FactSage Practical
MSE302

Practical 4. Equilib Module

Acknowledgements

The teaching team of MSE302 is grateful to:

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Professor Elmira Moosavi (ETS)

Professor Arthur Pelton (CRCT)

Professors In-Ho Jung and M. –A. Van Ende (Seoul National University)

Dr. Sina Mostaghel (SNC-Lavalin)

Professor Kinnor Chattopadhyay (UofT)

Drs. Daigen Fukayama, Takahiro Sasaki (RCCM)

Drs. Moritz to Baden and Guixuan Wu (GTT Technologies)

Outline

Some Important Thermodynamic Terms

Term	Physical Meaning
Heat Capacity C_P	The amount of heat required to raise the temperature of **the system** by 1 K during an isobaric process.
Enthalpy H	Total energy of the system. The change in Enthalpy refers to the amount of heat that is exchanged with the surroundings during an isobaric process.
Entropy S	A thermodynamic function that is used to determine the process spontaneity. The entropy for an isolated system always increases for spontaneous processes.
Gibbs Energy G	A thermodynamic function that is used to determine the process spontaneity. The Gibbs energy of a closed system always decreases for spontaneous processes with constant temperature and pressure.
Fugacity (Gas Species)	A thermodynamic function that describes the deviation from the ideal gas behavior. It is sometimes named as **effective** partial pressure of gas species. For ideal gases, fugacity is numerically equal to partial pressure.
Activity (Solution Species)	A thermodynamic function that describes the deviation from the ideal solution behavior. It represents effective concentration of components in a solution. For ideal solutions, activity is numerically equal to mole fraction.

Equilib Module: Some Important Terms

Term	Physical Meaning
Fugacity_Total (Gas Phase) Activity_Total (Solution Phase) Activity (Compound)	Theses terms are considered as “phase activity”. When their value is 1, the phase is stable; otherwise, the phase is not stable. When their value is close to 1, this indicates that if the temperature and pressure change slightly, the phase might become stable.

Equilib Module: Basics

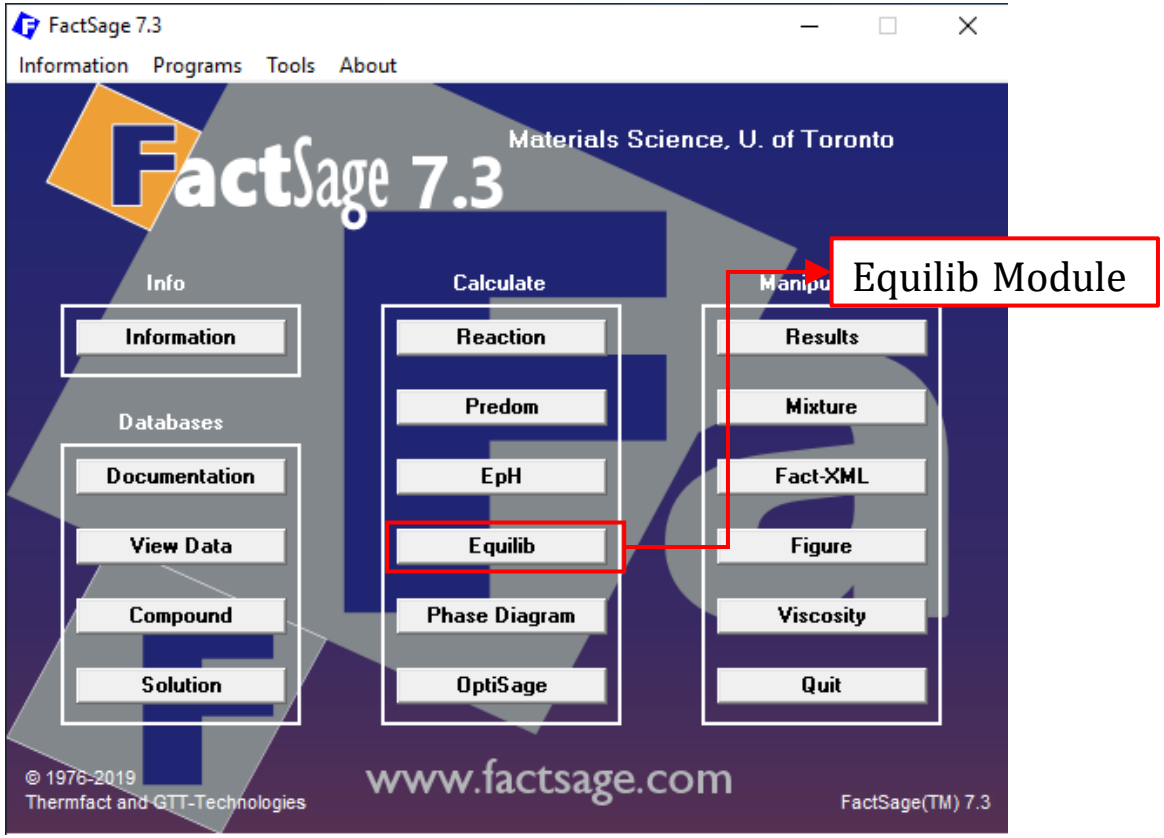
The Equilib Module is the **most powerful module** of FactSage.

- ✓ The module calculates the equilibrium for multiphase, multicomponent equilibria, with a wide variety of tabular and graphical output modes, under a large range of constraints (for example, given temperature, pressure, composition, etc.).
- ✓ The module uses the "Gibbs energy minimization" principle to find the phases that exist at equilibrium and their respective compositions & amounts.
- ✓ The module accesses both Compound and Solution databases.

Different from the Reaction Module, the Equilib Module does not require a well-defined reaction equation. The user only needs to tell the Equilib Module the input elements and the equilibrium conditions, and then the Equilib Module will calculate the products at equilibrium from the list of the **possible** phases the user has selected.

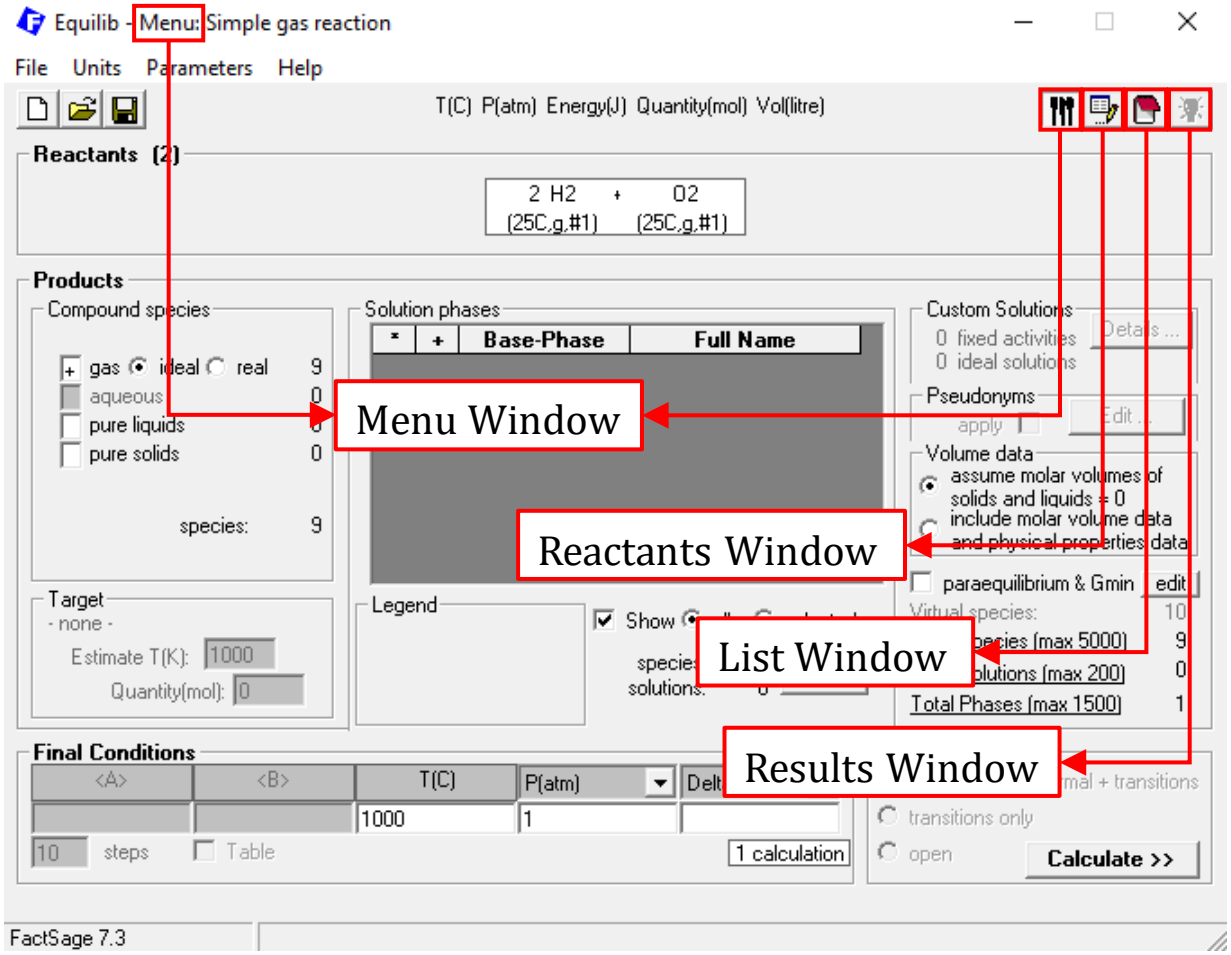
Equilib Module: Basics

Equilib Module in the home page**.**



Equilib Module: Basics

After you run the Equilib Module, you will see the following screen:



Equilib Module: Basics

General Steps in the Equilib Module

1. Define Reactants (Reactants Window)
2. Choose Databases (Reactants Window_Data Search)
3. Choose Units (Reactants Window_Units)
4. Input the amounts of reactants
5. Decide if the initial conditions should be defined (Reactants Window_Units)
6. Select Products (Menu Window)
7. Set up Final Conditions (Menu Window)
8. Calculate (Menu Window)

Note: you do not have to strictly follow these steps.

Equilib Module: Basics

A Note on "Initial Conditions"

The equilibrium that is calculated under given conditions is independent of the input species and only depends on the amounts of the various **elements** added (element matrix). For example, consider the following two scenarios:

(a) we add 1.0 mole of chalcopyrite ($CuFeS_2$) and 1.0 mole of oxygen (O_2) into the smelter; or,

(b) we add 0.5 mole of Cu_2O, 1.0 mole of hematite (Fe_2O_3), 1.0 mole of sulfur gas (S_2), and 0.25 mole of oxygen (O_2) into the smelter.

Note in both scenarios, the number of moles of elements added:

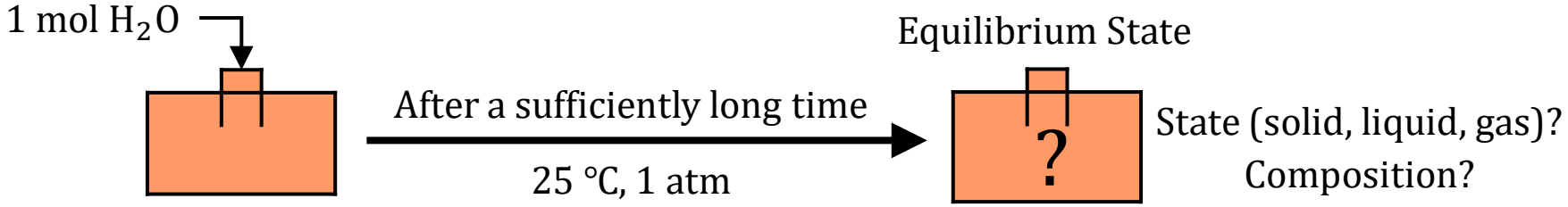
Cu: 1.0, Fe: 2.0, S: 2.0, and O: 2.0.

If the temperature and pressure in the smelter are maintained at the same level, the final products when the system reaches equilibrium must be same for the above two scenarios, although the heat of reaction will be different.

Equilib Module: H_2O Equilibrium

We will start with a simple example: H_2O.

Say we have 1 mole of H_2O. We would like to know when the system reaches equilibrium at 25 °C and 1 atm, what phase(s) are present and what are their compositions.



Equilib Module: H_2O Equilibrium

Before we use the Equilib Module, let us perform some manual calculations so we can better understand how FactSage works based on **the Gibbs energy minimization** principle.

[Problem] Find the equilibrium state for 1 mole of H_2O at 25 °C and 1 atm.

[Step 1] First, the system at equilibrium must meet the requirement of **mass conservation**, that is, **2 mole of hydrogen** and **1 mole of oxygen**. Clearly, there are an **infinite** number of ways (or, system configuration) so that this requirement can be met. **A few of them** are listed below:

(1) 1 mole of H_2O (s), i.e., ice

(2) 1 mole of H_2O (l), i.e., liquid water

(3) 1 mole of H_2O (g), i.e., water vapor

(4) 1 mole of H_2 (g) + 0.5 mole of O_2 (g) etc.

Equilib Module: H_2O Equilibrium

[Step 2] We can use the FactPS database to calculate the Gibbs energy for the above system configurations at 25 °C and 1 atm (**next page**).

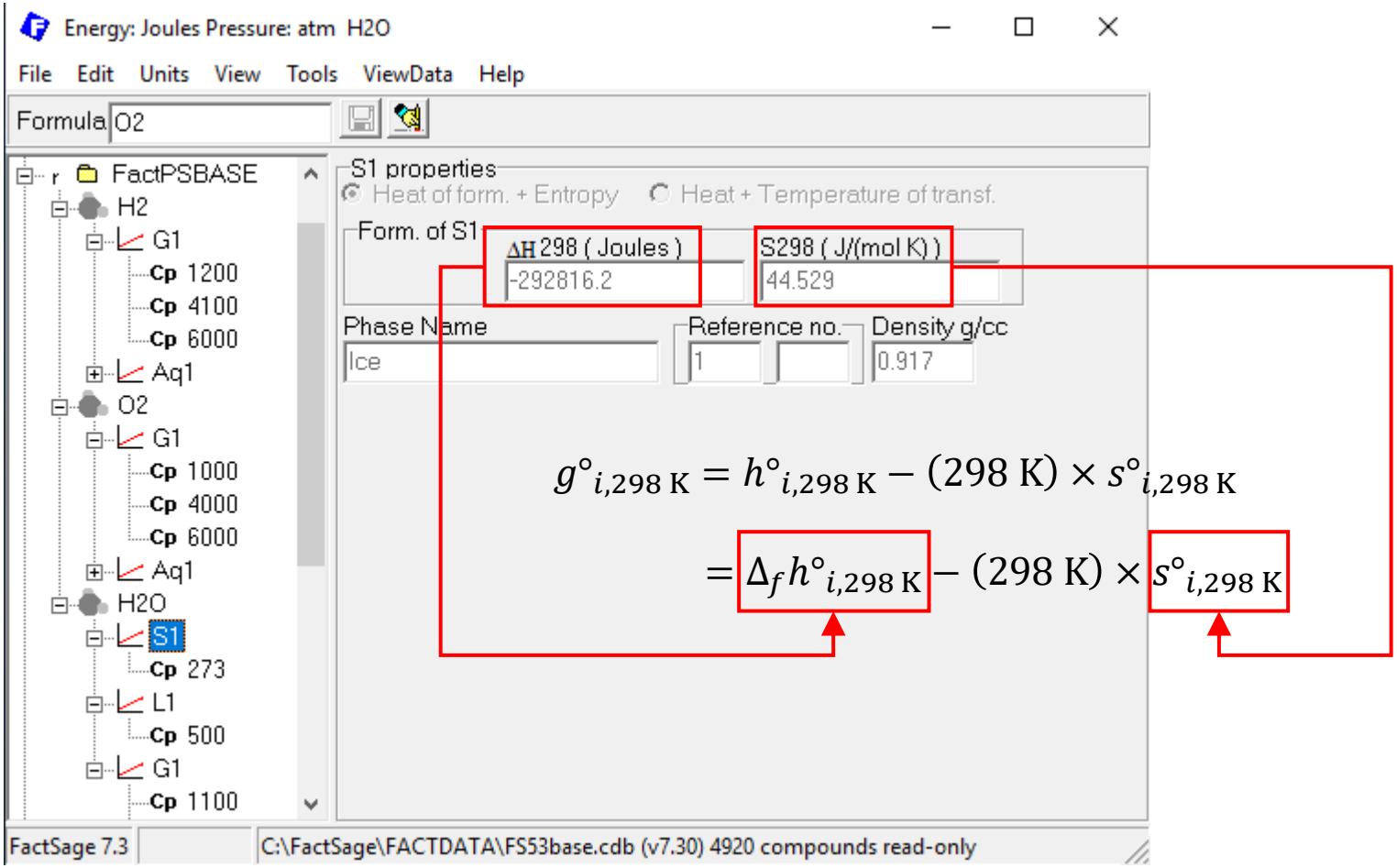
(1) −306.09 kJ (2) −306.69 kJ (3) −298.10 kJ (4) −71.86 kJ

[Step 3] The system at equilibrium should possess the minimum Gibbs energy. Therefore, the equilibrium state should be configuration (2).

A Note: the Gibbs energy minimizer in FactSage employs an efficient algorithm (Lagrange's Multipliers, FactSage-Teach) that can find the system configuration with the minimum Gibbs energy under the constraints of mass balance.

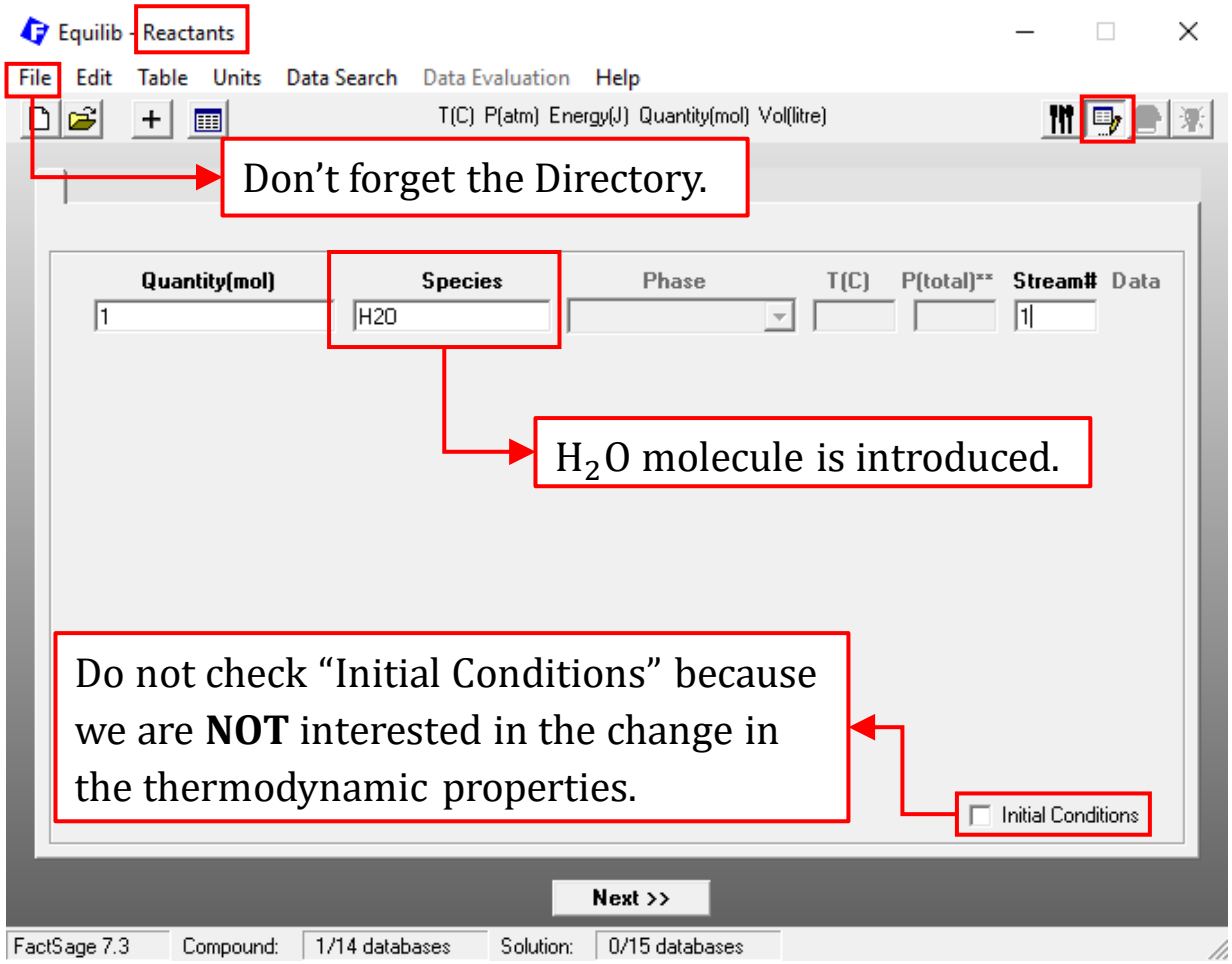
Equilib Module: H_2O Equilibrium

Compound Module: FactPS



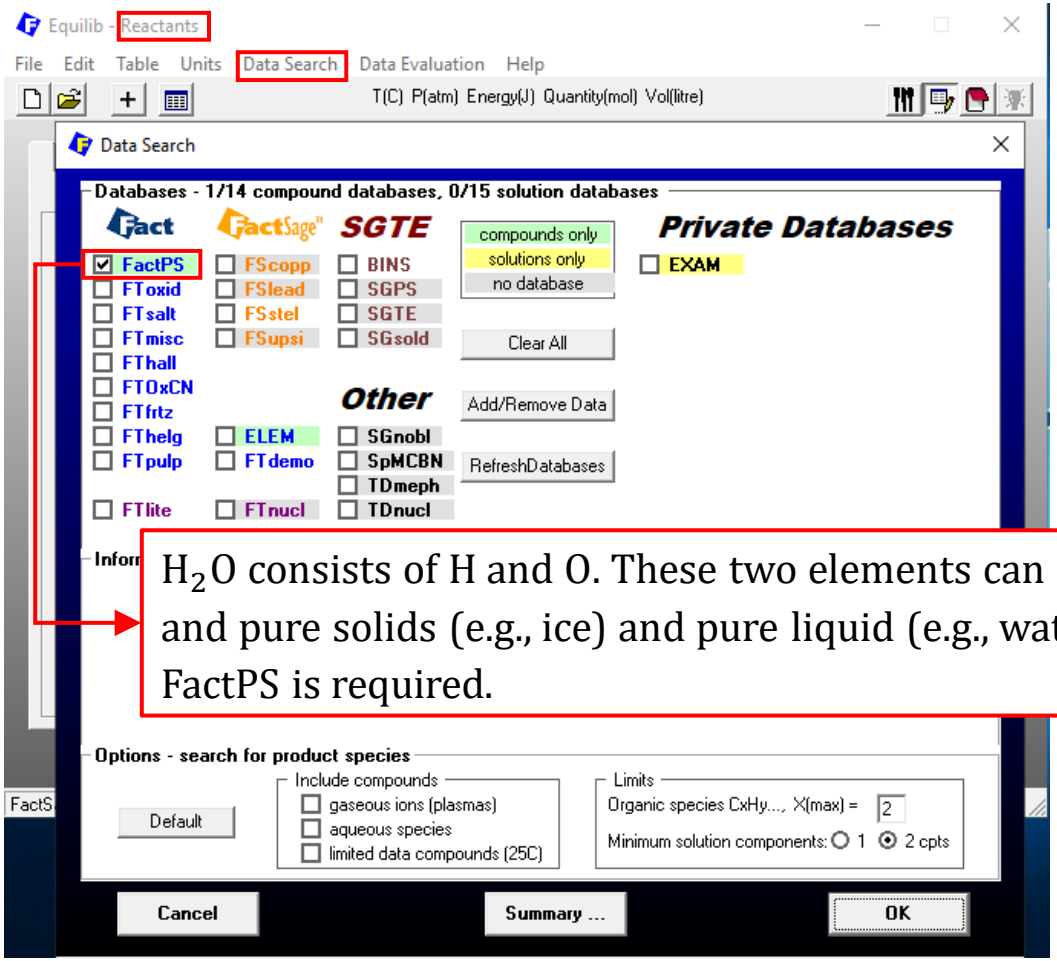
Equilib Module: H_2O Equilibrium

Reactants Window: Define Reactants



Equilib Module: H_2O Equilibrium

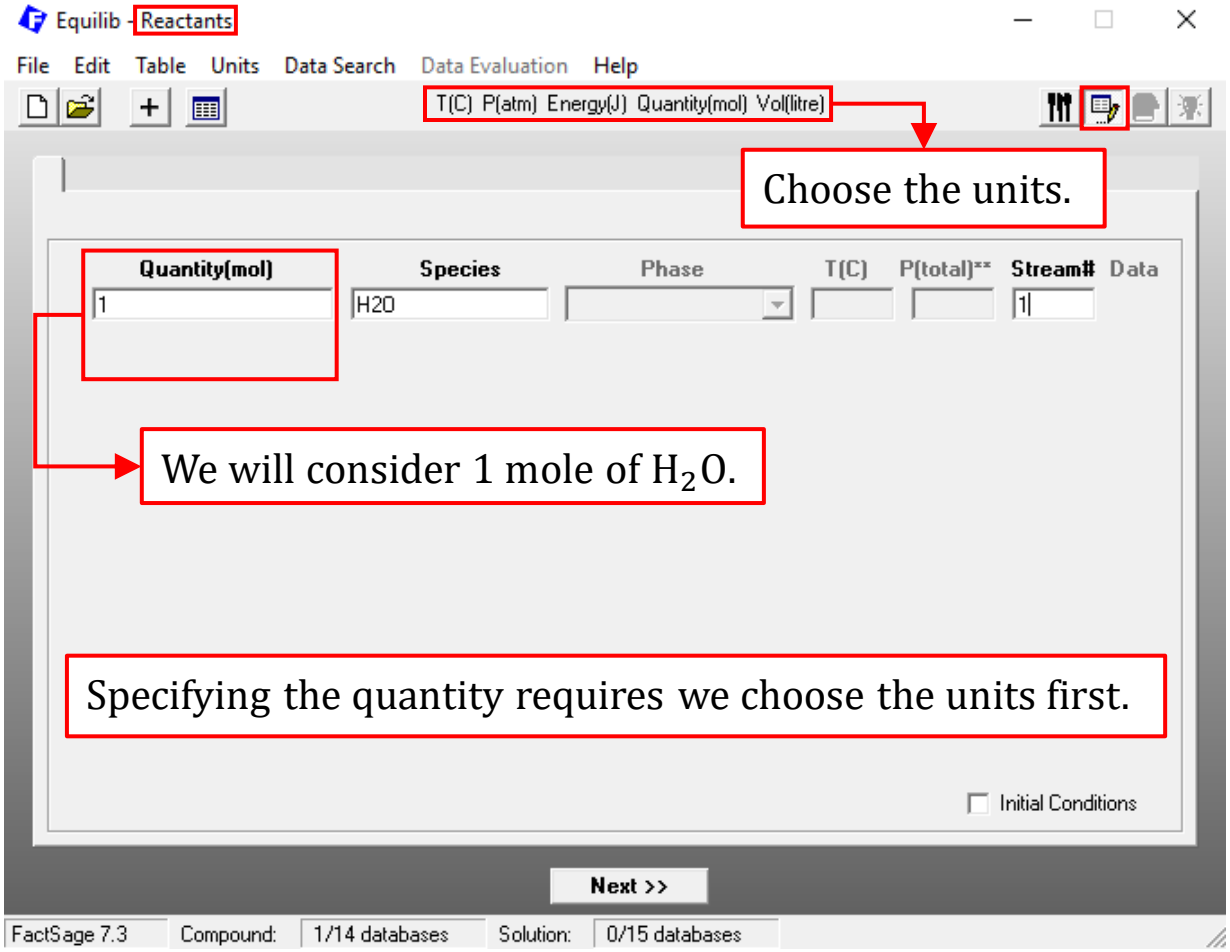
Reactants Window: Database(s)



H_2O consists of H and O. These two elements can only form gaseous species and pure solids (e.g., ice) and pure liquid (e.g., water). Therefore, only FactPS is required.

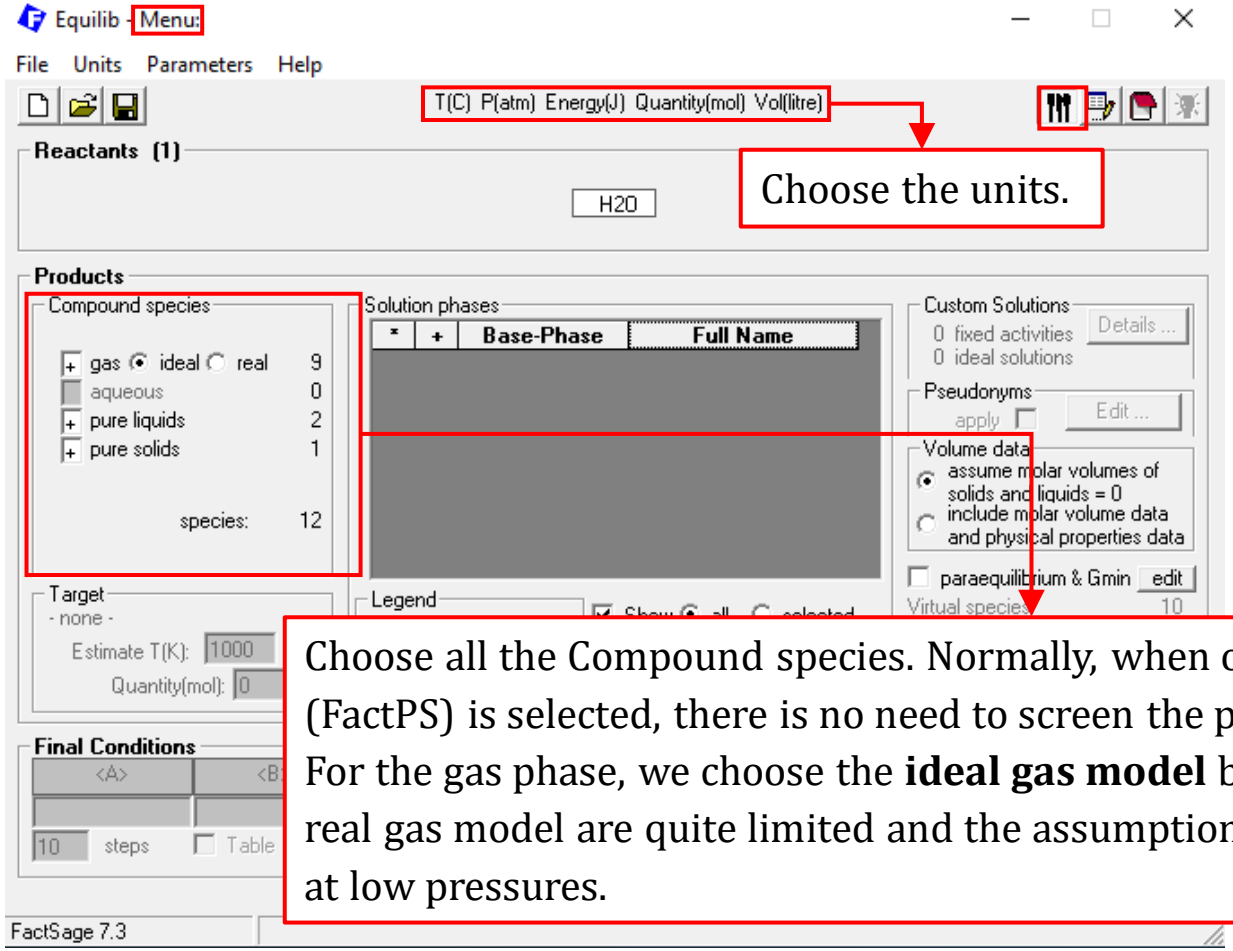
Equilib Module: H_2O Equilibrium

Reactants Window: Choose Units and Input the Quantity of Species



Equilib Module: H_2O Equilibrium

Menu Window: Selection of Products (Compounds and Solution Phases)

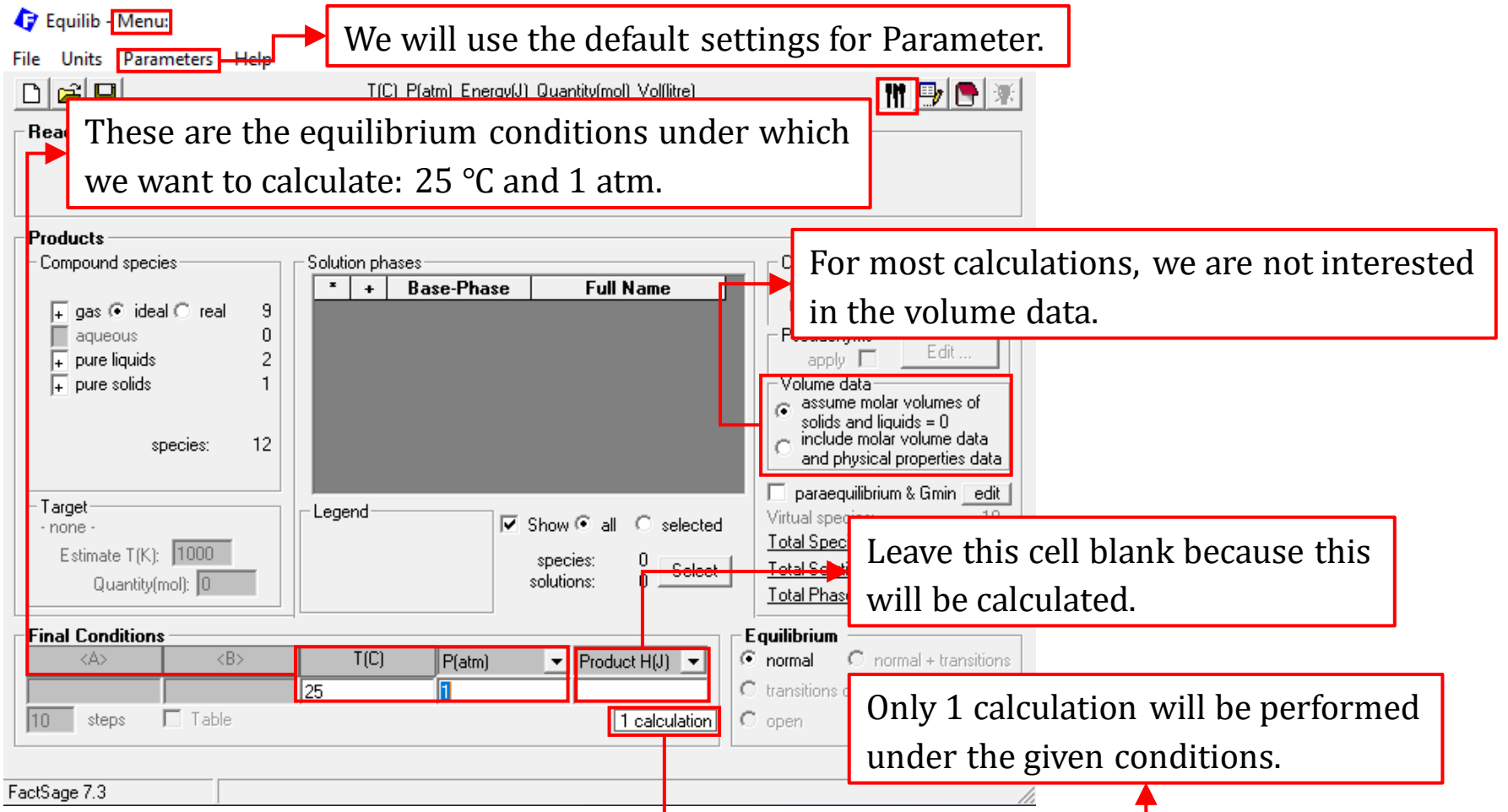


Choose all the Compound species. Normally, when only one compound database (FactPS) is selected, there is no need to screen the phases from the list.

