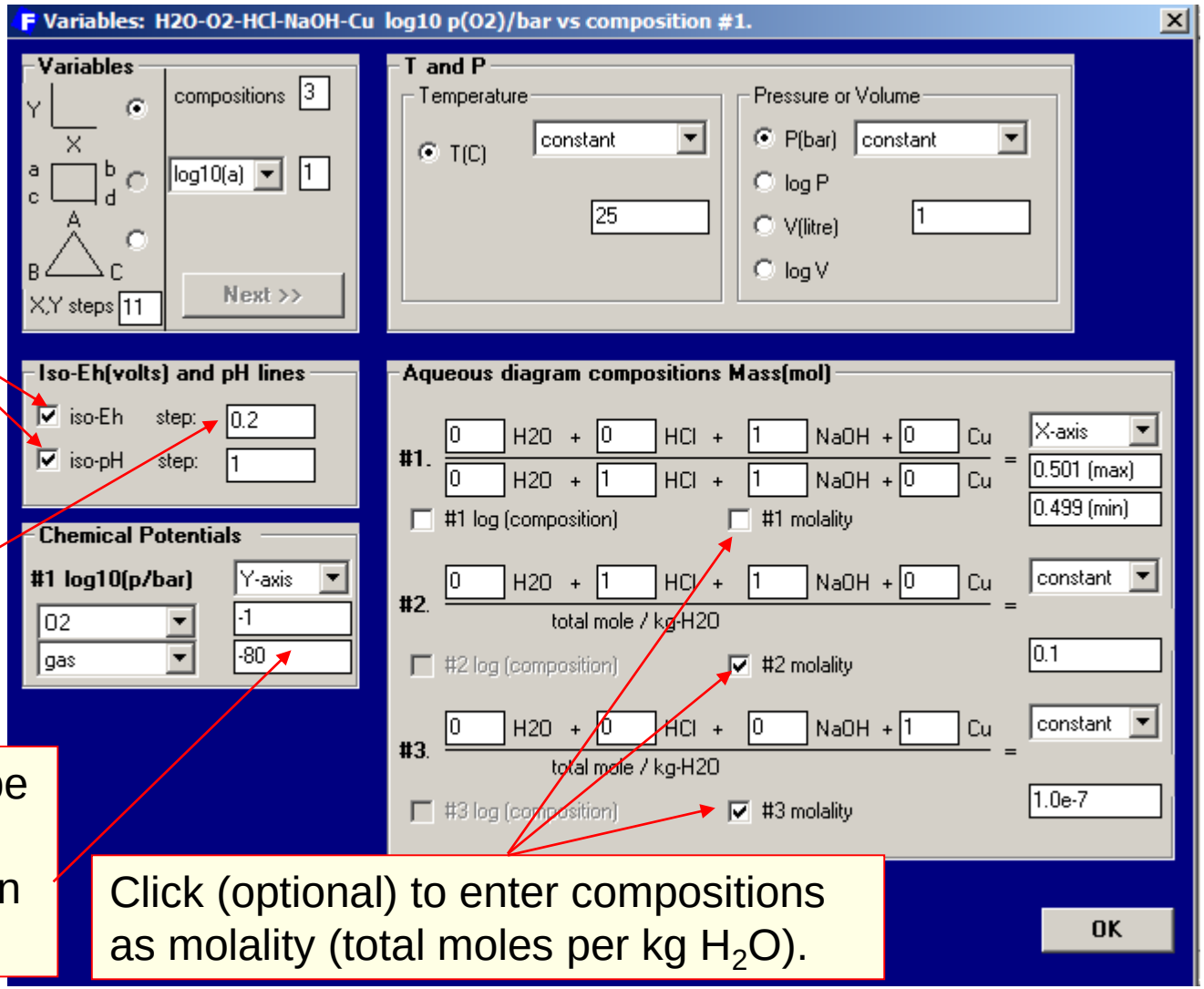
→ (Entry continued from previous Slide – Menu window)

Select.



Even if the gas phase is never a stable phase in the calculated diagram, it must nevertheless be selected if **iso-Eh** and **iso-pH lines** are to be plotted.

→ (Entry continued from previous Slide – Variables window)



Click to plot **iso-Eh** and **iso-pH** lines.

Enter steps. Upper and lower limits are selected automatically.

Default limits which can be edited. (The upper limit should not be greater than the total pressure.)

Click (optional) to enter compositions as molality (total moles per kg H_2O).

<u>Note</u>: If **mass units** of grams or pounds are selected, entry of compositions as **molalities** will not be permitted.

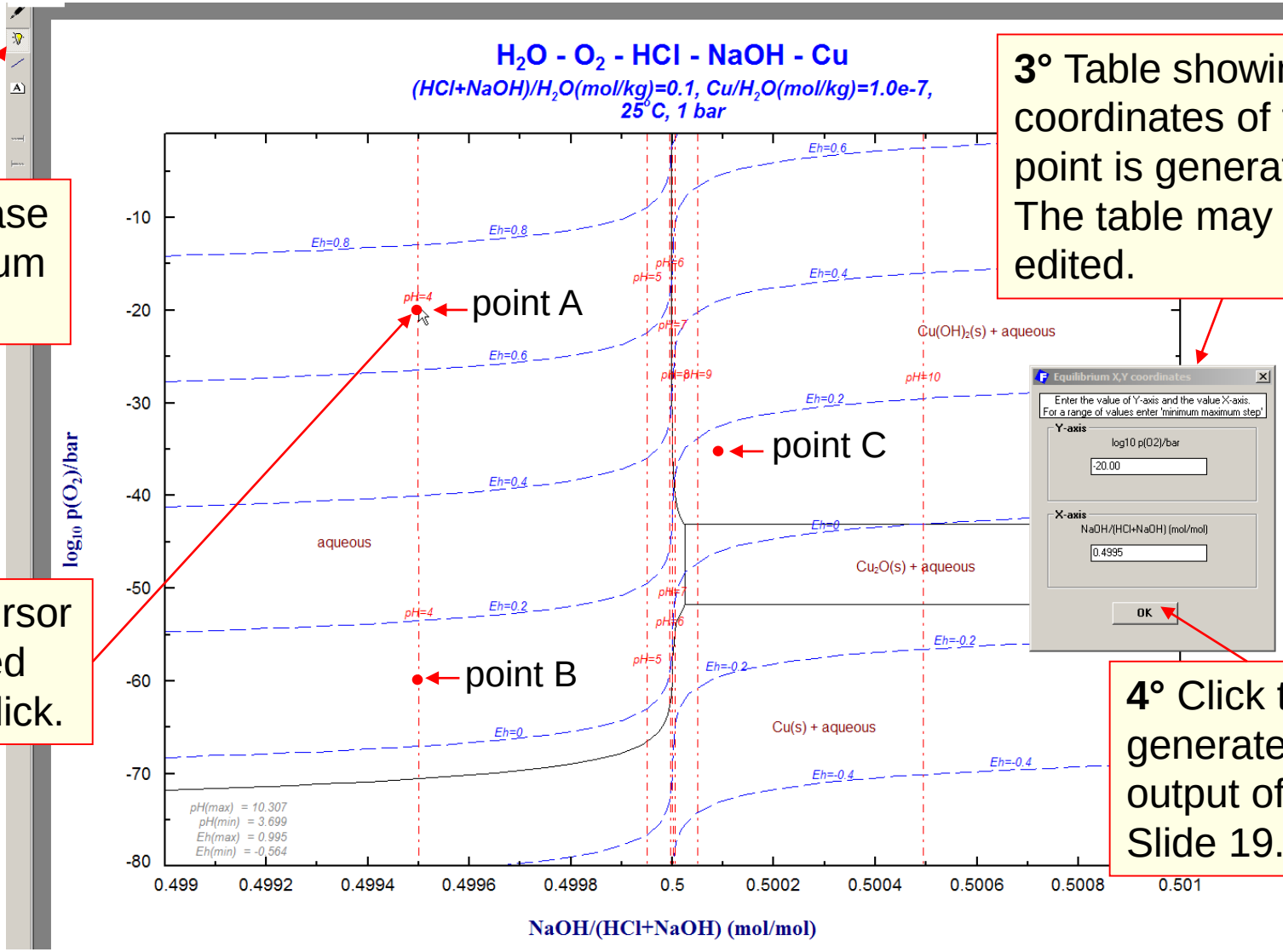
Calculating the equilibrium state at a point on the diagram

1° Click phase equilibrium mode.

2° Place cursor at a selected point and click.

3° Table showing coordinates of the point is generated. The table may be edited.

4° Click to generate output of Slide 19.11.



Equilibrium state at **point A** on Slide 19.10

In the single-phase aqueous region

```
log10 p(O2)/bar = -20,   NaOH/(HCl+NaOH) (mol/mol)   = 0.4995
==============================================================

 H2O  +  O2  +  HCl  +  NaOH  +

 Cu  =

 + 8.9915E-10 O2

 0          mol   gas_ideal
          (25 C, 1 bar,      a=3.1710E-02)
          ( 3.1710E-02       H2O
          + 2.5576E-12       HCl
          + 1.0000E-20       O2
          + 9.3341E-26       Cl2
          + 3.2818E-28       HOCl
          + 1.0871E-31       Cl
          + 2.8454E-32       H2
          + ......................

 + 1.0009     mol   aqueous
   (18.052 gram, 1.0009 mol)
          (25 C, 1 bar,      a=1.0000)
          ( 55.508           H2O_liquid
          + 5.0005E-02       Cl[-]
          + 4.9905E-02       Na[+]
          + 9.9711E-05       H[+]
          + 9.9911E-08       Cu[2+]
          + 9.8934E-11       OH[-]
          + 3.7501E-14       CuCl2[-]
          + 9.1944E-17       Cu[+]
          + ......................
          (Eh= 0.696 V, pH= 4.001)
```

Gas phase is not stable.

Since total pressure is 1.0 bar, these are the equilibrium H_2O, O_2 and H_2 partial pressures.

1.0 kg H_2O contains 55.508 moles. These concentrations of the ions are therefore their molalities.

At this oxidation potential, the Cu is almost entirely in the (2+) oxidation state (cf: Slide 19.2).

Eh and **pH** at **point A**.

Equilibrium state at **point B** on Slide 19.10

In the single-phase aqueous region

```
log10 p(O2)/bar = -60,  NaOH/(HCl+NaOH) (mol/mol)  = 0.4995
==============================================================

 H2O  +  O2  +  HCl  +  NaOH  +

 Cu  =

 + 4.4969E-10 O2

   0          mol   gas_ideal
            (25 C, 1 bar,      a=3.1710E-02)
            ( 3.1710E-02       H2O
            + 2.8454E-12       H2
            + 2.5601E-12       HCl
            + ........................
            + 1.0000E-60       O2
            + ........................

 + 1.0009     mol   aqueous
   (18.052 gram, 1.0009 mol)
            (25 C, 1 bar,      a=1.0000)
            ( 55.508           H2O_liquid
            + 5.0005E-02       Cl[-]
            + 4.9905E-02       Na[+]
            + 9.9811E-05       H[+]
            + 9.9640E-08       CuCl2[-]
            + 2.4430E-10       Cu[+]
            + 9.8835E-11       OH[-]
            + 2.6573E-11       Cu[2+]
            + ........................
            (Eh= 0.105 V, pH= 4.001)
```

At this oxidation potential, the Cu is almost entirely in the (1+) oxidation state (mainly as $CuCl_2[-]$) (cf: Slide 19.2).

Eh and **pH** at **point B**.

Equilibrium state at **point C** on Slide 19.10

In the 2-phase ($Cu(OH)_2$ + aqueous) region

```
log10 p(O2)/bar = -35,  NaOH/(HCl+NaOH) (mol/mol)  = 0.5001
==============================================================

 H2O  +  O2  +  HCl  +  NaOH  +

 Cu  =

 + 8.9814E-10 O2

   O          mol   gas_ideal
            (25 C, 1 bar,      a=3.1710E-02)
            ( 3.1710E-02       H2O
            + 1.2647E-17       HCl
            + 8.9978E-25       H2
            + 1.0000E-35       O2
            + ..........

 + 1.0009     mol   aqueous
   (18.052 gram, 1.0009 mol)
            (25 C, 1 bar,      a=1.0000)
            ( 55.508           H2O_liquid
            + 4.9965E-02       Na[+]
            + 4.9945E-02       Cl[-]
            + 1.9983E-05       OH[-]
            + 4.9366E-10       H[+]
            + 2.2442E-10       CuCl2[-]
            + 5.5154E-13       Cu[+]
            + 5.2766E-13       Cu[2+]
            + ..................
            (Eh= 0.161 V, pH= 9.307)

 + 1.7942E-09 mol   Cu(OH)2_solid
   (1.7505E-07 gram, 1.7942E-09 mol)
            (25 C, 1 bar, S1, a=1.0000)
```

1.0 kg H_2O.

Virtually all the Cu has precipitated as $Cu(OH)_2$.

(55.508) (1.7942 x 10^{-9}) = 1.0 x 10^{-7} moles Cu.

$H^+ + e^- = ½ H_2$

$$(Eh) = \Delta G / F = -(RT / F)(\ln P_{H_2} - \ln a_{H^+})$$

$$(Eh) = (2.303RT / F)(-1/2 \log_{10} P_{H_2} - pH) \qquad [1]$$

where: a_{H^+} = activity of $H^+ \approx m\ (H^+)$

F = Faraday's constant

$pH = -\log_{10} a_{H^+}$

Also:

$H_2O\ (liq) = H_2(g) + ½\ O_2\ (g)$

$$K = P_{H_2} P_{O_2}^{1/2} / a_{H_2O}$$

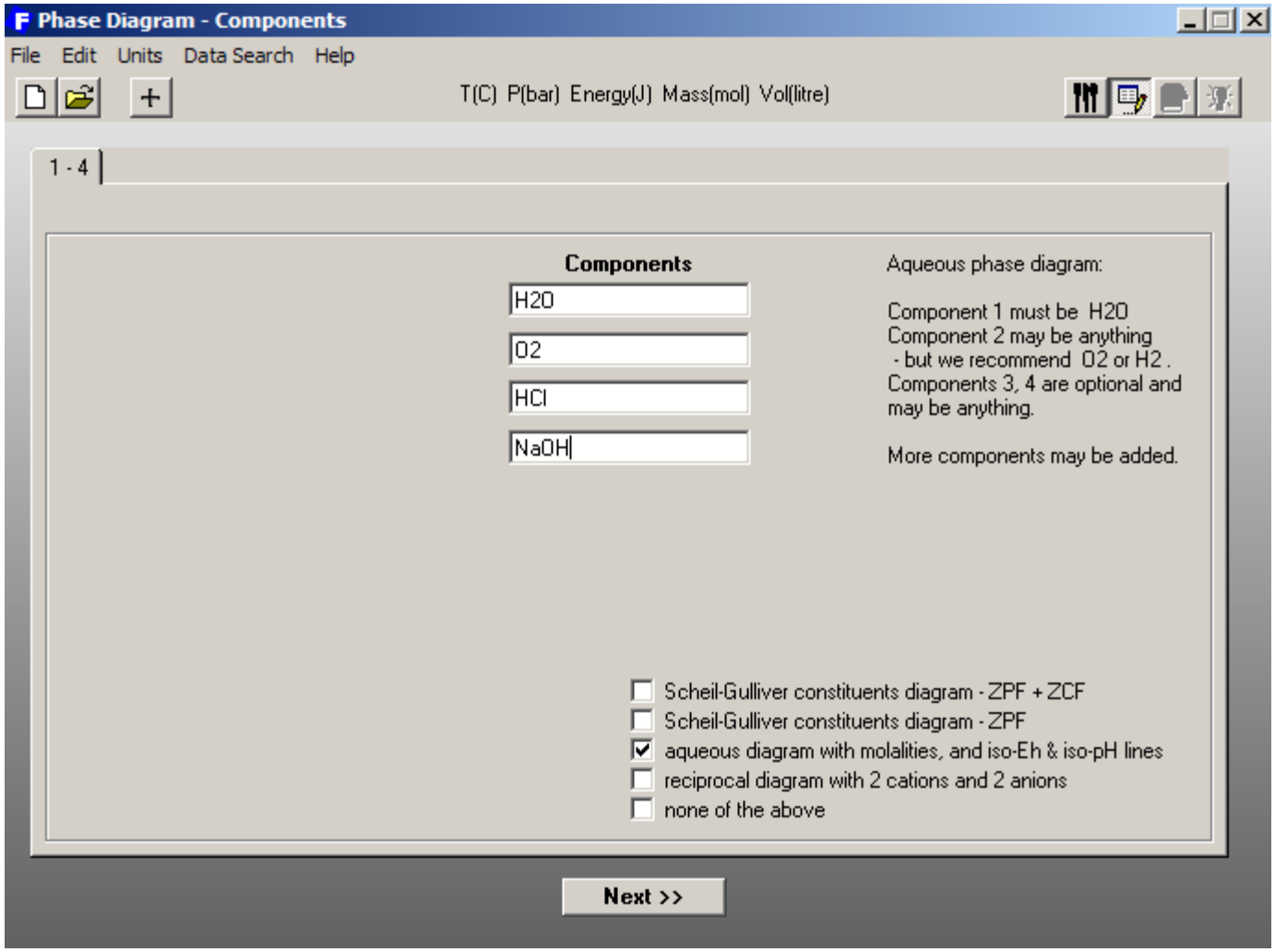
where $a_{H_2O} \approx 1.0$

substituting into Eq. [1] gives:

$$Eh = (2.303RT / F)(1/4 \log P_{O_2} - pH - 1/2 \log K + \log a_{H_2O}) \qquad [2]$$

