FactSage Practical
MSE302

Practical 3. Phase Diagram Calculation

Acknowledgements

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Phase Diagram Calculations in FactSage

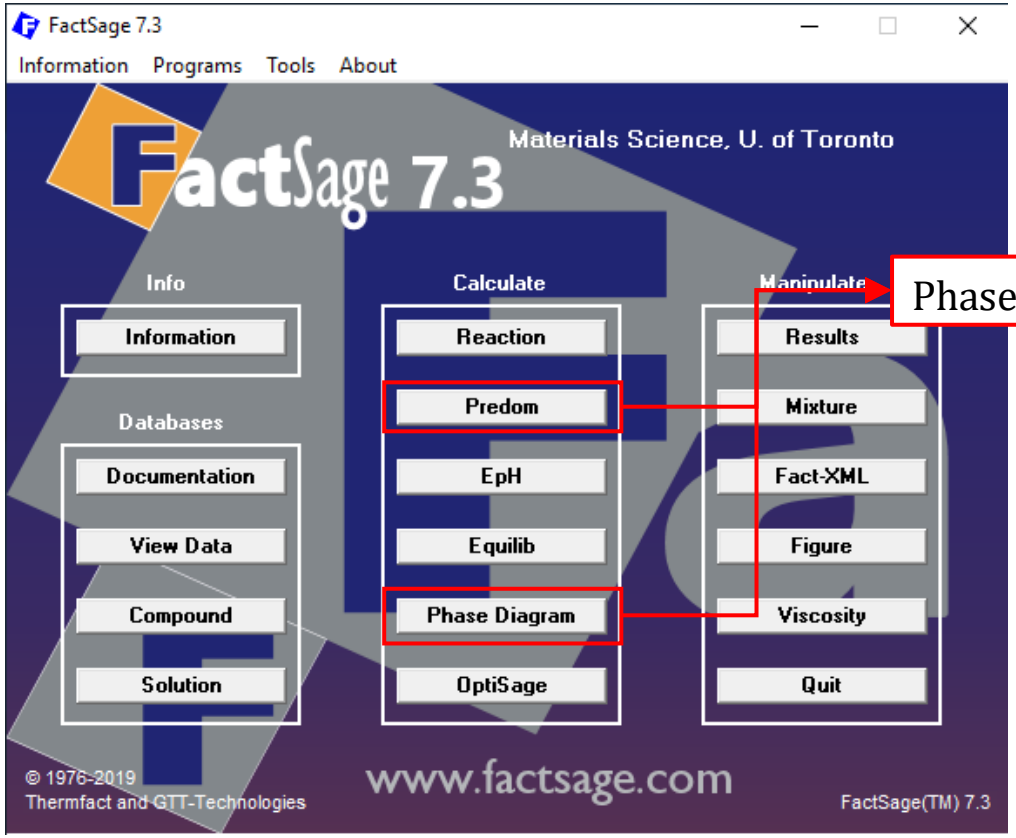
We have already shown in the *FactSage Overview* that there are three modules which are available in FactSage 7.3 for the calculation of phase diagrams:

- ✓ **Predom Module**.
- ✓ **EpH Module**.
- ✓ **Phase Diagram Module**.

In MSE302, since our focus is mainly on the **non-aqueous system**, the EpH module will not be discussed. However, you should be aware that in fields of electrochemistry and hydrometallurgy, the EpH module has found wide applications.

Phase Diagram Calculations in FactSage

Predom Module and **Phase Diagram** Module



Phase Diagram Calculation.

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Practical 3. Phase Diagram Calculation

Predom Module

Predominance Diagram

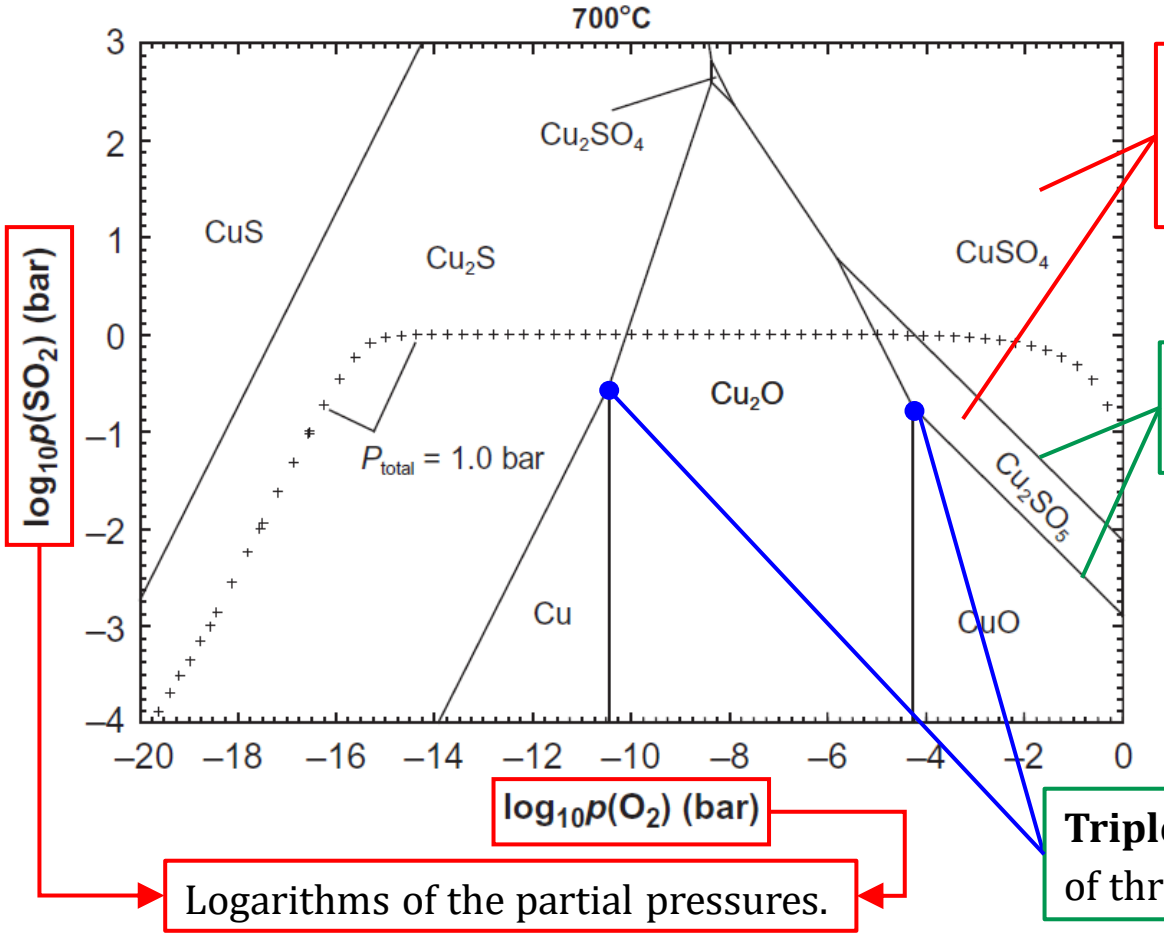
The **predominance diagrams** are a particularly simple type of phase diagram that have many applications in the fields of hot corrosion, chemical vapor deposition, etc.

Let us discuss the construction of a predominance diagram using the Cu-SO_2-O_2 system.

Pelton, Phase Diagrams and Thermodynamic Modeling of Solutions, 2019 (Chapter 2.4.3)

Predominance Diagram: Theoretical Basis

Predominance Diagram of the Cu-SO_2-O_2 System at 700 °C



Areas: domains of stability of various solid compounds of Cu, S and O.

Lines (univariant): coexistence of two solid phases (in equilibrium)

Triple (Invariant) Points: coexistence of three solid phases (in equilibrium).

Logarithms of the partial pressures.

Pelton, Phase Diagrams and Thermodynamic Modeling of Solutions, 2019 (Chapter 2.4.3)

Predominance Diagram: Theoretical Basis

A **predominance diagram** can be constructed by calculating the lines which indicate the coexistence of two solid compounds. The detailed procedure has been discussed by Bale et al.

We formulate a reaction for the formation of each solid phase, always from 1.0 mol of Cu and involving the gaseous species whose pressures are used as the axes; here, we use SO_2 and O_2.

$$Cu + 0.5O_2 = CuO;\ \Delta_r g = \Delta_r g^\circ + RT\ln\left[\left(P_{O_2}\right)^{-0.5}\right]$$

$$Cu + 0.25O_2 = 0.5CuO;\ \Delta_r g = \Delta_r g^\circ + RT\ln\left[\left(P_{O_2}\right)^{-0.25}\right]$$

$$Cu + SO_2 = CuS + O_2;\ \Delta_r g = \Delta_r g^\circ + RT\ln\left[\left(P_{O_2}\right)^{1}\left(P_{SO_2}\right)^{-1}\right]$$

$$Cu + SO_2 + O_2 = CuSO_4;\ \Delta_r g = \Delta_r g^\circ + RT\ln\left[\left(P_{O_2}\right)^{-1}\left(P_{SO_2}\right)^{-1}\right]$$

At equilibrium, $\Delta_r g = 0$, and $\log\left(P_{SO_2}\right)$~$\log\left(P_{O_2}\right)$ can be calculated.

Bale et al. Can. Metall. Q. 25, 107-112
Pelton, Phase Diagrams and Thermodynamic Modeling of Solutions, 2019 (Chapter 2.4.3)

Predominance Diagram: Theoretical Basis

You can repeat the above procedure for the formation of Cu_2S, Cu_2SO_4, and Cu_2SO_5.

You may note that in some equilibrium equations, there is no P_{O_2} or P_{SO_2}. This means that the equilibrium between two solid compounds are independent of P_{O_2} or P_{SO_2}, and the lines would be horizontal or vertical.

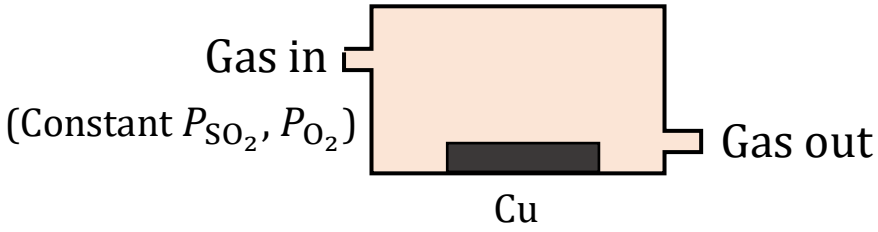
Also, by reformulating the reaction for the formation of each solid phase, in terms of, for example, S_2 and O_2 rather than SO_2 and O_2, a predominance diagram with logarithms of P_{S_2} and P_{O_2} as axes can be constructed.

Pelton, Phase Diagrams and Thermodynamic Modeling of Solutions, 2019 (Chapter 2.4.3)

Predominance Diagram: Theoretical Basis

Application I of Predominance Diagram

Say we introduce a large amount of SO_2 and O_2 into a system, the gas mixture reacts with a small amount of Cu. Because the amount of Cu is small, the change in the gas composition is negligible. If we adjust P_{SO_2} and P_{O_2}, different products would result. A predominance diagram of Cu-SO_2-O_2 can be used to study this problem.

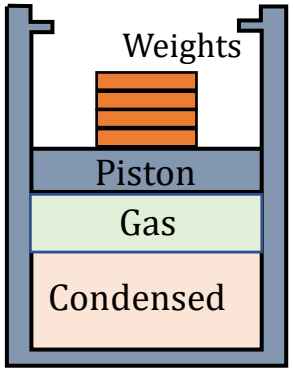


Pelton, Phase Diagrams and Thermodynamic Modeling of Solutions, 2019 (Chapter 2.4.3)

Predominance Diagram: Theoretical Basis

Application II of Predominance Diagram

You may notice from the predominance diagram of the Cu-SO_2-O_2 system, there is a curve shown by the crosses. Along this curve, the **total (hydrostatic) pressure** is 1.0 bar.



We can fix a constant **hydrostatic** pressure of 1 bar by placing the system in a cylinder fitted with a piston (left graph). Under this condition, if the gas phase is present, then the gas phase consists not only of SO_2 and O_2, but also of other species such as S_2, S_3, O_3, etc. whose equilibrium partial pressures can be calculated.

It is noted that when the total (hydrostatic) pressure is controlled, P_{SO_2} and P_{O_2} can not be independently varied.

Pelton, Phase Diagrams and Thermodynamic Modeling of Solutions, 2019 (Chapter 2.4.3)

Predominance Diagram: Theoretical Basis

Application II of Predominance Diagram

The cross line is used to study the system's equilibria when we have a closed system and the total (hydrostatic) pressure is controlled. Above the total pressure line, the total pressure is greater than 1.0 bar even though the sum of the partial pressures of SO_2 and O_2 might be less than 1.0 bar. Caution must therefore be exercised using such diagrams. If the total pressure is **no** greater than 1.0 bar, states above the $P_{\text{total}} = 1.0$ bar are inaccessible. In other words, the calculated diagram for a total (hydrostatic) pressure of 1.0 bar terminates at this line.

Pelton, Phase Diagrams and Thermodynamic Modeling of Solutions, 2019 (Chapter 2.4.3)

Predom Module: Cu-S-O System

The Predom Module allows you to calculate predominance diagrams. These diagrams are calculated under quite restrictive conditions.

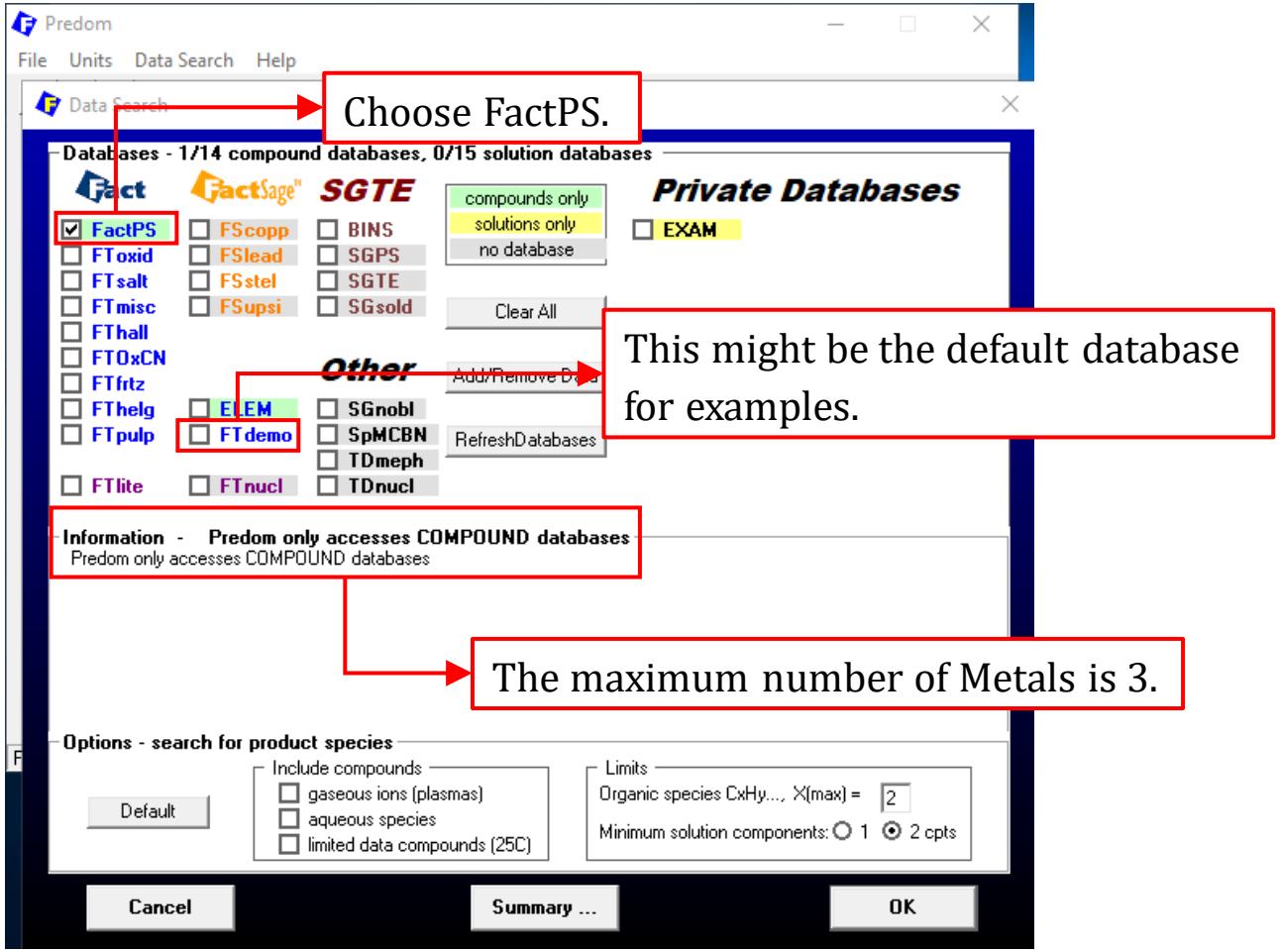
- ✓ **Only** compound databases are accessed.
- ✓ Temperature is fixed (isothermal calculation).

The partial pressures are permitted to vary for non-metallic species, and the total pressure which is the sum of the partial pressures of all species can also vary.

Again, before you work on your project, check the Directory!!!

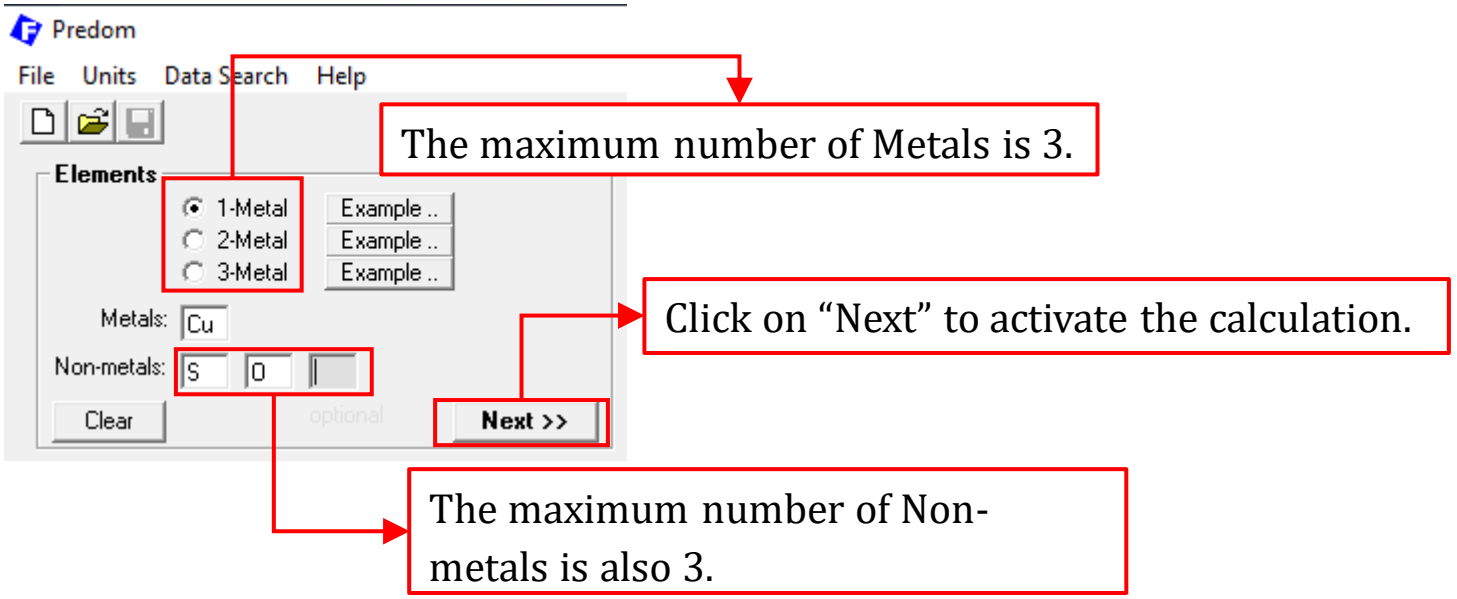
Predom Module: Cu-S-O System

Database Selection



Predom Module: Cu-S-O System

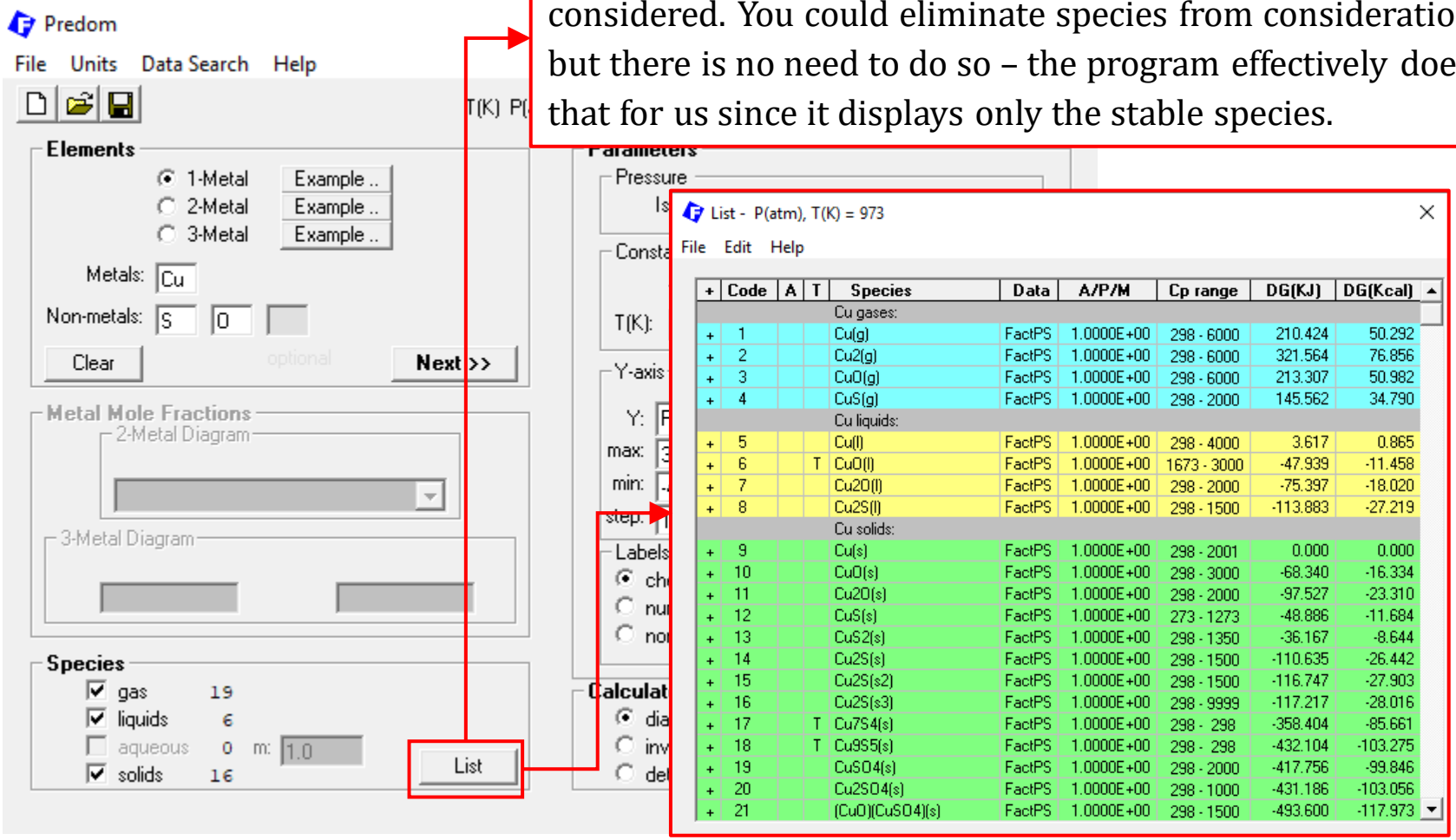
Define **Elements**: Metals and Non-metals



Predom Module: Cu-S-O System

Define **List of Species**

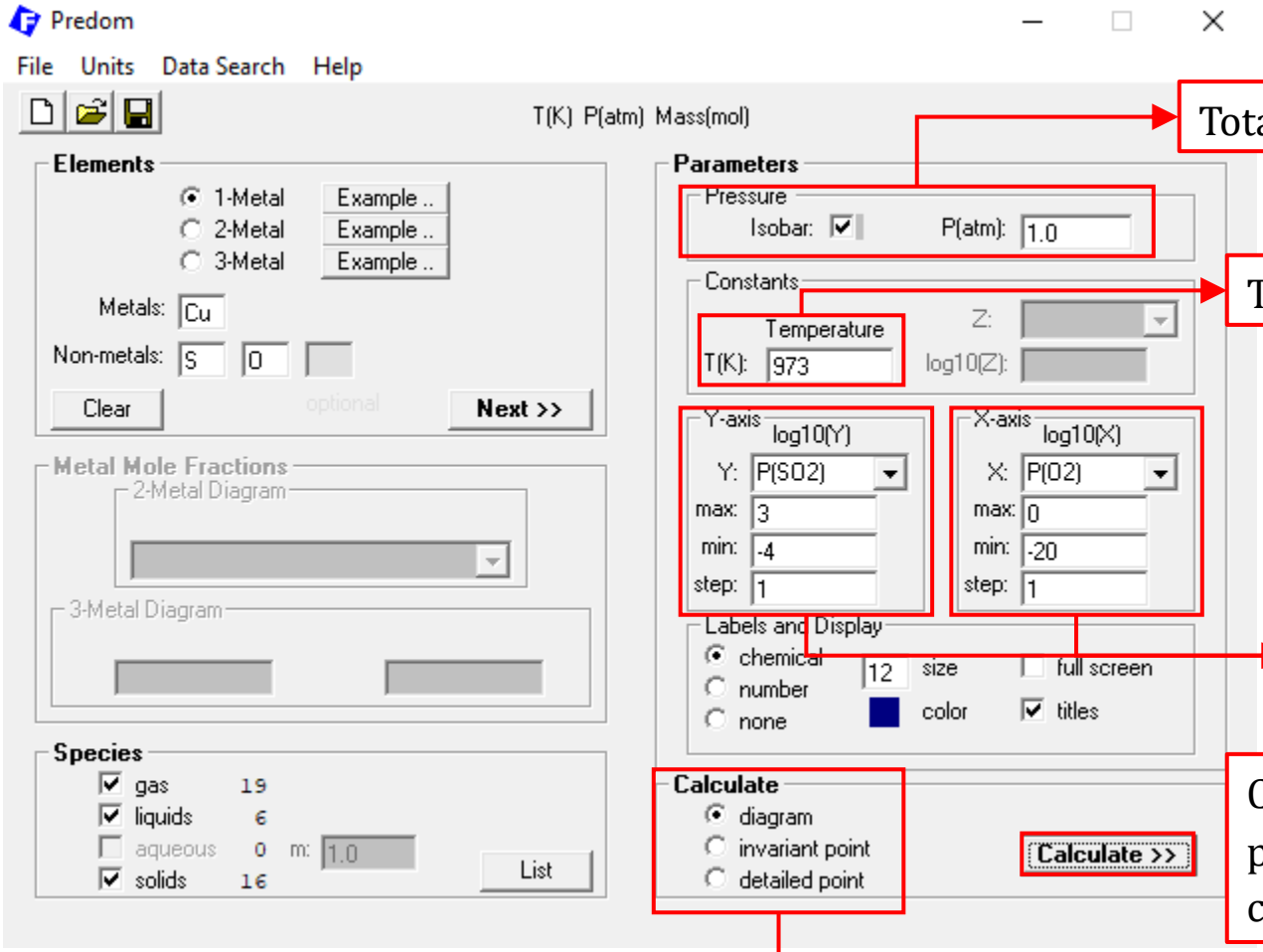
Click on "List" to see all the species that are going to be considered. You could eliminate species from consideration, but there is no need to do so – the program effectively does that for us since it displays only the stable species.



+	Code	A	T	Species	Data	A/P/M	Cp range	DG(KJ)	DG(Kcal)
				Cu gases:					
+	1			Cu(g)	FactPS	1.0000E+00	298 - 6000	210.424	50.292
+	2			Cu2(g)	FactPS	1.0000E+00	298 - 6000	321.564	76.856
+	3			CuO(g)	FactPS	1.0000E+00	298 - 6000	213.307	50.982
+	4			CuS(g)	FactPS	1.0000E+00	298 - 2000	145.562	34.790
				Cu liquids:					
+	5			Cu(l)	FactPS	1.0000E+00	298 - 4000	3.617	0.865
+	6		T	CuO(l)	FactPS	1.0000E+00	1673 - 3000	-47.939	-11.458
+	7			Cu2O(l)	FactPS	1.0000E+00	298 - 2000	-75.397	-18.020
+	8			Cu2S(l)	FactPS	1.0000E+00	298 - 1500	-113.883	-27.219
				Cu solids:					
+	9			Cu(s)	FactPS	1.0000E+00	298 - 2001	0.000	0.000
+	10			CuO(s)	FactPS	1.0000E+00	298 - 3000	-68.340	-16.334
+	11			Cu2O(s)	FactPS	1.0000E+00	298 - 2000	-97.527	-23.310
+	12			CuS(s)	FactPS	1.0000E+00	273 - 1273	-48.886	-11.684
+	13			CuS2(s)	FactPS	1.0000E+00	298 - 1350	-36.167	-8.644
+	14			Cu2S(s)	FactPS	1.0000E+00	298 - 1500	-110.635	-26.442
+	15			Cu2S(s2)	FactPS	1.0000E+00	298 - 1500	-116.747	-27.903
+	16			Cu2S(s3)	FactPS	1.0000E+00	298 - 9999	-117.217	-28.016
+	17		T	Cu7S4(s)	FactPS	1.0000E+00	298 - 298	-358.404	-85.661
+	18		T	Cu9S5(s)	FactPS	1.0000E+00	298 - 298	-432.104	-103.275
+	19			CuSO4(s)	FactPS	1.0000E+00	298 - 2000	-417.756	-99.846
+	20			Cu2SO4(s)	FactPS	1.0000E+00	298 - 1000	-431.186	-103.056
+	21			(CuO)(CuSO4)(s)	FactPS	1.0000E+00	298 - 1500	-493.600	-117.973

Predom Module: Cu-S-O System

Define **Parameters**: Pressures and Temperature



Total hydrostatic pressure.

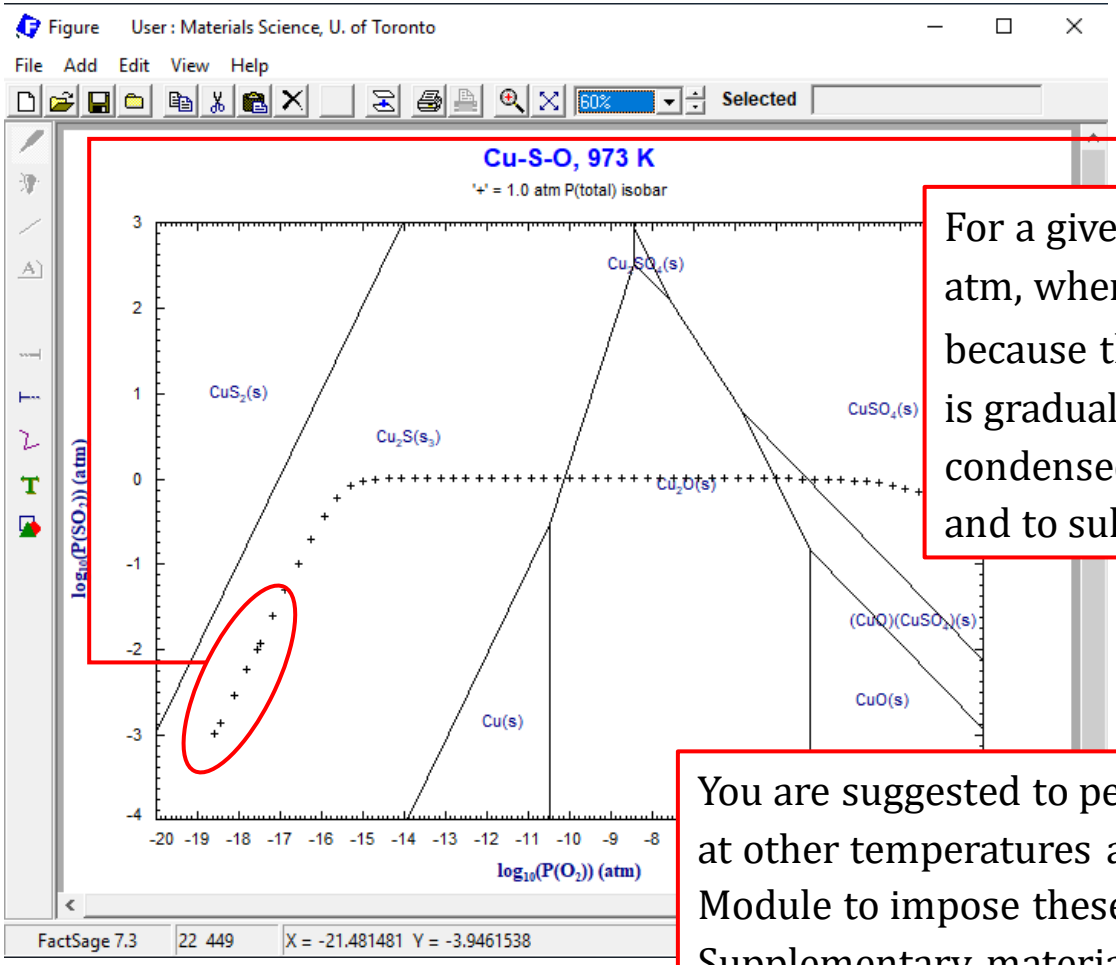
Temperature is 700 °C.

Axes: partial pressures of species.

Choose “diagram”. The triple points can be calculated by choosing “invariant point”.

Predom Module: Cu-S-O System

Define **Parameters**: Pressures and Temperature

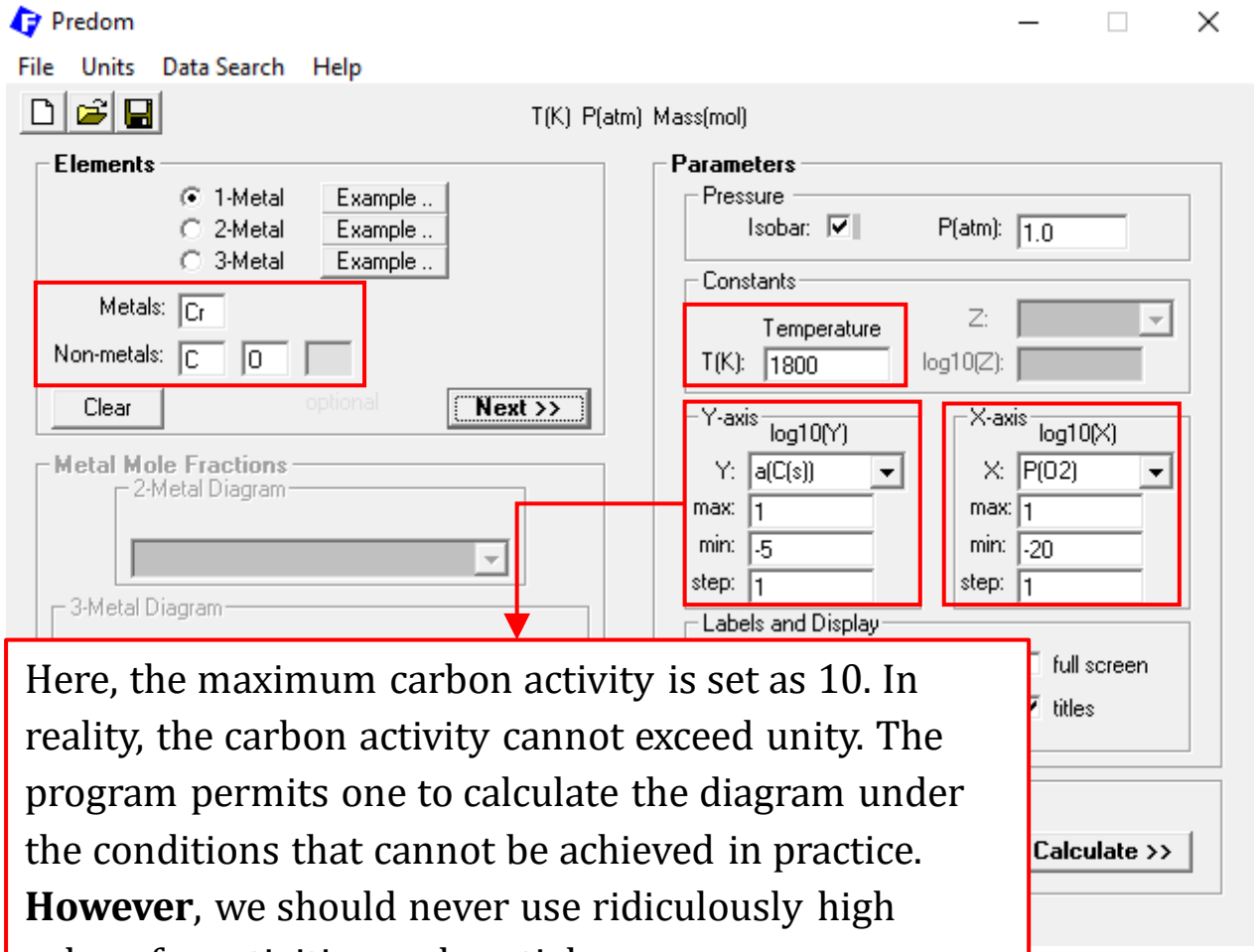


For a given total hydrostatic pressure of 1 atm, when P_{O_2} is low, P_{SO_2} is also low. This is because that P_{S_2} is high. As P_{O_2} increases, S_2 is gradually converted to SO_2 and the condensed phases go from a sulfide to oxide, and to sulfate.

You are suggested to perform the calculations at other temperatures and use the Figure Module to impose these diagrams (See the Supplementary material).

Predom Module: Cr-C-O System

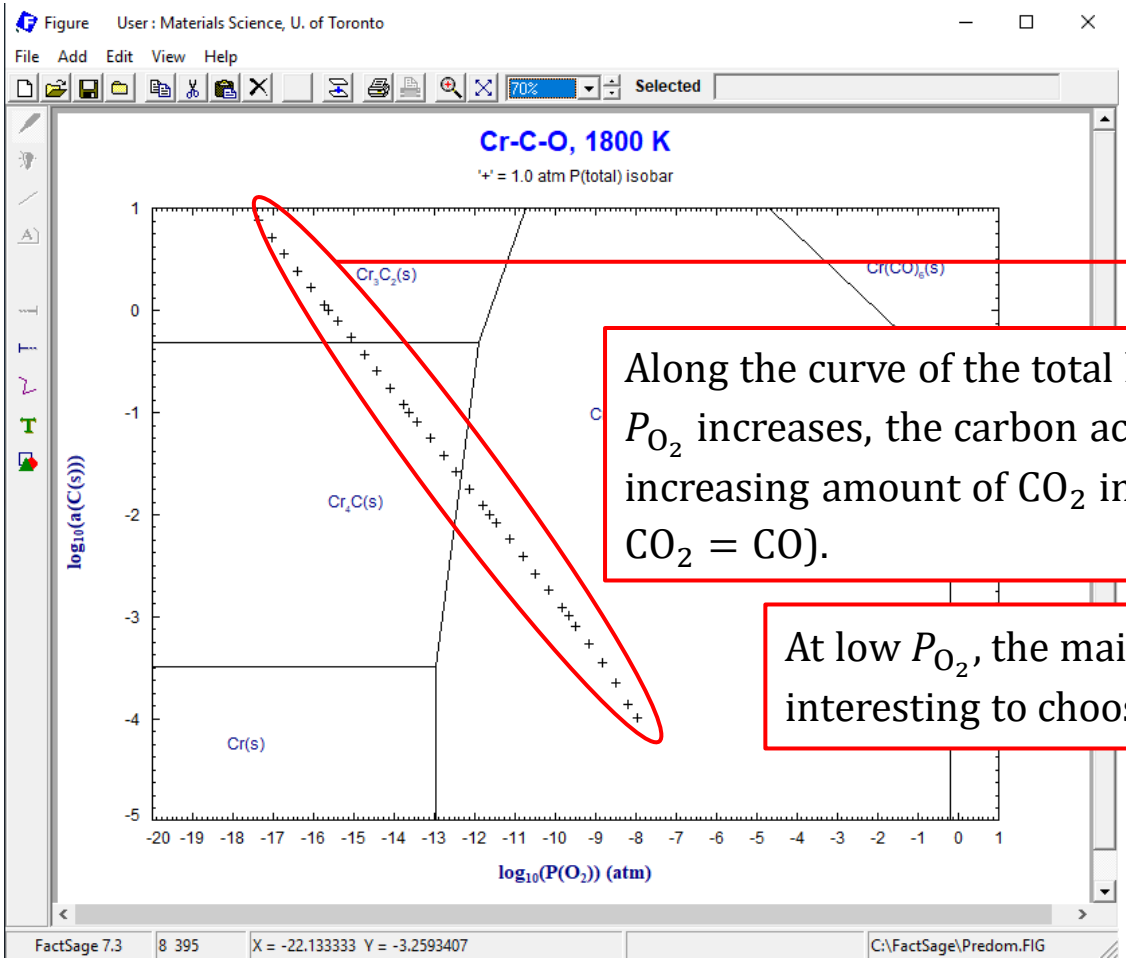
The second example we will look at is the Cr-C-O system at 1800 K.



Here, the maximum carbon activity is set as 10. In reality, the carbon activity cannot exceed unity. The program permits one to calculate the diagram under the conditions that cannot be achieved in practice. **However**, we should never use ridiculously high values for activities and partial pressures.

Predom Module: Cr-C-O System

The second example we will look at is the Cr-C-O system at 1800 K.

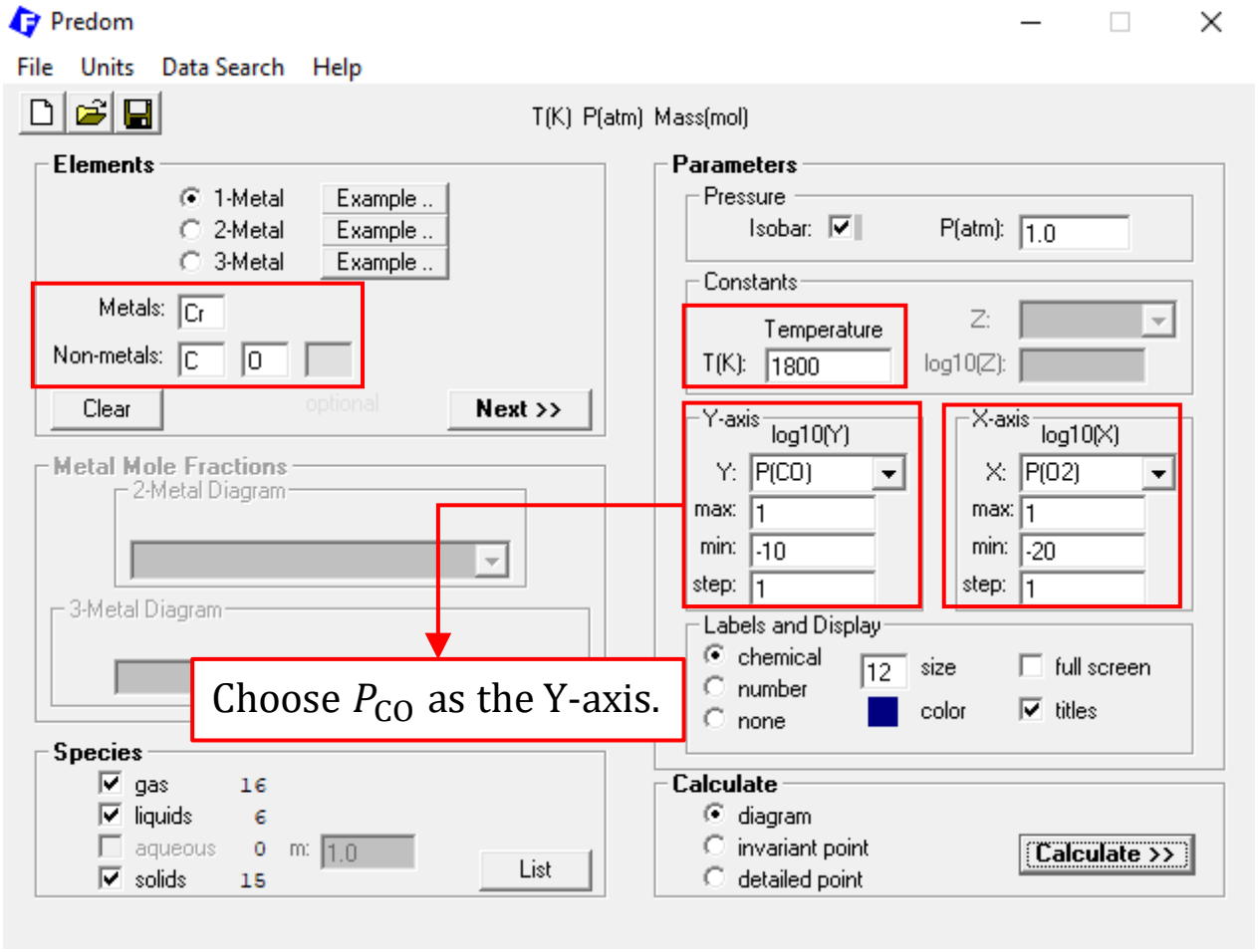


Along the curve of the total hydrostatic pressure of 1 atm, as P_{O_2} increases, the carbon activity is dropping because of an increasing amount of CO_2 in the gas phase (consider: $C + CO_2 = CO$).

At low P_{O_2}, the main gas species is CO. It is therefore interesting to choose P_{CO} as the Y-axis.

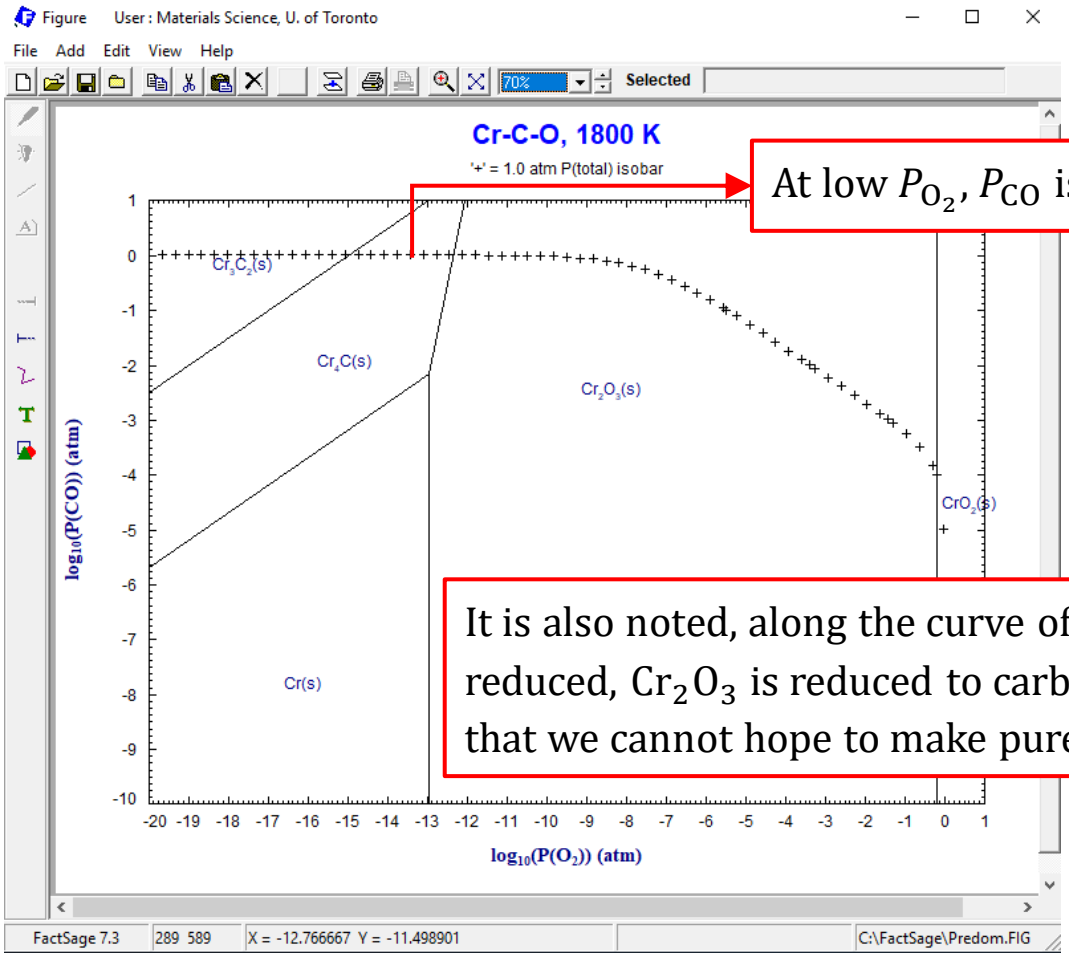
Predom Module: Cr-C-O System

The second example we will look at is the Cr-C-O system at 1800 K.



Predom Module: Cr-C-O System

The second example we will look at is the Cr-C-O system at 1800 K.



At low P_{O_2}, P_{CO} is close to unity.

It is also noted, along the curve of the total pressure of 1 atm, as P_{O_2} is reduced, Cr_2O_3 is reduced to carbide, but not metallic Cr. This reveals that we cannot hope to make pure Cr metal by carbothermic reduction.

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Practical 3. Phase Diagram Calculation

Phase Diagram Module: Unary and Binary System

Phase Diagram Module

Phase diagrams are a **graphical representation of phase equilibria**, showing the phases at equilibrium with respect to temperature, pressure, etc. We have already shown various types of phase diagrams for systems containing stoichiometric compounds as well as solution phases in lectures. For binary systems, the most common type is $T \sim X_B$ diagram.

The **Phase Diagram Module** is a very powerful module and is superior to the Predom Module in many ways. However, it takes a lot of care to use it correctly. The general rules of constructing **single-valued** phase diagrams is thoroughly discussed by Pelton.

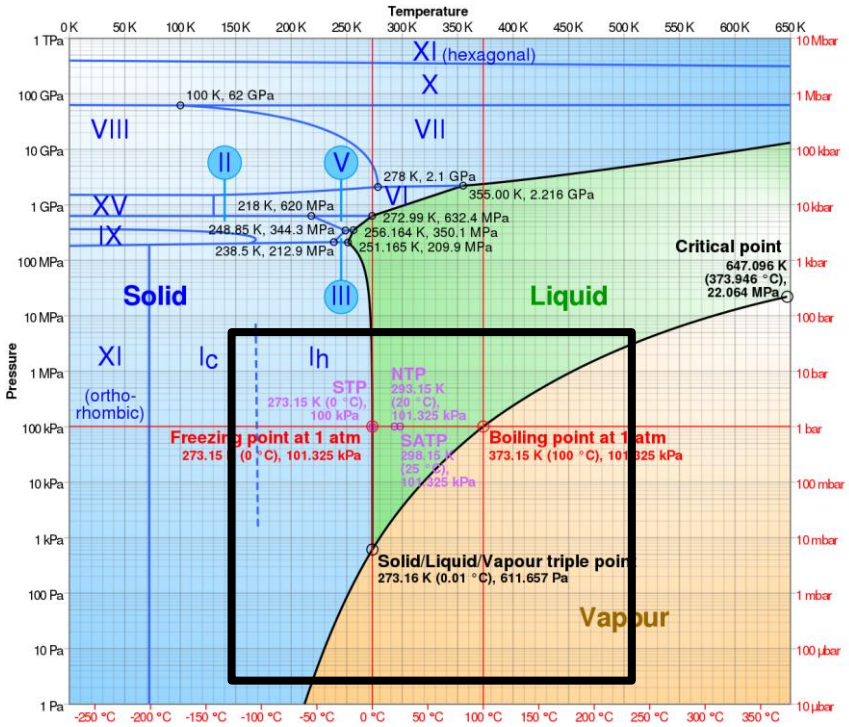
Like the Equilib Module, selection of databases, especially, solution database, and selection of the phases that may exist at equilibrium are quite challenging for high-order systems. Always consult the Documentation Module!!!

Pelton, Phase Diagrams and Thermodynamic Modeling of Solutions, 2019 (Chapter 7.5)

Phase Diagram Module: H_2O

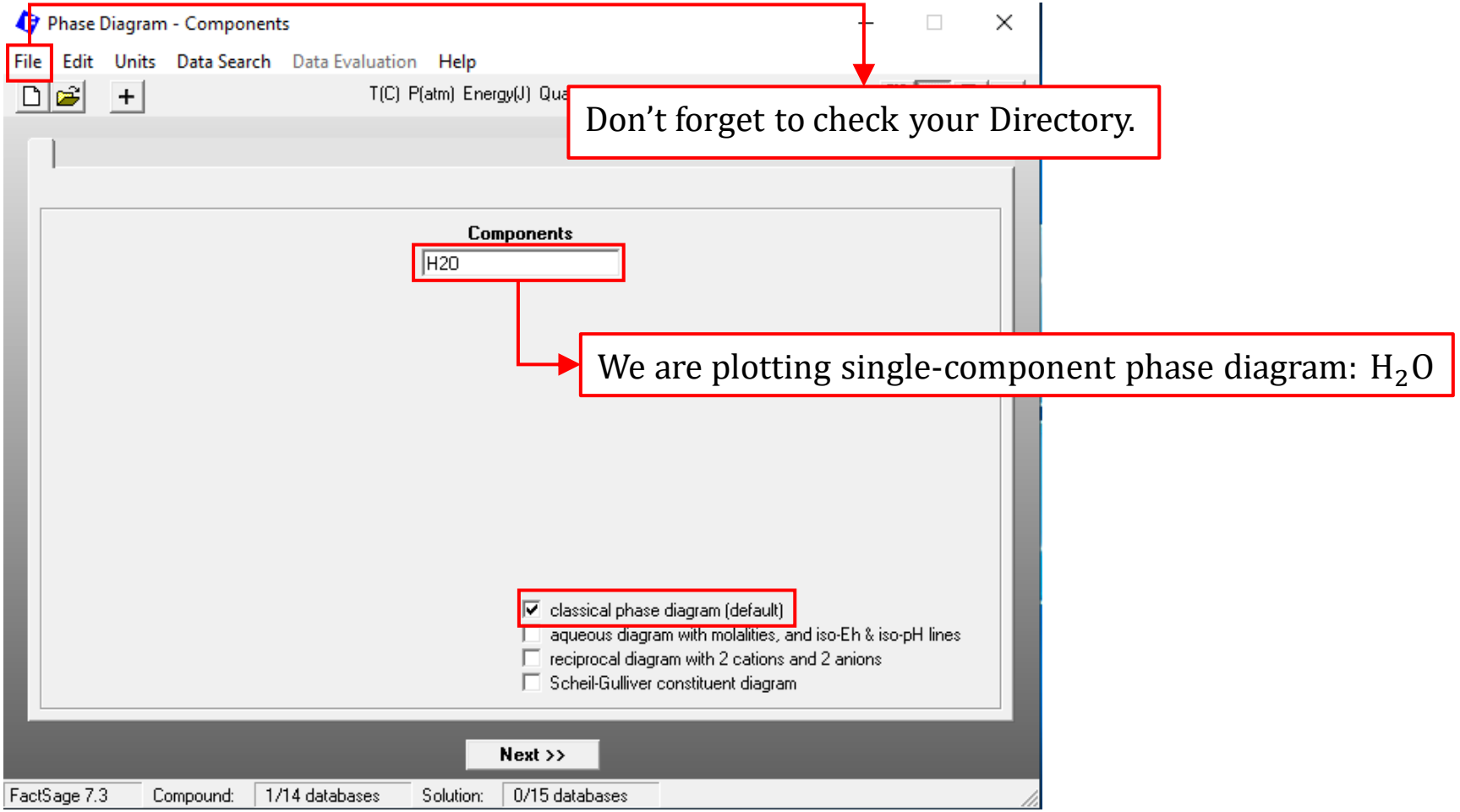
Let us start with a simple example: unary phase diagram of H_2O. We would like to know how the equilibrium between **water vapor**, **liquid water** and **ice** is shifted when the system's pressure and temperature are varied.