For the gas phase, we choose the **ideal gas model** because the gas species in the real gas model are quite limited and the assumption of ideal gas model is valid at low pressures.

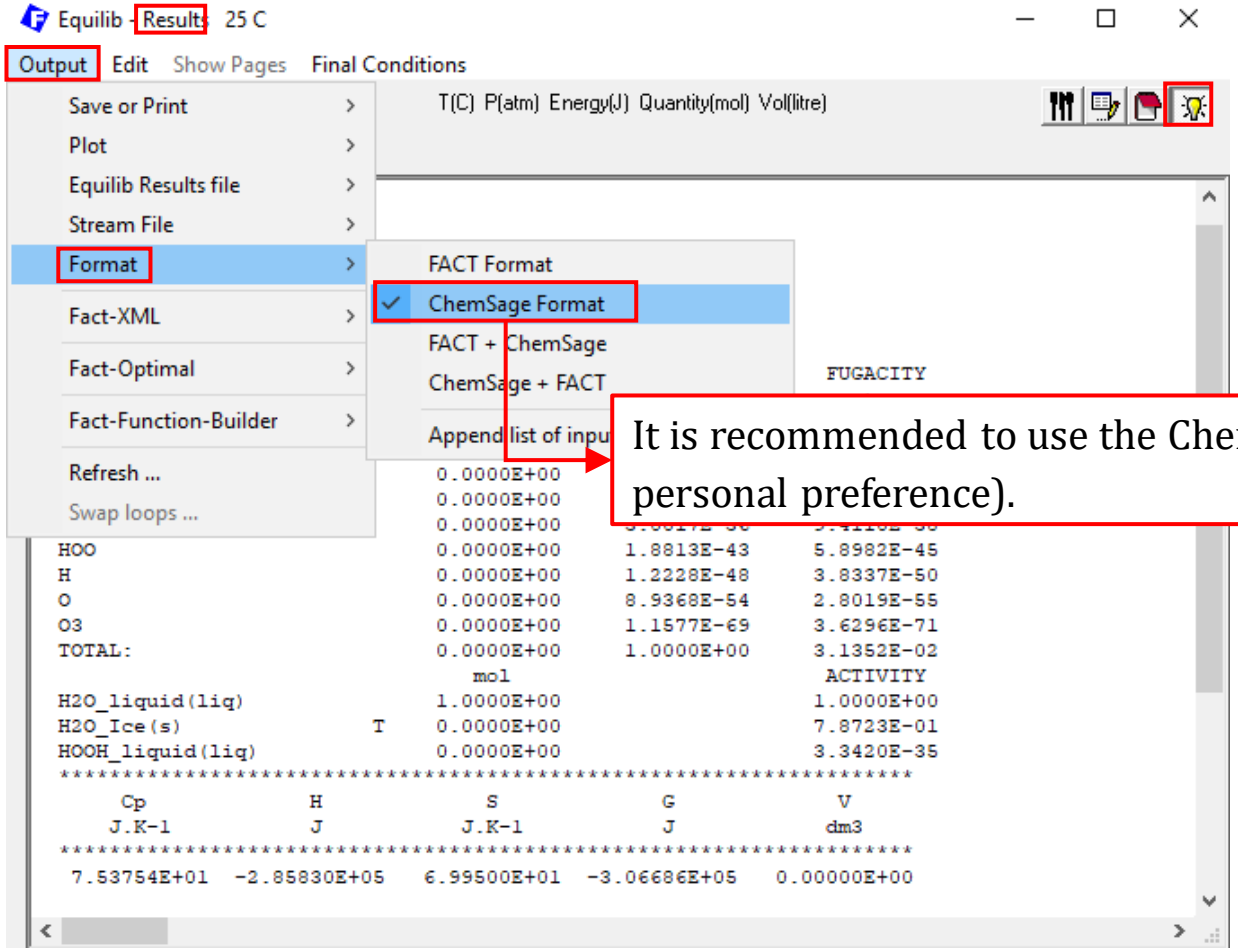
Equilib Module: H_2O Equilibrium

Menu Window: Set up the Final Conditions



Equilib Module: H_2O Equilibrium

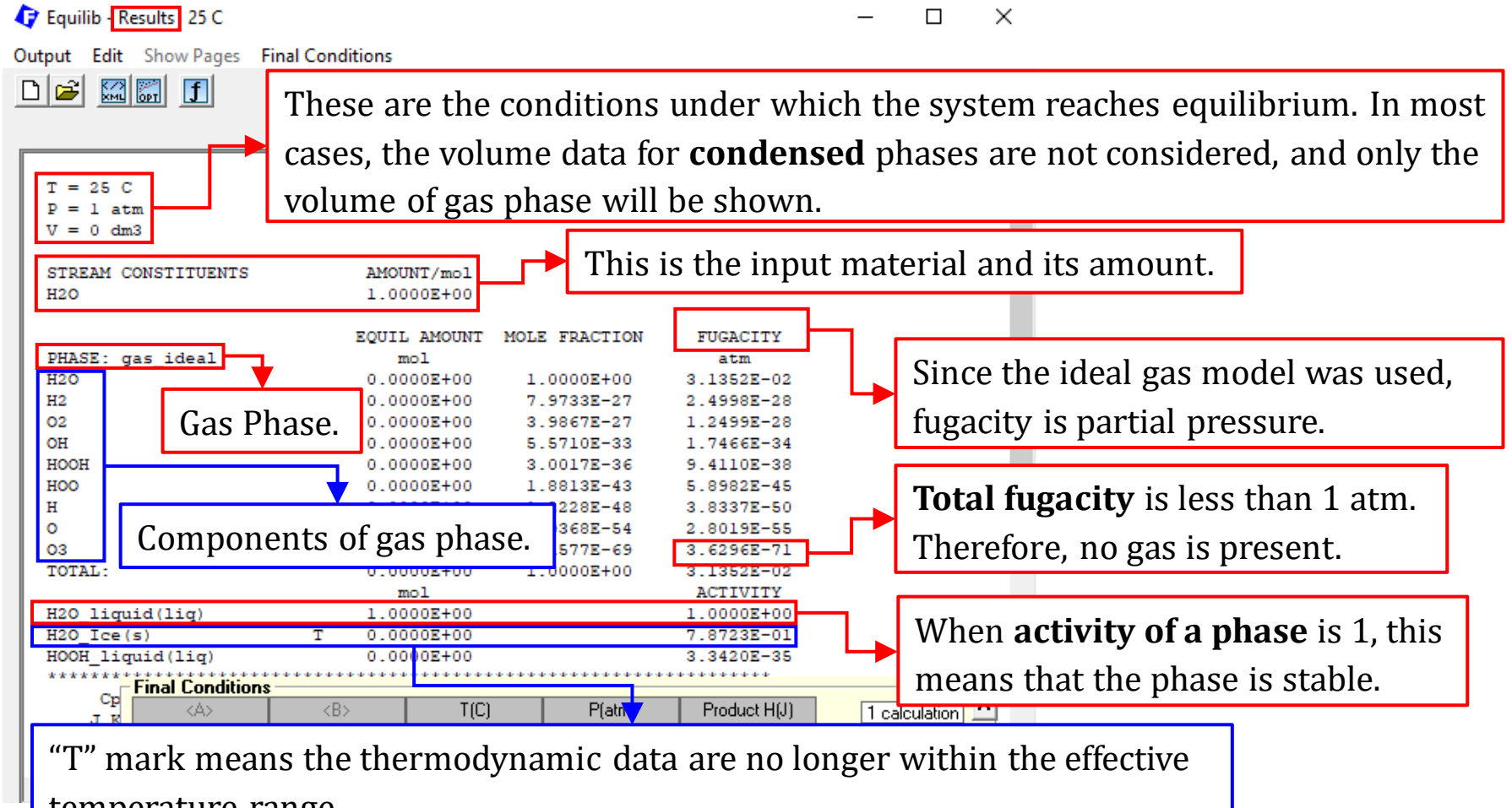
Results: ChemSage Format



It is recommended to use the ChemSage format (just personal preference).

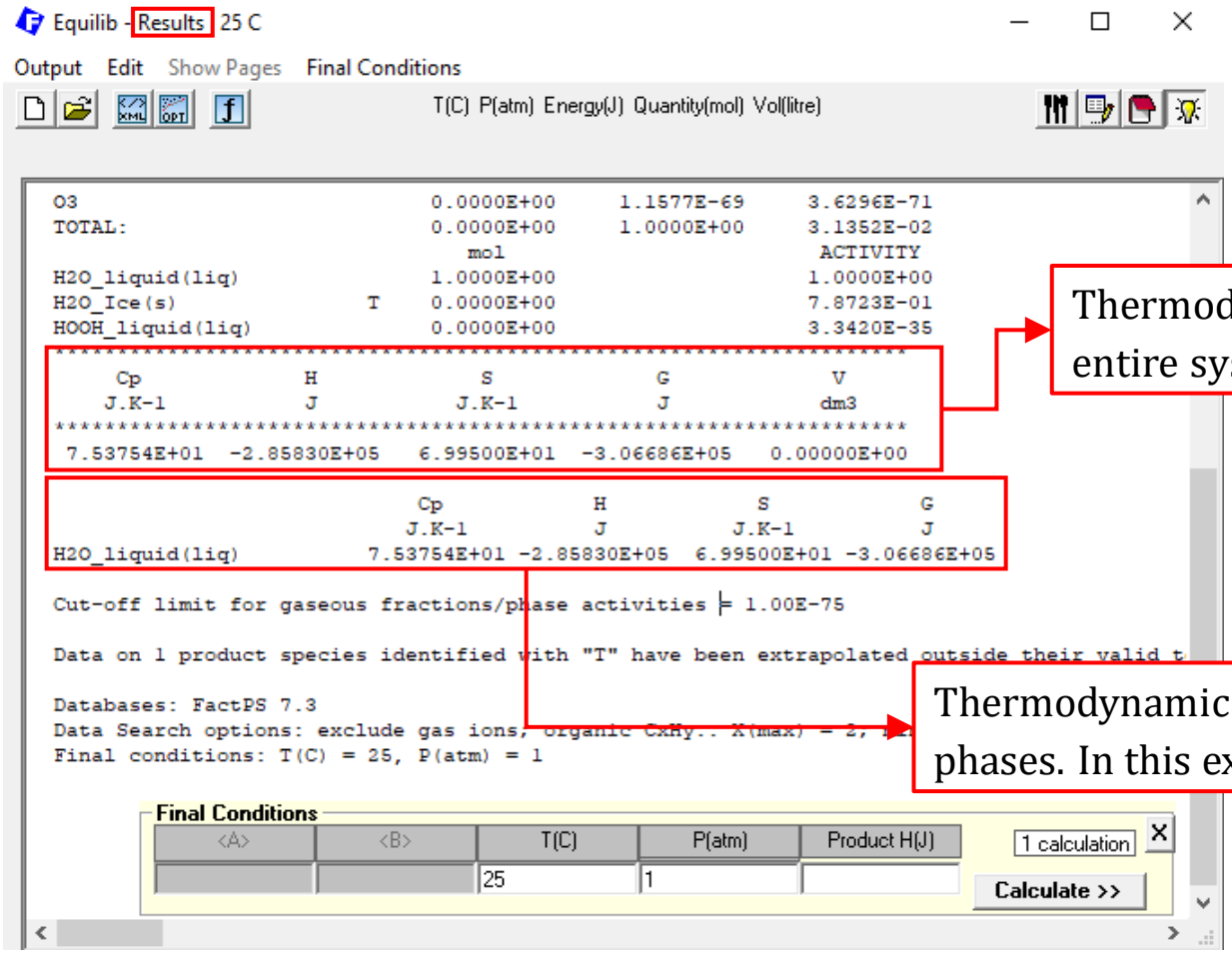
Equilib Module: H_2O Equilibrium

Results: ChemSage Format



Equilib Module: H_2O Equilibrium

Results: ChemSage Format

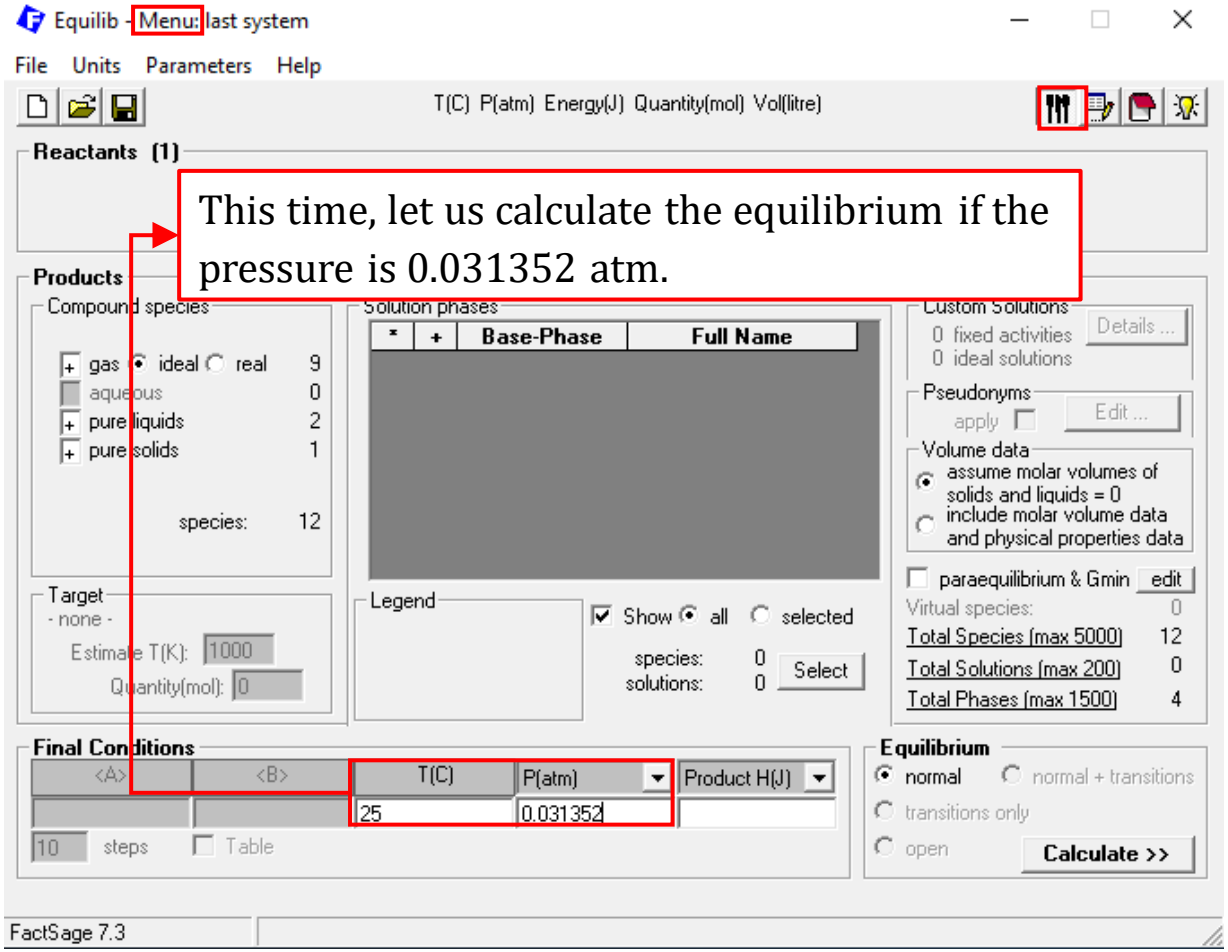


Thermodynamic quantities of the entire system.

Thermodynamic quantities of stable phases. In this example, only liquid water.

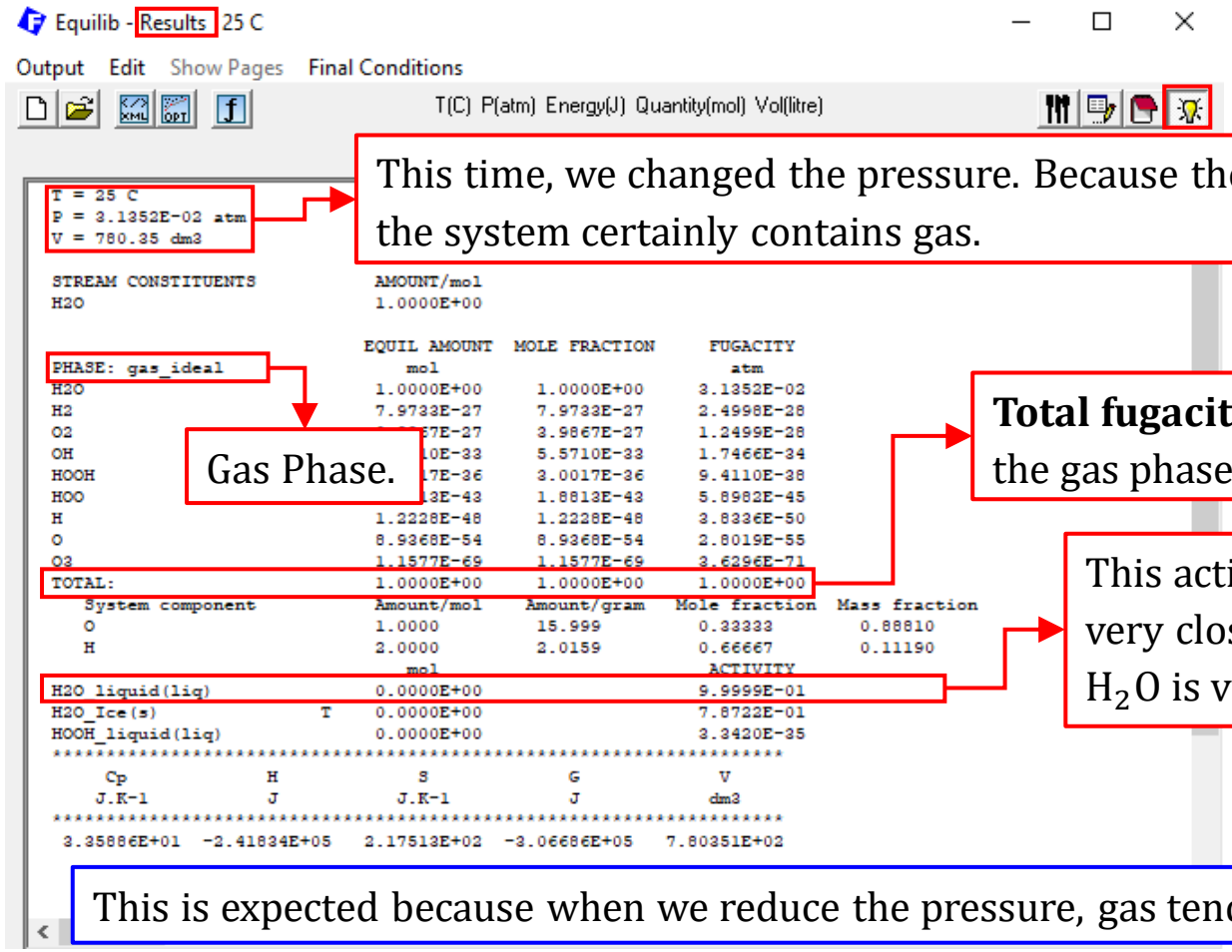
Equilib Module: H_2O Equilibrium

Menu Window: Set up the Final Conditions



Equilib Module: H_2O Equilibrium

Results: ChemSage Format



This time, we changed the pressure. Because the volume is not zero, this time the system certainly contains gas.

Gas Phase.

Total fugacity is 1 atm. This means the gas phase is stable.

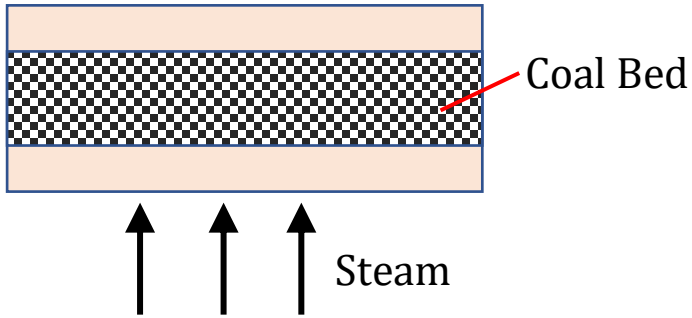
This activity of liquid H_2O is not 1, but very close to 1. This means that liquid H_2O is very close to be a stable phase.

This is expected because when we reduce the pressure, gas tends to be stable.

Equilib Module: Gasification of Coal

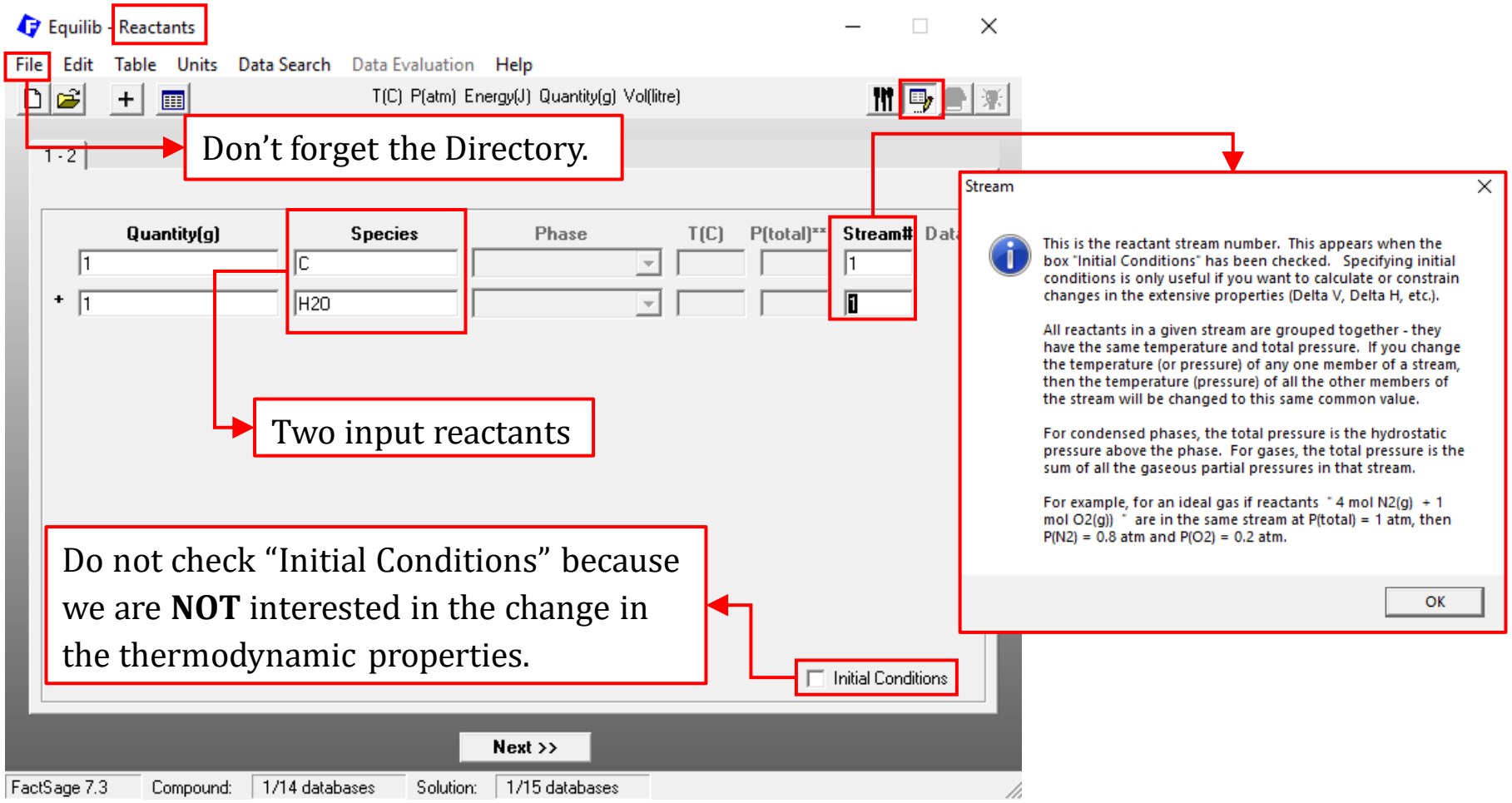
The second example we will be looking at is the gasification of coal by steam.

Say we inject the hot steam into a coal bed. The temperature of the coal bed is maintained at 1000 K, and the pressure at 10 atm. We would like to know what species are obtained at equilibrium as well as their respective amounts.



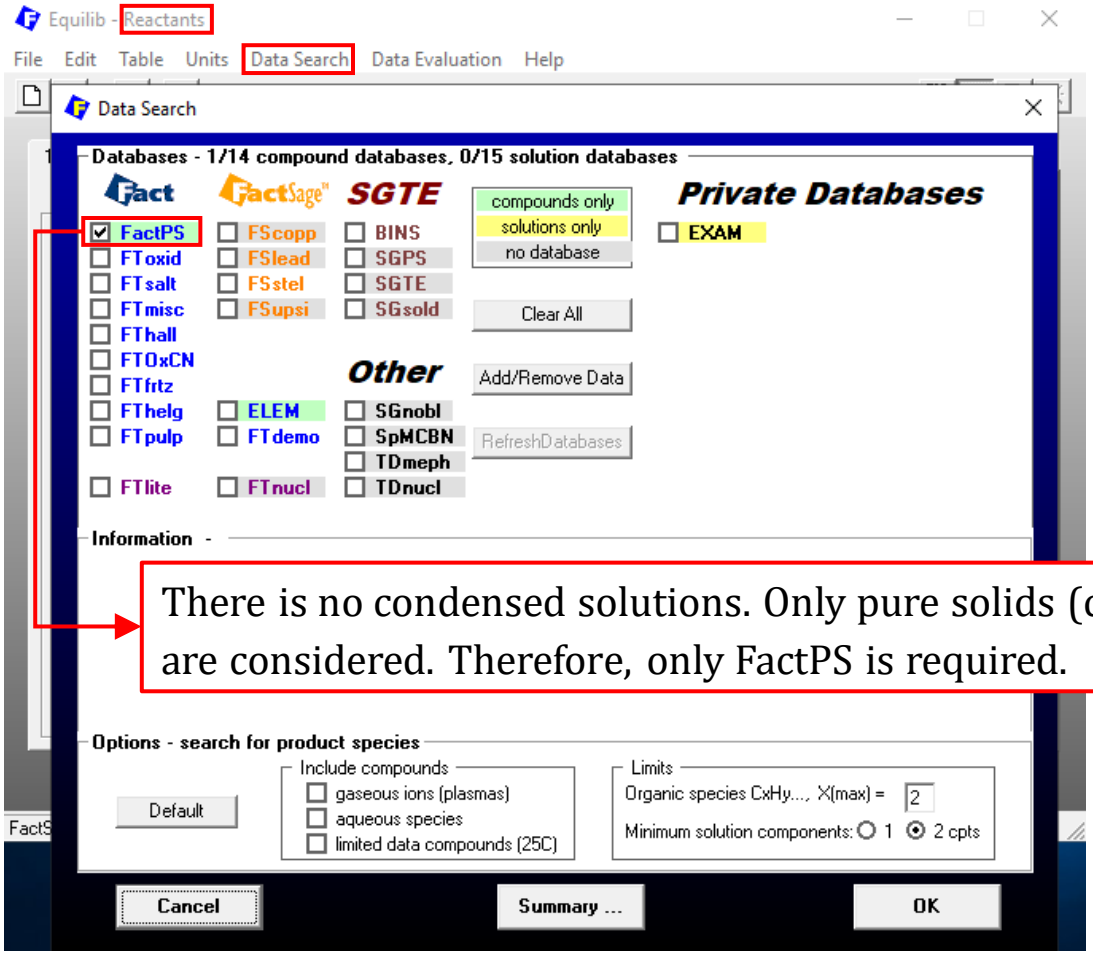
Equilib Module: Gasification of Coal

Reactants Window: Define Reactants



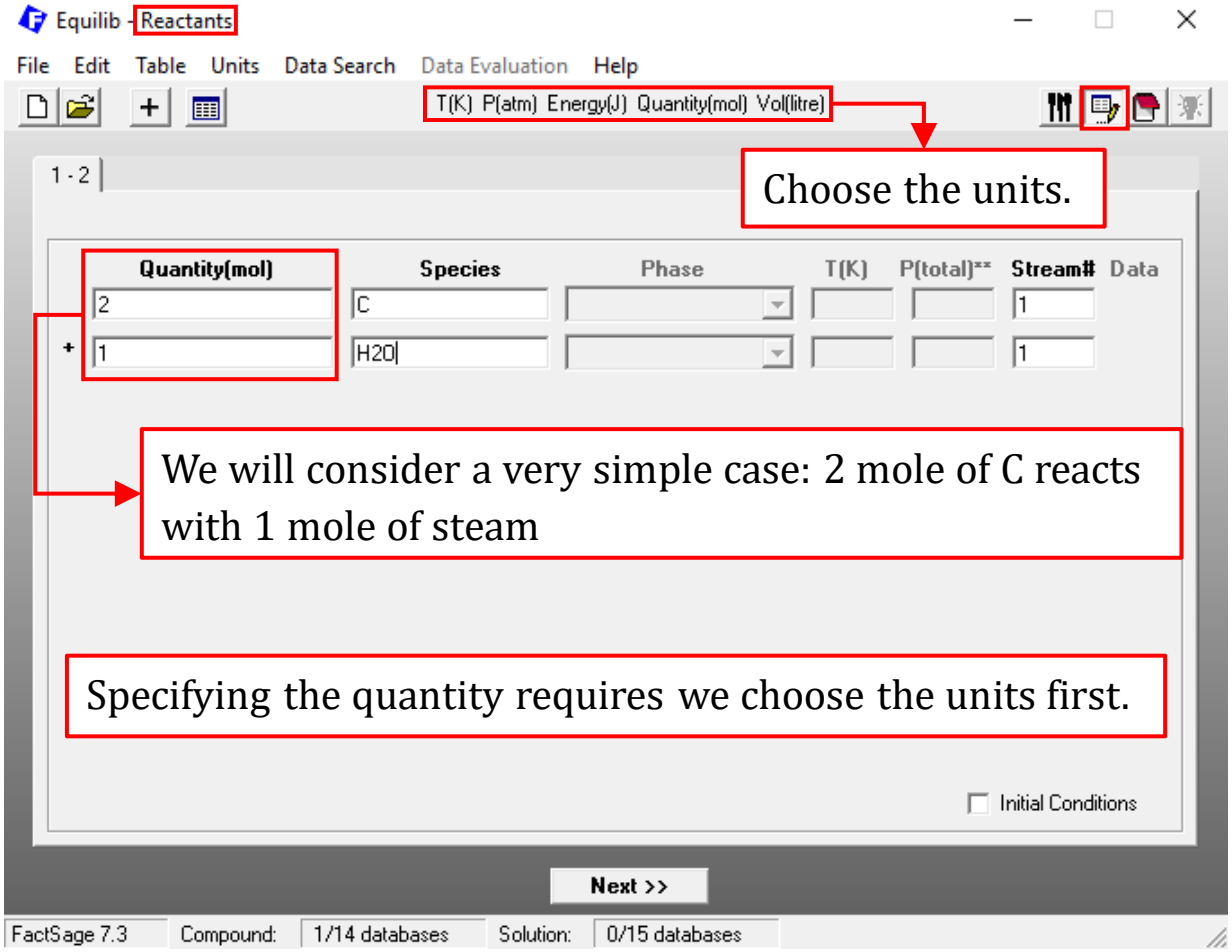
Equilib Module: Gasification of Coal

Reactants Window: Database(s)