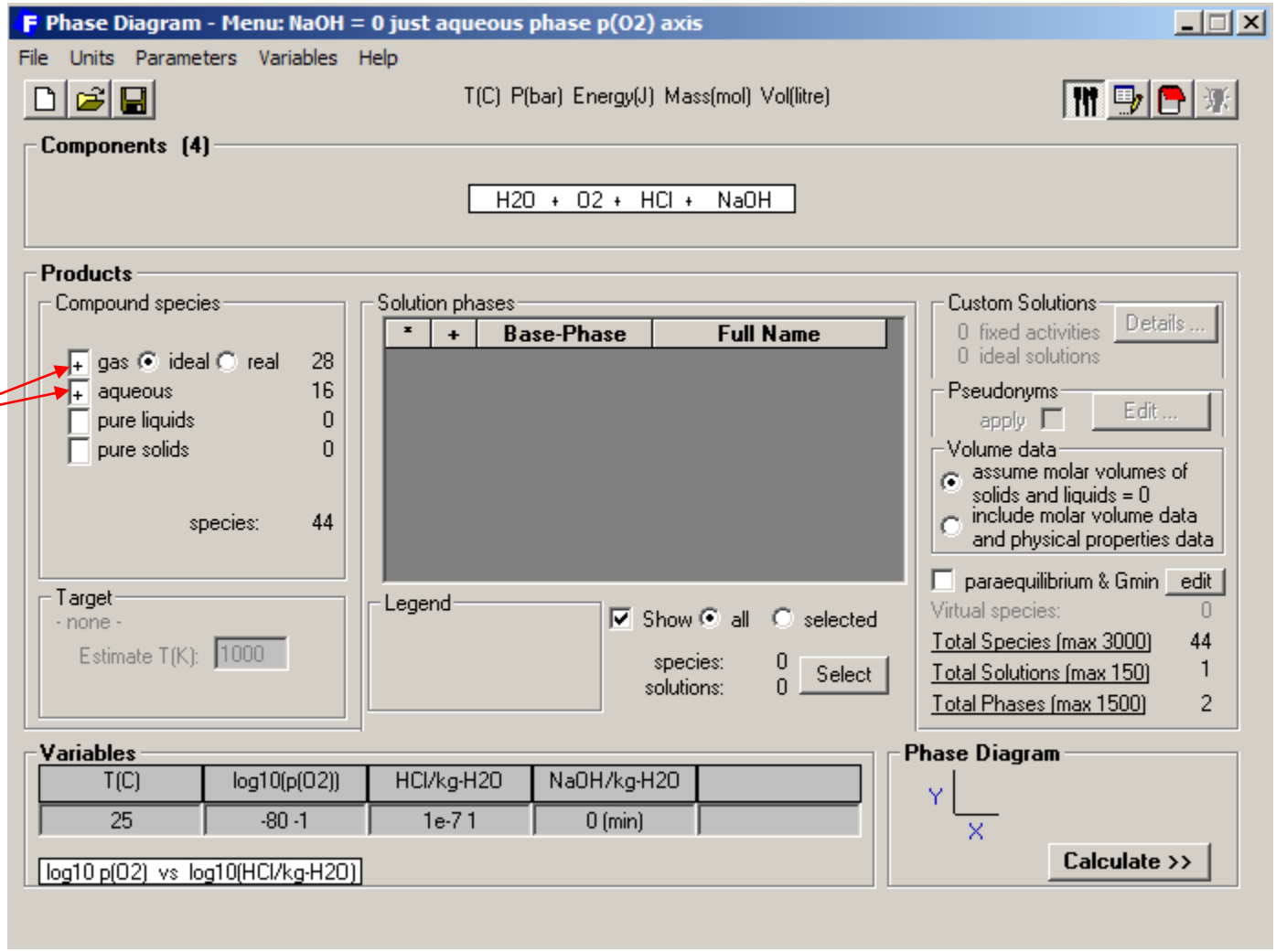
Eqs. [1,2] are illustrated on Slides 19.18, 19.19 and 19.21.

Entry to illustrate relationships among **log $P(O_2)$, Eh and pH**

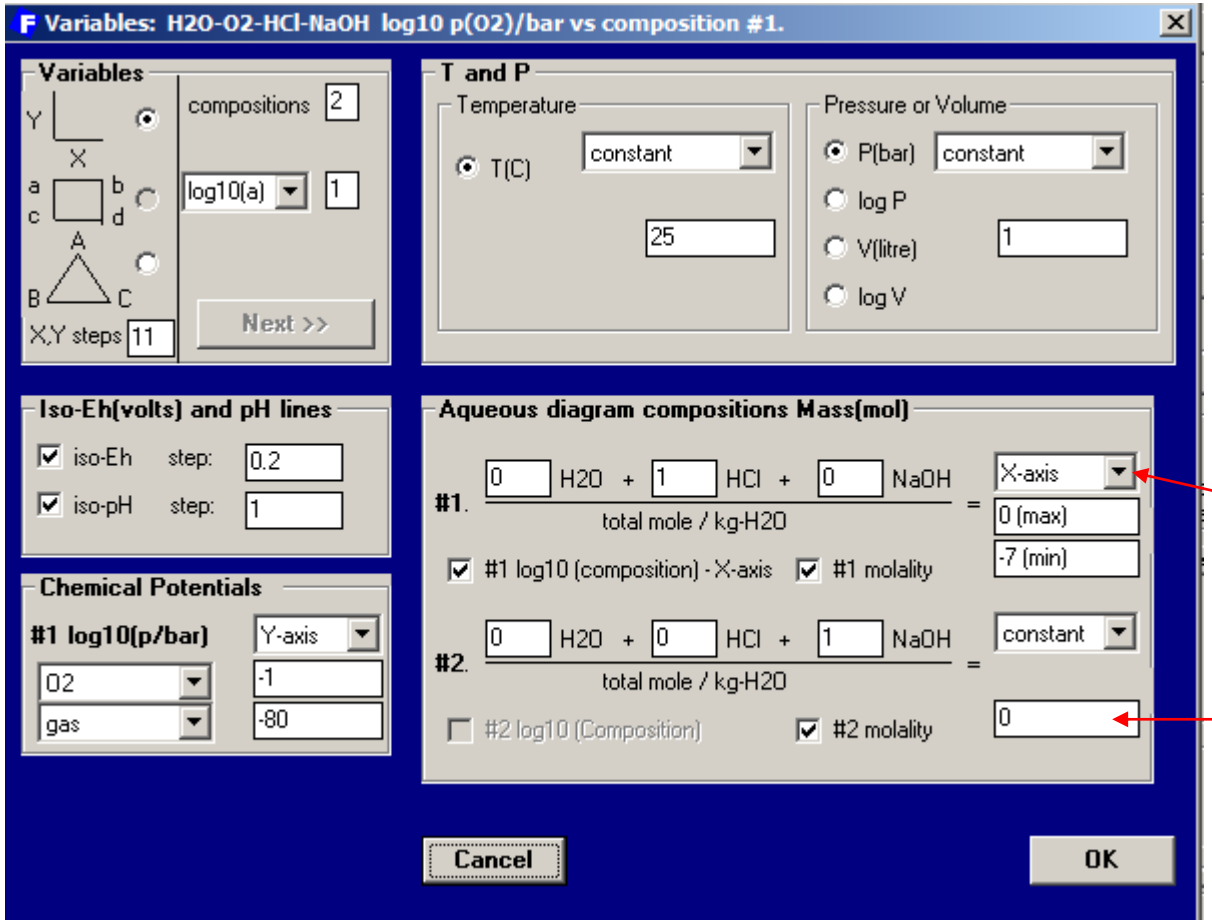


→ (Entry continued from previous Slide – Menu window)

Choose only gas and aqueous.



(Entry continued from previous Slide – Variables window)

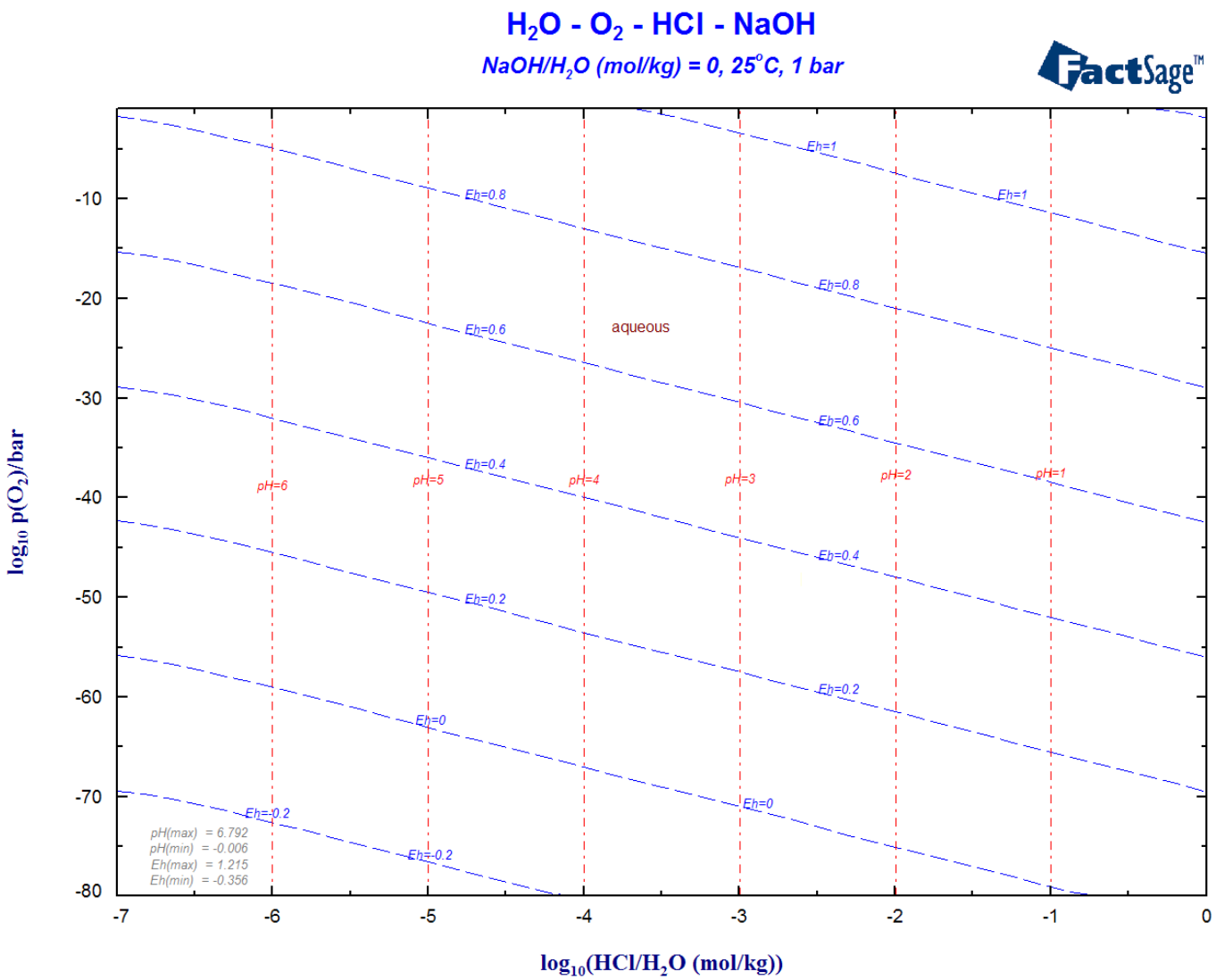


X-axis is log of molality of HCl.

Zero amount NaOH.

Single-phase aqueous diagram illustrating relationship among **log P(O_2)**, **Eh**&**pH**

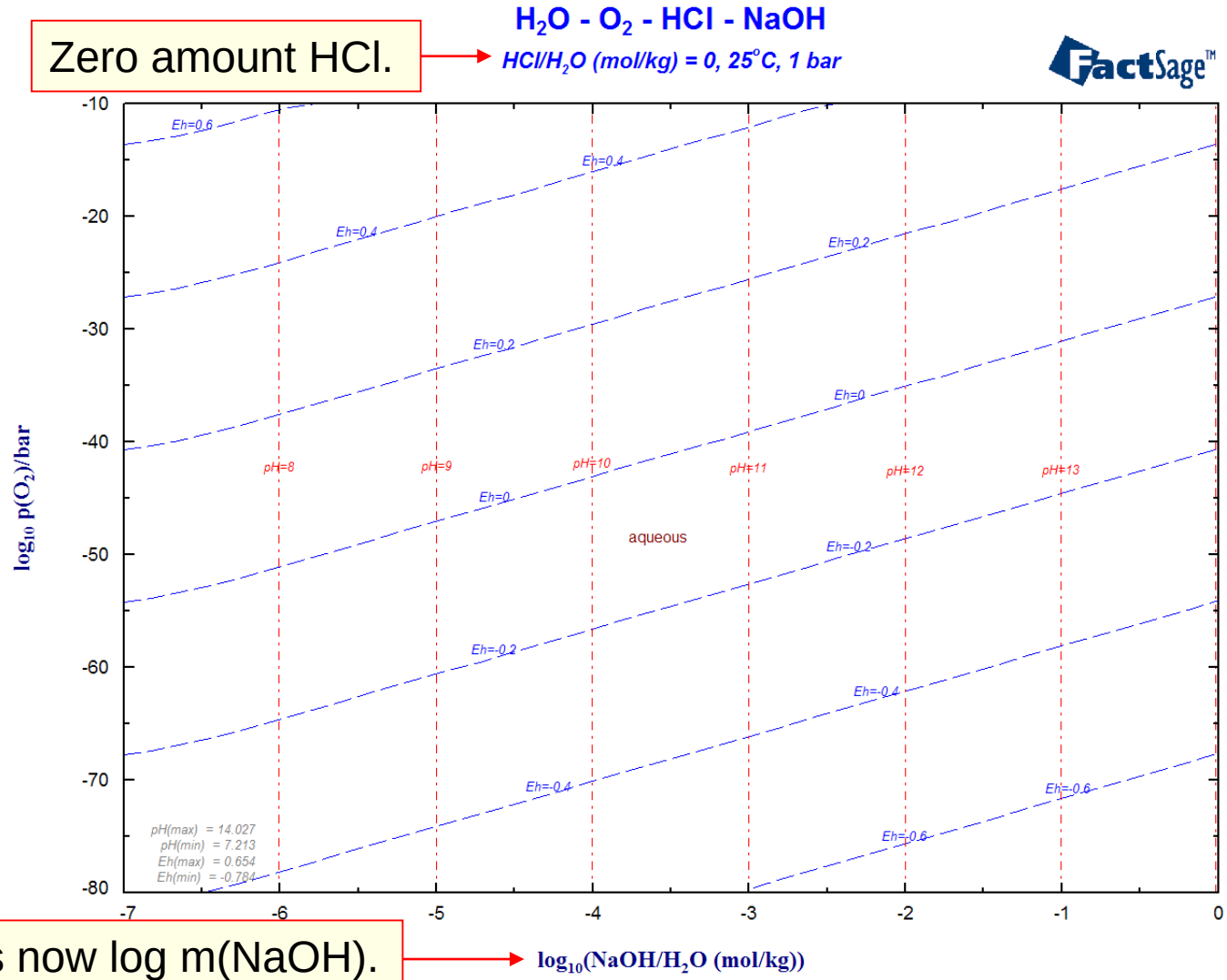
This slide illustrates Eq [2] of Slide 19.14



Single-phase aqueous diagram illustrating relationship among **log P(O_2)**, **Eh&pH**

This slide also illustrates Eq [2] of Slide 19.14

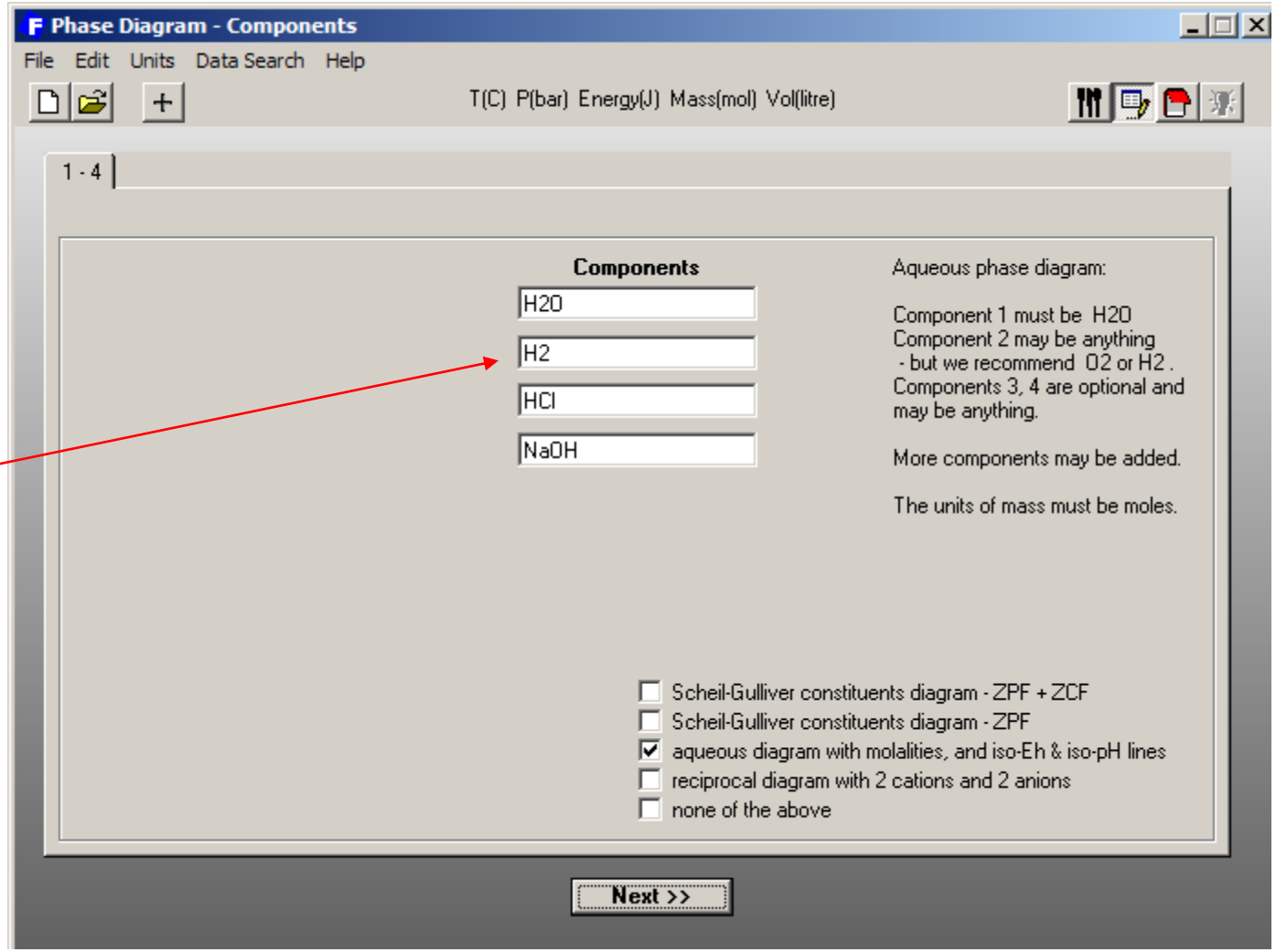
Zero amount HCl.