We would like to plot a diagram that is the similar to the graph below.



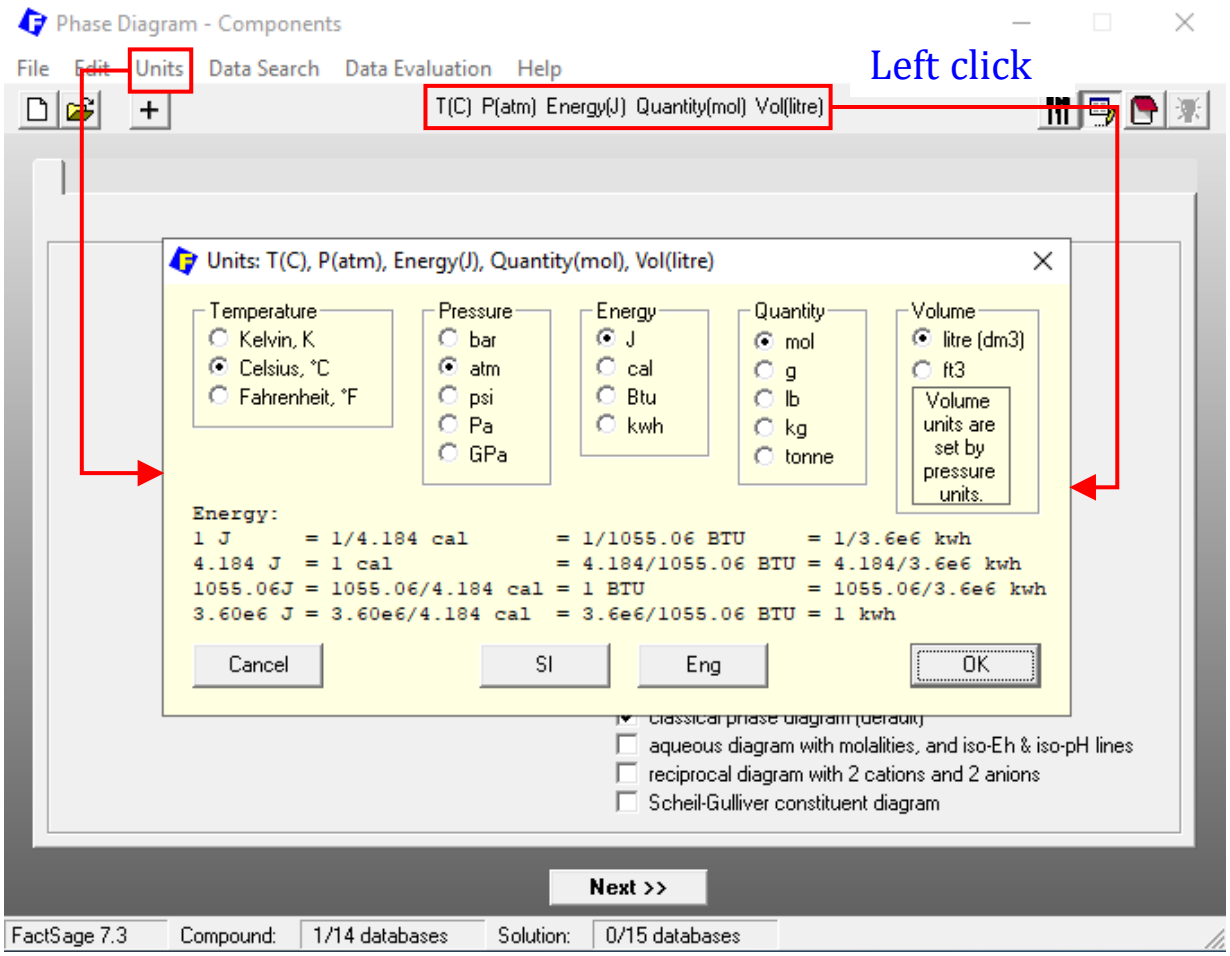
Phase Diagram Module: H_2O

Components Window: Define Components



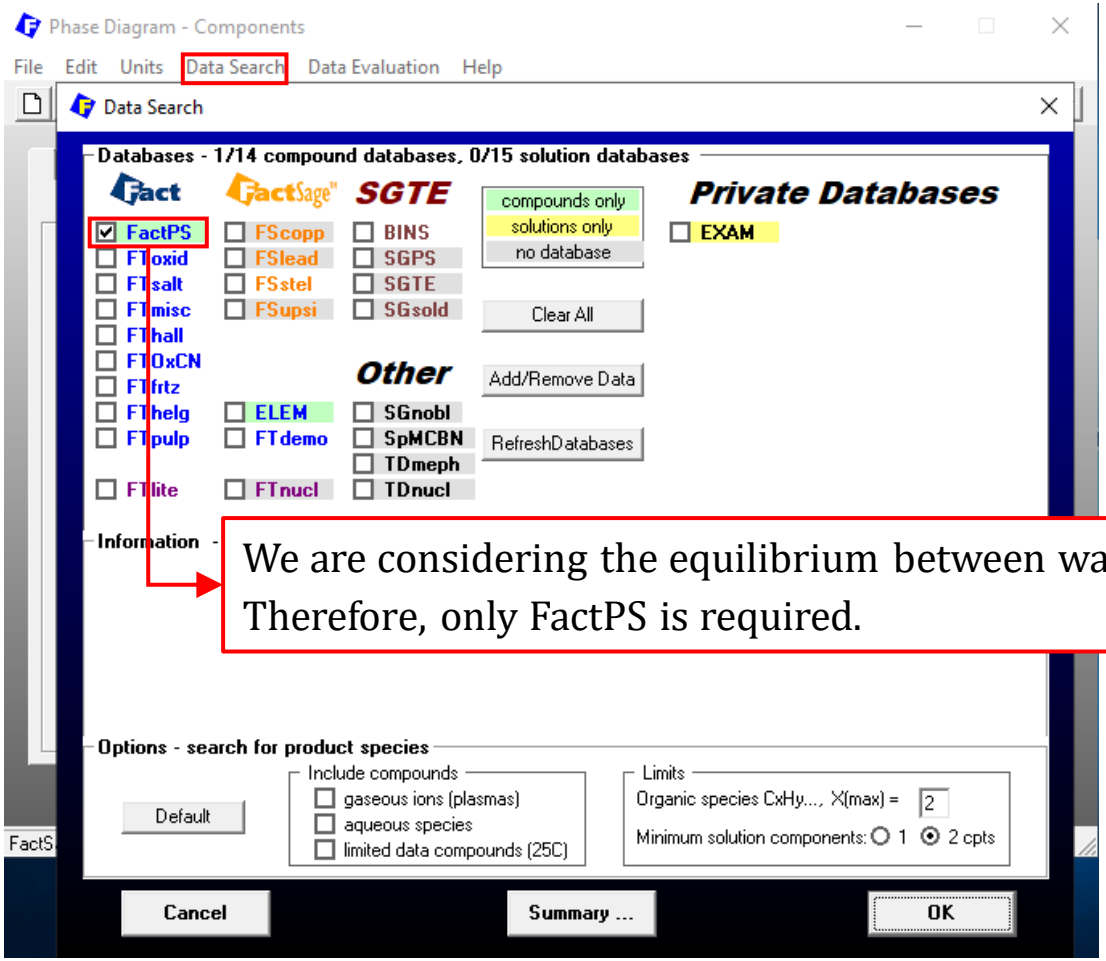
Phase Diagram Module: H_2O

Components Window: Choose Units



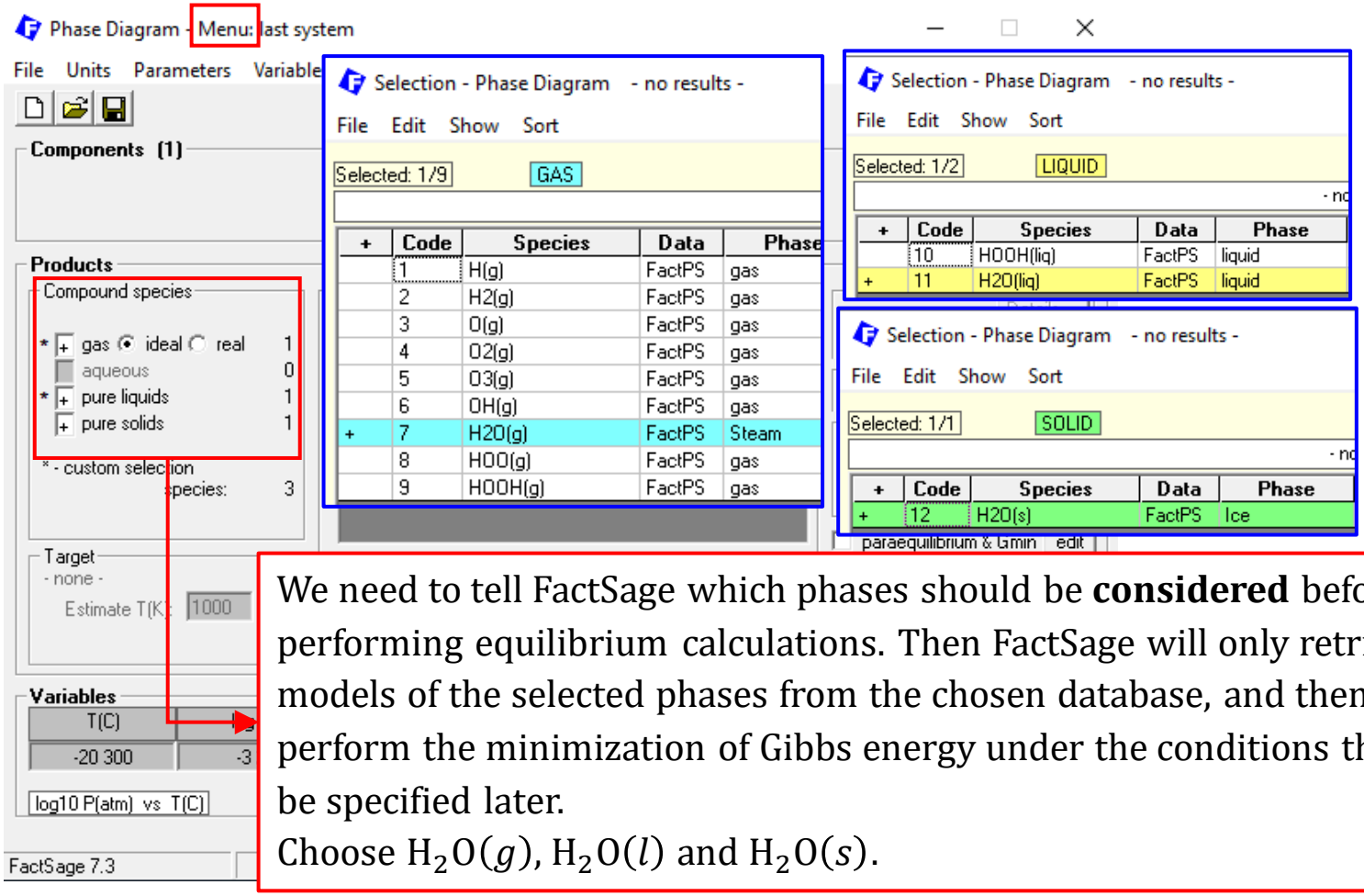
Phase Diagram Module: H_2O

Components Window: Choose Database(s)



Phase Diagram Module: H_2O

Menu Window: Choose Products/Phases (Compounds and Solution Phases)

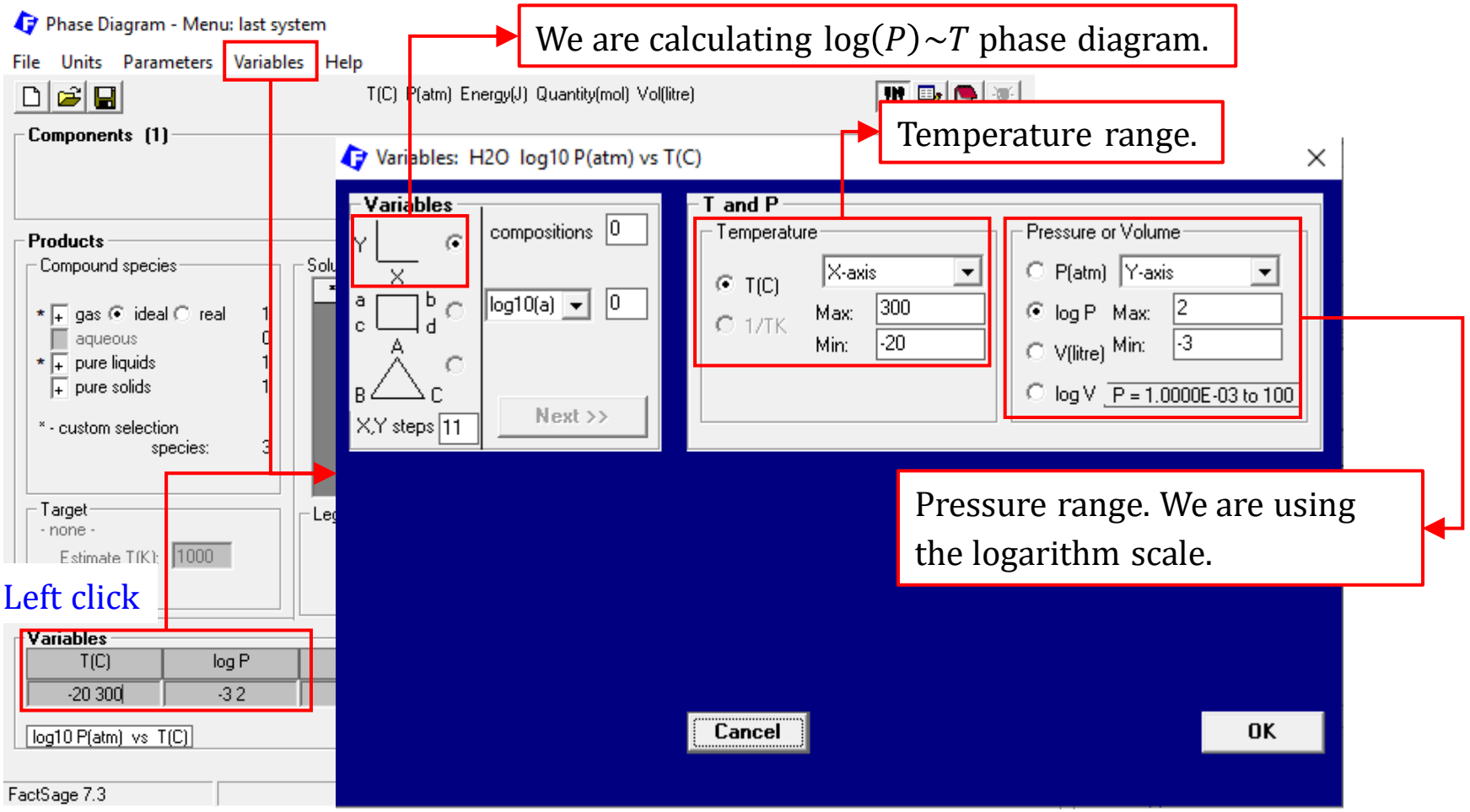


We need to tell FactSage which phases should be **considered** before performing equilibrium calculations. Then FactSage will only retrieve the models of the selected phases from the chosen database, and then perform the minimization of Gibbs energy under the conditions that will be specified later.

Choose $H_2O(g)$, $H_2O(l)$ and $H_2O(s)$.

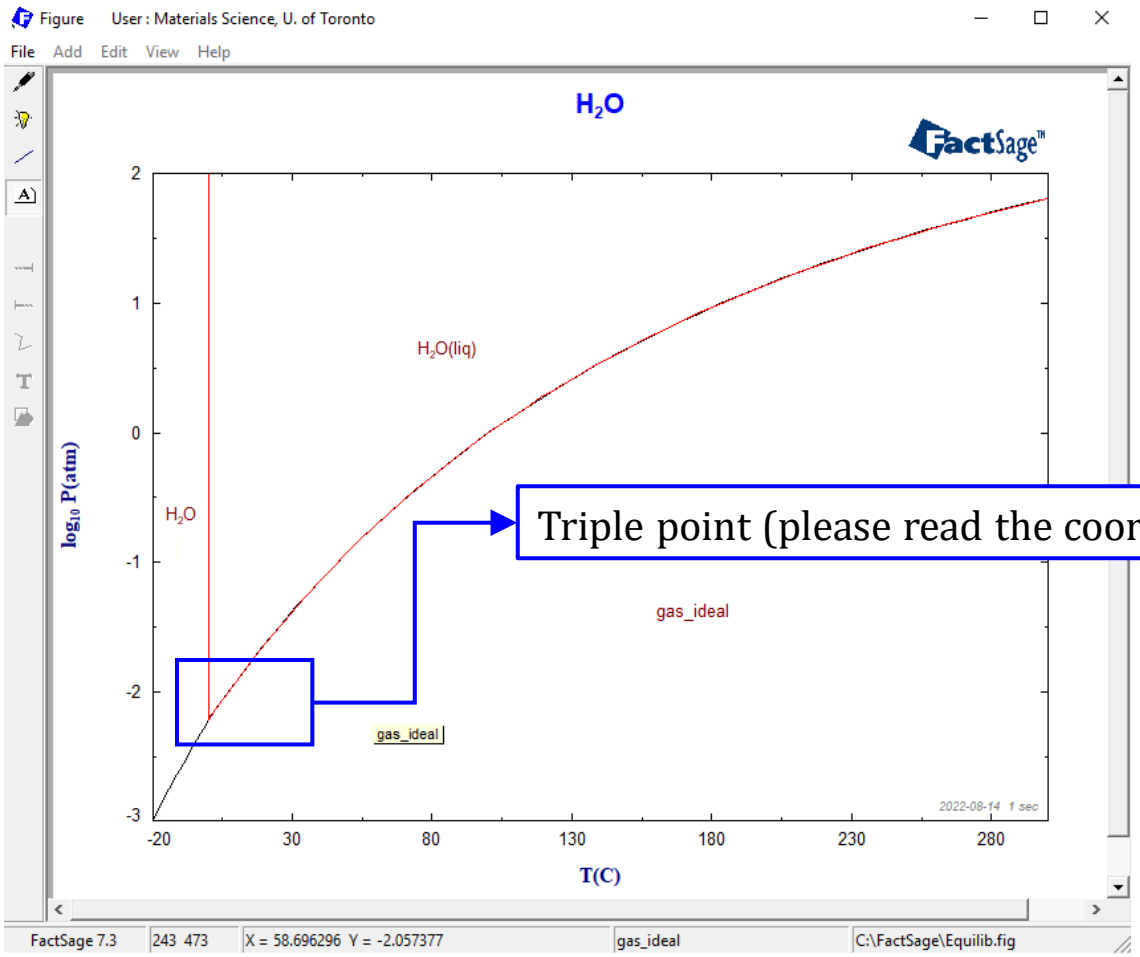
Phase Diagram Module: H_2O

Menu Window: Choose Variables



Phase Diagram Module: H_2O

Results



Triple point (please read the coordinates).

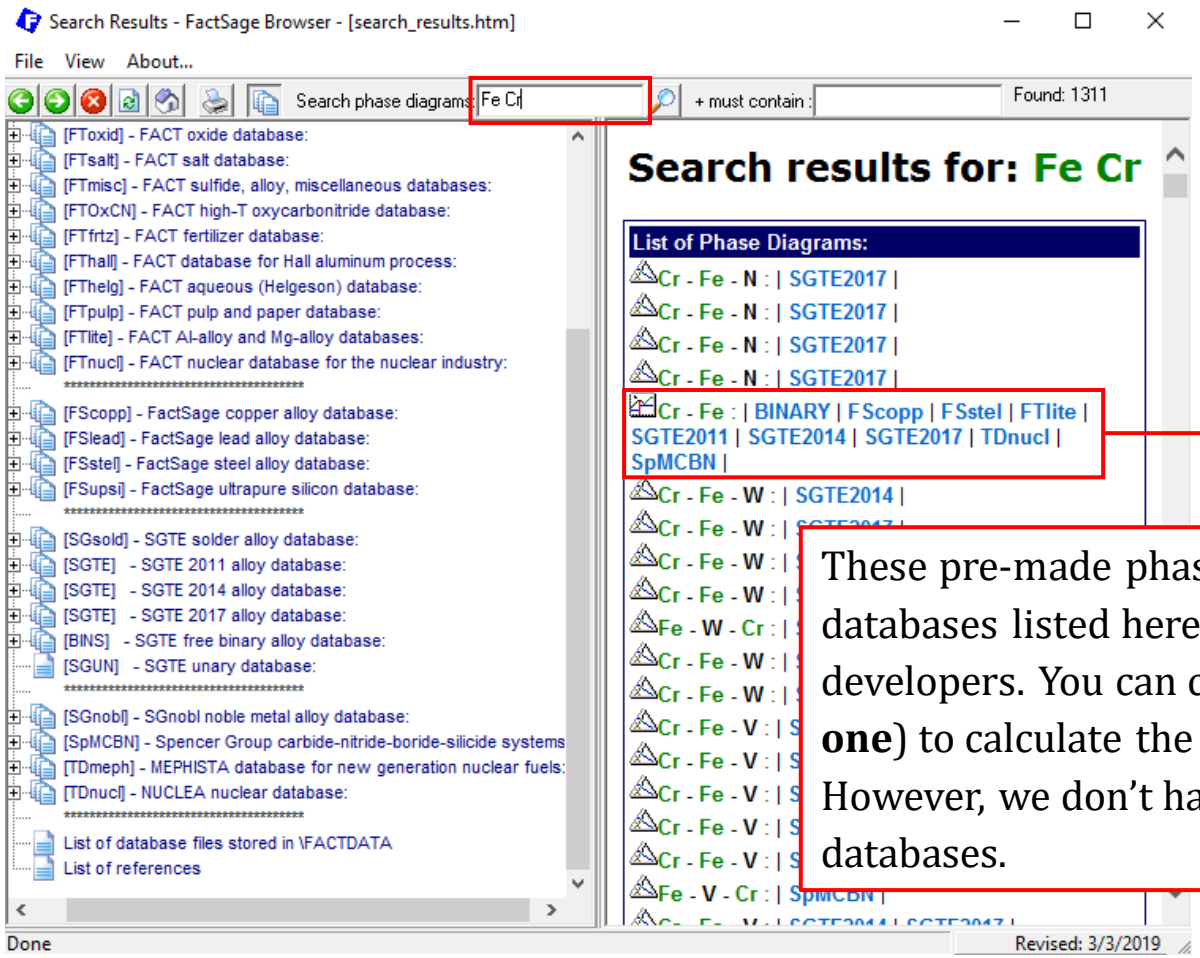
Phase Diagram Module: Fe-Cr System

The second example guides you through the calculation of the $T \sim X_B$ diagrams for binary alloy system.

Say we would like to calculate the Fe-Cr phase diagram. We are aware that in this system, both **stoichiometric compounds** and **solution phases** could exist. Therefore, we need to determine which database(s) should be used. To do this, we could either use the search function in the **Documentation** Module, or use the **View Data** Module.

Phase Diagram Module: Fe-Cr System

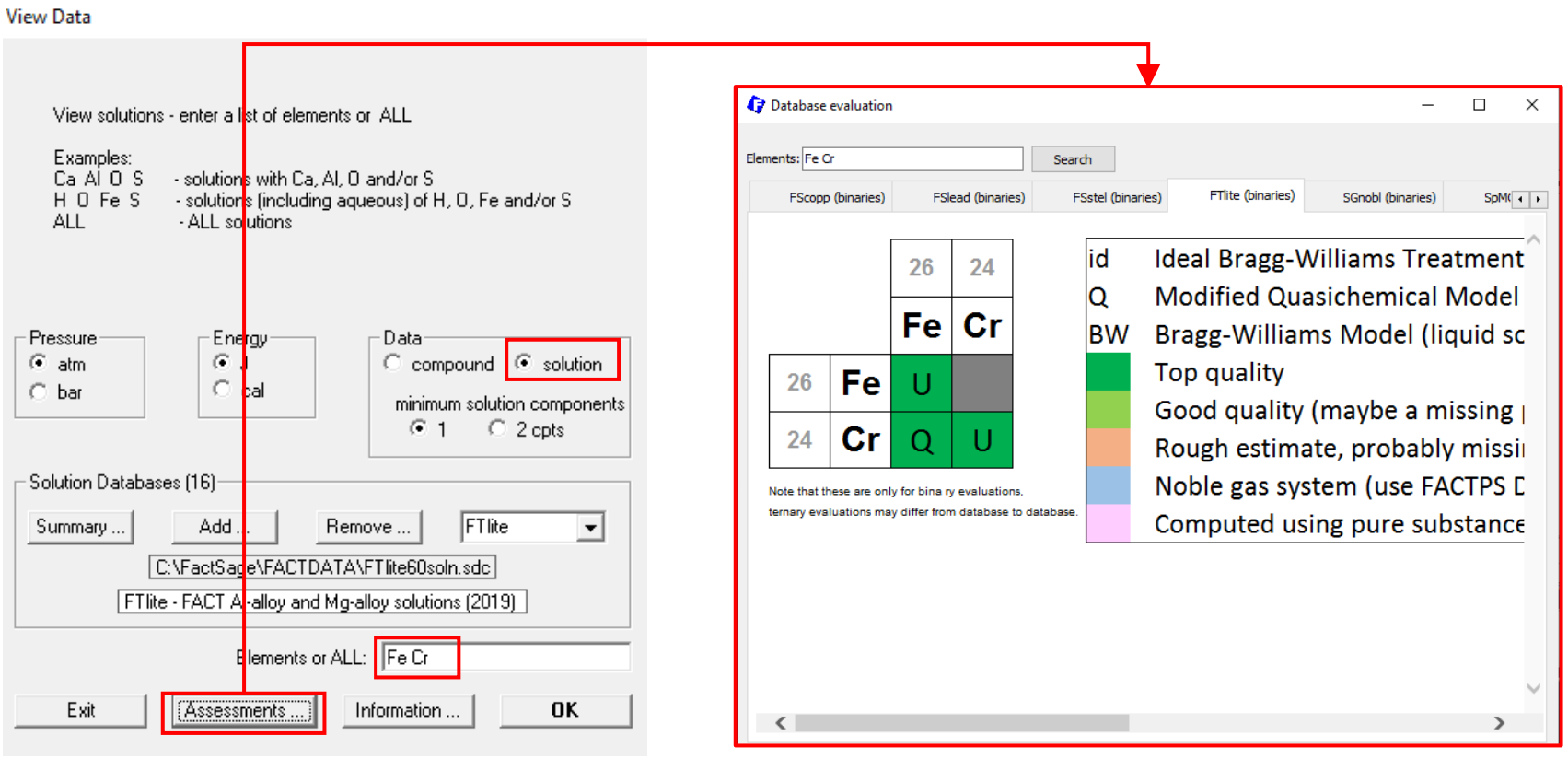
Search the Fe-Cr system in the Documentation Module.



These pre-made phase diagrams using the databases listed here are provided by FactSage developers. You can choose one of them (**ONLY one**) to calculate the Fe-Cr phase diagram. However, we don't have the access to all these databases.

Phase Diagram Module: Fe-Cr System

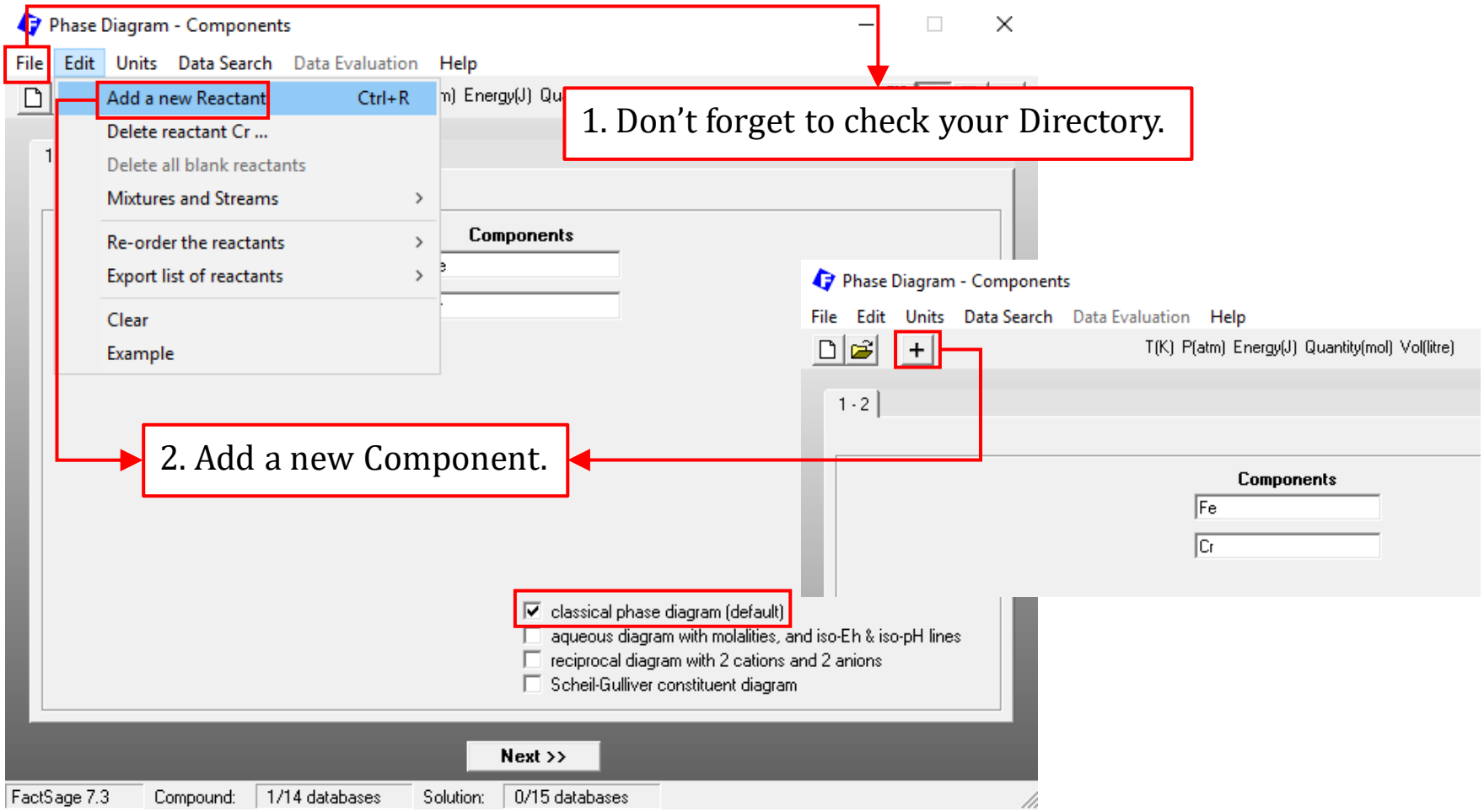
View the model quality for the Fe-Cr system in the View Data Module.



The above information from the Documentation Module and View Data Module indicates that FTlite could be used to calculate the Fe-Cr system.

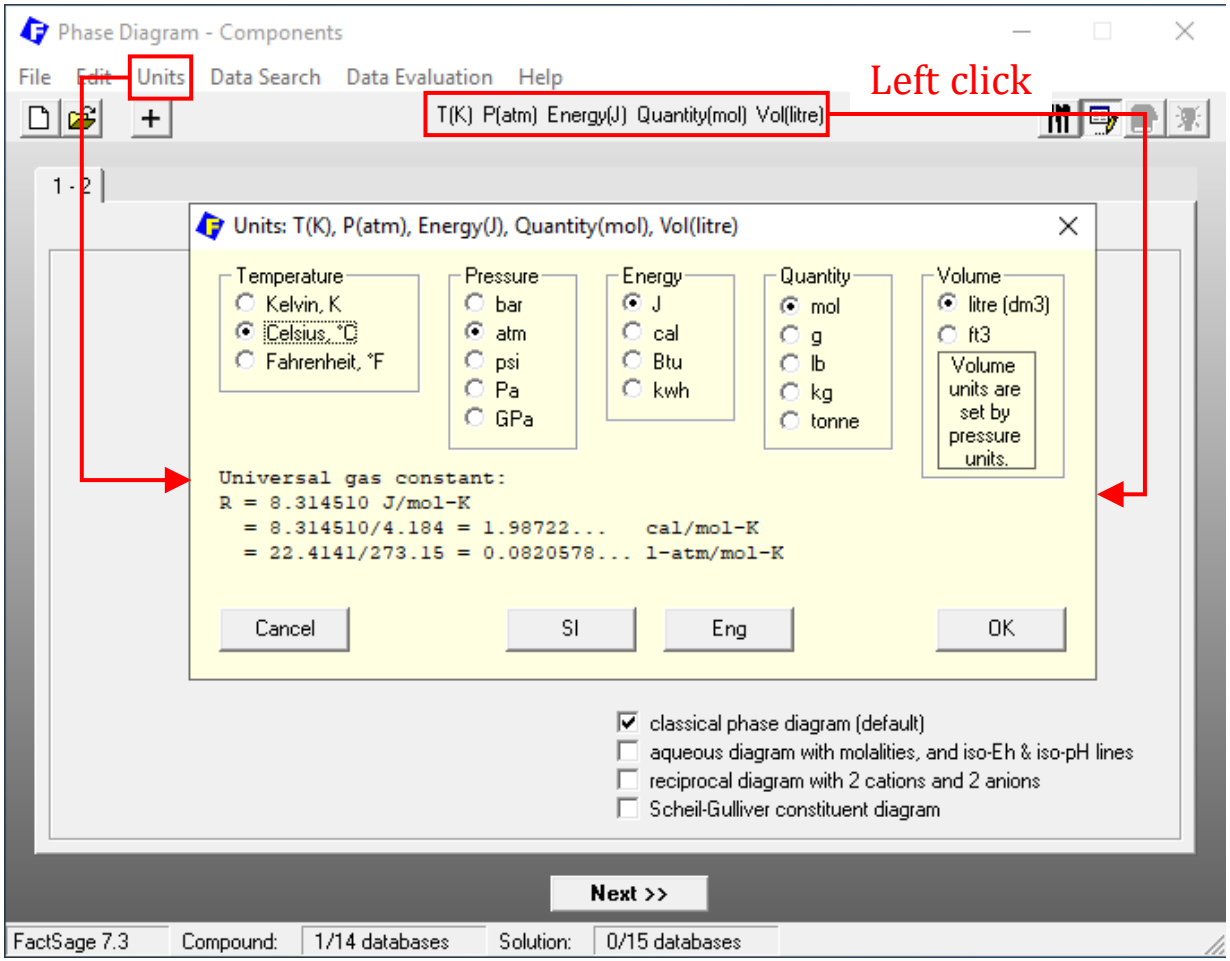
Phase Diagram Module: Fe-Cr System

Components Window: Define Components



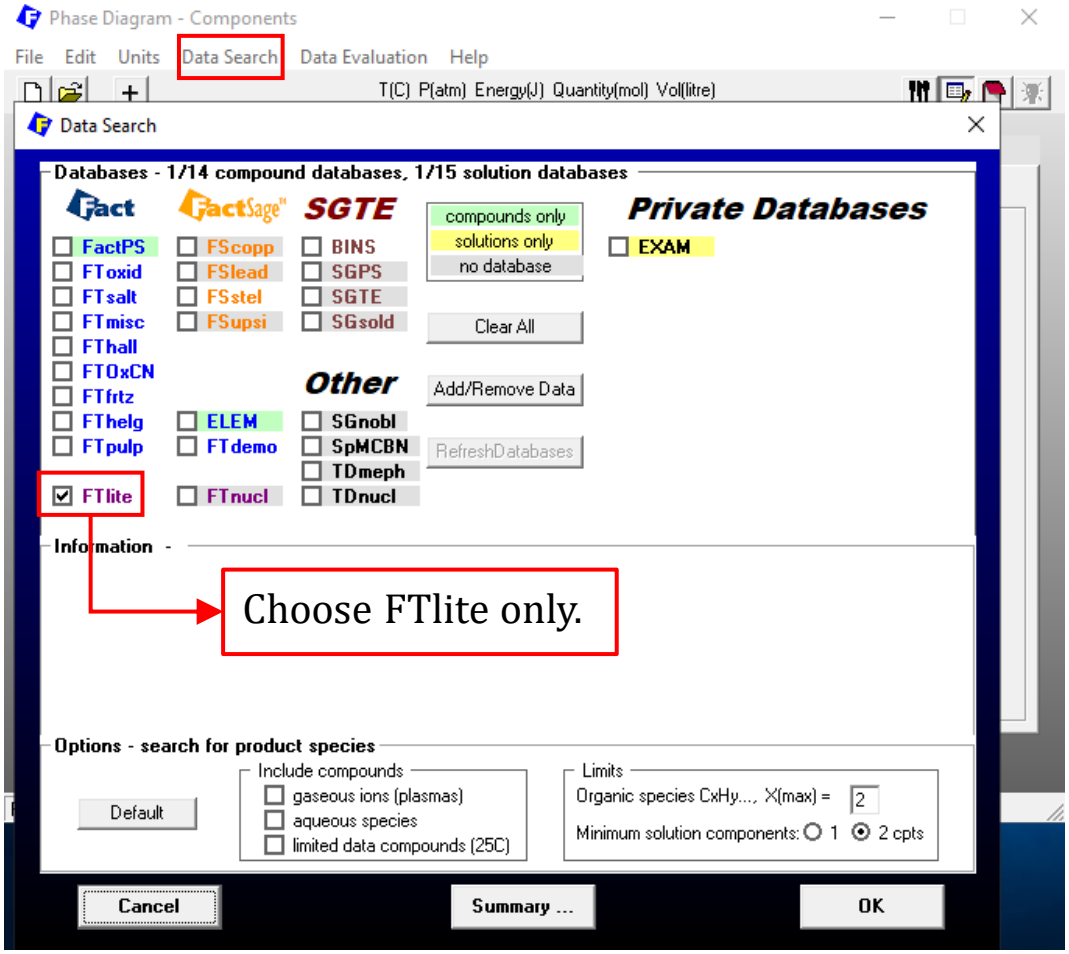
Phase Diagram Module: Fe-Cr System

Components Window: Choose Units



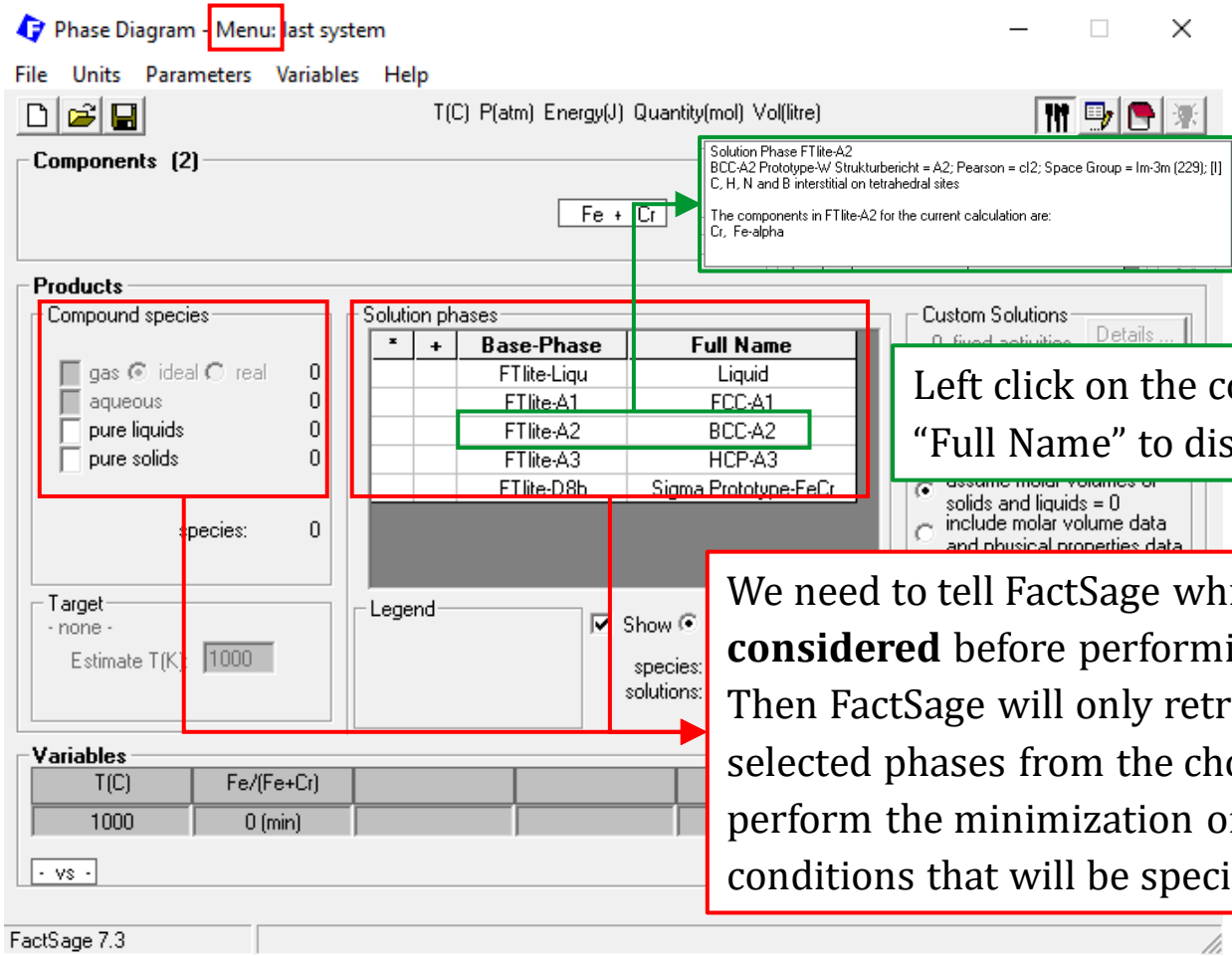
Phase Diagram Module: Fe-Cr System

Components Window: Choose Database(s)



Phase Diagram Module: Fe-Cr System

Menu Window: Choose Products/Phases (Compounds and Solution Phases)

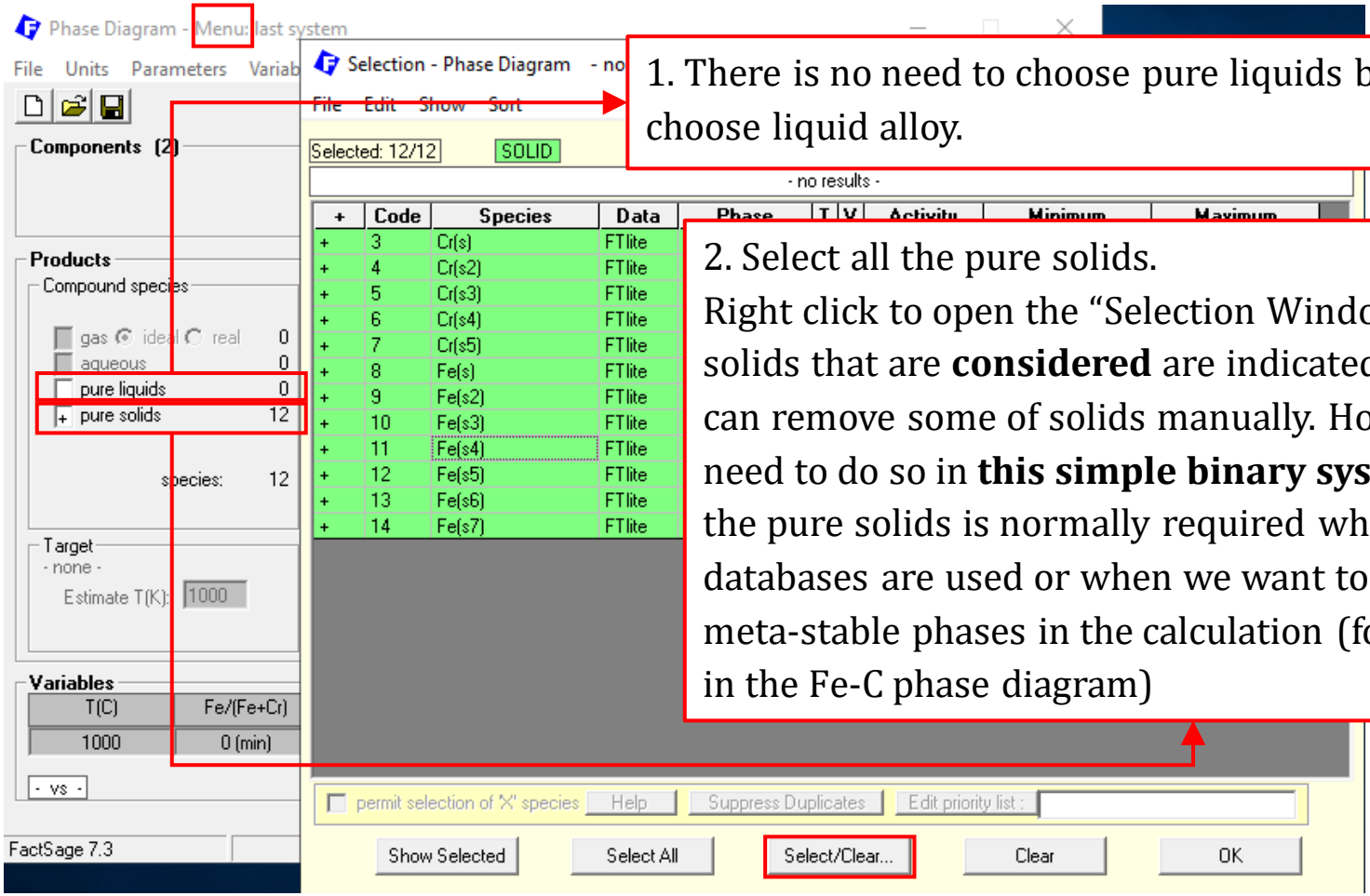


Left click on the column of "Base-Phase" or "Full Name" to display the solution description.

We need to tell FactSage which phases should be **considered** before performing equilibrium calculations. Then FactSage will only retrieve the models of the selected phases from the chosen database, and then perform the minimization of Gibbs energy under the conditions that will be specified later.

Phase Diagram Module: Fe-Cr System

Menu Window: Choose Products/Phases (Compounds and Solution Phases)

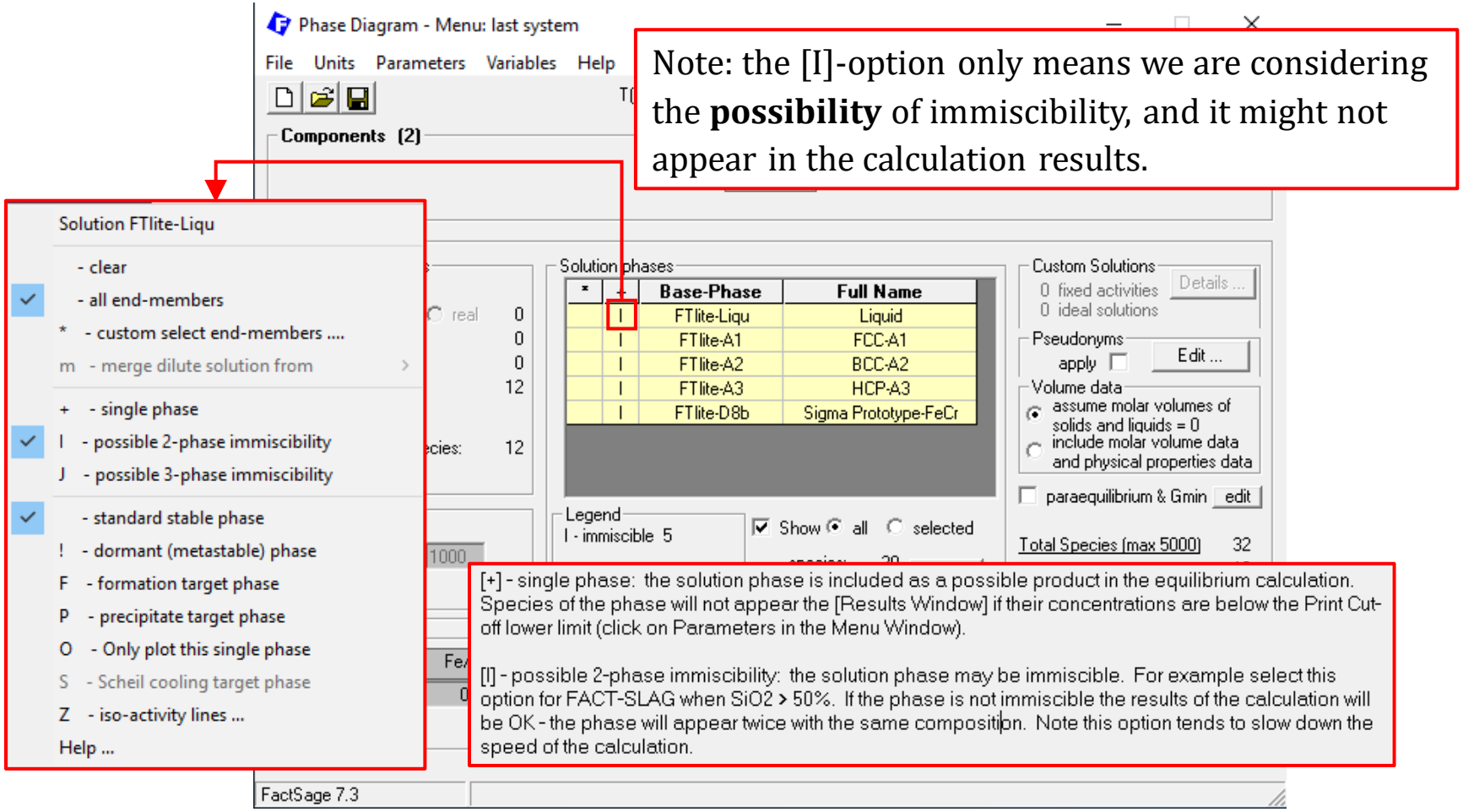


1. There is no need to choose pure liquids because we will choose liquid alloy.

2. Select all the pure solids.
Right click to open the "Selection Window". All the pure solids that are **considered** are indicated by a sign "+". You can remove some of solids manually. However, there is no need to do so in **this simple binary system**. Screening of the pure solids is normally required when multiple databases are used or when we want to include some meta-stable phases in the calculation (for example, Fe_3C in the Fe-C phase diagram)

Phase Diagram Module: Fe-Cr System

Menu Window: Choose Products/Phases (Compounds and Solution Phases)



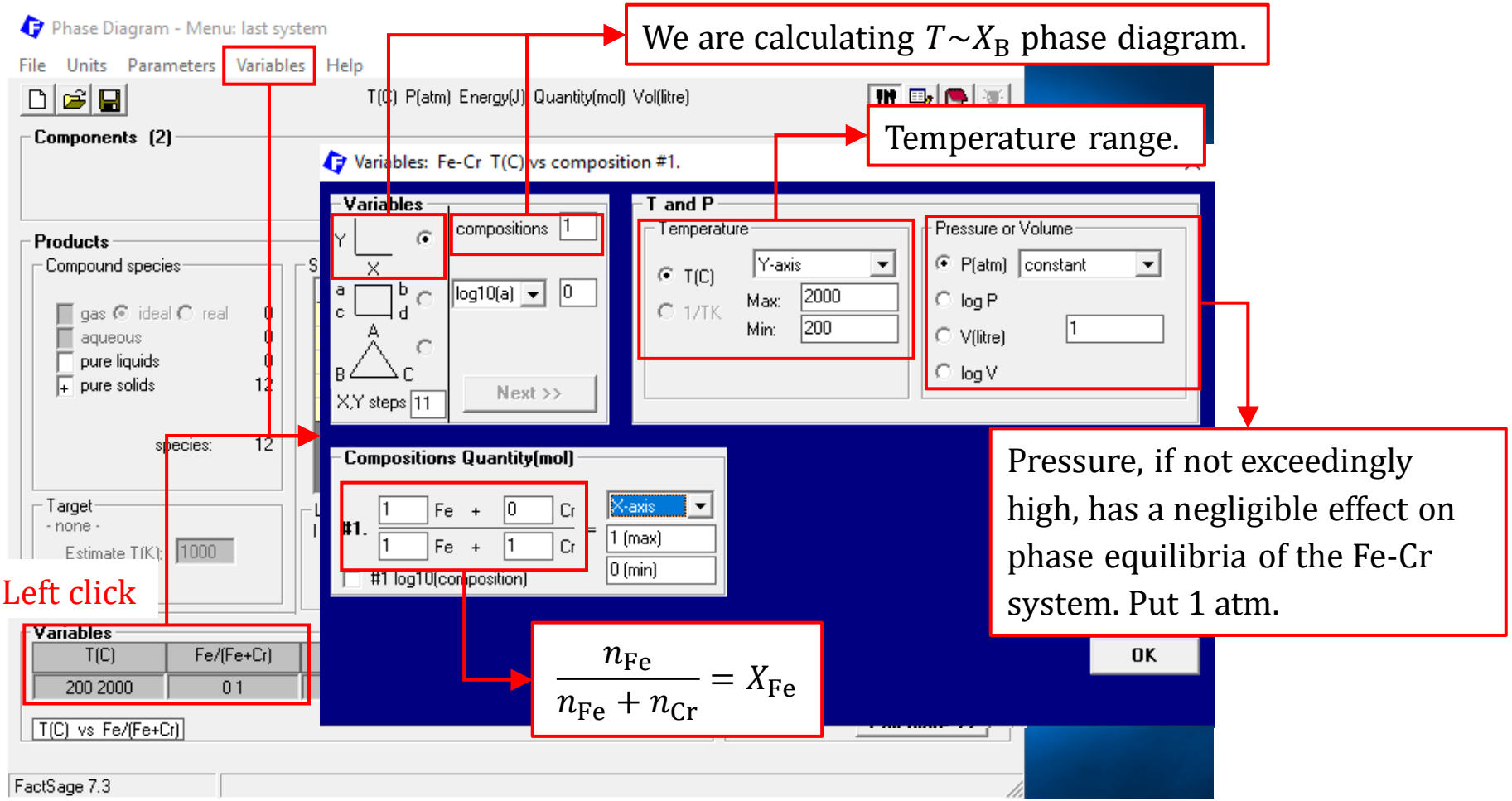
Phase Diagram Module: Fe-Cr System

Menu Window: Choose Products/Phases (Compounds and Solution Phases)

A Note: for the calculation of phase diagrams of a **binary** system which has been optimized in the FactSage databases, we normally use the default settings when choose phases, that is, all pure solids and all solutions (some default setting is [I]-option). However, when calculating higher-order systems which requires the selection of multiple databases, caution must be exercised and screening of certain phases is necessary.