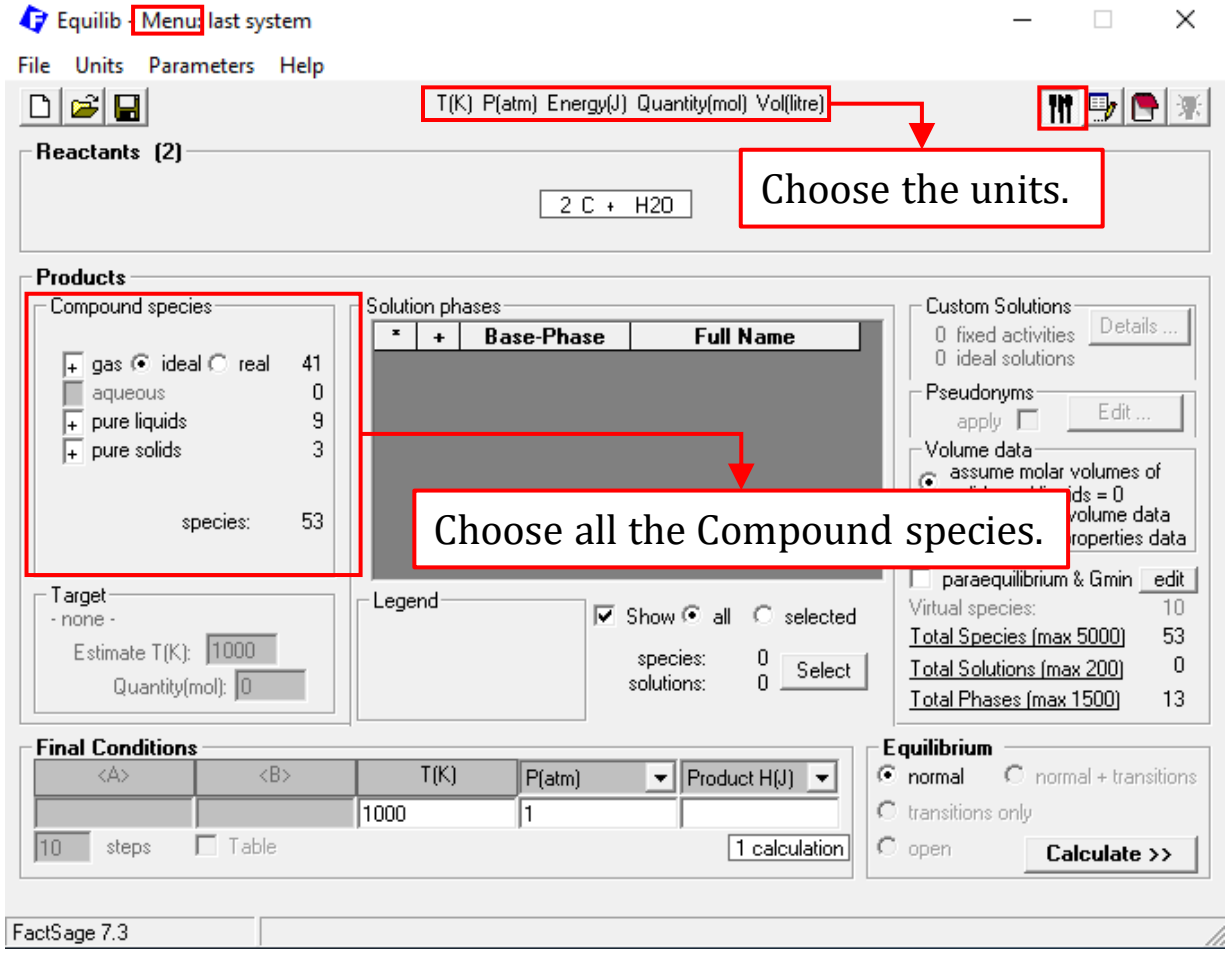
Equilib Module: Gasification of Coal

Reactants Window: Choose Units and Input the Quantity of Species



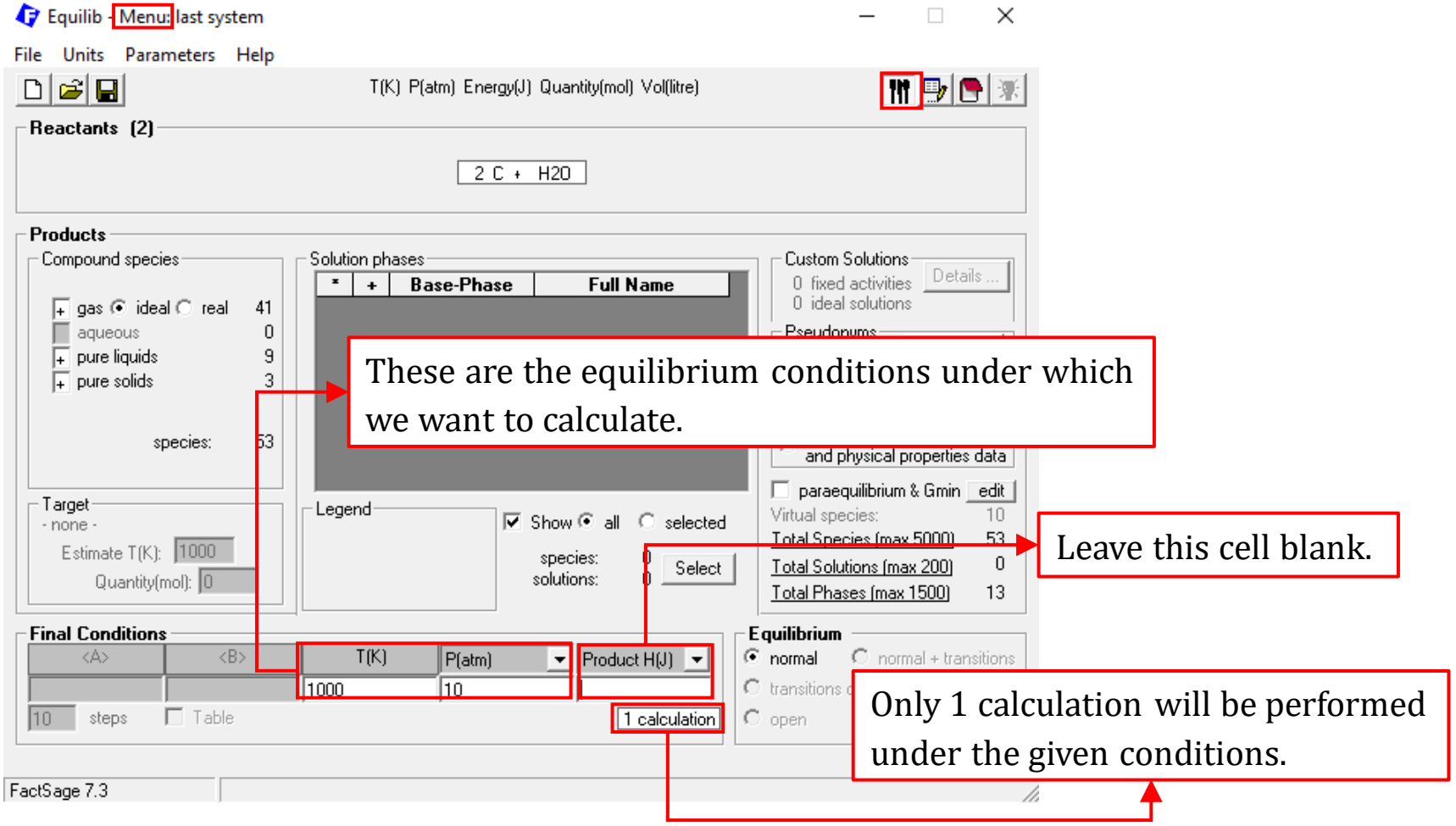
Equilib Module: Gasification of Coal

Menu Window: Selection of Products (Compounds and Solution Phases)



Equilib Module: Gasification of Coal

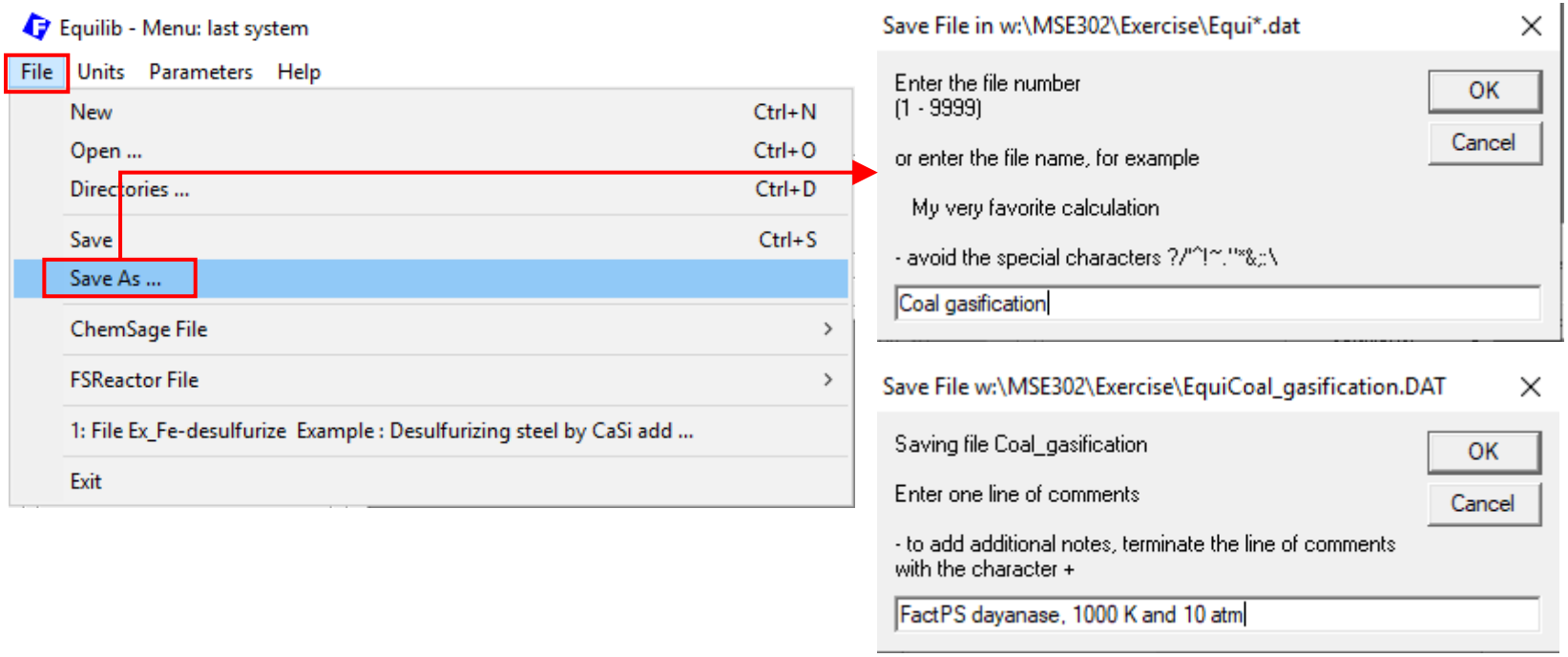
Menu Window: Set up the Final Conditions



Equilib Module: Gasification of Coal

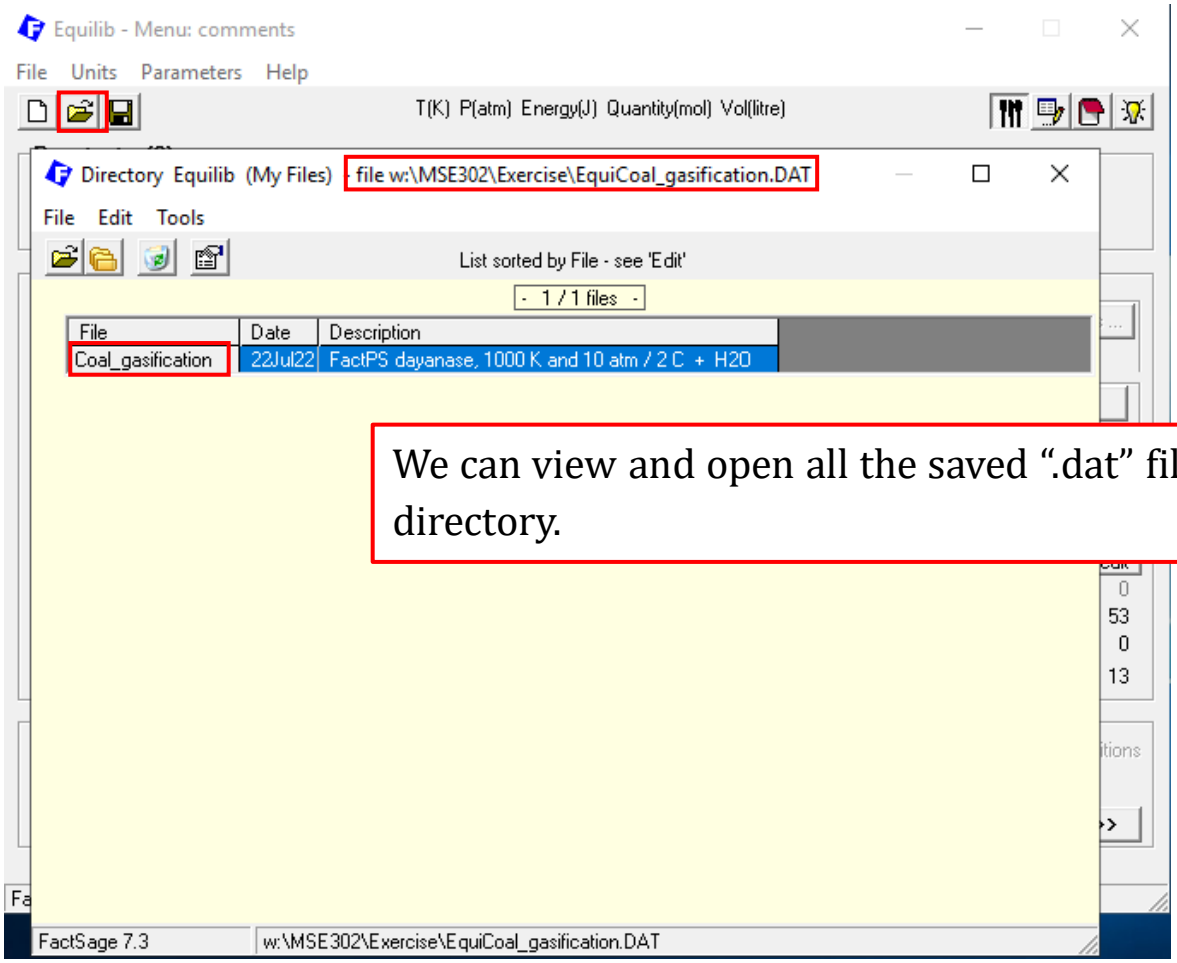
Save the Equilib settings: ".dat" file

In the Equilib Module, we can save the settings for a calculation as a ".dat" file.



Equilib Module: Gasification of Coal

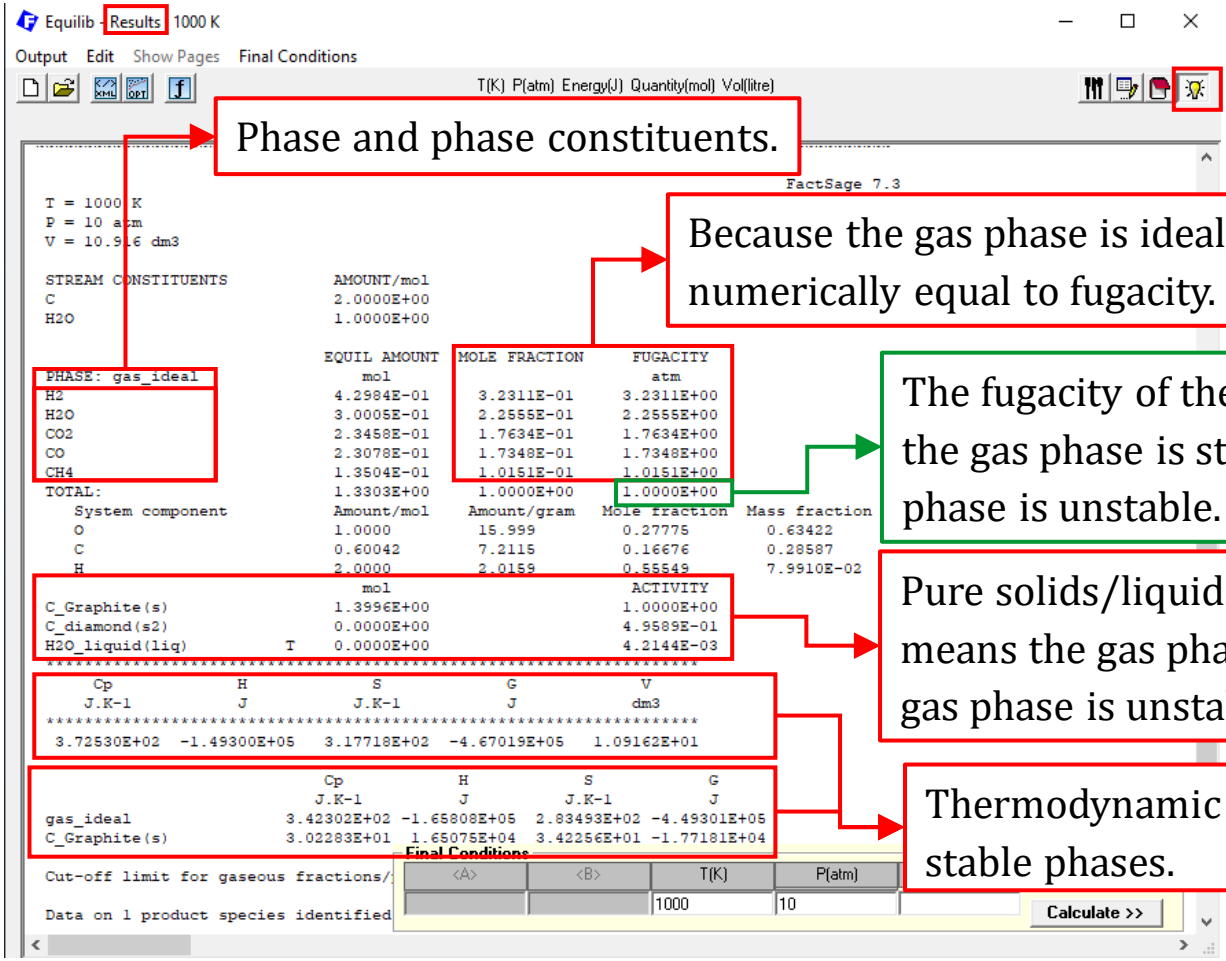
Open the ".dat" file



We can view and open all the saved ".dat" files from the directory.

Equilib Module: Gasification of Coal

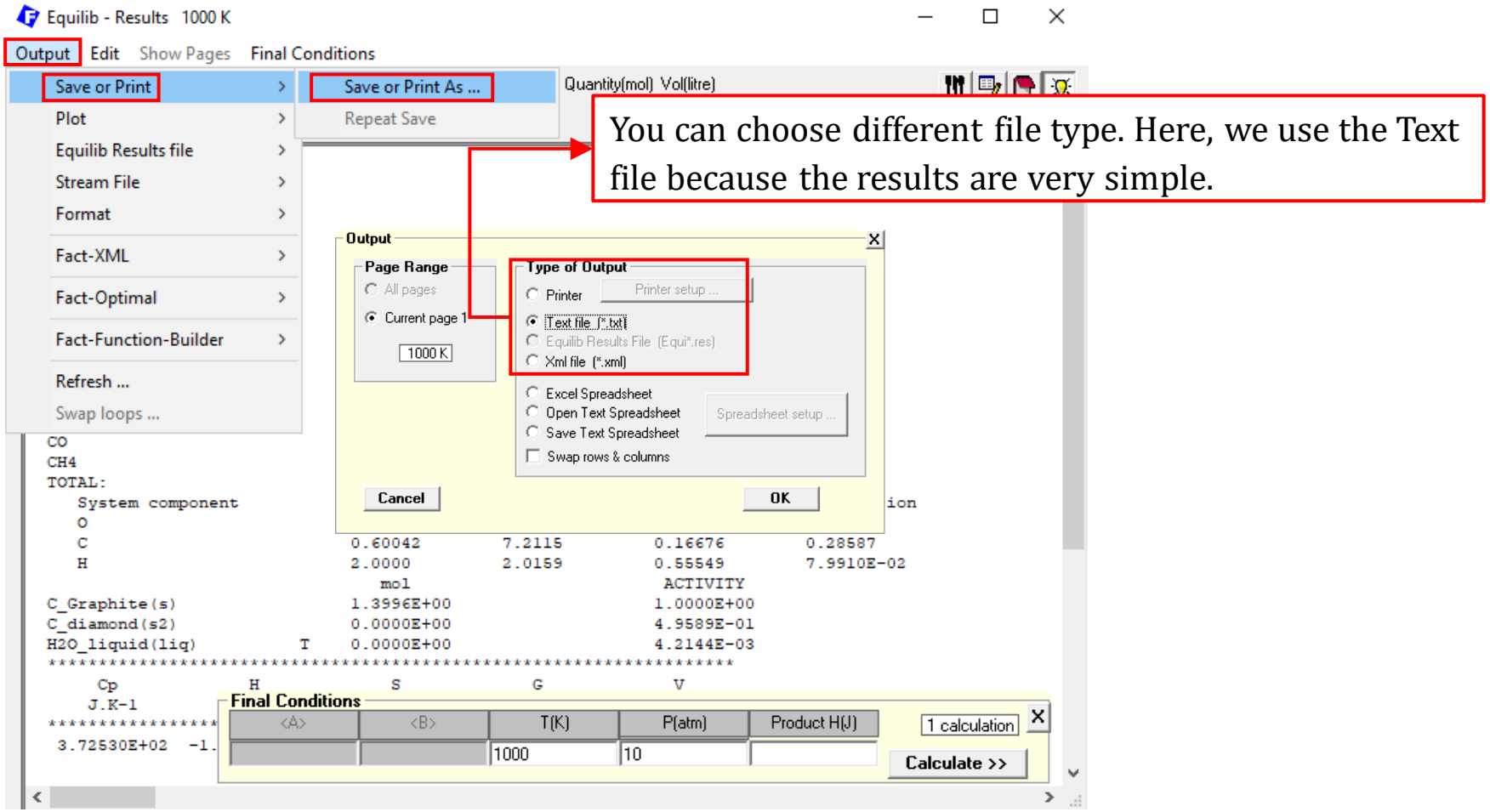
Results: ChemSage Format



Pelton, Phase Diagrams and Thermodynamic Modeling of Solutions, 2019 (Chapter 5.12)

Equilib Module: Gasification of Coal

Save the Results: Spreadsheet Format



Equilib Module: Recovery of Tin from Tin Cans

The third example is to recover tin from tin cans by chlorination, represented by the following reaction:

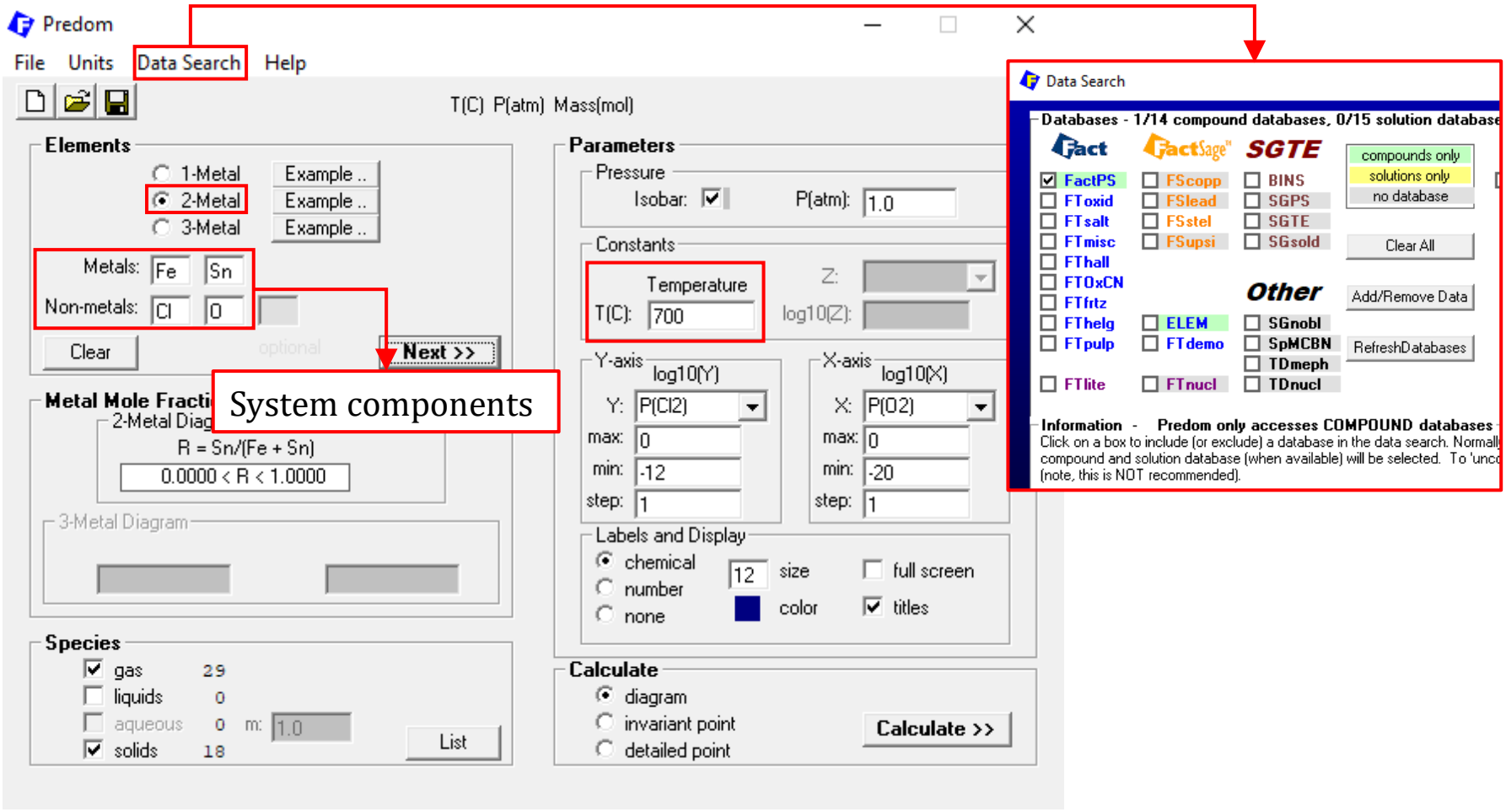
$$Sn + 2Cl_2 = SnCl_4$$

Tin cans are made of tin-coated steel. Progressive chlorination of tin results in the exposure of iron. To avoid the chlorination of iron which would lower the grade of $SnCl_4$, oxygen is introduced to form Fe_2O_3. This means that we need to study the thermodynamics of the Fe-Sn-Cl-O system for this chlorination process if the steel is considered to consist of pure iron. Under the controlled conditions, the desired solid products should be $SnCl_4$ and Fe_2O_3.

To help you better understand the underlying thermodynamic principle on which the above process is based, the predominance diagram of the Fe-Sn-Cl-O system was calculated.

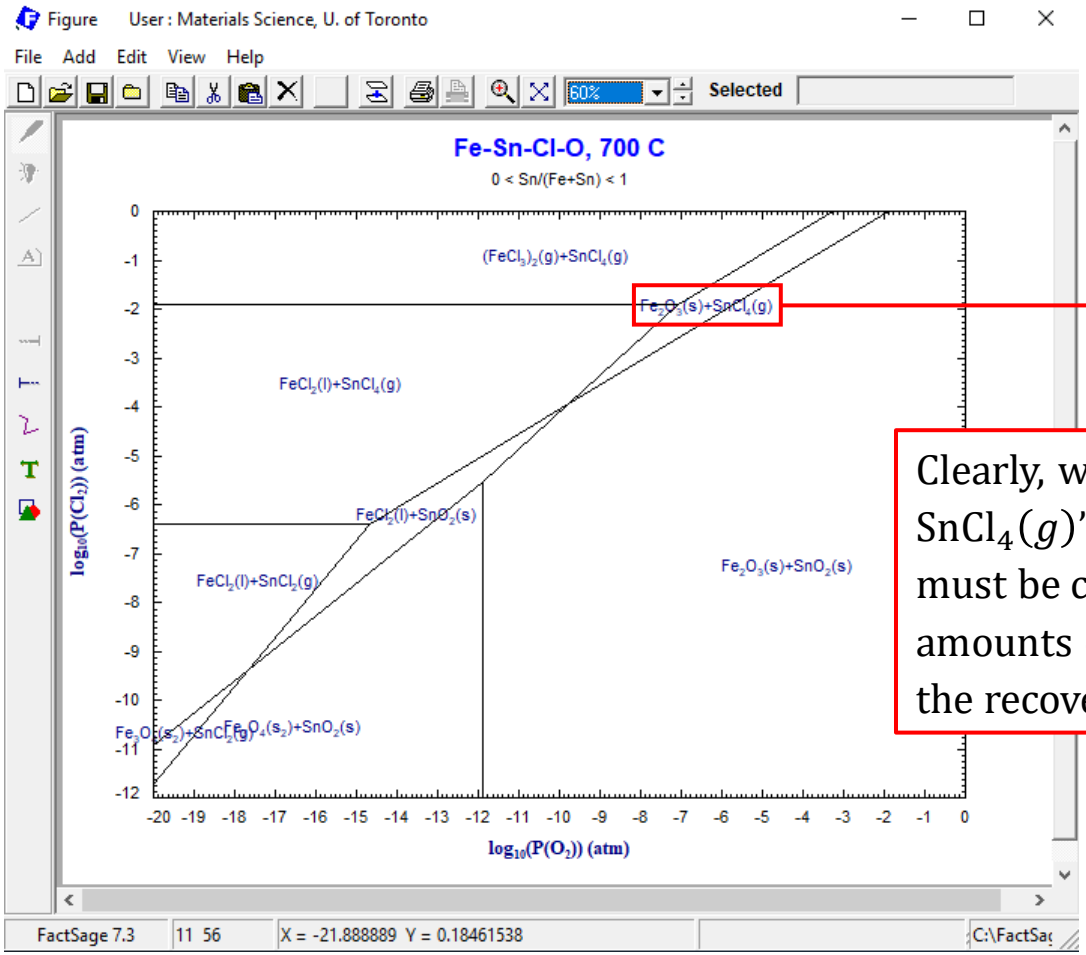
Equilib Module: Recovery of Tin from Tin Cans

Predominance Diagram of the Fe-Sn-Cl-O System at 700 °C.



Equilib Module: Recovery of Tin from Tin Cans

Predominance Diagram of the Fe-Sn-Cl-O System at 700 °C.



Clearly, when the system exists as "$Fe_2O_3(s) + SnCl_4(g)$", the partial pressure of O_2 and Cl_2 must be carefully controlled. That is, the input amounts of O_2 and Cl_2 are the key factors in the recovery of high-grade $SnCl_4$.

Equilib Module: Recovery of Tin from Tin Cans

Part I.

Let us start with a simple calculation. Say we are recovering 1.0 mol of Sn, and the exposed iron is **assumed** to be 0.2 mol. Clearly, the minimum number of moles of Cl_2 is 2.0 mol when all Sn is recovered as $SnCl_4$; and the minimum number of moles of O_2 when all the exposed iron is oxidized to Fe_2O_3 is 0.15 mol.

$$1.0 \text{ mol Sn} + 2.0 \text{ Cl}_2 = 1.0 \text{ mol SnCl}_4$$

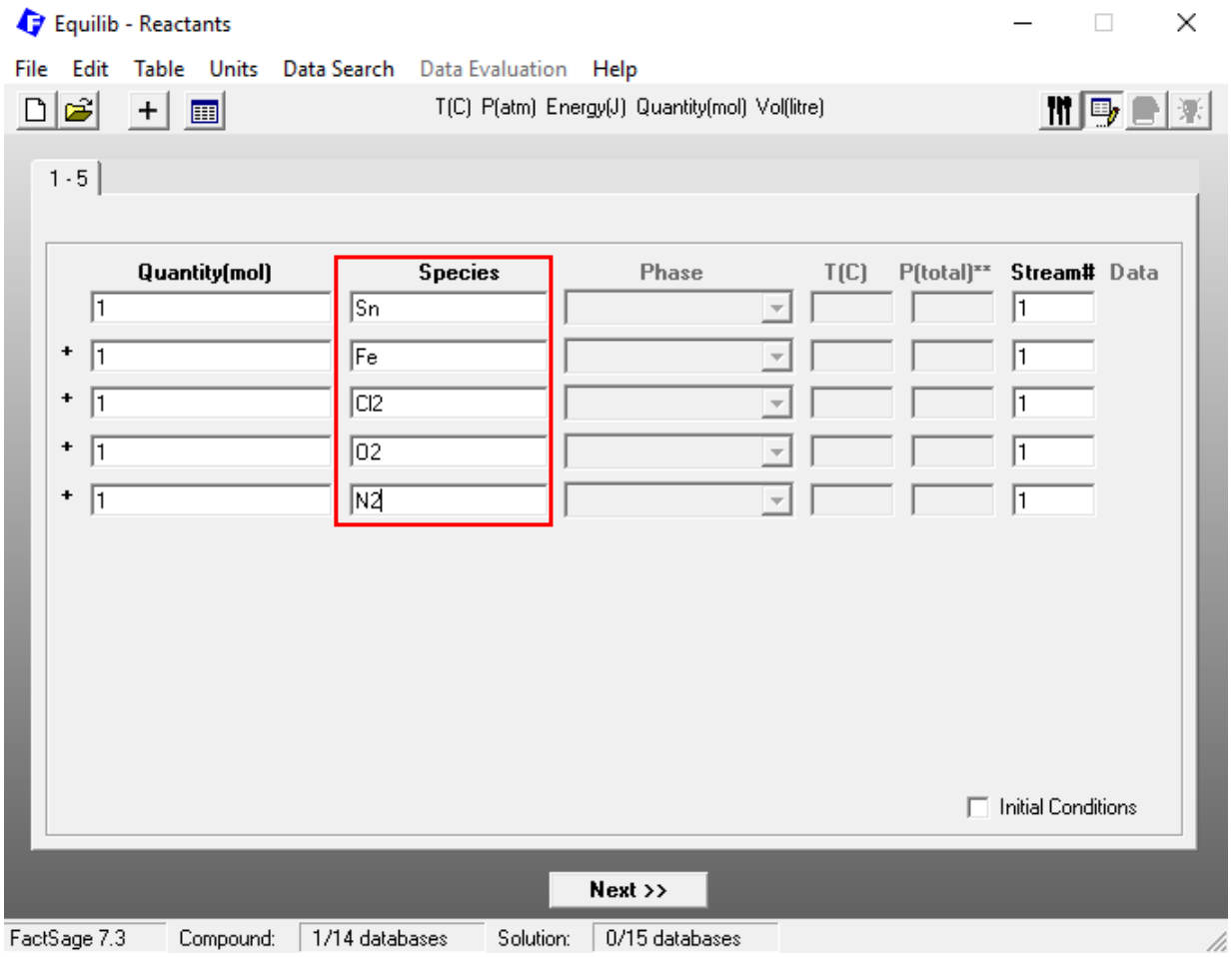
$$0.2 \text{ mol Fe} + 0.15 \text{ O}_2 = 1.0 \text{ mol Fe}_2\text{O}_3$$

Of course, if O_2 is supplied from air (21 vol.% O_2 + 79 vol.% N_2), then the number of moles of N_2 is 3.76×0.15 mol = 0.564 mol.

Also, we assume all the reactants are introduced into the reactor at room temperature.