X-axis is now log m(NaOH).

Entry to illustrate relationship among log $P(H_2)$, Eh and pH

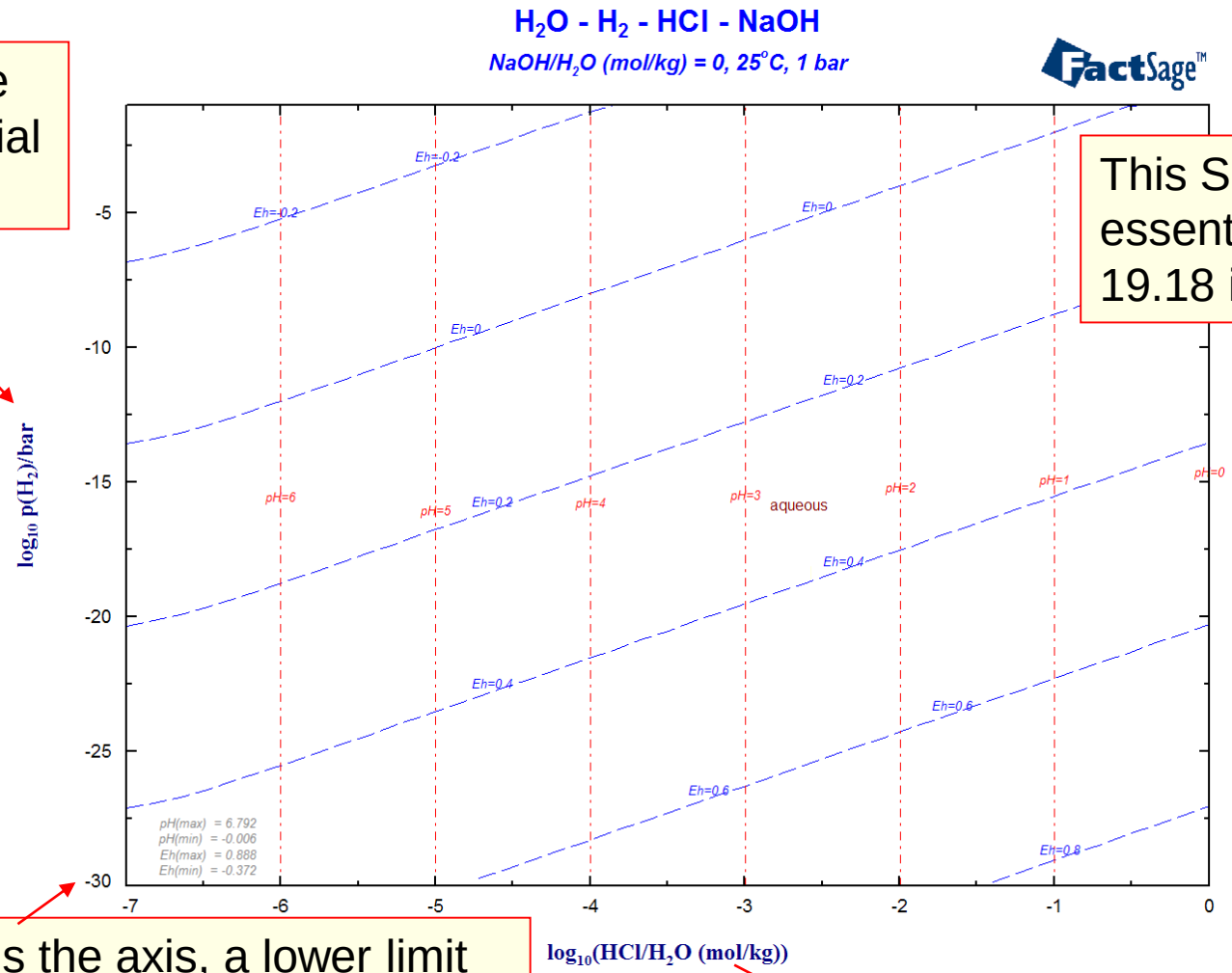
Enter H_2 as a component instead of O_2.



Single-phase aqueous diagram illustrating relationship among **log P(H_2)**, **Eh&pH**

This Slide illustrates Eq [1] of Slide 19.14

Y-axis is now the reduction potential **logP(H_2).**



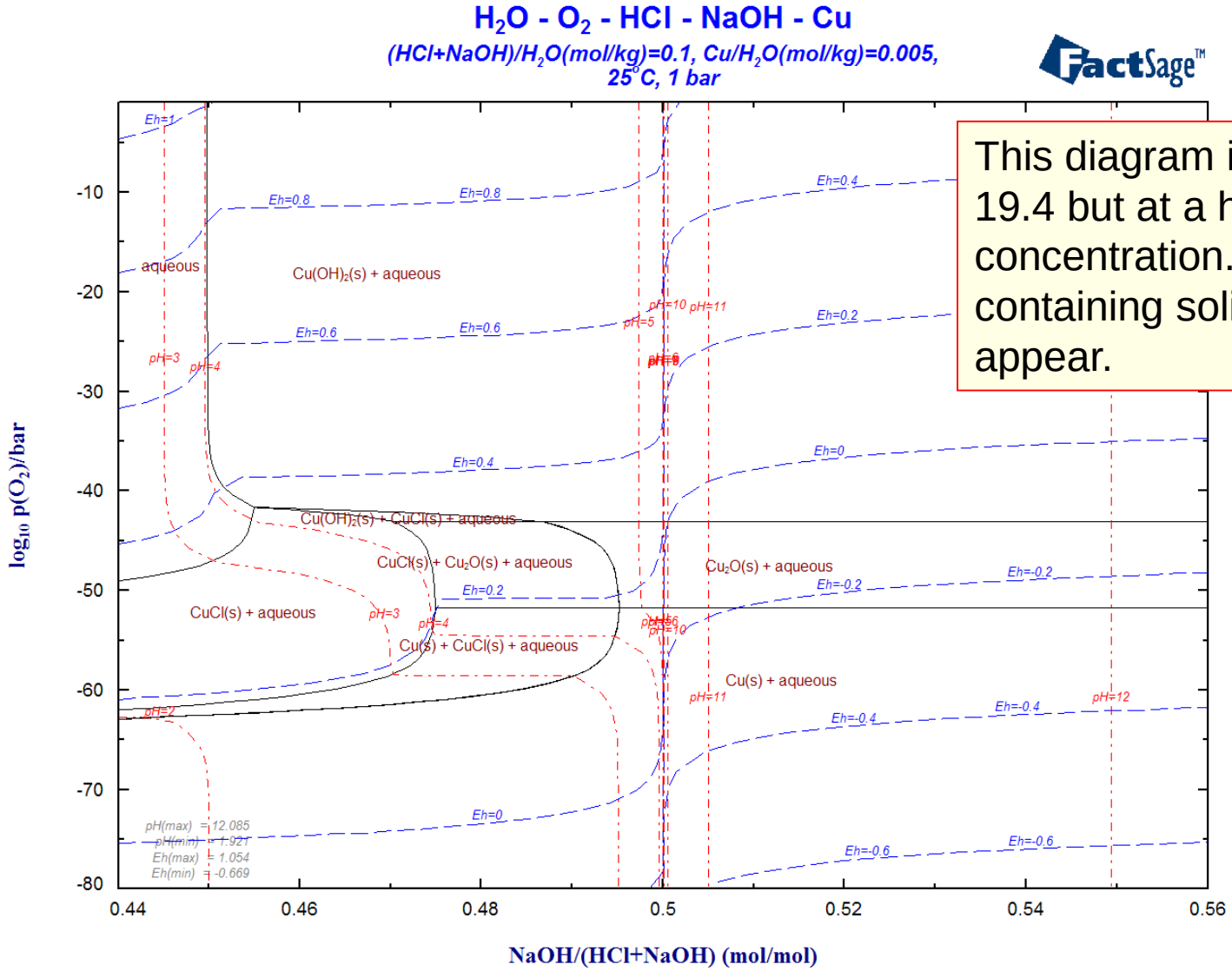
This Slide is essentially Slide 19.18 inverted.

When **logP(H_2)** is the axis, a lower limit of approximately **-30** is recommended.

log m(HCl).

H_2O-O_2-HCl-NaOH-Cu Aqueous Phase Diagram

logP(O_2) versus molar ratio NaOH/(HCl + NaOH) at constant molalities m(Cu) = 0.005 and (m(HCl) + m(NaOH)) = 0.1 (Aqueous phase of **FactPS** was used)



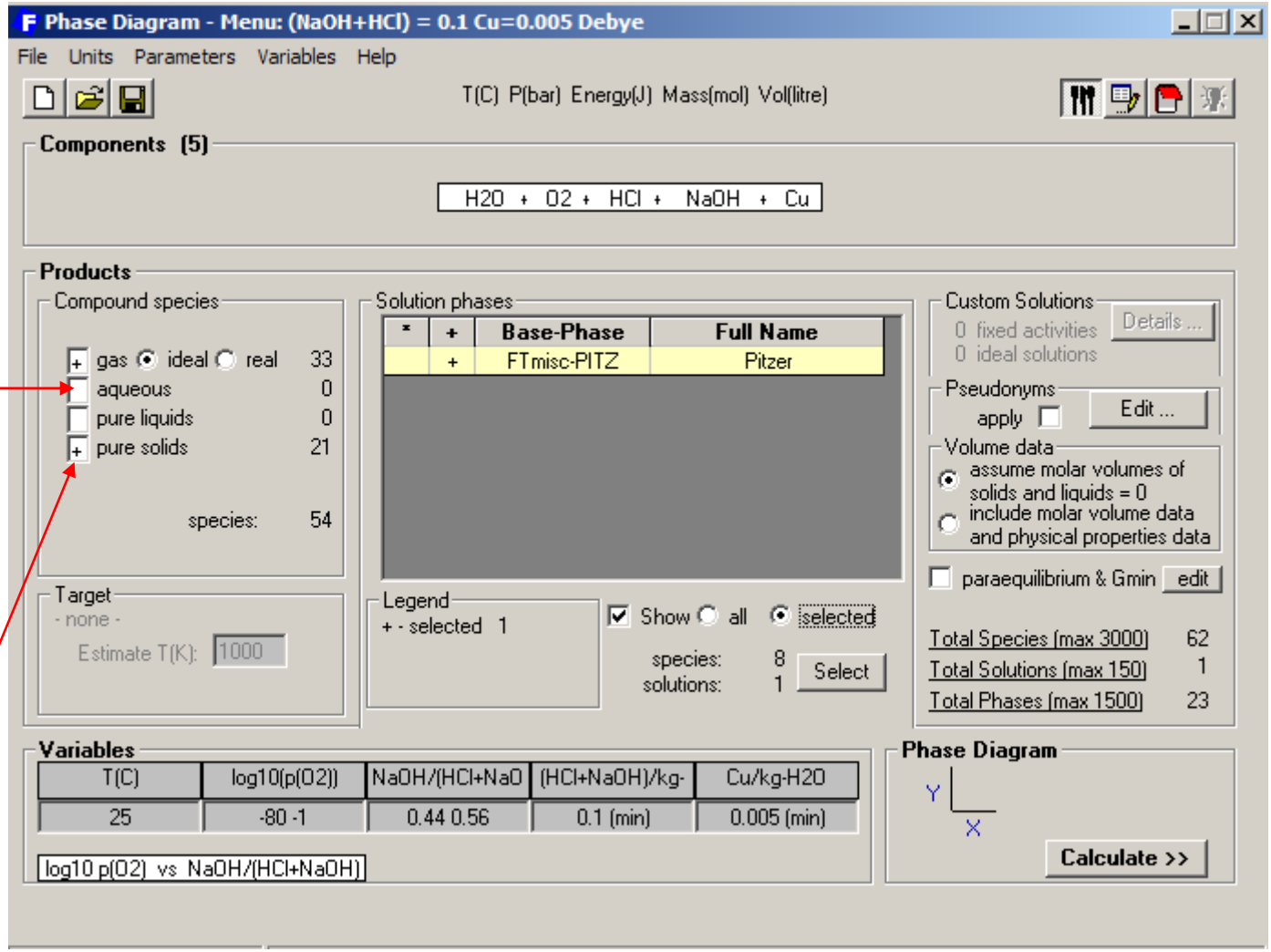
This diagram is like Slide 19.4 but at a higher Cu concentration. Fields containing solid CuCl now appear.

Using the **non-ideal Pitzer aqueous solution** in the **FTmisc** database

Input to calculate a diagram like Slide 19.22

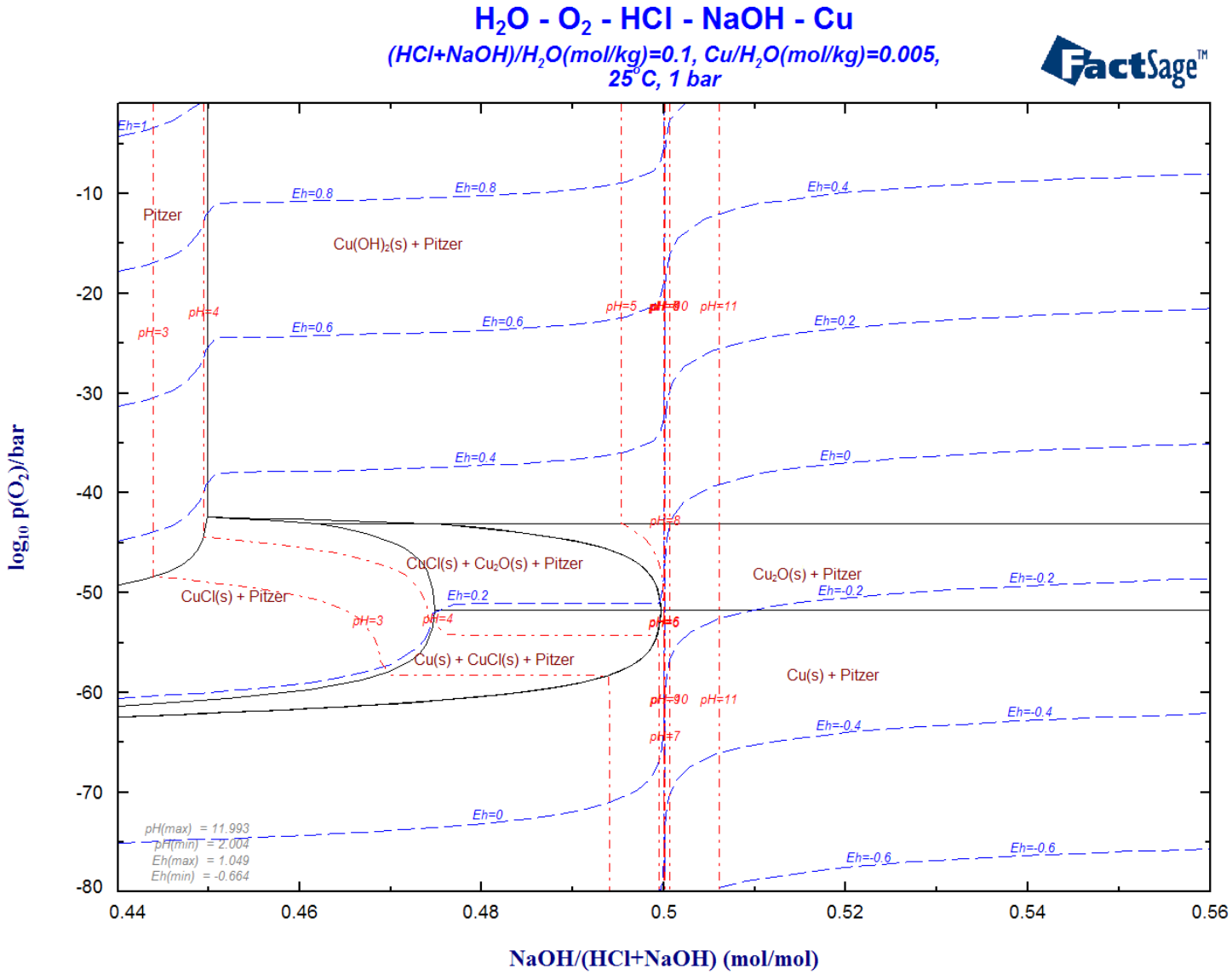
Never select more than one aqueous phase in a calculation.