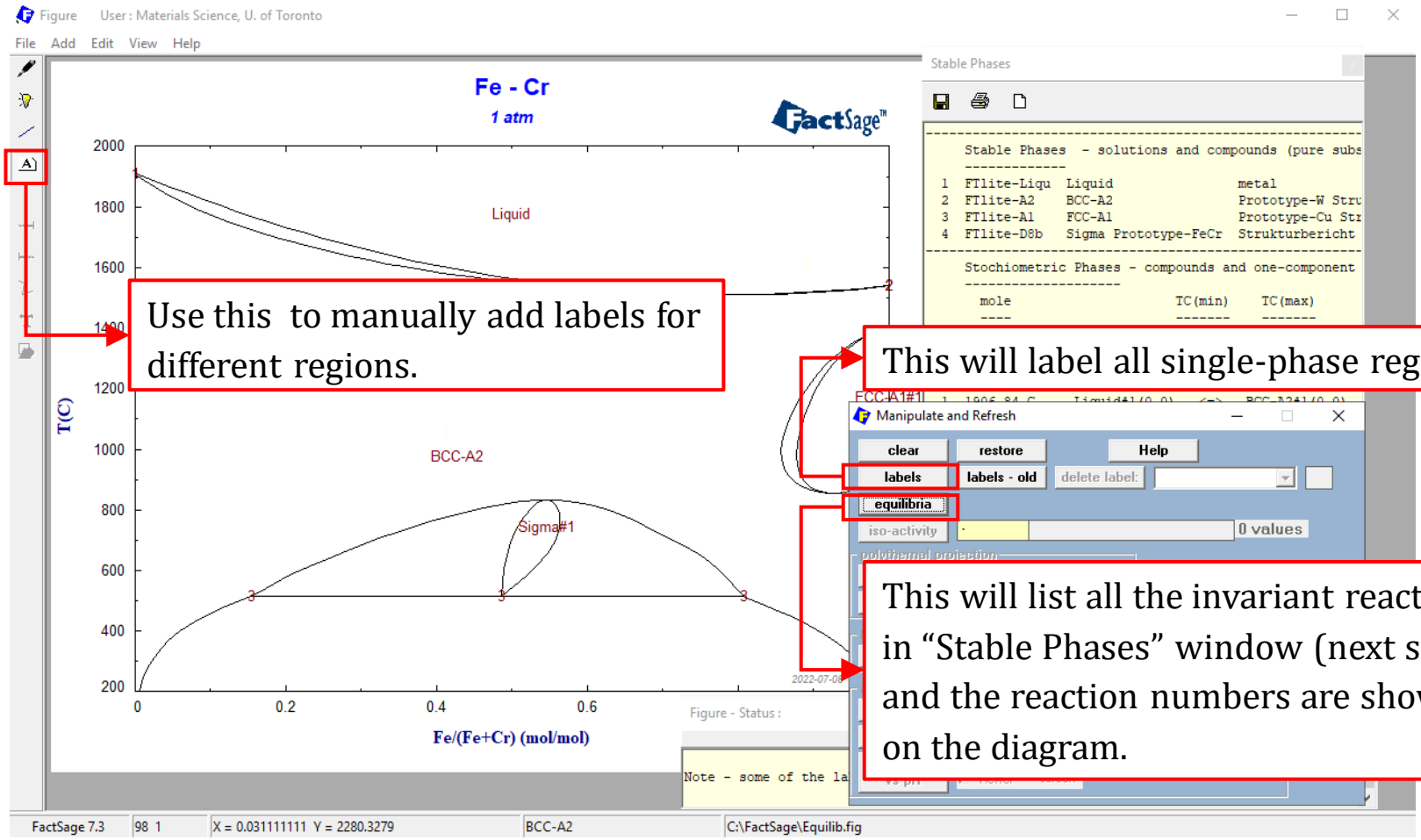
Phase Diagram Module: Fe-Cr System

Menu Window: Choose Variables



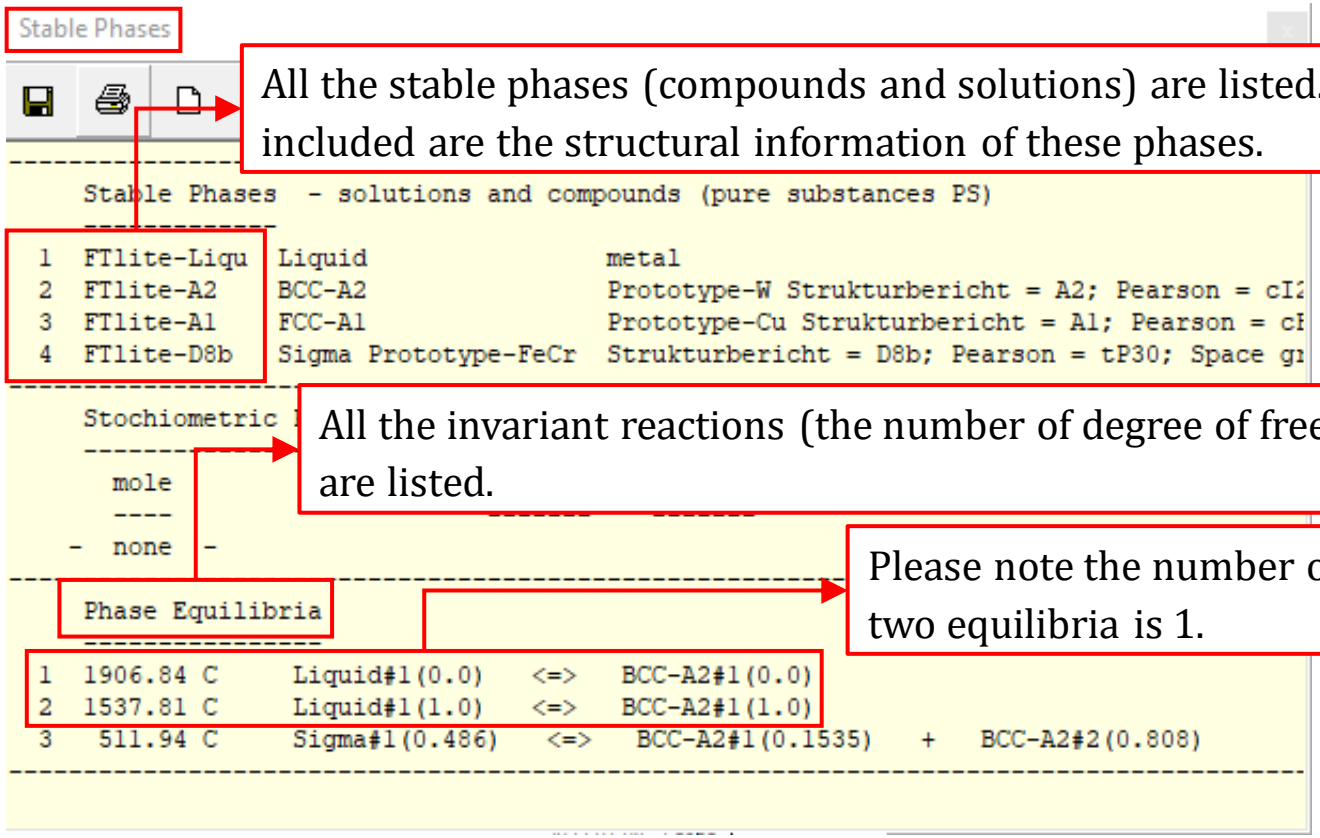
Phase Diagram Module: Fe-Cr System

Results: Click on "Calculate" to generate the phase diagram.



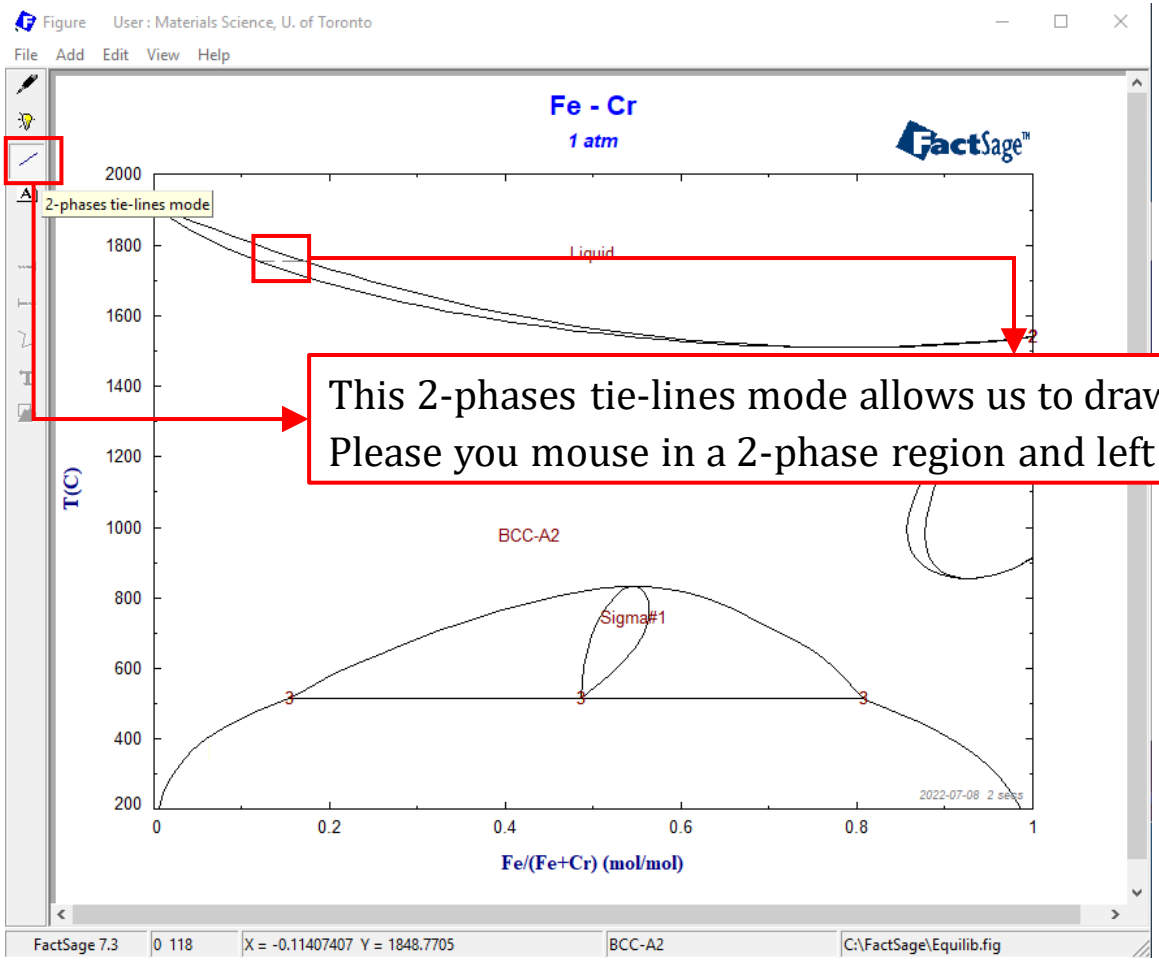
Phase Diagram Module: Fe-Cr System

Results: Click on "Calculate" to generate the phase diagram.



Phase Diagram Module: Fe-Cr System

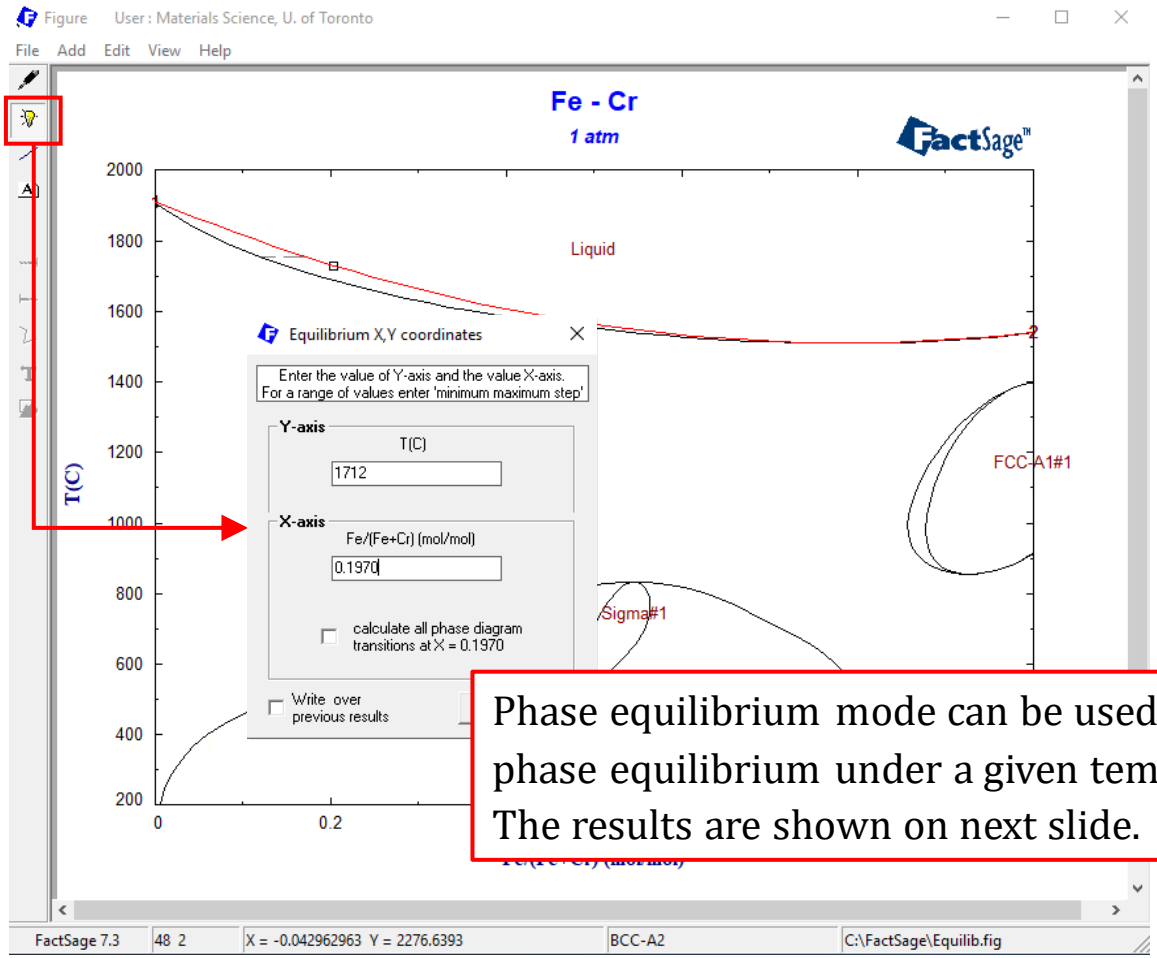
Results: 2-phases tie-lines mode



This 2-phases tie-lines mode allows us to draw tie lines in a 2-phase region. Please you mouse in a 2-phase region and left click.

Phase Diagram Module: Fe-Cr System

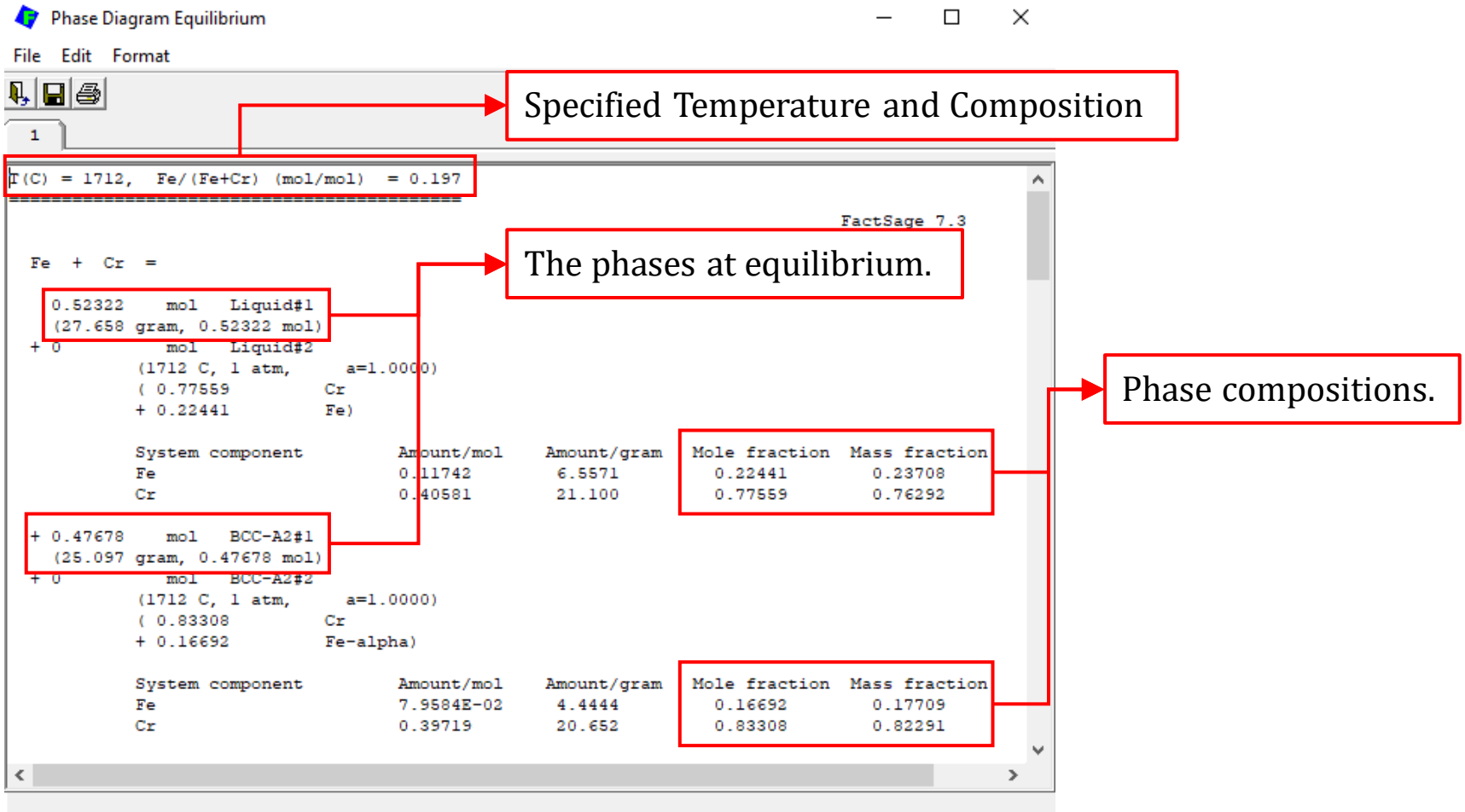
Results: phase equilibrium mode



Phase equilibrium mode can be used to quickly calculate the phase equilibrium under a given temperature and composition. The results are shown on next slide.

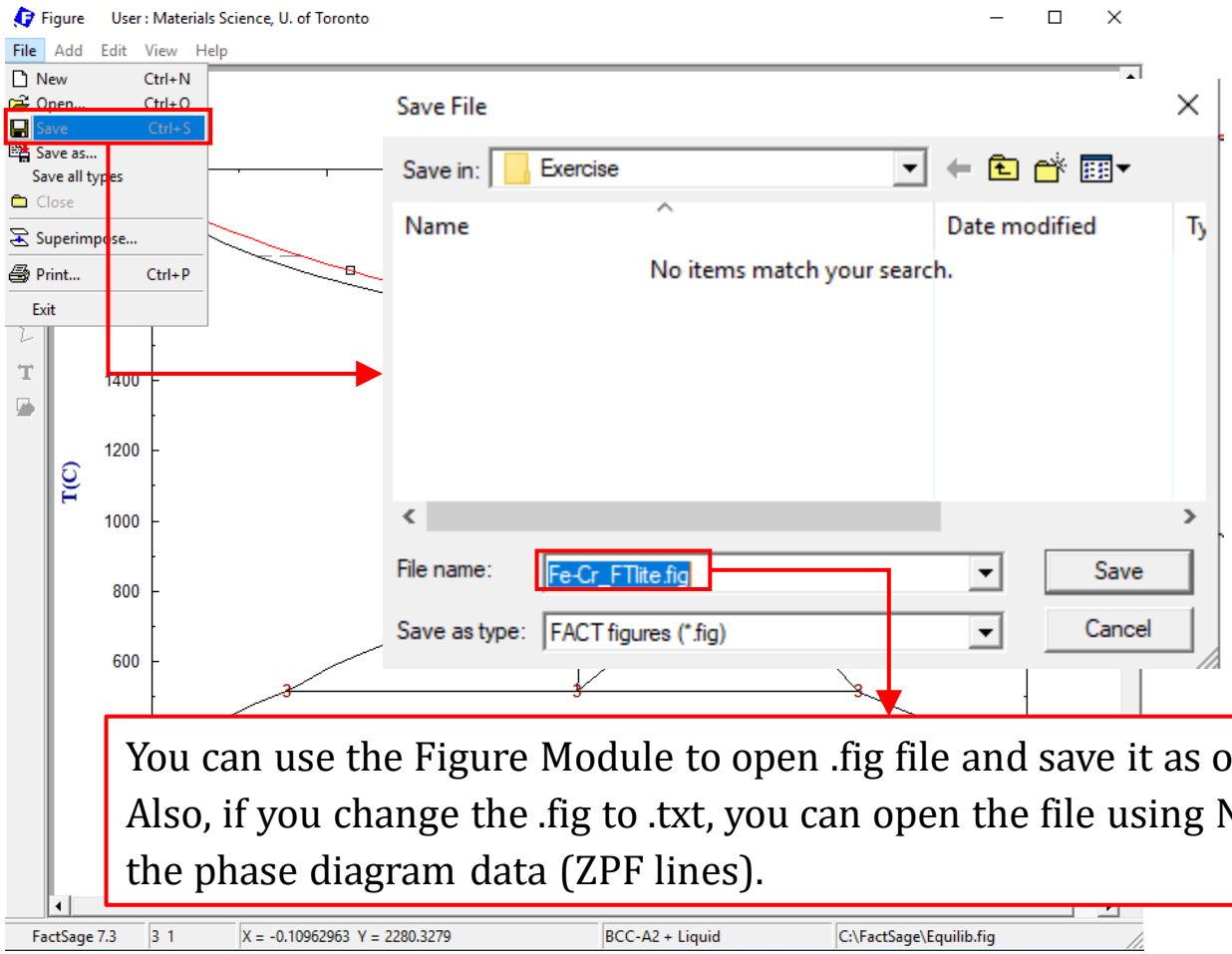
Phase Diagram Module: Fe-Cr System

Results: phase equilibrium mode



Phase Diagram Module: Fe-Cr System

Save Results



You can use the Figure Module to open .fig file and save it as other graph format. Also, if you change the .fig to .txt, you can open the file using NotePad and extract all the phase diagram data (ZPF lines).

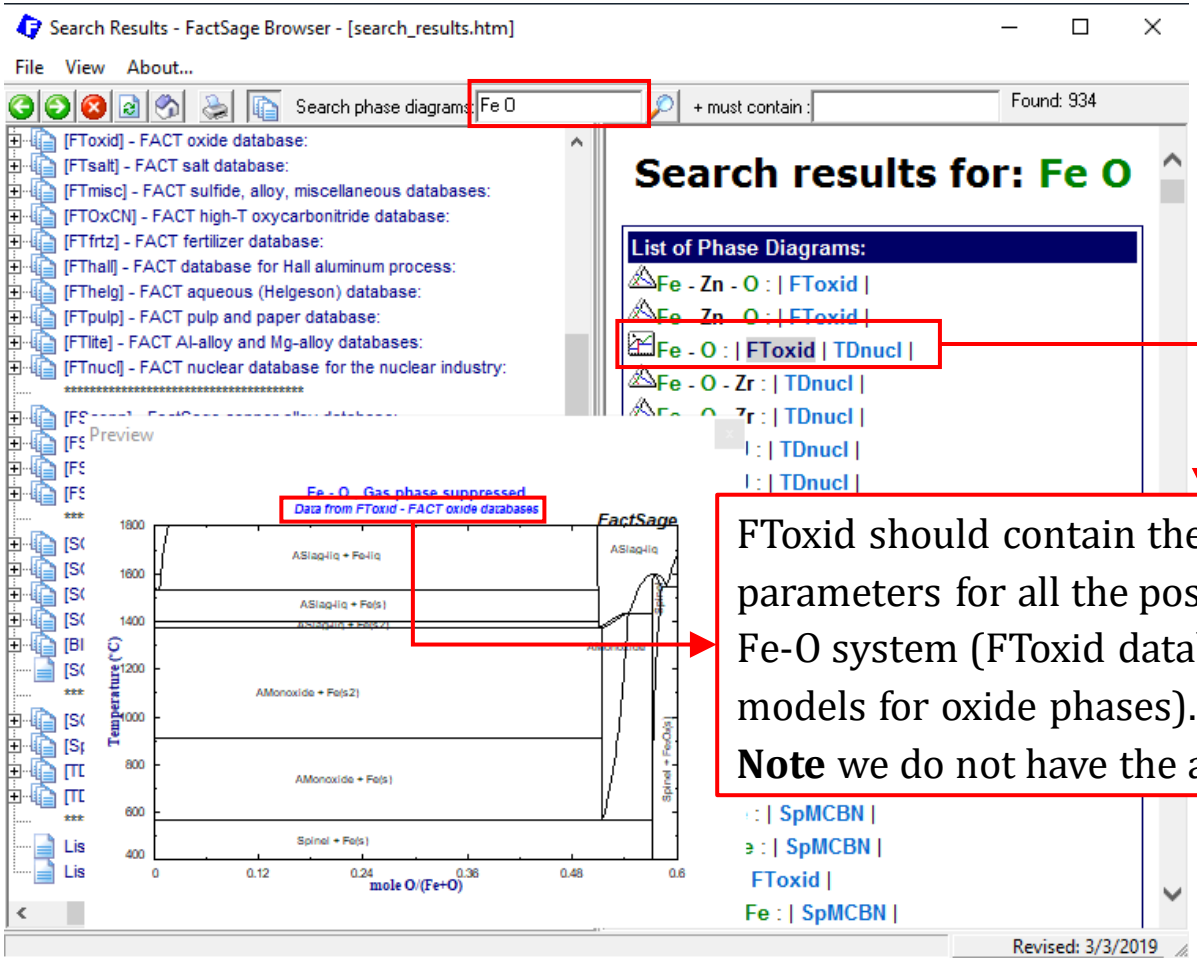
Phase Diagram Module: Fe-O_2 System

The third example guides you through the calculation of the $T \sim X_B$ diagrams as well as two-potential phase diagrams. We will use the Fe-O_2 system as the example.

First, let us calculate the $T \sim X_B$ diagram for the Fe-O_2 system.

Phase Diagram Module: Fe-O_2 System

Search the Fe-O (not Fe-O_2) system in the Documentation Module.

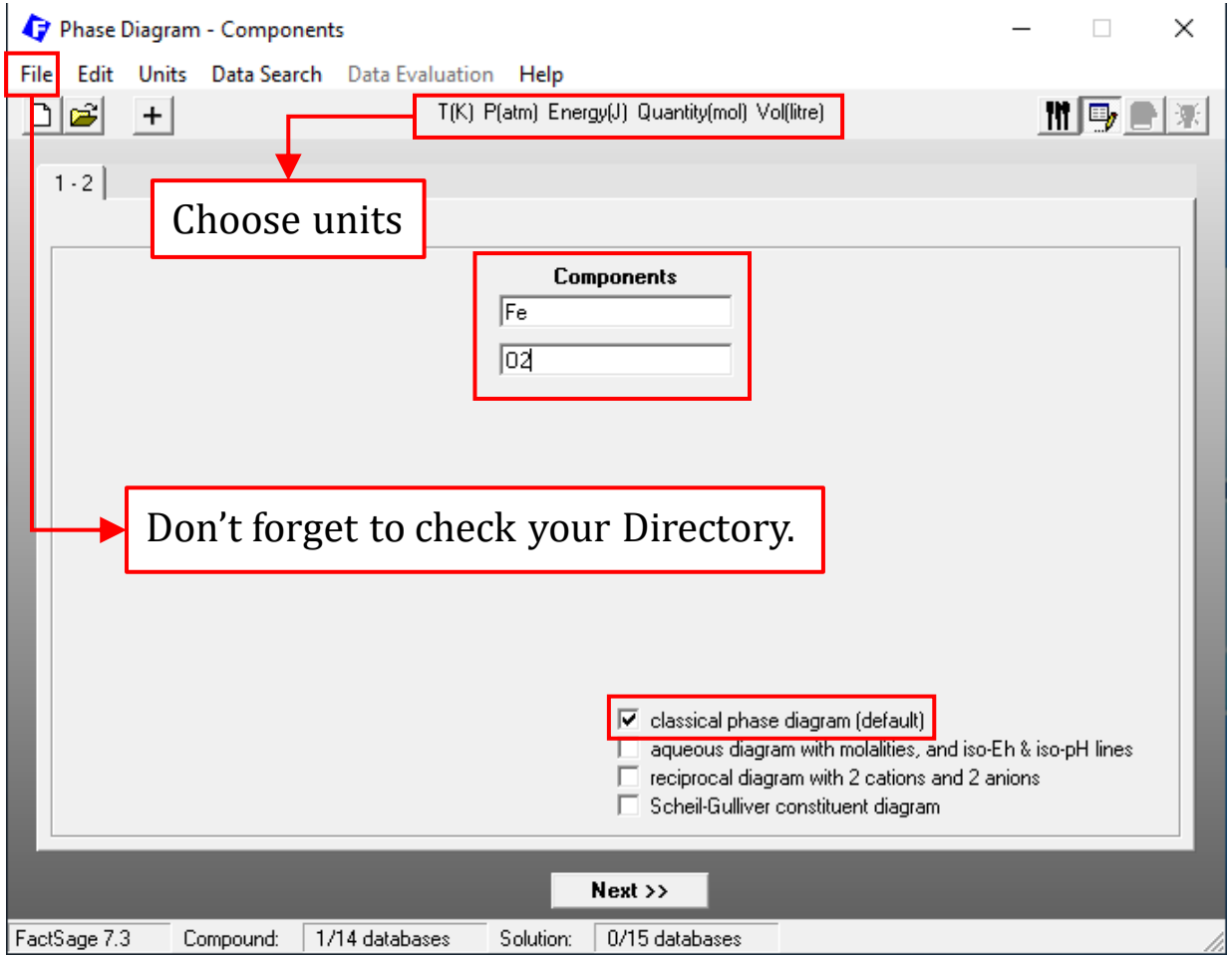


FToxid should contain the optimized model parameters for all the possible **oxide** phases in the Fe-O system (FToxid database only contains the models for oxide phases).

Note we do not have the access to TDnucl database.

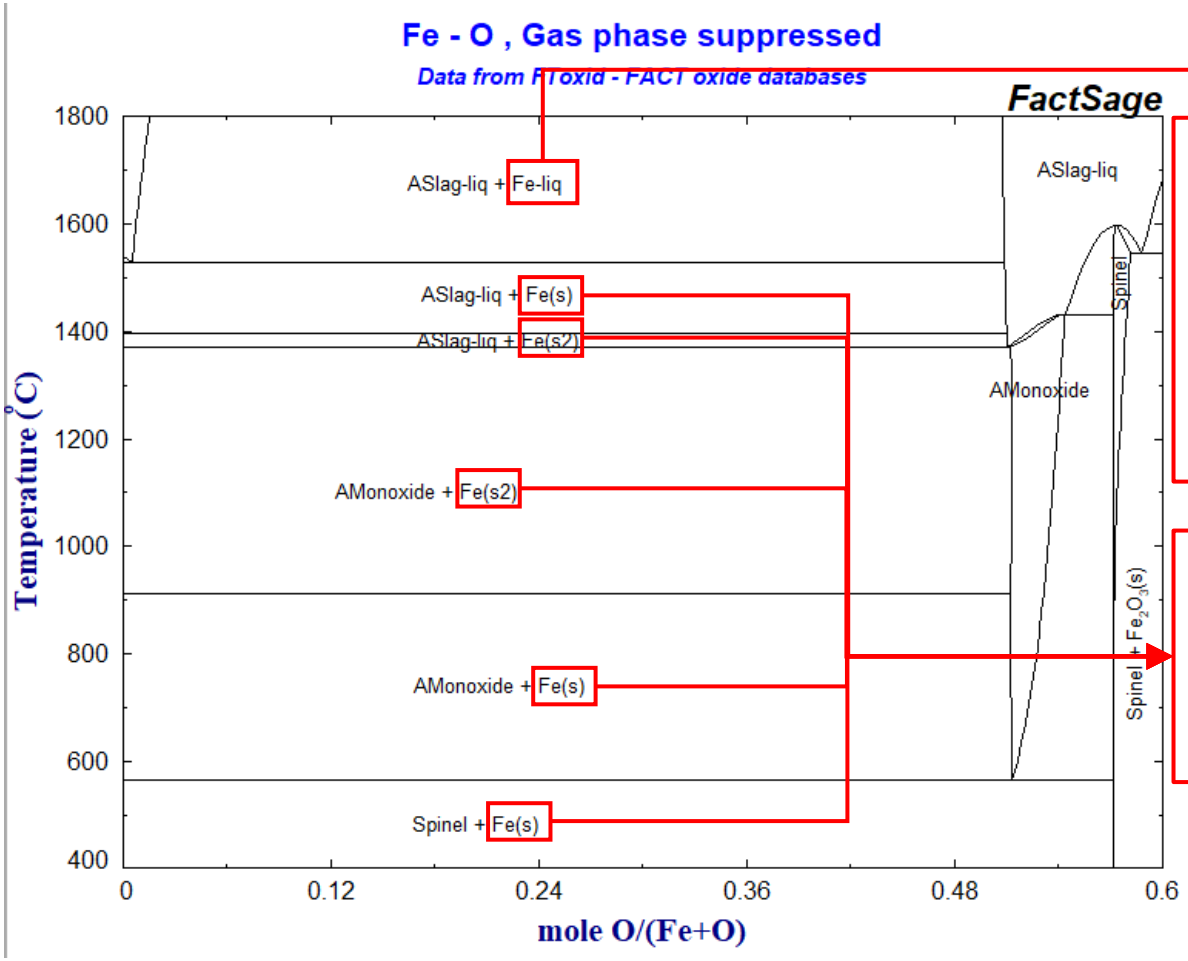
Phase Diagram Module: Fe-O_2 System

Components Window: Define Components



Phase Diagram Module: Fe-O_2 System

Before we choose the database(s), let us check the pre-made phase diagram.



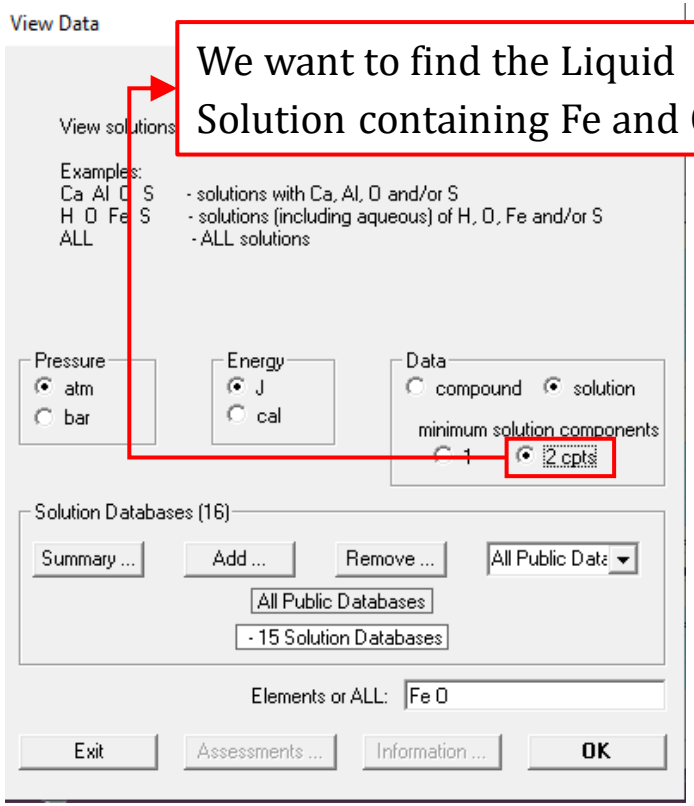
Note: the Fe-Liq phase is a solution phase. Limited amounts of oxygen are dissolved in liquid Fe. However, FToxid does not contain a phase model for Fe-Liq which is **liquid metal**.

These Fe structures have no solubility for oxygen. However, FToxid does not contain phase models for pure metals.

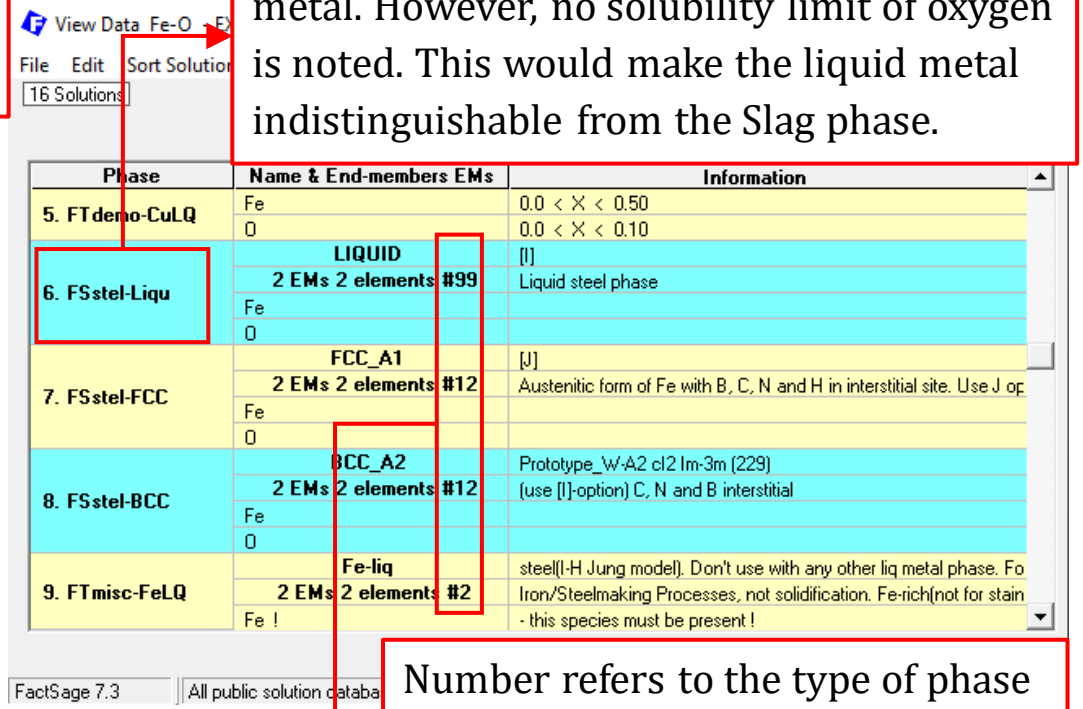
Phase Diagram Module: Fe-O_2 System

We use the View Data Module to determine which other databases are needed.

First, check the Liquid Solution.



We want to find the Liquid Solution containing Fe and O.



This **might** be a suitable phase for the liquid metal. However, no solubility limit of oxygen is noted. This would make the liquid metal indistinguishable from the Slag phase.

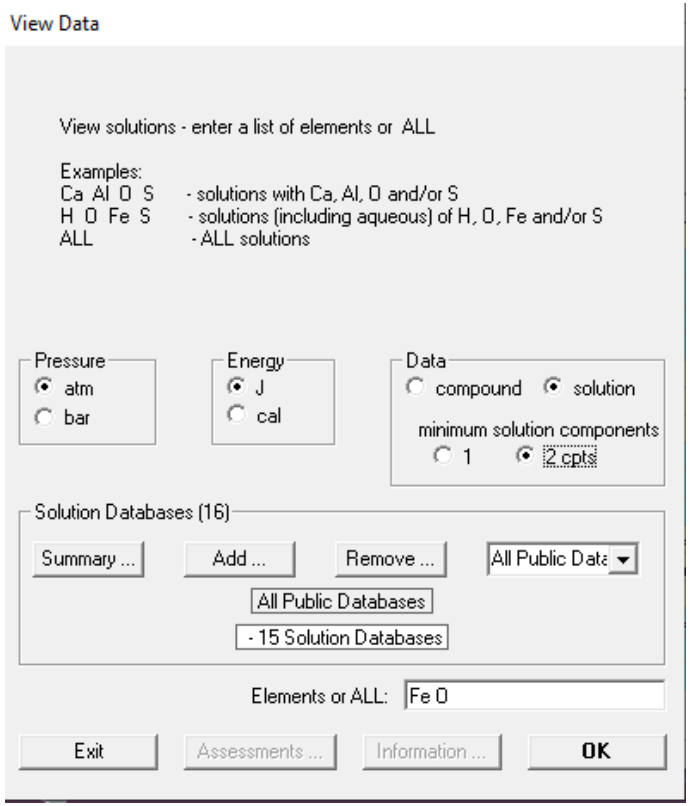
Number refers to the type of phase model. See the supplementary of Solution Module.

Note: there is no need to check the FTdemo database.

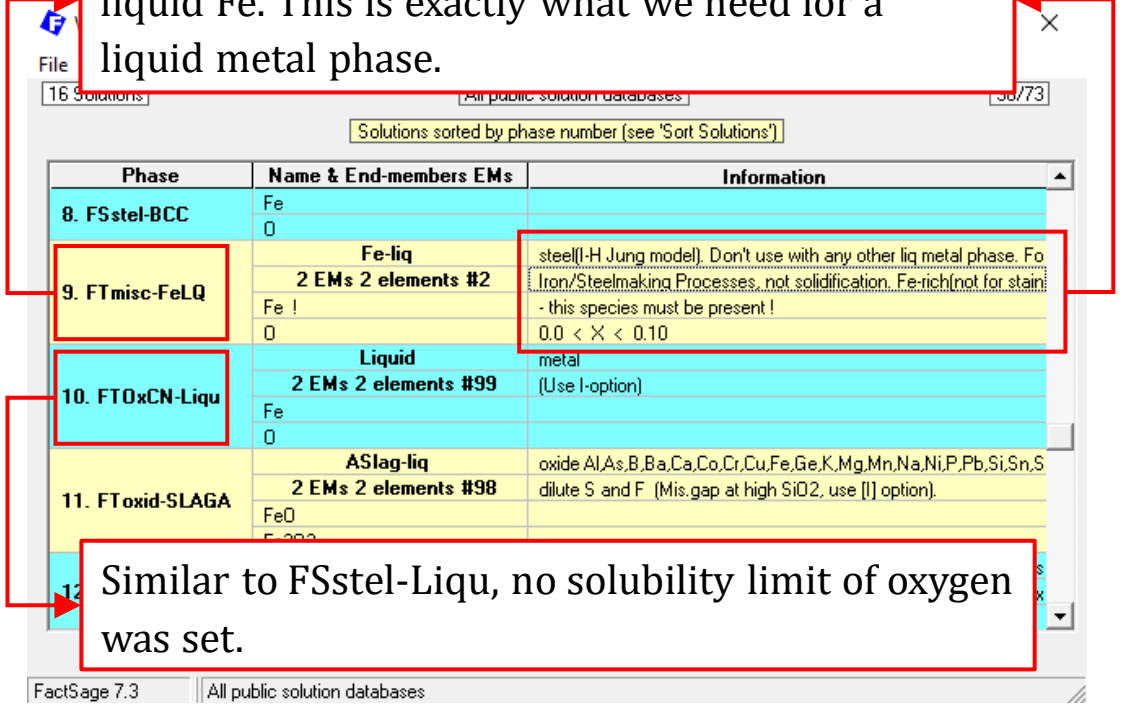
Phase Diagram Module: Fe-O_2 System

We use the View Data Module to determine which other databases are needed.

First, check the Liquid Metal.



This phase sets the solubility limit of oxygen in liquid Fe. This is exactly what we need for a liquid metal phase.



Similar to FSstel-Liqu, no solubility limit of oxygen was set.

Note: there is no need to check the FTdemo database.

Phase Diagram Module: Fe-O_2 System

We use the View Data Module to determine which other databases are needed.

First, check the Liquid Metal.

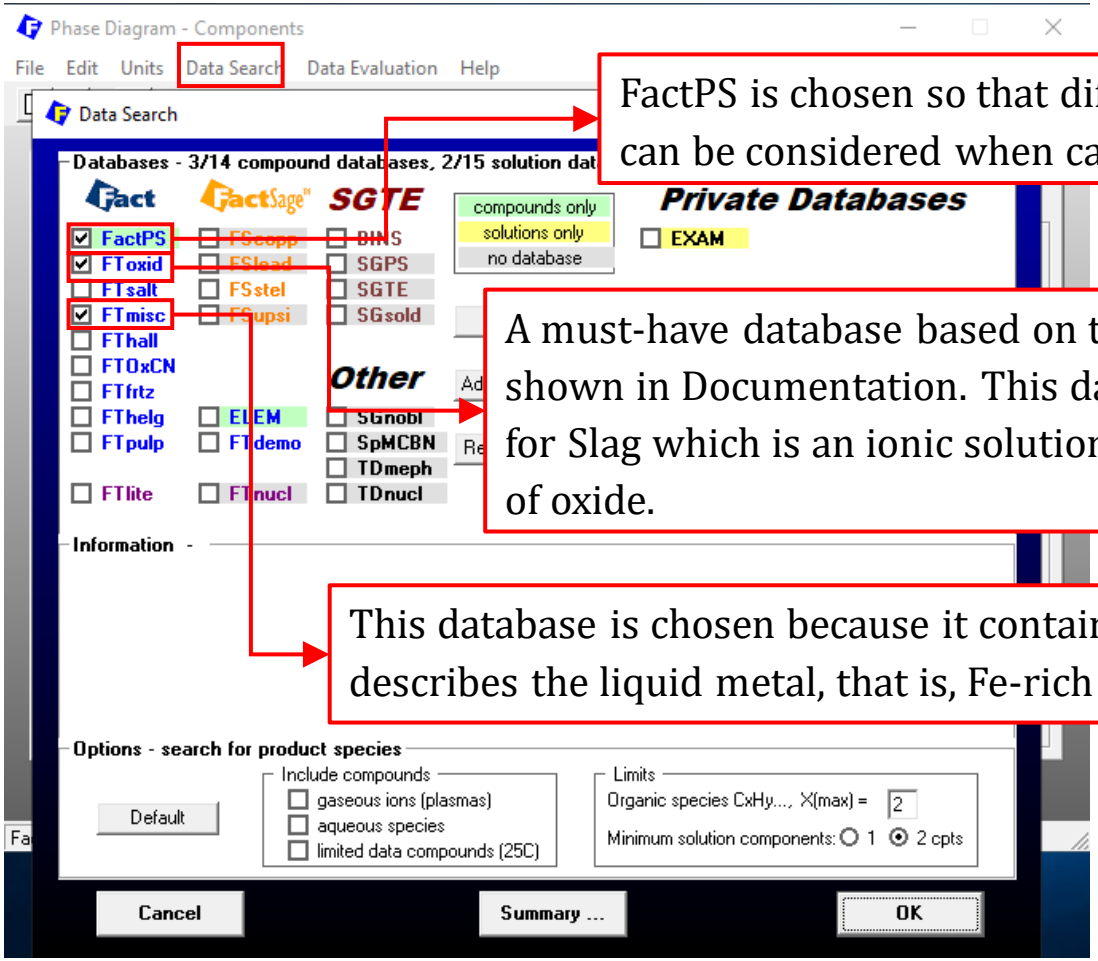
The above information shows that FTmisc-FeLQ is probably the best candidate for the liquid metal phase. Therefore, FTmisc database should be chosen.

For the solid **metallic Fe** phases, since the solubility is very low, you can choose either FactPS database which ignores the solubility of oxygen, or FSstel database which considers the dissolution of oxygen (FSstel-BCC and FSstel-FCC). Here, we choose FactPS .

Now let us reproduce the Fe-O phase diagram before we calculate the Fe-O_2 phase diagram.

Phase Diagram Module: Fe-O_2 System

Components Window: Choose Database(s)



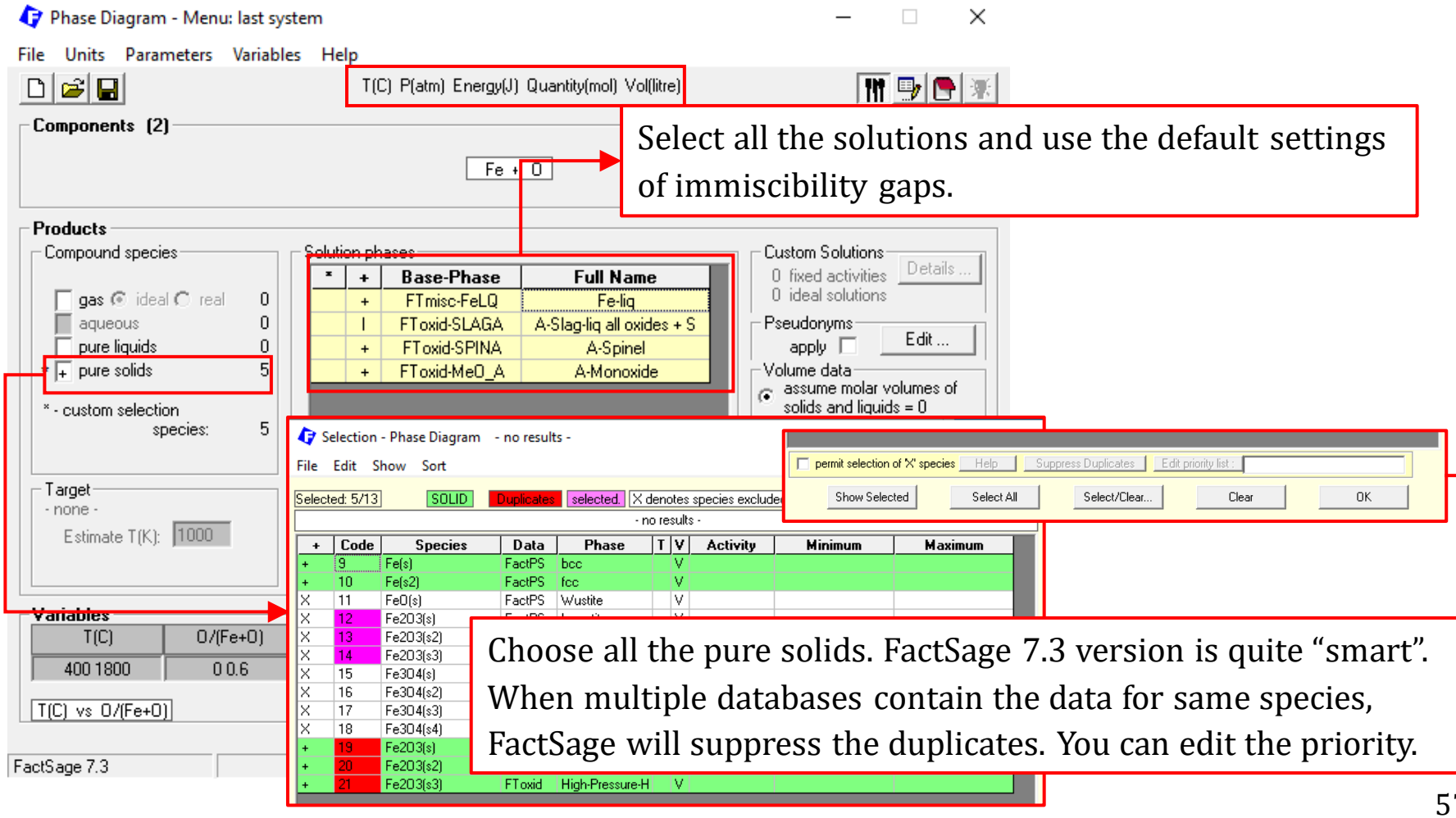
FactPS is chosen so that different solid pure Fe structures can be considered when calculating the phase diagram.

A must-have database based on the pre-made phase diagram shown in Documentation. This database includes the models for Slag which is an ionic solution and other solid solutions of oxide.

This database is chosen because it contains the model which describes the liquid metal, that is, Fe-rich solution.