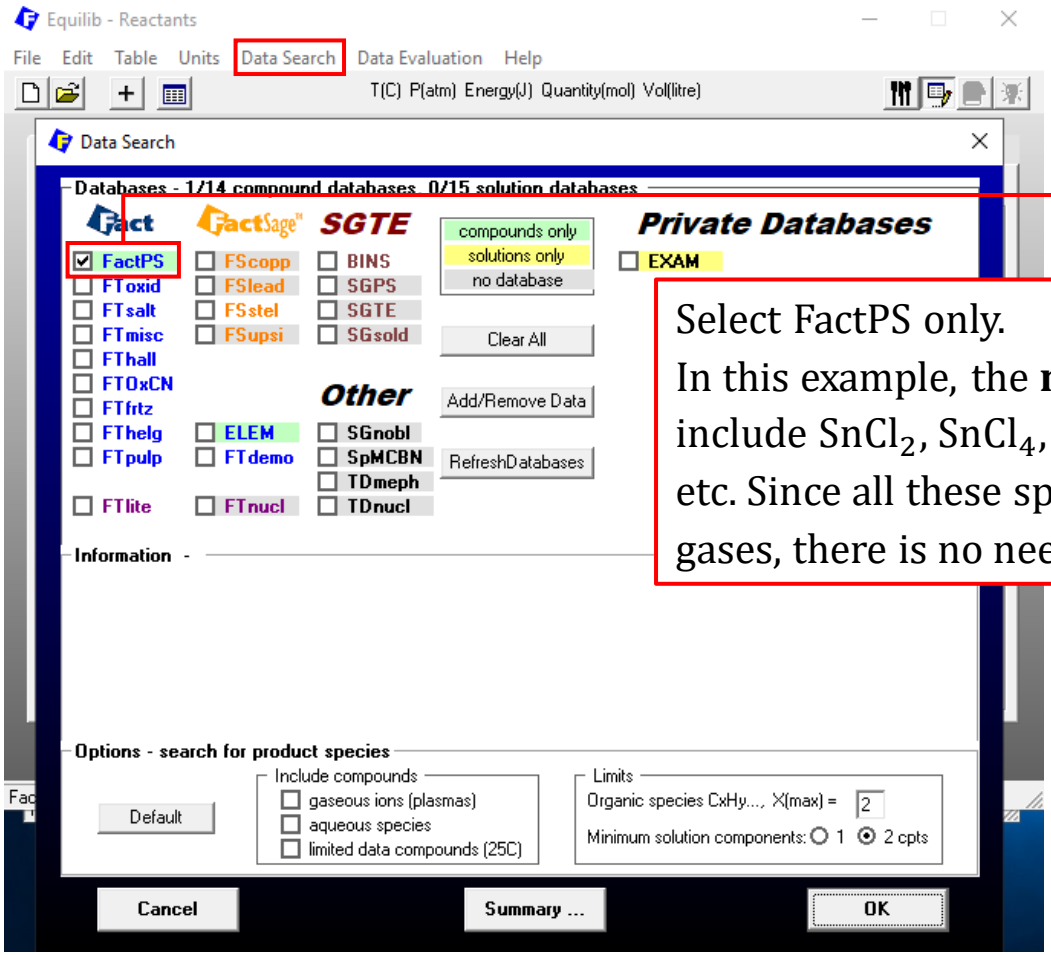
Equilib Module: Recovery of Tin from Tin Cans

Reactants Window: Define Reactants (Species)



Equilib Module: Recovery of Tin from Tin Cans

Reactants Window: Select Database(s)

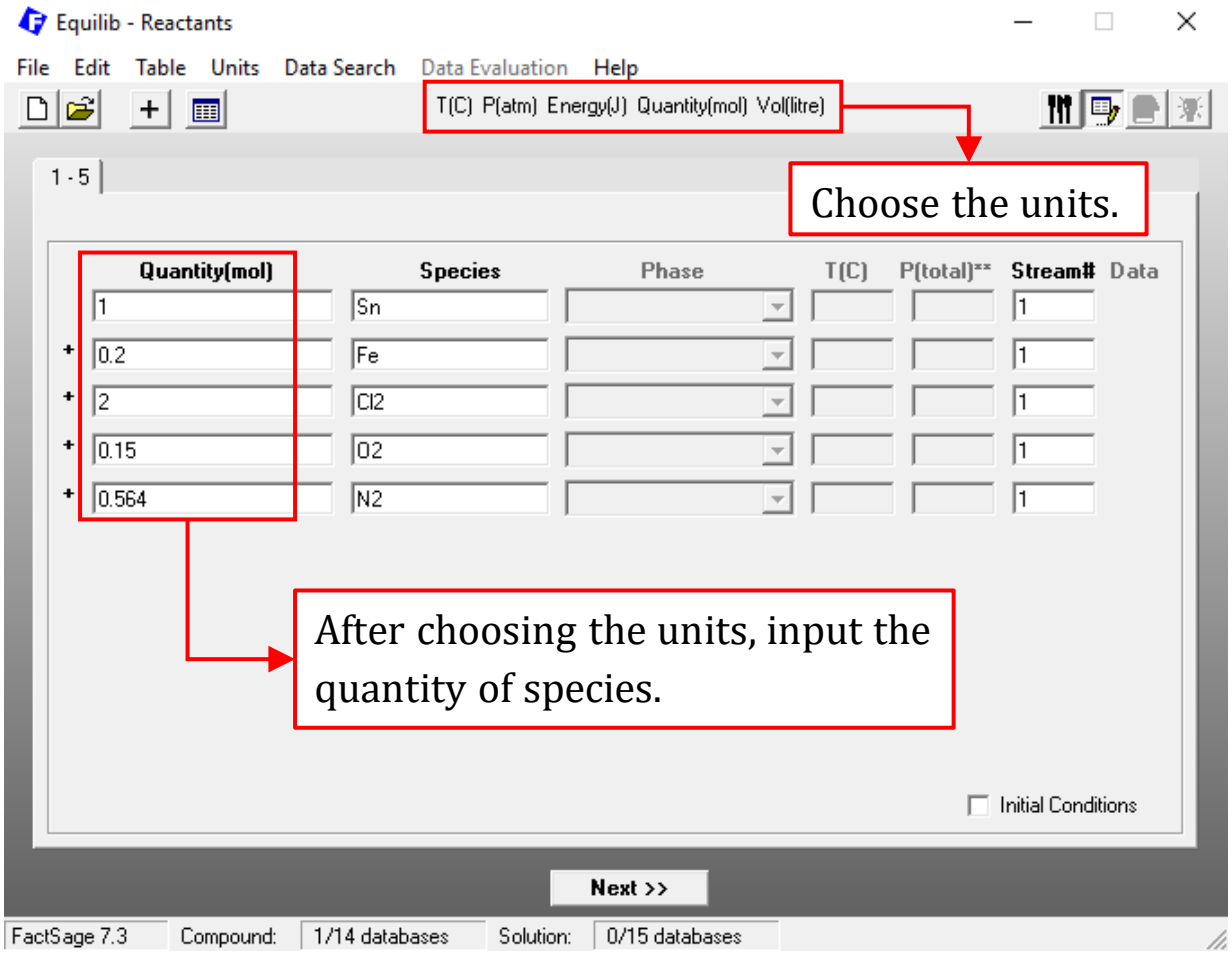


Select FactPS only.

In this example, the **major** species we are interested in include $SnCl_2$, $SnCl_4$, SnO_2, $FeCl_2$, $FeCl_3$, Fe_2O_3, Cl_2, O_2, N_2, etc. Since all these species are either pure solids/liquid or gases, there is no need to choose any solution database.

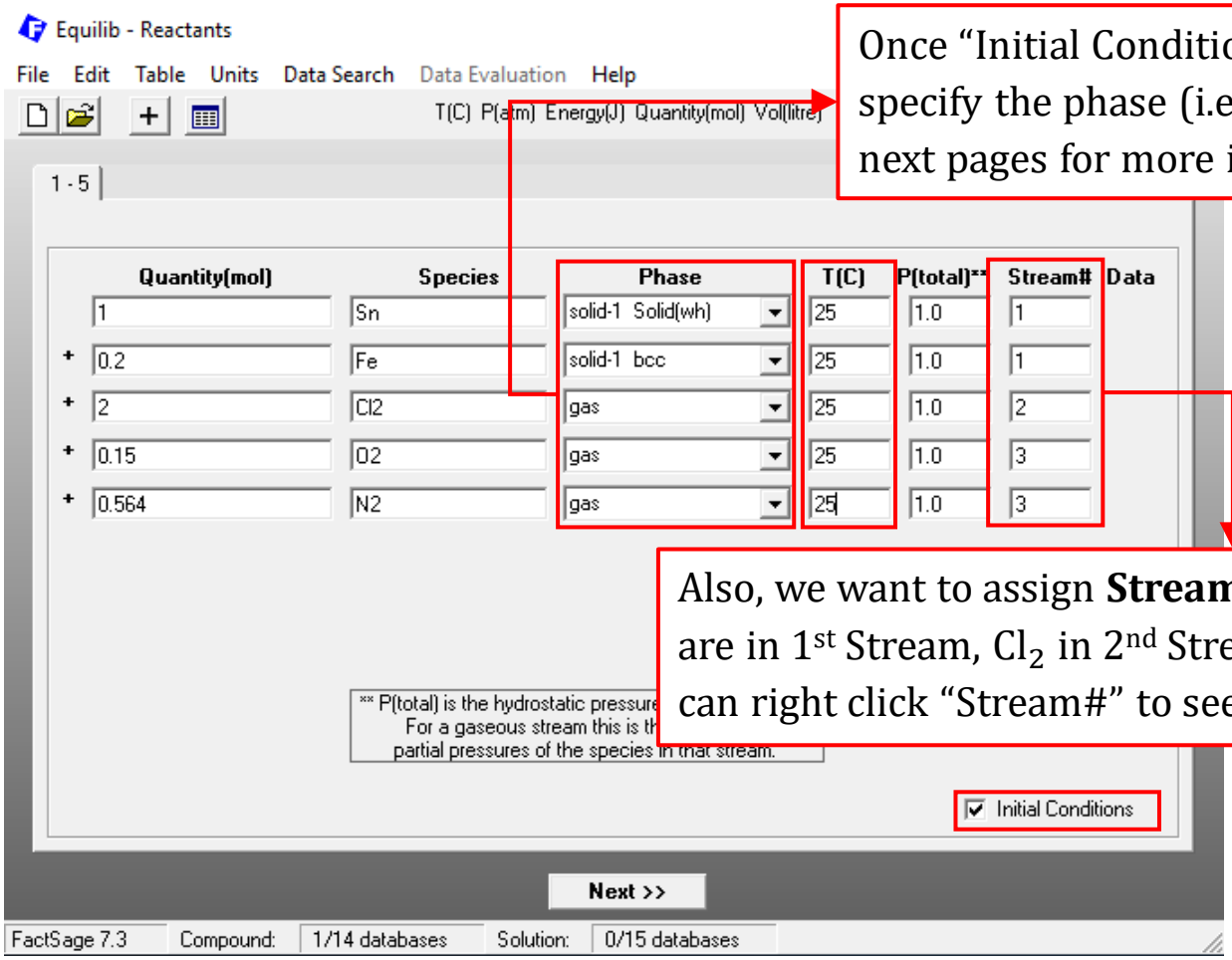
Equilib Module: Recovery of Tin from Tin Cans

Reactants Window: Choose Units and Input the Quantity of Species



Equilib Module: Recovery of Tin from Tin Cans

Reactants Window: Choose "Initial Conditions"

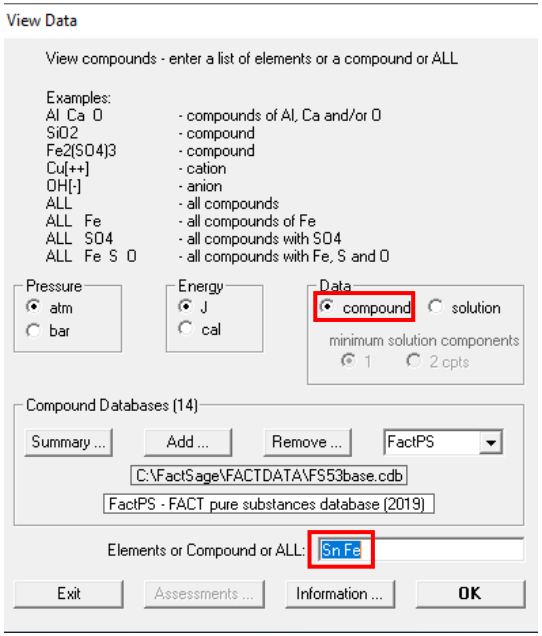


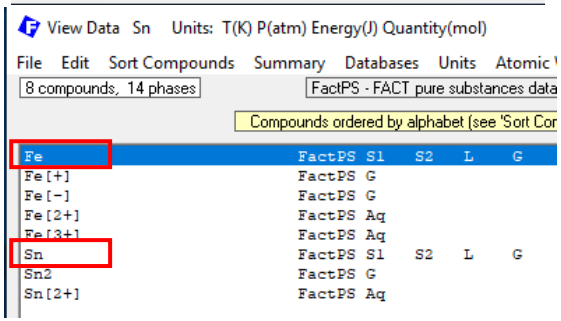
Once "Initial Conditions" is checked, we need to specify the phase (i.e., structure) of species (see next pages for more information).

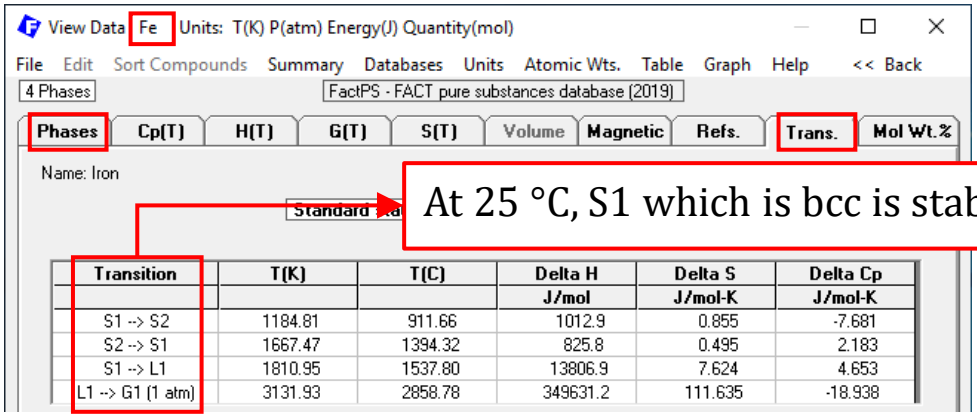
Also, we want to assign **Stream#** to the reactants (Sn and Fe are in 1st Stream, Cl_2 in 2nd Stream, and air in 3rd Stream). You can right click "Stream#" to see more details.

Equilib Module: Recovery of Tin from Tin Cans

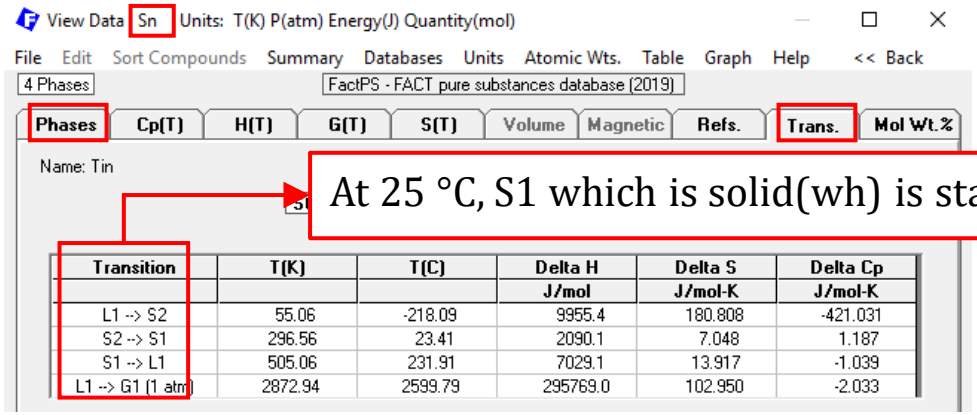
View Data Module: Structure of Sn and Fe at 25 °C, 1 atm







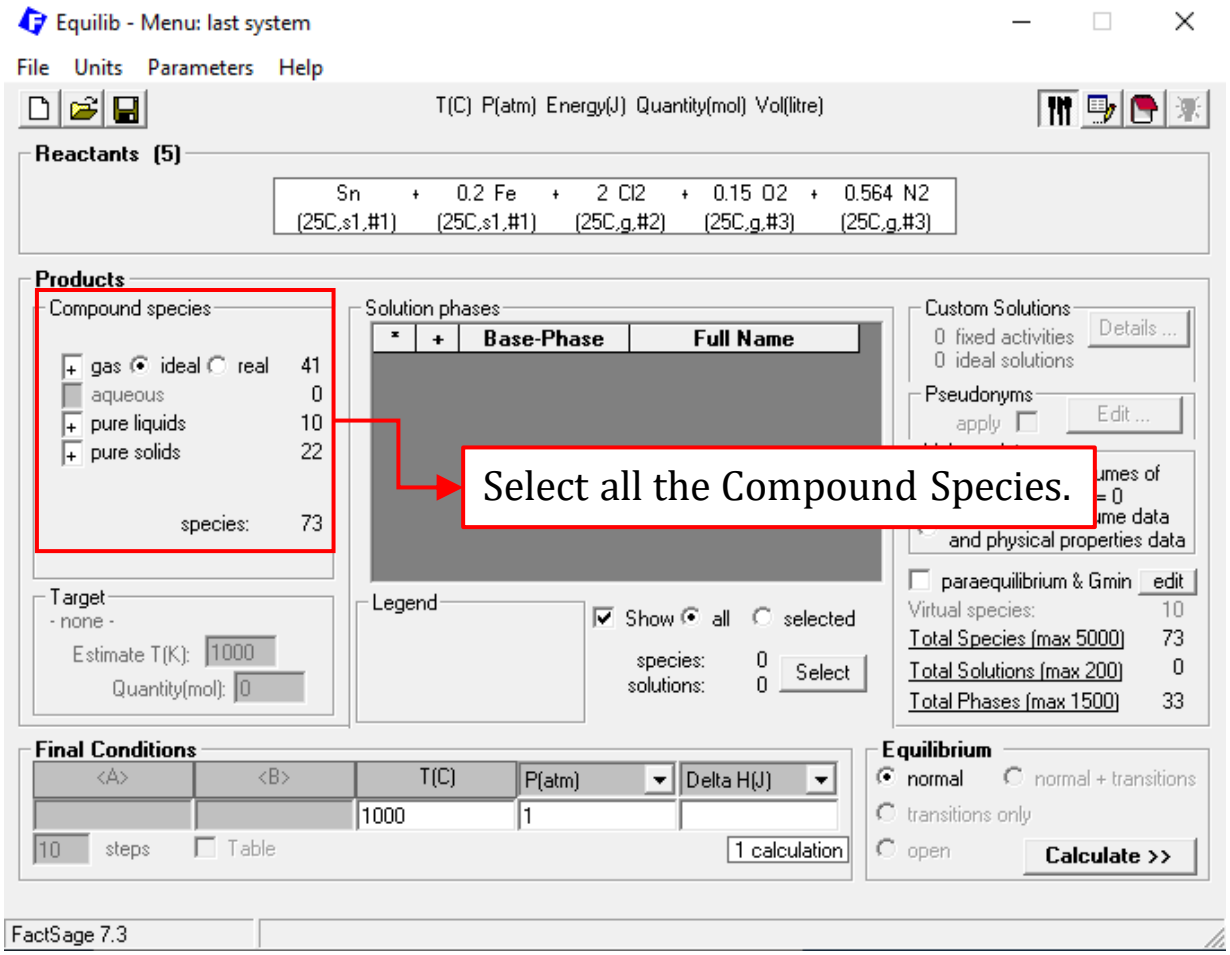
Transition	T(K)	T(C)	Delta H J/mol	Delta S J/mol-K	Delta Cp J/mol-K
S1 --> S2	1184.81	911.66	1012.9	0.855	-7.681
S2 --> S1	1667.47	1394.32	825.8	0.495	2.183
S1 --> L1	1810.95	1537.80	13806.9	7.624	4.653
L1 --> G1 (1 atm)	3131.93	2858.78	349631.2	111.635	-18.938



Transition	T(K)	T(C)	Delta H J/mol	Delta S J/mol-K	Delta Cp J/mol-K
L1 --> S2	55.06	-218.09	9955.4	180.808	-421.031
S2 --> S1	296.56	23.41	2090.1	7.048	1.187
S1 --> L1	505.06	231.91	7029.1	13.917	-1.039
L1 --> G1 (1 atm)	2872.94	2599.79	295769.0	102.950	-2.033

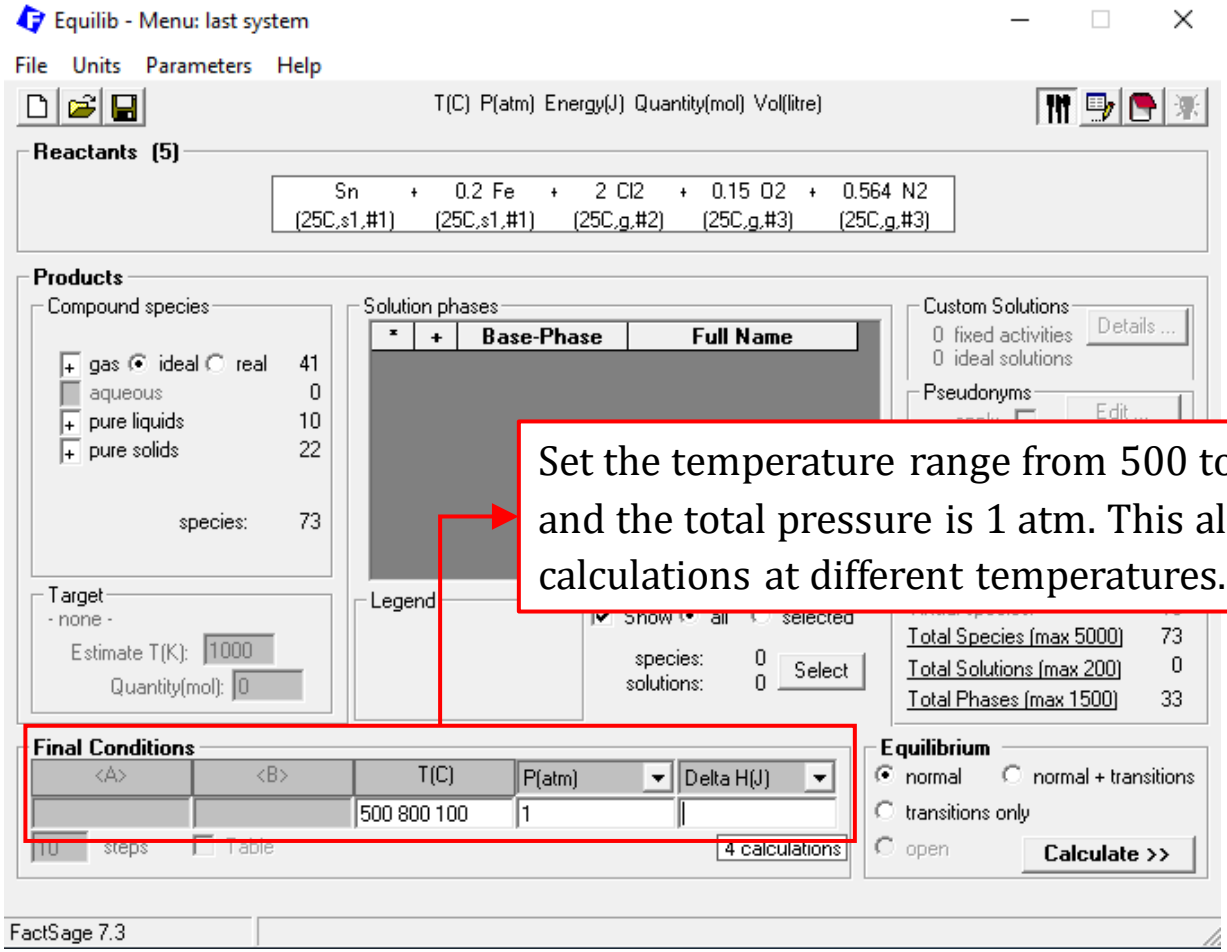
Equilib Module: Recovery of Tin from Tin Cans

Menu Window: Select the Products



Equilib Module: Recovery of Tin from Tin Cans

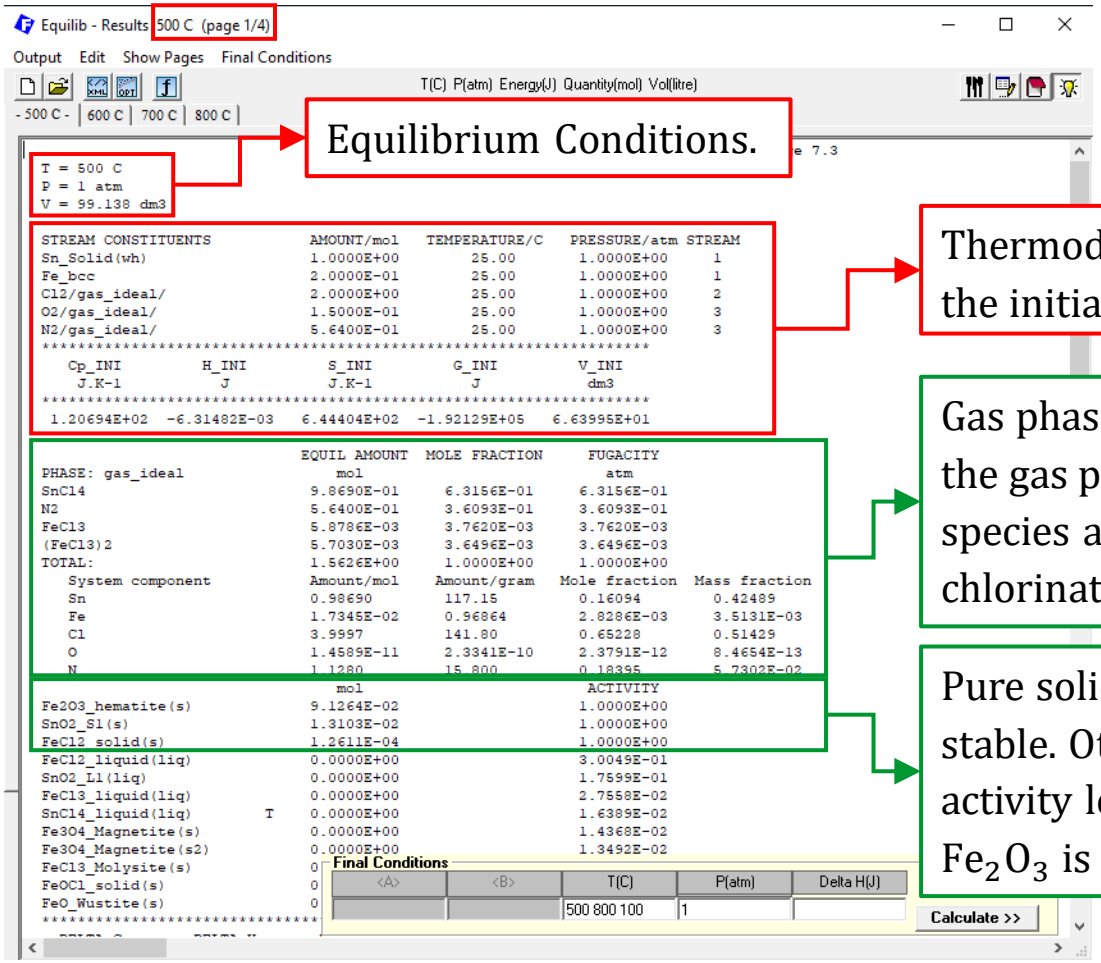
Menu Window: Set the Final Conditions



Set the temperature range from 500 to 800 °C at 100 °C intervals, and the total pressure is 1 atm. This allows us to perform 4 calculations at different temperatures.

Equilib Module: Recovery of Tin from Tin Cans

Results: (Here, we again use the ChemSage format)



Equilibrium Conditions.

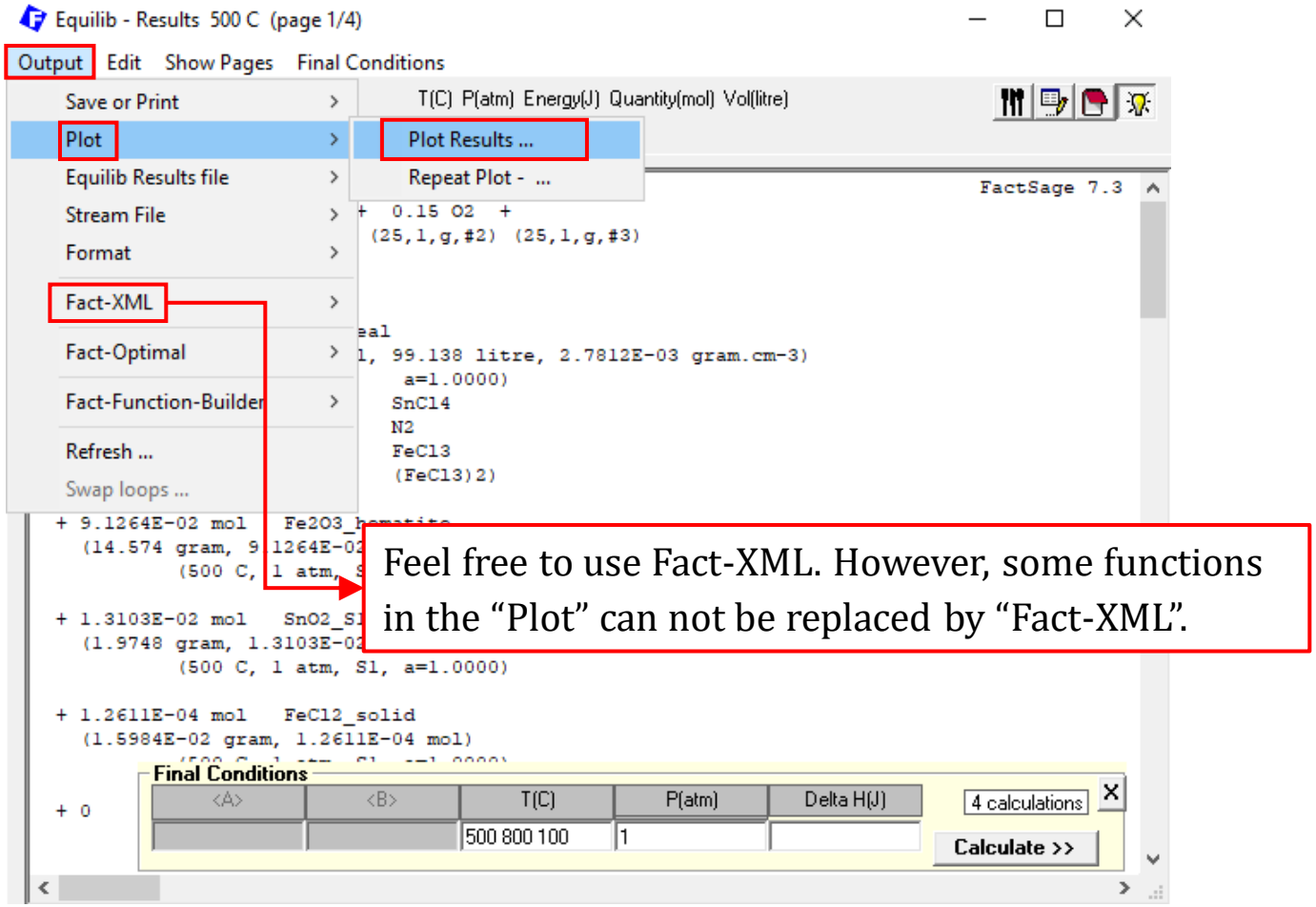
Thermodynamic properties of the system at the initial state.

Gas phase: the total fugacity is 1 which means the gas phase is stable. The major gaseous species are $SnCl_4$ and N_2. This means Sn is chlorinated and removed very efficiently.

Pure solids: Fe_2O_3, SnO_2, and $FeCl_2$ are stable. Other compound species have an activity less than 1, which are not stable. Also, Fe_2O_3 is the major species.