Pure solids are taken from **FactPS** database.



Using FTmisc non-ideal Pitzer aqueous solution

Compare to Slide 19.22



Some phase boundaries are displaced from their positions in Slide 19.22 because ionic interactions are now taken into account.

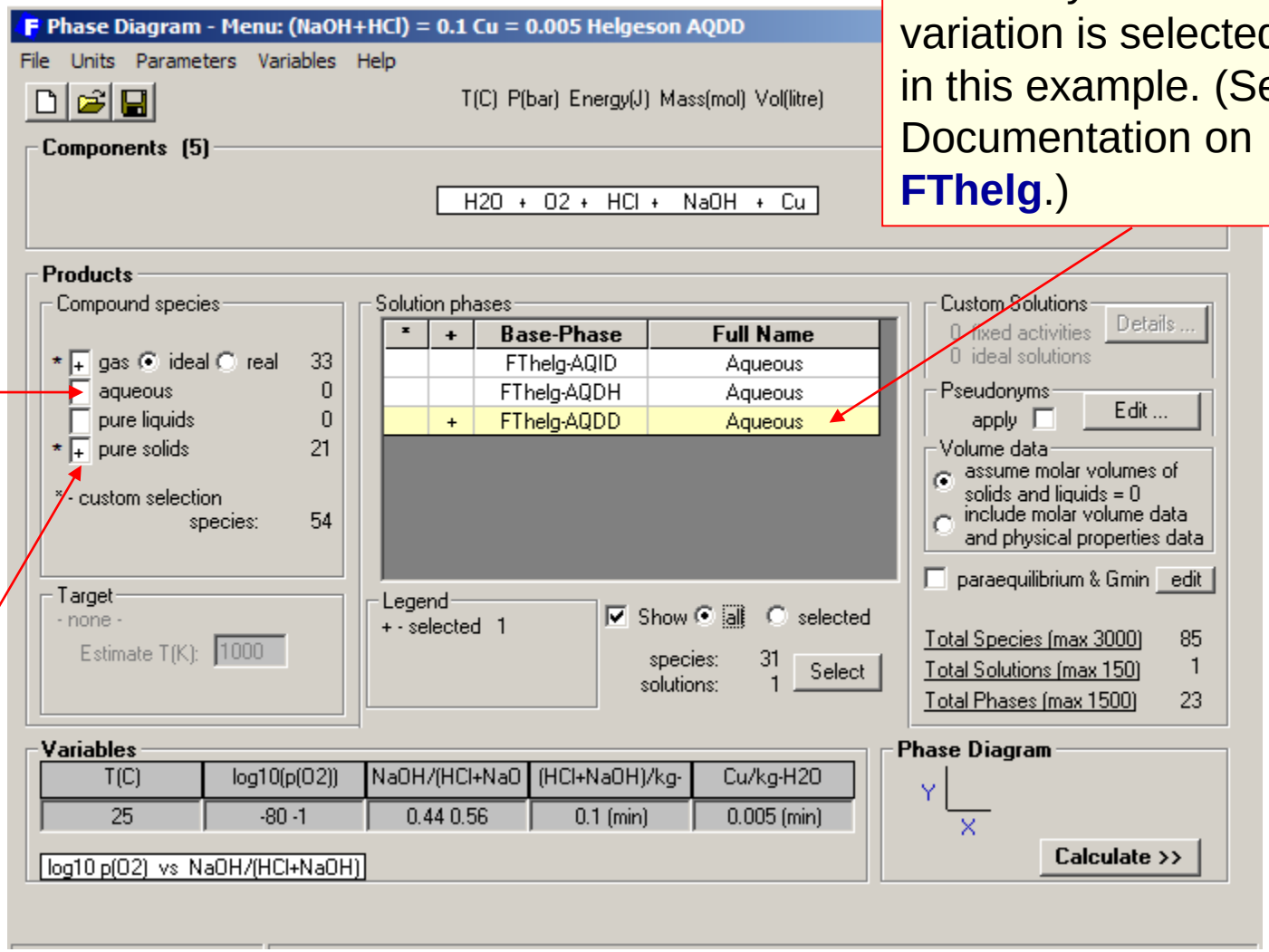
Using **FThelg** **non-ideal Helgeson aqueous solution**

Input to calculate a diagram like Slide 19.22

The Debye-Davies variation is selected in this example. (See Documentation on **FThelg**.)

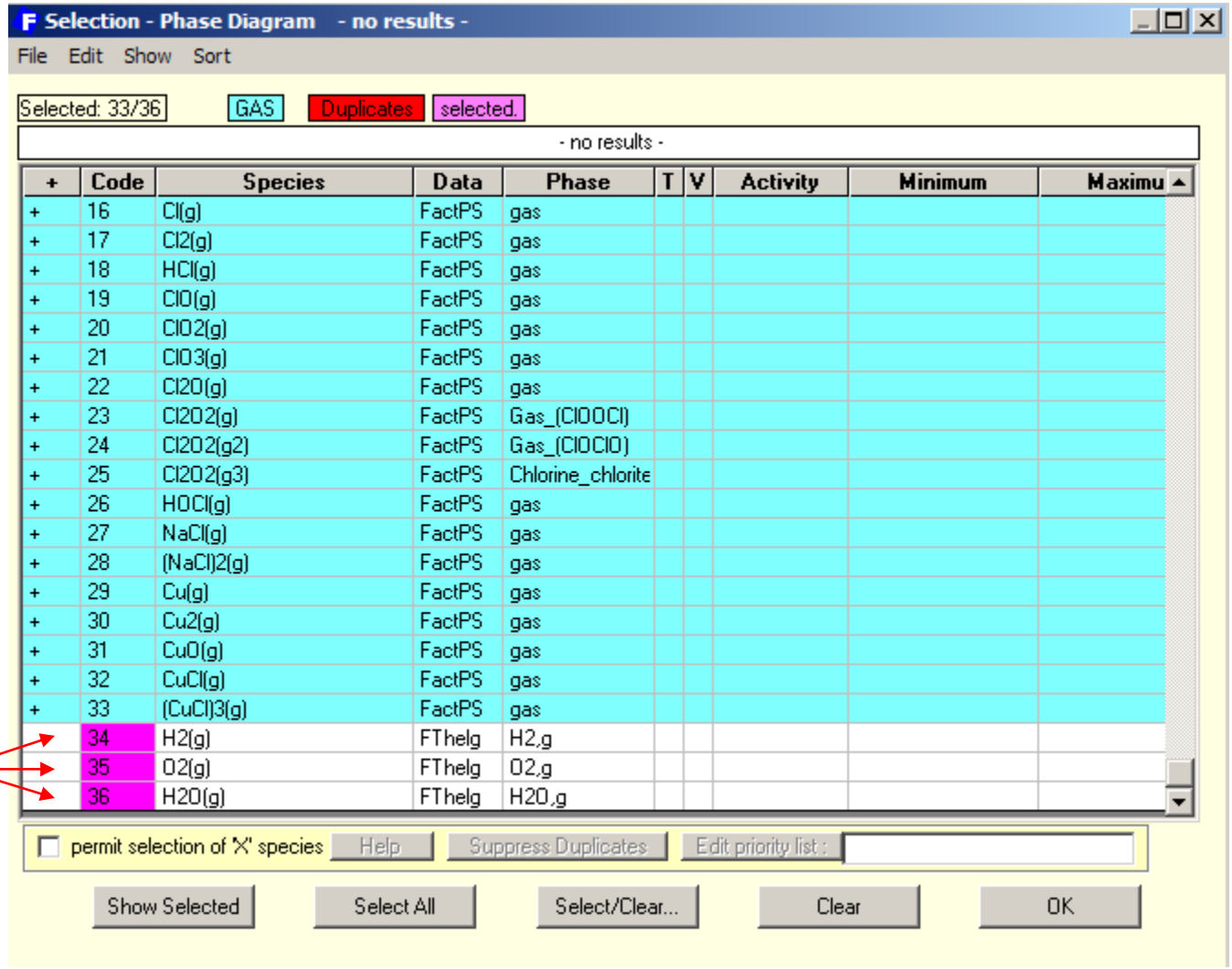
Never select more than one aqueous phase in a calculation.

Solids taken from **FactPS** (See next Slide).



Non-ideal Helgeson aqueous solution – Selection window «gas»

- Right click on «gas» in Slide 19.25
- Then de-select all species that are duplicated in the **FactPS** and **FThelg** databases.

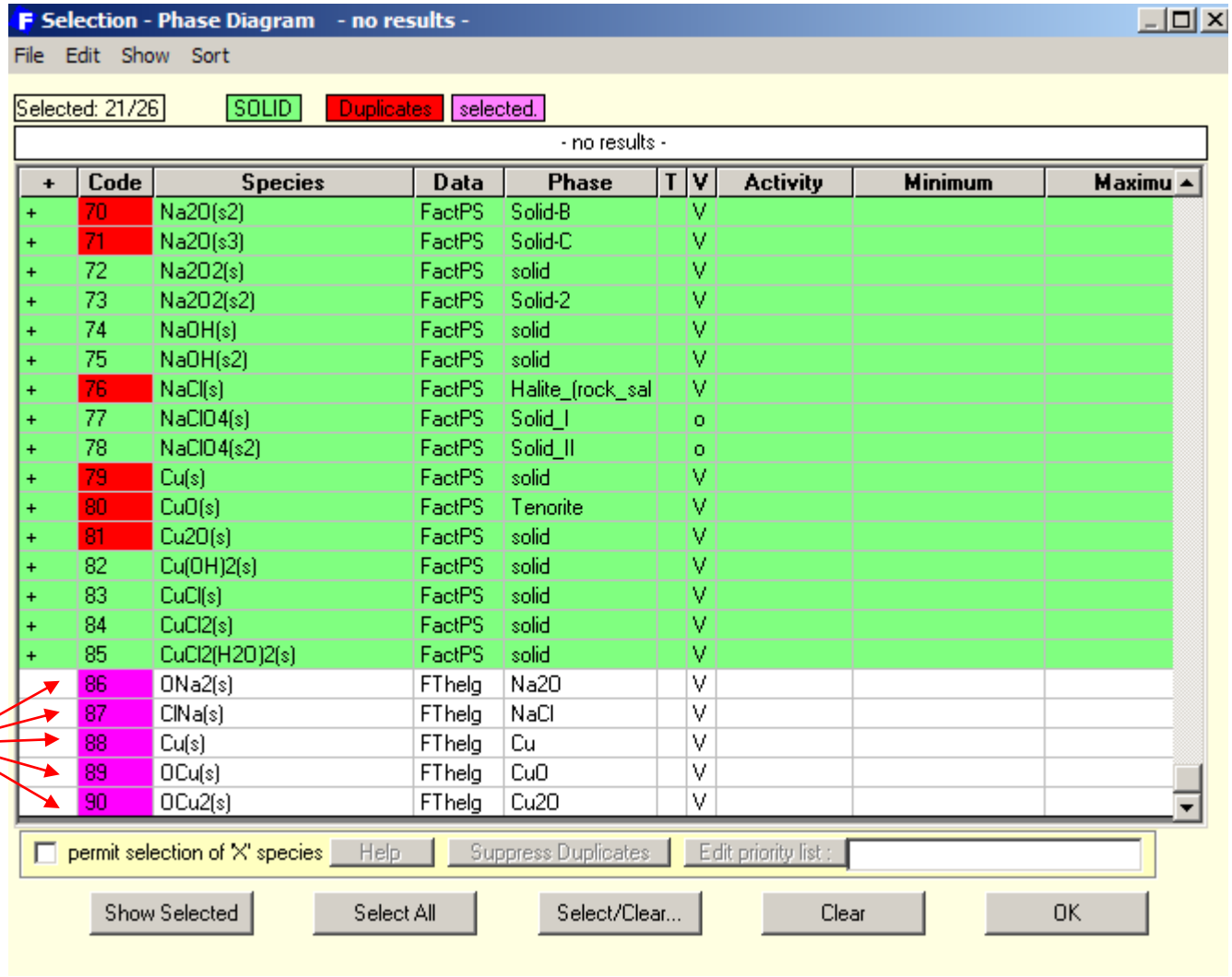


+	Code	Species	Data	Phase	T	V	Activity	Minimum	Maximu
+	16	Cl(g)	FactPS	gas					
+	17	Cl2(g)	FactPS	gas					
+	18	HCl(g)	FactPS	gas					
+	19	ClO(g)	FactPS	gas					
+	20	ClO2(g)	FactPS	gas					
+	21	ClO3(g)	FactPS	gas					
+	22	Cl2O(g)	FactPS	gas					
+	23	Cl2O2(g)	FactPS	Gas_(ClOOCl)					
+	24	Cl2O2(g2)	FactPS	Gas_(ClOClO)					
+	25	Cl2O2(g3)	FactPS	Chlorine_chlorite					
+	26	HOCl(g)	FactPS	gas					
+	27	NaCl(g)	FactPS	gas					
+	28	(NaCl)2(g)	FactPS	gas					
+	29	Cu(g)	FactPS	gas					
+	30	Cu2(g)	FactPS	gas					
+	31	CuO(g)	FactPS	gas					
+	32	CuCl(g)	FactPS	gas					
+	33	(CuCl)3(g)	FactPS	gas					
	34	H2(g)	FThelg	H2,g					
	35	O2(g)	FThelg	O2,g					
	36	H2O(g)	FThelg	H2O,g					

De-select.

Non-ideal Helgeson aqueous solution – Selection window «pure solids»

- Right click on «pure solids» in Slide 19.25
- Then select species from one database or the other.

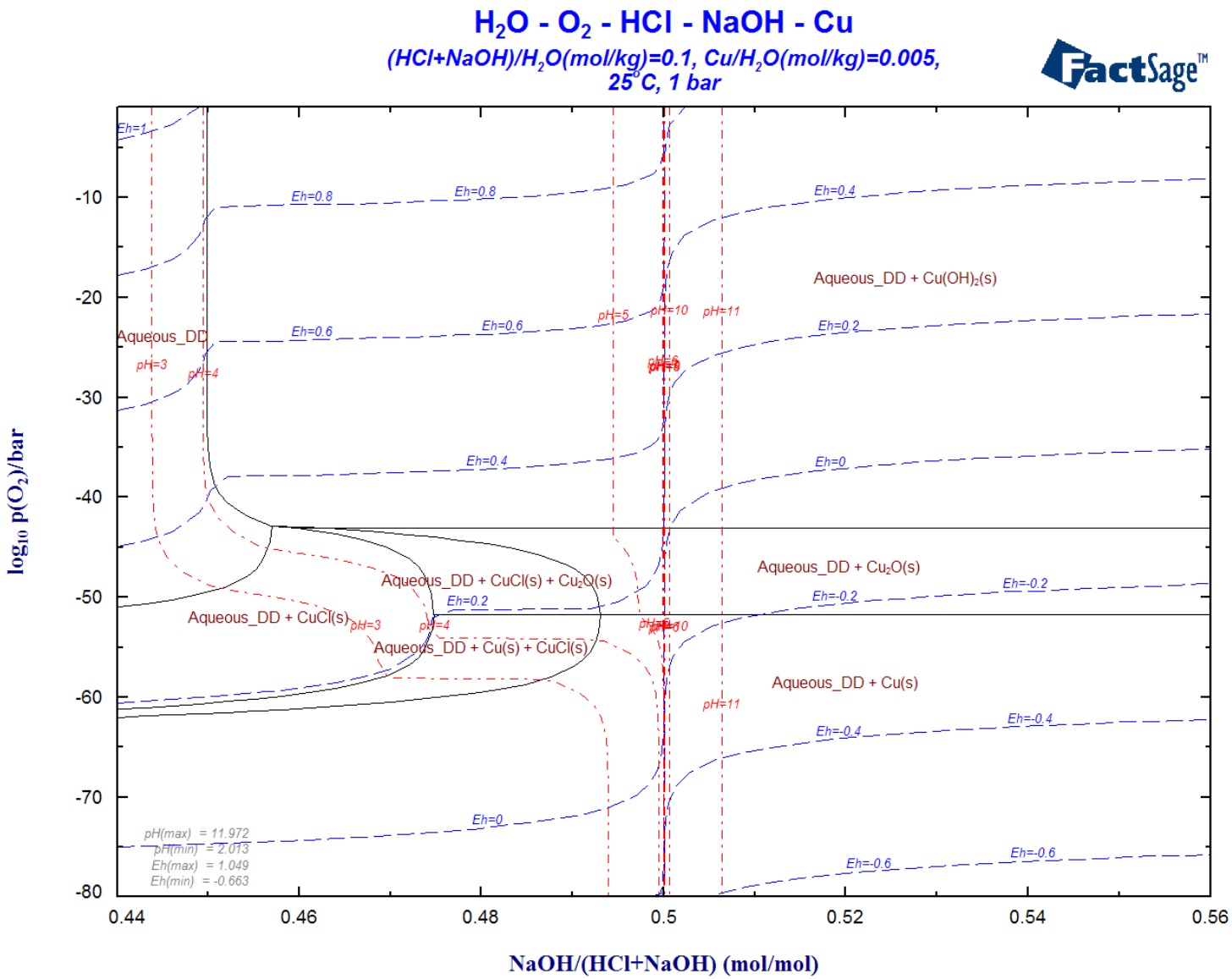


+	Code	Species	Data	Phase	T	V	Activity	Minimum	Maximu
+	70	Na2O(s2)	FactPS	Solid-B		V			
+	71	Na2O(s3)	FactPS	Solid-C		V			
+	72	Na2O2(s)	FactPS	solid		V			
+	73	Na2O2(s2)	FactPS	Solid-2		V			
+	74	NaOH(s)	FactPS	solid		V			
+	75	NaOH(s2)	FactPS	solid		V			
+	76	NaCl(s)	FactPS	Halite_(rock_sal		V			
+	77	NaClO4(s)	FactPS	Solid_I		o			
+	78	NaClO4(s2)	FactPS	Solid_II		o			
+	79	Cu(s)	FactPS	solid		V			
+	80	CuO(s)	FactPS	Tenorite		V			
+	81	Cu2O(s)	FactPS	solid		V			
+	82	Cu(OH)2(s)	FactPS	solid		V			
+	83	CuCl(s)	FactPS	solid		V			
+	84	CuCl2(s)	FactPS	solid		V			
+	85	CuCl2(H2O)2(s)	FactPS	solid		V			
	86	ONa2(s)	FThelg	Na2O		V			
	87	ClNa(s)	FThelg	NaCl		V			
	88	Cu(s)	FThelg	Cu		V			
	89	OCu(s)	FThelg	CuO		V			
	90	OCu2(s)	FThelg	Cu2O		V			

De-select.