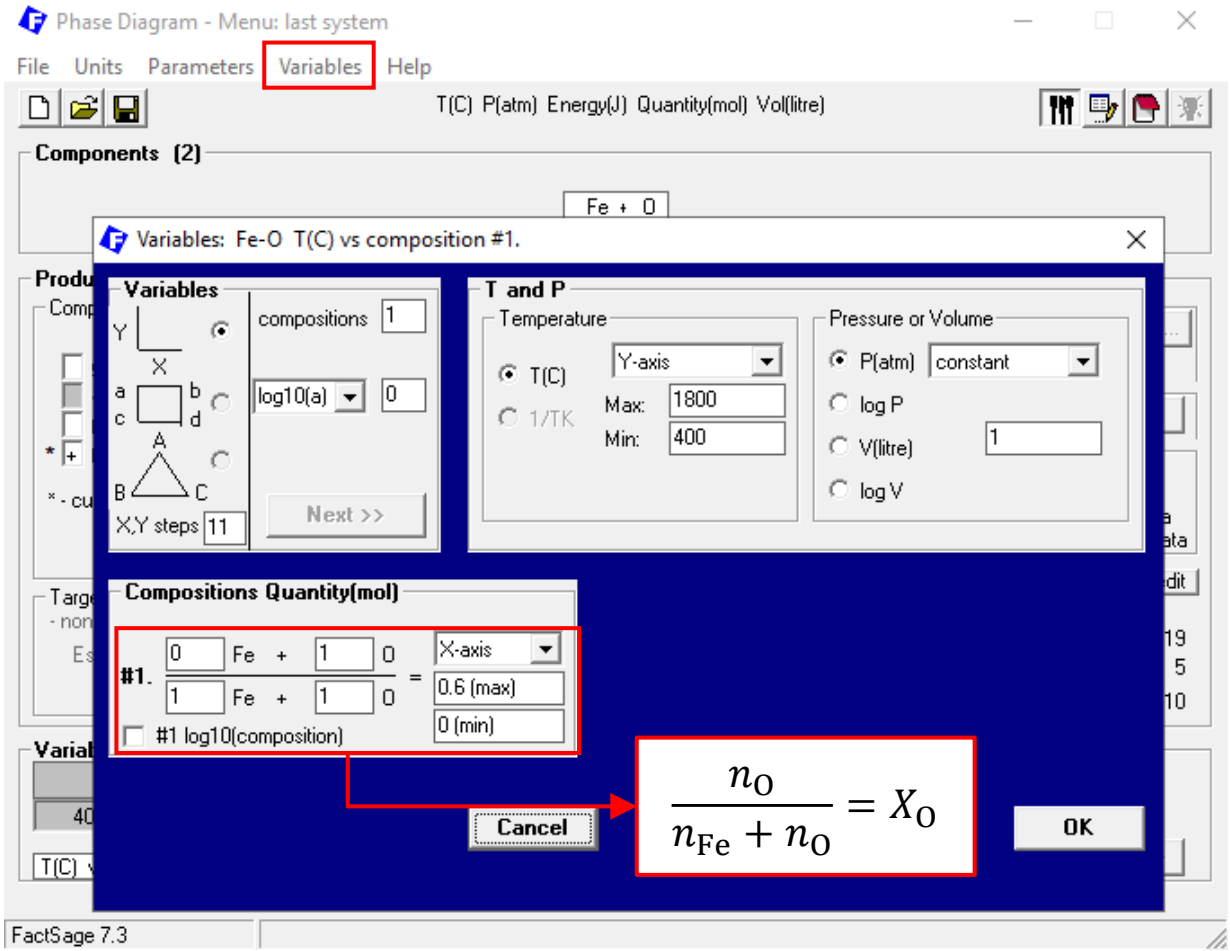
Phase Diagram Module: Fe-O_2 System

Menu Window: Choose Products/Phases (Compounds and Solution Phases)



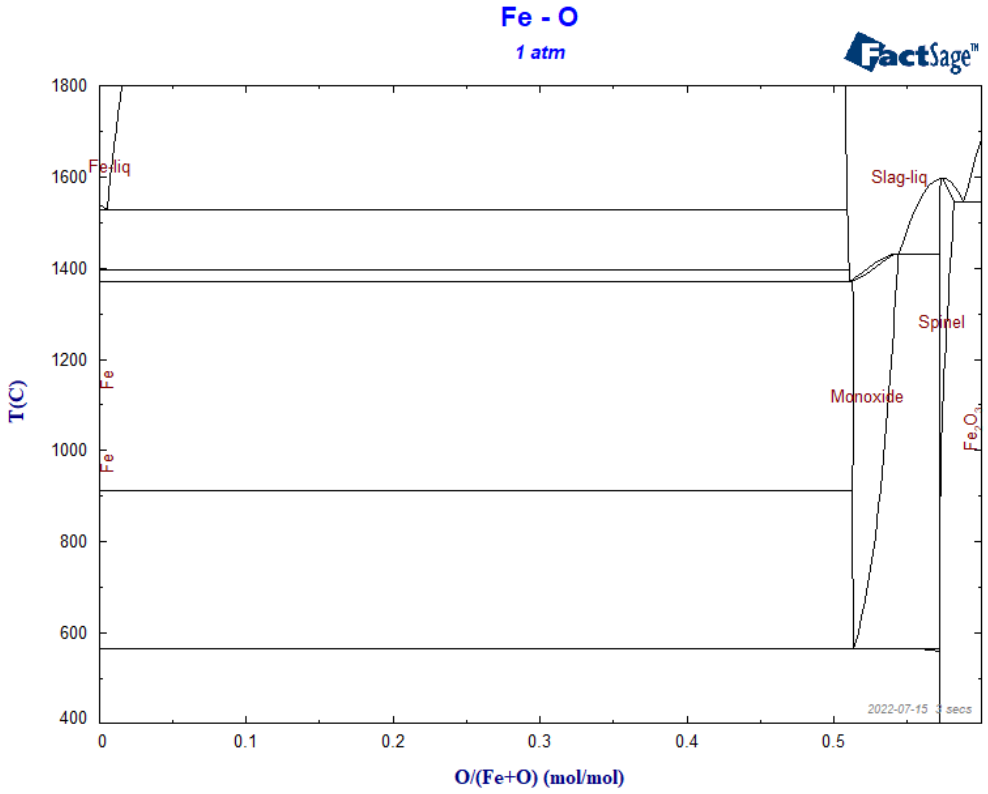
Phase Diagram Module: Fe-O_2 System

Menu Window: Choose Variables



Phase Diagram Module: Fe-O_2 System

Results: Fe-O Phase Diagram ($T \sim X_O$ Phase Diagram)



Stable Phases

Stochiometric Phases - compounds and one-component solutions

	mole		TC(min)	TC(max)
1	0.0000	Fe(s)	400.00	1537.79
2	0.0000	Fe(s2)	911.66	1394.32
3	0.6000	Fe2O3(s)	400.00	1684.45

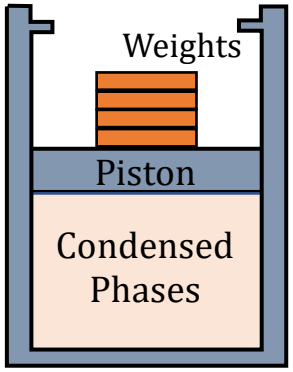
Phase Equilibria

1	1544.89 C	Slag-liq#1(0.5879)	<=>	Spinel(0.5815)	+	Fe2O3(s)(0.6)
2	1537.80 C	Fe-liq(0.0)	<=>	Fe(s)(0.0)		
3	1526.92 C	Fe-liq(0.005514)	<=>	Fe(s)(0.0)	+	Slag-liq#1(0.5088)
4	1430.24 C	Monoxide(0.5435)	<=>	Slag-liq#1(0.5434)	+	Spinel(0.5714)
5	1394.32 C	Fe(s2)(0.0)	<=>	Fe(s)(0.0)	+	Slag-liq#1(0.51)
6	1370.50 C	Slag-liq#1(0.5103)	<=>	Fe(s2)(0.0)	+	Monoxide(0.5124)
7	911.66 C	Fe(s)(0.0)	<=>	Fe(s2)(0.0)	+	Monoxide(0.5124)
8	563.55 C	Monoxide(0.5132)	<=>	Fe(s)(0.0)	+	Spinel(0.5714)

Phase Diagram Module: Fe-O_2 System

A Note on the Fe-O Phase Equilibrium: "Gas Suppression" Condition

It is worth noting that the Fe-O phase diagram shown on Slide does not include the gas phase. That is, the gas phase is suppressed.



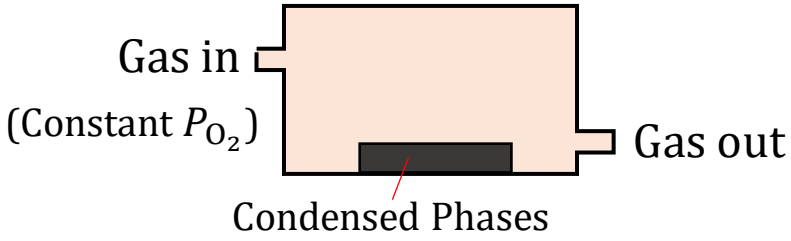
Say we fix a constant **hydrostatic** pressure of 1 atm by placing the condensed phases in a cylinder fitted with a piston (left graph). If the total gas pressure at equilibrium (i.e., sum of the partial pressures exerted by the gaseous species in the vapor phase generated by incomplete vaporization of the components) is less than 1 atm, there will be no gas phase present. This condition is referred to as "gas suppression" condition. Clearly, if we heat or cool the system, the **overall** composition of the condensed phases remain constant.

Pelton, Phase Diagrams and Thermodynamic Modeling of Solutions, 2019 (Chapter 7.8)

Phase Diagram Module: Fe-O_2 System

A Note on the Fe-O Phase Equilibrium: Fixed Oxygen Potential

Different from the previous condition under which the composition of the condensed phases remains unchanged, another condition is to control the oxygen content in the gas phase, i.e., constant partial pressure P_{O_2}.

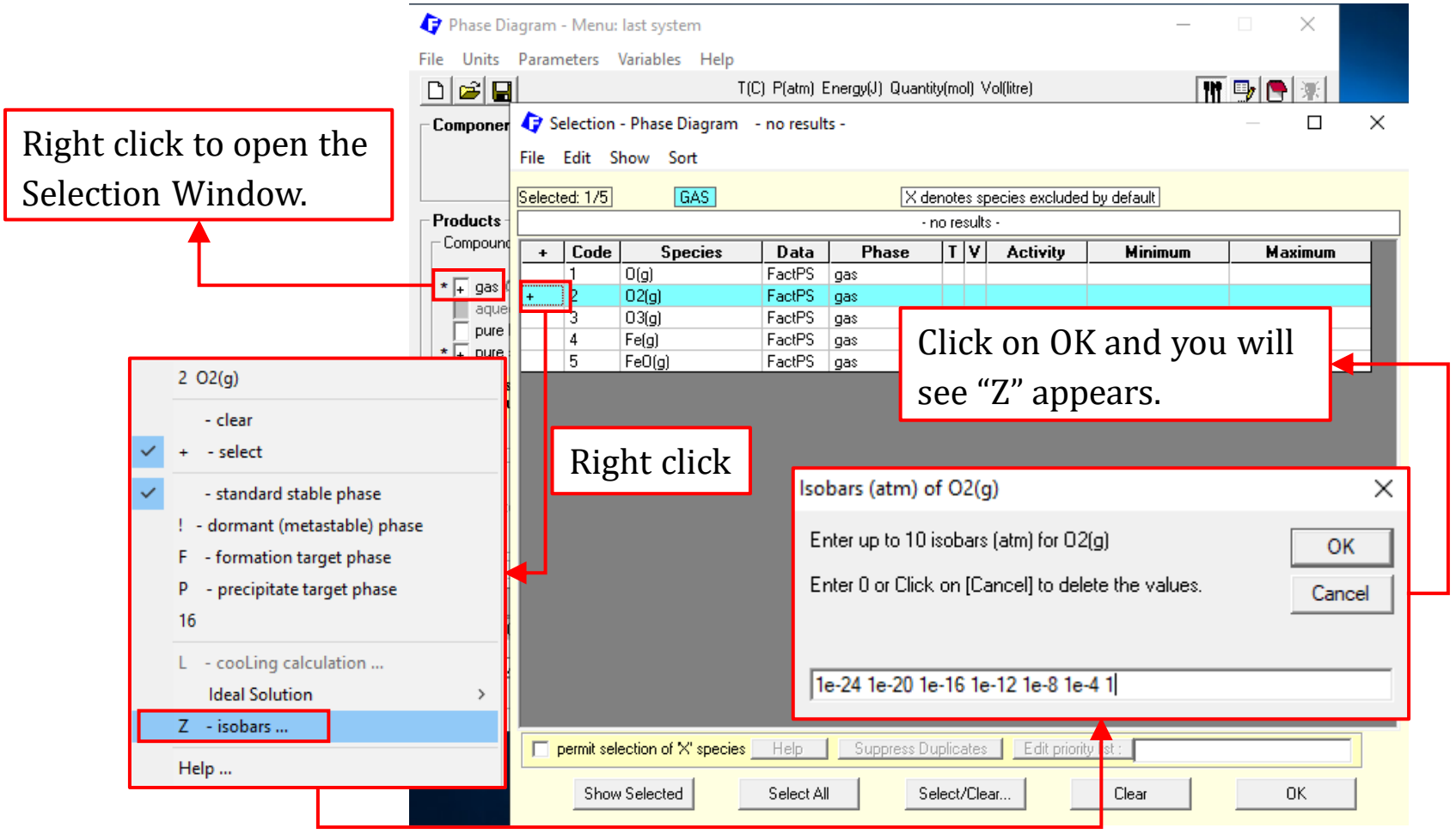


Note: the mass ratio of gas to condensed phases is large enough so that the composition of gas-in and that gas-out is same.

When the above system reaches equilibrium, the condensed phases (solid and/or liquid) are equilibrated with a gas phase with fixed P_{O_2}. Say we wish to fix P_{O_2} in the range of 10^{-24} to 1 atm. Now let us plot the oxygen isobars on the Fe-O phase diagram.

Phase Diagram Module: Fe-O_2 System

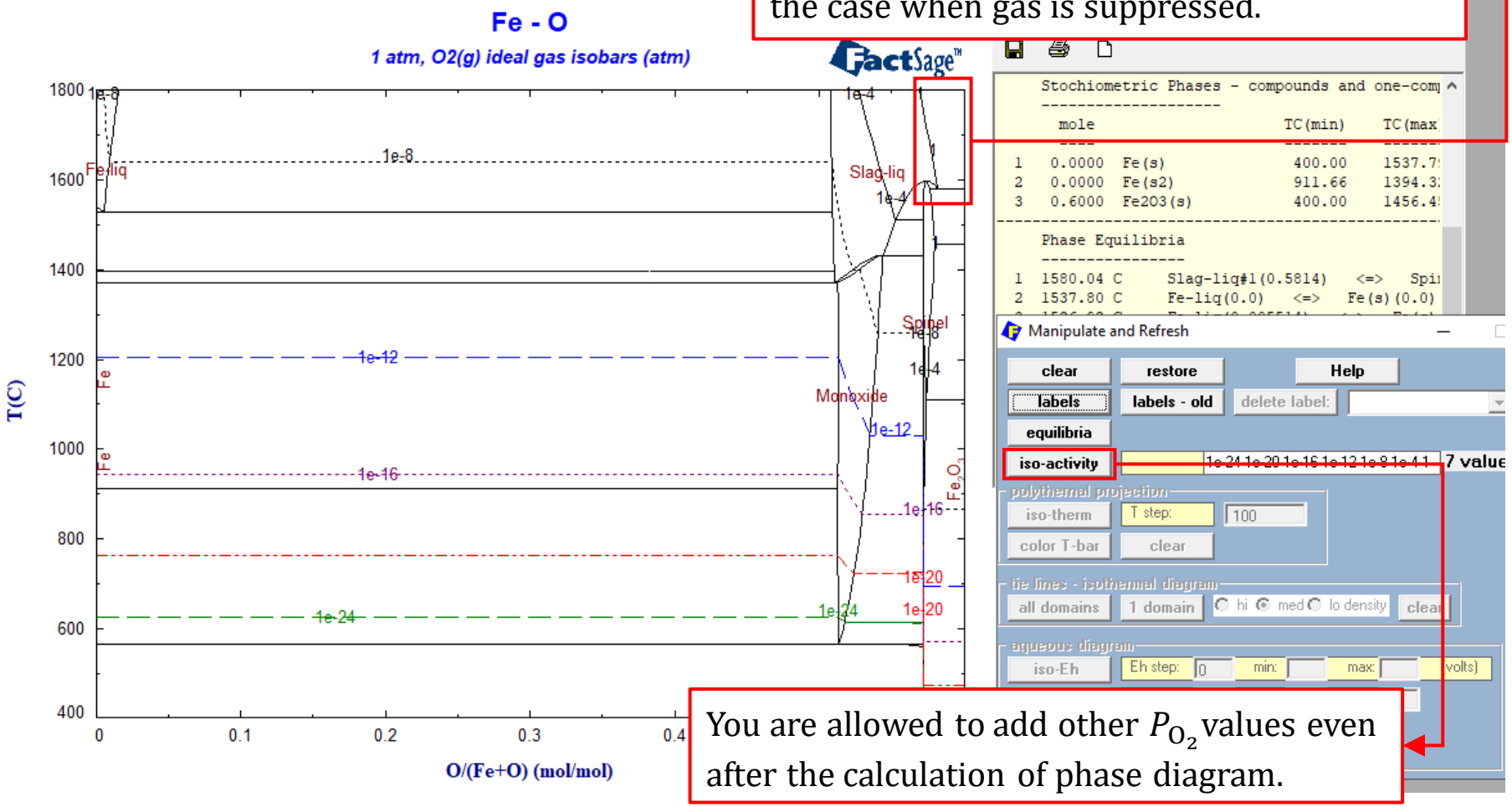
Back to the Menu Window (Slide)



Phase Diagram Module: Fe-O_2 System

Back to the Menu Window (Slide)

You may noticed this region is different from the case when gas is suppressed.



You are allowed to add other P_{O_2} values even after the calculation of phase diagram.

Phase Diagram Module: Fe-O_2 System

A Note on the Fe-O Phase Equilibrium: Fixed Oxygen Potential

The calculated Fe-O phase diagram with the P_{O_2} isobars can be used to study a heating or cooling process.

Say we are controlling the oxygen partial pressure $P_{O_2} = 10^{-8}$ atm. From the calculated Fe-O phase diagram, it is seen that along the line of $P_{O_2} = 10^{-8}$ atm, the highest temperature is > 1800 °C, and the condensed phase should be pure iron. Now, if we cool this system while keeping the oxygen partial pressure constant (10^{-8} atm), the composition of the condensed phase will be changed along the line of $P_{O_2} = 10^{-8}$ atm because of the oxidation.

The above simple analysis shows that the variables, i.e., temperature, composition of the condensed phases and P_{O_2} are correlated. As West and Saunders commented that the partial pressure of oxygen is a function of both temperature and composition.

West and Saunders, Ternary Phase Diagrams in Materials Science, 3rd Edition, 2002

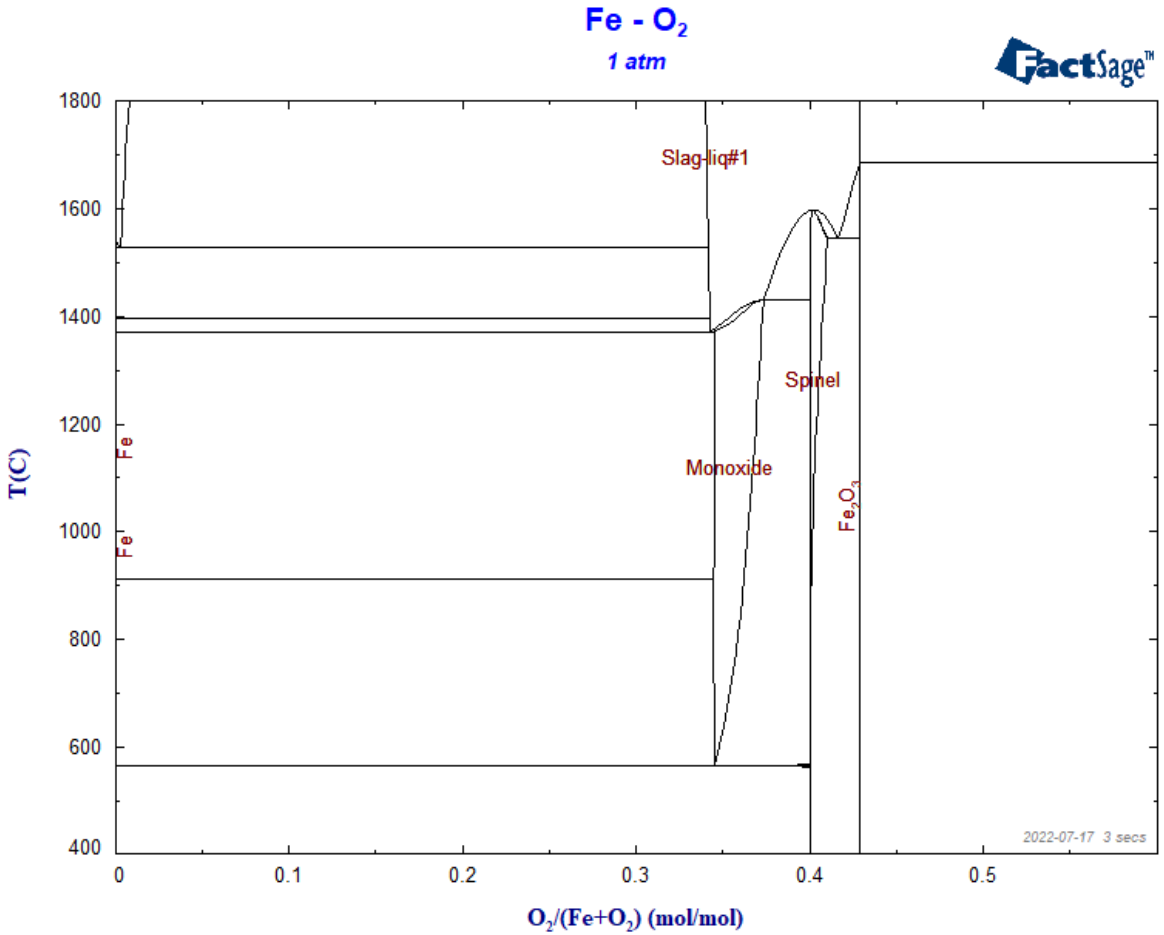
Phase Diagram Module: Fe-O_2 System

Now, we have successfully reproduce the Fe-O phase diagram shown in the Documentation. To calculate the Fe-O_2 phase diagram, we need to change the component "O" to "O_2", but do not change the phase selection.

You can calculate either the condition under which the gas phase is suppressed, or the condition of fixed P_{O_2}. Here, we only show the calculation when the gas phase is suppressed.

Phase Diagram Module: Fe-O_2 System

Results: Fe-O_2 Phase Diagram ($T \sim X_{O_2}$ Phase Diagram)



Phase Diagram Module: Fe-O_2 System

Next, let us look at two-potential phase diagrams. We will again use the Fe-O_2 system as the example to calculate $T \sim \mu_{O_2}$ (thermal potential~chemical potential) for the Fe-O_2 system.

You might ask why we want to use μ_{O_2} as a variable? From the master equation, we know,

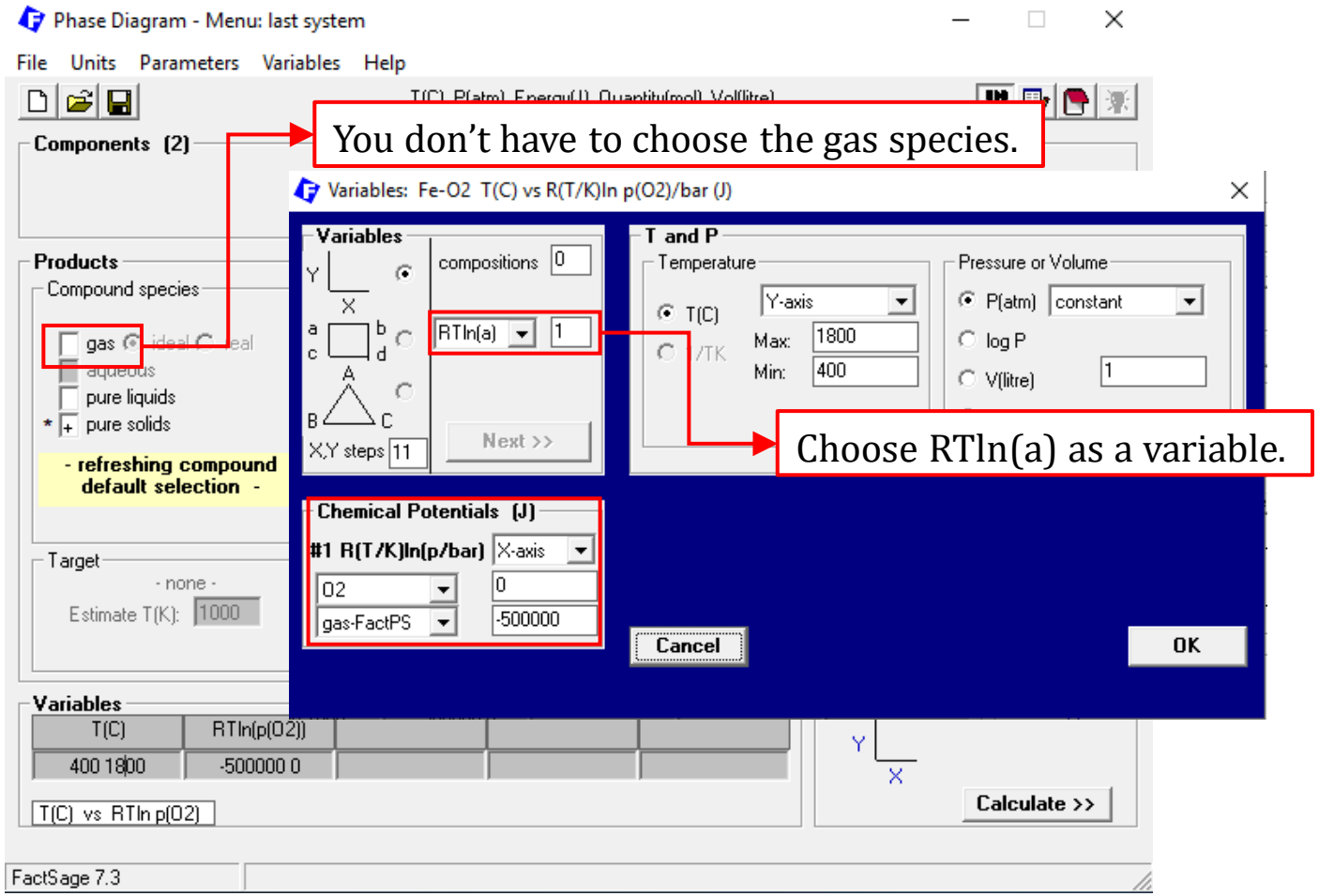
$$\mu_{O_2} = \mu^\circ_{O_2} + RT\ln\left(P_{O_2}\right)$$

This means that, the topology of the $T \sim \mu_{O_2}$ diagram is same to that of the $T \sim RT\ln\left(P_{O_2}\right)$ diagram. **Clearly**, we are very interested in the effect of P_{O_2} on the phase equilibria. However, you should note that the topology of the $T \sim \mu_{O_2}$ diagram is different from that of the $T \sim \ln\left(P_{O_2}\right)$ diagram.

Pelton, Phase Diagrams and Thermodynamic Modeling of Solutions, 2019 (Chapter 7)

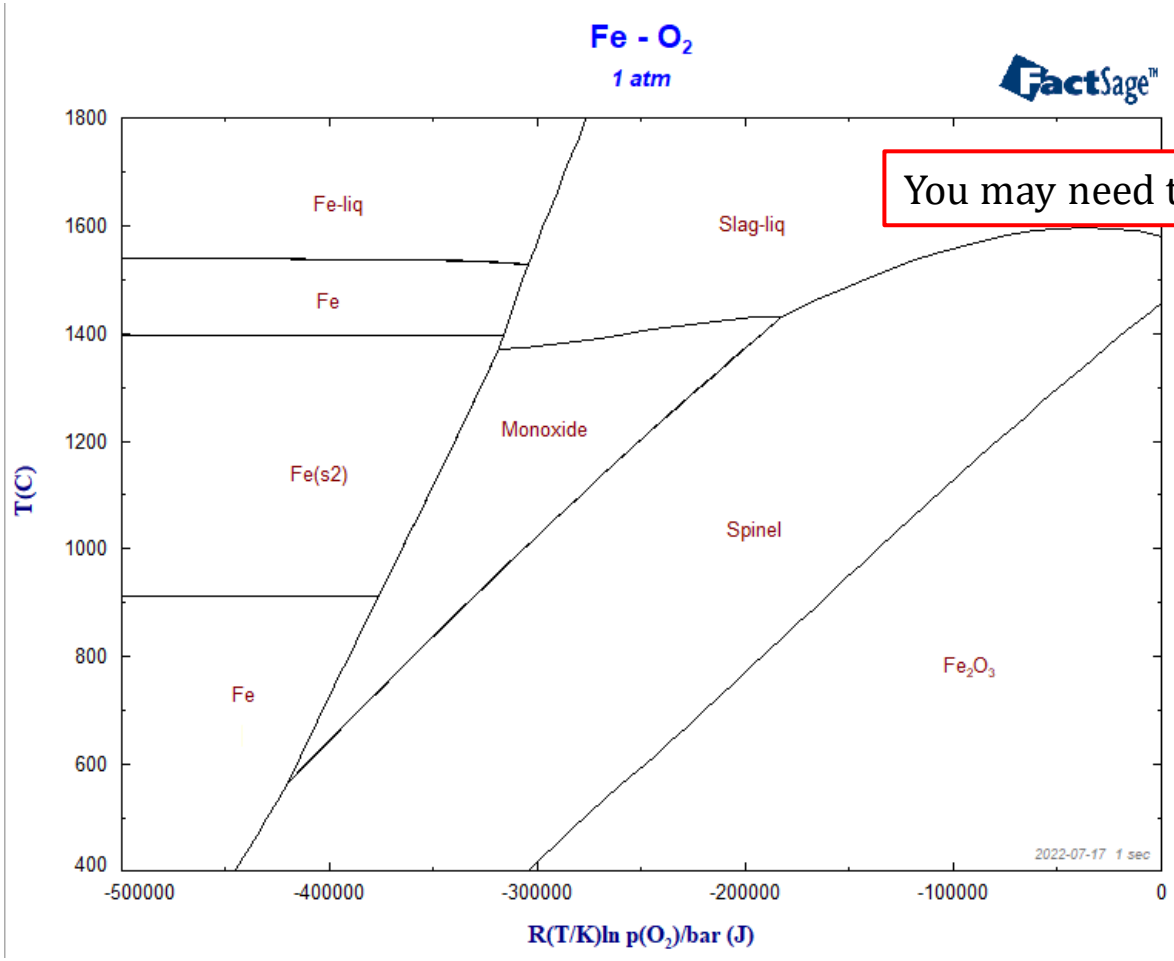
Phase Diagram Module: Fe-O_2 System

Back to the Menu Window, and activate the Variables Window



Phase Diagram Module: Fe-O_2 System

Results: Fe-O_2 Phase Diagram (Two-potential Phase Diagram)



You may need to add labels manually.

This is a very useful diagram. It shows the stability regions of various condensed phases.

FactSage Practical
MSE302

Practical 3. Phase Diagram Calculation

Phase Diagram Module: Ternary System

Phase Diagram Module

The phase diagram for a ternary system requires a space model. Because of this, we normally calculate **isothermal sections** and **liquidus projections** which are easier to view in a 2D space.

The Phase Diagram Module can be used to calculate above phase diagrams for ternary systems. Two examples will be presented, one is metallic system and the other is oxide system.

A Note: most binaries have been critically assessed using existing experimental data and therefore the binary phase diagrams reported by different accessors (or model developers) generally agree with each other. However, this is not true for ternary and higher-order systems. Since the amount of work in measuring even one isothermal section of a relatively simple **ternary** phase diagram is enormous, most of ternary phase diagrams and higher-order phase diagrams are estimates extrapolated from critically evaluated binaries, and validated using limited amounts of experimental data.

Phase Diagram Module: Al-Mg-Zn System

Let us review the FTlite database. Go to the Documentation Module, navigate to "[FTlite] – FACT Al-Alloy and Mg-alloy databases", and open the PDF document of "general description and list of optimized systems".

Al Alloys
Ag, **Al**, As, Au, **B**, **Ba**, **Be**, **Bi**, **C**, **Ca**, **Ce**, **Co**, **Cr**, **Cu**, **Dy**, **Er**, **Eu**, **Fe**, Ga, **Gd**, **Ge**, **H**, Hf, **Ho**, **In**, **K**, **La**, **Li**, **Lu**, **Mg**, **Mn**, N, **Na**, Nb, **Nd**, **Ni**, P, **Pb**, **Pr**, **Sb**, **Sc**, **Si**, **Sm**, **Sn**, **Sr**, Ta, **Tb**, **Ti**, **Tm**, **V**, W, **Y**, **Yb**, **Zn**, **Zr**
Mg Alloys
Ag, **Al**, **B**, **Ba**, **Be**, **Bi**, **C**, **Ca**, **Ce**, **Co**, **Cr**, **Cu**, **Dy**, **Er**, **Eu**, **Fe**, **Ga**, **Gd**, **Ge**, **H**, **Ho**, **In**, **K**, **La**, **Li**, **Lu**, **Mg**, **Mn**, **Na**, **Nb**, **Nd**, **Ni**, **Pb**, **Pr**, **Sb**, **Sc**, **Si**, **Sm**, **Sn**, **Sr**, **Tb**, **Ti**, **Tm**, **V**, **Y**, **Yb**, **Zn**, **Zr**
Color codes
Red : Al or Mg **Blue** : Major alloying elements (full optimisations of binary systems with **Al** and **Mg** and with several minor alloying elements, **Al-Mg-Xx** ternary systems evaluated (good for Al+Mg-rich regions), several quaternary systems included); **Green** : Minor alloying elements (full optimisations of binary systems with Al and Mg); Black : Optimized for the **Al-Zz** system and few **Al-Xx-Zz** and **Al-Yy-Zz** systems;

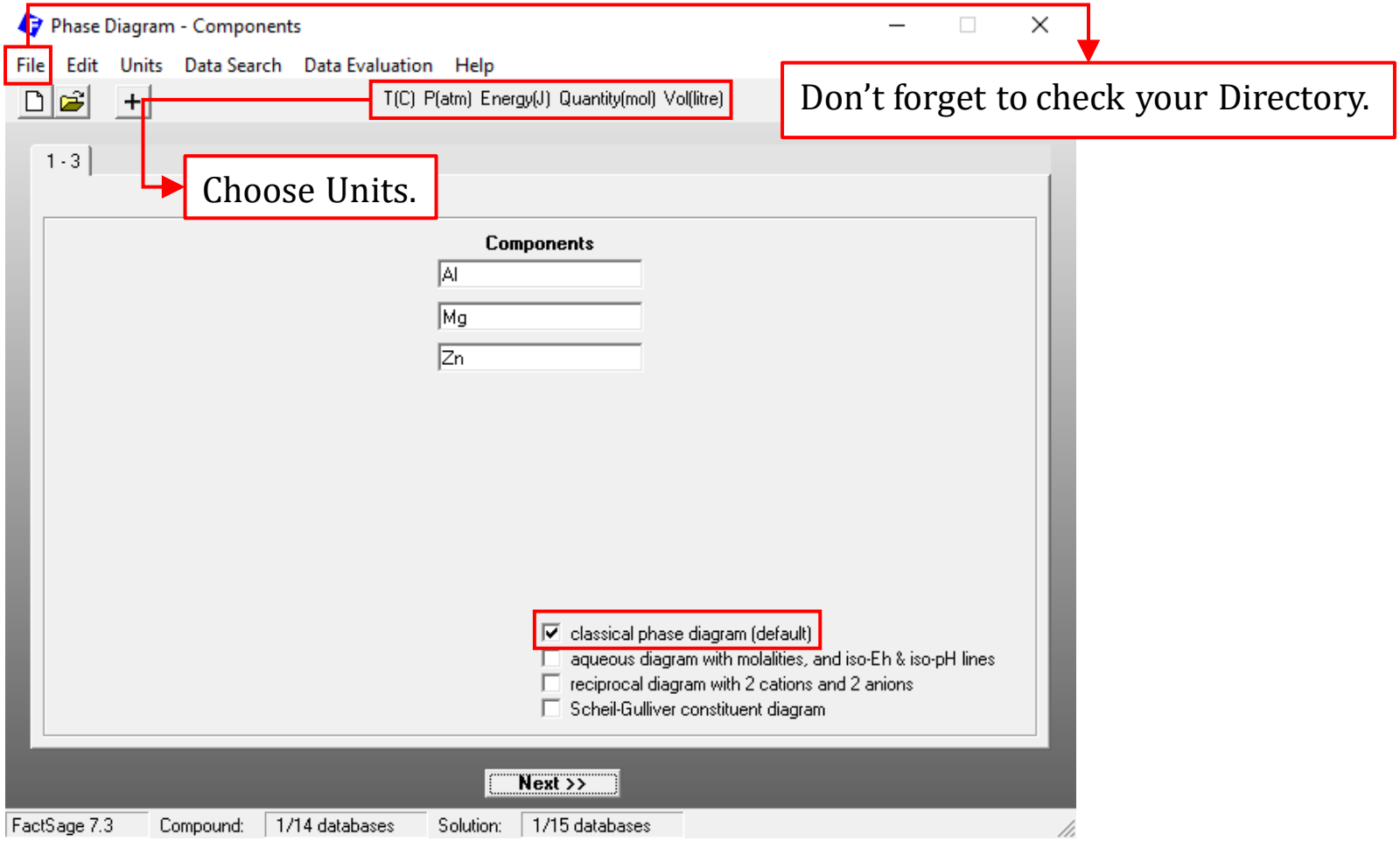
Phase Diagram Module: Al-Mg-Zn System

The above description shows that the FTlite database could be used to calculate the Al-Mg-Zn system.

Note: for the FTlite database, no pre-made phase diagram for ternary systems by CRCT (only binary systems) is available. That is, you won't be able to find the Al-Mg-Zn phase diagrams calculated using the FTlite database from the Documentation Module. You might be able to find a few Al-Mg-Zn phase diagrams calculated using the SGTE (alloy) database. Unfortunately, we do not have the access to the SGTE database.

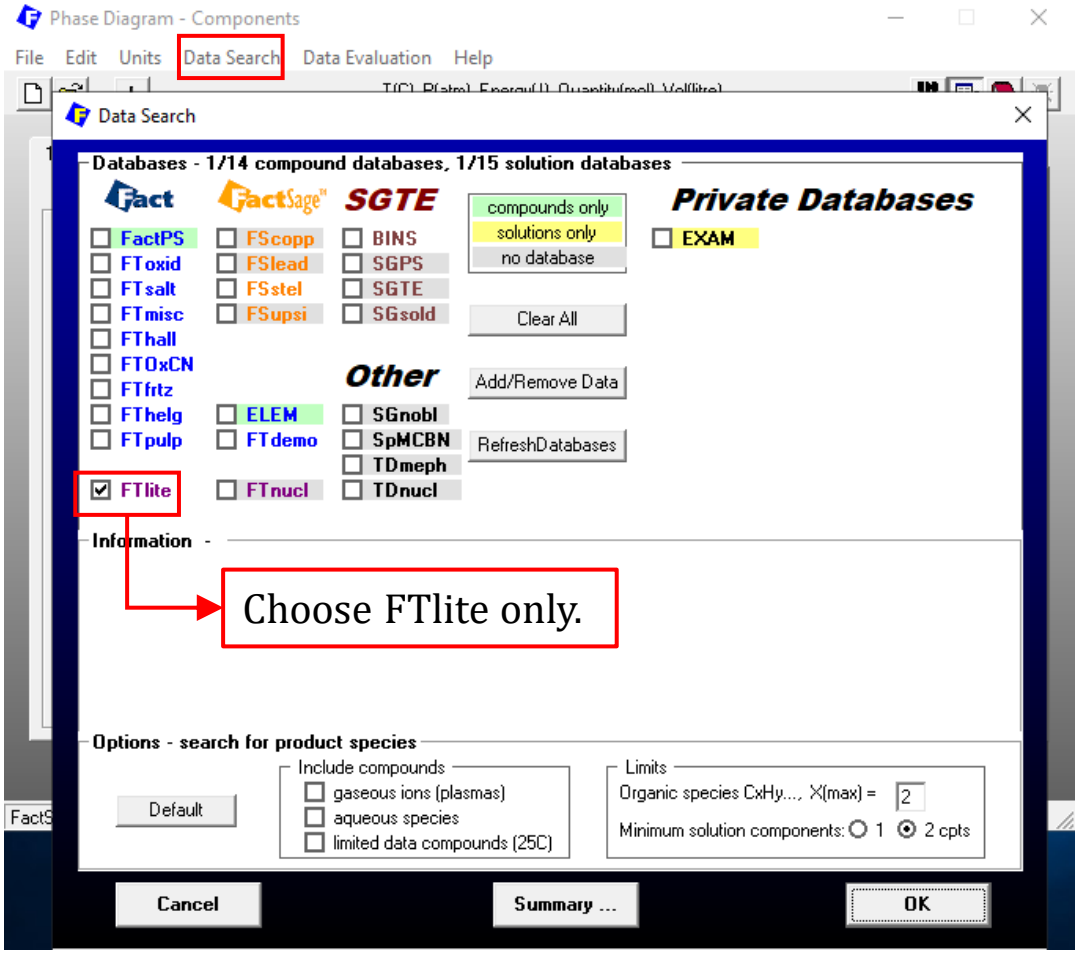
Phase Diagram Module: Al-Mg-Zn System

Components Window: Define Components



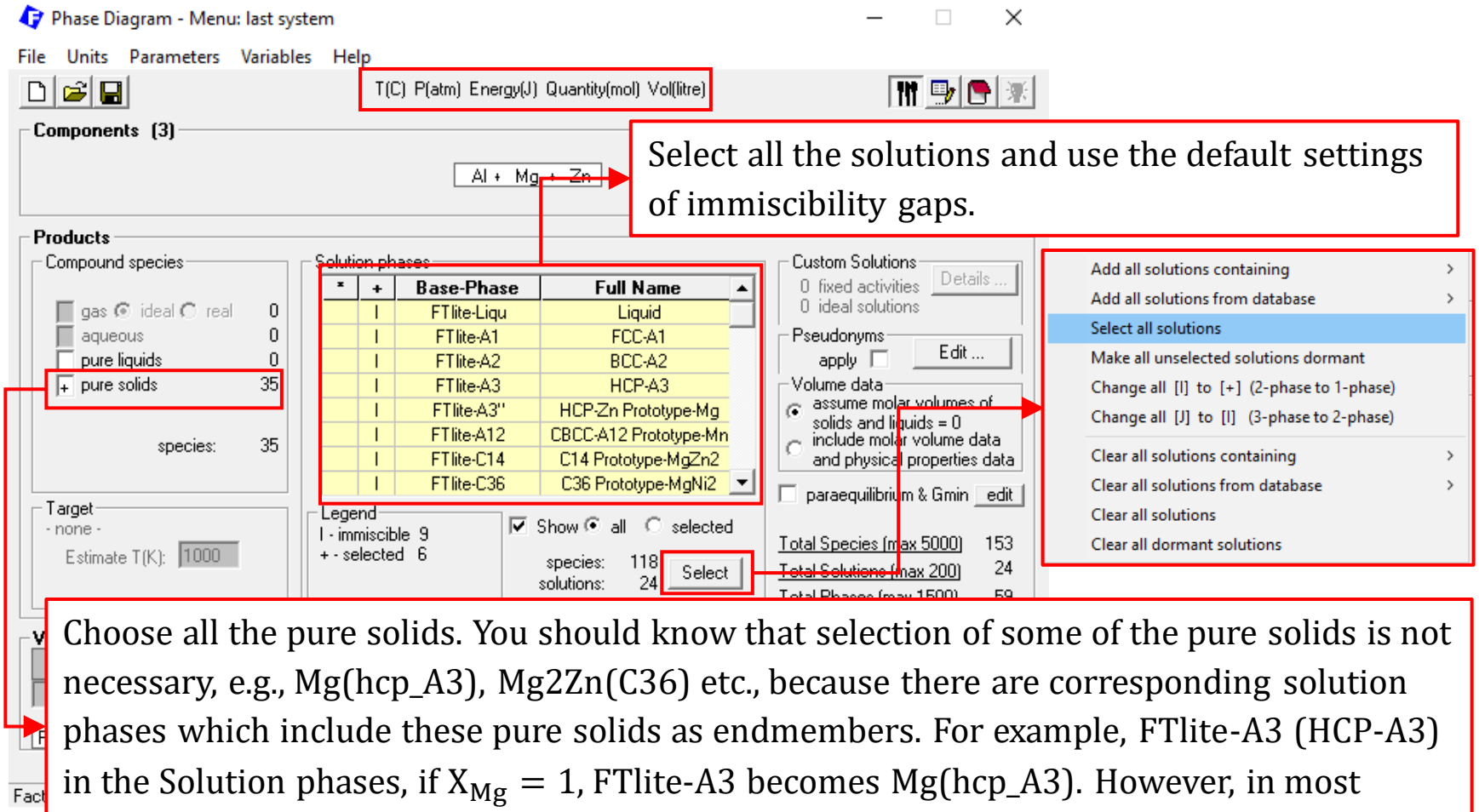
Phase Diagram Module: Al-Mg-Zn System

Components Window: Choose Database(s)



Phase Diagram Module: Al-Mg-Zn System

Menu Window: Choose Products/Phases (Compounds and Solution Phases)



Select all the solutions and use the default settings of immiscibility gaps.

Choose all the pure solids. You should know that selection of some of the pure solids is not necessary, e.g., Mg(hcp_A3), Mg2Zn(C36) etc., because there are corresponding solution phases which include these pure solids as endmembers. For example, FTlite-A3 (HCP-A3) in the Solution phases, if $X_{Mg} = 1$, FTlite-A3 becomes Mg(hcp_A3). However, in most cases, it does no harm if these phases are selected.

Phase Diagram Module: Al-Mg-Zn System

A Note on the Selection of Products/Phases

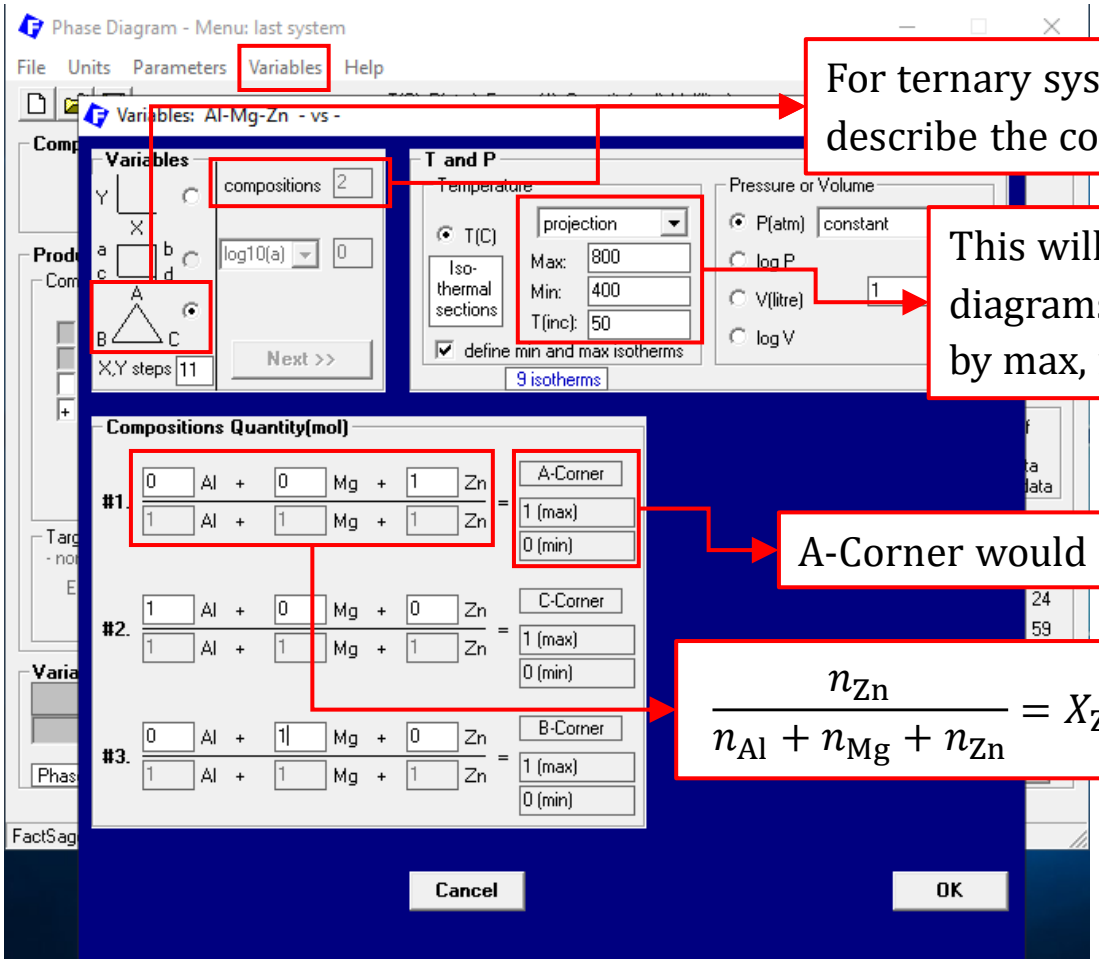
To make FactSage more user-friendly, the developers of **commercial** databases have added some key features to the databases, for example:

- ✓ [+], [I], and [J] indicate the possibility of miscibility, two-phase immiscibility, and three-phase immiscibility.
- ✓ All the endmembers of solution phases are included in the pure solids.

These features permit the FactSage users who do not have a good knowledge of thermodynamics to perform relatively reliable calculations for simple systems. **However**, for complex real-world problems, an advanced FactSage user always performs screening of products to avoid the appearance of unreasonable phases in the equilibrium calculations.

Phase Diagram Module: Al-Mg-Zn System

Menu Window: Set up the Variables (Liquidus Projections)



For ternary systems, we use Gibbs triangle to describe the composition (only 2 are needed).

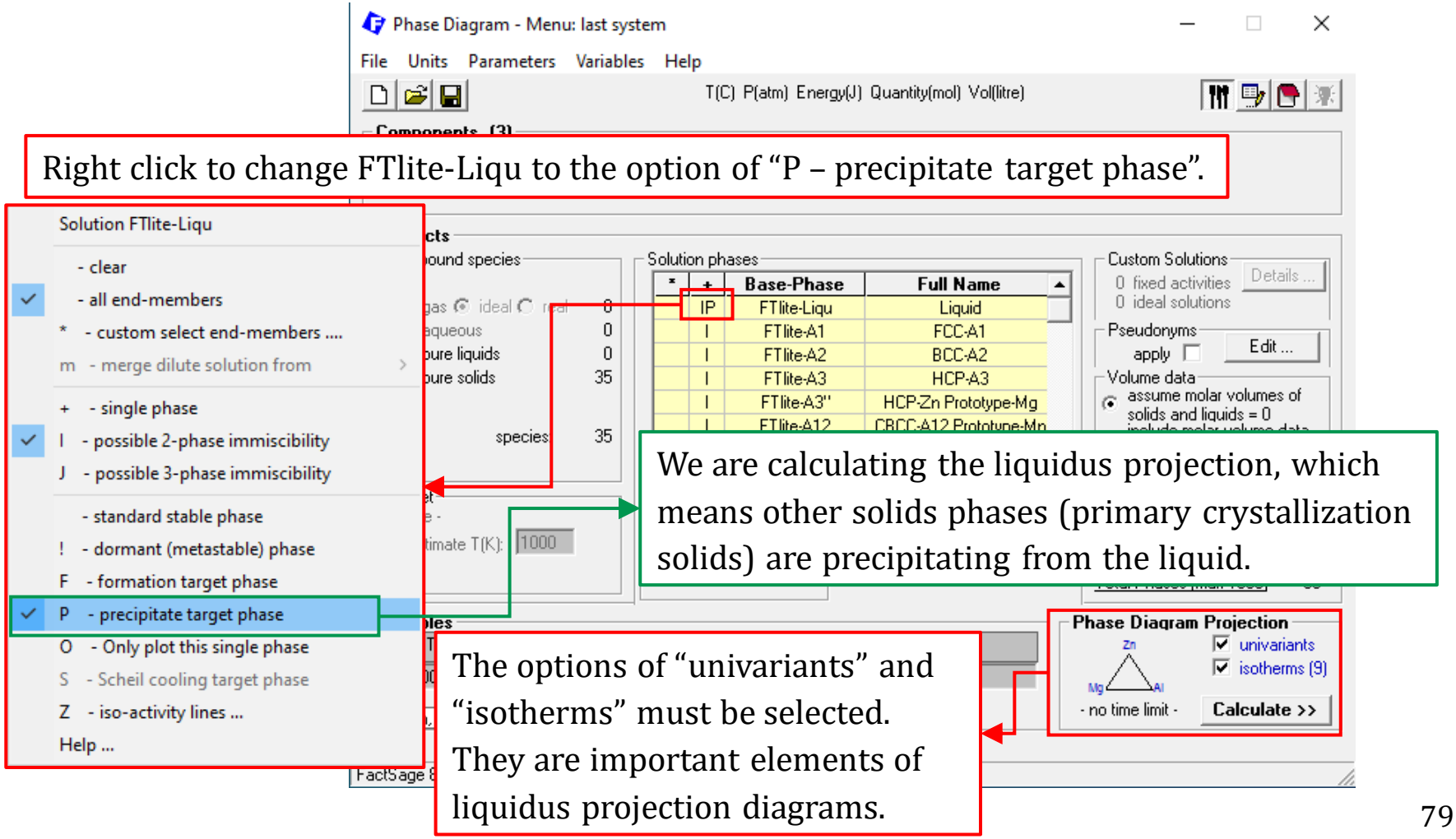
This will permit the calculation of projection diagrams. Also, the isotherms are specified by max, min and increments.