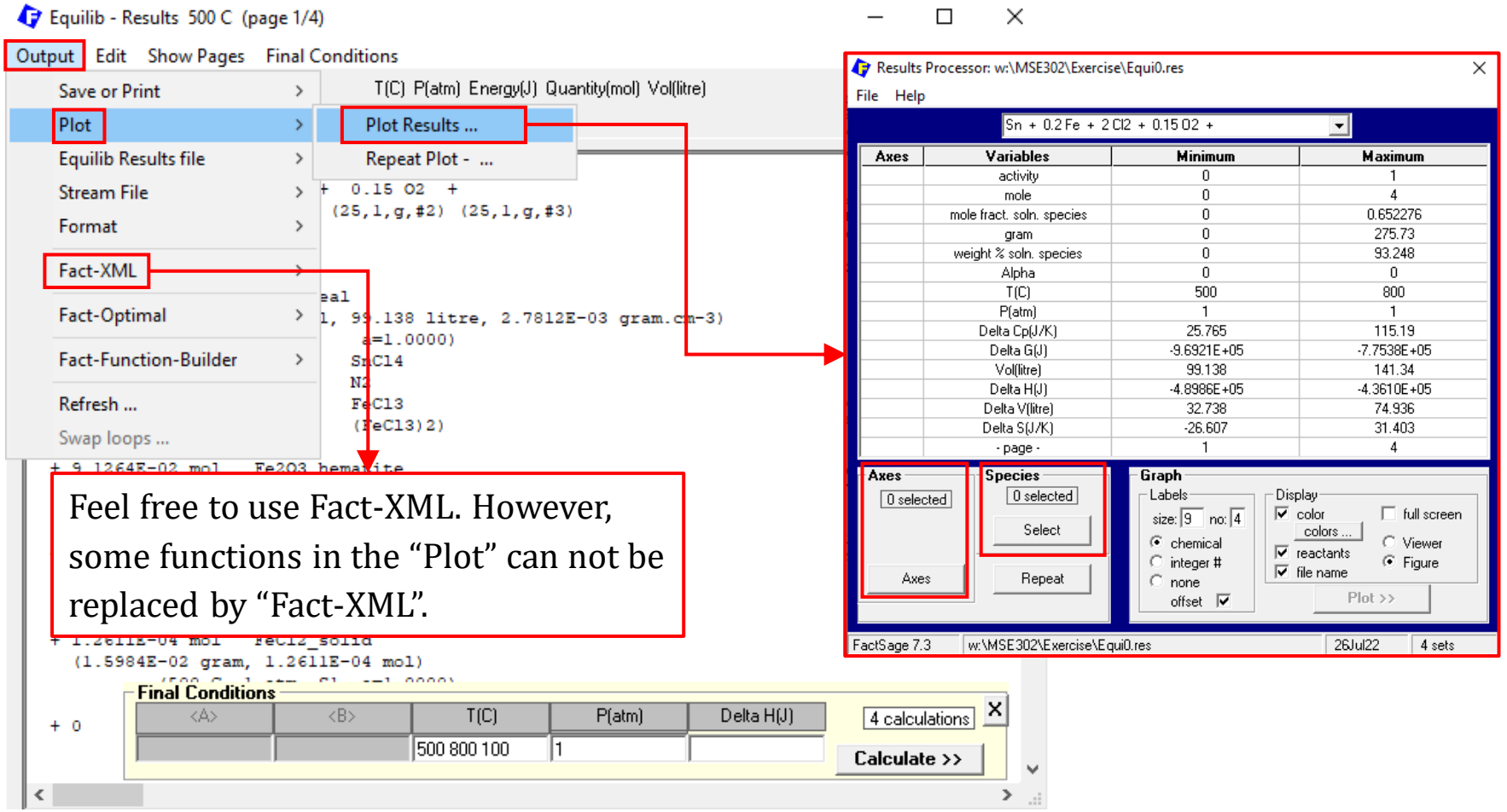
Equilib Module: Recovery of Tin from Tin Cans

Results: let us plot the data (this time we use Output\Plot)



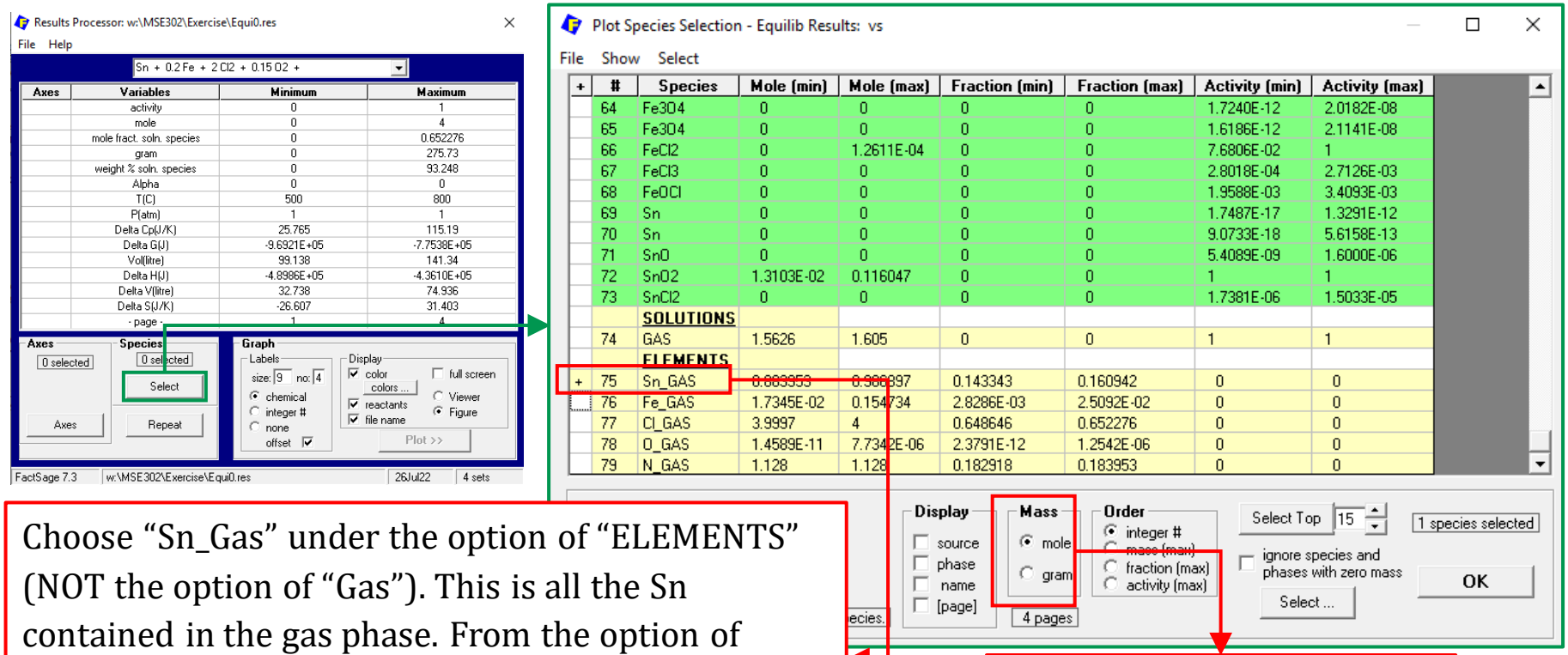
Equilib Module: Recovery of Tin from Tin Cans

Results: let us plot the data (this time we use Output\Plot)



Equilib Module: Recovery of Tin from Tin Cans

Results: let us plot the data (this time we use Output\Plot)

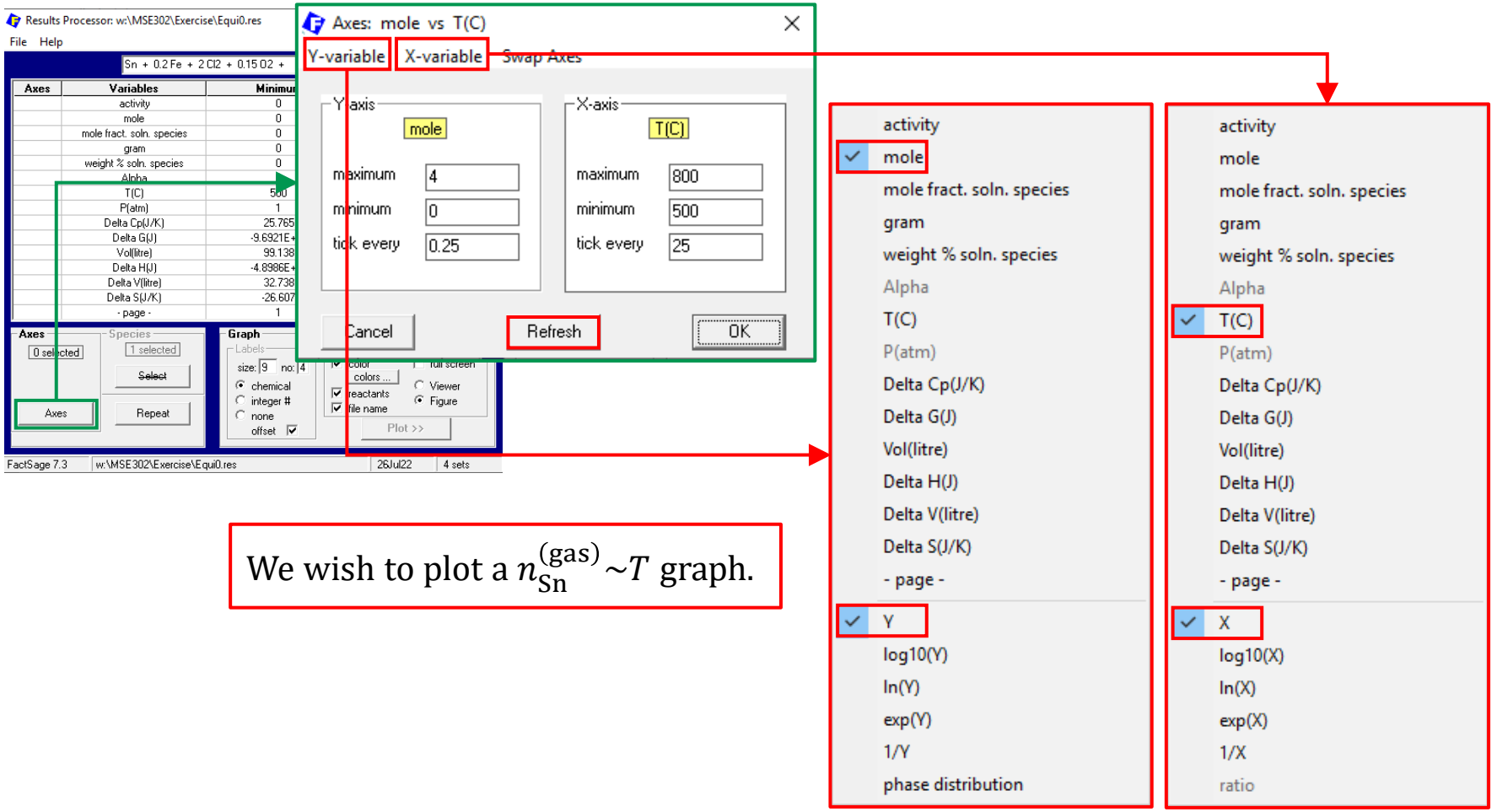


Choose "Sn_Gas" under the option of "ELEMENTS" (NOT the option of "Gas"). This is all the Sn contained in the gas phase. From the option of "Gas", you would see Sn exists as Sn, Sn_2, SnO, SnO_2, O_2Sn_2, O_3Sn_3, O_4Sn_4, SnCl, $SnCl_2$, and **$SnCl_4$** (major species of Sn carrier).

Choose "mole" as Mass unit.

Equilib Module: Recovery of Tin from Tin Cans

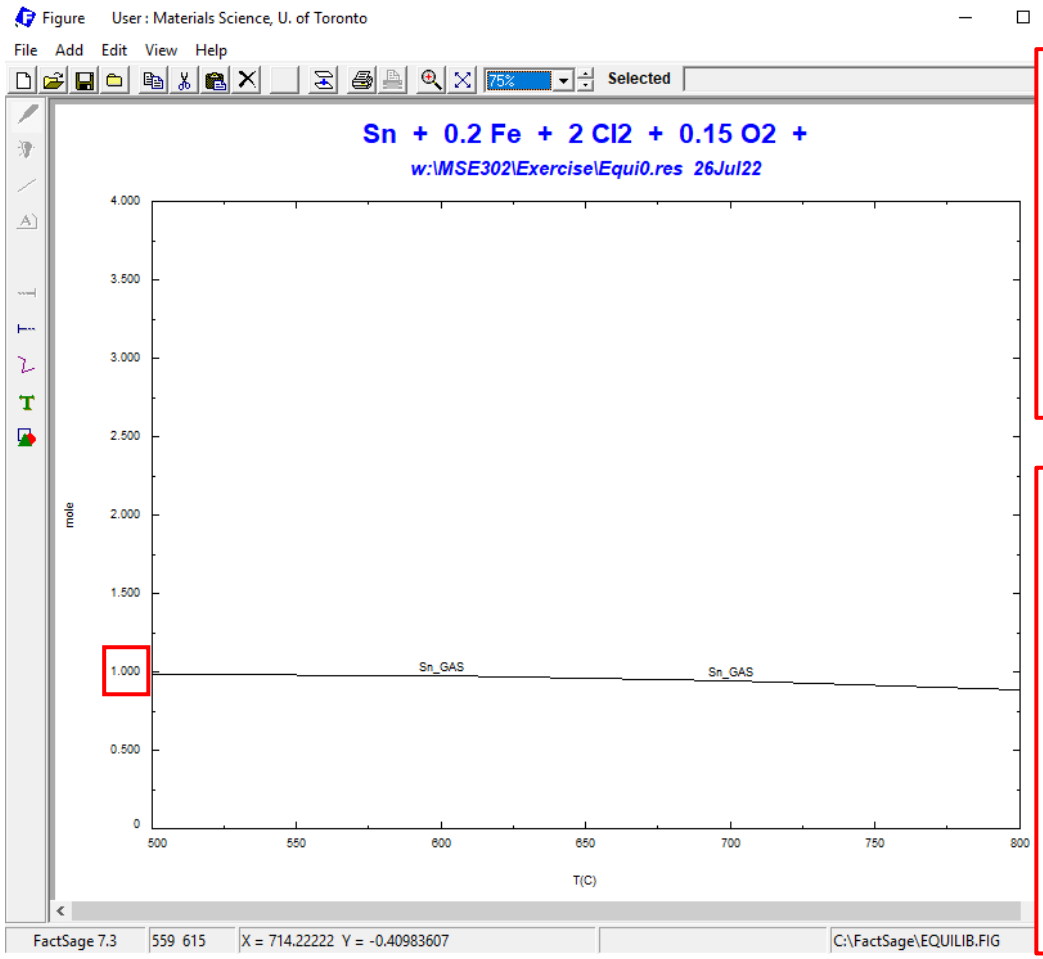
Results: let us plot the data (this time we use Output\Plot)



We wish to plot a $n_{\mathrm{Sn}}^{(\mathrm{gas})} \sim T$ graph.

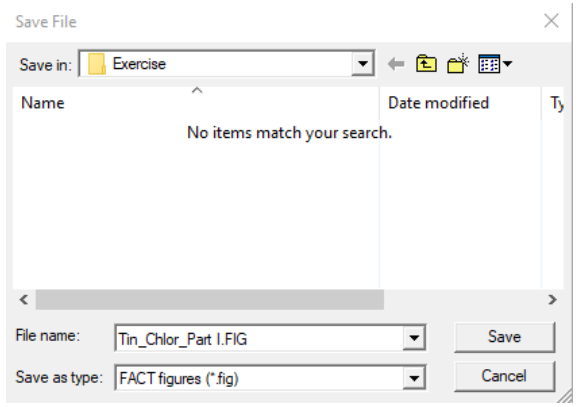
Equilib Module: Recovery of Tin from Tin Cans

Results: let us plot the data (this time we use Output\Plot)



As seen from the graph, the total amount of Sn in the gas phase is close to 1.0 mol at the four temperatures we investigated. This means that essentially all the Sn is recovered (Recall the total Sn input is 1.0 mol).

Save the graph.



Equilib Module: Recovery of Tin from Tin Cans

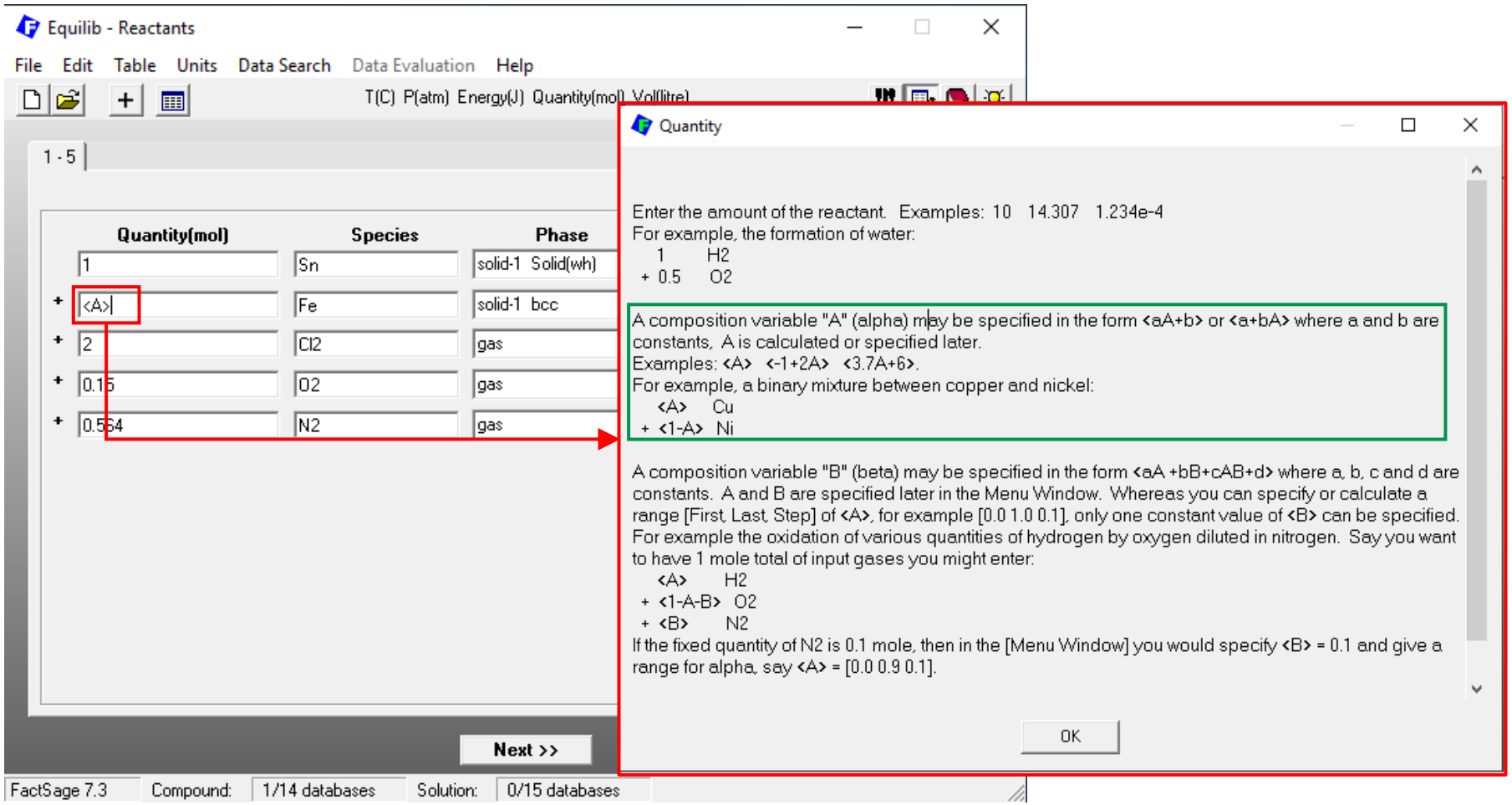
Part II.

For Part II, we will be looking at what happens if the amount of oxygen supplied is not sufficient to oxidize the exposed iron.

Assume the amount of the exposed iron is a variable: for 1 mol of Sn, the amount of the exposed iron varies from 0.2 to 0.6 mol. The temperature is fixed at 600 °C.

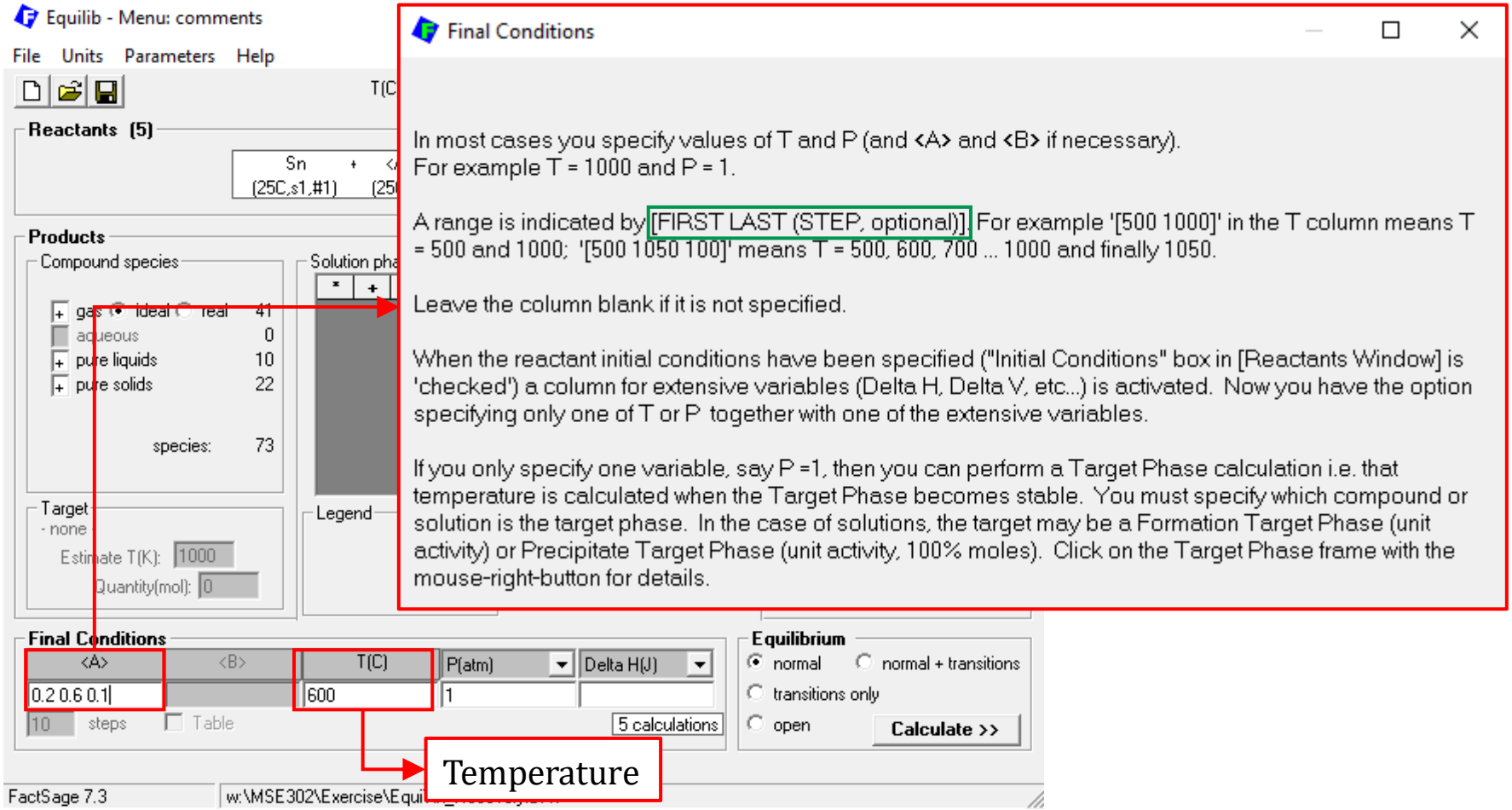
Equilib Module: Recovery of Tin from Tin Cans

Back to the Reactants Window:



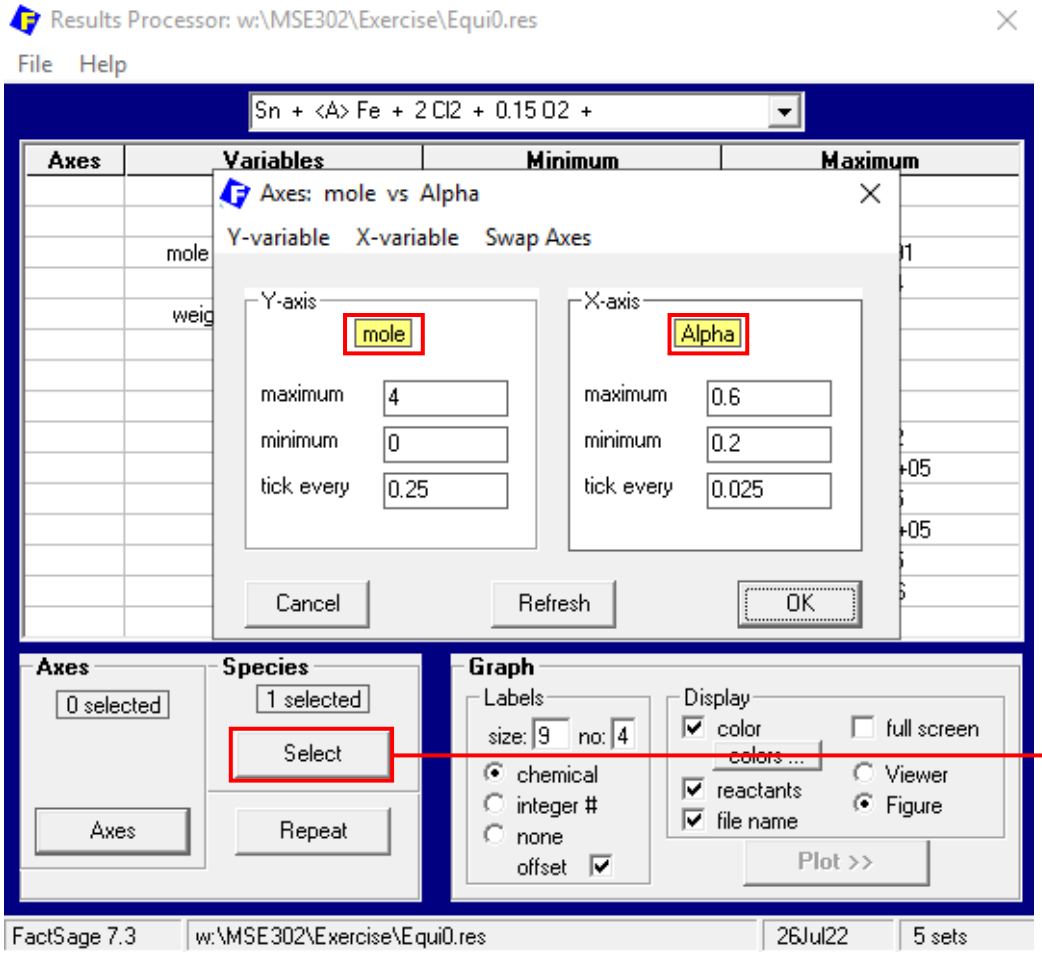
Equilib Module: Recovery of Tin from Tin Cans

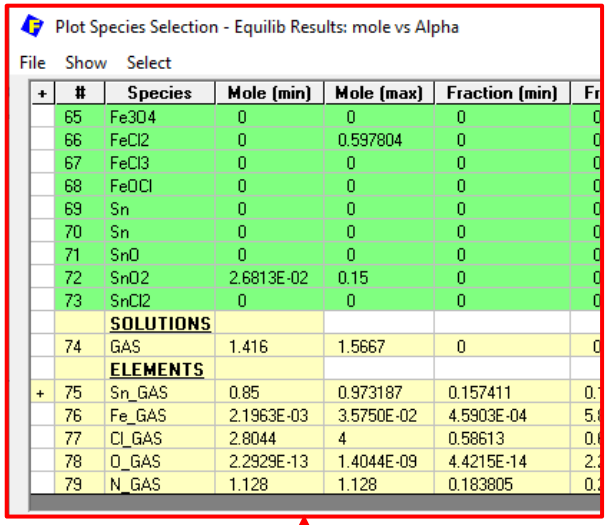
Menu Window



Equilib Module: Recovery of Tin from Tin Cans

Results: plot the $n_{Sn}^{(gas)}$ ~<Alpha> graph

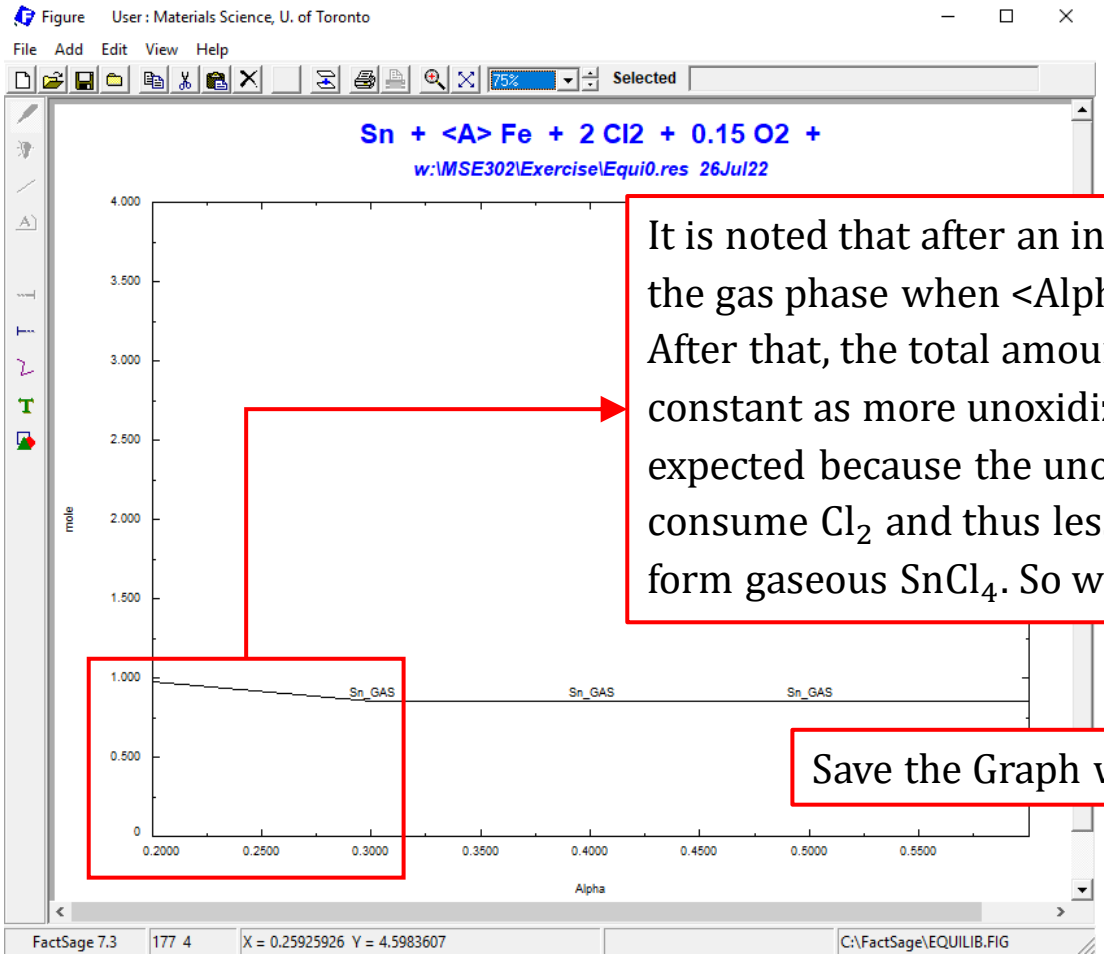




+	#	Species	Mole (min)	Mole (max)	Fraction (min)	Fr
	65	Fe3O4	0	0	0	0
	66	FeCl2	0	0.597804	0	0
	67	FeCl3	0	0	0	0
	68	FeOCl	0	0	0	0
	69	Sn	0	0	0	0
	70	Sn	0	0	0	0
	71	SnO	0	0	0	0
	72	SnO2	2.6813E-02	0.15	0	0
	73	SnCl2	0	0	0	0
		SOLUTIONS				
	74	GAS	1.416	1.5667	0	0
		ELEMENTS				
+	75	Sn_GAS	0.85	0.973187	0.157411	0.1
	76	Fe_GAS	2.1963E-03	3.5750E-02	4.5903E-04	5.0
	77	Cl_GAS	2.8044	4	0.58613	0.0
	78	O_GAS	2.2929E-13	1.4044E-09	4.4215E-14	2.2
	79	N_GAS	1.128	1.128	0.183805	0.2

Equilib Module: Recovery of Tin from Tin Cans

Results: plot the $n_{Sn}^{(gas)}$ ~<Alpha> graph

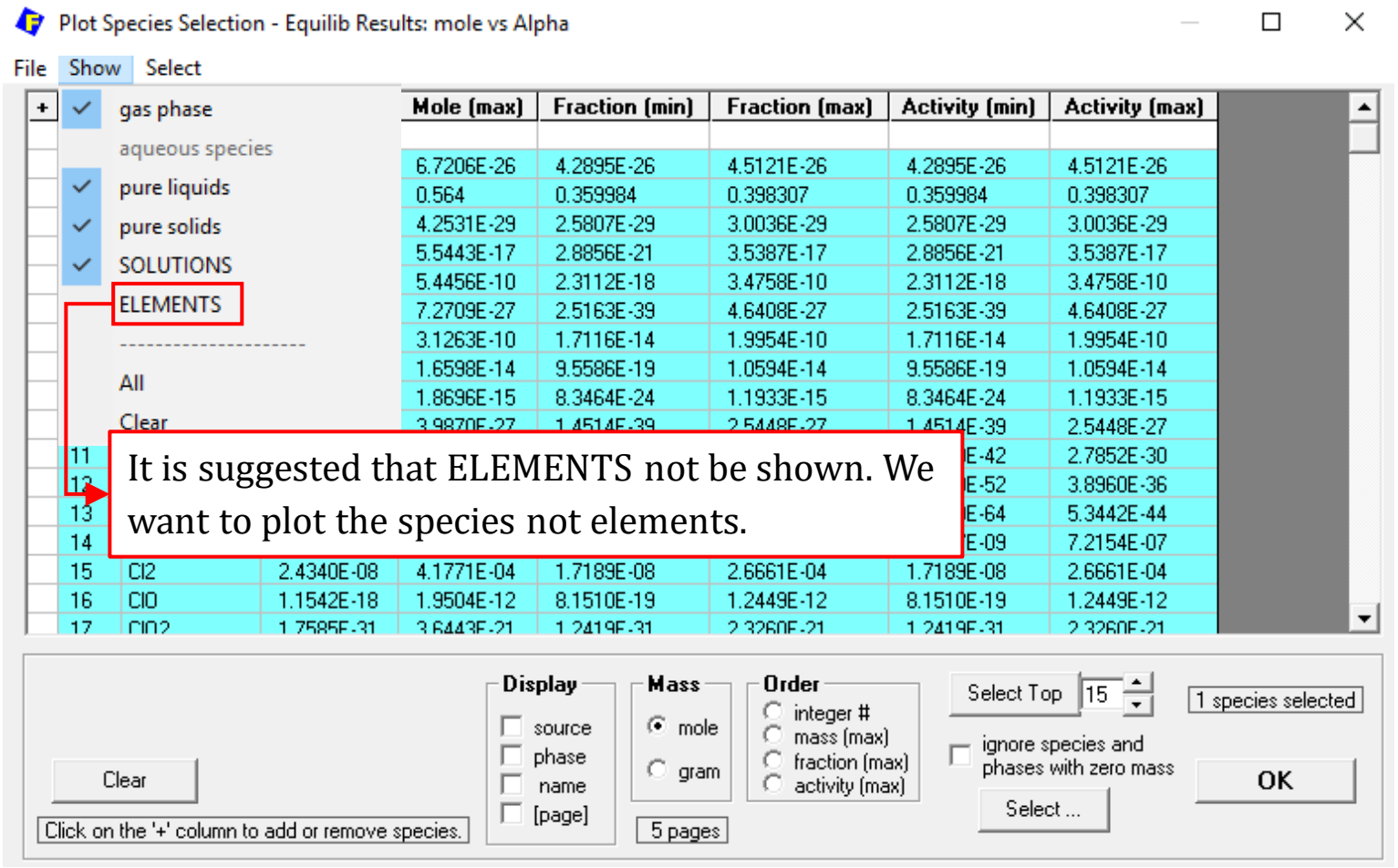


It is noted that after an initial drop in the total amount of Sn in the gas phase when <Alpha> increases from 0.2 to 0.3 mol. After that, the total amount of Sn in the gas phase remains constant as more unoxidized iron is available. This is not expected because the unoxidized iron would presumably consume Cl_2 and thus less Cl_2 is available to chloridize Sn to form gaseous $SnCl_4$. So what is going on?