Using FThelg non-ideal Helgeson aqueous solution

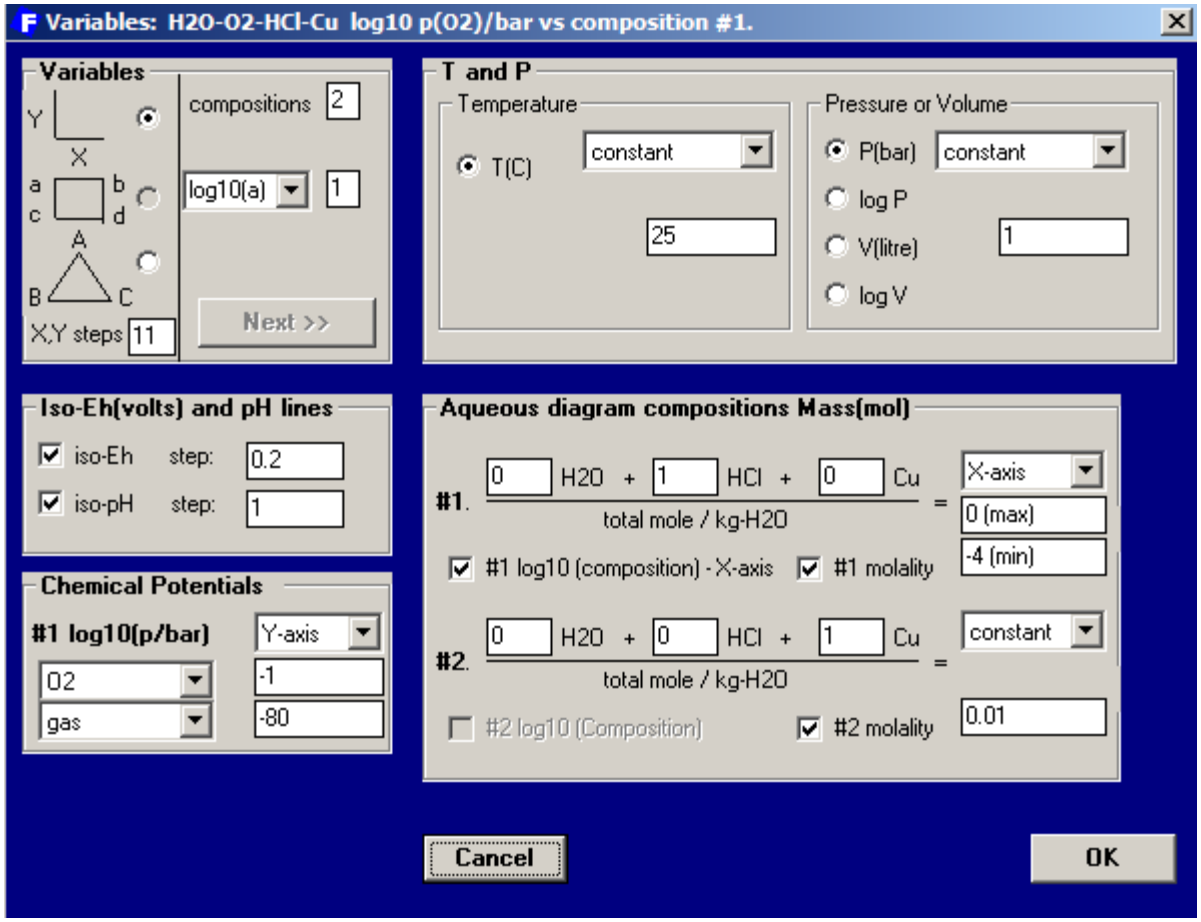
Compare to Slide 19.22



Some phase boundaries are displaced from their positions in Slide 19.22 because ionic interactions are now taken into account.

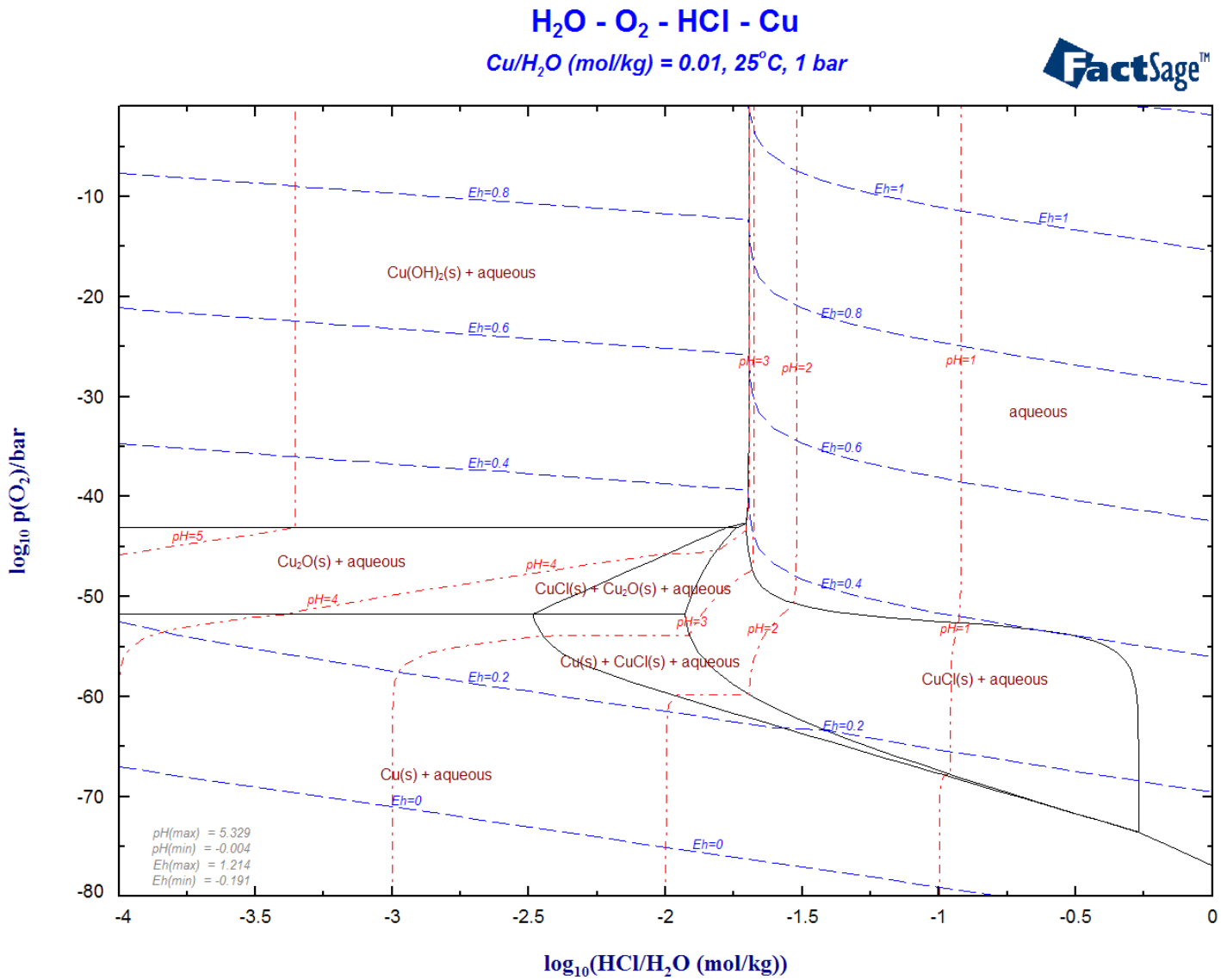
Input for an aqueous H_2O-O_2-HCl-Cu diagram

log m(HCl) as x-axis and oxidation potential as y-axis at constant m(Cu) = 0.01



Aqueous H_2O-O_2-HCl-Cu diagram

log m(HCl) as x-axis and oxidation potential as y-axis at constant m(Cu) = 0.01

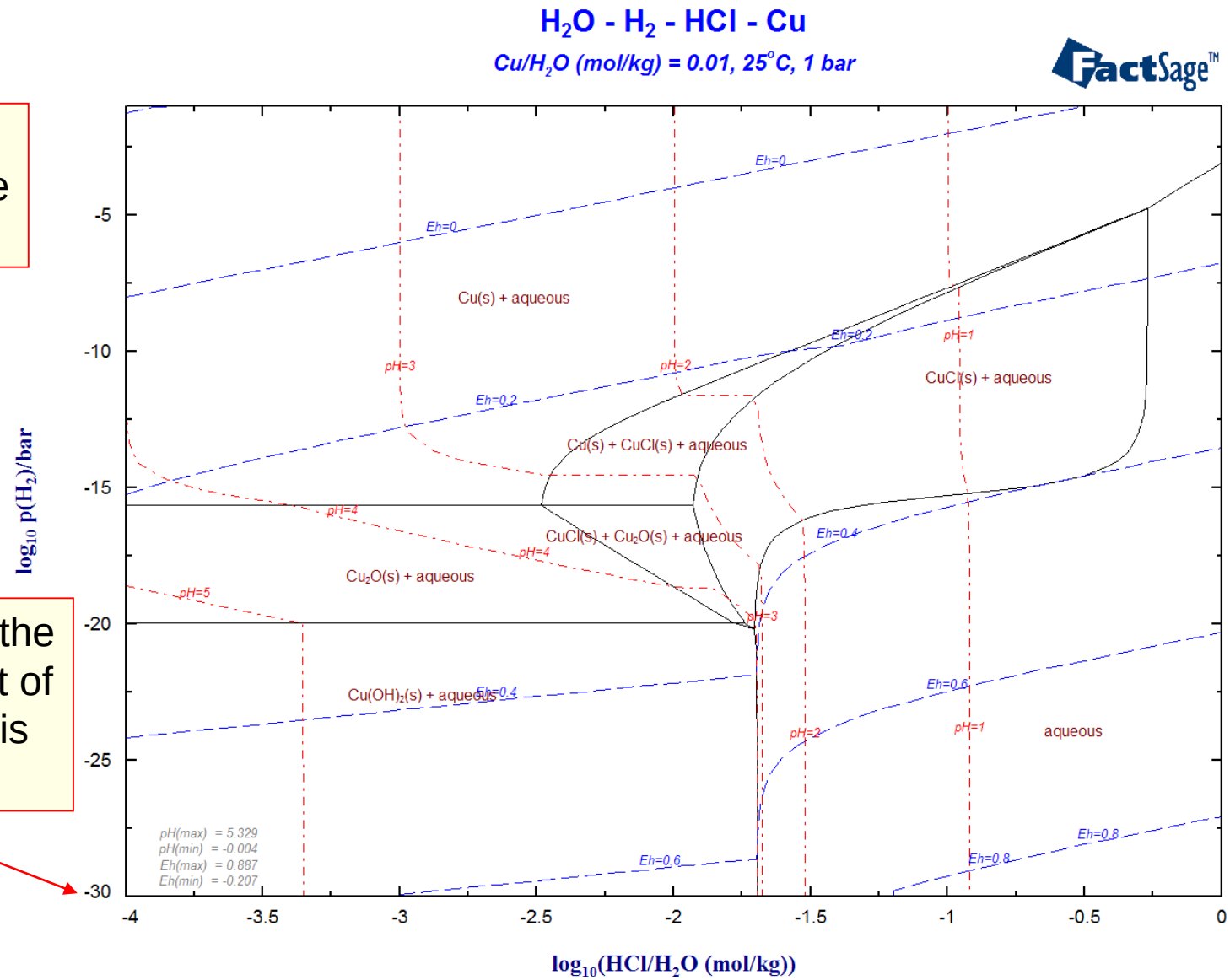


H_2O-O_2-HCl-Cu diagram

log m(HCl) as x-axis and reduction potential, log P(H_2), as y-axis

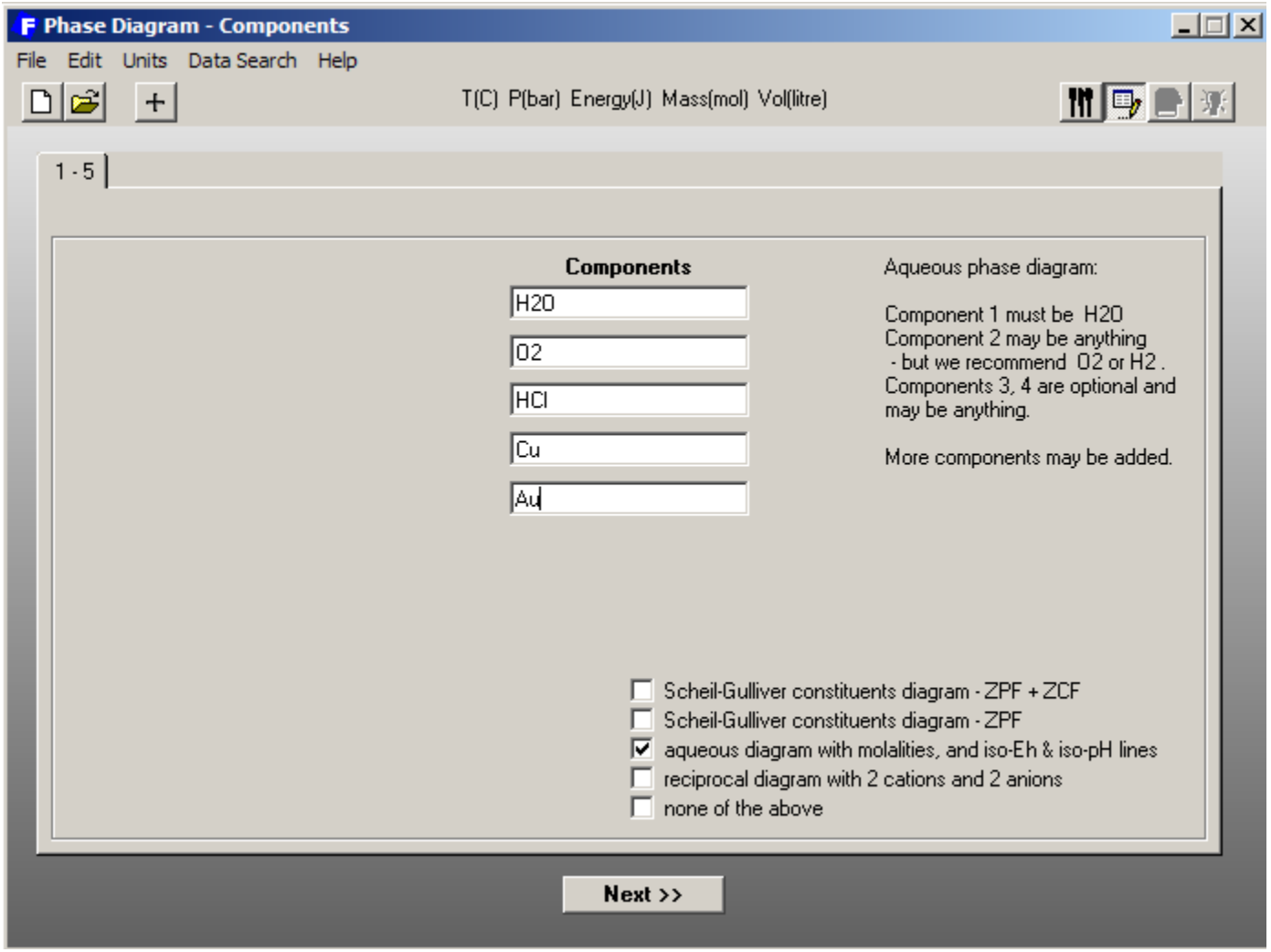
This diagram is, essentially, Slide 19.30 inverted.