A-Corner would be Zn.

$$\frac{n_{\mathrm{Zn}}}{n_{\mathrm{Al}} + n_{\mathrm{Mg}} + n_{\mathrm{Zn}}} = X_{\mathrm{Zn}}$$

Phase Diagram Module: Al-Mg-Zn System

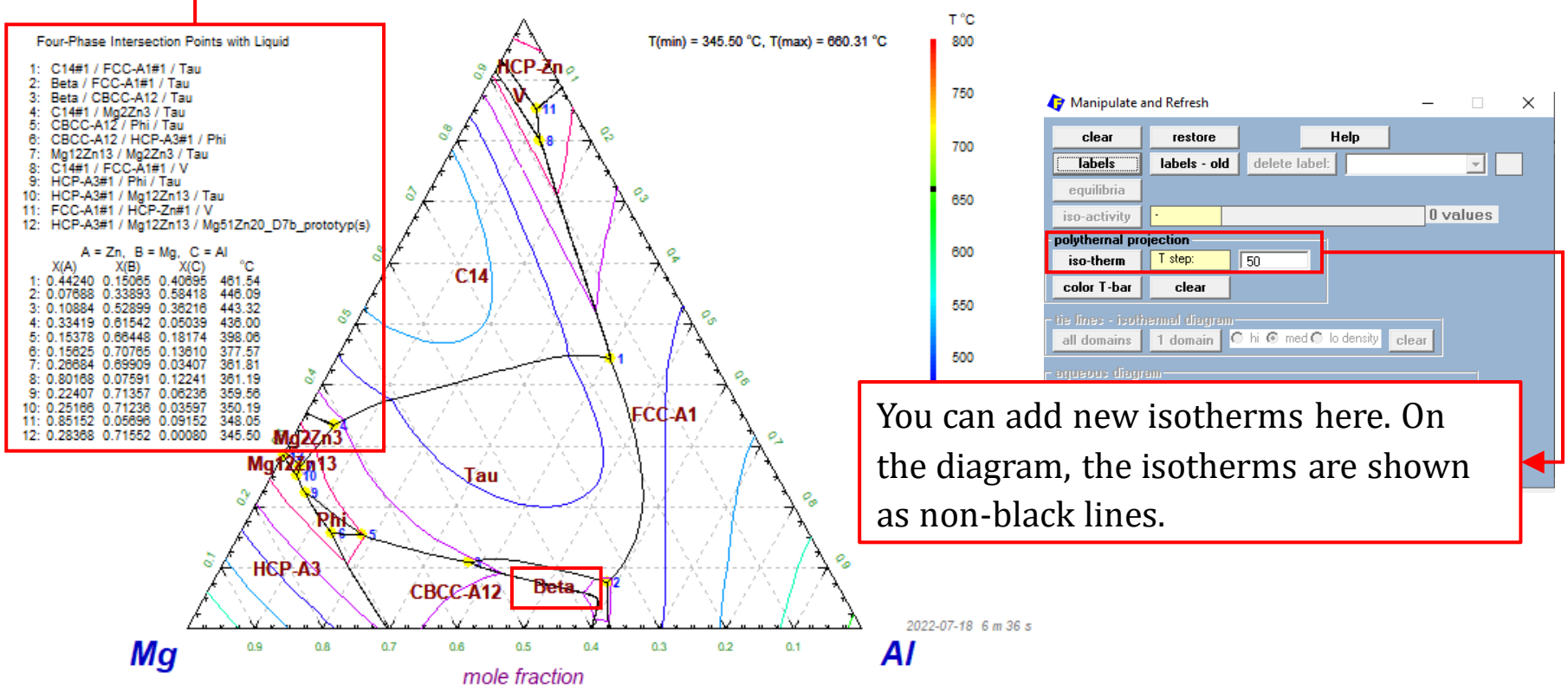
Menu Window: Choose Products/Phases (Compounds and Solution Phases)



Phase Diagram Module: Al-Mg-Zn System

Results: Liquidus Projection of the Al-Mg-Zn System (FTlite Database)

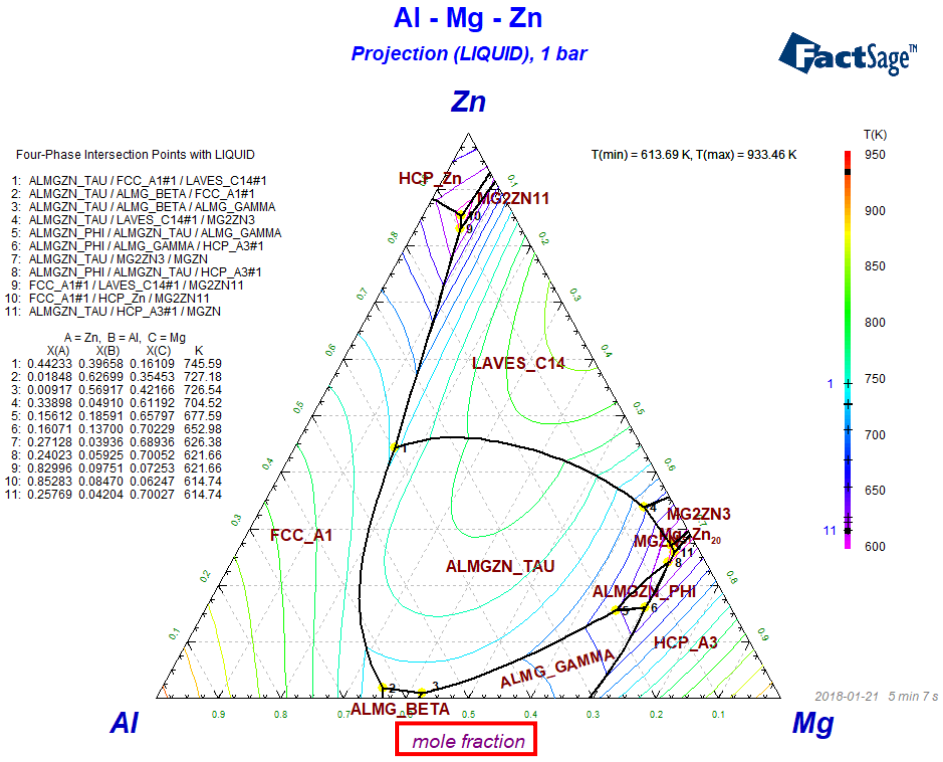
All the invariant reactions.

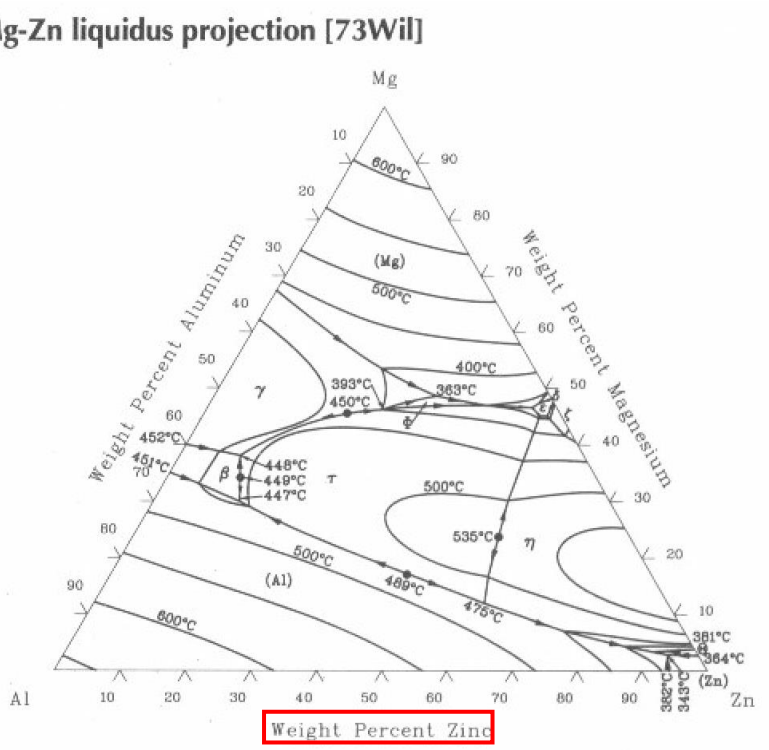


You can add new isotherms here. On the diagram, the isotherms are shown as non-black lines.

Phase Diagram Module: Al-Mg-Zn System

Comparison with the diagrams from SGTE2017 and ASM Handbook.

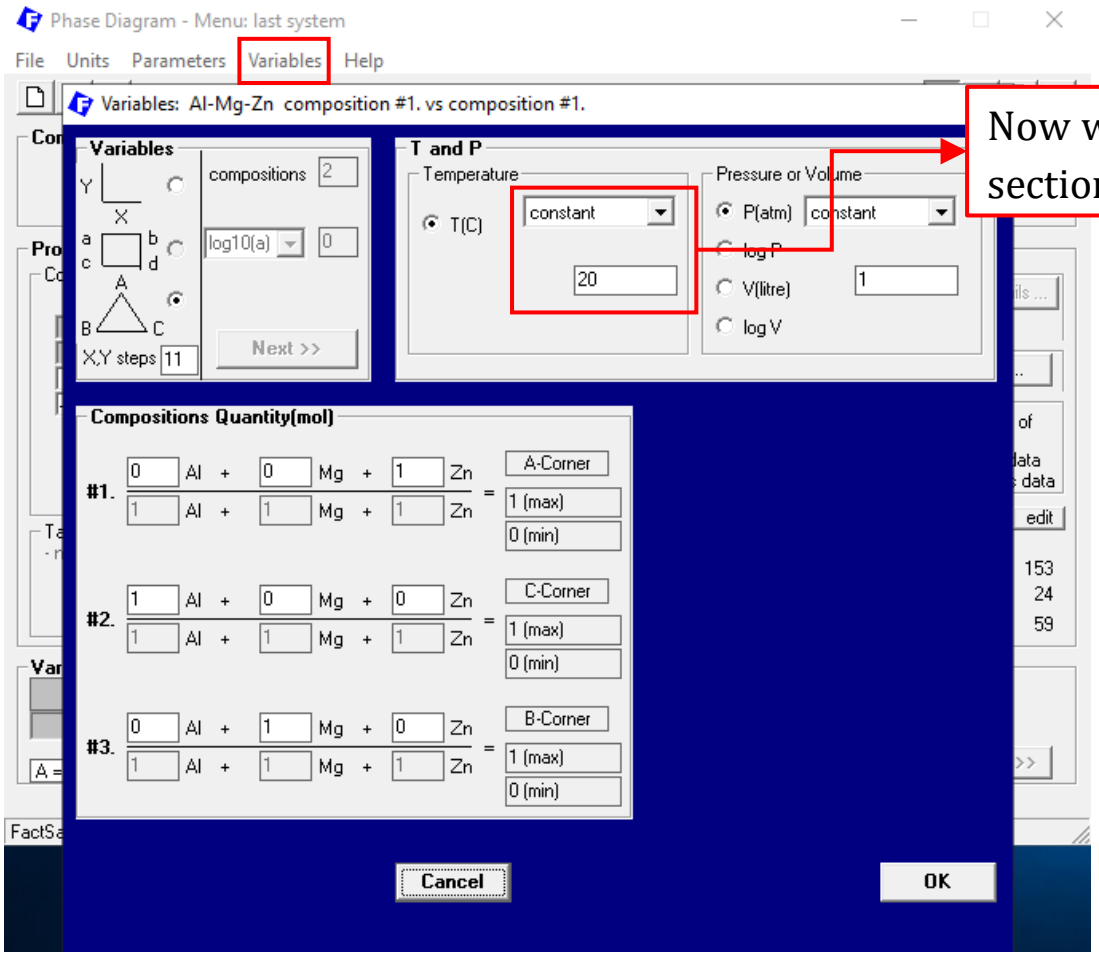




Don't be surprised if you find that the discrepancy exists for the liquidus Al-Mg-Zn projections from different sources. After all, they are all just estimates!!!

Phase Diagram Module: Al-Mg-Zn System

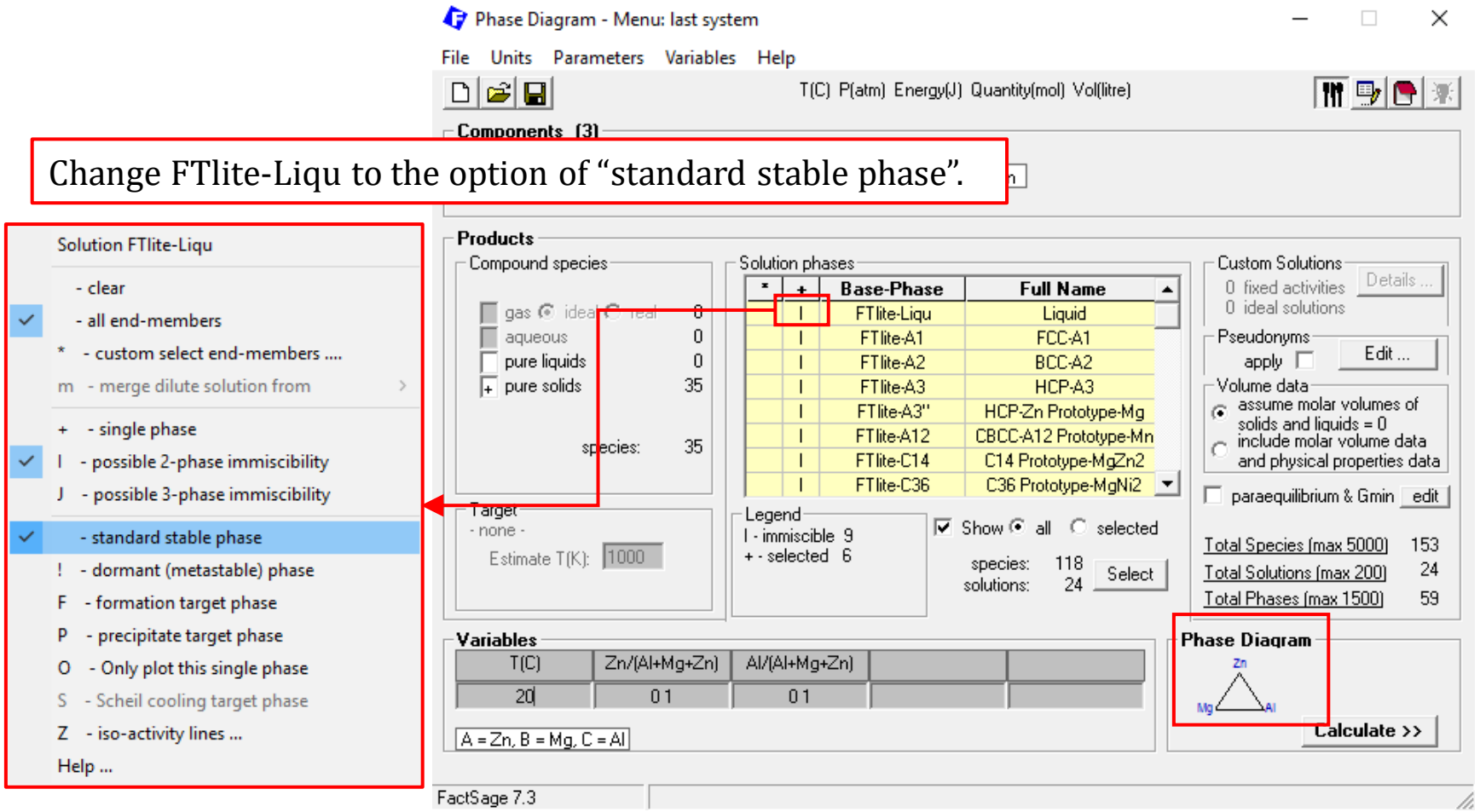
Back to Variable Window (Slide): Isothermal Sections



Now we want to calculate the isothermal section of the Al-Mg-Zn system at 20 °C.

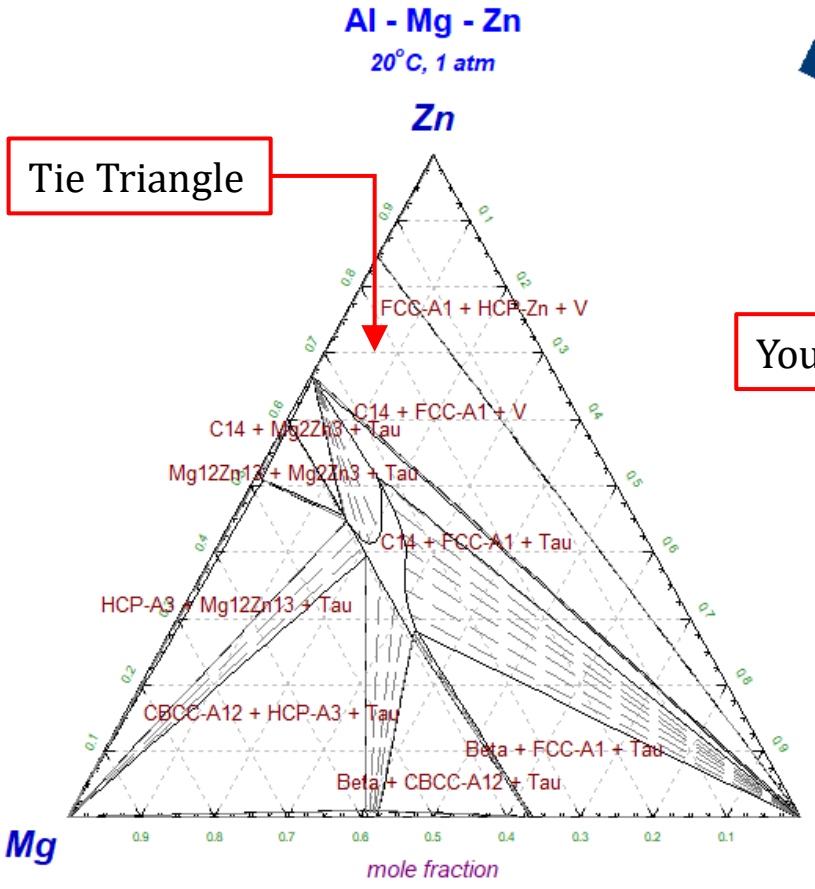
Phase Diagram Module: Al-Mg-Zn System

Menu Window: Choose Products/Phases (Compounds and Solution Phases)



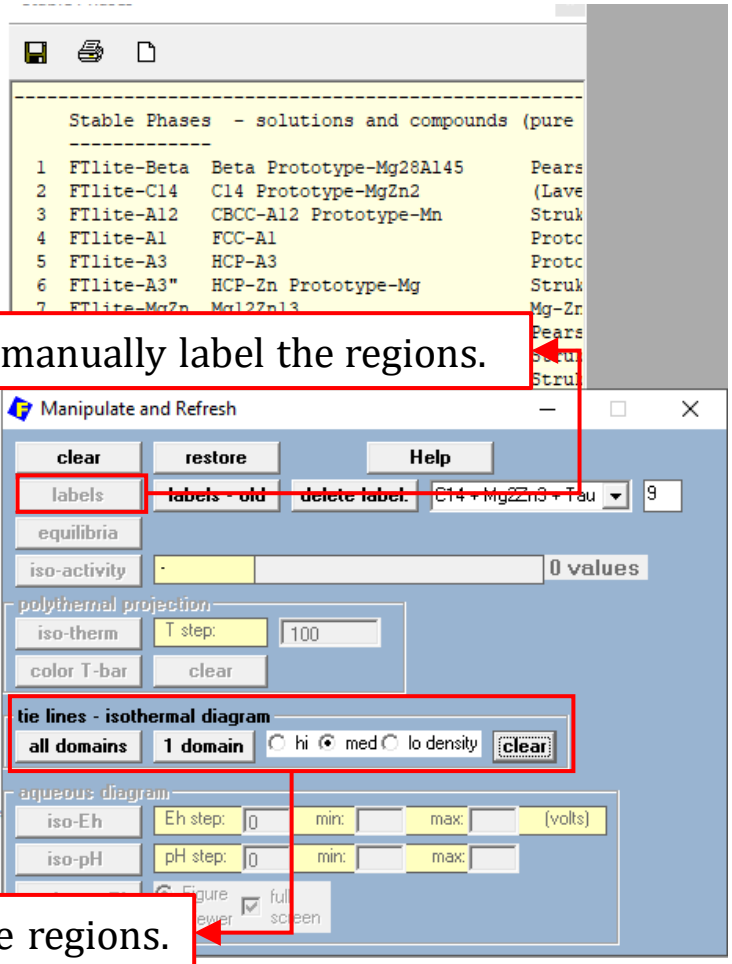
Phase Diagram Module: Al-Mg-Zn System

Results: Isothermal Section of the Al-Mg-Zn System (FTlite Database)



Tie Triangle

FactSage™

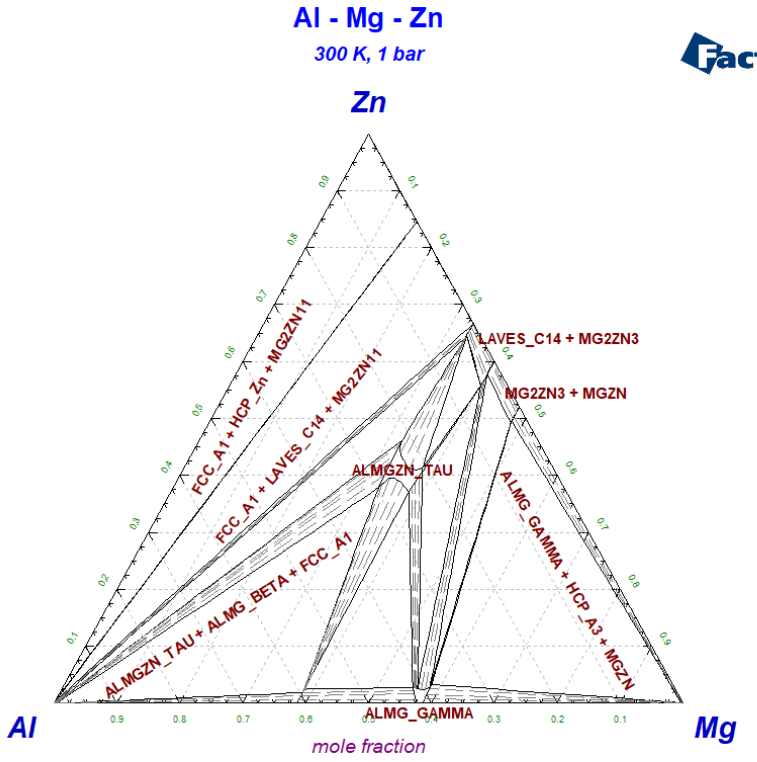


You need to manually label the regions.

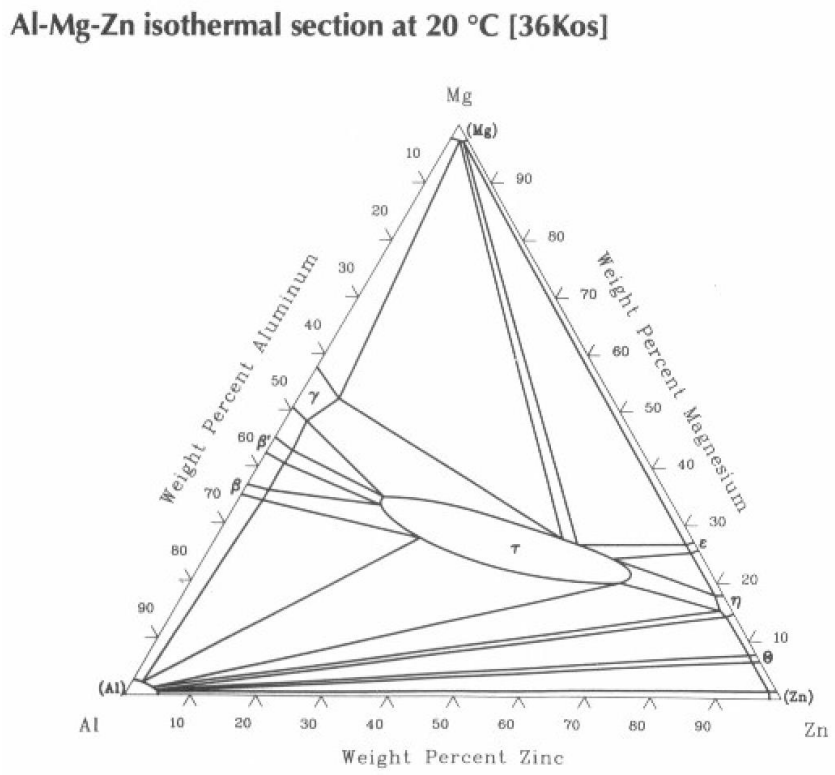
This allows us to plot the tie lines for two-phase regions.

Phase Diagram Module: Al-Mg-Zn System

Comparison with the diagrams from SGTE2017 and ASM Handbook.



FactSage™



Again, there is a discrepancy between different phases diagrams reported from different sources.

Phase Diagram Module: SiO_2-CaO-Al_2O_3 System

Now let us calculate an oxide system which consists of SiO_2, CaO, and Al_2O_3. It is worth mentioning that the ternary SiO_2-CaO-Al_2O_3 phase diagram is actually an isopleth of the quaternary Si-Ca-Al-O system along the line:

$$n_O = 2n_{Si} + n_{Ca} + 1.5n_{Al}$$

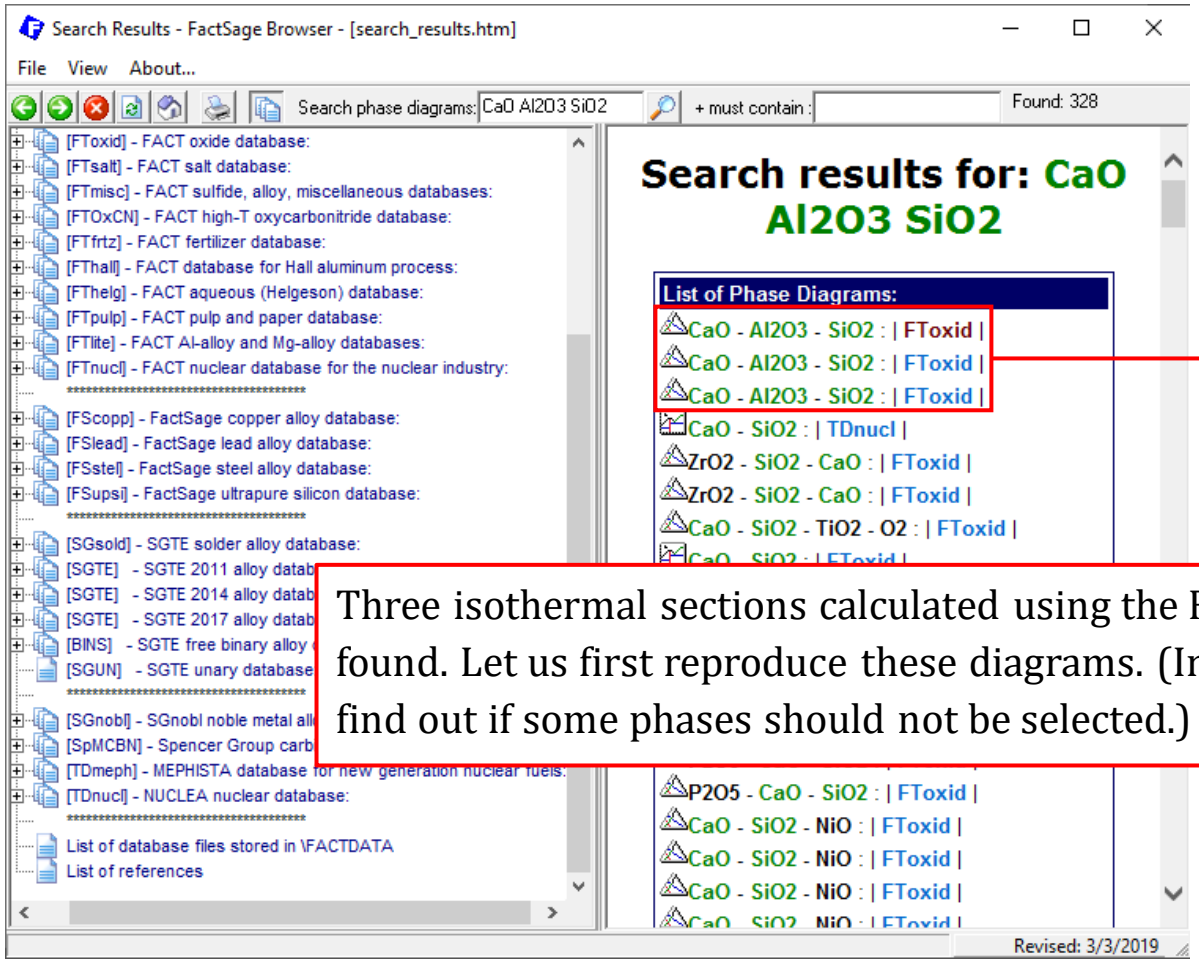
This relationship is met in every condensed phases. Therefore, strictly speaking, the ternary SiO_2-CaO-Al_2O_3 phase diagram is a "**quasi-**" ternary phase diagram.

You also should note that the pressure, more specifically, P_{O_2}, has a negligible effect on the phase equilibria of the SiO_2-CaO-Al_2O_3 system because all the metals have only one oxidation state.

Pelton, Phase Diagrams and Thermodynamic Modeling of Solutions, 2019 (Chapter 6)

Phase Diagram Module: SiO_2-CaO-Al_2O_3 System

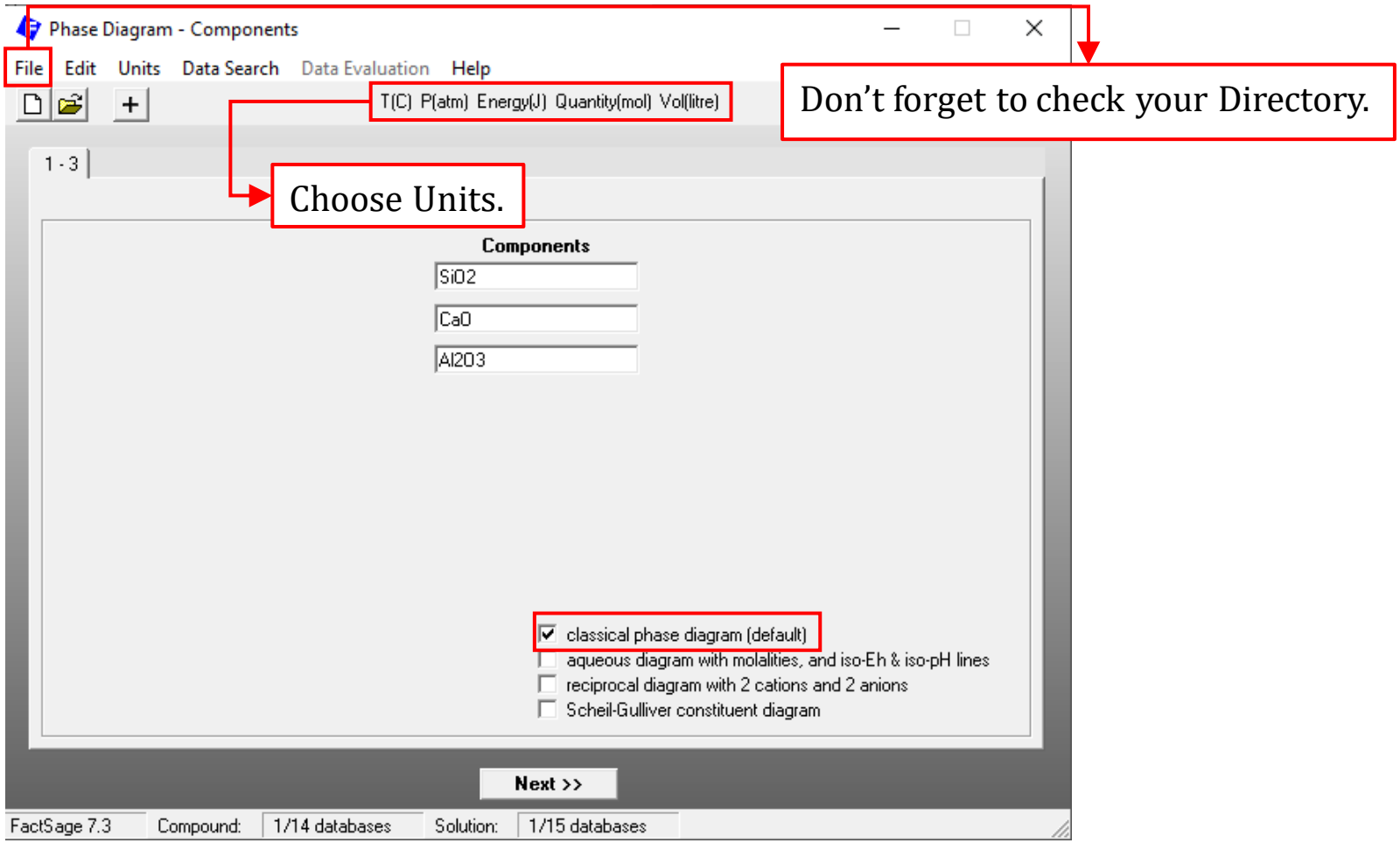
First, let us search this system in the Documentation Module.



Three isothermal sections calculated using the FToxid database are found. Let us first reproduce these diagrams. (In doing so, we will find out if some phases should not be selected.)

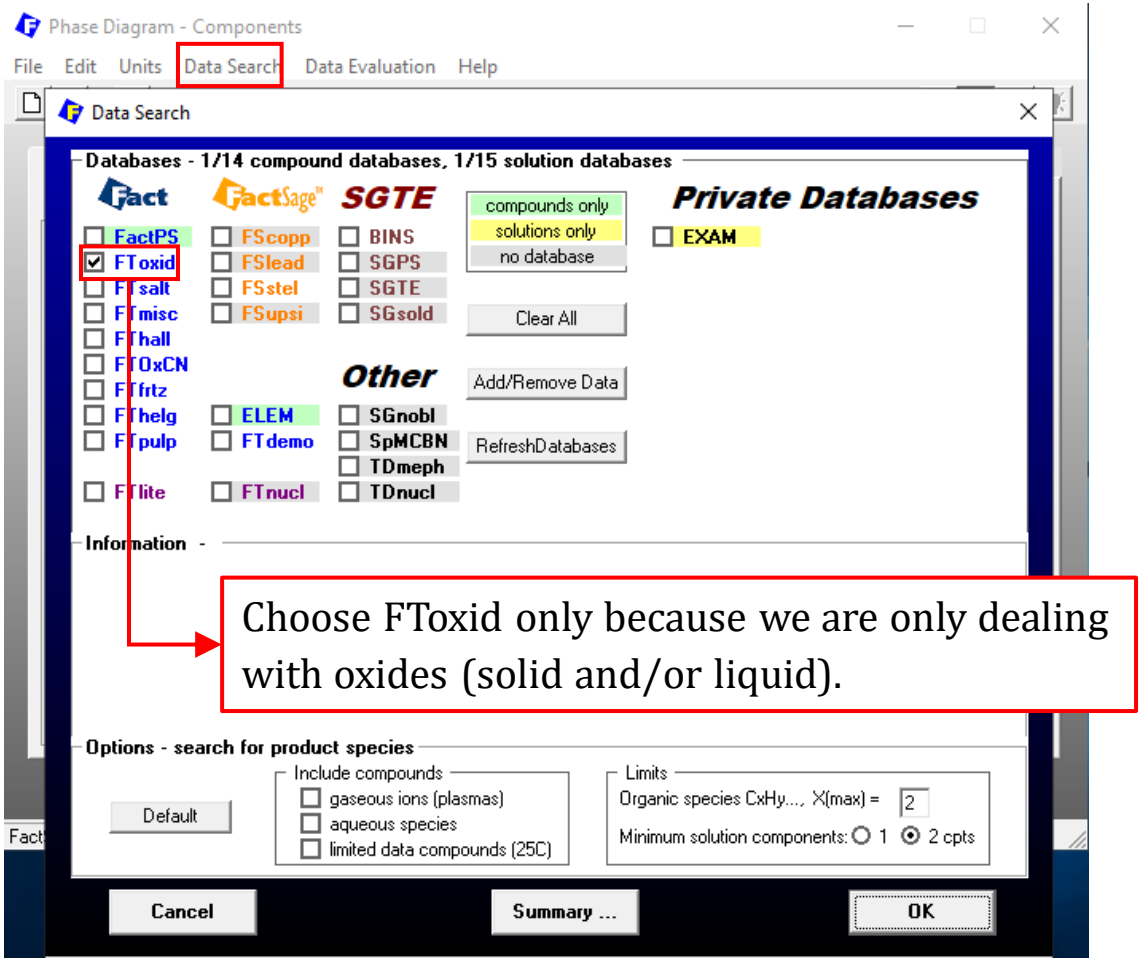
Phase Diagram Module: SiO_2-CaO-Al_2O_3 System

Components Window: Define Components



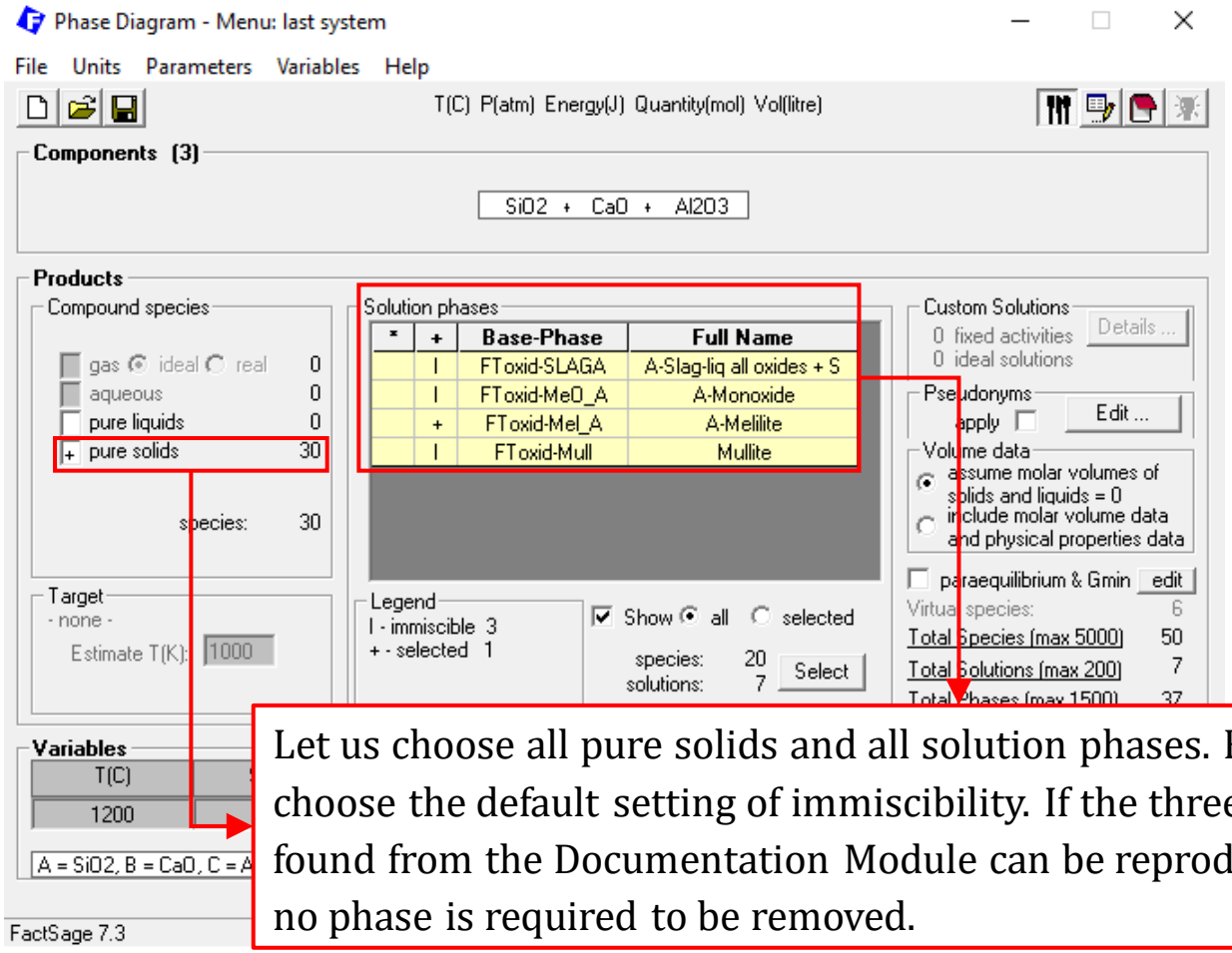
Phase Diagram Module: SiO_2-CaO-Al_2O_3 System

Components Window: Choose Database(s)



Phase Diagram Module: SiO_2-CaO-Al_2O_3 System

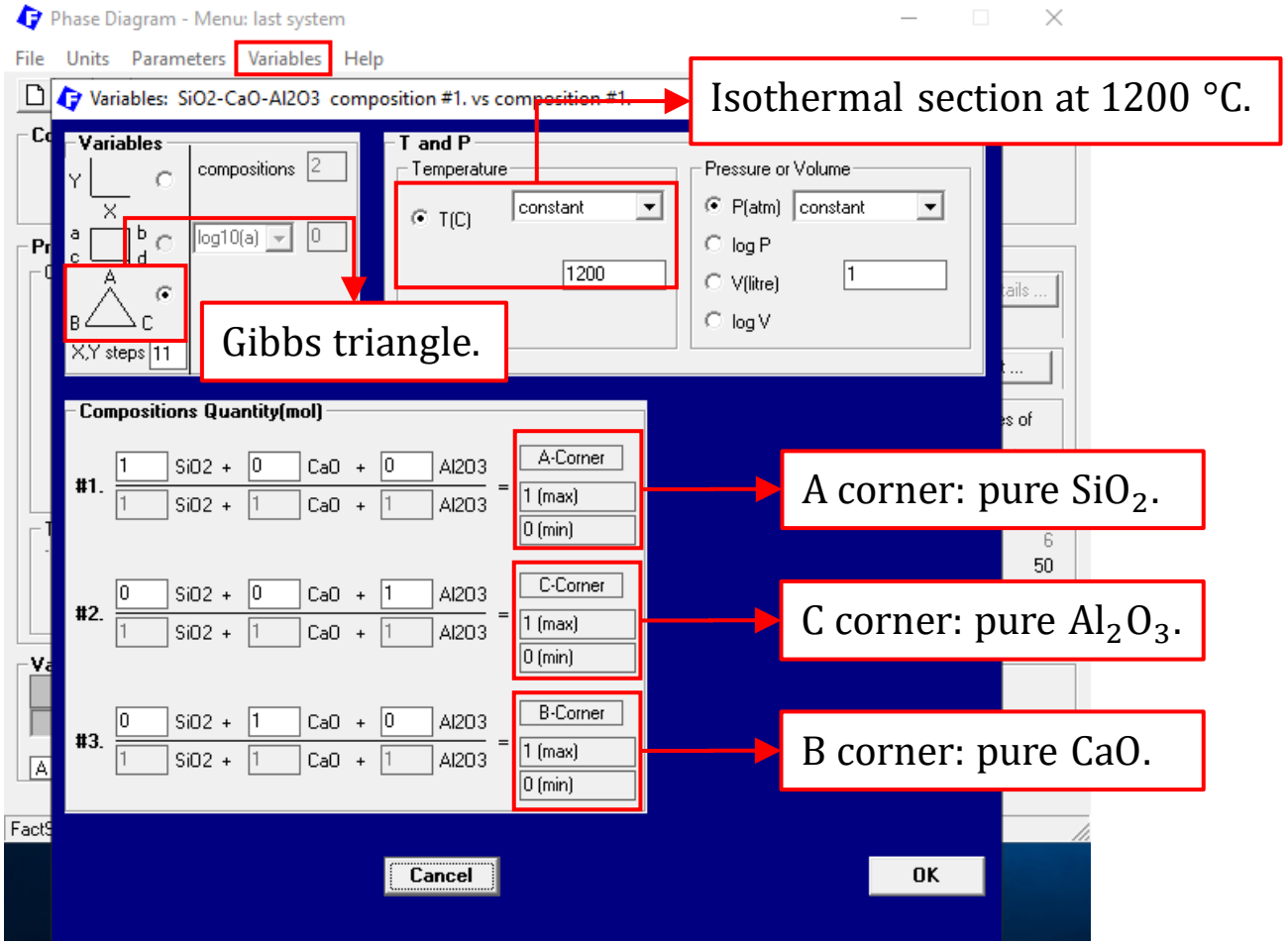
Menu Window: Choose Products/Phases (Compounds and Solution Phases)



Let us choose all pure solids and all solution phases. For solution phases, choose the default setting of immiscibility. If the three isothermal sections found from the Documentation Module can be reproduced, then probably no phase is required to be removed.

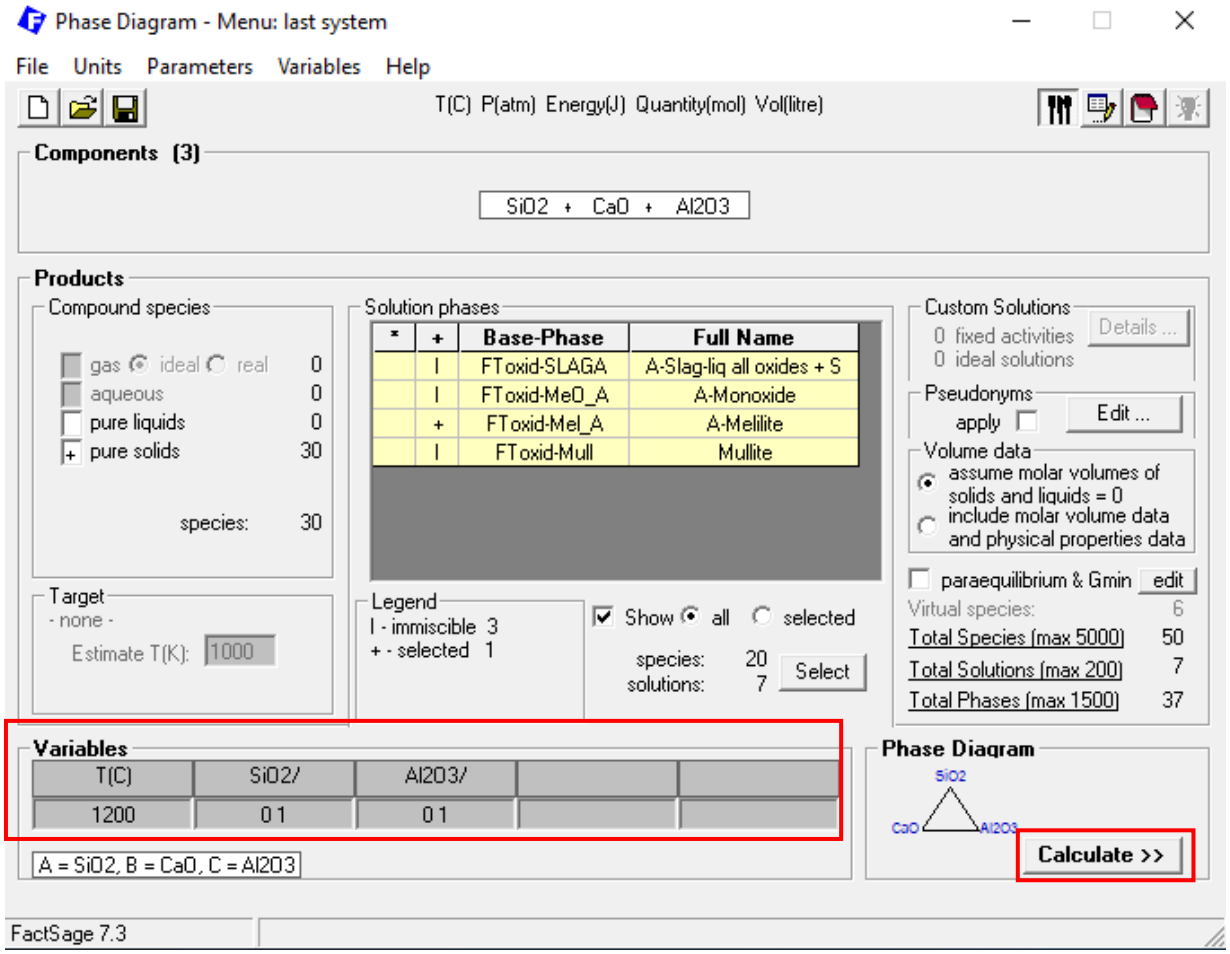
Phase Diagram Module: SiO_2-CaO-Al_2O_3 System

Menu Window: Set up the Variables (Isothermal Sections)



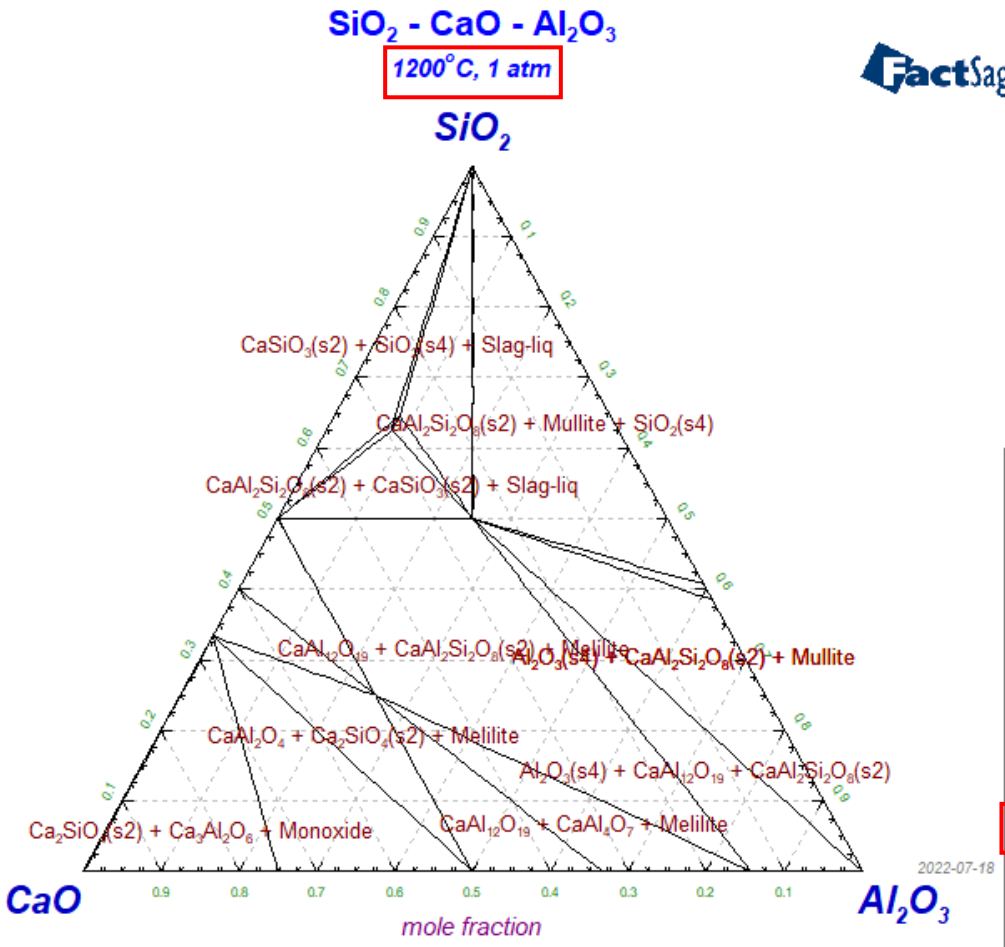
Phase Diagram Module: SiO_2-CaO-Al_2O_3 System

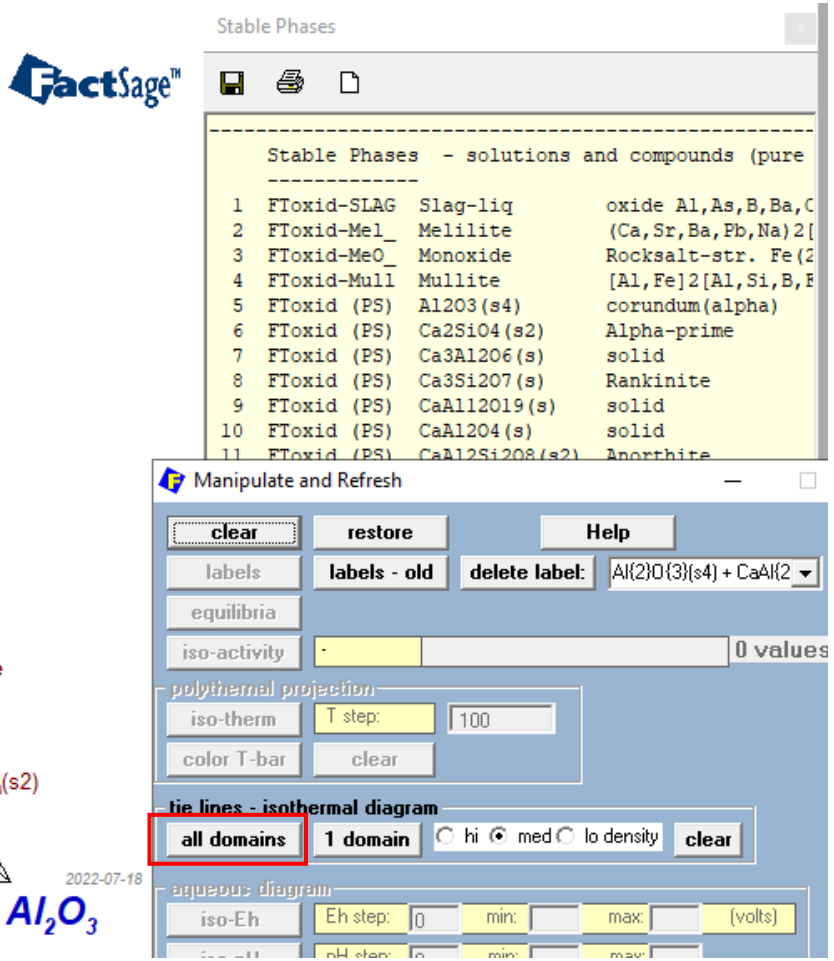
Menu Window: Set up the Variables



Phase Diagram Module: SiO_2-CaO-Al_2O_3 System

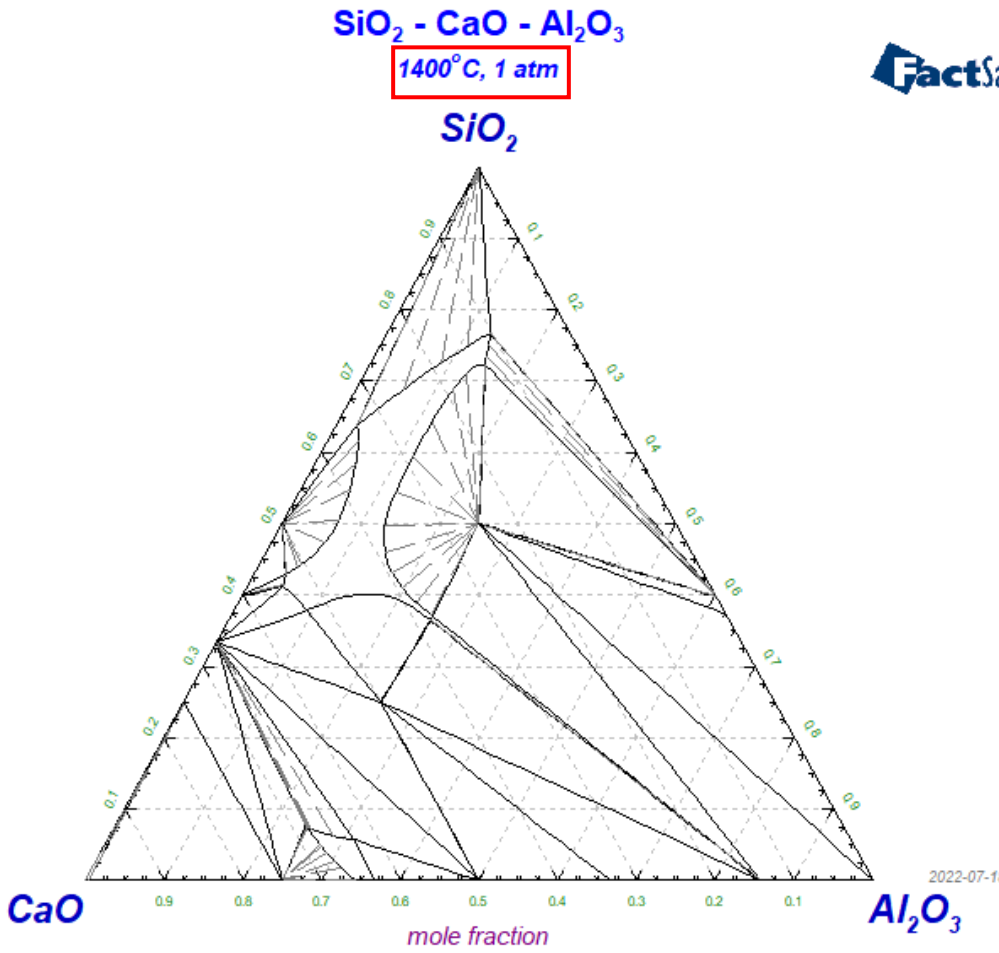
Results: Isothermal Section of the SiO_2-CaO-Al_2O_3 System (FToxid Database)