Save the Graph with the name "Tin_Chlor_Part II"

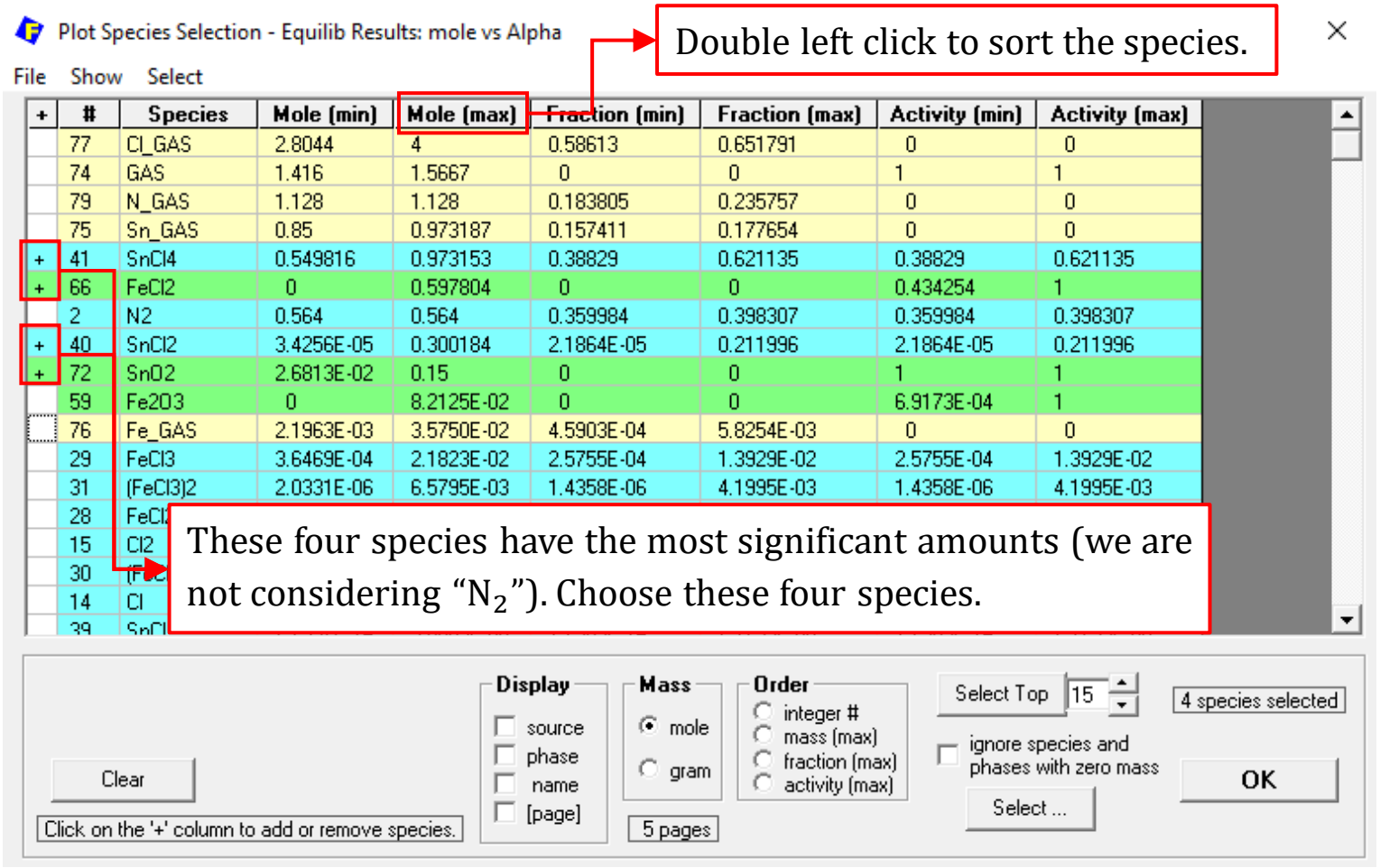
Equilib Module: Recovery of Tin from Tin Cans

Results: plot the amounts of major species



Equilib Module: Recovery of Tin from Tin Cans

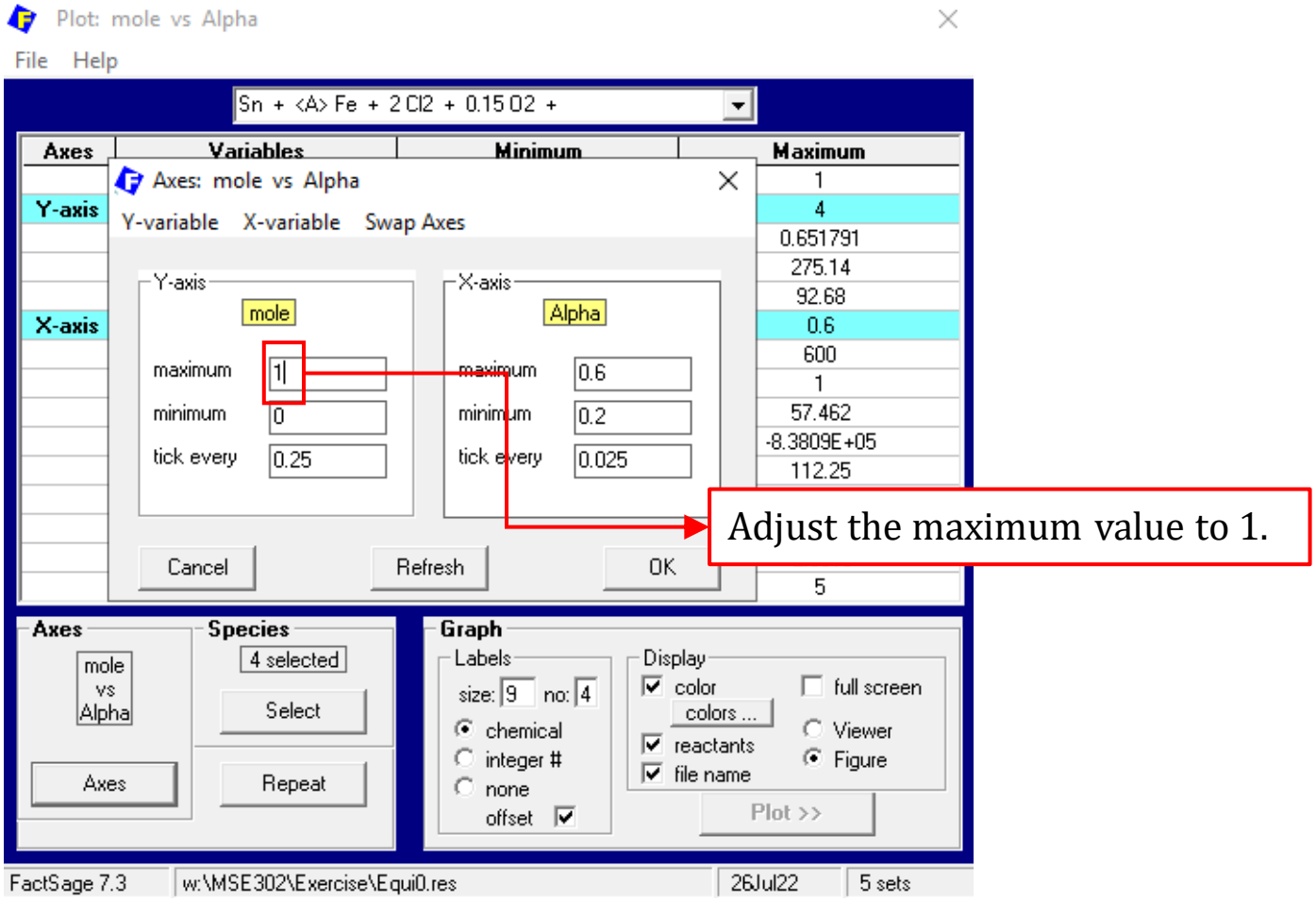
Results: plot the amounts of major species



+	#	Species	Mole (min)	Mole (max)	Fraction (min)	Fraction (max)	Activity (min)	Activity (max)
	77	Cl_GAS	2.8044	4	0.58613	0.651791	0	0
	74	GAS	1.416	1.5667	0	0	1	1
	79	N_GAS	1.128	1.128	0.183805	0.235757	0	0
	75	Sn_GAS	0.85	0.973187	0.157411	0.177654	0	0
+	41	SnCl4	0.549816	0.973153	0.38829	0.621135	0.38829	0.621135
+	66	FeCl2	0	0.597804	0	0	0.434254	1
	2	N2	0.564	0.564	0.359984	0.398307	0.359984	0.398307
+	40	SnCl2	3.4256E-05	0.300184	2.1864E-05	0.211996	2.1864E-05	0.211996
+	72	SnO2	2.6813E-02	0.15	0	0	1	1
	59	Fe2O3	0	8.2125E-02	0	0	6.9173E-04	1
	76	Fe_GAS	2.1963E-03	3.5750E-02	4.5903E-04	5.8254E-03	0	0
	29	FeCl3	3.6469E-04	2.1823E-02	2.5755E-04	1.3929E-02	2.5755E-04	1.3929E-02
	31	(FeCl3)2	2.0331E-06	6.5795E-03	1.4358E-06	4.1995E-03	1.4358E-06	4.1995E-03
	28	FeCl						
	15	Cl2						
	30	(Fe						
	14	Cl						
	39	SnCl						

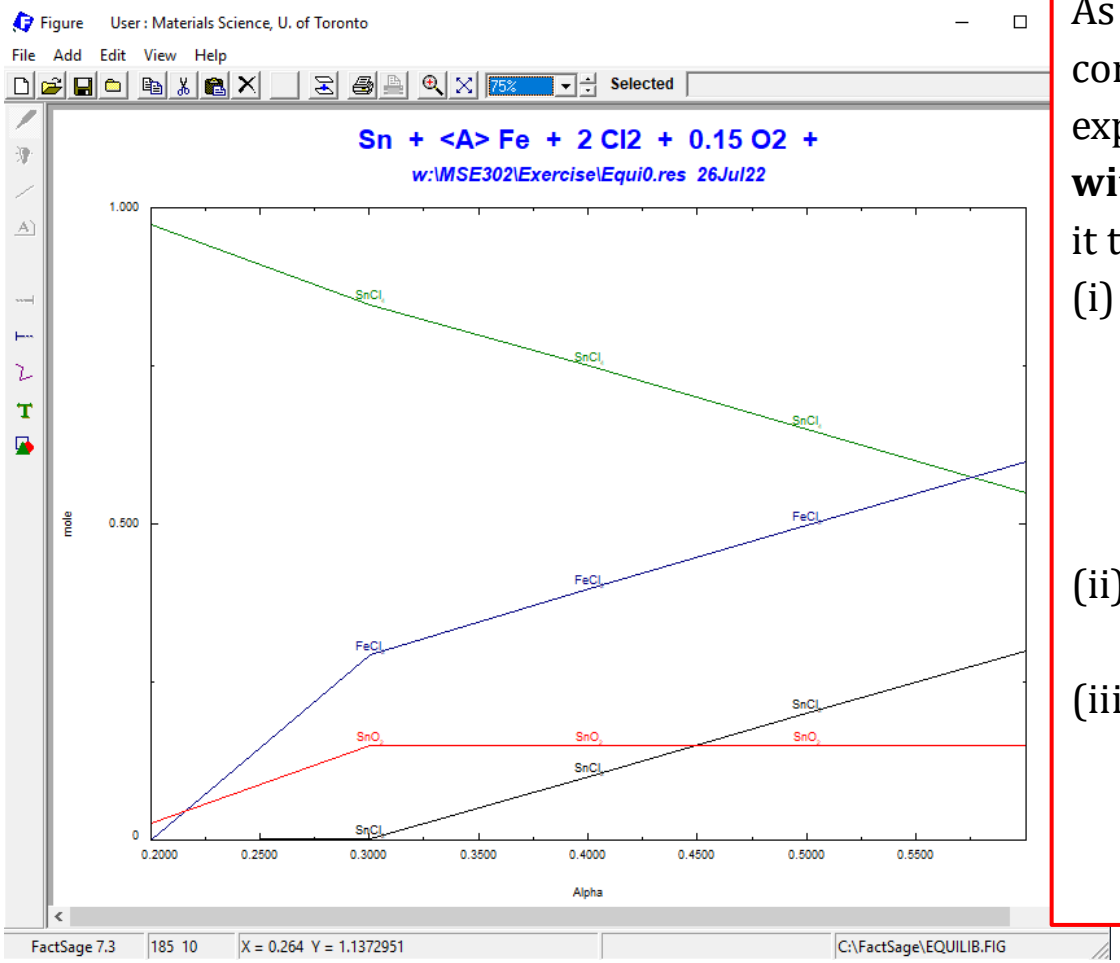
Equilib Module: Recovery of Tin from Tin Cans

Results: plot the amounts of major species



Equilib Module: Recovery of Tin from Tin Cans

Results: plot the amounts of major species



As seen from the graph, there is a complex chemistry occurring as more exposed iron is available for reaction **without adequate oxygen** to convert it to Fe_2O_3.

(i) Some Sn forms solid SnO_2 and this would represent a Sn loss since SnO_2 is not volatile and will remain with the solid waste stream.

(ii) Some Cl_2 is wasted by reaction with iron to form solid $FeCl_2$.

(iii) The Sn volatilization does remain "respectable" because of the formation of stannous chloride $SnCl_2$ in the gas phase.

Equilib Module: Recovery of Tin from Tin Cans

Part III (Process Control)

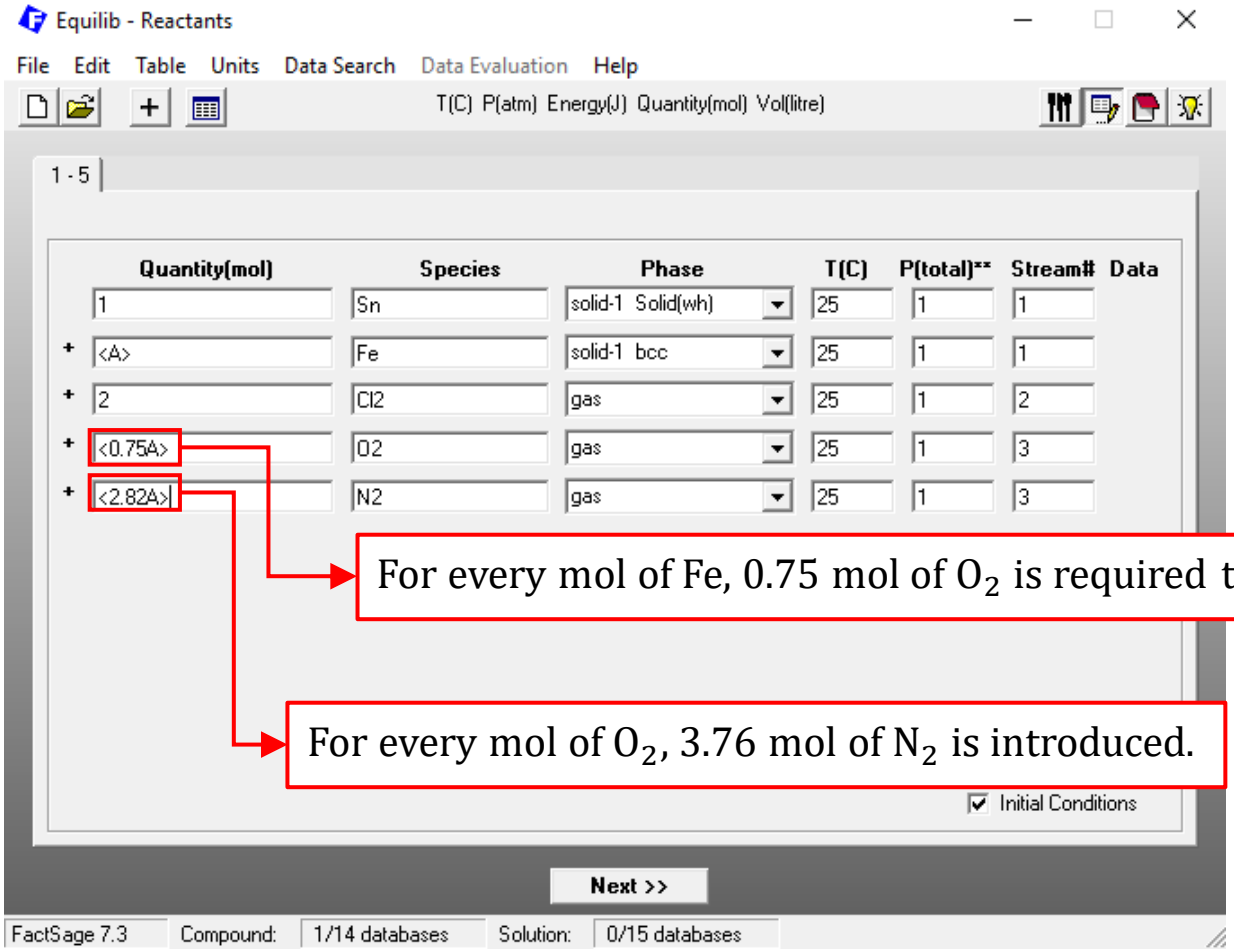
The above calculations can be used to guide the production. If significant quantities of $FeCl_2$ are detected in the outlet product stream, then this is a sign that we need to add more O_2 (i.e., air) to oxidize the metallic iron to Fe_2O_3. The **secret** in operating this tin recovery process efficiently is to maintain the oxygen flow to keep the iron as Fe_2O_3, but not to over-oxidize the metals, either.

Bearing this in mind, let us simulate the process in FactSage.

Note: in the actual tin recovery process, the amount of the exposed iron is unknown, and the assumption of 0.2 mol of the exposed iron for 1 mol of Sn in Part I calculation is not universally valid.

Equilib Module: Recovery of Tin from Tin Cans

Back to the Reactants Window

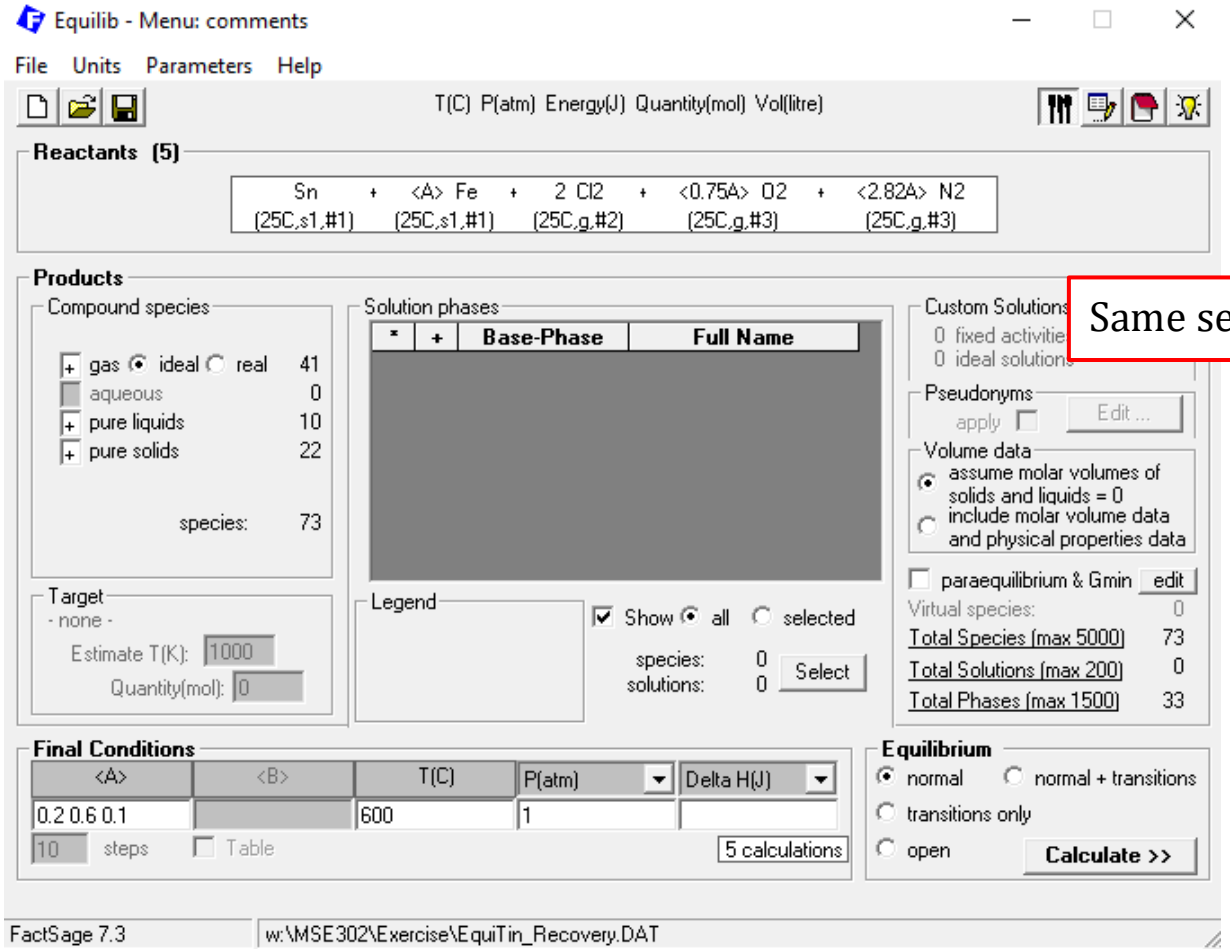


For every mol of Fe, 0.75 mol of O_2 is required to form 0.5 mol of Fe_2O_3.

For every mol of O_2, 3.76 mol of N_2 is introduced.

Equilib Module: Recovery of Tin from Tin Cans

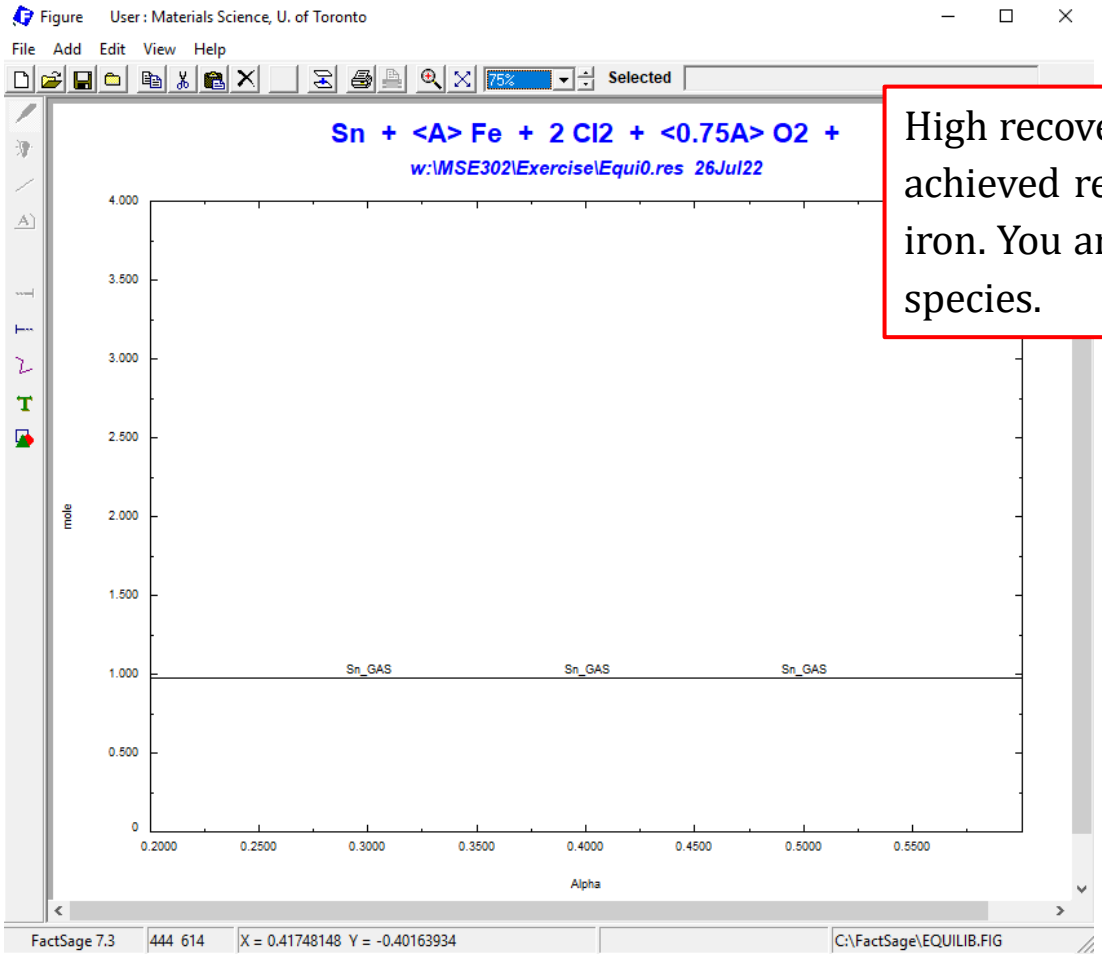
Menu Window



Same settings as Slide.

Equilib Module: Recovery of Tin from Tin Cans

Results: plot the $n_{Sn}^{(gas)}$ ~<Alpha> graph



High recoveries of Sn to the gas phase are achieved regardless of the amount of exposed iron. You are recommended to check the major species.

Plot Species Selection - Equilib Results: mole vs Alpha

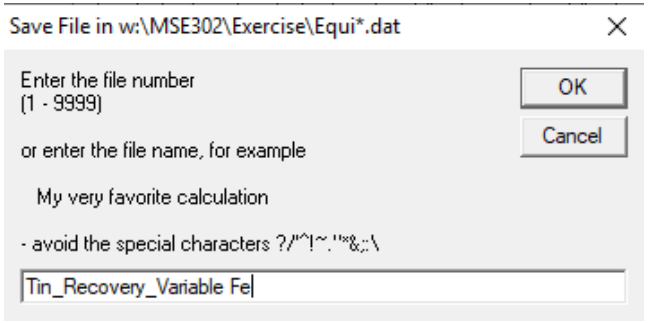
File Show Select

+	#	Species	Mole (min)	Mole (max)	Fractio
	77	Cl_GAS	4	4	0.4765E
	79	N_GAS	1.128	3.384	0.1838C
	74	GAS	1.5667	2.6965	0
	2	N2	0.564	1.692	0.3599E
	41	SnCl4	0.972948	0.973195	0.36082
	75	Sn_GAS	0.972994	0.973233	0.11592
	59	Fe2O3	8.2125E-02	0.281996	0
	76	Fe_GAS	3.5690E-02	3.6009E-02	4.2903E
	72	SnO2	2.6767E-02	2.7006E-02	0
	29	FeCl3	2.1823E-02	2.4992E-02	9.2683E
	31	(FeCl3)2	5.0137E-03	6.5795E-03	1.8593E
	28	FeCl2	6.8357E-04	9.0366E-04	3.3513E
	15	Cl2	4.1771E-04	5.3951E-04	2.0008E
	40	SnCl2	3.4256E-05	4.5637E-05	1.6925E

Equilib Module: Recovery of Tin from Tin Cans

Save the Graph and Equilib settings: ".dat" file

Save the Graph with the name "Tin_Chlor_Part III". Also, go back to the Menu Window, save the Equilib settings as a ".dat" file.



Equilib Module: Recovery of Tin from Tin Cans

A Note on the Real-world Production

In the actual production, with the majority of Sn being recovered as $SnCl_4$ to the gas phase, Fe_2O_3 that forms on the exposed iron will become a "protective" layer. Consequently, the amount of O_2 required will be difficult to predict ahead of time, and we will need to monitor the process for free Cl_2 and $FeCl_2$ to ensure that we:

(a) add enough chlorine – we will need to keep the free Cl_2 at around 2% in the gas phase; and,

(b) add enough air to prevent iron chlorination.

For the commercial-scale production, an effective operating strategy that has been proven successful is to monitor the **oxygen** level in the off-gas and to control the feed rates of **chlorine** and **oxygen** (in air) to match the amounts of iron and tin that are actually reacting.

The following exercise focuses on the tin chlorination process with variable **oxygen** and **chlorine**.

Equilib Module: Recovery of Tin from Tin Cans

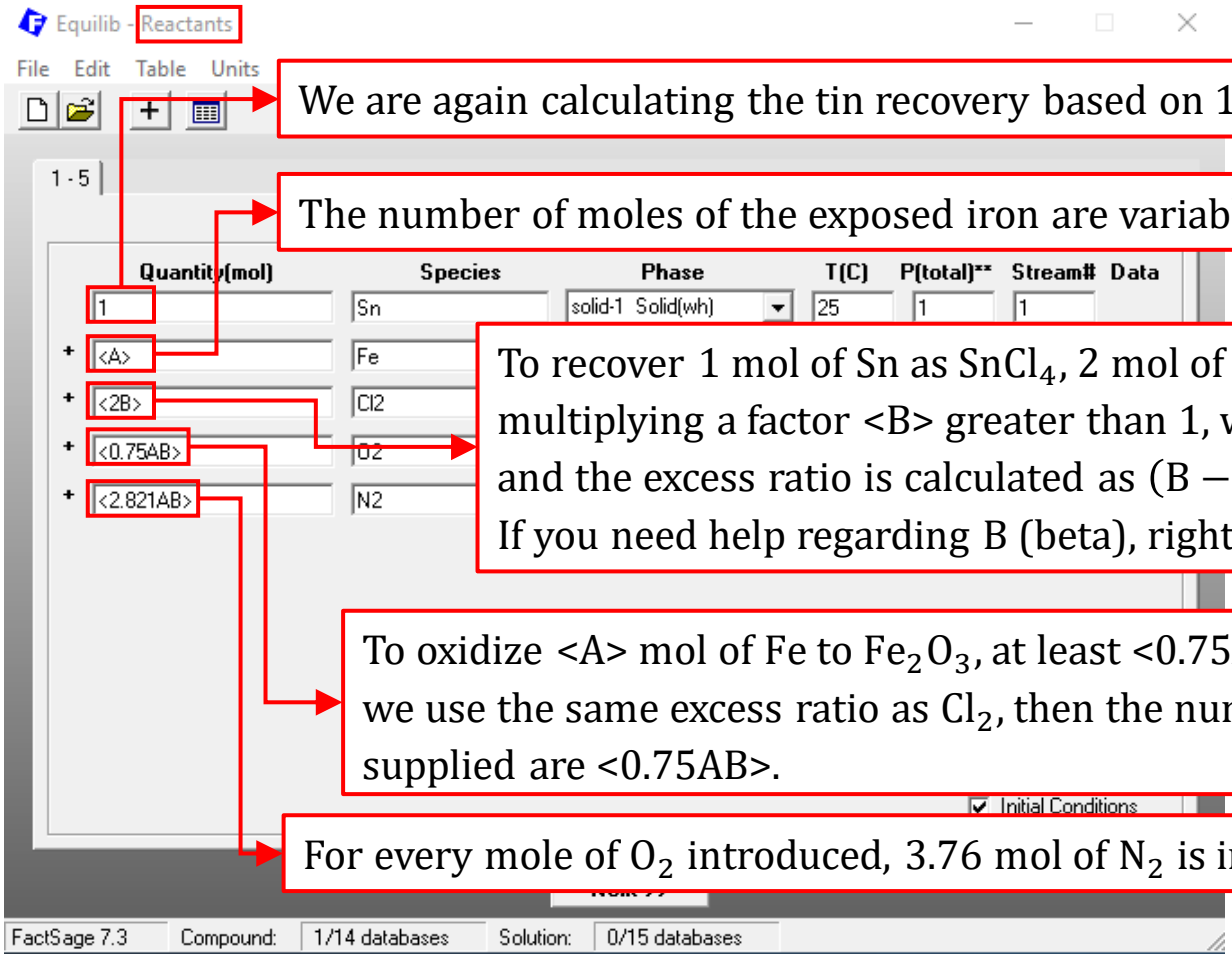
Exercise 1. A Small Excess of Both Chlorine and Oxygen

In the first exercise, we will supply excess **chlorine** and **oxygen** to the reactor. In doing so, we will have some oxygen that can be measured in the product stream and some excess chlorine (that we can absorb and reuse). By having a (small) excess of both the reacting gases, we ensure that there will always be a driving force for the reactions we want.

For simplicity, we shall assume chlorine and oxygen that are supplied have the same excess ratio.

Equilib Module: Recovery of Tin from Tin Cans

Exercise 1. A Small Excess of Both Chlorine and Oxygen



We are again calculating the tin recovery based on 1 mol of Sn.

The number of moles of the exposed iron are variable.

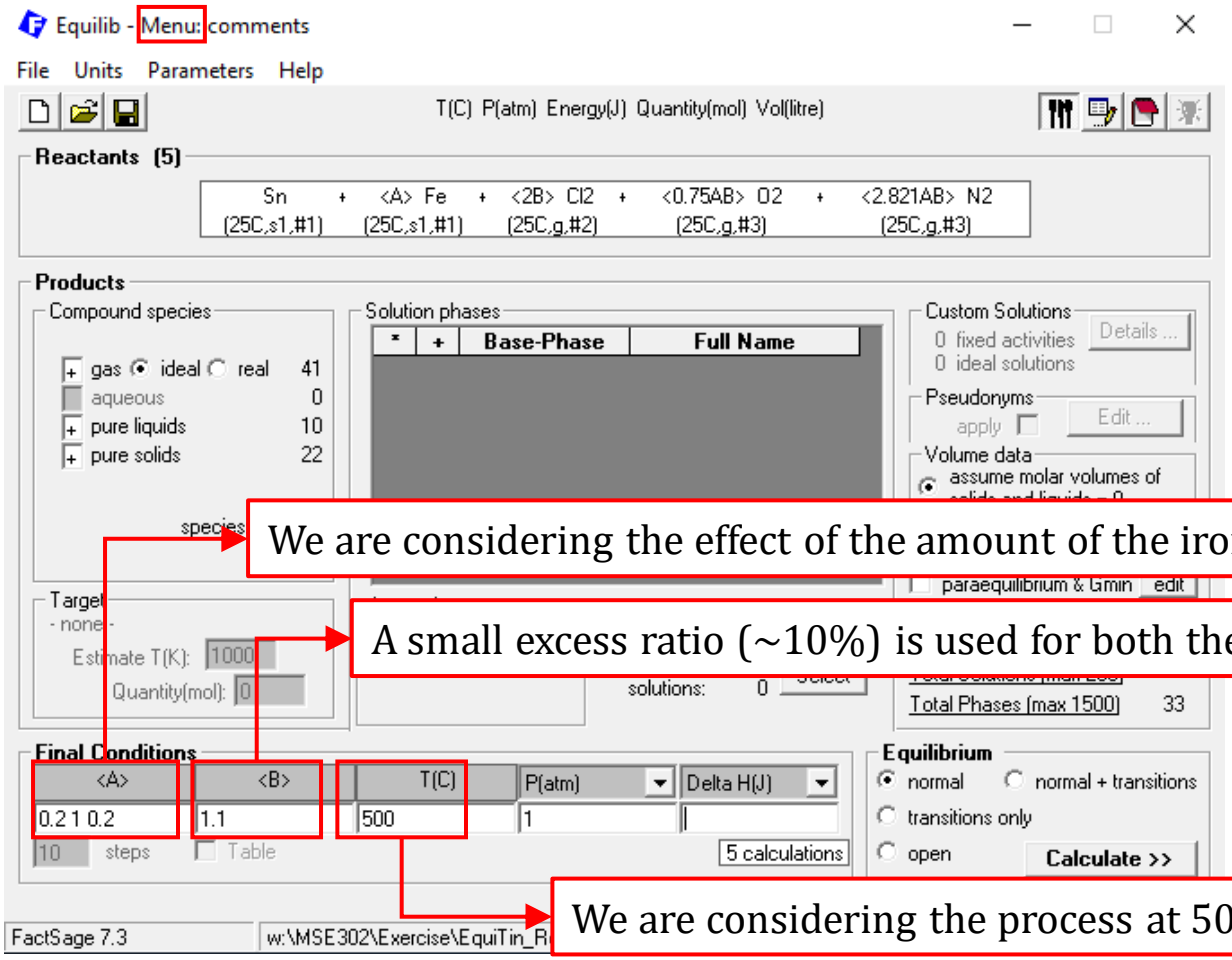
To recover 1 mol of Sn as $SnCl_4$, 2 mol of Cl_2 are required. By multiplying a factor <B> greater than 1, we are providing excess Cl_2, and the excess ratio is calculated as $(B - 1) \times 100\%$.
If you need help regarding B (beta), right click to open "Help".