When log **P(H_2)** is the y-axis, a lower limit of approximately **-30** is recommended.

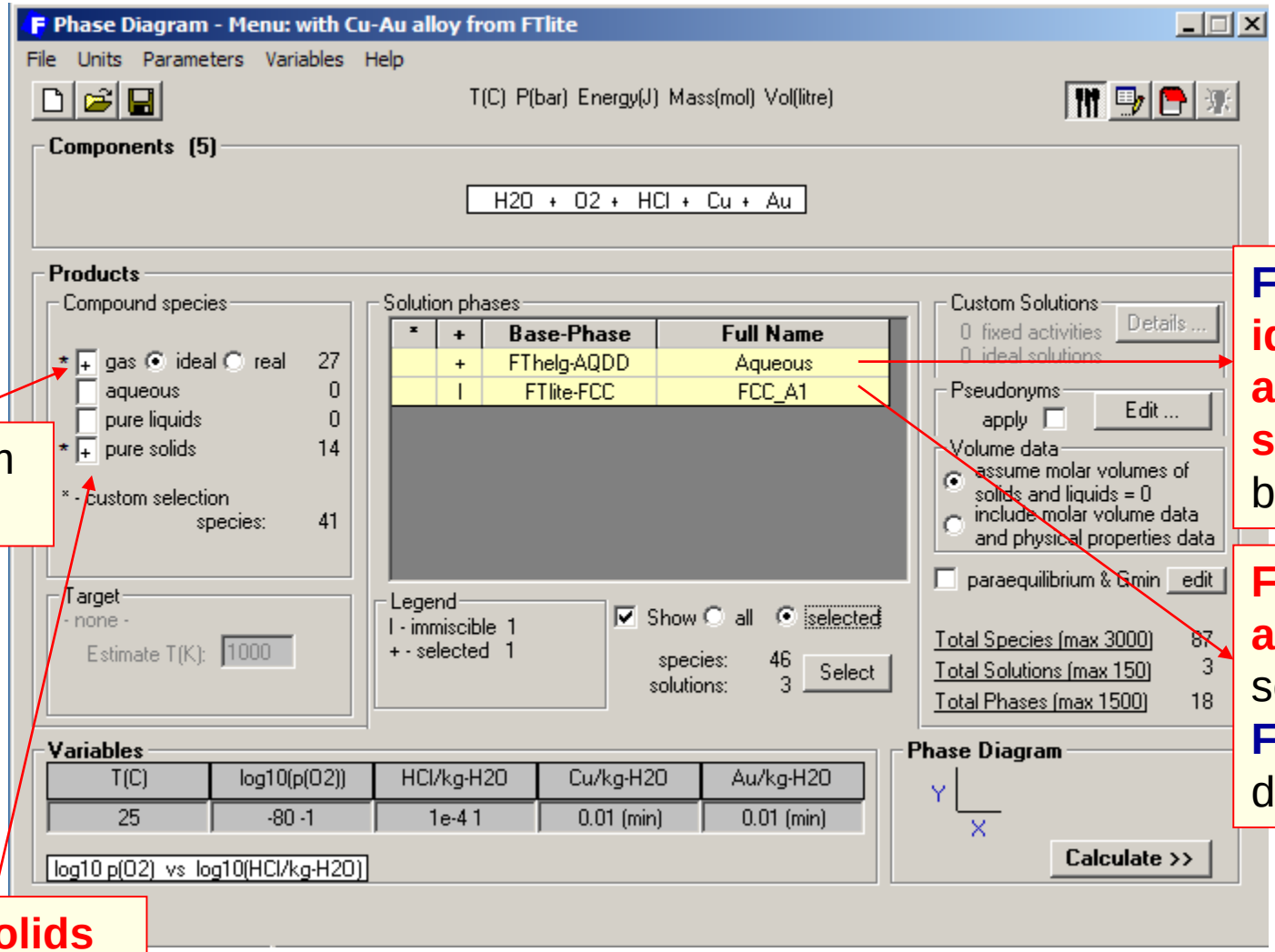


Calculating an aqueous phase diagram with a non-ideal **Cu-Au** alloy

Components window



→ (Input continued from previous Slide – Menu window)



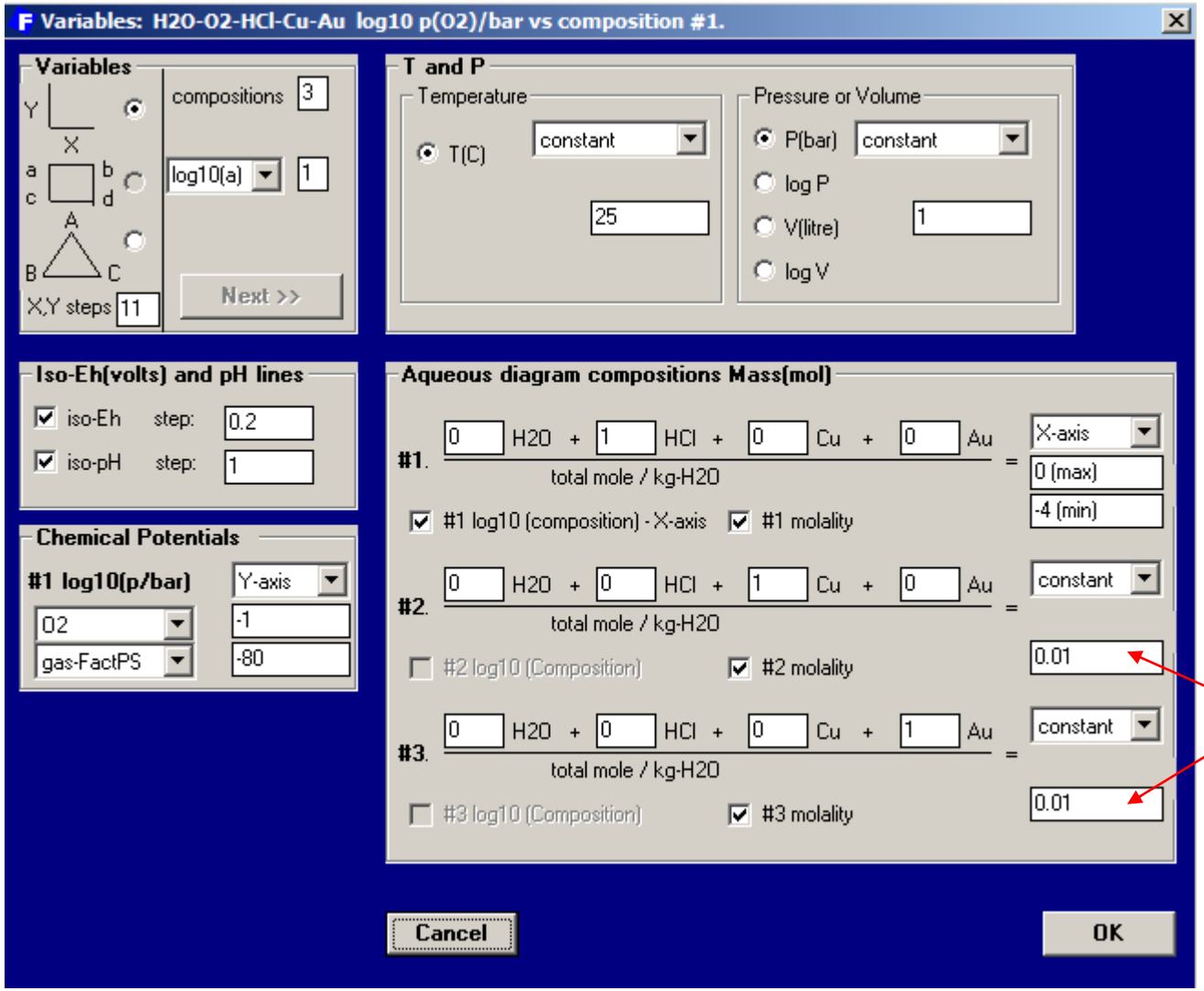
Gas from **FactPS**.

FThelg non-ideal aqueous solution has been selected.

FCC Cu-Au alloy solution selected from **Ftlite** database.

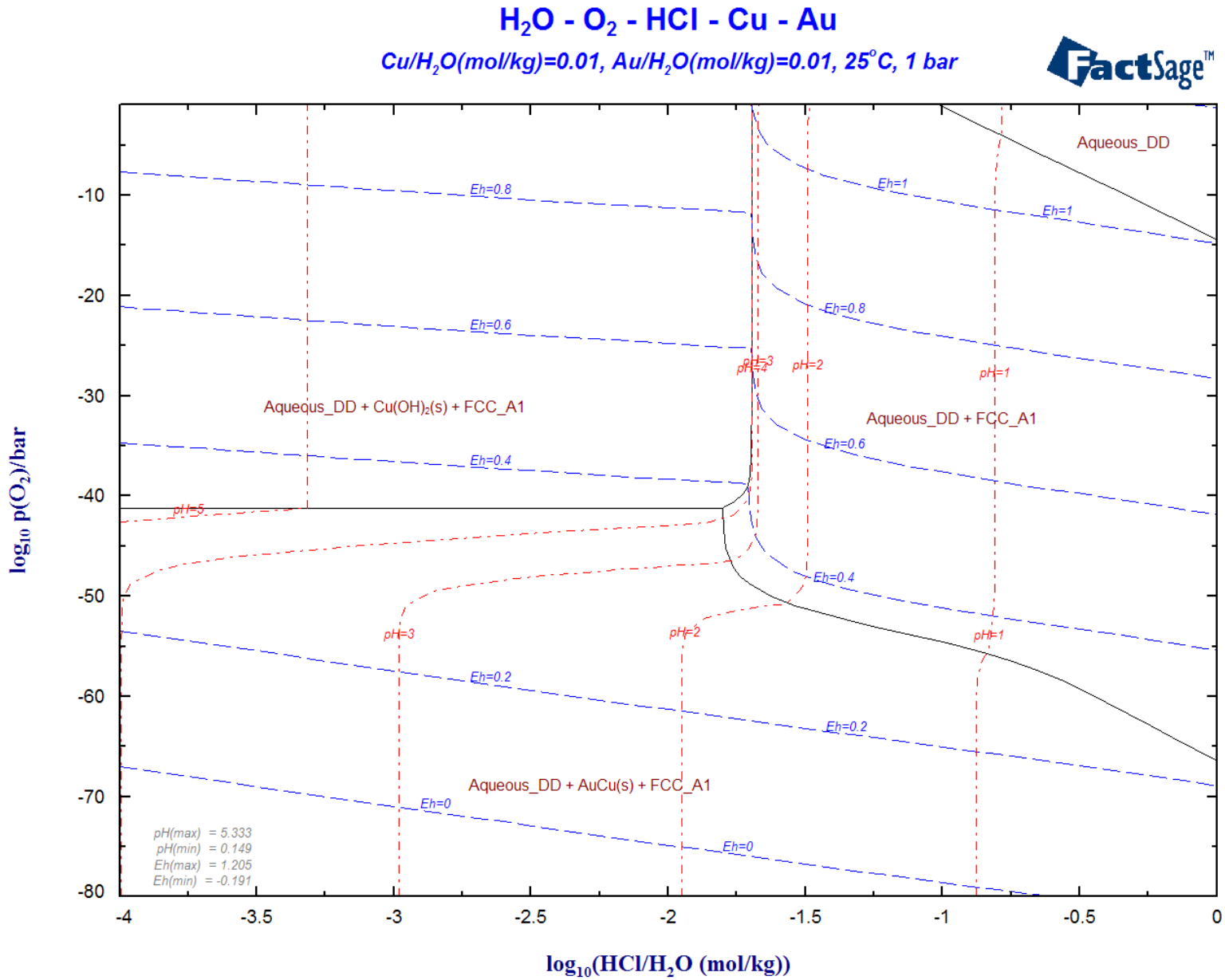
Pure solids from **FactPS**.

(Input continued from previous Slide – Variables window)



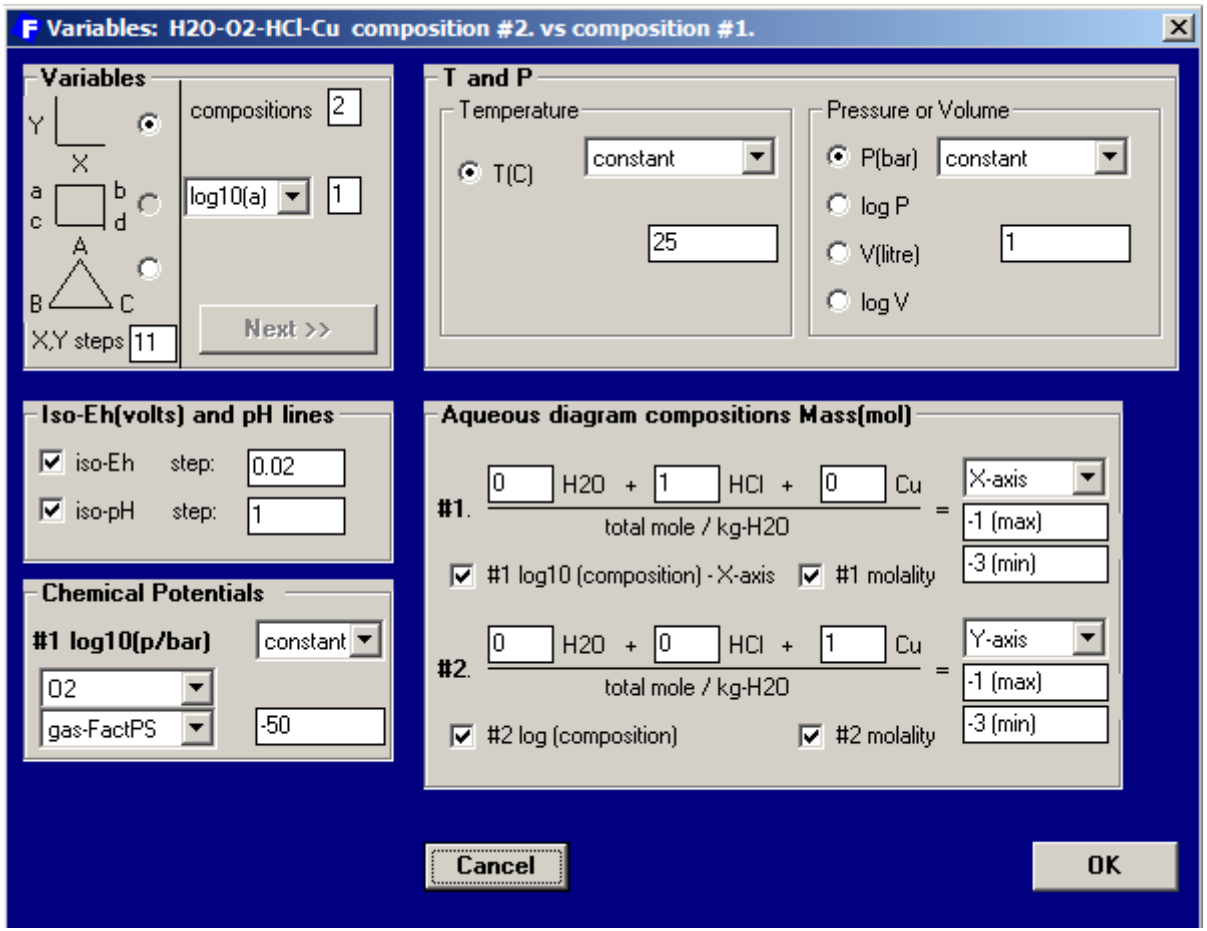
Molalities of Cu and Au held constant.