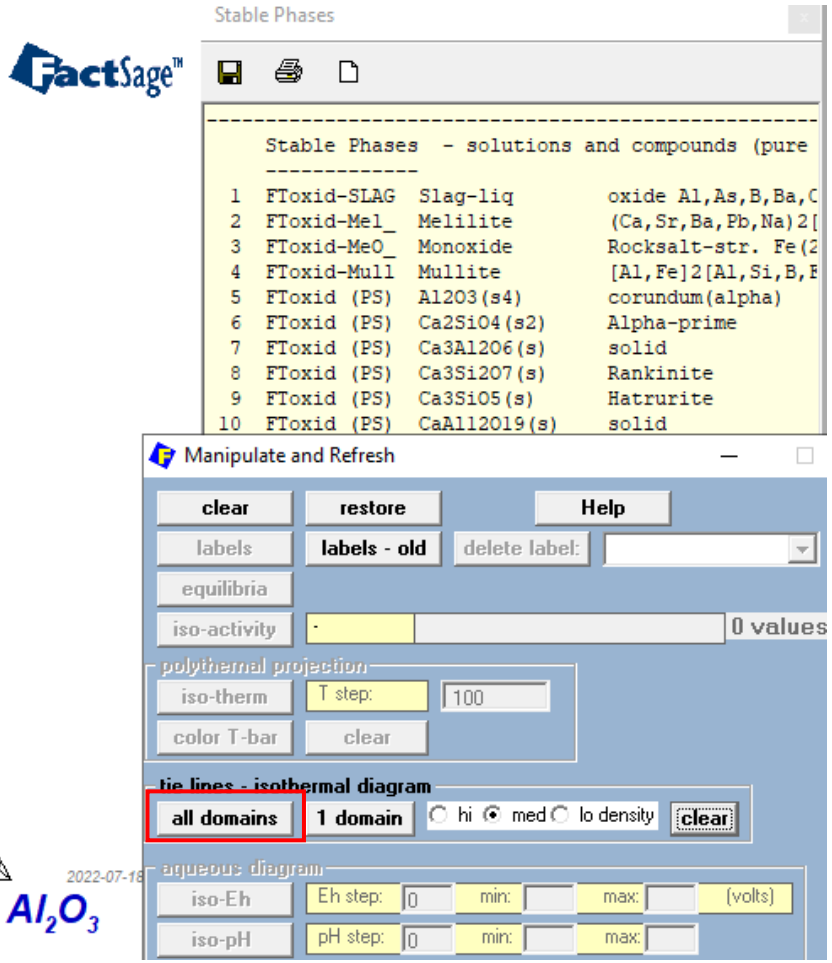




Phase Diagram Module: SiO_2-CaO-Al_2O_3 System

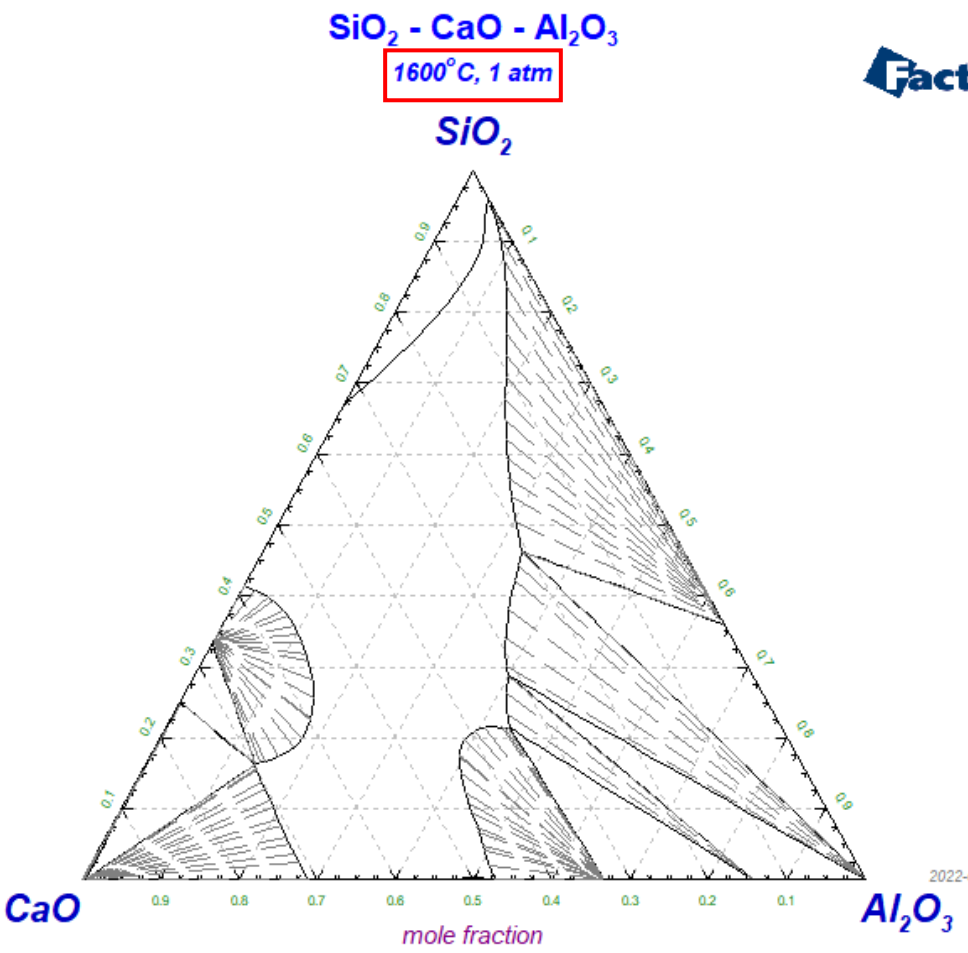
Results: Isothermal Section of the SiO_2-CaO-Al_2O_3 System (FToxid Database)

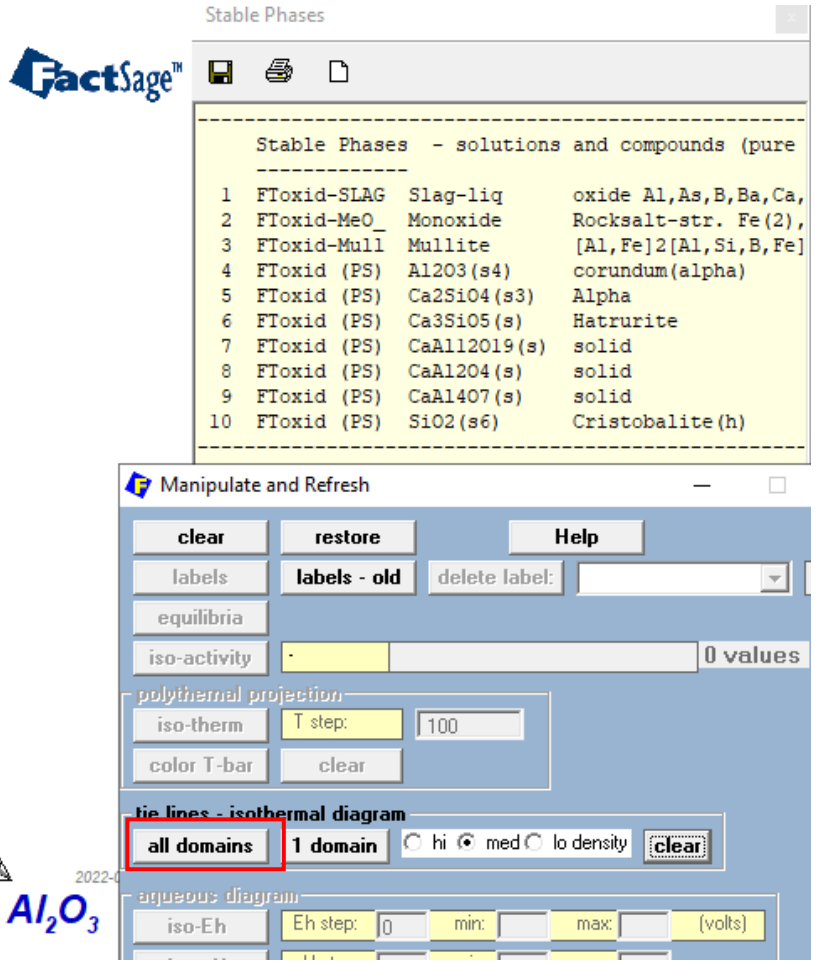




Phase Diagram Module: SiO_2-CaO-Al_2O_3 System

Results: Isothermal Section of the SiO_2-CaO-Al_2O_3 System (FToxid Database)





Phase Diagram Module: SiO_2-CaO-Al_2O_3 System

Comparison with the three pre-made isothermal sections indicates that choosing all the pure solids and solution phases from the FToxid database permits one to generate reliable phase diagrams for the SiO_2-CaO-Al_2O_3 system.

Now, we can calculate the isothermal sections at other temperatures using the same selection of the phases. Please try to calculate the isothermal sections at 1800 °C, 1500 °C, and 1100 °C.

Phase Diagram Module: SiO_2-CaO-Al_2O_3 System

Before we calculate the liquidus projection of the SiO_2-CaO-Al_2O_3 system, let us think about the following question:

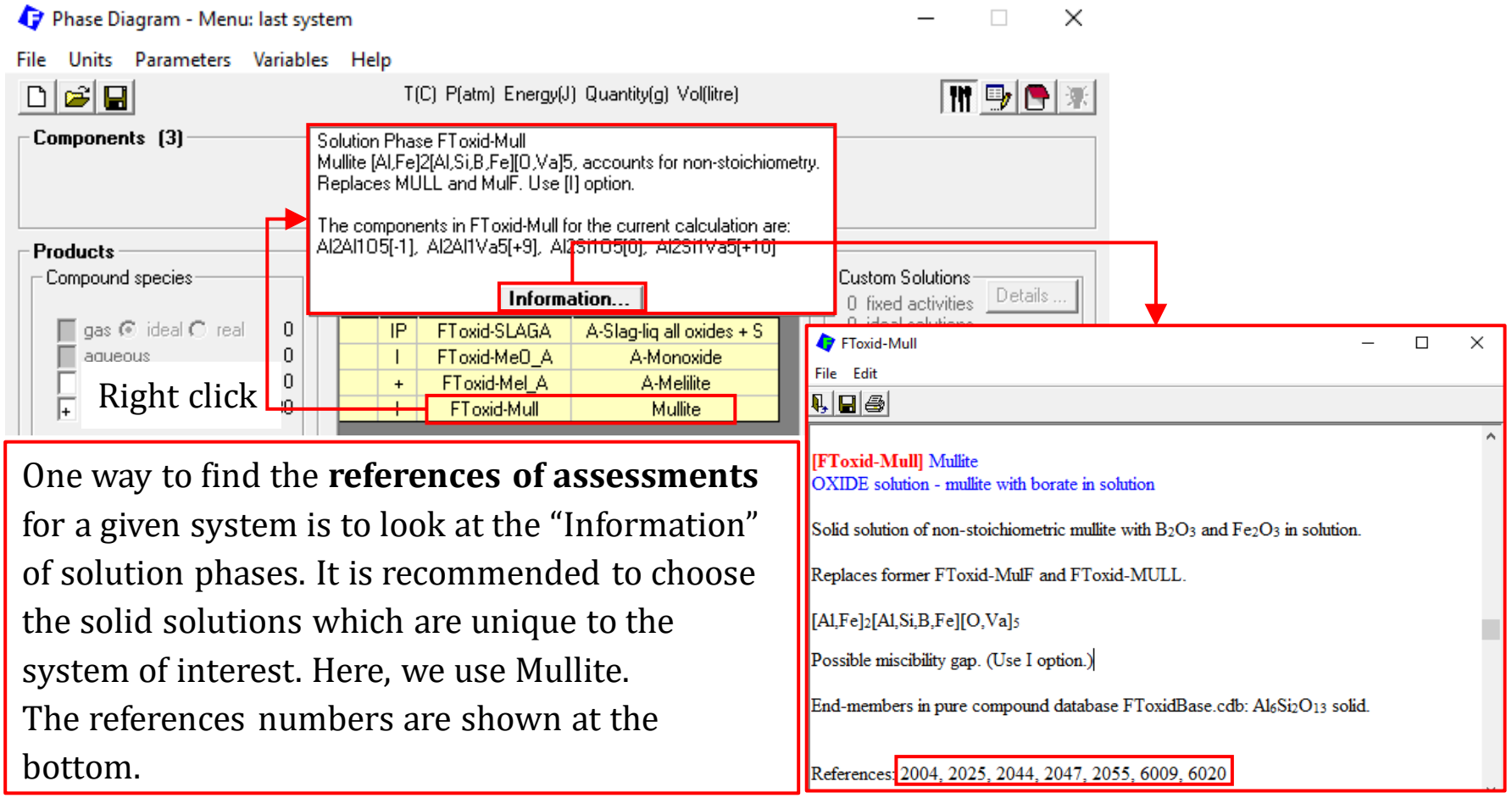
Who critically assessed the SiO_2-CaO-Al_2O_3 system?

The development of CALPHAD databases (e.g., FactSage databases) is based on numerous thermodynamic assessment work for binaries, ternaries, etc. These work was either published in journals or communicated internally.

For FactSage, the references of thermodynamic assessments are complied as "List of references" in the Documentation Module. Then the next question is how can we find the references which were used to build the FactSage databases?

Phase Diagram Module: SiO_2-CaO-Al_2O_3 System

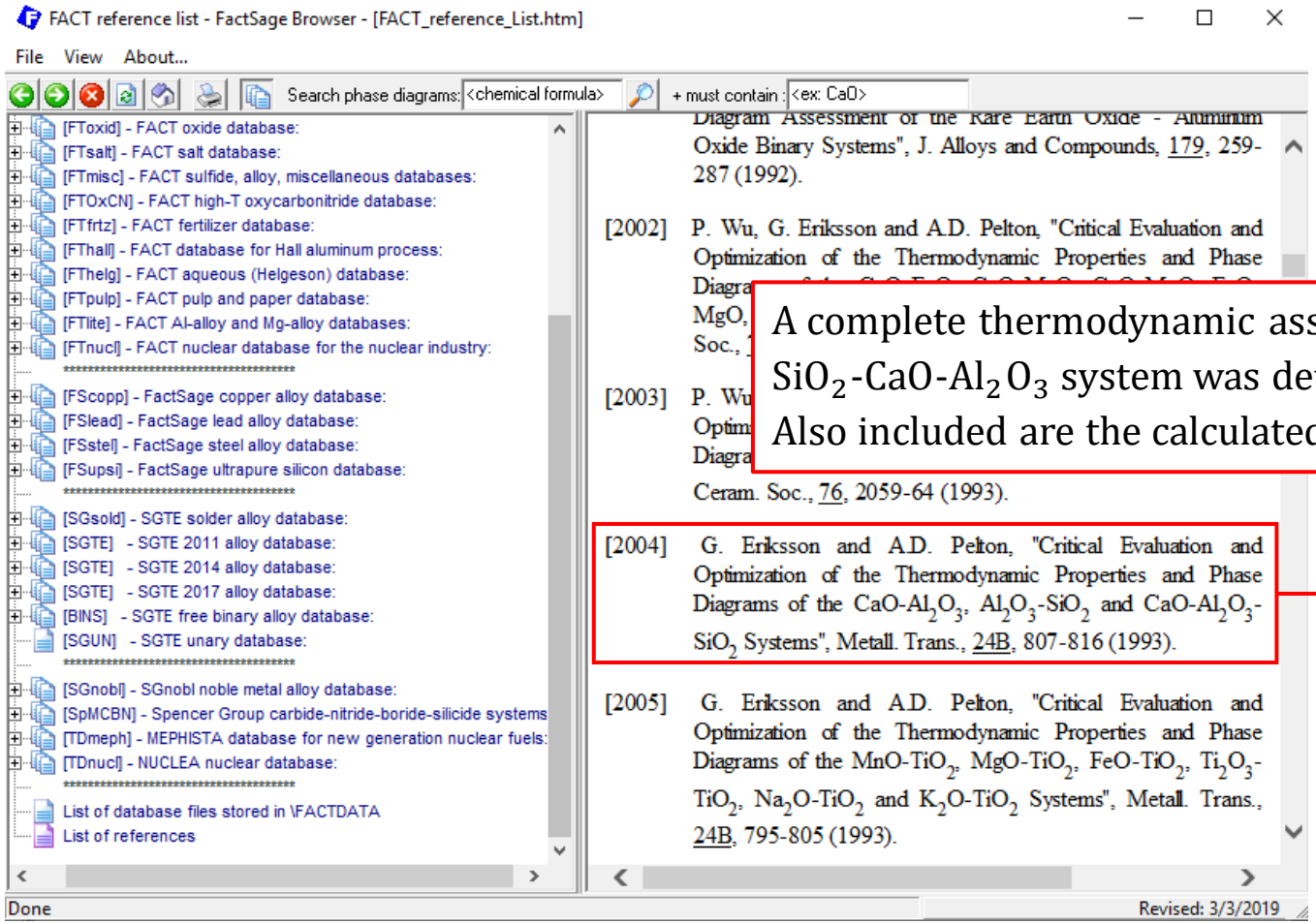
What are the references used for the SiO_2-CaO-Al_2O_3 system?



One way to find the **references of assessments** for a given system is to look at the "Information" of solution phases. It is recommended to choose the solid solutions which are unique to the system of interest. Here, we use Mullite.
The references numbers are shown at the bottom.

Phase Diagram Module: SiO_2-CaO-Al_2O_3 System

What are the references used for the SiO_2-CaO-Al_2O_3 system?



A complete thermodynamic assessment for the SiO_2-CaO-Al_2O_3 system was detailed in this paper. Also included are the calculated phase diagrams.

Link

Phase Diagram Module: SiO_2-CaO-Al_2O_3 System

What are the references used for the SiO_2-CaO-Al_2O_3 system?

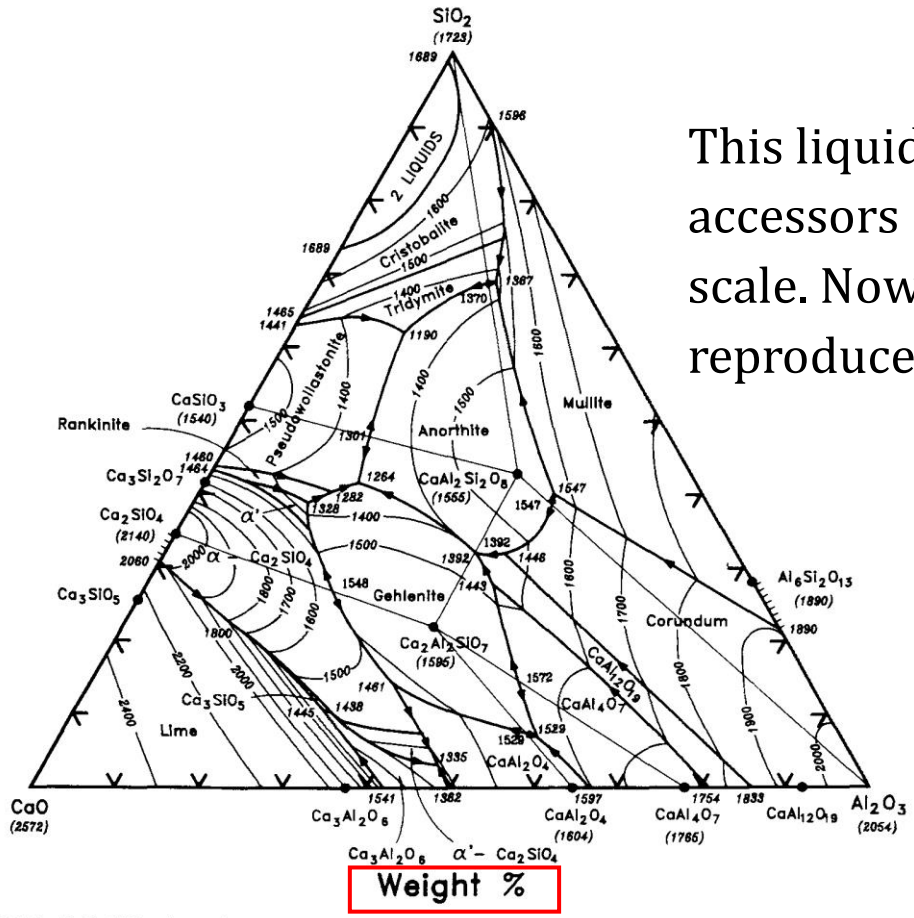


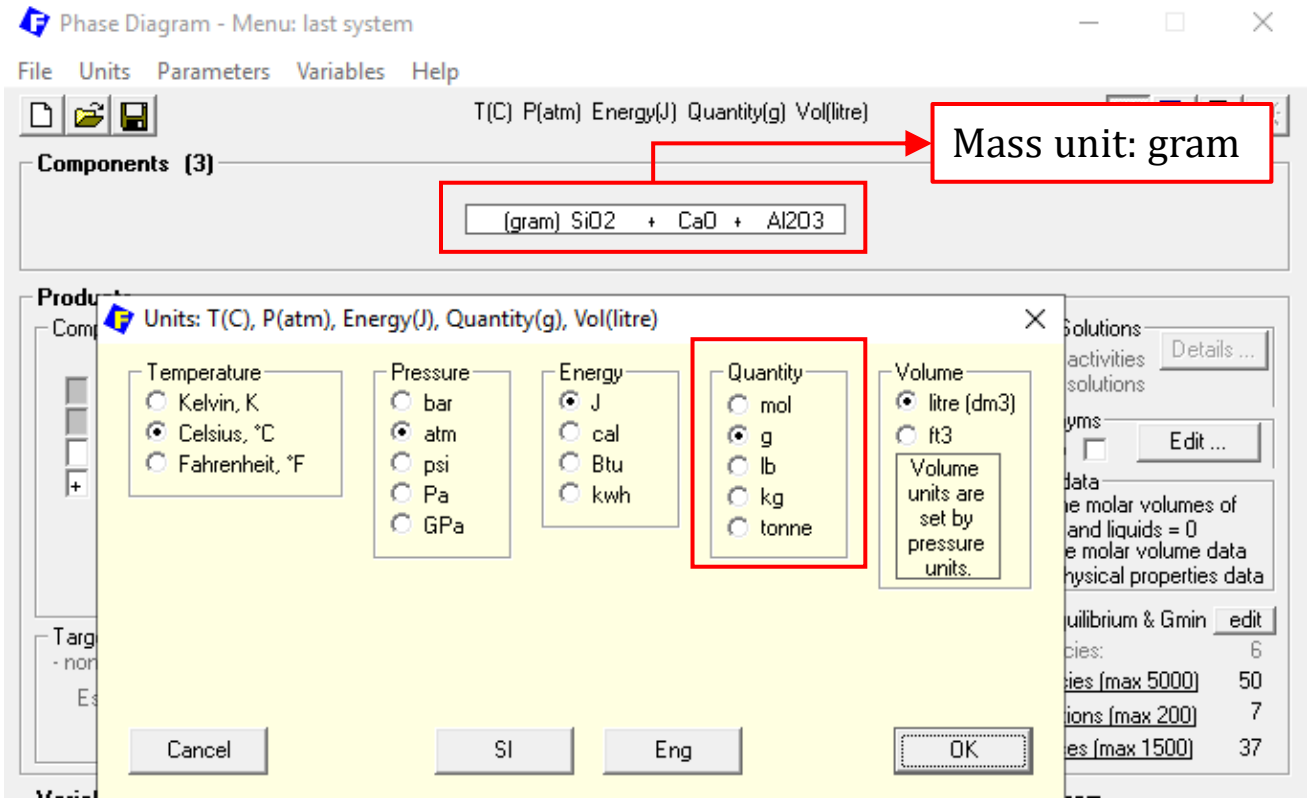
Fig. 5—Optimized CaO-Al_2O_3-SiO_2 phase diagram. Temperature in °C.

This liquidus projection calculated by the accessors used wt.% as compositional scale. Now let us use FactSage – FToxid to reproduce this phase diagram.

Eriksson and Pelton, Metallurgical Transactions B, Vol.24, No. 5, pp807-816 (1993)

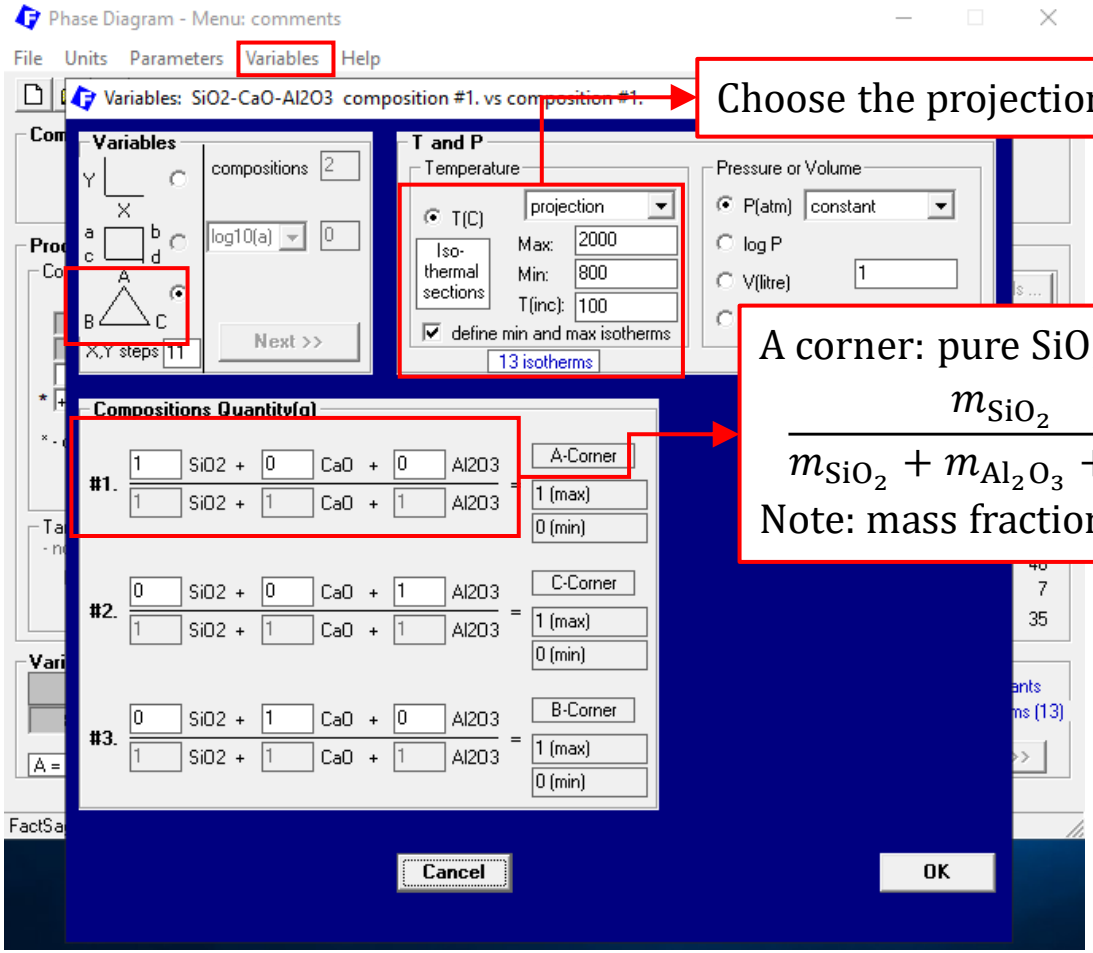
Phase Diagram Module: SiO_2-CaO-Al_2O_3 System

Back to the Menu Window (Slide): Change the mass unit to gram.



Phase Diagram Module: SiO_2-CaO-Al_2O_3 System

Back to the Variables Window (Slide)



Choose the projection option and set the isotherms.

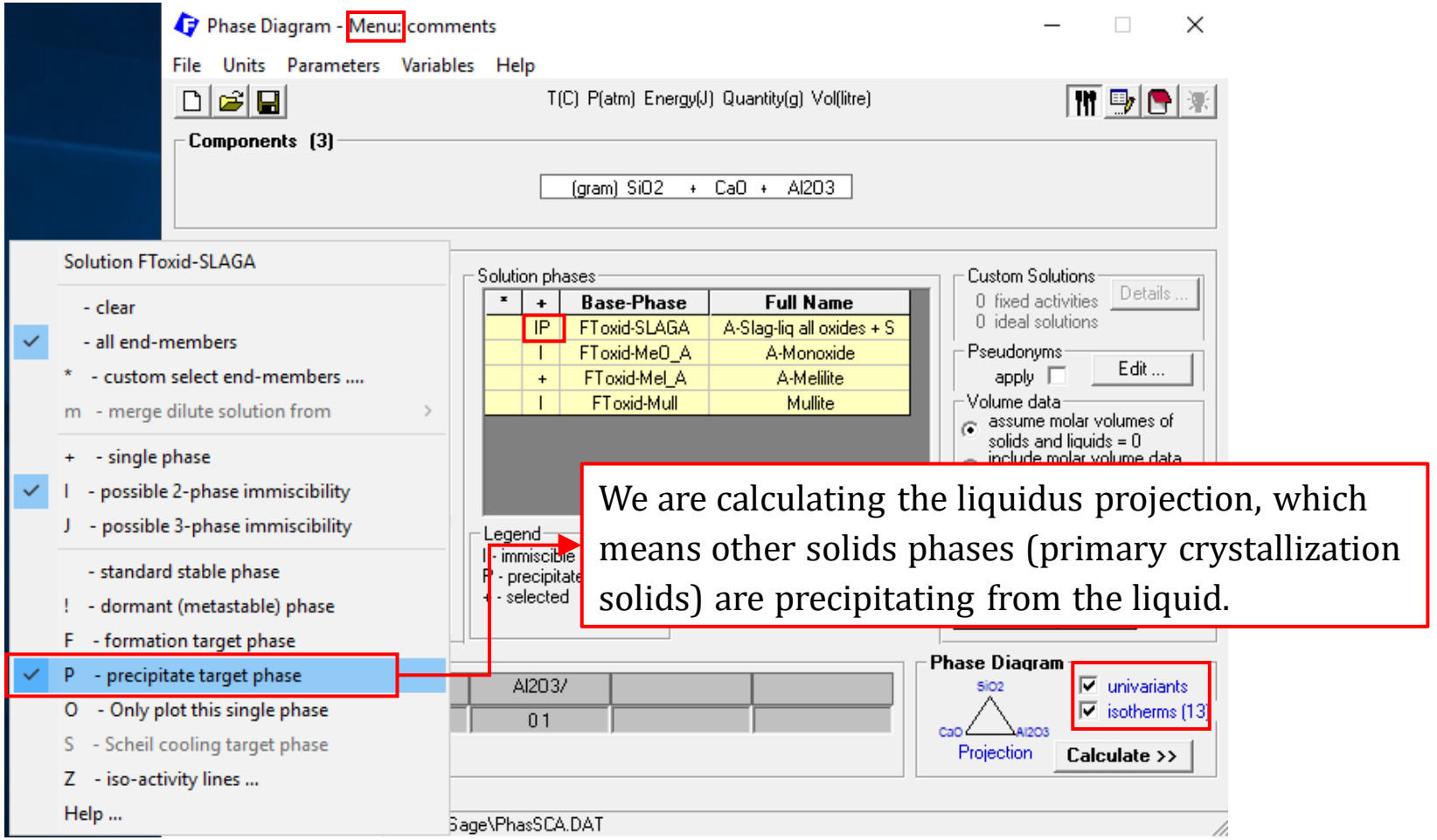
A corner: pure SiO_2.

$$\frac{m_{SiO_2}}{m_{SiO_2} + m_{Al_2O_3} + m_{CaO}} = \text{mass fraction}_{SiO_2}$$

Note: mass fraction is not wt.%.

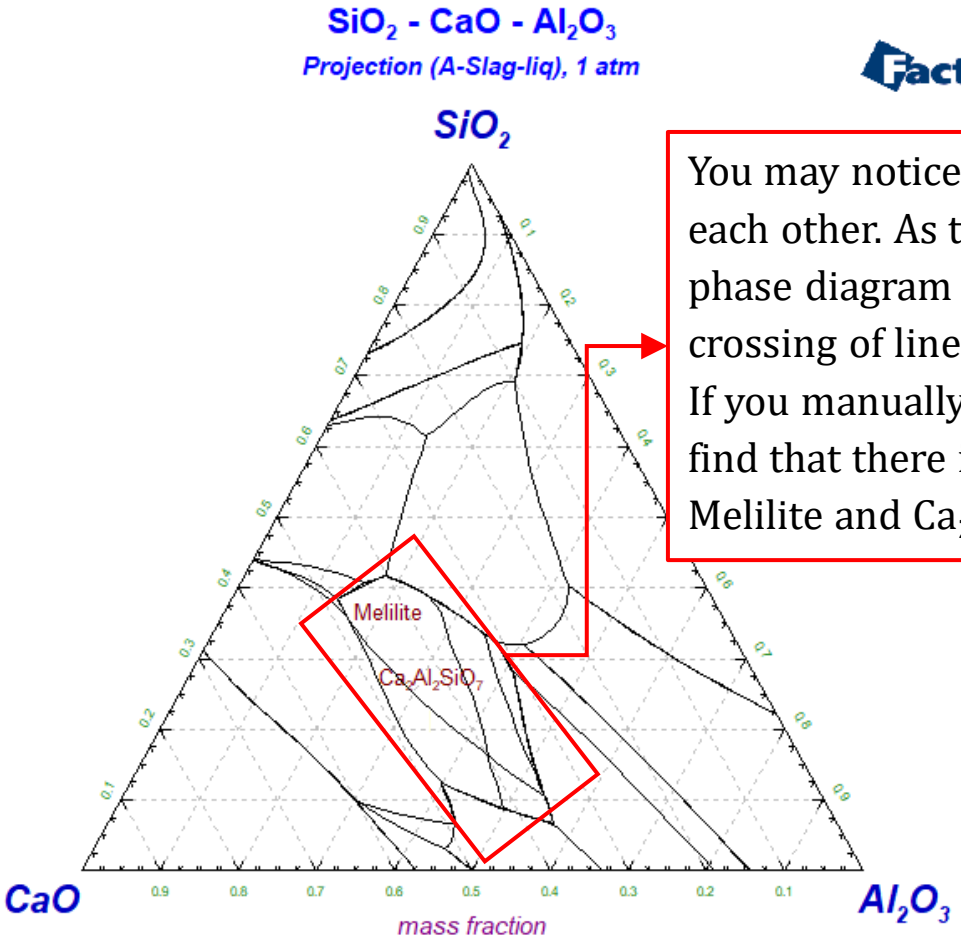
Phase Diagram Module: SiO_2-CaO-Al_2O_3 System

Menu Window (Slide): Choose Liquid (Slag) as the precipitate target phase.



Phase Diagram Module: SiO_2-CaO-Al_2O_3 System

Results: the Liquidus Projection of the SiO_2-CaO-Al_2O_3 System



You may notice there are lines which cross with each other. As the equilibrium state shown on a phase diagram must be uniquely defined, the crossing of lines is not permitted.
If you manually label the phase regions, you will find that there is a region which is labeled both as Melilite and $Ca_2Al_2SiO_7$.

Phase Diagram Module: SiO_2-CaO-Al_2O_3 System

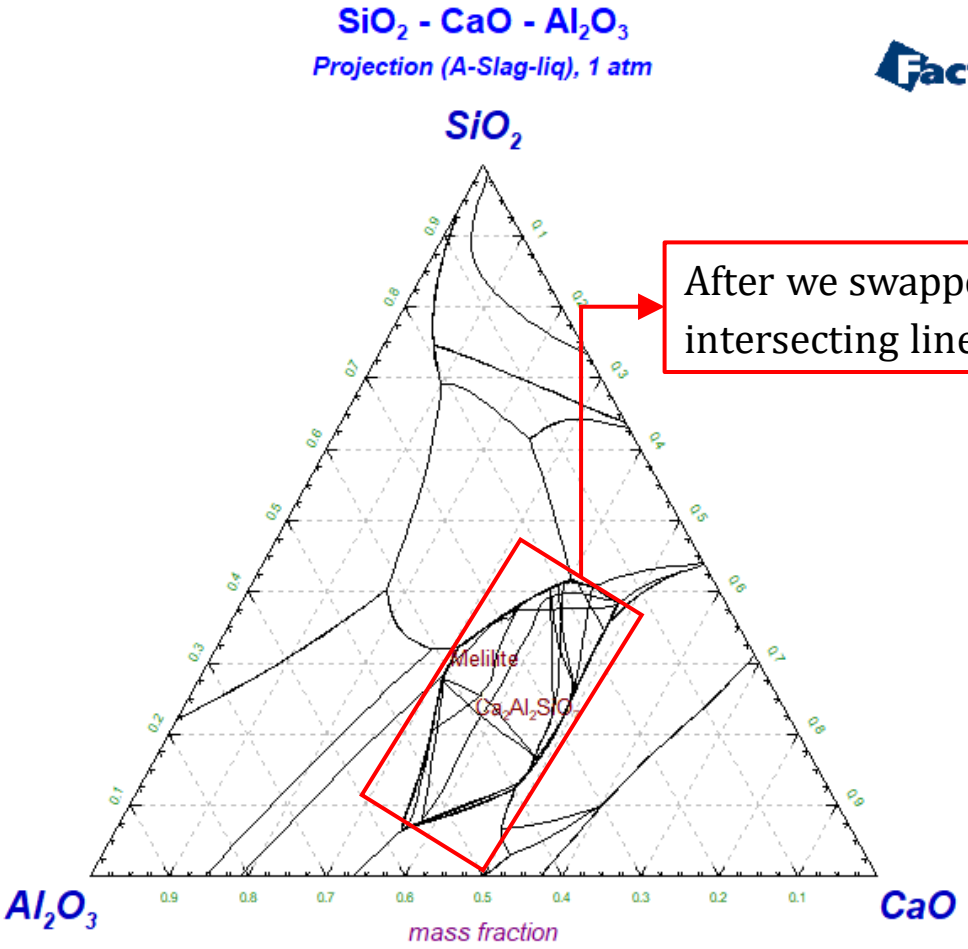
The issue of having crossing or redundant lines when calculating the liquidus projection is usually because we choose both the solution phase and its **endmembers** from pure solids.

It is worth mentioning that the topology of the space model for a ternary system like the SiO_2-CaO-Al_2O_3 system is quite complex. When FactSage is performing the "Gibbs energy minimization" calculation, if there are two Gibbs energy functions of which the values are close (e.g., the Gibbs energy of a solution phase and its endmembers), the calculation which gives single-value solutions might be challenging. Furthermore, the algorithm of the "Gibbs energy minimization" is based on numerical methods (not analytical!!!). Because of this, if we rearrange the A, B, and C corner, the complexity of the "Gibbs energy minimization" might be different, and the diagrams might look slightly different. Actually, one strategy of resolving the issue when the calculated phase diagram contains crossing and redundant lines is to switch the components at the A, B, and C corner.

Hack, FactSage Tech (FactSage\Information\FactSage-Tech)

Phase Diagram Module: SiO_2-CaO-Al_2O_3 System

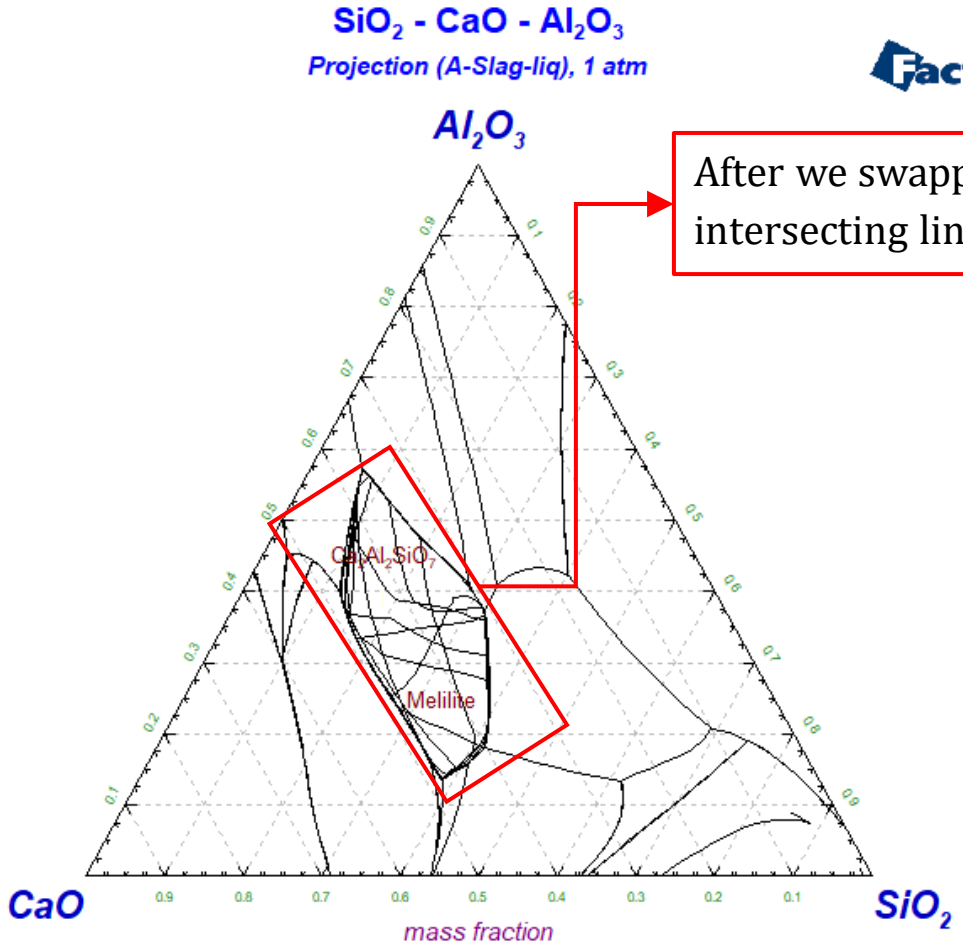
Results: the Liquidus Projection of the SiO_2-CaO-Al_2O_3 System



After we swapped Al_2O_3 and CaO, crossing and intersecting lines still are present.

Phase Diagram Module: SiO_2-CaO-Al_2O_3 System

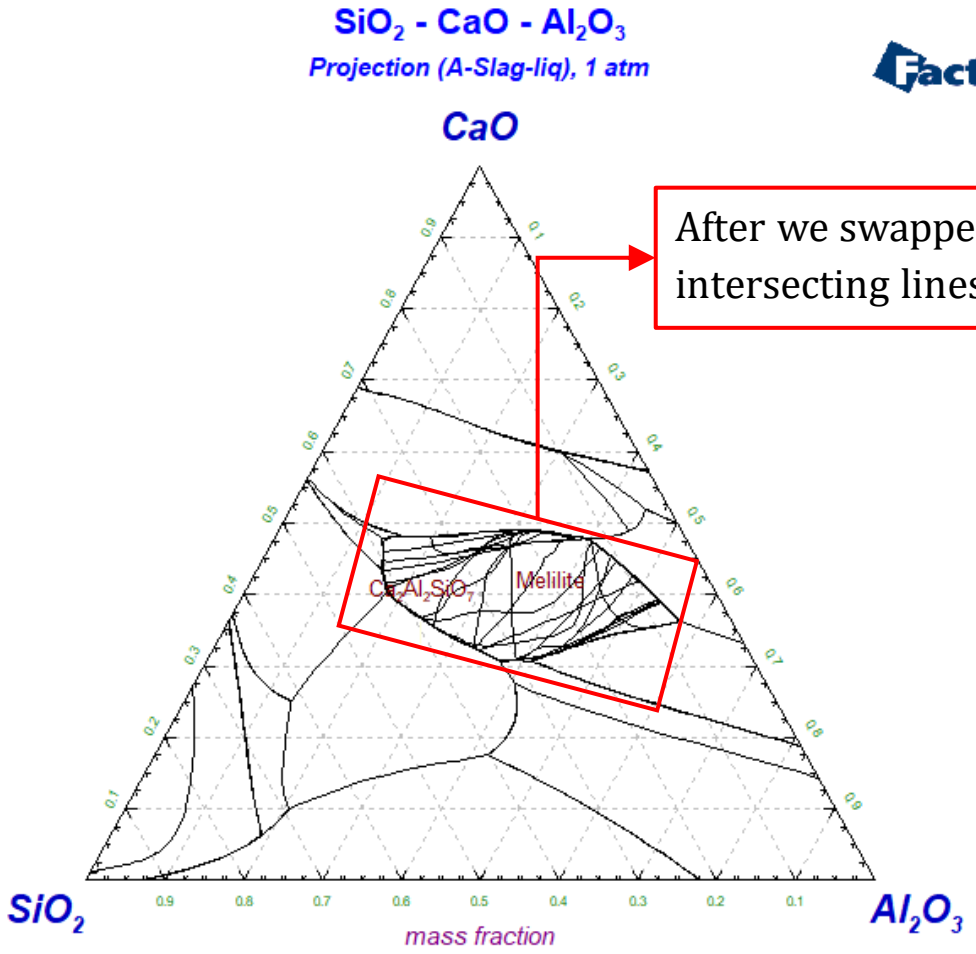
Results: the Liquidus Projection of the SiO_2-CaO-Al_2O_3 System



After we swapped SiO_2 and Al_2O_3, crossing and intersecting lines still are present.

Phase Diagram Module: SiO_2-CaO-Al_2O_3 System

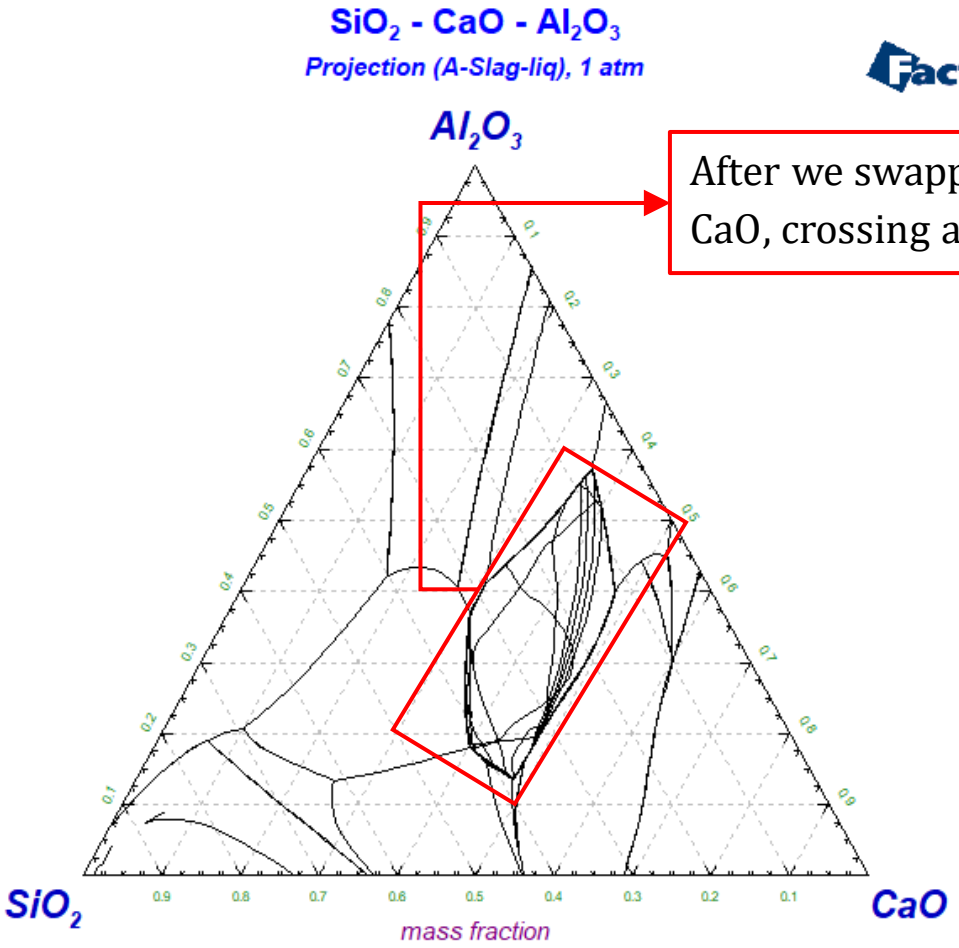
Results: the Liquidus Projection of the SiO_2-CaO-Al_2O_3 System



After we swapped SiO_2 and CaO, crossing and intersecting lines still are present.

Phase Diagram Module: SiO_2-CaO-Al_2O_3 System

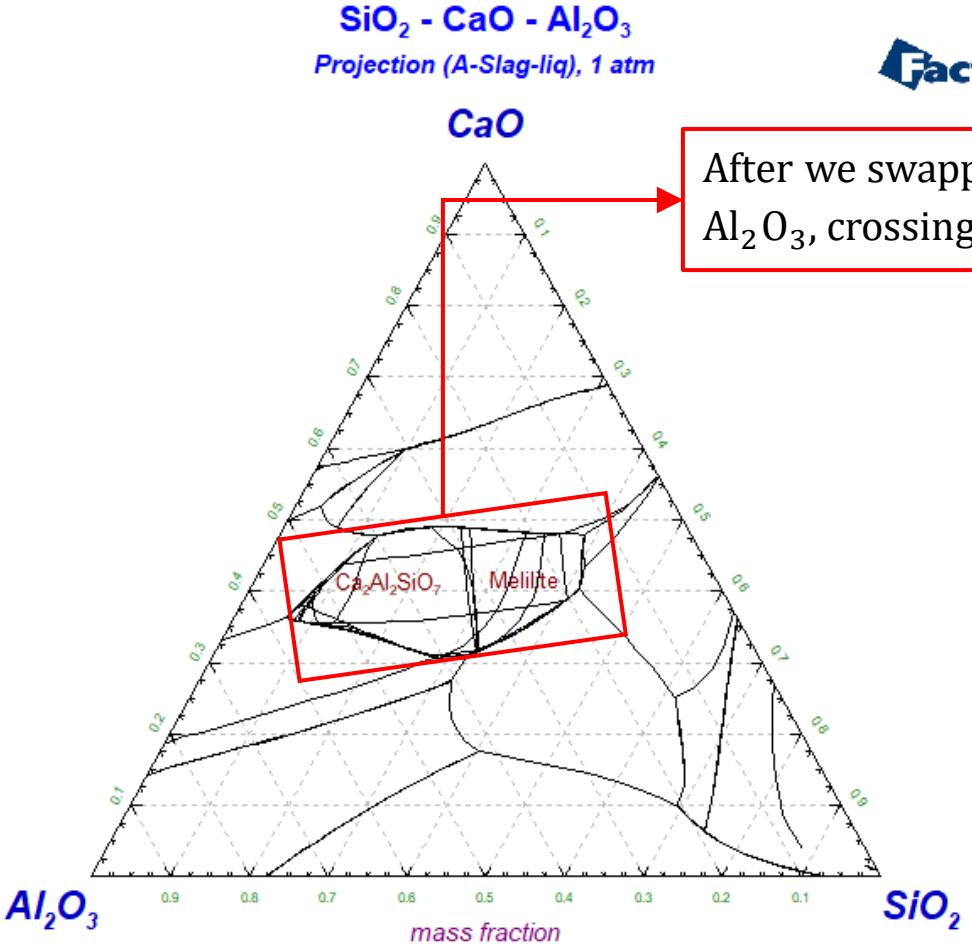
Results: the Liquidus Projection of the SiO_2-CaO-Al_2O_3 System



After we swapped SiO_2 and Al_2O_3, then SiO_2 and CaO, crossing and intersecting lines still are present.

Phase Diagram Module: SiO_2-CaO-Al_2O_3 System

Results: the Liquidus Projection of the SiO_2-CaO-Al_2O_3 System



After we swapped SiO_2 and CaO, and then SiO_2 and Al_2O_3, crossing and intersecting lines still are present.