To oxidize <A> mol of Fe to Fe_2O_3, at least <0.75A> mol of O_2 are required. If we use the same excess ratio as Cl_2, then the number of moles of O_2 that are supplied are <0.75AB>.

For every mole of O_2 introduced, 3.76 mol of N_2 is introduced.

Equilib Module: Recovery of Tin from Tin Cans

Exercise 1. A Small Excess of Both Chlorine and Oxygen



We are considering the effect of the amount of the iron that is reacting.

A small excess ratio (~10%) is used for both the input chlorine and oxygen.

We are considering the process at 500 °C.

Equilib Module: Recovery of Tin from Tin Cans

Exercise 1. A Small Excess of Both Chlorine and Oxygen

After the calculation, plot the total amount of Sn in the gas phase. For varying amounts of iron reacting, is the recovery of Sn efficient? What are the levels of oxygen and chlorine in the off-gas?

Equilib Module: Recovery of Tin from Tin Cans

Exercise 2. Adding Too Much Air

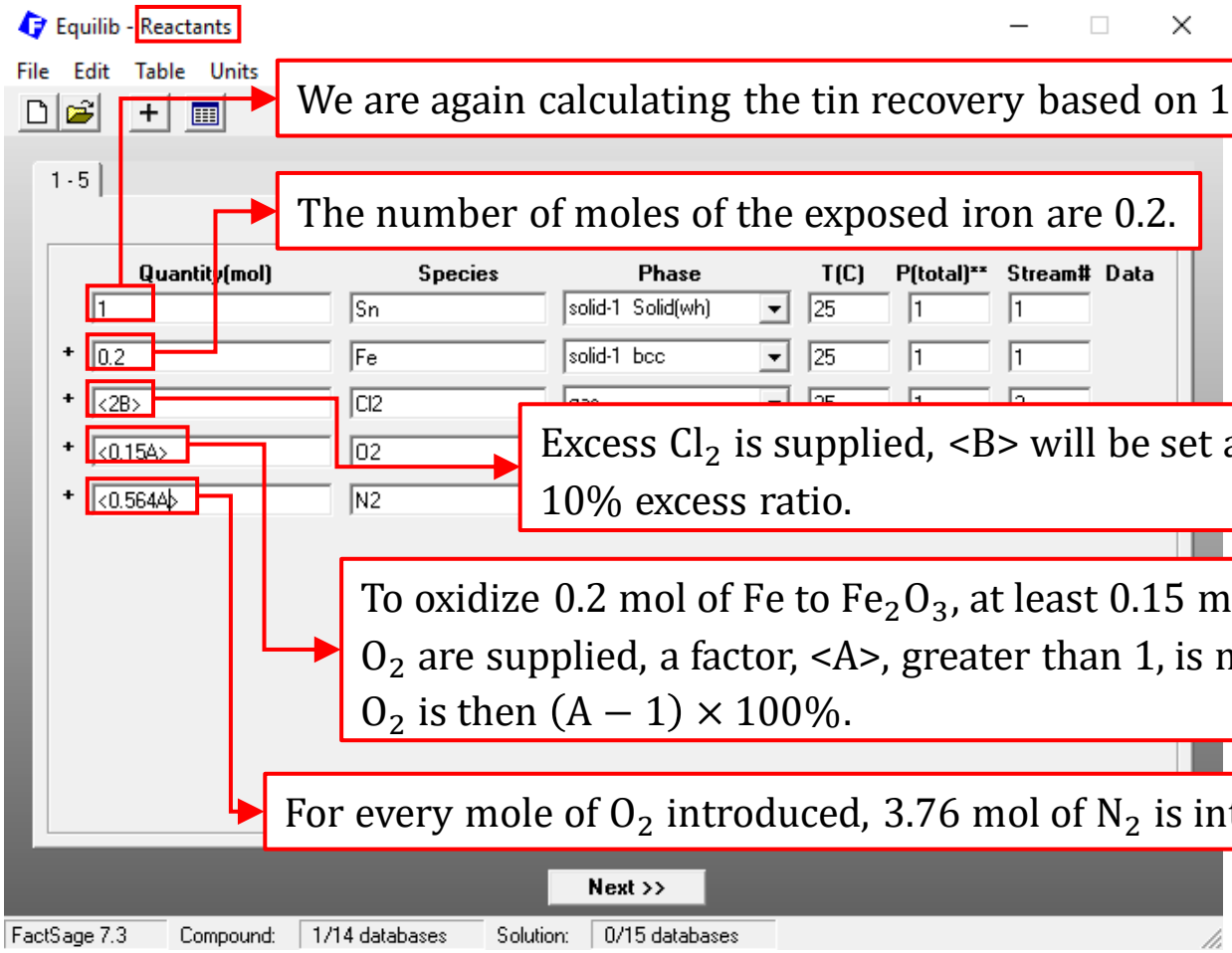
In the second exercise, we will consider the situation if the process is out of control and too much air is introduced to the reactor.

We will consider the fixed amount of the exposed iron: for 1 mol of Sn, 0.2 mol of the exposed iron. For the input chlorine, the excess ratio is set as 10%.

Let us vary the amount of oxygen supplied.

Equilib Module: Recovery of Tin from Tin Cans

Exercise 2. Adding Too Much Air



We are again calculating the tin recovery based on 1 mol of Sn.

The number of moles of the exposed iron are 0.2.

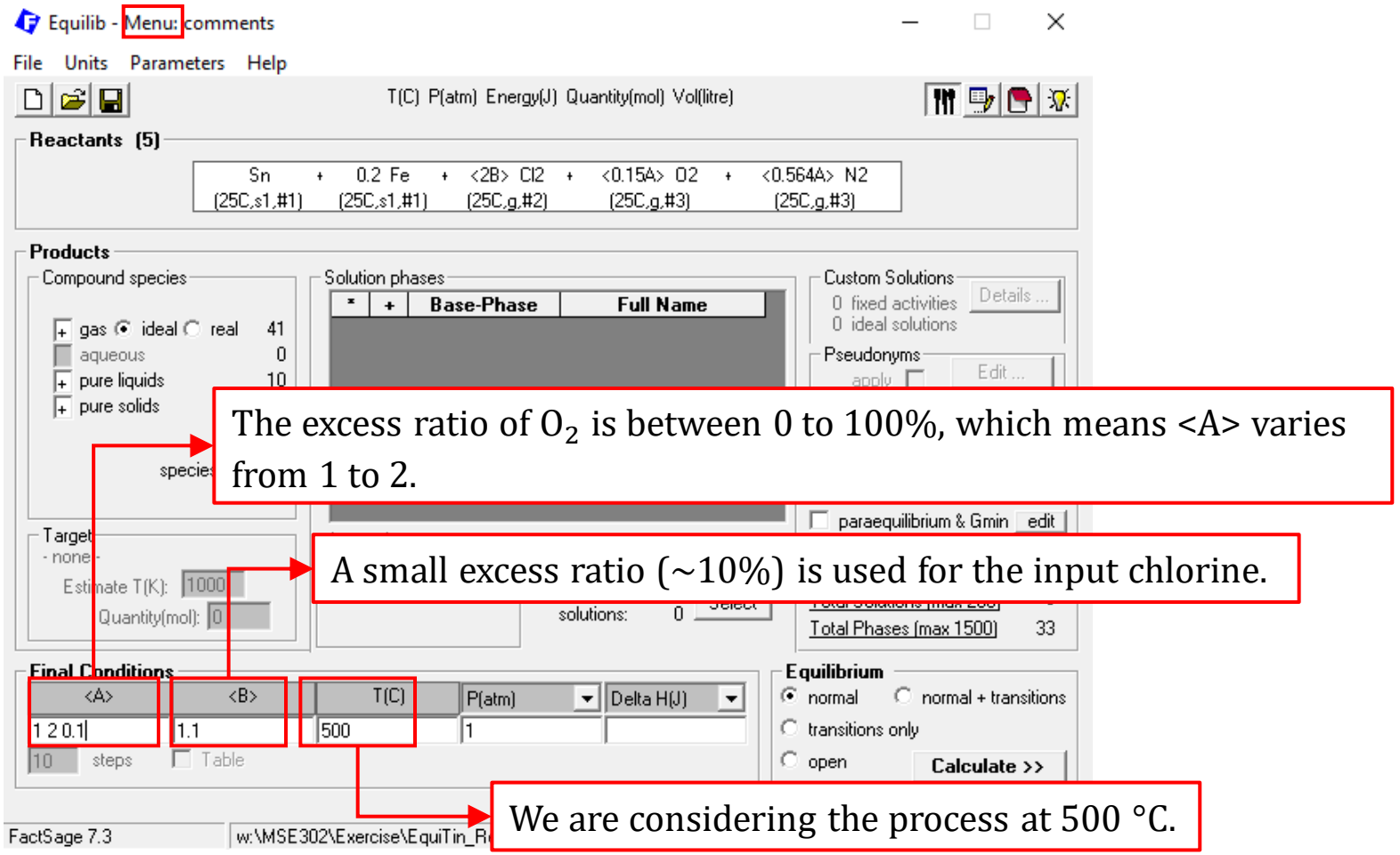
Excess Cl_2 is supplied, <B> will be set as 1.1 (Menu Window) to give 10% excess ratio.

To oxidize 0.2 mol of Fe to Fe_2O_3, at least 0.15 mol of O_2 are required. If excess O_2 are supplied, a factor, <A>, greater than 1, is multiplied. The excess ratio of O_2 is then $(A - 1) \times 100\%$.

For every mole of O_2 introduced, 3.76 mol of N_2 is introduced.

Equilib Module: Recovery of Tin from Tin Cans

Exercise 2. Adding Too Much Air



The excess ratio of O_2 is between 0 to 100%, which means <A> varies from 1 to 2.

A small excess ratio (~10%) is used for the input chlorine.

We are considering the process at 500 °C.

Equilib Module: Recovery of Tin from Tin Cans

Exercise 2. Adding Too Much Air

After the calculation, plot the number of moles of $SnCl_4(g)$, $Cl_2(g)$, $Fe_2O_3(s)$ and $SnO_2(s)$ against <A>. With increasing the excess oxygen supplied, is Sn efficiently recovered to the gas stream? Why?

Also, plot the mole fraction of oxygen in the off-gas against <A>. If the oxygen level in the off-gas is measured and it reaches ~150 ppm, you would know to cut back on the air feed to the reactor. This means that it would be possible, at least in principle, to use an oxygen analyzer to drive an air flow control valve.

Note that the partial pressure of oxygen does not rise very steeply with excess air, because it is "buffered" by the formation of SnO_2. The formation of SnO_2 means that less chlorine is used for chlorination of Sn so that chlorine will rise in tandem with oxygen, and the chlorine is present at much higher concentrations (please plot the mole fraction of chlorine in the off-gas against <A>).

Equilib Module: Recovery of Tin from Tin Cans

Exercise 2. Adding Too Much Air

In an actual process, the excess Cl_2 supplied to the reactor would result in the presence of free Cl_2 in the off-gas. It would be necessary to keep the free Cl_2 in the off-gas in a range of 11~20 vol.%, or even higher, to provide the driving force for the chlorination process. This requires a careful control of the addition rate of chlorine. The free Cl_2 in the off-gas can be recovered and recycled.

Equilib Module: Recovery of Tin from Tin Cans

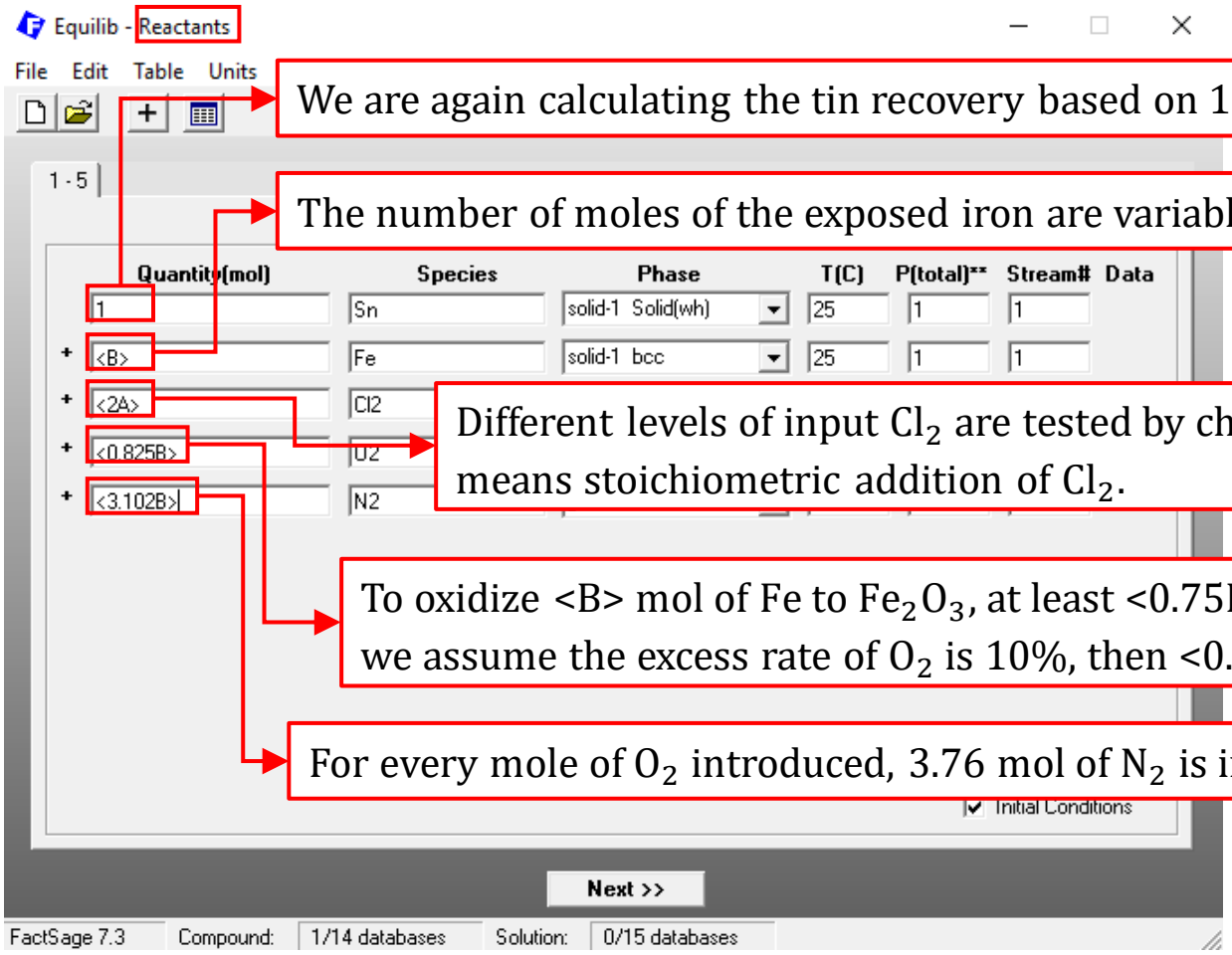
Exercise 3. Changing the Amounts of Both Chlorine and Iron to the Reactor

In the third exercise, we will be looking at the effects of the varying amounts of both Cl_2 and the exposed iron that reacts on the chlorination process. This can be done by setting the amounts of Cl_2 and iron as variables (next page).

Note: when <B> is used, the calculations are repeated for each value.

Equilib Module: Recovery of Tin from Tin Cans

Exercise 3. Changing the Amounts of Both Chlorine and Iron to the Reactor



We are again calculating the tin recovery based on 1 mol of Sn.

The number of moles of the exposed iron are variable <B>.

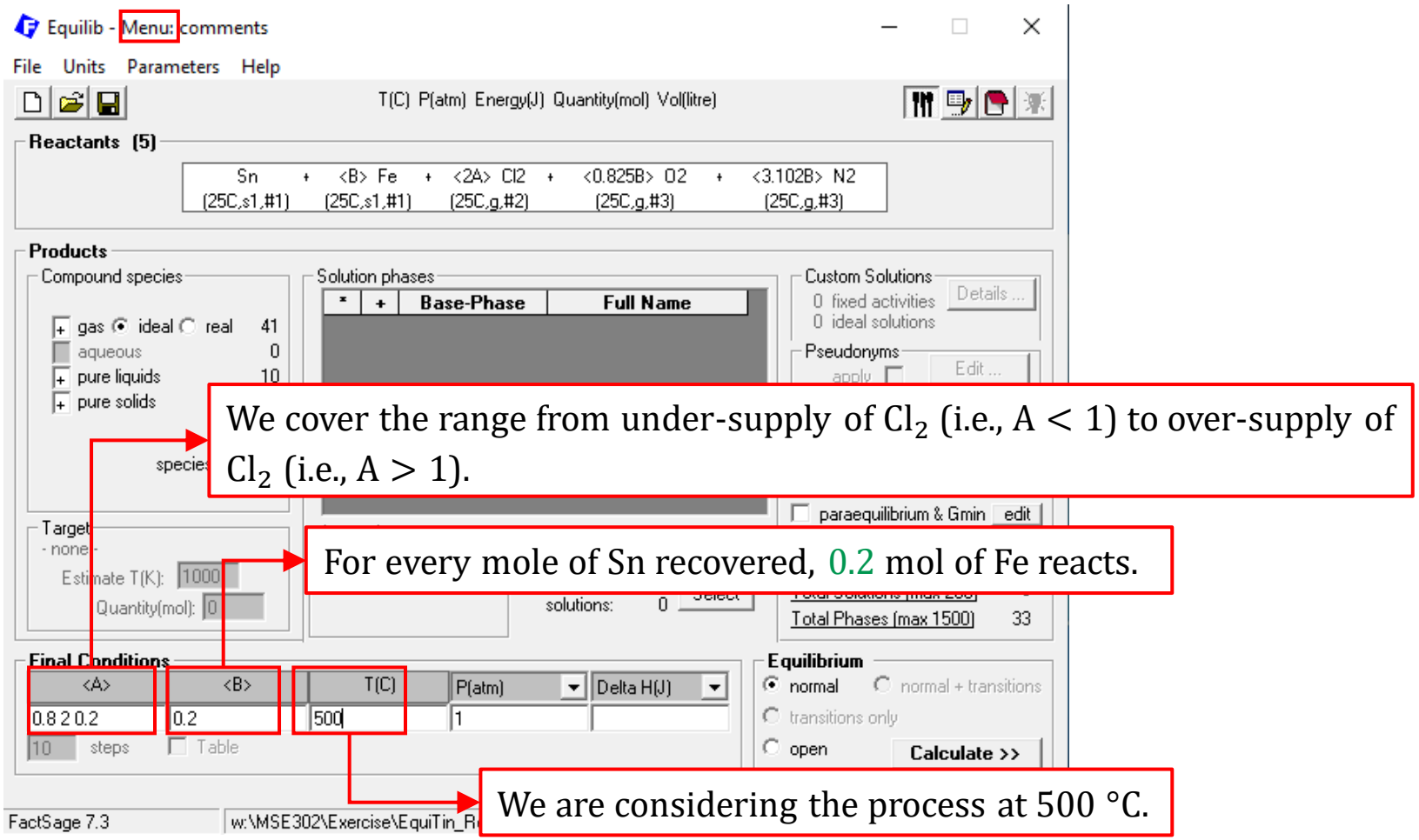
Different levels of input Cl_2 are tested by changing <A>: $A = 1$ means stoichiometric addition of Cl_2.

To oxidize <B> mol of Fe to Fe_2O_3, at least <0.75B> mol of O_2 are required. If we assume the excess rate of O_2 is 10%, then <0.825B> mol of O_2 are added.

For every mole of O_2 introduced, 3.76 mol of N_2 is introduced.

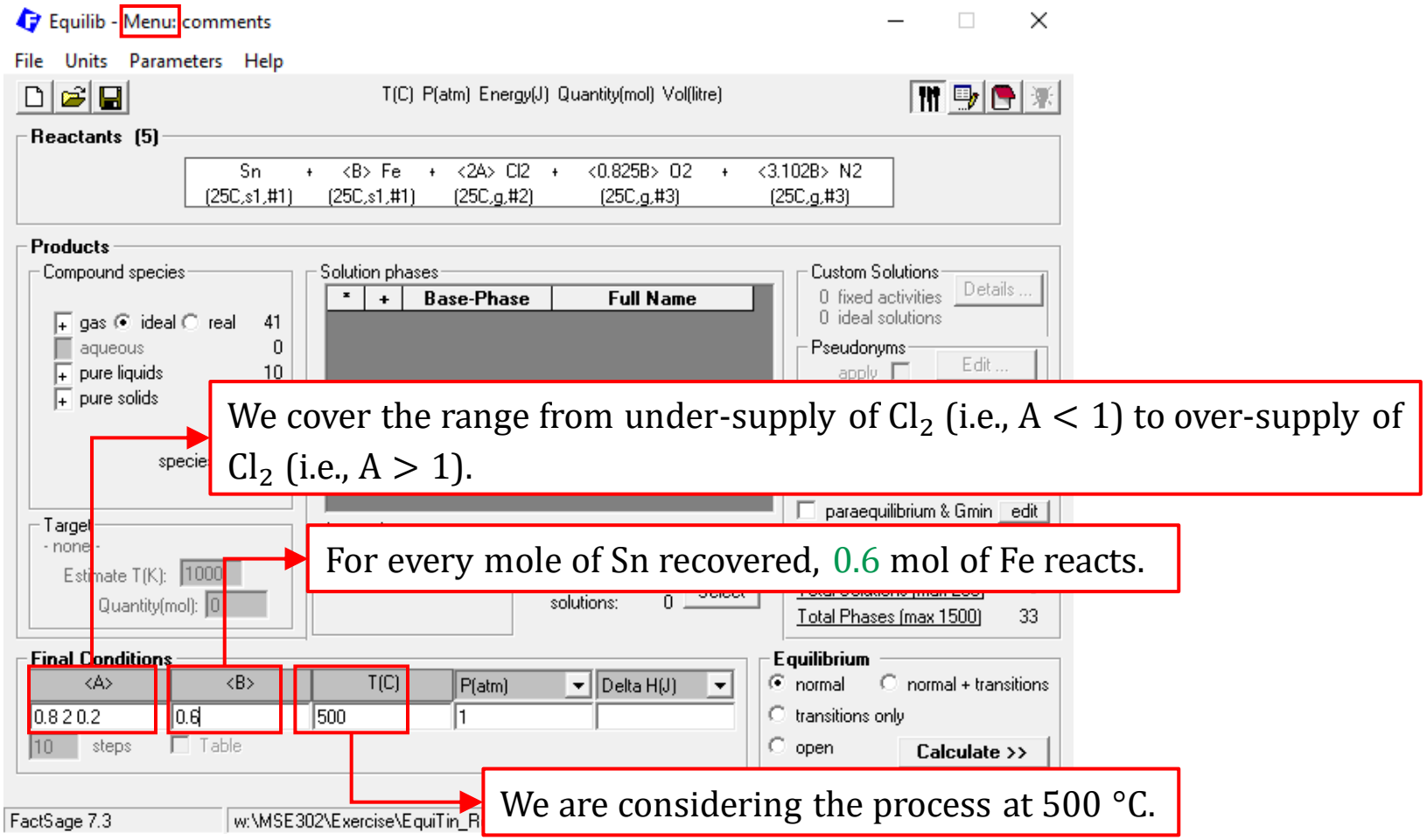
Equilib Module: Recovery of Tin from Tin Cans

Exercise 3. Changing the Amounts of Both Chlorine and Iron to the Reactor



Equilib Module: Recovery of Tin from Tin Cans

Exercise 3. Changing the Amounts of Both Chlorine and Iron to the Reactor



Equilib Module: Recovery of Tin from Tin Cans

Exercise 3. Changing the Amounts of Both Chlorine and Iron to the Reactor

After each calculation with different <B>, plot the levels of oxygen and chlorine in the off-gas (e.g., mol fraction) against <A>.

Save the three graphs and use the Figure Module to superimpose them. Make sure you use different line types so that the conditions can be differentiated.

(a) From the superimposed graph, can you see the correlation between the oxygen level in the off-gas and the chlorine supplied to the reactor?

(b) Can you suggest proper operating conditions (i.e., <A> and <B> values) based on the total Sn recovered to the gas phase?

(c) Given $B = 2$, if we wish to increase the recovery of Sn to the gas phase, should we increase or decrease the excess rate of O_2?

Equilib Module: Recovery of Tin from Tin Cans

Final Thought

You need to be aware that all the above calculations that have been performed using FactSage are equilibrium calculations. The real process may behave differently, because of kinetics.

Equilib Module: Oxidation of Iron

The oxidation of metals is one of the very important chemical reactions. Take the oxidation of iron for example. The species that may exist at equilibrium include metallic iron (bcc, fcc) and various types of iron oxides. The thermodynamic data for metallic iron are stored in FactPS, and the data for oxides can be found in both FactPS and FToxid. (You should use the View Data Module to check the Compounds and Solutions for the Fe-O system)

Reminder: when multiple thermodynamic databases are selected, special care must be taken so that the same compound is selected only once.

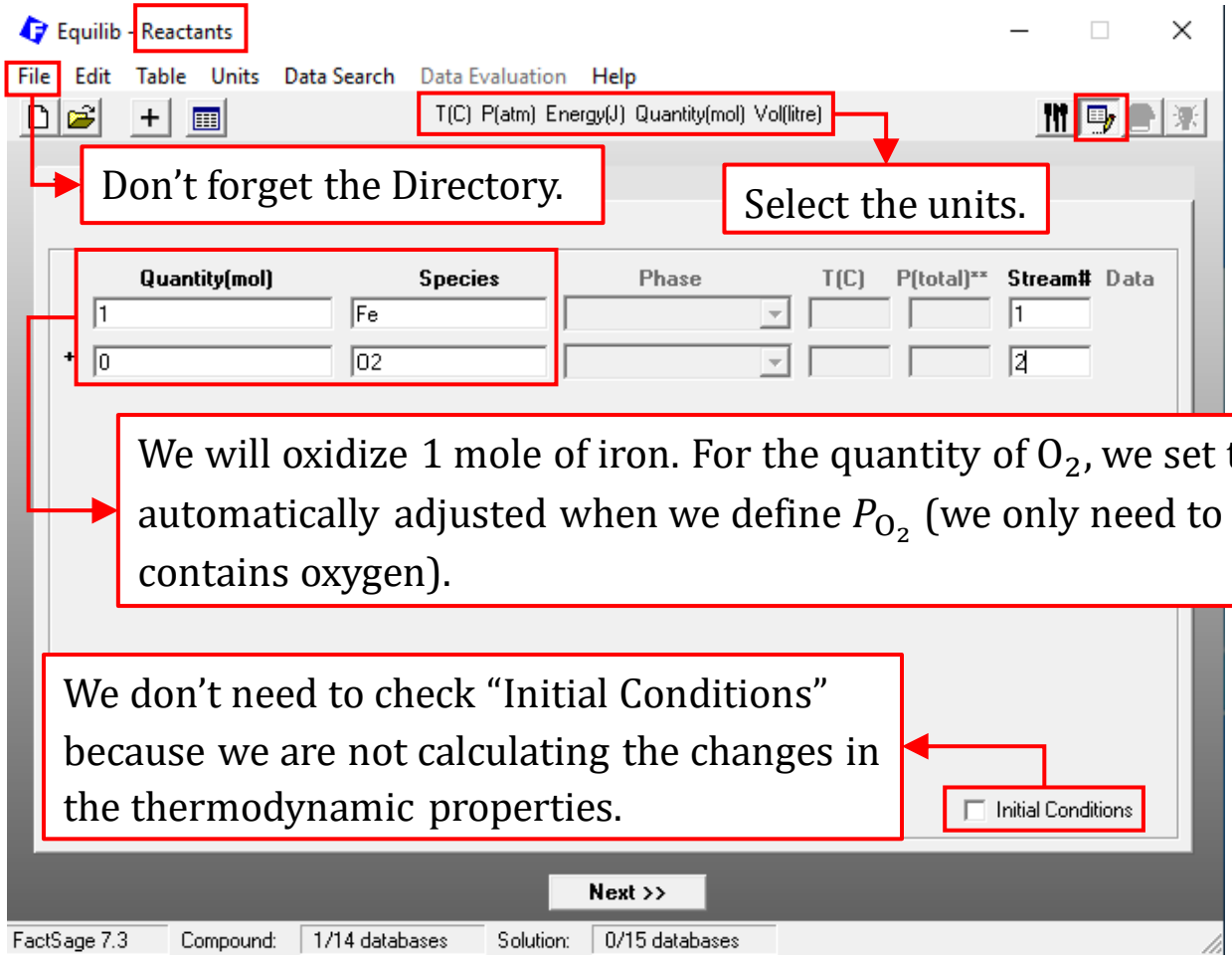
For iron oxides, iron can take the oxidation state of Fe^{2+} and Fe^{3+}. To aid your understanding, we can view Fe^{2+} and Fe^{3+} as two separate species. The relative amounts of Fe^{2+} and Fe^{3+} depend on the oxygen potential (i.e., oxygen partial pressure). Therefore, when calculating the equilibrium involving the metal oxides with different oxidation states, the oxygen partial pressure, P_{O_2}, must be specified. The input amount of the gas component will be automatically adjusted so that the desired P_{O_2} is met.

Equilib Module: Oxidation of Iron

Let us study the oxidation of iron by looking at the dependence of the oxidation state of iron on the oxygen partial pressure. We will adjust P_{O_2} and see what iron oxide is stable. We will fix the temperature at 1400 °C, the pressure at 1 atm.

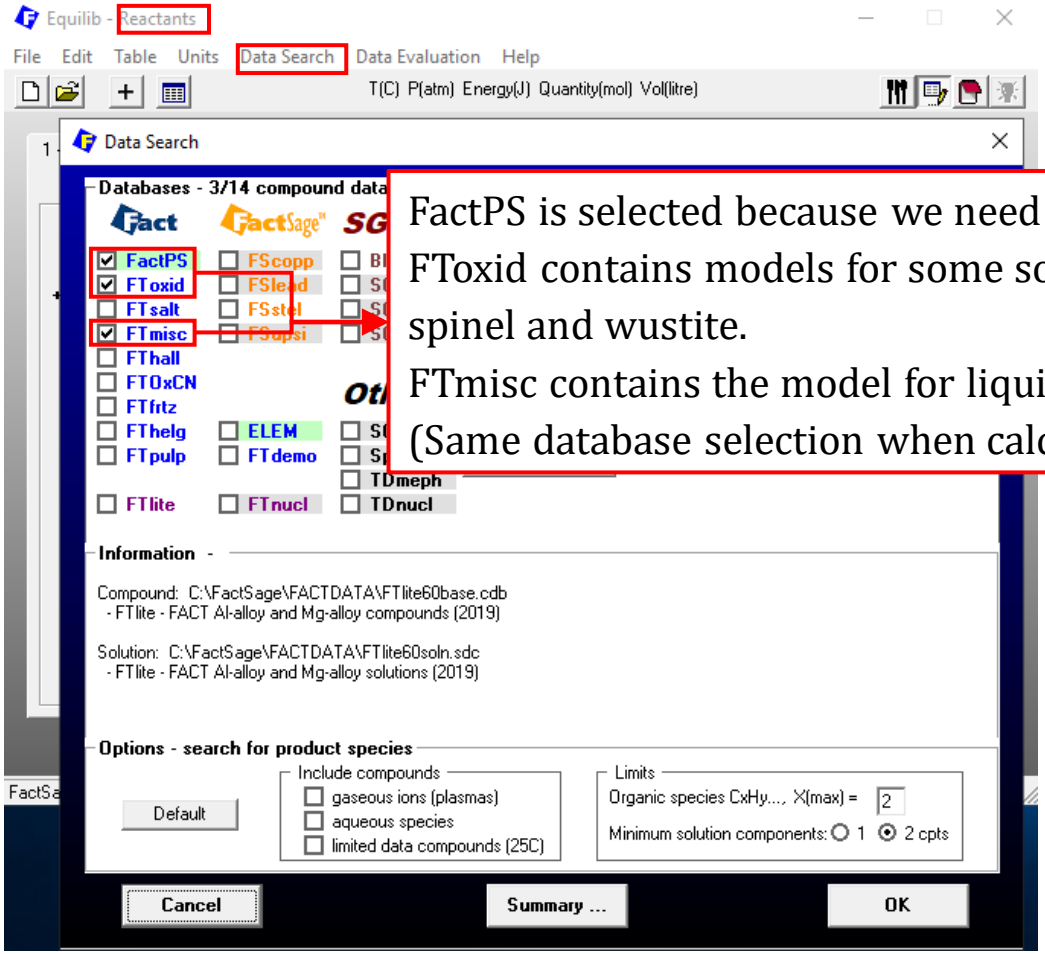
Equilib Module: Oxidation of Iron

Reactants Window



Equilib Module: Oxidation of Iron

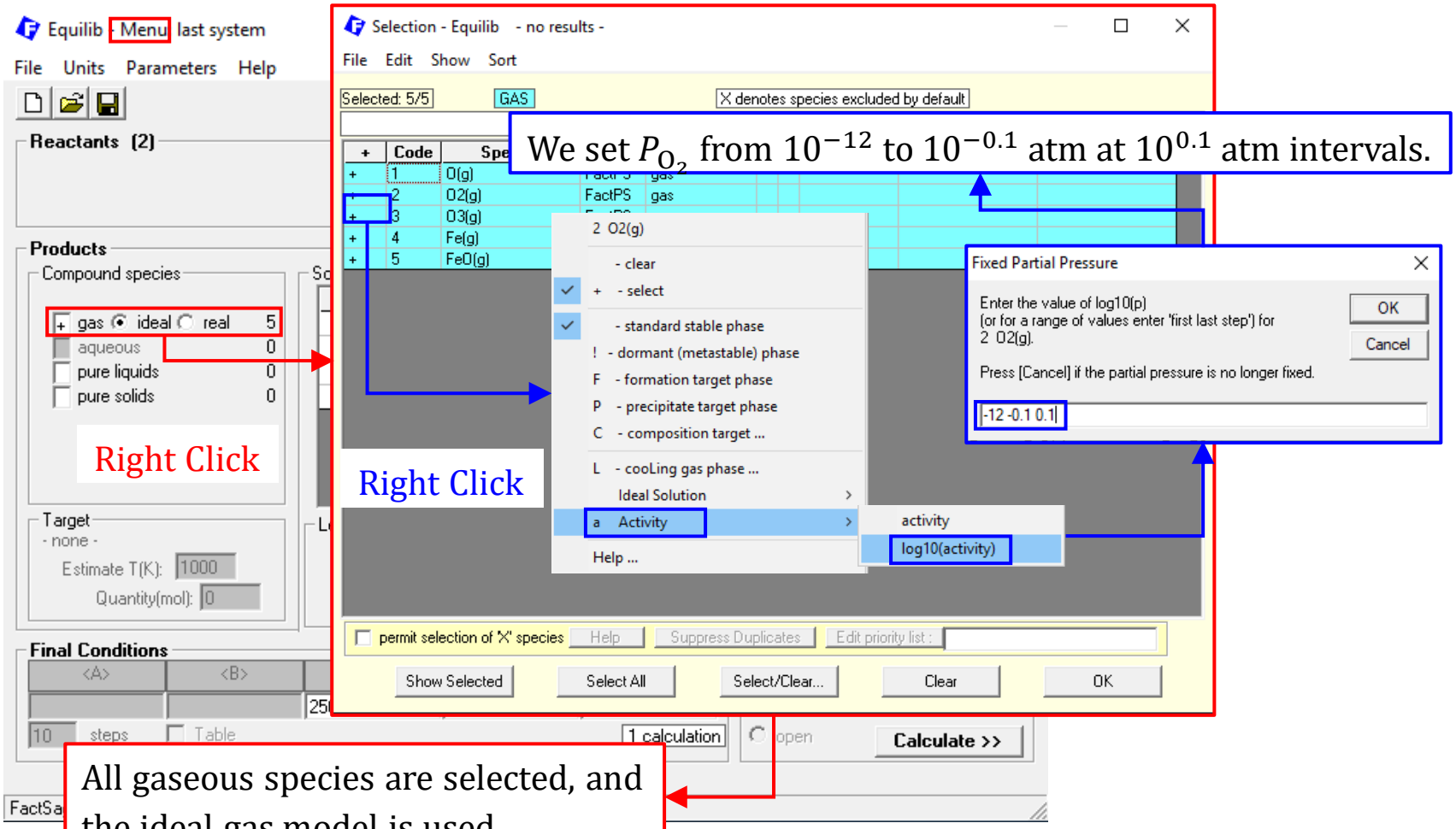
Reactants Window: Database(s)



FactPS is selected because we need to consider $O_2(g)$.
FToxid contains models for some solid solutions of iron oxide, for example, spinel and wustite.
FTmisc contains the model for liquid Fe with limited solubility of oxygen. (Same database selection when calculating the Fe-O_2 phase diagram.)