Aqueous phase diagram involving a non-ideal alloy of Cu and Au



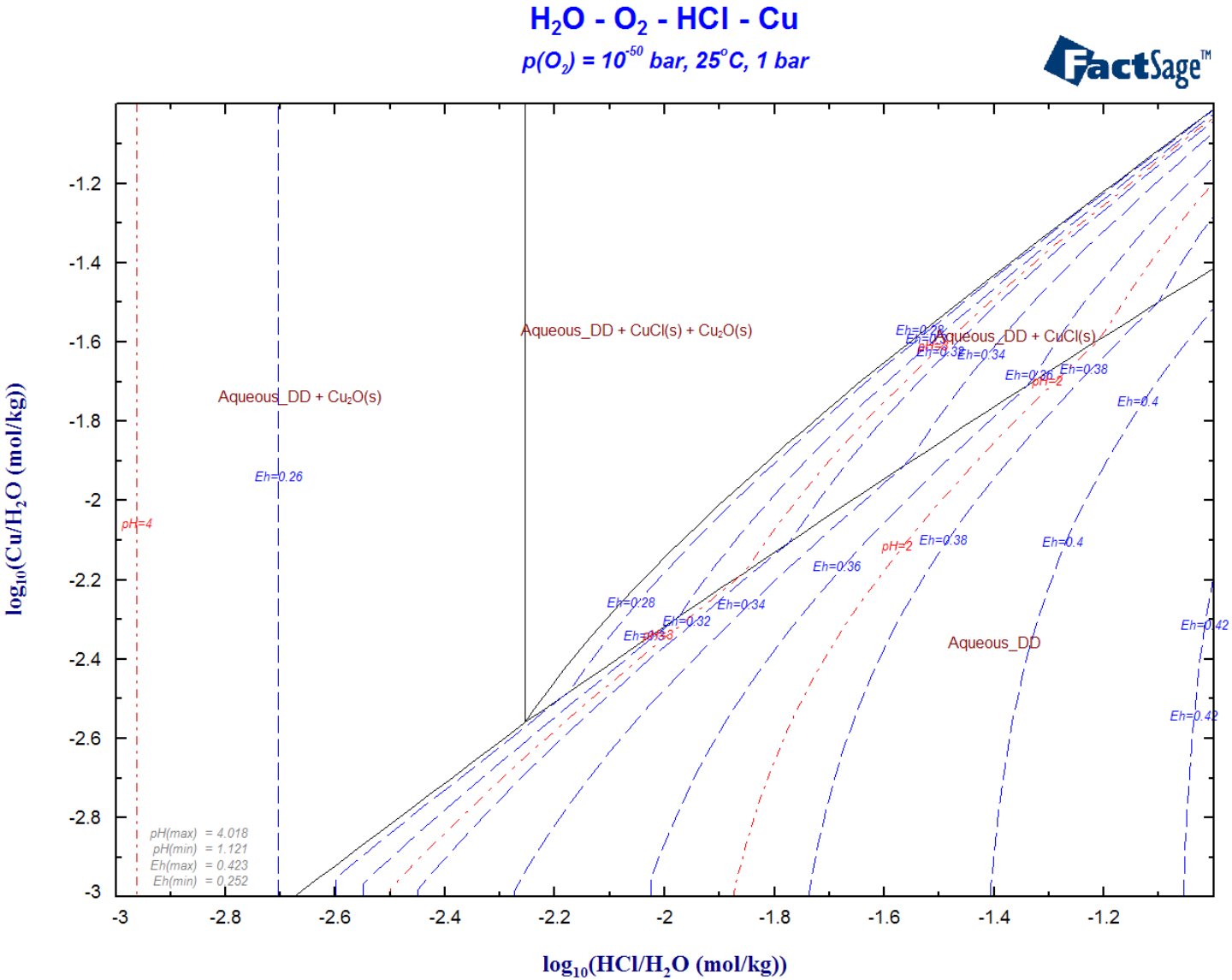
Calculation of an H_2O-O_2-HCl-Cu aqueous diagram

log m(HCl) versus log m(Cu) at constant oxygen potential – Variables window



H_2O-O_2-HCl-Cu aqueous diagram

m(HCl) versus log m(Cu) at constant oxygen potential



Using Zero Phase Fraction lines in graphs

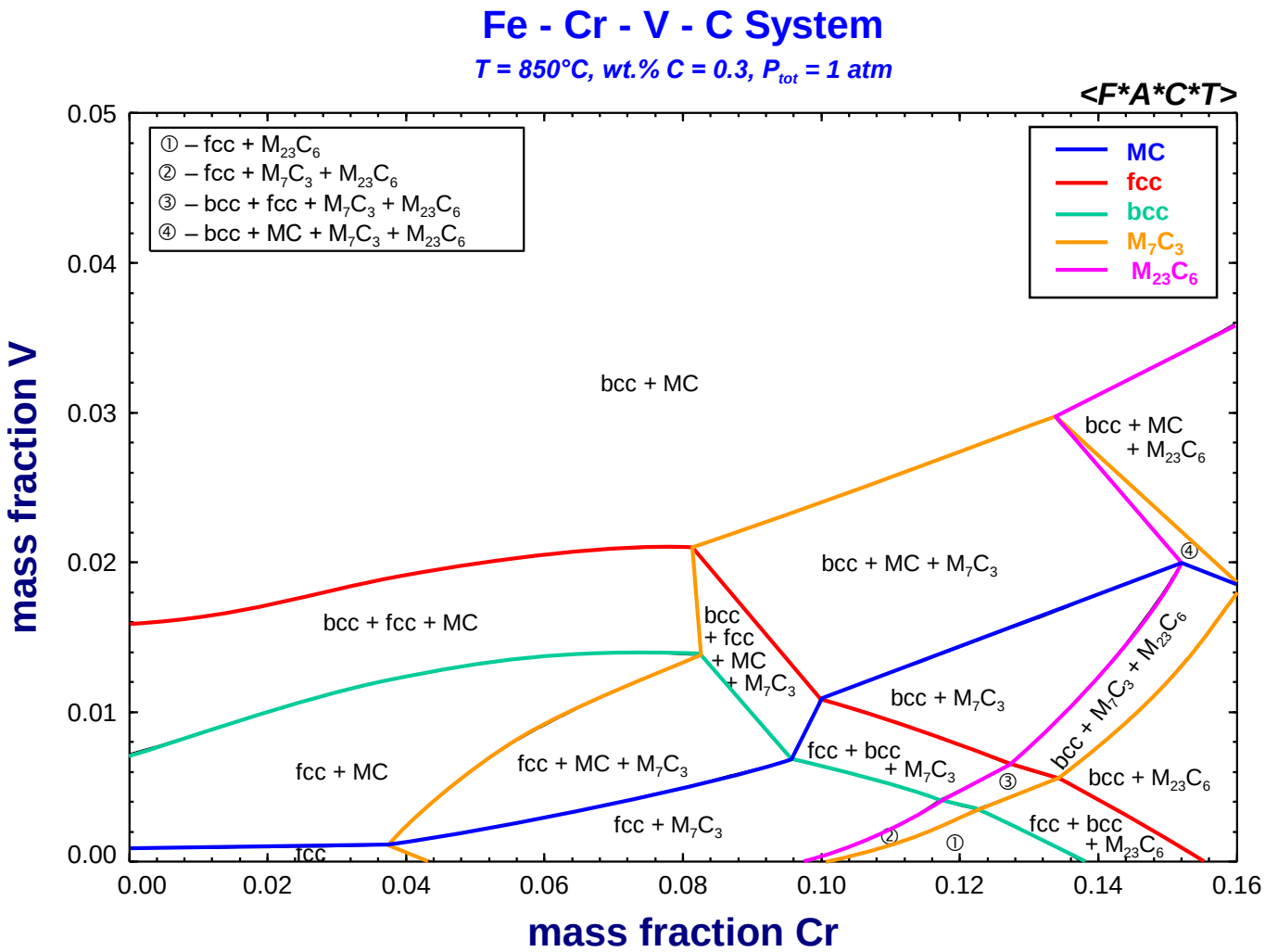
Zero Phase Fraction (ZPF) lines are essential for the calculation and interpretation of the resulting phase diagrams.

ZPF lines constitute the set of phase boundaries in a phase diagram that depict the outer edge of appearance (zero phase fraction) of a particular phase. When crossing the line the phase either appears or disappears depending on the direction.

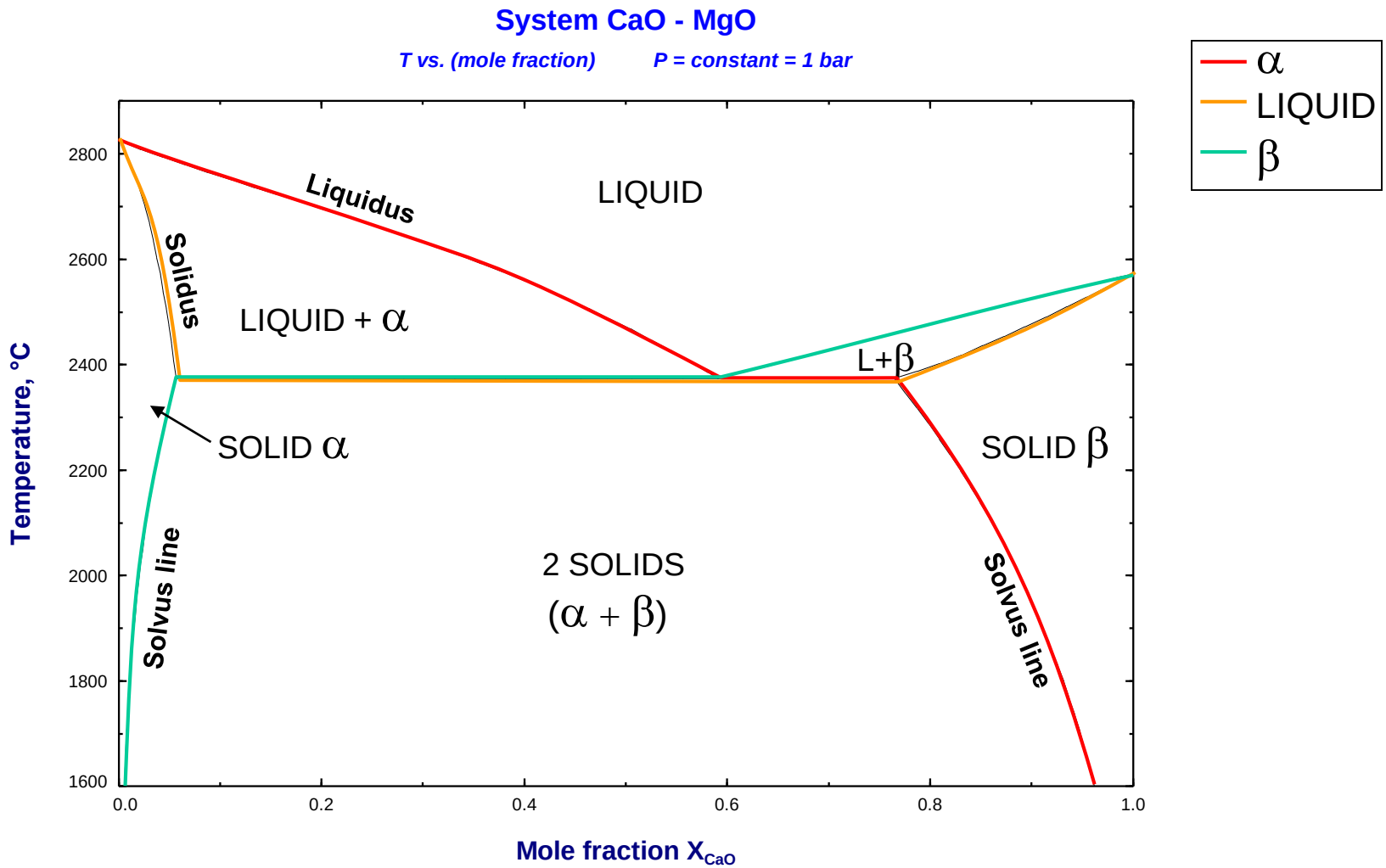
The following three slides show examples of calculated phase diagrams with the ZPF lines marked in color. Slides 15.1 and 15.2 are easy to understand since they both have at least one compositional axis.

Note however, that it is also possible to mark ZPF lines in a predominance area type diagram (slide 15.3) although no phase amounts are given in this type of diagram. As a result the phase boundaries are marked with two colors since the lines themselves are the two phase «fields», i.e. each line is a boundary for TWO phases.

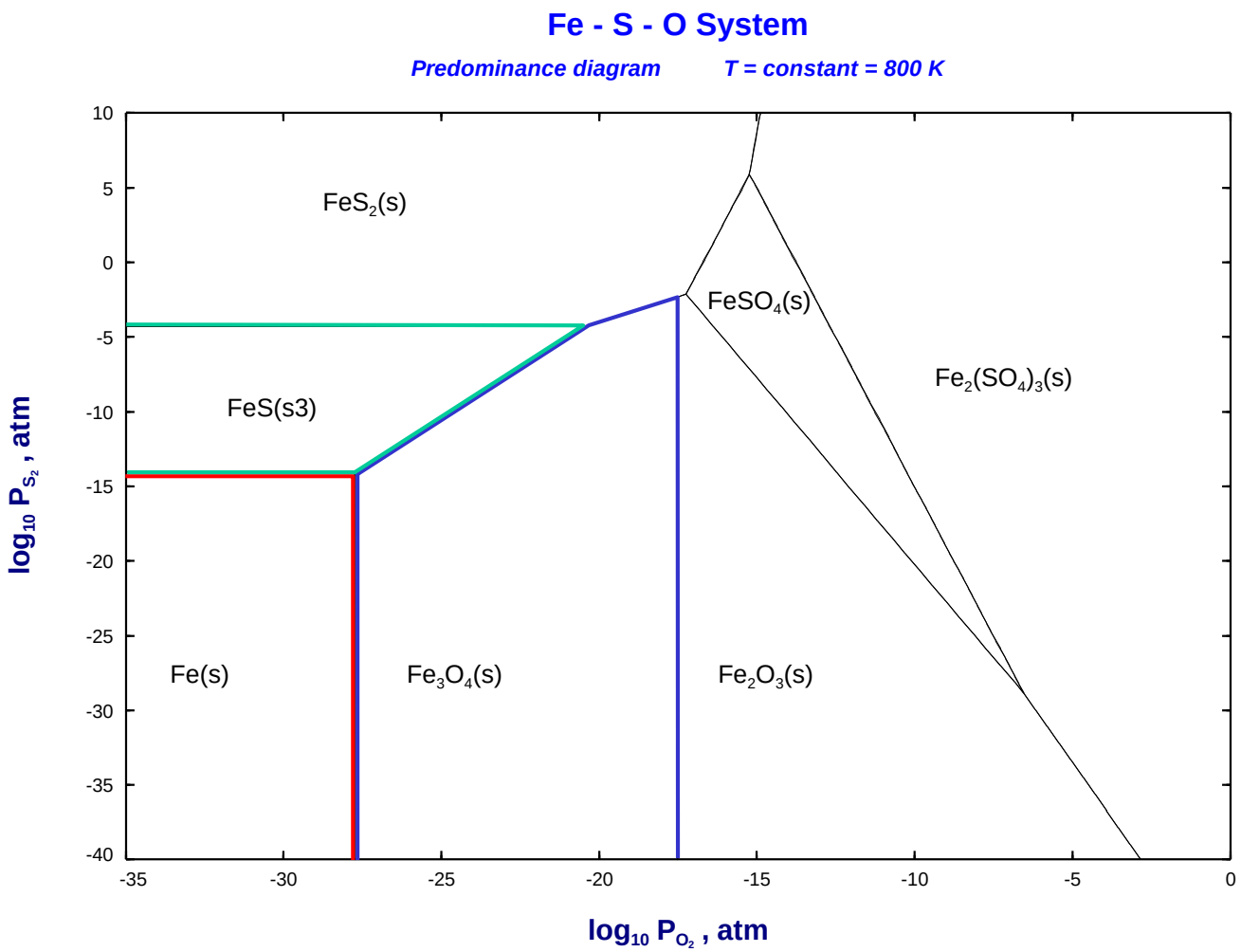
Zero Phase Fraction (ZPF) Lines



Zero Phase Fraction (ZPF) Lines



Fe - S - O Predominance diagram (ZPF lines)



Generalized rules for phase diagrams

The following two slides show the rules for the choice of axes variables such that proper phase diagrams result from the calculation.

The basic relationship for these rules is given by the **Gibbs-Duhem equation** which interrelates a set of potential variables with their respective conjugate extensive variables.

Only one variable from each pair may be used in the definition of the axes variables. If extensive properties are to be used ratios of these need to be employed in the definition of the axes variables.

N-Component System (A-B-C-…-N)

Extensive variable	Corresponding potential
q_i	$\phi_i = \left(\frac{\partial U}{\partial q_i}\right)_{q_j}$
S	T
V	$-P$
n_A	μ_A
n_B	μ_B
.	.
.	.
.	.
n_N	μ_N

$$dU = TdS - PdV + \sum \mu_i dn_i = \sum \phi_i dq_i$$

Gibbs-Duhem: $$SdT + VdP + \sum n_i d\mu_i = \sum q_i d\phi_i = 0$$

N-component system

(1) Choose n potentials: $\phi_1, \phi_2, \ldots, \phi_n \quad (n \le N+1)$

(2) From the non-corresponding extensive variables ($q_{n+1}, q_{n+2}, \ldots$), form (N+1-n) independent ratios ($Q_{n+1}, Q_{n+2}, \ldots, Q_{N+1}$).

Example:

$$Q_i = \frac{q_i}{\sum_{j=n+1}^{N+2} q_j} \qquad (n+1 \le i \le N+1)$$

[$\phi_1, \phi_2, \ldots, \phi_n$; $Q_{n+1}, Q_{n+2}, \ldots, Q_{N+1}$] are then the ($N$+1) variables of which 2 are chosen as axes and the remainder are held constant.

Using the **rules for classical cases**

The following four slides show how the rules outlined above are employed for the selection of proper axes in the case of

the T vs x diagram of the system **CaO-MgO**

and

the log $P(S_2)$ vs log $P(O_2)$ diagram for the system **Fe-Cr-S_2-O_2**.

The calculated phase diagrams are also shown.