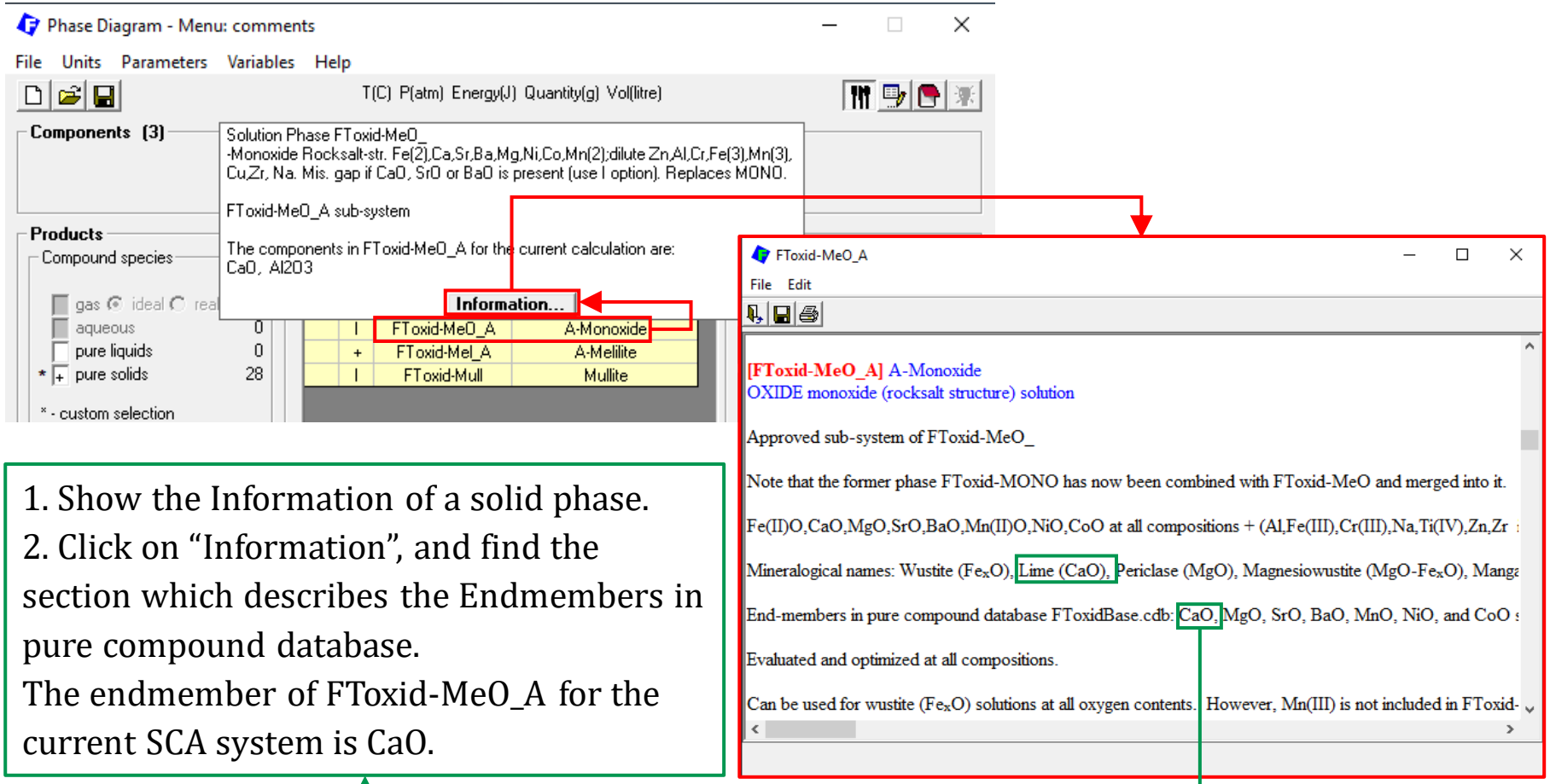
Phase Diagram Module: SiO_2-CaO-Al_2O_3 System

The above phase diagram calculations show that the process of "Gibbs energy minimization" might be impeded when both the solution phases and some pure solids which are the endmembers of these solution phases are selected.

How to resolve the issue of having crossing and intersecting lines? The solution is very simple: remove all the pure solids which are the endmembers of the solution phases.

Phase Diagram Module: SiO_2-CaO-Al_2O_3 System

Find the endmembers of solid phases

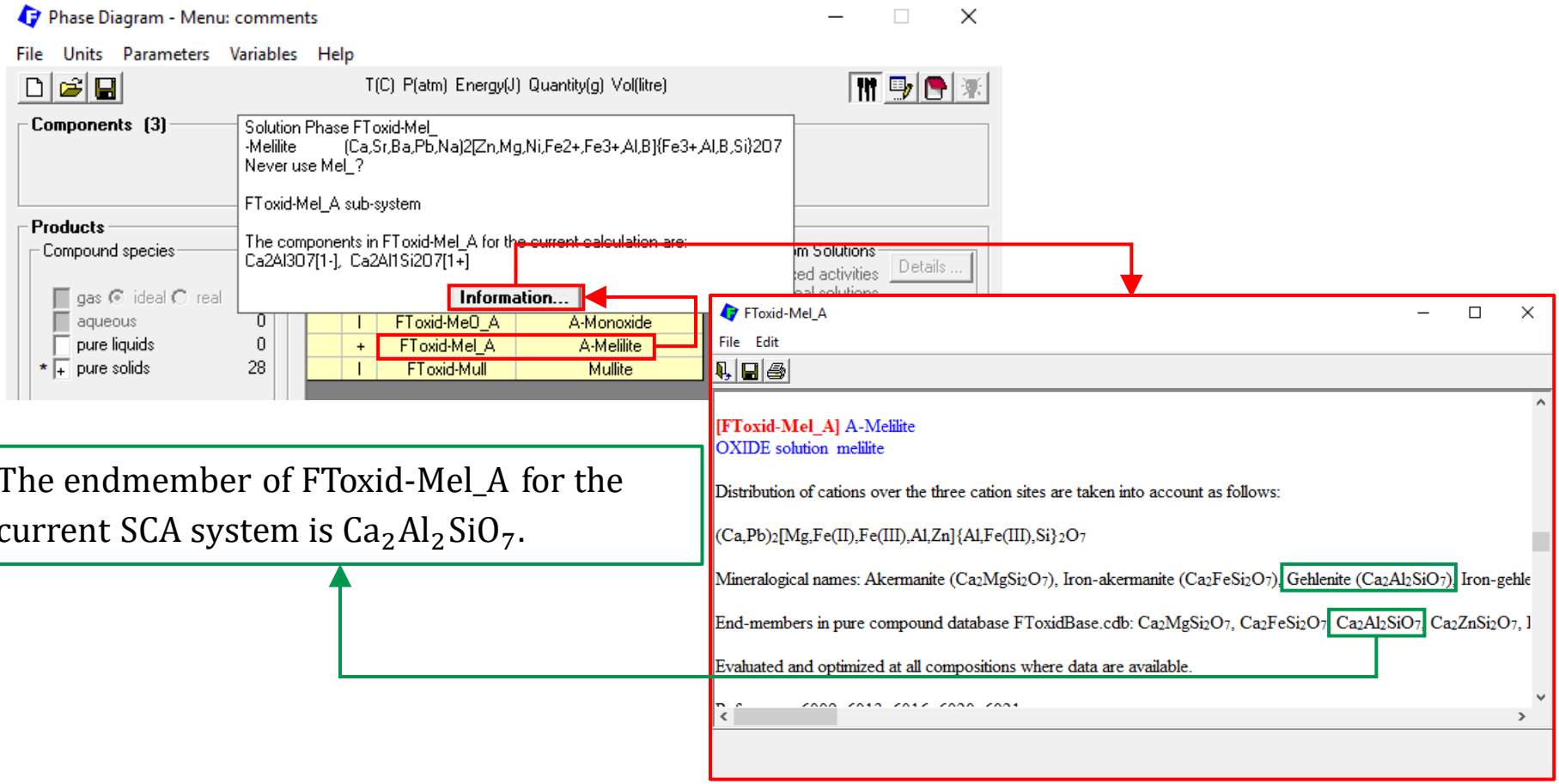


1. Show the Information of a solid phase.
2. Click on “Information”, and find the section which describes the Endmembers in pure compound database.

The endmember of FToxid-MeO_A for the current SCA system is CaO.

Phase Diagram Module: SiO_2-CaO-Al_2O_3 System

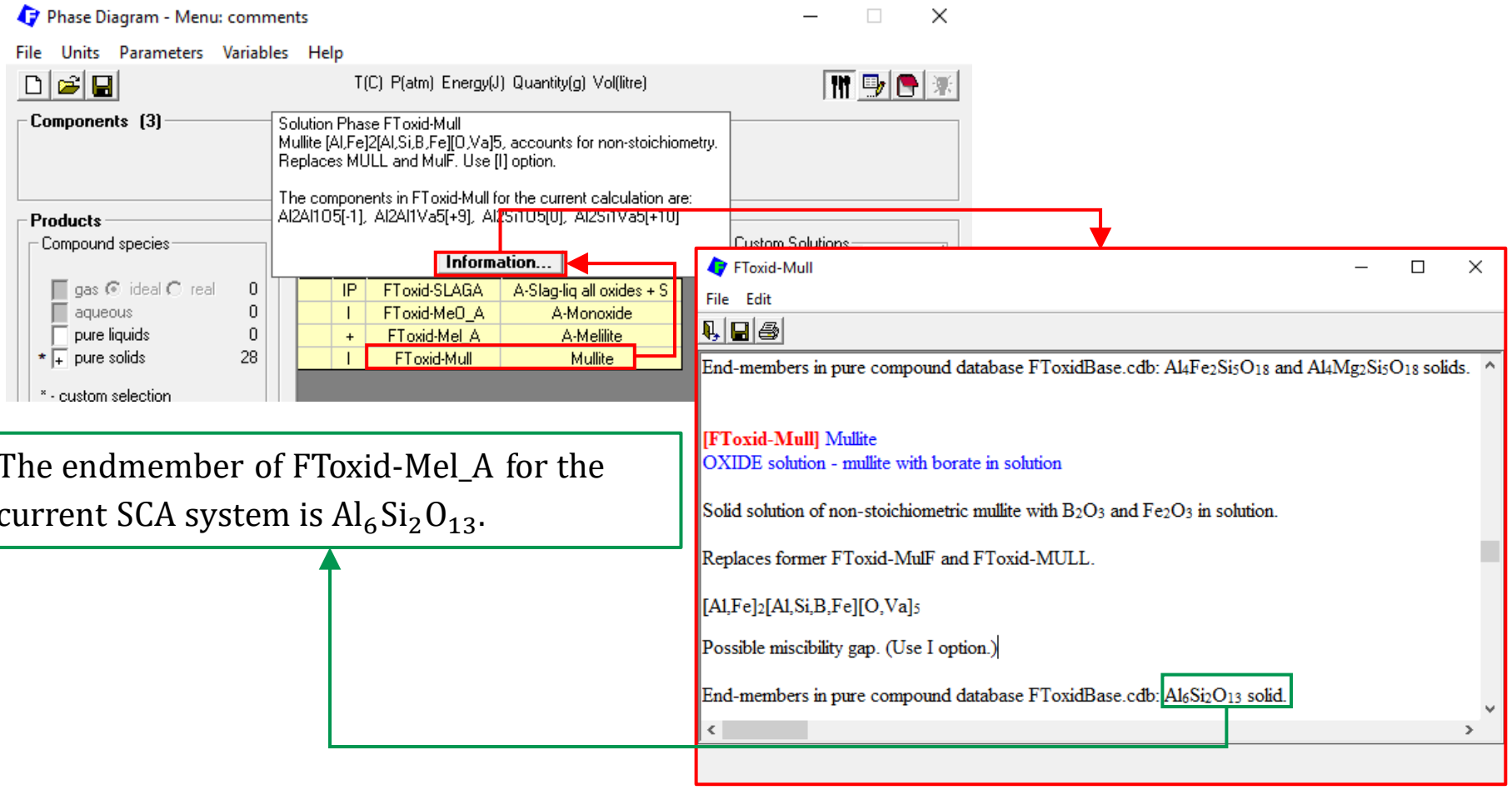
Find the endmembers of solid phases



The endmember of FToxid-Mel_A for the current SCA system is $Ca_2Al_2SiO_7$.

Phase Diagram Module: SiO_2-CaO-Al_2O_3 System

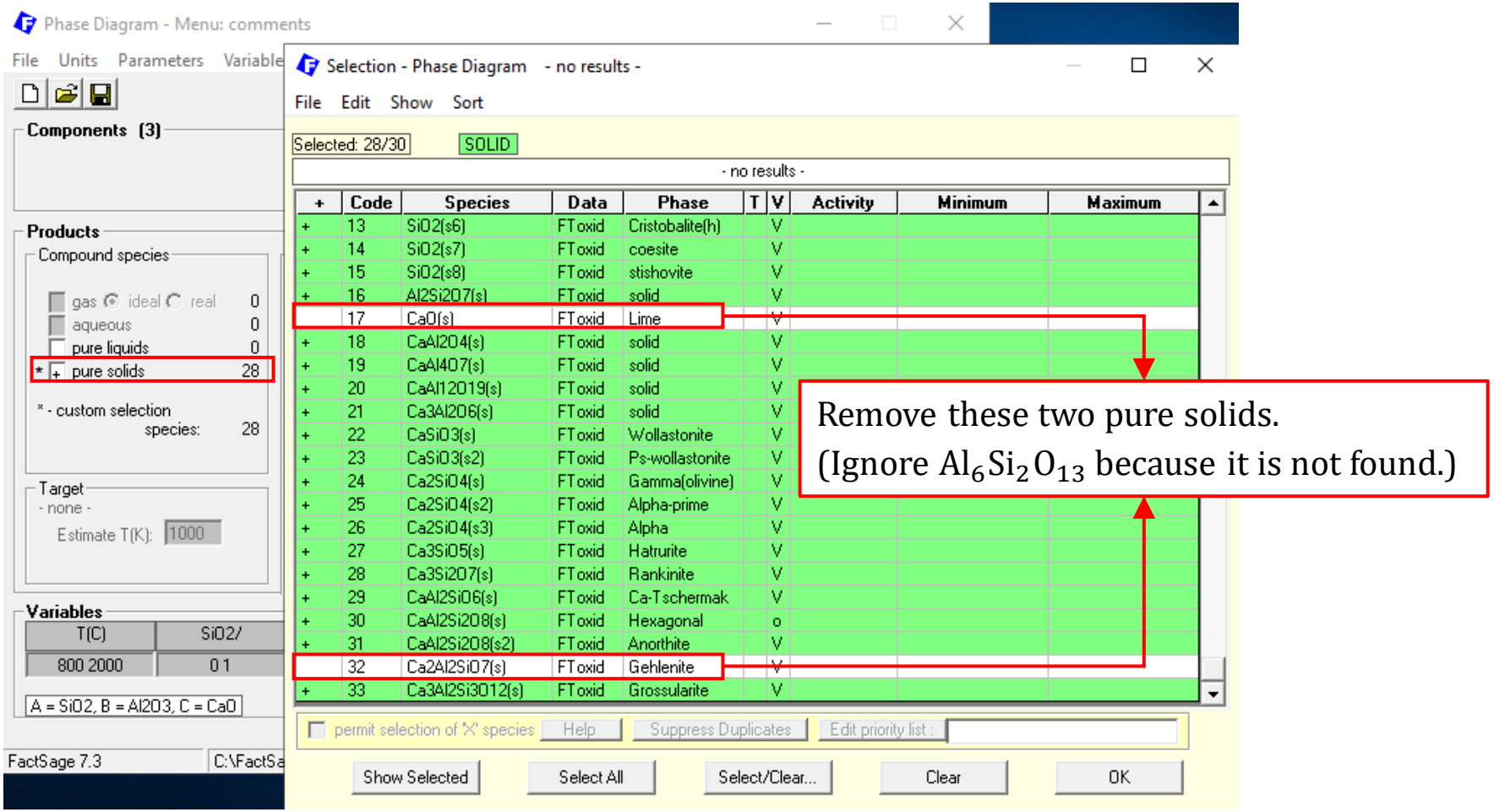
Find the endmembers of solid phases



The endmember of FToxid-Mel_A for the current SCA system is $Al_6Si_2O_{13}$.

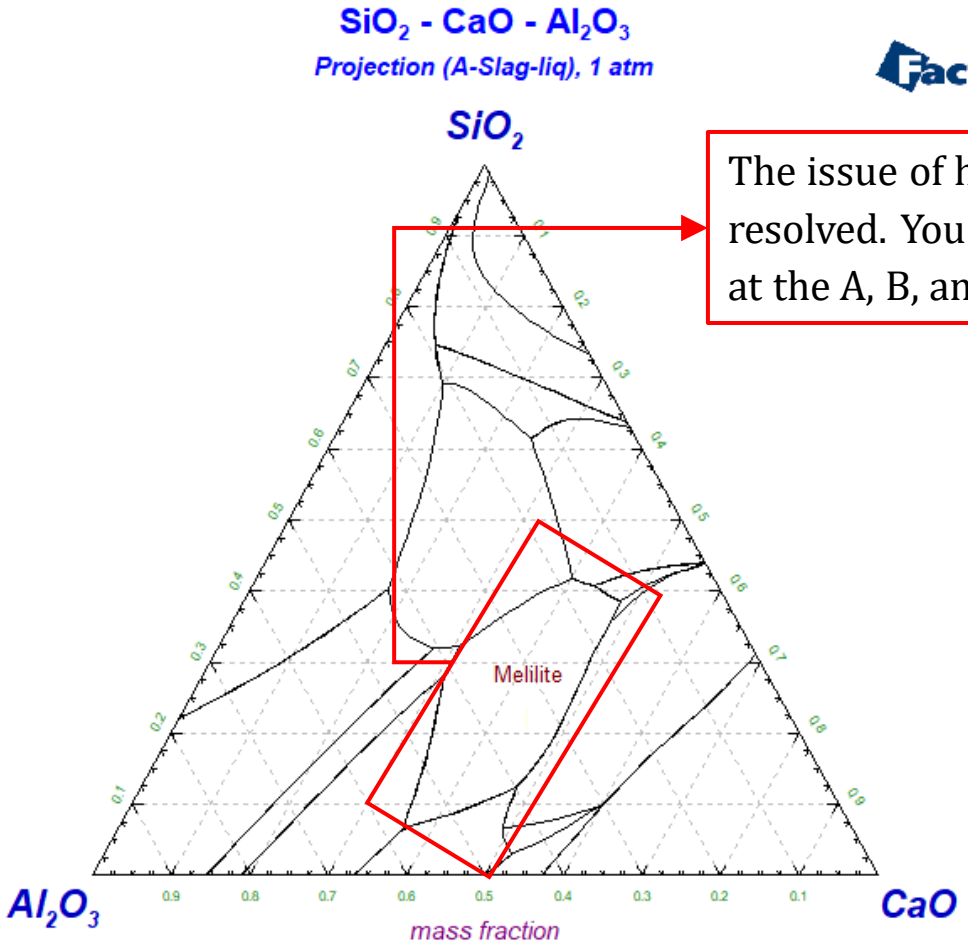
Phase Diagram Module: SiO_2-CaO-Al_2O_3 System

Remove the endmembers of solid phases from pure solids



Phase Diagram Module: SiO_2-CaO-Al_2O_3 System

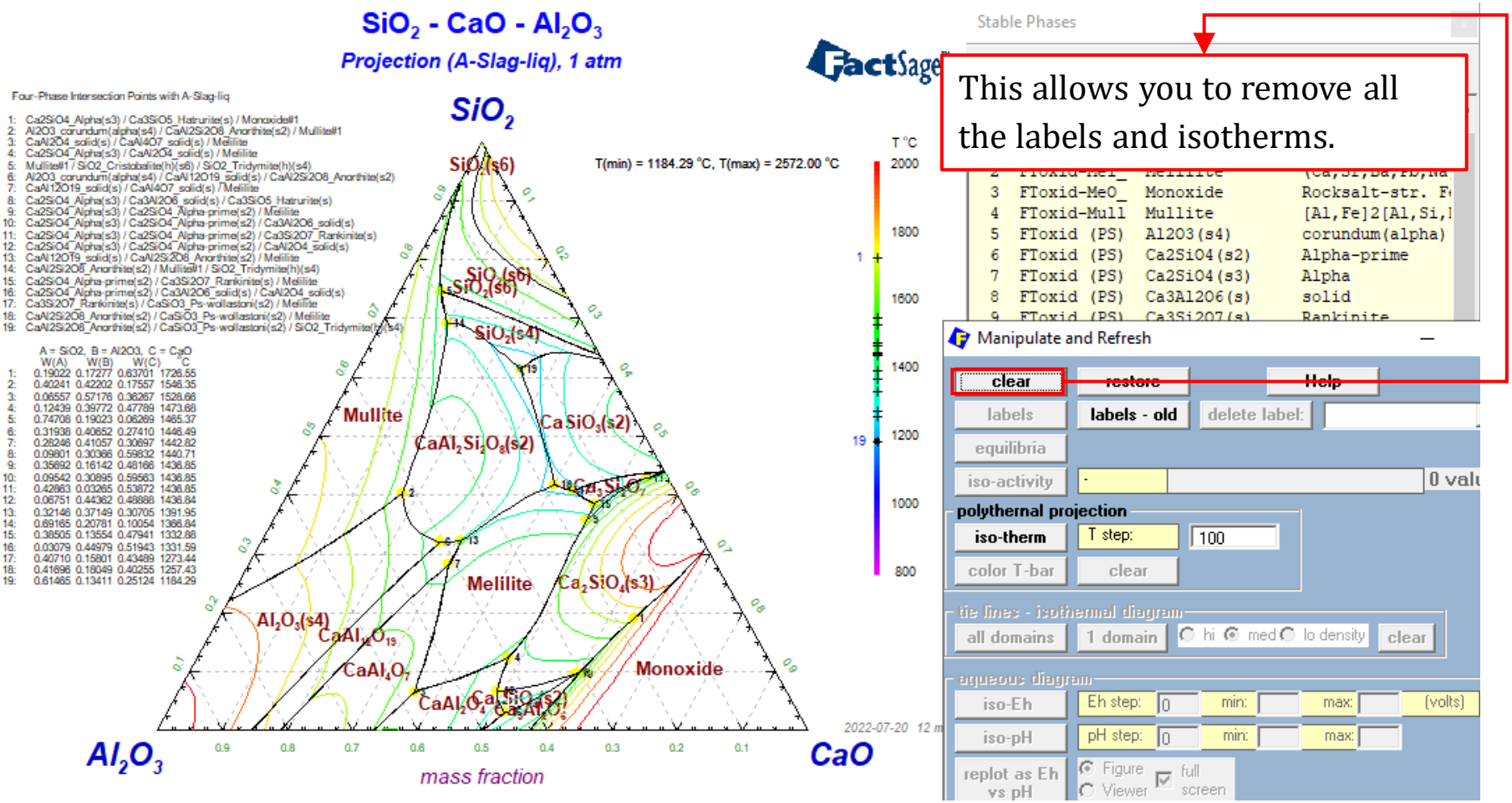
Then, perform the phase diagram calculation again.



The issue of having crossing and intersecting lines is resolved. You can try other component arrangements at the A, B, and C corner.

Phase Diagram Module: SiO_2-CaO-Al_2O_3 System

Results: the Liquidus Projection of the SiO_2-CaO-Al_2O_3 System.



This allows you to remove all the labels and isotherms.

Phase Diagram Module: SiO_2-CaO-Al_2O_3 System

A Note on the Phase Selection:

Although the selection of CaO and $Ca_2Al_2SiO_7$ from the list of pure solids did not produce any redundant lines when the isothermal sections were calculated, it is still recommended that all the endmembers of the solutions phases be removed.

Comparison with the phase diagram reported by Eriksson and Pelton:

You might notice that the liquidus projection of the SCA system calculated by the current FToxid database is not exactly same to the one reported by Eriksson and Pelton (CRCT Team). This is because FToxid is being constantly updated by CRCT to improve the accuracy of models and to include other oxides.

Eriksson and Pelton, Metallurgical Transactions B, Vol.24, No. 5, pp807-816 (1993)

Phase Diagram Module: MgF_2-CaF_2 System

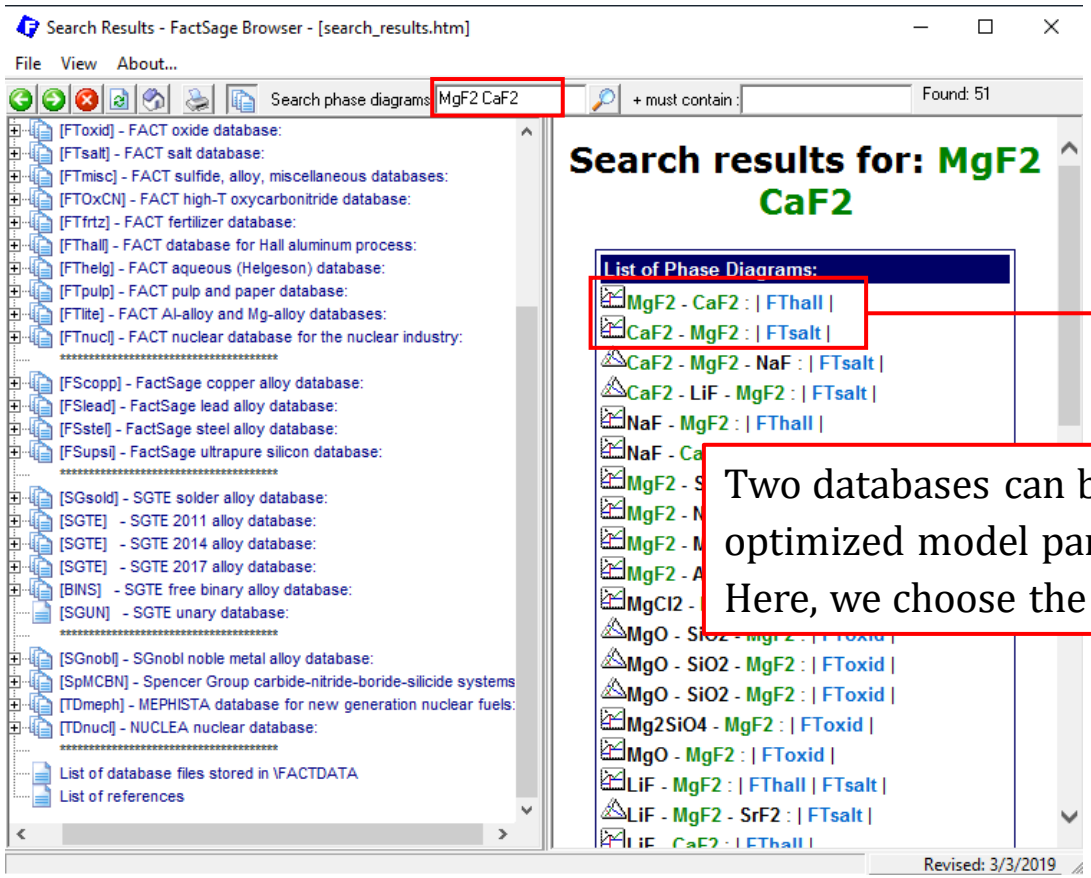
From previous examples, it is seen that the FactSage databases (e.g,, FTlite, FToxid) always contain a model for **liquid solution**. The model usually gives a quite accurate description of the interactions between solution constituents. In most cases, the model is non-ideal solution model. However, the Phase Diagram Module permits one to choose instead of non-ideal liquid solution from the FactSage databases, an ideal liquid solution.

Say we are looking at a simple eutectic system, MgF_2-CaF_2. Let us calculate the phase diagram of the MgF_2-CaF_2 system using both the ideal solution model and the non-ideal solution model for the liquid MgF_2-CaF_2 solution.

Note: for these two scenarios, only the liquid phase is different.

Phase Diagram Module: MgF_2-CaF_2 System

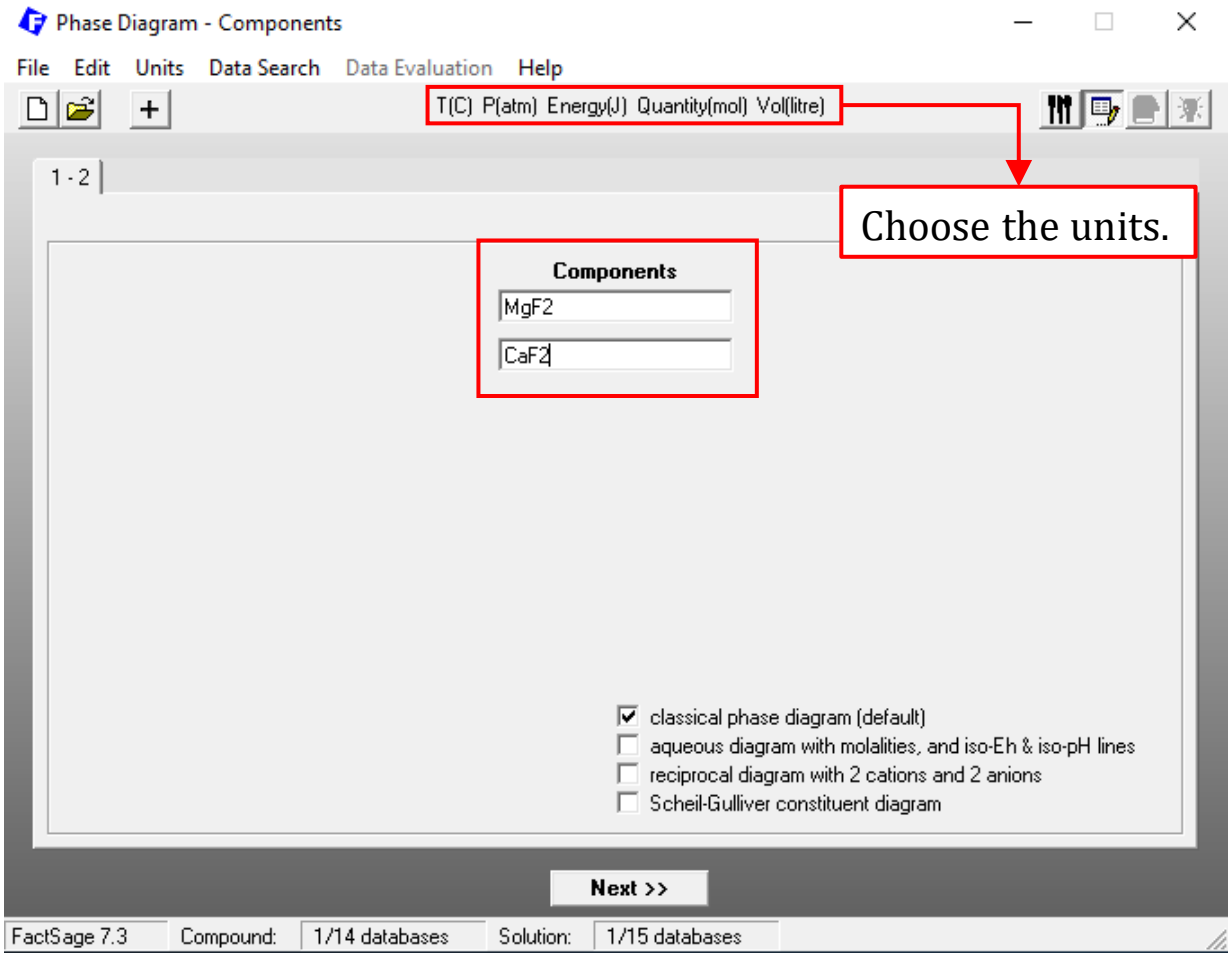
First, find the FactSage database that can be used to calculate the phase diagram of the MgF_2-CaF_2 system.



Two databases can be used, and both of them contain the optimized model parameters for the MgF_2-CaF_2 system. Here, we choose the FTsalt database.

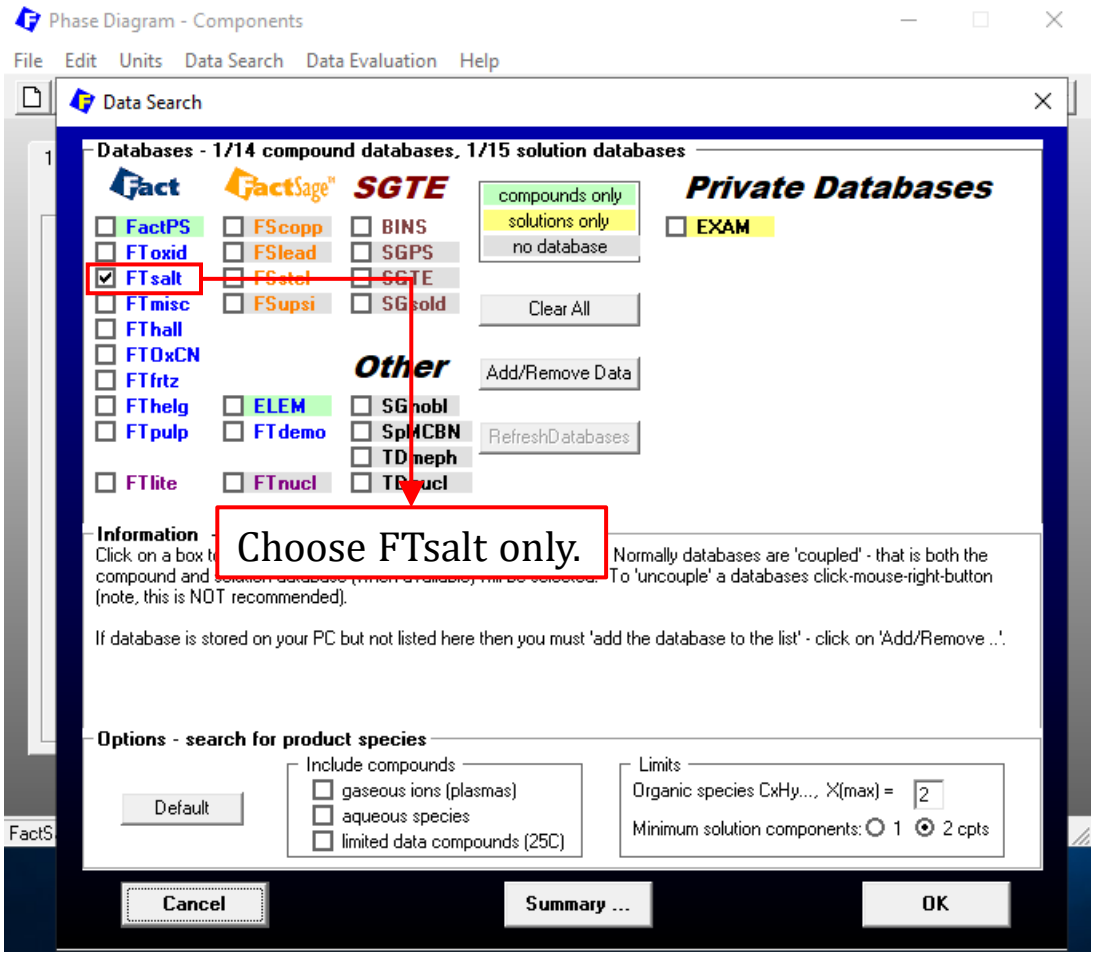
Phase Diagram Module: MgF_2-CaF_2 System

Components Window: Define Components



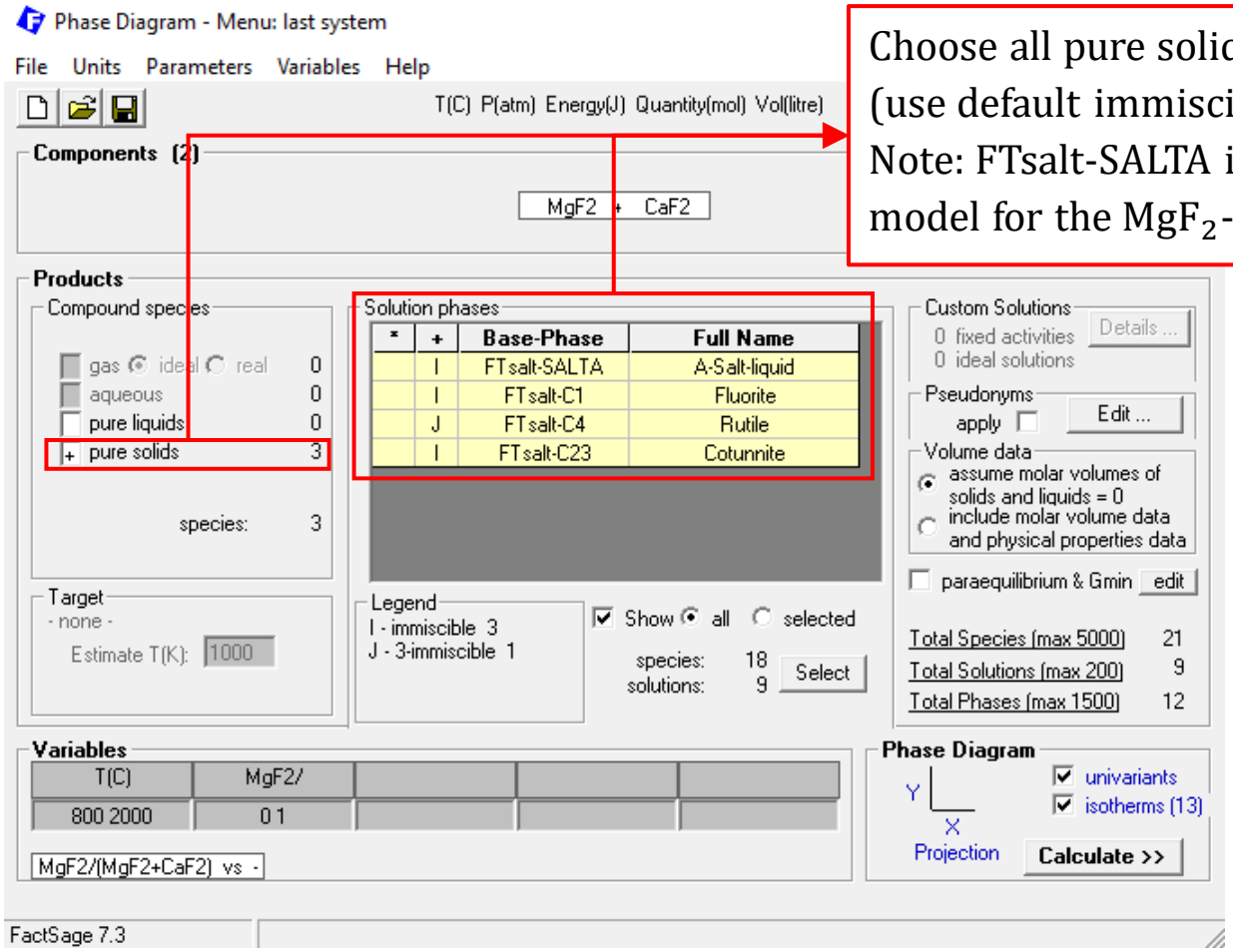
Phase Diagram Module: MgF_2-CaF_2 System

Components Window: Choose Database(s)



Phase Diagram Module: MgF_2-CaF_2 System

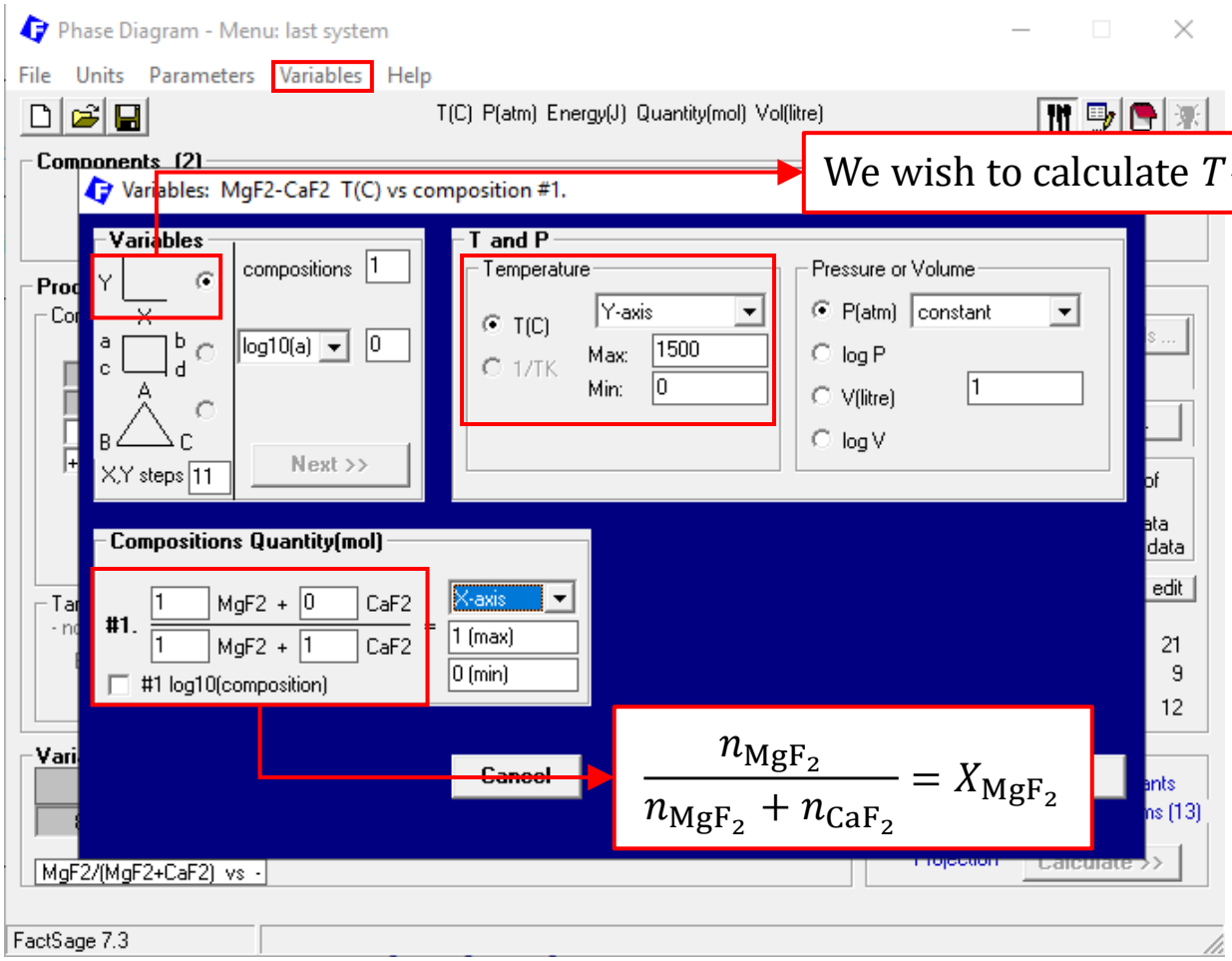
Menu Window: Choose Products/Phases (Compounds and Solution Phases)



Choose all pure solids and all solution phases (use default immiscibility settings).
Note: FTsalt-SALTA is the non-ideal solution model for the MgF_2-CaF_2 liquid.

Phase Diagram Module: MgF_2-CaF_2 System

Menu Window: Set up the Variables

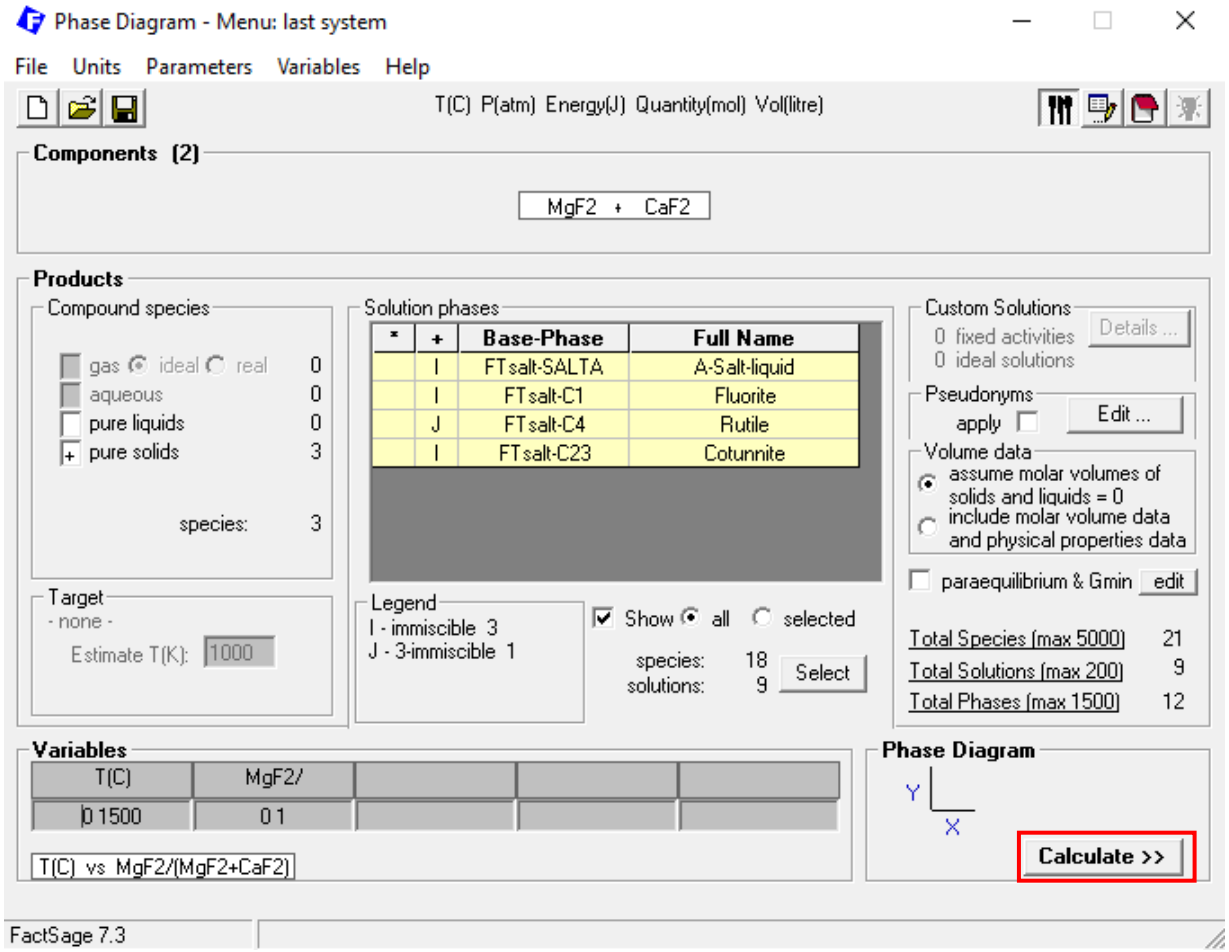


We wish to calculate $T \sim X_B$ type of phase diagram.

$$\frac{n_{MgF_2}}{n_{MgF_2} + n_{CaF_2}} = X_{MgF_2}$$

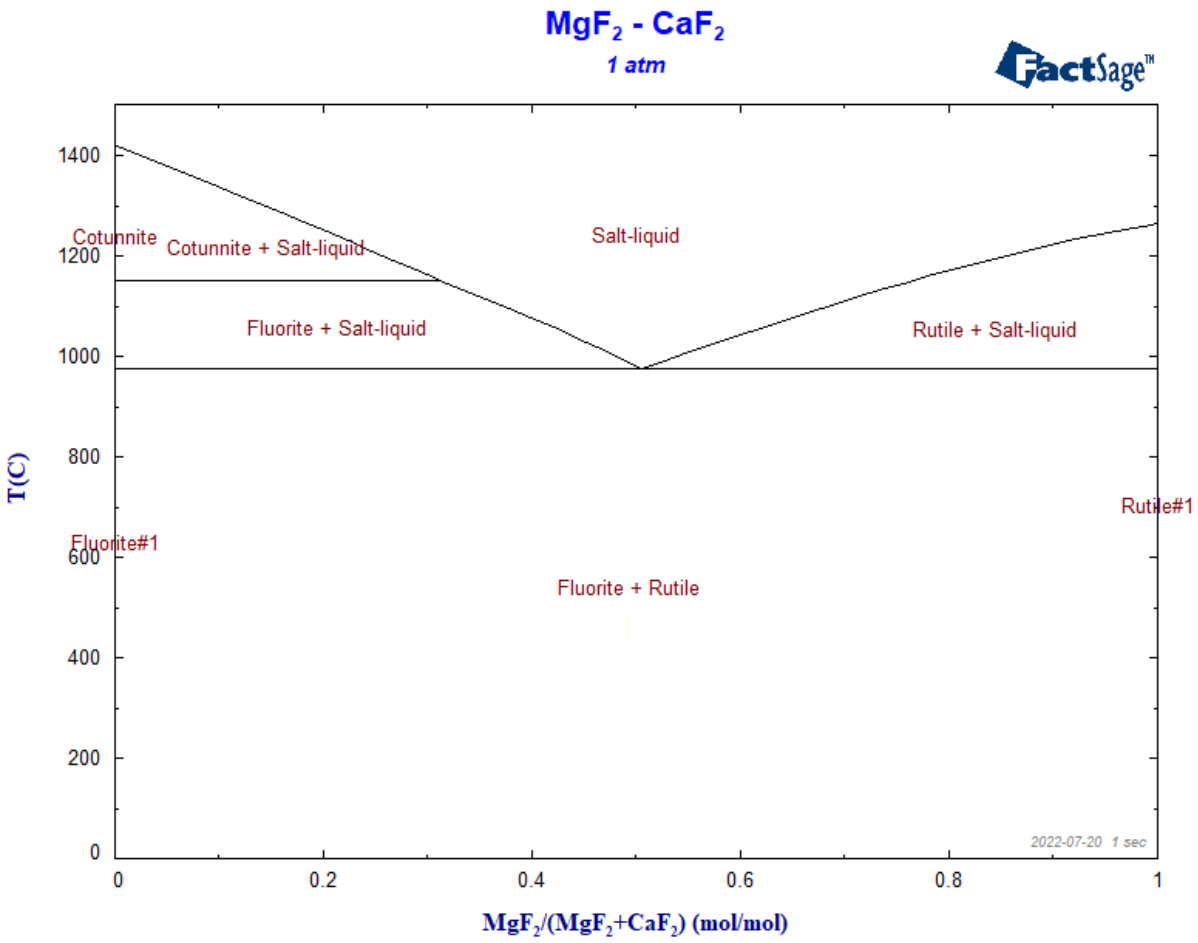
Phase Diagram Module: MgF_2-CaF_2 System

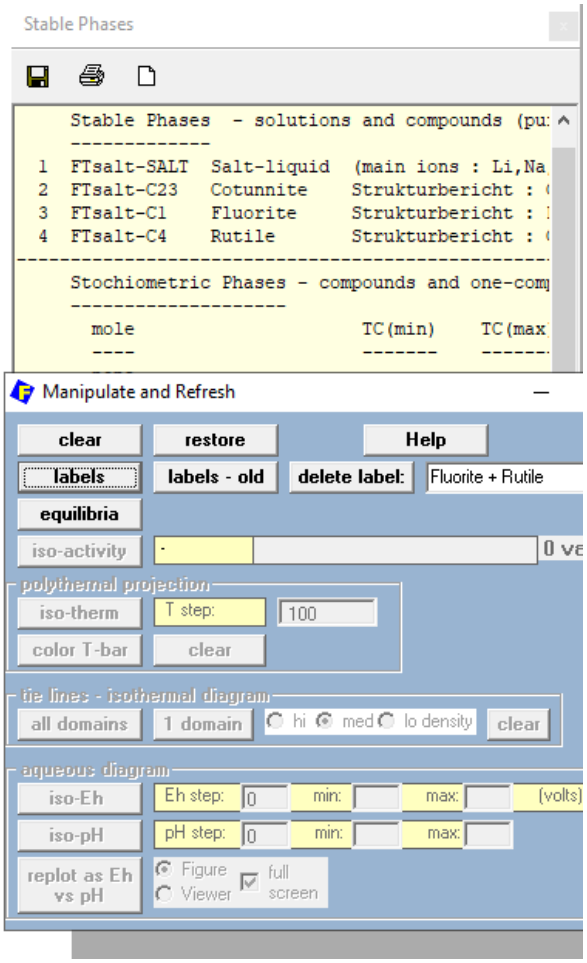
Menu Window: Calculate



Phase Diagram Module: MgF_2-CaF_2 System

Results: the MgF_2-CaF_2 Phase Diagram



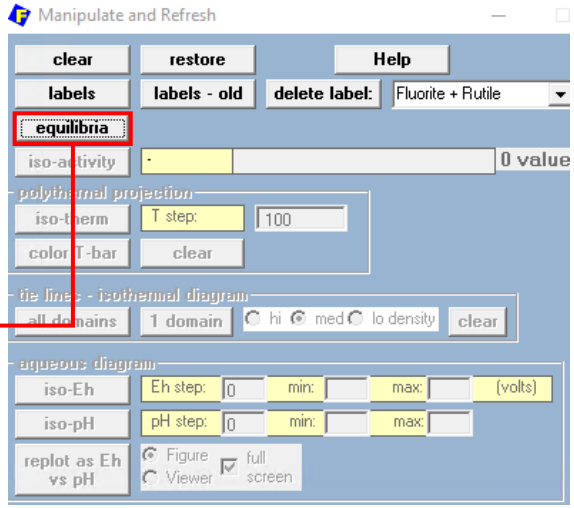


Phase Diagram Module: MgF_2-CaF_2 System

Results: Invariant Reactions

Stable Phases

```
    Stable Phases  - solutions and compounds (pure substances PS)
    -------------
 1  FTsalt-SALT  Salt-liquid  (main ions : Li,Na,K,Rb,Cs,Mg,Ca,Sr,Ba,Al,Fe[2+,3+],Mn,Co,Ni,Zn,Pb,L
 2  FTsalt-C23   Cotunnite    Strukturbericht : C23; Pearson : oP12; Space group : Pnma (62); Prot
 3  FTsalt-C1    Fluorite     Strukturbericht : FCC_C1; Pearson : cF12; Space group : Fm-3m (225);
 4  FTsalt-C4    Rutile       Strukturbericht : C4; Pearson : tP6; Space group : P42/mnm (136); Pr
-------------------------------------------------------------------------------------------------
    Stochiometric Phases - compounds and one-component solutions
    --------------------
      mole                    TC(min)    TC(max)
      ----                    -------    -------
   -  none  -
-------------------------------------------------------------------------------------------------
    Phase Equilibria
    ----------------
 1  1418.05 C     Salt-liquid#1(0.0)    <=>   Cotunnite#1(0.0)
 2  1262.85 C     Salt-liquid#1(1.0)    <=>   Rutile#1(1.0)
 3  1150.85 C     Fluorite#1(0.0002255)    <=>   Cotunnite#1(0.0002255)    +   Salt-liquid#1(0.3109)
 4   974.01 C     Salt-liquid#1(0.5047)    <=>   Fluorite#1(0.0003127)    +   Rutile#1(0.9997)
-------------------------------------------------------------------------------------------------
```

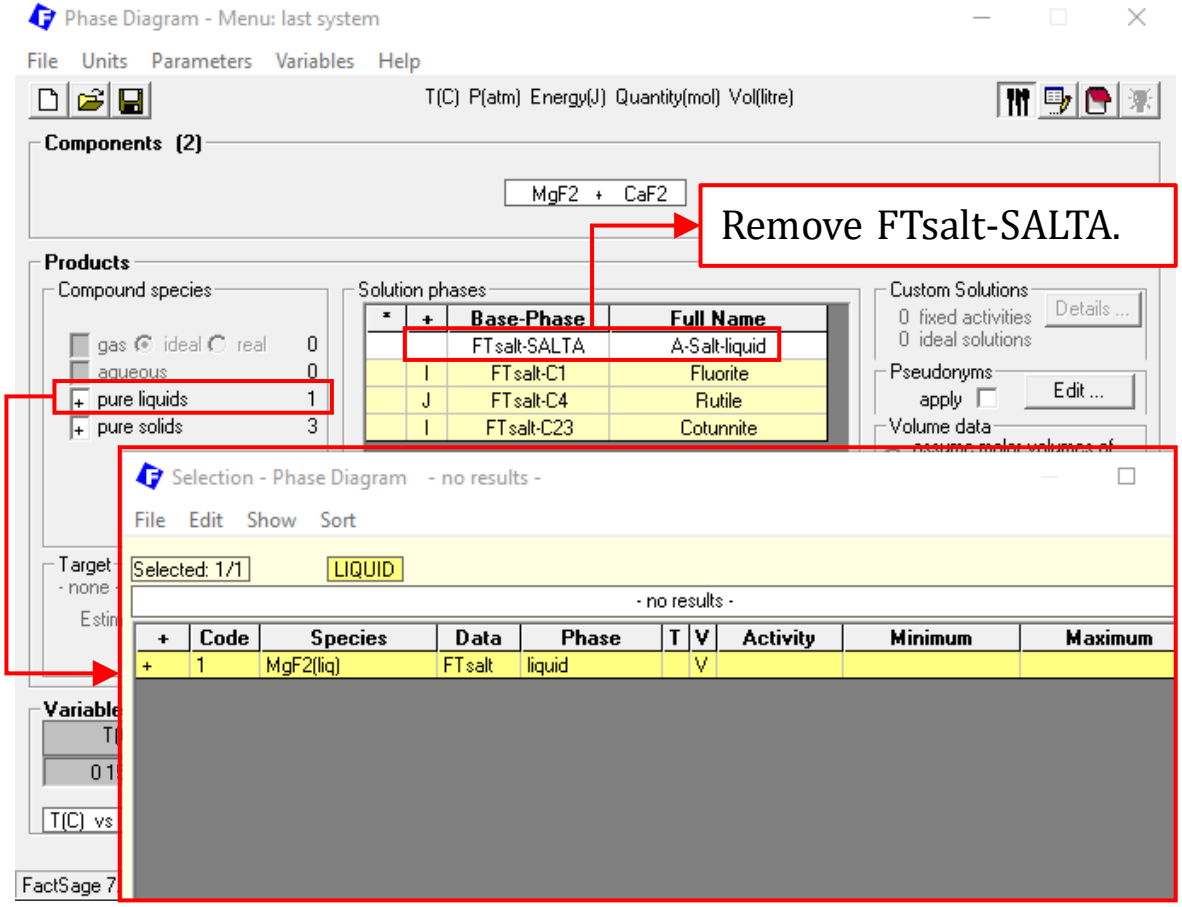


The invariant reaction labeled as “4” is the eutectic reaction.

Phase Diagram Module: MgF_2-CaF_2 System

Now, let us choose the MgF_2-CaF_2 liquid which is modeled as an ideal solution.

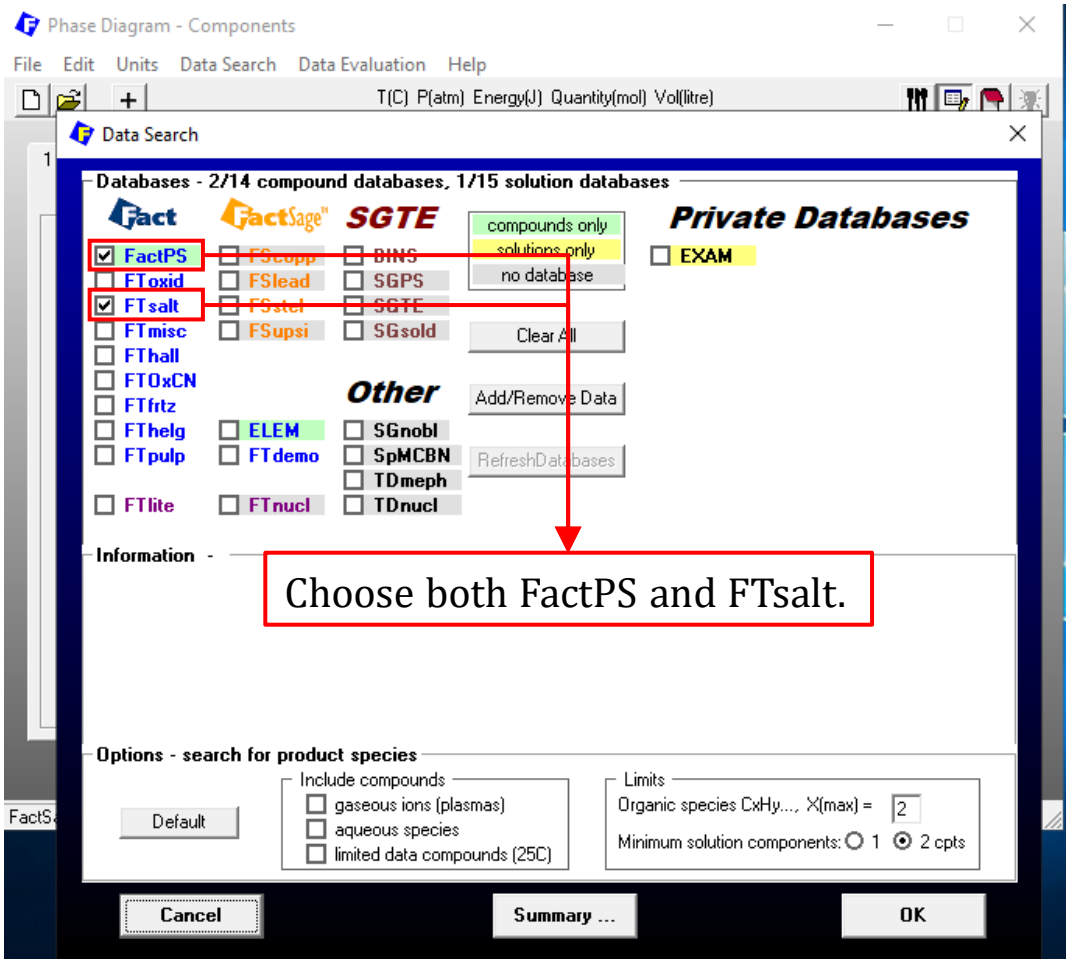
Back to the Menu Window.



To define an ideal liquid MgF_2-CaF_2 solution, we need both pure liquid MgF_2 and pure liquid CaF_2. However, the FTsalt database does not include the model for pure liquid CaF_2. Therefore, another database (normally FactPS) must be used.

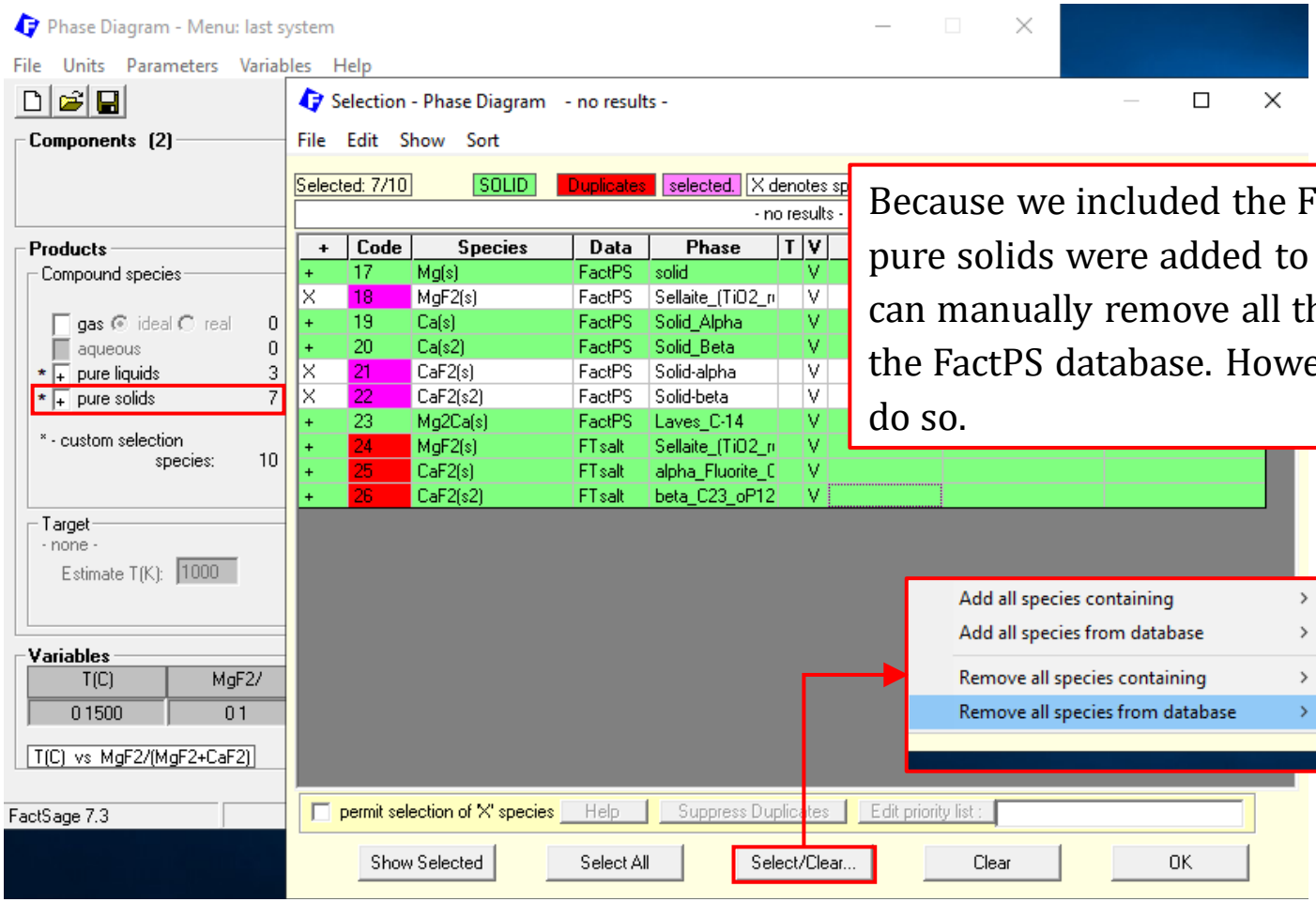
Phase Diagram Module: MgF_2-CaF_2 System

Bac to Components Window: Add FactPS



Phase Diagram Module: MgF_2-CaF_2 System

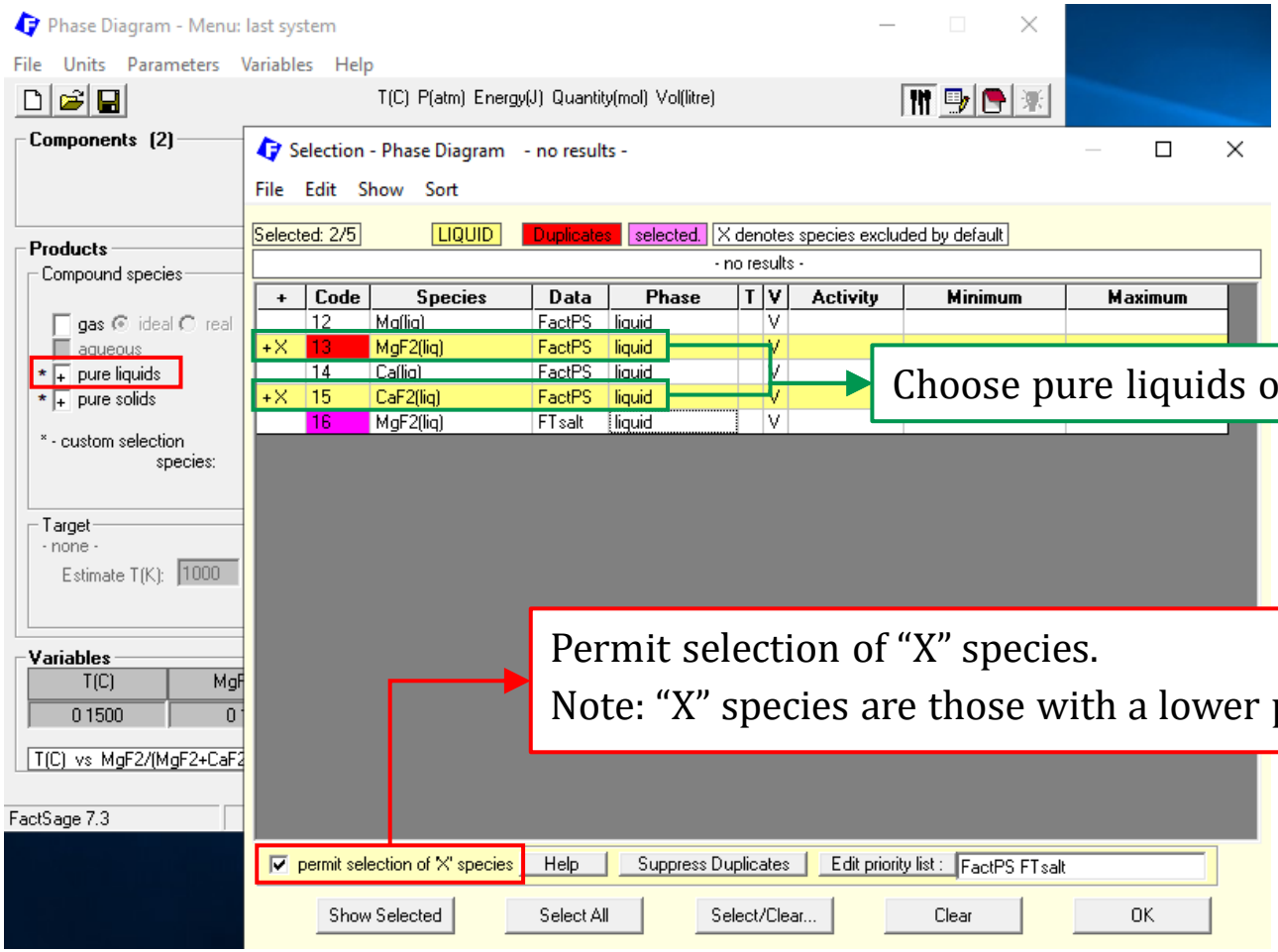
Pure Solids: Remove all the pure solids from the FactPS database



Because we included the FactPS database, more pure solids were added to the selection list. We can manually remove all the pure solids from the FactPS database. However, you don't have to do so.

Phase Diagram Module: MgF_2-CaF_2 System

Pure Liquids: Define Ideal Liquid MgF_2-CaF_2 Solution

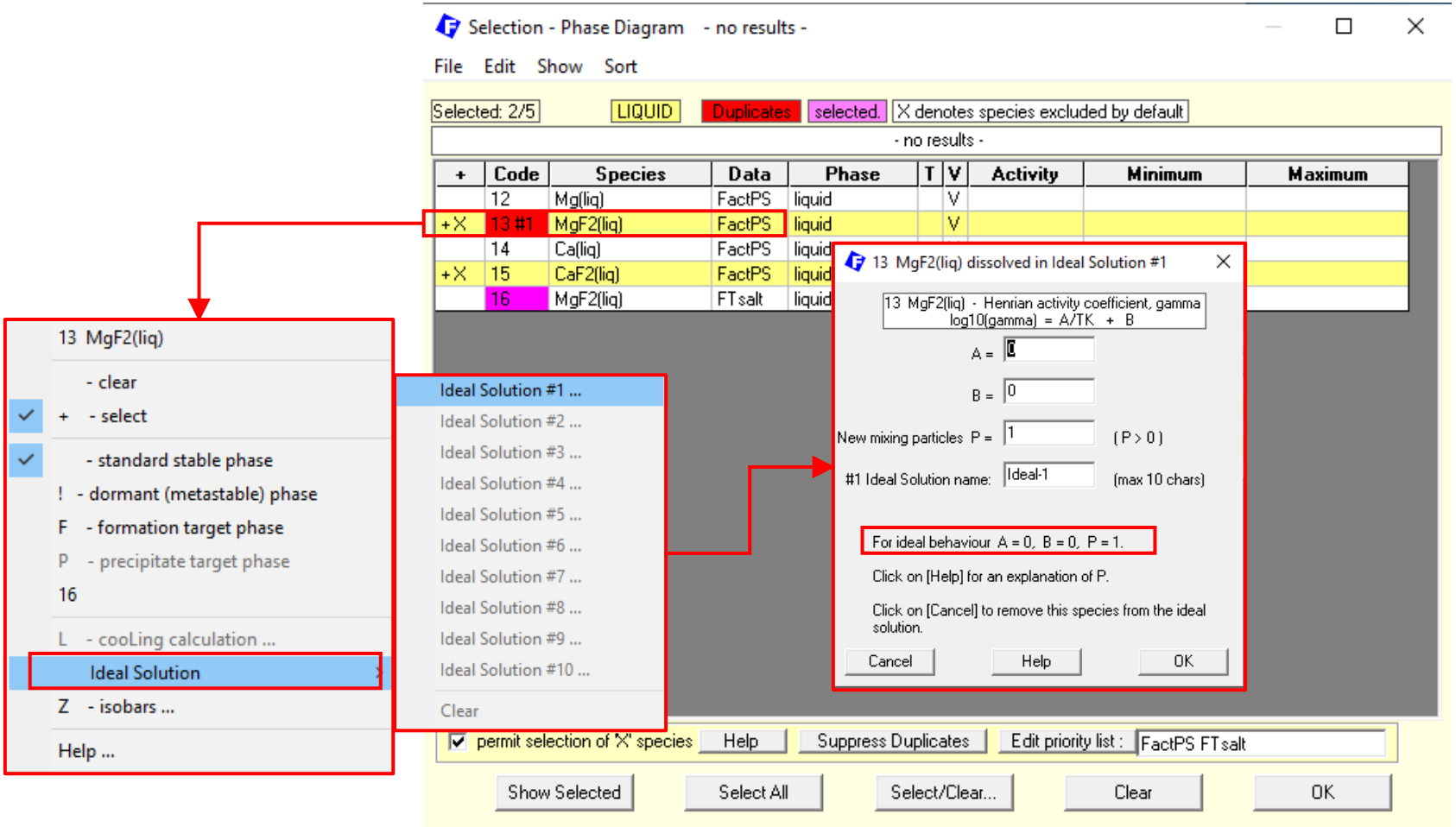


Choose pure liquids of MgF_2 and CaF_2.

Permit selection of "X" species.
Note: "X" species are those with a lower priority.

Phase Diagram Module: MgF_2-CaF_2 System

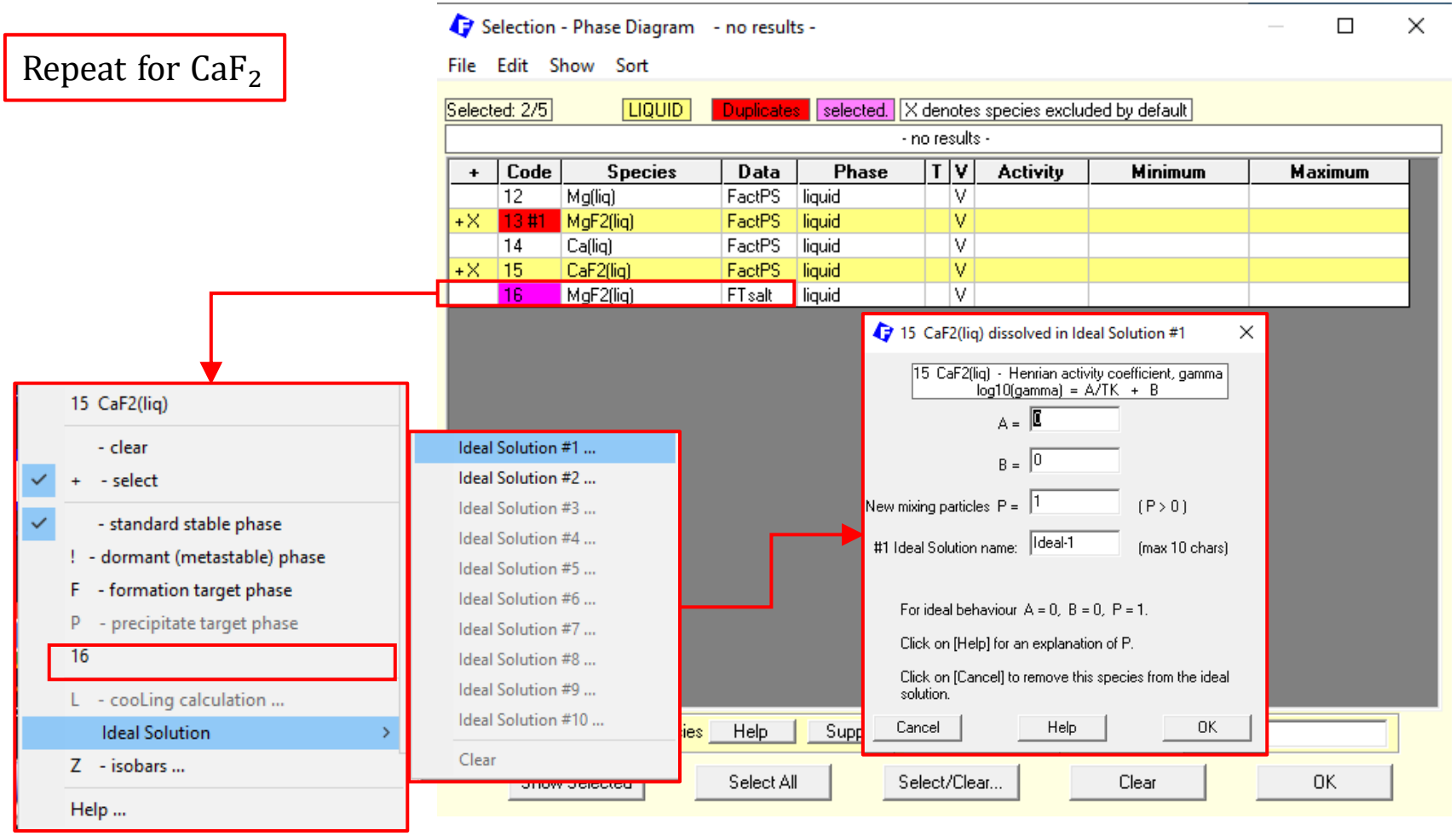
Pure Liquids: Define Ideal Liquid MgF_2-CaF_2 Solution



Phase Diagram Module: MgF_2-CaF_2 System

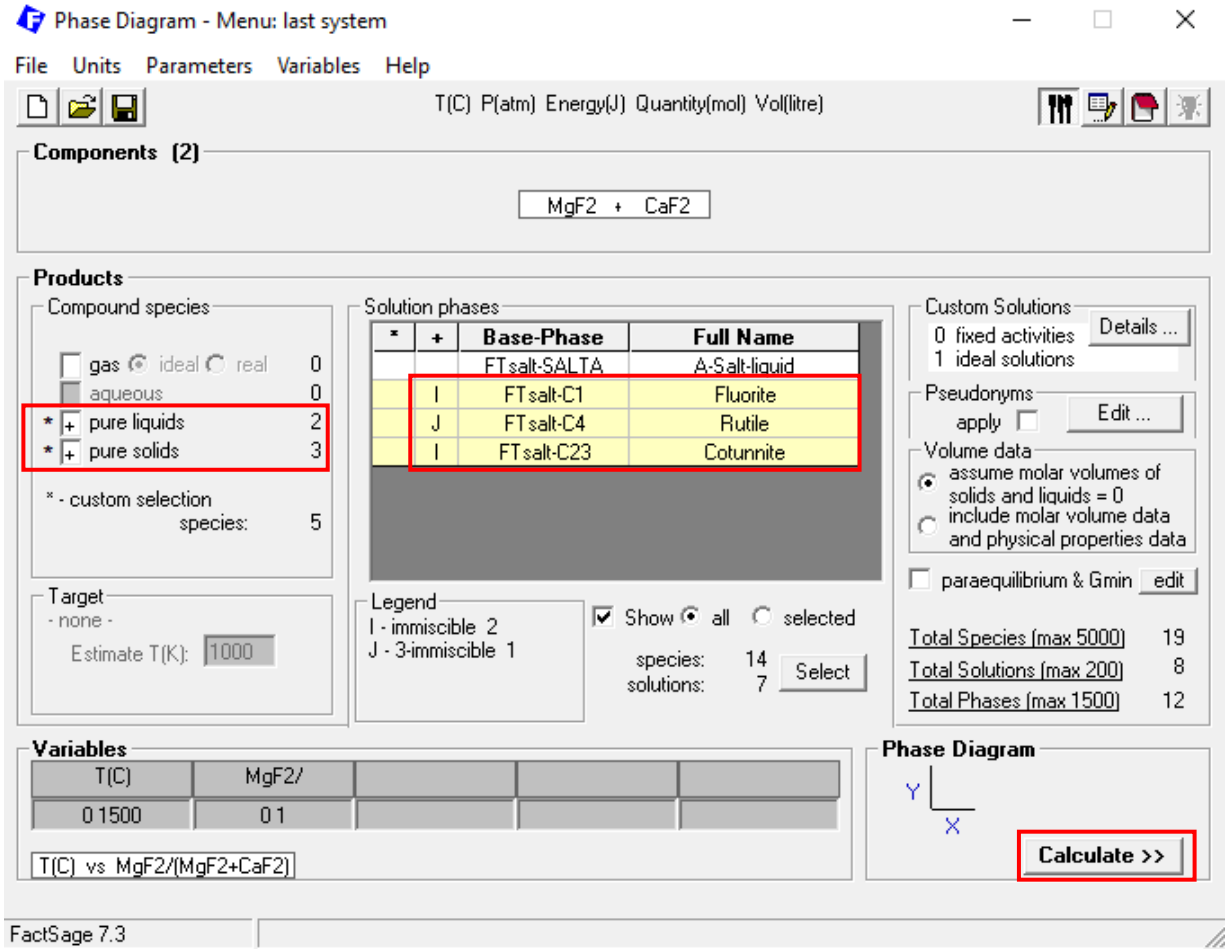
Pure Liquids: Define Ideal Liquid MgF_2-CaF_2 Solution

Repeat for CaF_2



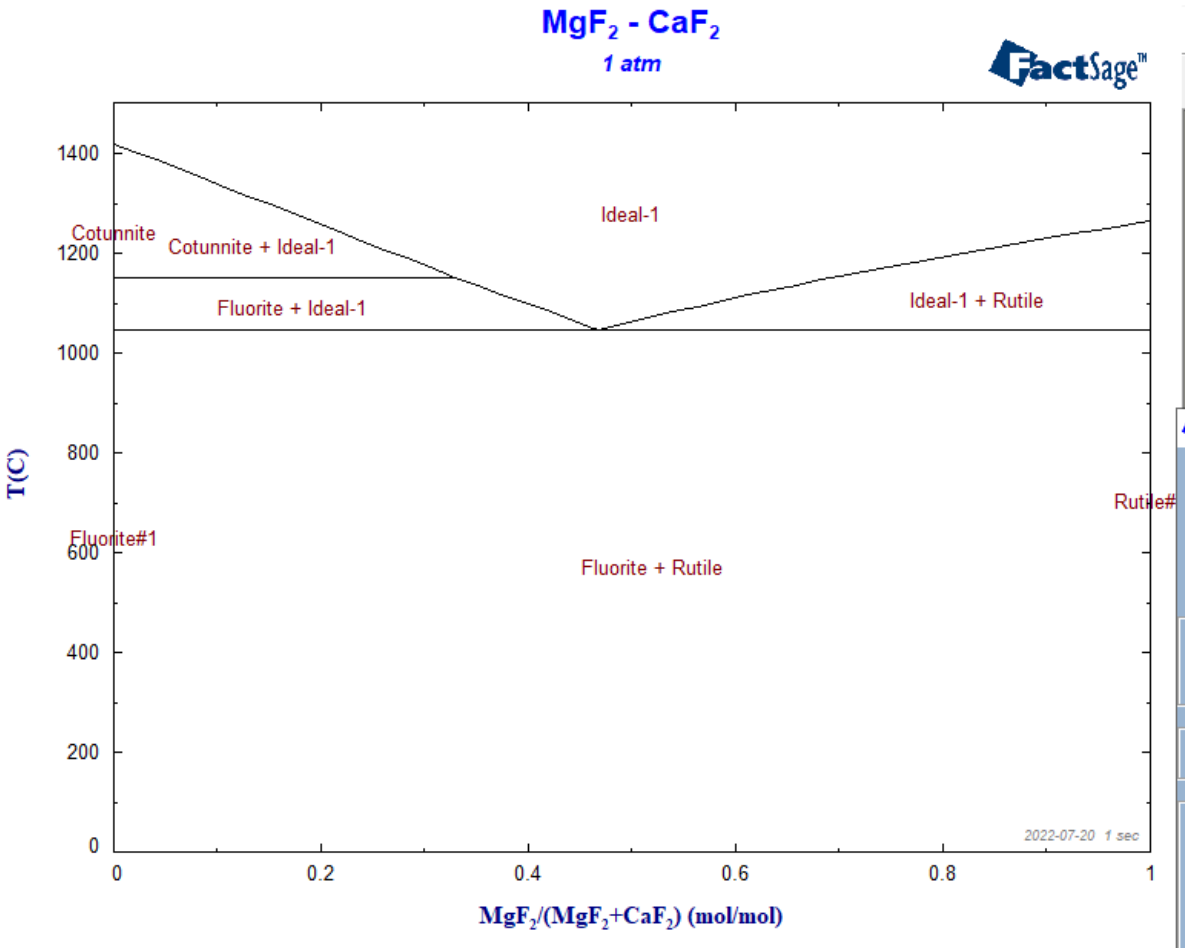
Phase Diagram Module: MgF_2-CaF_2 System

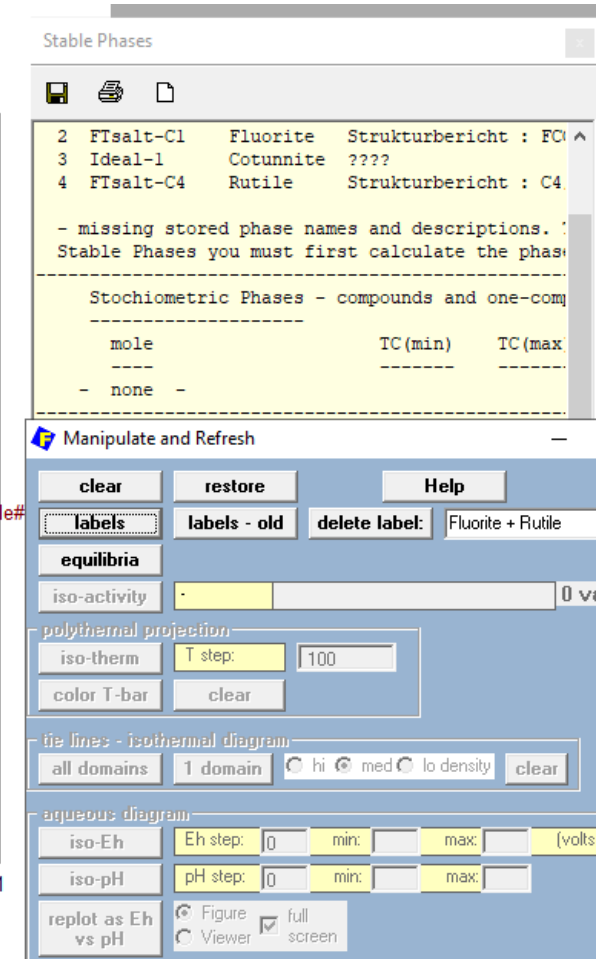
Menu Window: Calculate when the liquid solution is ideal



Phase Diagram Module: MgF_2-CaF_2 System

Results: the MgF_2-CaF_2 Phase Diagram (when the liquid solution is ideal)





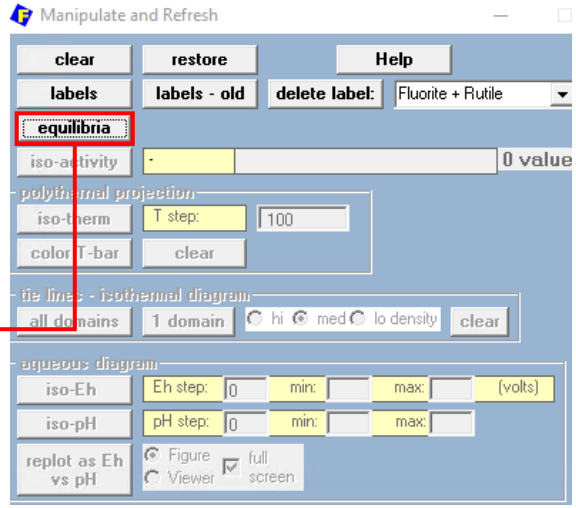
Phase Diagram Module: MgF_2-CaF_2 System

Results: Invariant Reactions (when the liquid solution is ideal)

Stable Phases

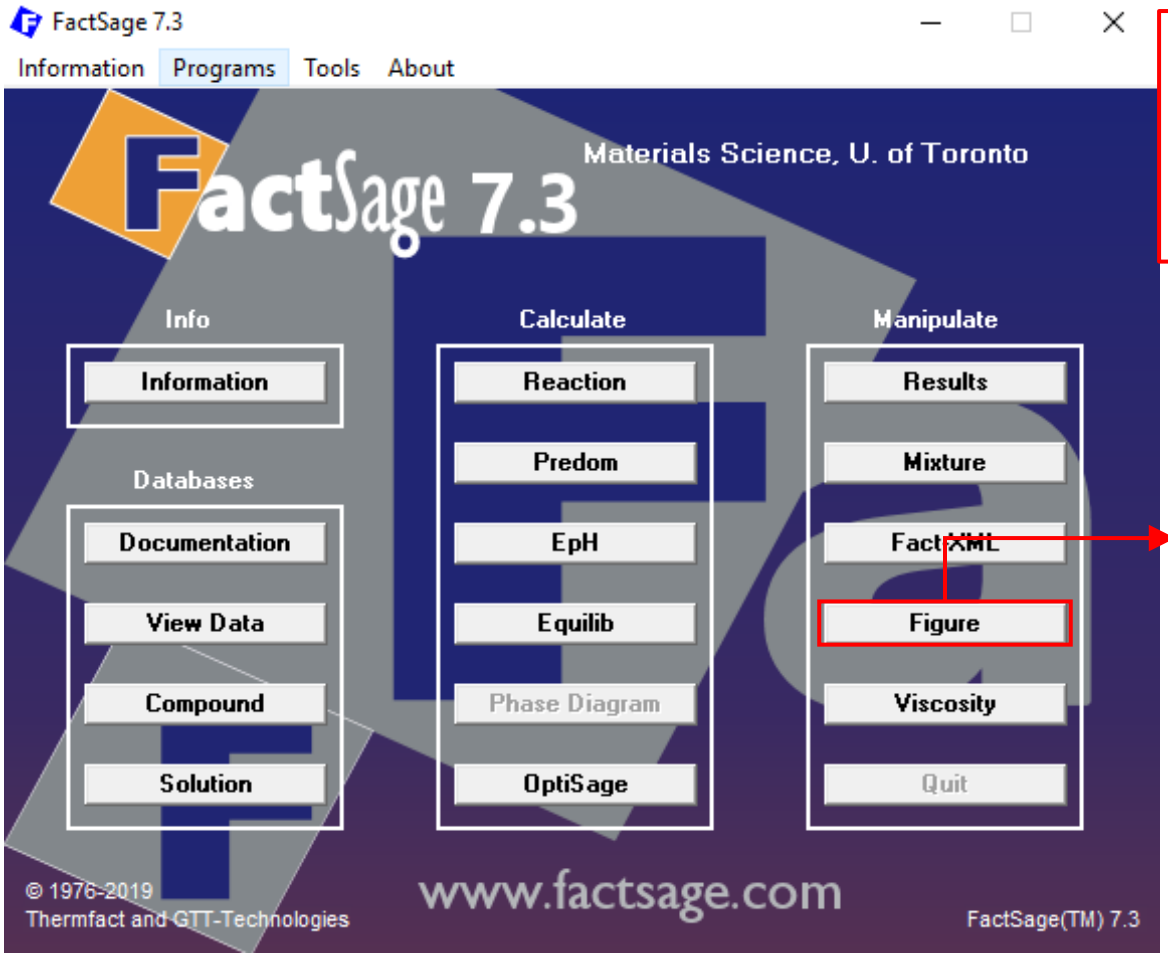
```
 1  FTsalt-C23    Cotunnite  Strukturbericht : C23; Pearson : oP12; Space group : Pnma (62); Pr
 2  FTsalt-C1     Fluorite   Strukturbericht : FCC_C1; Pearson : cF12; Space group : Fm-3m (225
 3  Ideal-1       Cotunnite  ????
 4  FTsalt-C4     Rutile     Strukturbericht : C4; Pearson : tP6; Space group : P42/mnm (136);

 - missing stored phase names and descriptions. To list all the
 Stable Phases you must first calculate the phase diagram.
-------------------------------------------------------------------------------------------------
    Stochiometric Phases - compounds and one-component solutions
    --------------------
      mole                    TC(min)     TC(max)
      ----                    -------     -------
   -  none  -
-------------------------------------------------------------------------------------------------
    Phase Equilibria
    ----------------
 1  1417.86 C     Ideal-1(0.0)    +    (1.0)   <=>   Cotunnite#1(0.0)
 2  1262.85 C     Ideal-1(0.0)    +    (1.0)   <=>   Rutile#1(0.0)
 3  1150.85 C     Fluorite#1(0.0004005)    <=>    Cotunnite#1(0.0004005)    +    Ideal-1(0.3274)
 4  1045.02 C     Ideal-1(0.4676)    <=>    Fluorite#1(0.000483)    +    Rutile#1(0.9995)
-------------------------------------------------------------------------------------------------
```



Phase Diagram Module: MgF_2-CaF_2 System

Comparison: Open the Figure Module

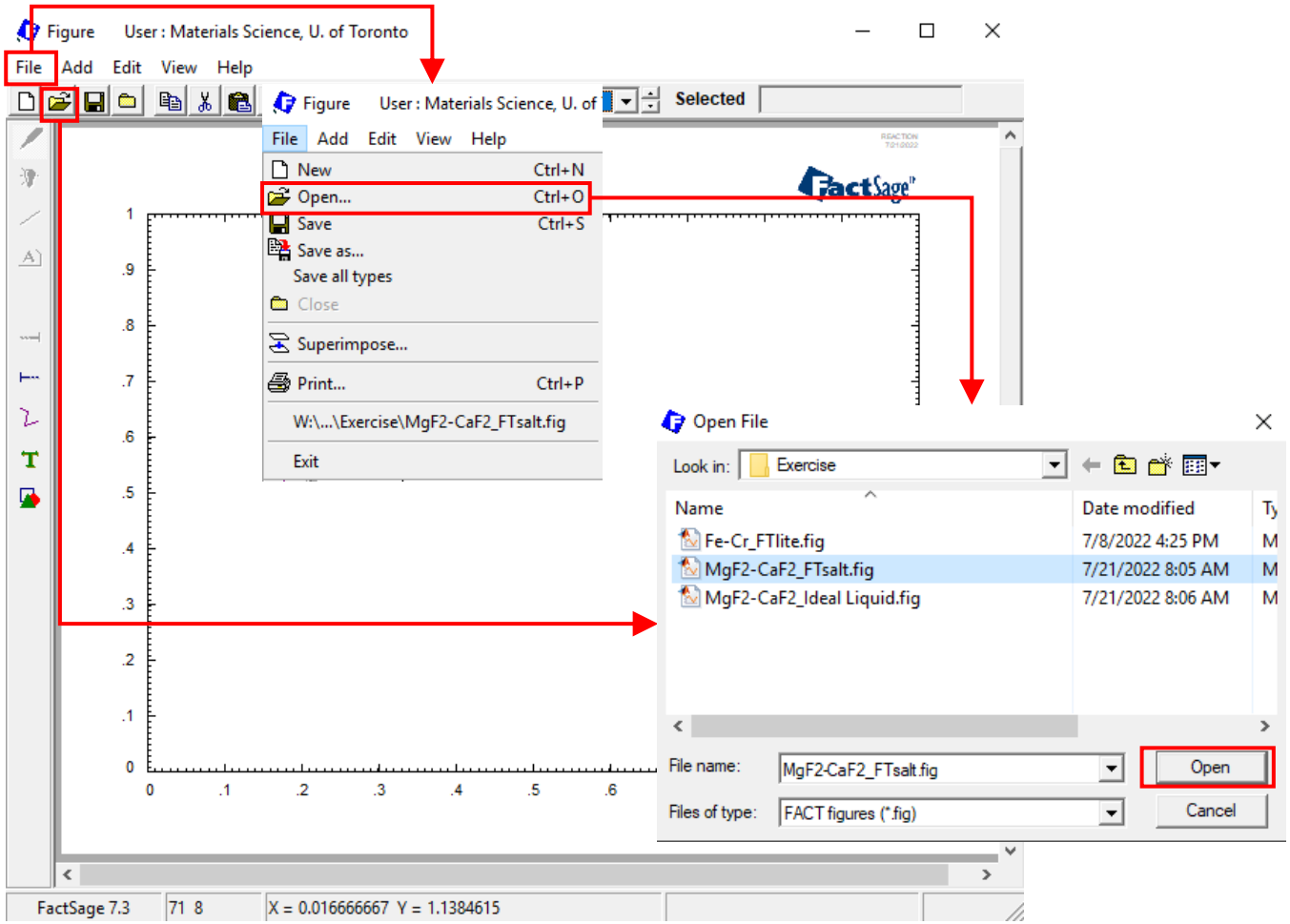


We will use the Figure Module to superimpose the two phases diagrams of the MgF_2-CaF_2 system.

Run Figure

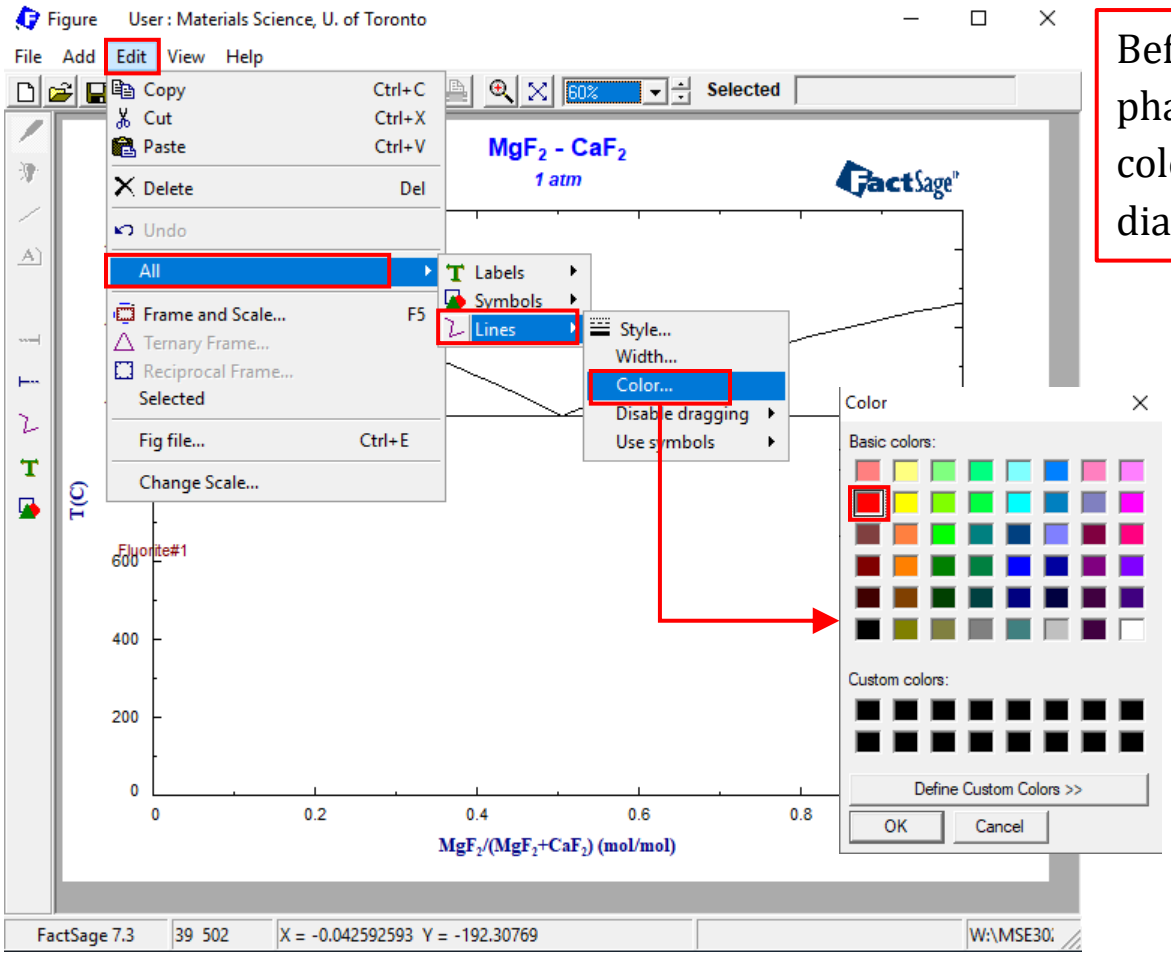
Phase Diagram Module: MgF_2-CaF_2 System

Comparison: Open the first phase diagram



Phase Diagram Module: MgF_2-CaF_2 System

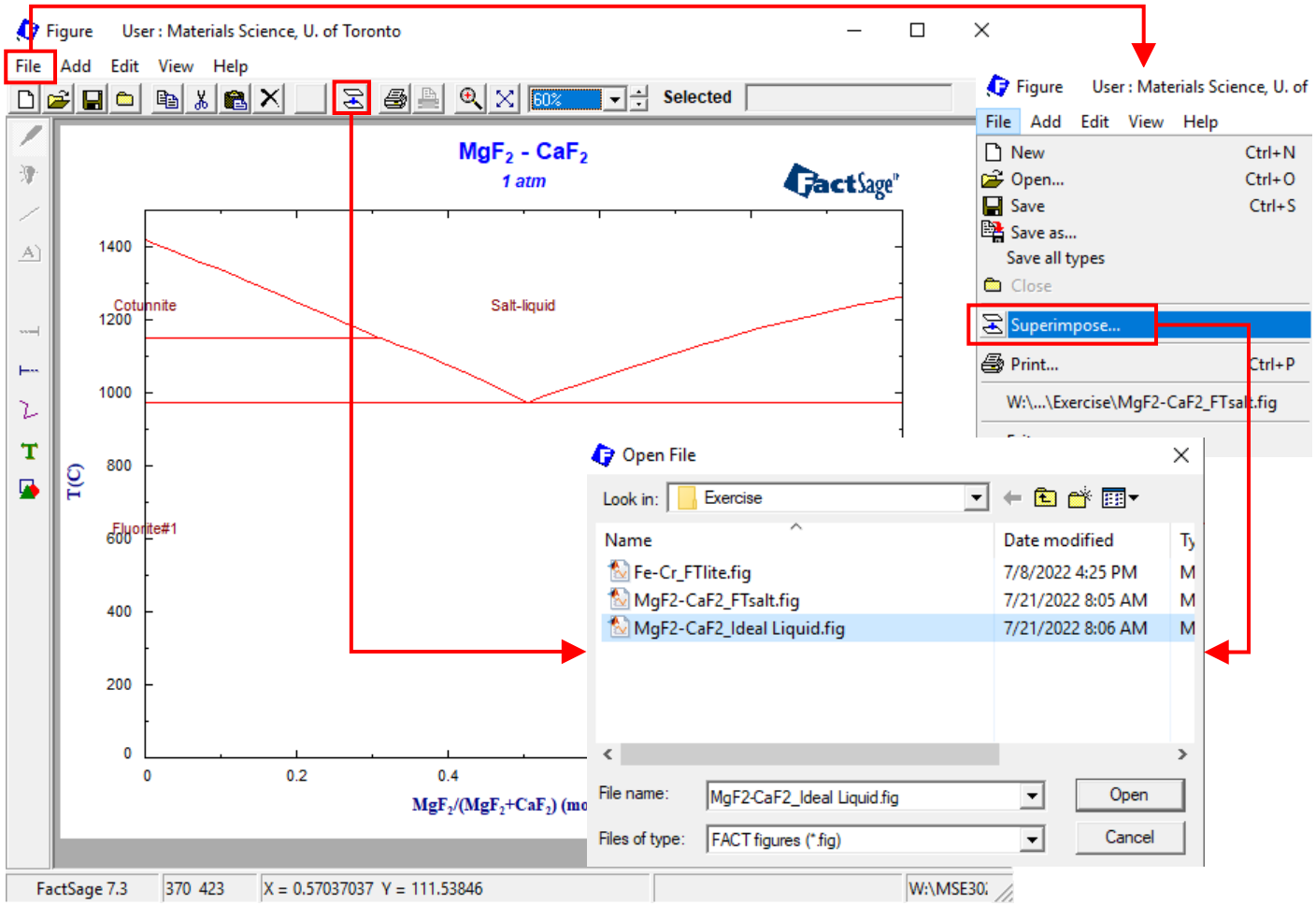
Comparison: Open the first phase diagram



Before we superimpose the second phase diagram, let us change the color of lines on the first phase diagram (FTsalt-SALTA) to red.

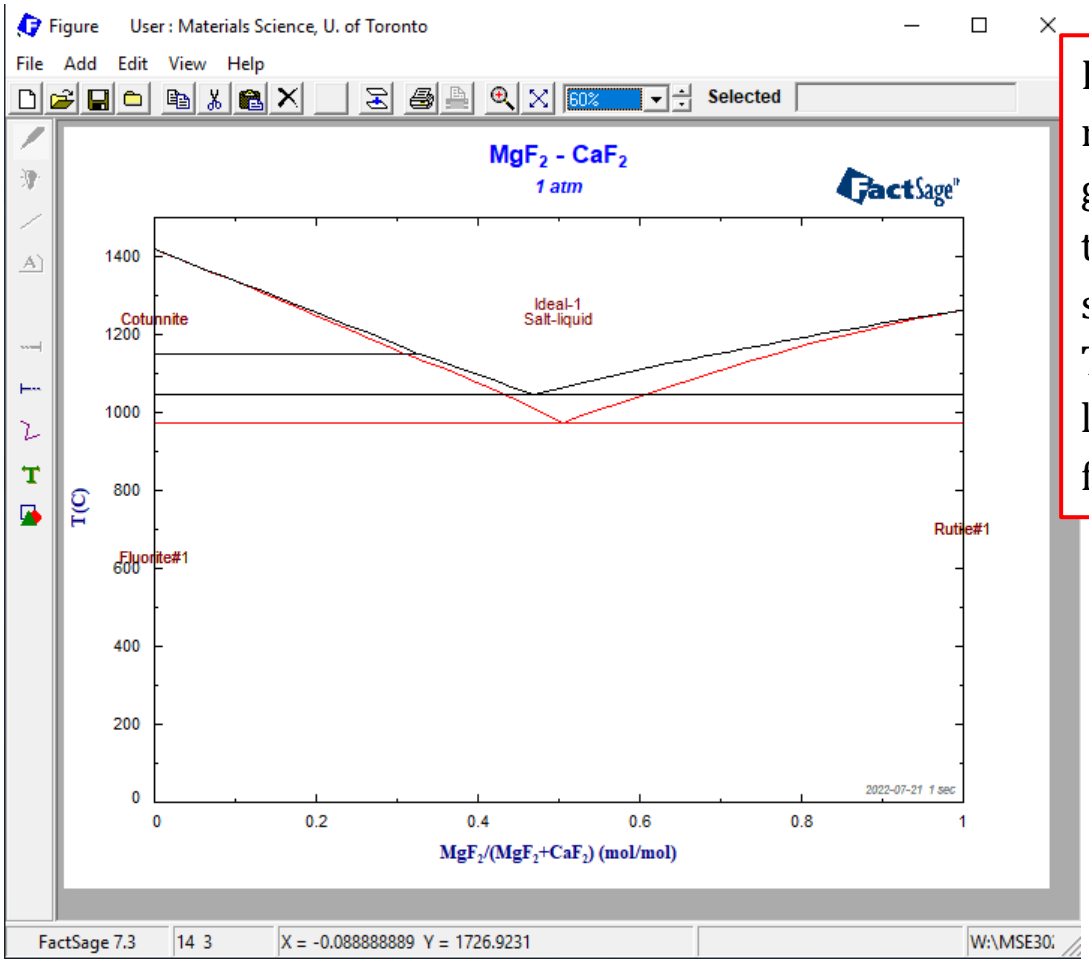
Phase Diagram Module: MgF_2-CaF_2 System

Comparison: Superimpose the second phase diagram



Phase Diagram Module: MgF_2-CaF_2 System

Comparison: Superimpose the second phase diagram



It is seen that the real liquid solution model (FTsalt-SALTA, labeled as red) gives lower liquidus lines and eutectic temperature than if ideal liquid solution model is used.
This means that liquid MgF_2 and liquid CaF_2 exhibit negative deviation from ideality. (Reason?)

In-Class Exercise

Question 1.

Calculate the predominance diagram of the Mo-C-O system at 1400 K. Use $\log_{10}\left(P_{CO_2}/1\text{ atm}\right)$ as Y-axis, and $\log_{10}(P_{CO}/1\text{ atm})$ as X-axis.

For a total hydrostatic pressure of 1 atm, what are the pressures of CO_2 and CO when metallic Mo is stable with its carbide phase at 1400 K?

In-Class Exercise

Question 2.

Calculate the Al-Mg phase diagram. Label all the liquid and all solid phases. Then answer the following questions:

(a) What is the lowest melting point in the system?

(b) What is the maximum solubility of Mg in solid FCC Al?

(c) What is the maximum solubility of Al in solid HCP Mg?

(d) At 350 °C, what is the solubility limit of Mg in solid FCC Al? What is the solubility limit Al in solid HCP Mg?

(e) Over what range of temperature is the $Al_{30}Mg_{23}$ phase stable?

(f) What is the non-stoichiometric range of the gamma phase (CBCC-A12)?

In-Class Exercise

Question 3.

Calculate the phase diagram for the Fe-Cr-O_2 system at 1300 °C.

Use $\log_{10}\left(P_{O_2}/1\text{ atm}\right)$ as the Y-axis which varies from from -20 to 0, and use the mole fraction of Cr X_{Cr} as the X-axis which varies from 0 to 1. For an Fe-Cr alloy with the composition of $X_{Cr} = 0.18$, what is the maximum P_{O_2} that will permit this alloy to remain free of oxidation at 1300 °C?

In-Class Exercise

Question 4.

Calculate the "**quasi-**" binary phase diagram of the MgO-Al_2O_3 system. Find the temperature and specify the co-existing phases and reactions at all the invariant points.

In-Class Exercise

Question 5.

Choose FTlite database to calculate the liquidus projection of the Al-Mg-Si and isothermal sections at 500 and 1000 K (1 bar). Then compare them with the diagrams calculated by SGTE2017 database (available from Documentation).