MgO-CaO Binary System

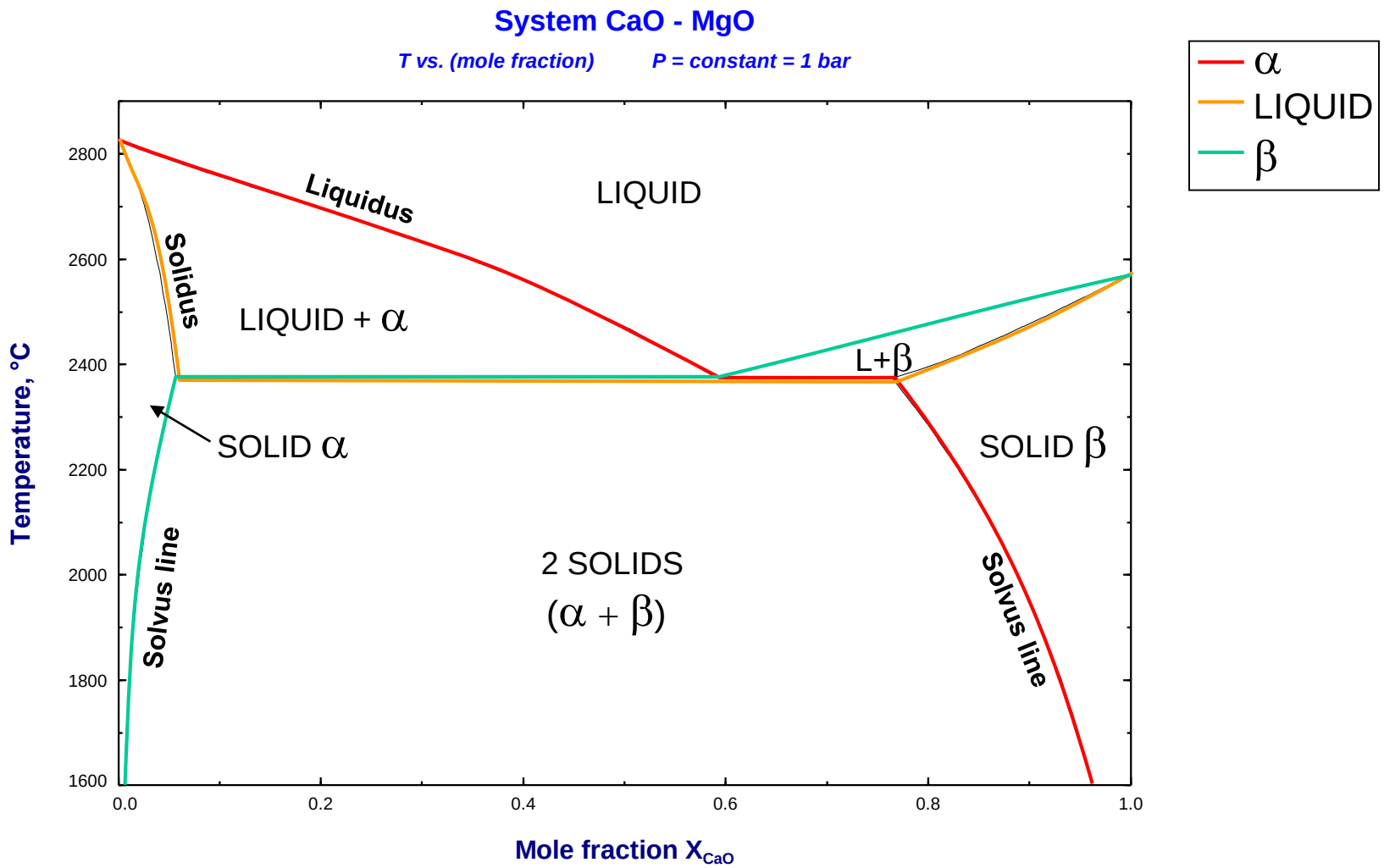
S	T
V	$-P$
n_{MgO}	μ_{MgO}
n_{CaO}	μ_{CaO}

$\phi_1 = T$	*y-axis*
$\phi_2 = -P$	*constant*

$$\left.\begin{array}{l} q_3 = n_{MgO} \\ q_4 = n_{CaO} \end{array}\right\} Q_3 = \frac{n_{CaO}}{\left(n_{MgO} + n_{CaO}\right)}$$

x-axis

T vs x diagram: CaO-MgO System, graphical output



Fe - Cr - S_2 - O_2 System

S	T
V	$-P$
n_{O_2}	μ_{O_2}
n_{S_2}	μ_{S_2}
n_{Fe}	μ_{Fe}
n_{Cr}	μ_{Cr}

$\phi_1 = T$ *constant*

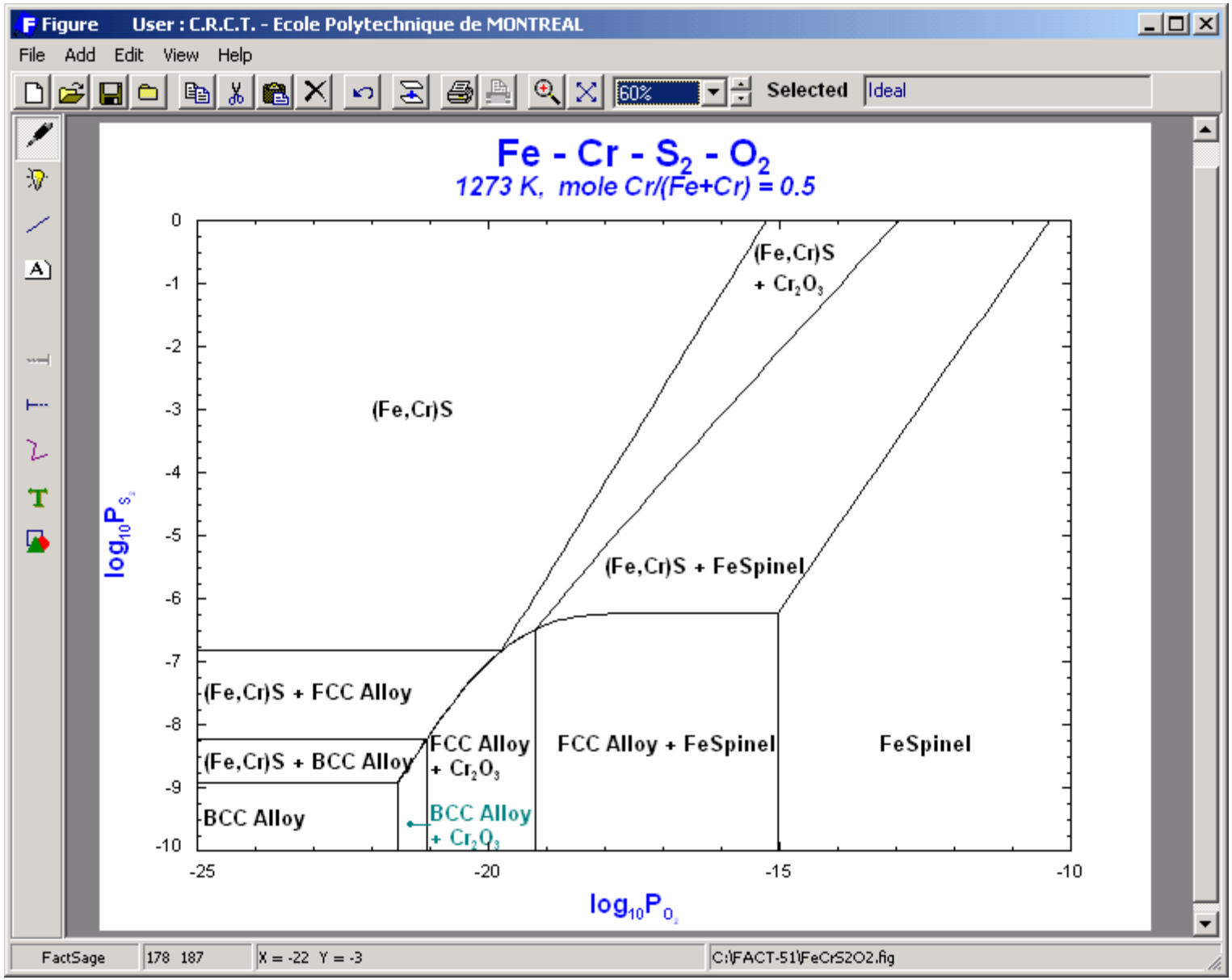
$\phi_2 = -P$ *constant*

$\phi_3 = \mu_{O_2}$ *x-axis*

$\phi_4 = \mu_{S_2}$ *y-axis*

$$\left.\begin{array}{l} q_5 = n_{Cr} \\ q_6 = n_{Fe} \end{array}\right\} Q_5 = \frac{n_{Cr}}{n_{Fe}}$$ *constant*

Predominance area diagram: Fe-Cr-S_2-O_2 System, graphical output



Breaking the rules: Diagrams but not phase diagrams

The following three diagrams will show how the «wrong» choice of axes variables, i.e. combinations which are not permitted according to the rules outlined in slides 14.1 and 14.2, leads to diagrams which
(1) are possible but not permitted in the input of the phase diagram module, and
(2) which are not true phase diagrams (because a unique equilibrium condition is not necessarily represented at every point).

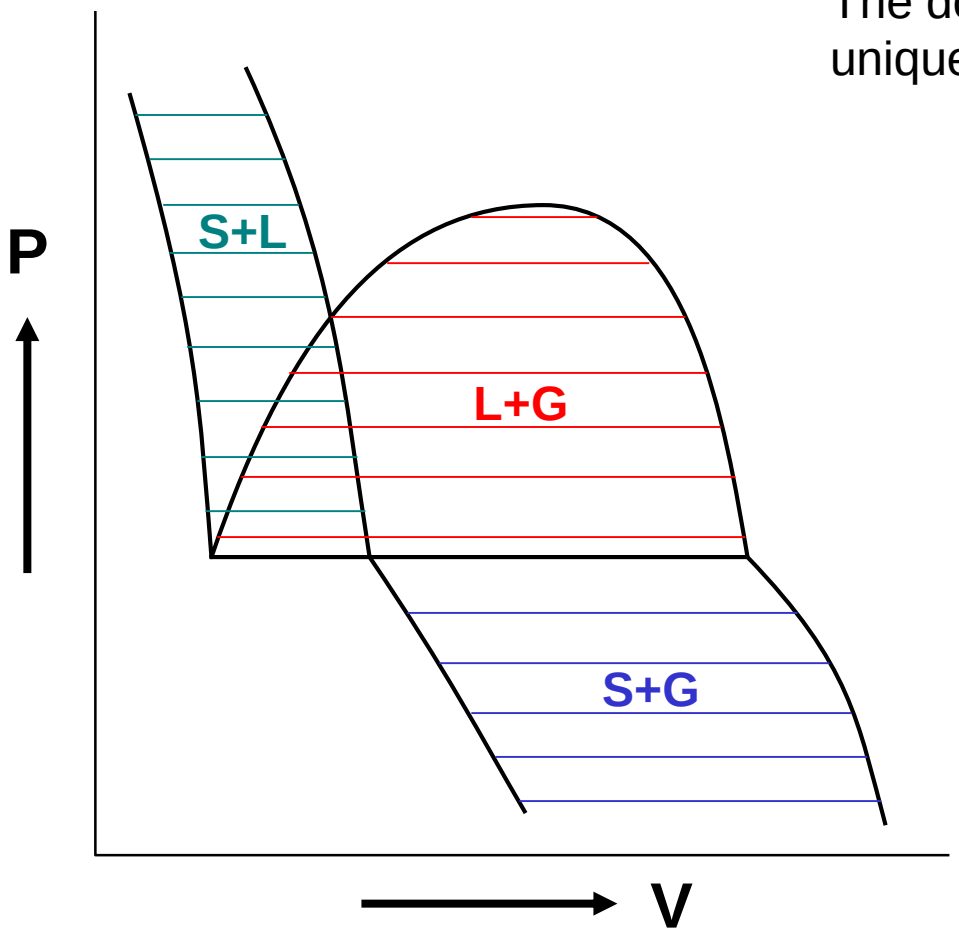
- A simple one component case is the P-V diagram for the **water** system with liquid, gas and solid (Slide 16.1).
- A more complexe case is shown for the ternary system **Fe-Cr-C** where one axis is chosen as activity of carbon while the other is mole fraction of Cr. The case shown is not a true phase diagram because of the way the mole fraction of Cr is defined:

  The total set of mole numbers, i.e. including the mole number of C, is used. Thus both the mole number *and* the activity of carbon are being used for the axes variables. This is *NOT* permitted for true phase diagrams.

Pressure vs. **Volume** diagram for H_2O

This is **NOT** a true phase diagram.

The double marked area can not be uniquely attributed to one set of phases.

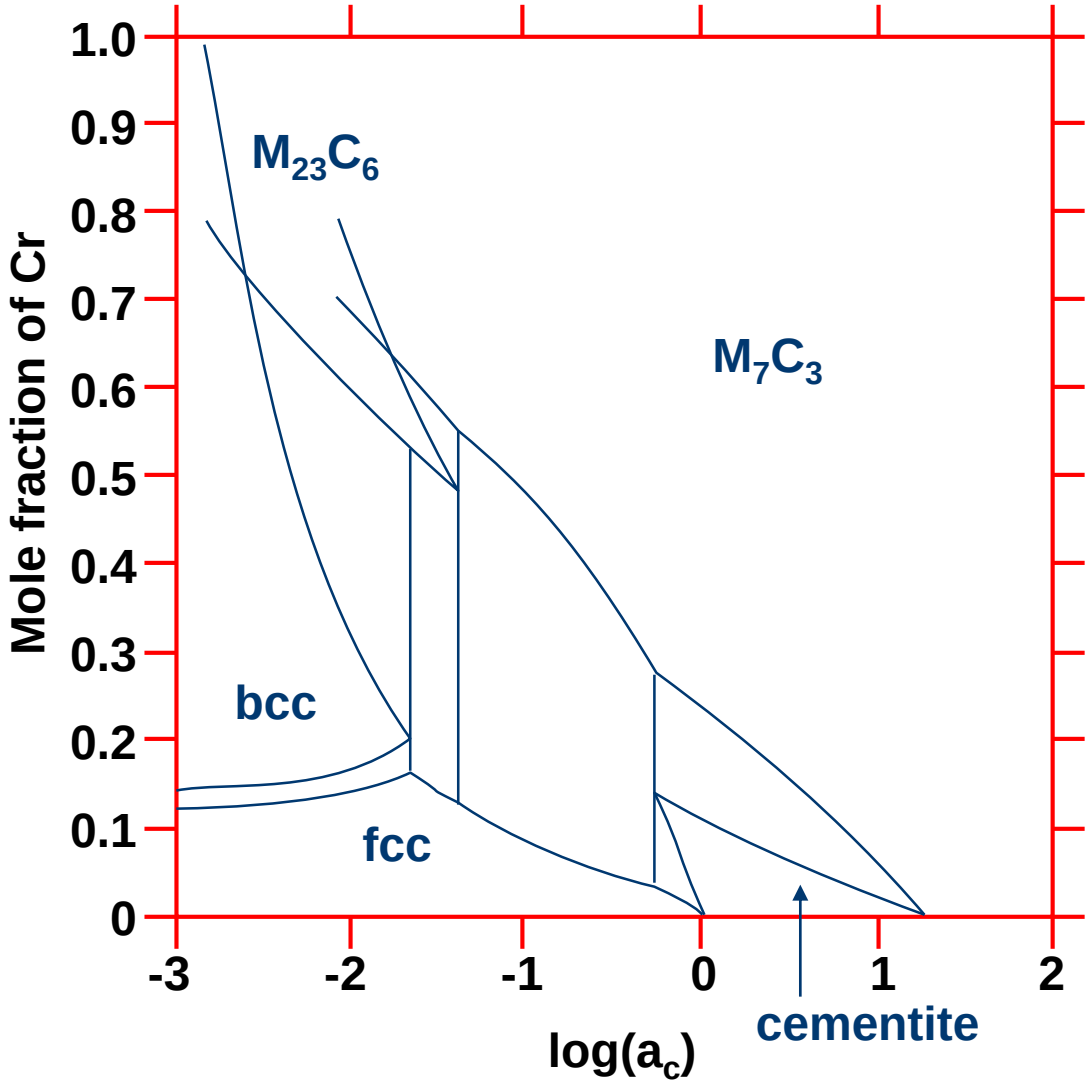


Fe - Cr - C System

S	T
V	$-P$
n_C	μ_C
n_{Fe}	μ_{Fe}
n_{Cr}	μ_{Cr}

$\phi_1 = T$	*constant*
$\phi_2 = -P$	*constant*
$\phi_3 = \mu_C \rightarrow a_C$	*x-axis*
$Q_4 = \dfrac{n_{Cr}}{(n_{Fe} + n_{Cr} + n_C)}$	**(NOT OK)**
$Q_4 = \dfrac{n_{Cr}}{(n_{Fe} + n_{Cr})}$	**(OK)** *y-axis*

Requirement: $\dfrac{dQ_j}{dq_i} = 0 \quad for \quad i \leq 3$

Fe - Cr - C system, T = 1300 K, $X_{Cr} = n_{Cr}/(n_{Fe} + n_{Cr} + n_C)$ vs a_C (carbon activity)

This is **NOT** a true phase diagram.
The areas with the **«swallow tails»** cannot be uniquely attributed to one set of phases.