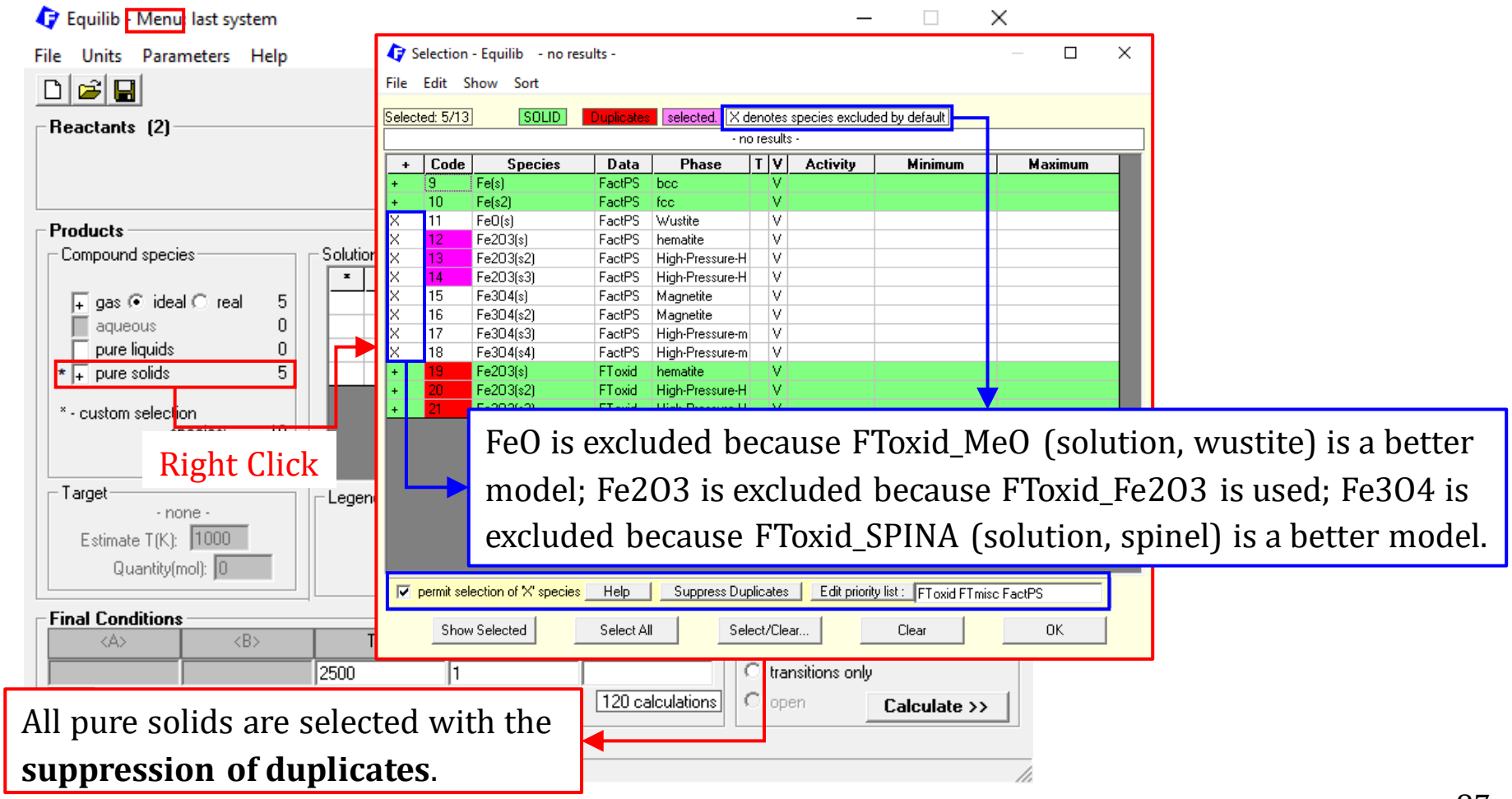
Equilib Module: Oxidation of Iron

Menu Window: Set P_{O_2}



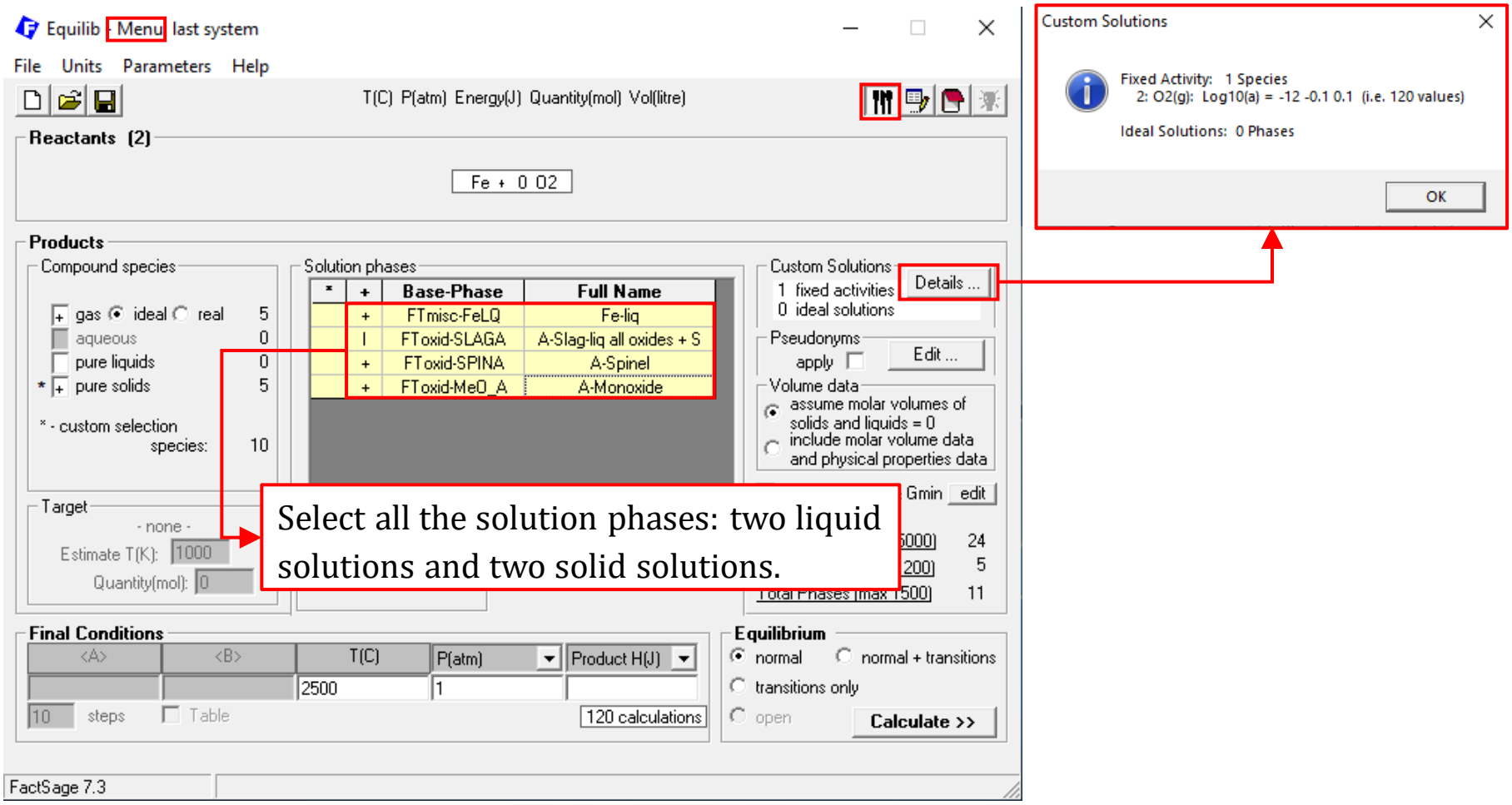
Equilib Module: Oxidation of Iron

Menu Window: Select Pure Solids



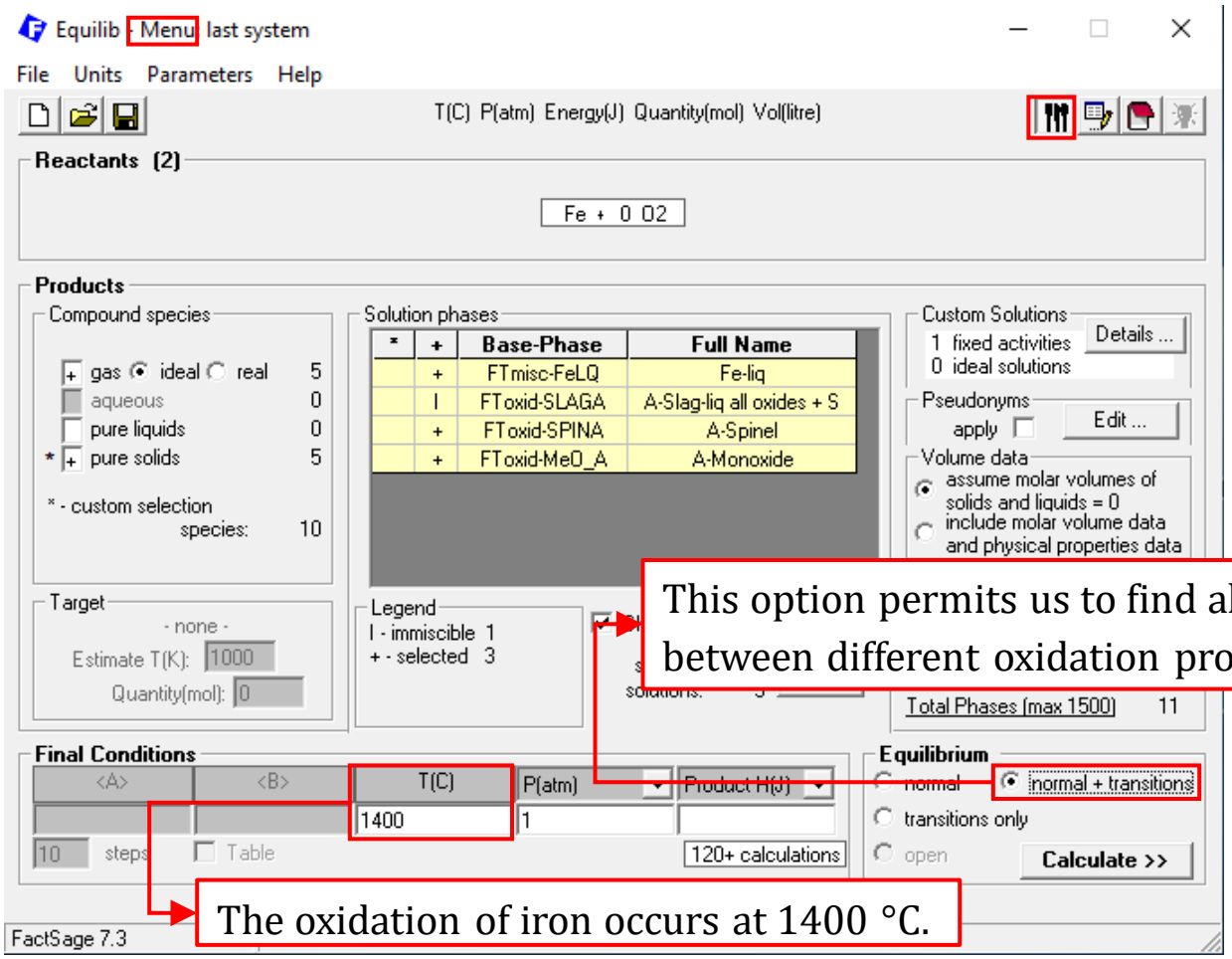
Equilib Module: Oxidation of Iron

Menu Window: Select Solution Phases



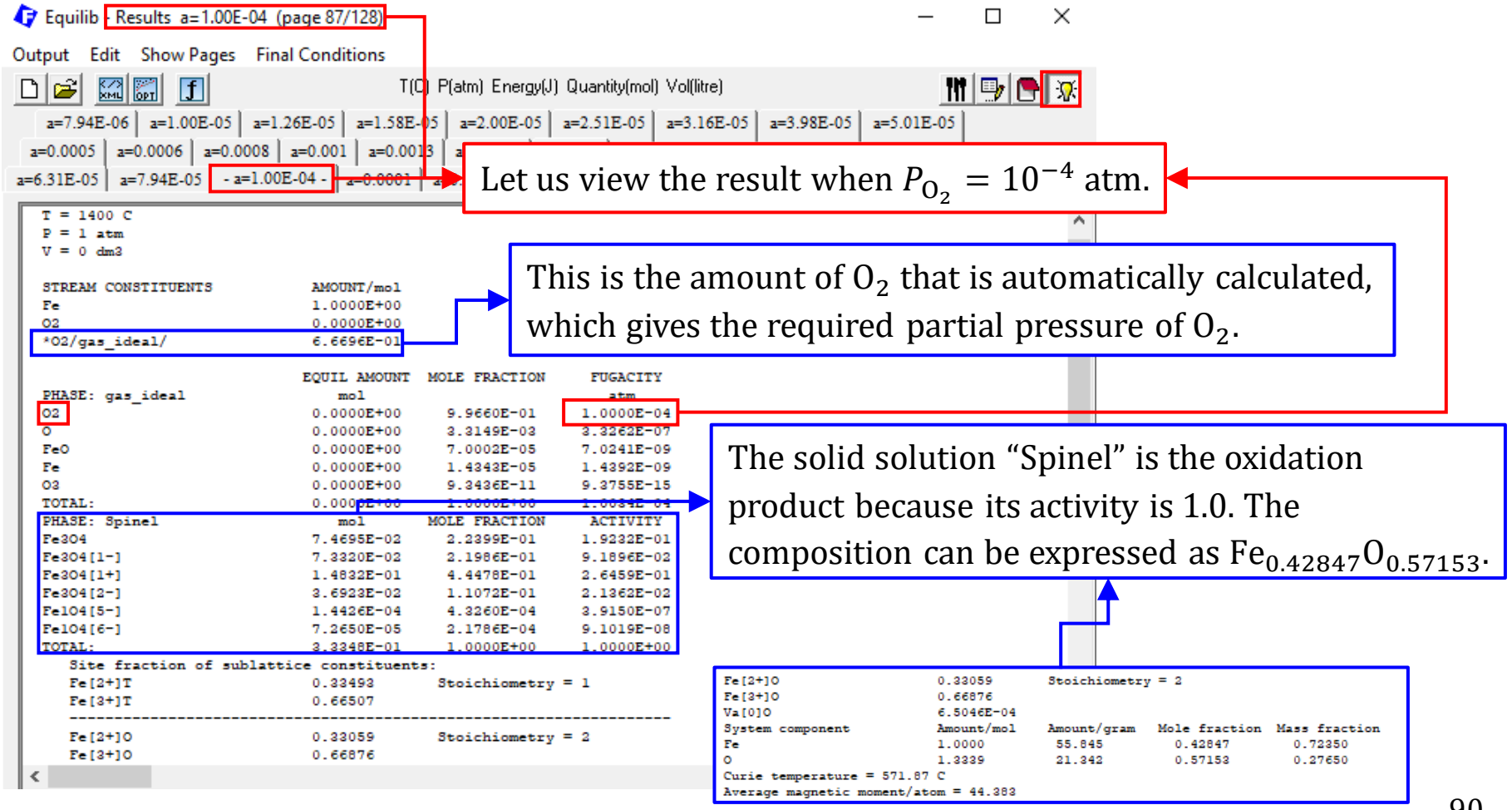
Equilib Module: Oxidation of Iron

Menu Window: Set Final Conditions



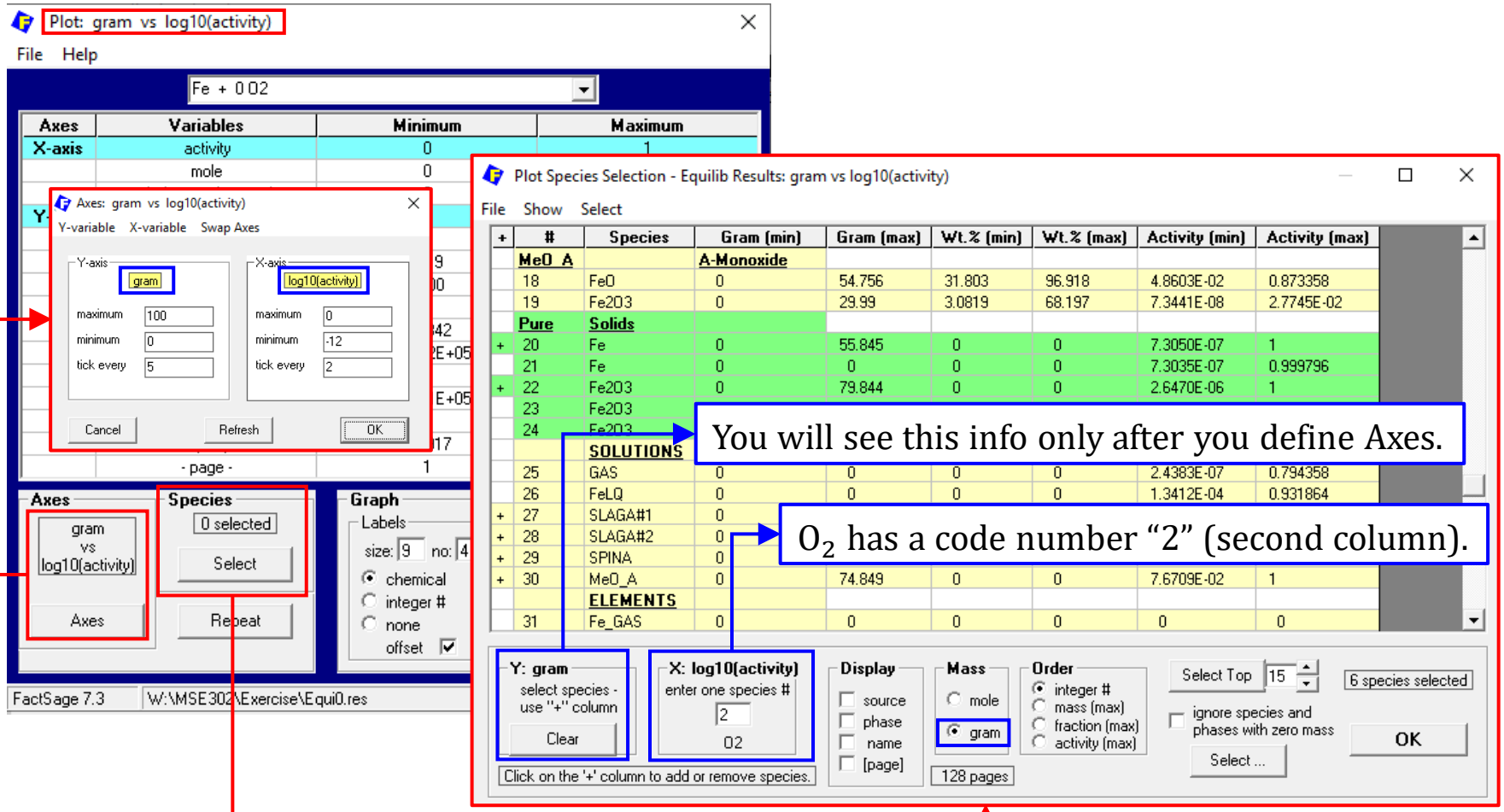
Equilib Module: Oxidation of Iron

Results: When $P_{O_2} = 10^{-4}$ atm



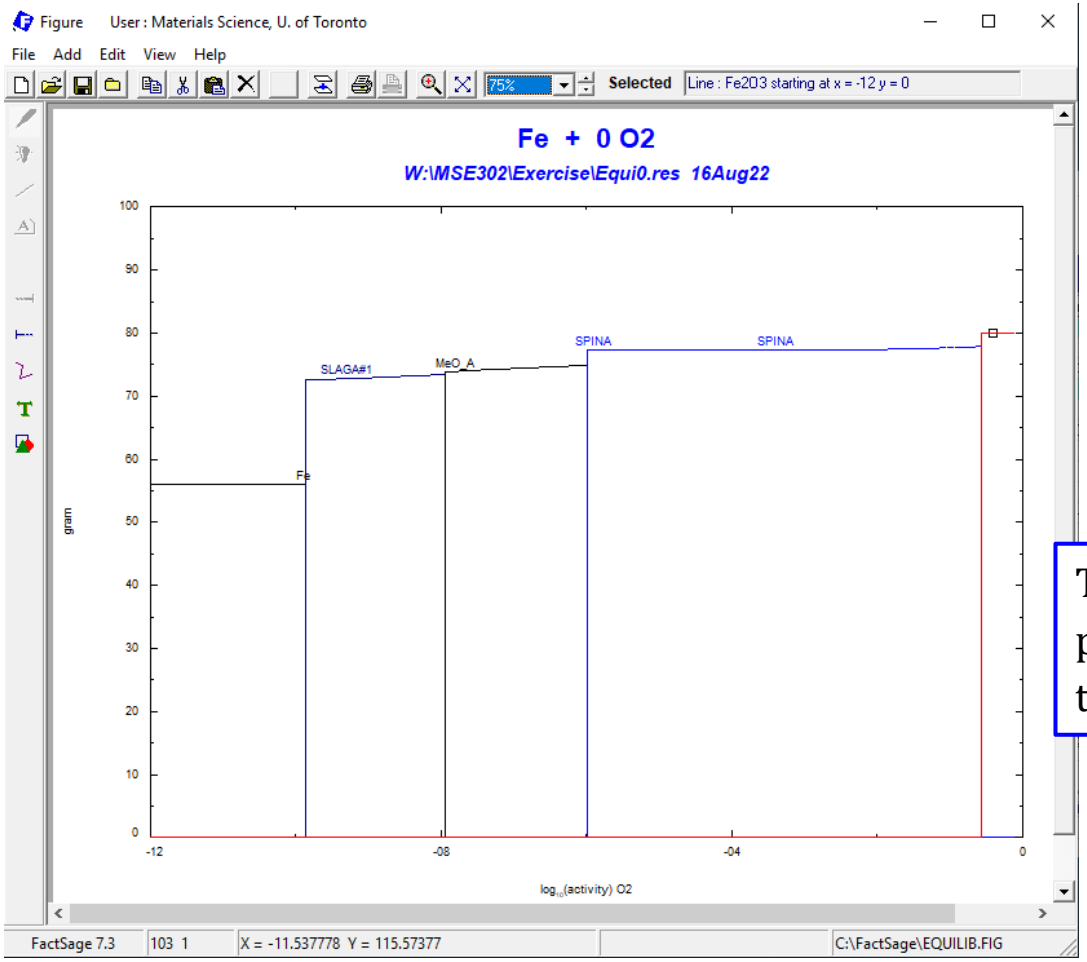
Equilib Module: Oxidation of Iron

Results: Plot the masses of oxidation products, i.e., gram~P_{O_2}.



Equilib Module: Oxidation of Iron

Results: Plot the masses of oxidation products, i.e., gram~P_{O_2}.



This graph shows that the oxidation products at 1400 °C are affected by the oxygen partial pressure.

Equilib Module: Mixing Properties

Recall we studied the **solution** properties by looking at an **isothermal mixing process** (Chapter 4.3). Now let us calculate some mixing properties using the Equilib Module.

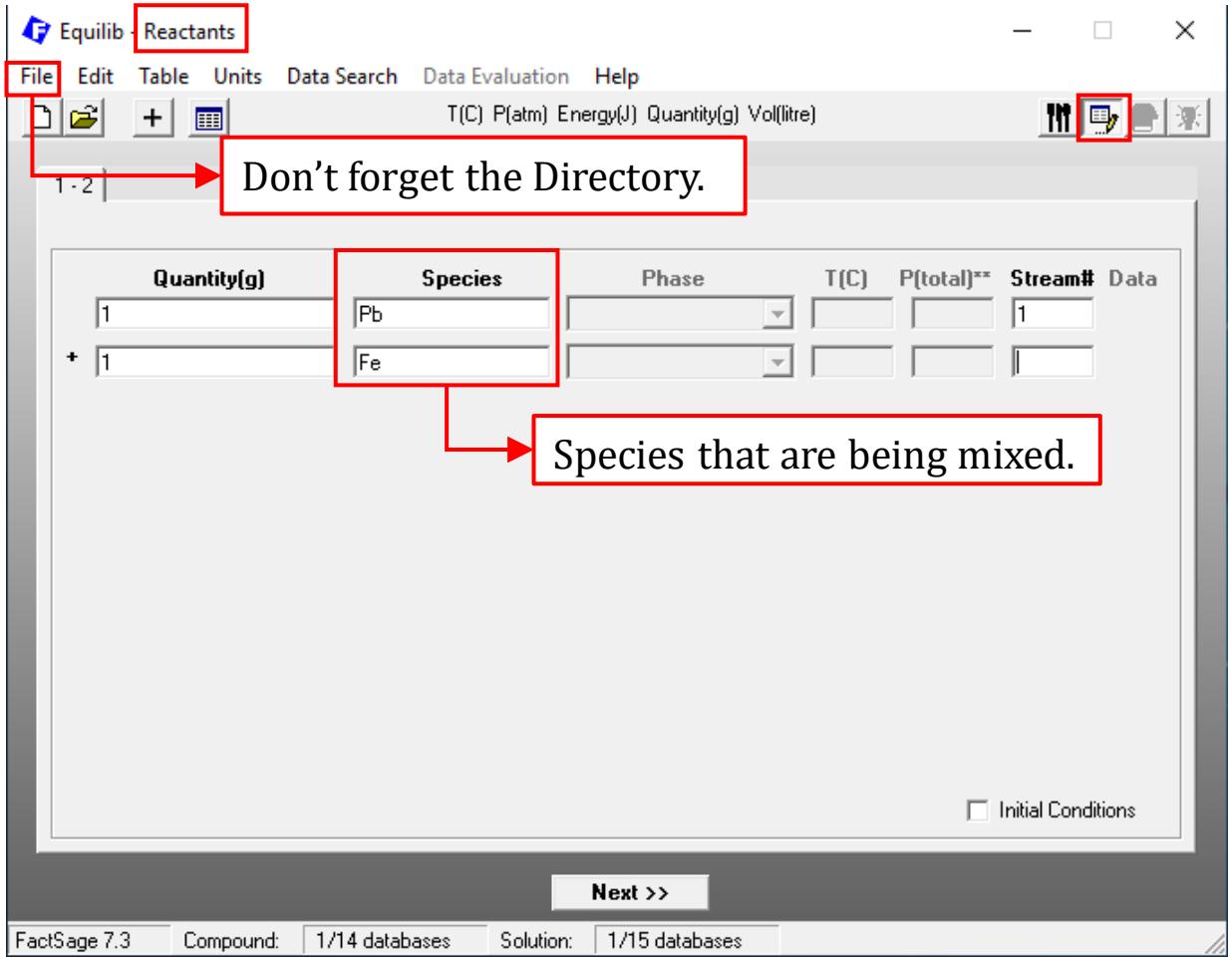
Say we would like to mix varying amounts of liquid Pb and liquid Fe at 2500 °C and 1 atm. We assume the total amount of Pb and Fe is 1 mole.

The mixing process can be described as the following:

$$X_{\mathrm{Pb}}\mathrm{Pb}(l) + (1 - X_{\mathrm{Pb}})\mathrm{Fe}(l) \xrightarrow{2500\ ^{\circ}\mathrm{C},1\ \mathrm{atm}} 1\ \mathrm{mole\ Solution}$$

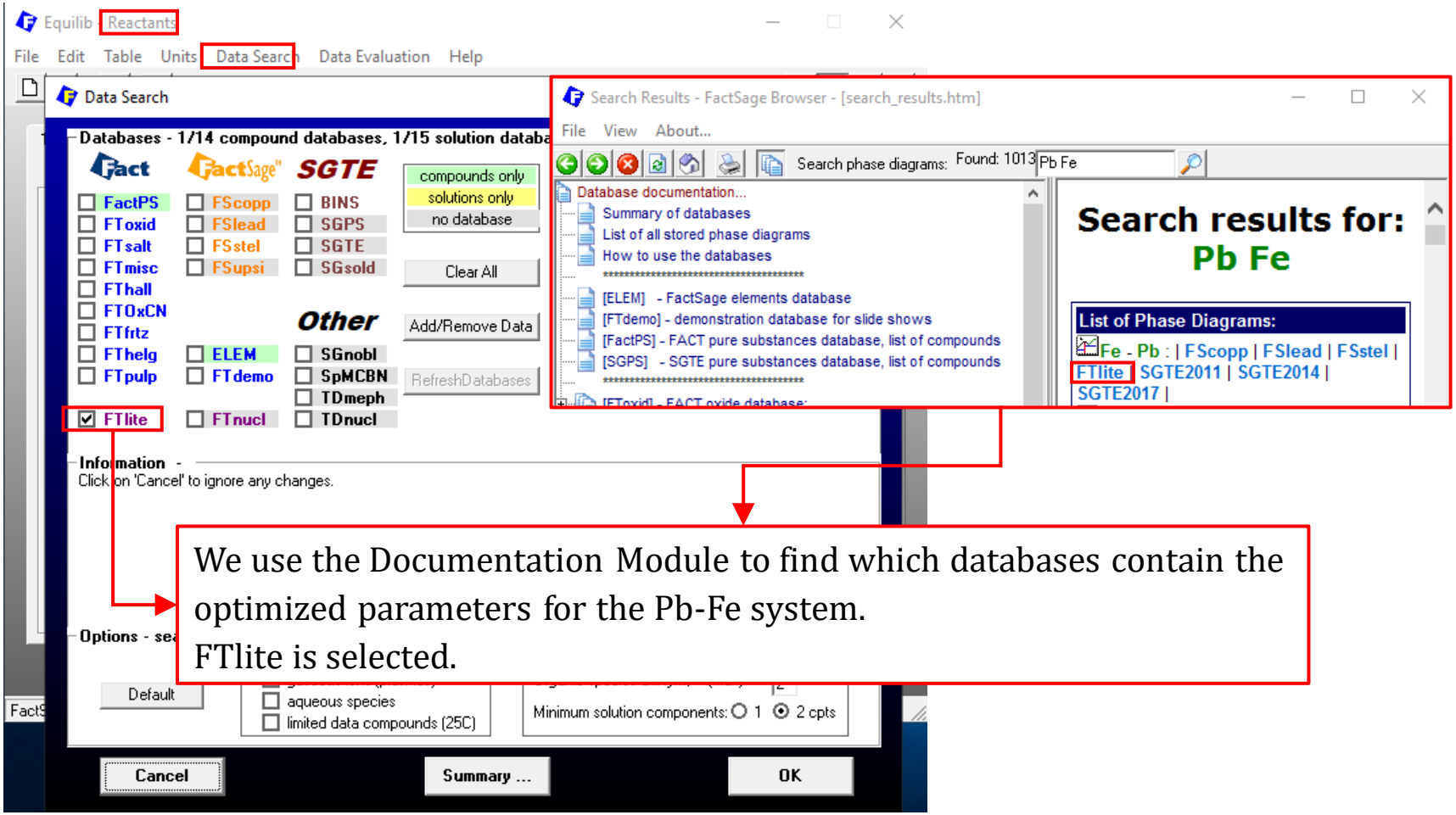
Equilib Module: Mixing Properties

Reactants Window: Define Reactants



Equilib Module: Mixing Properties

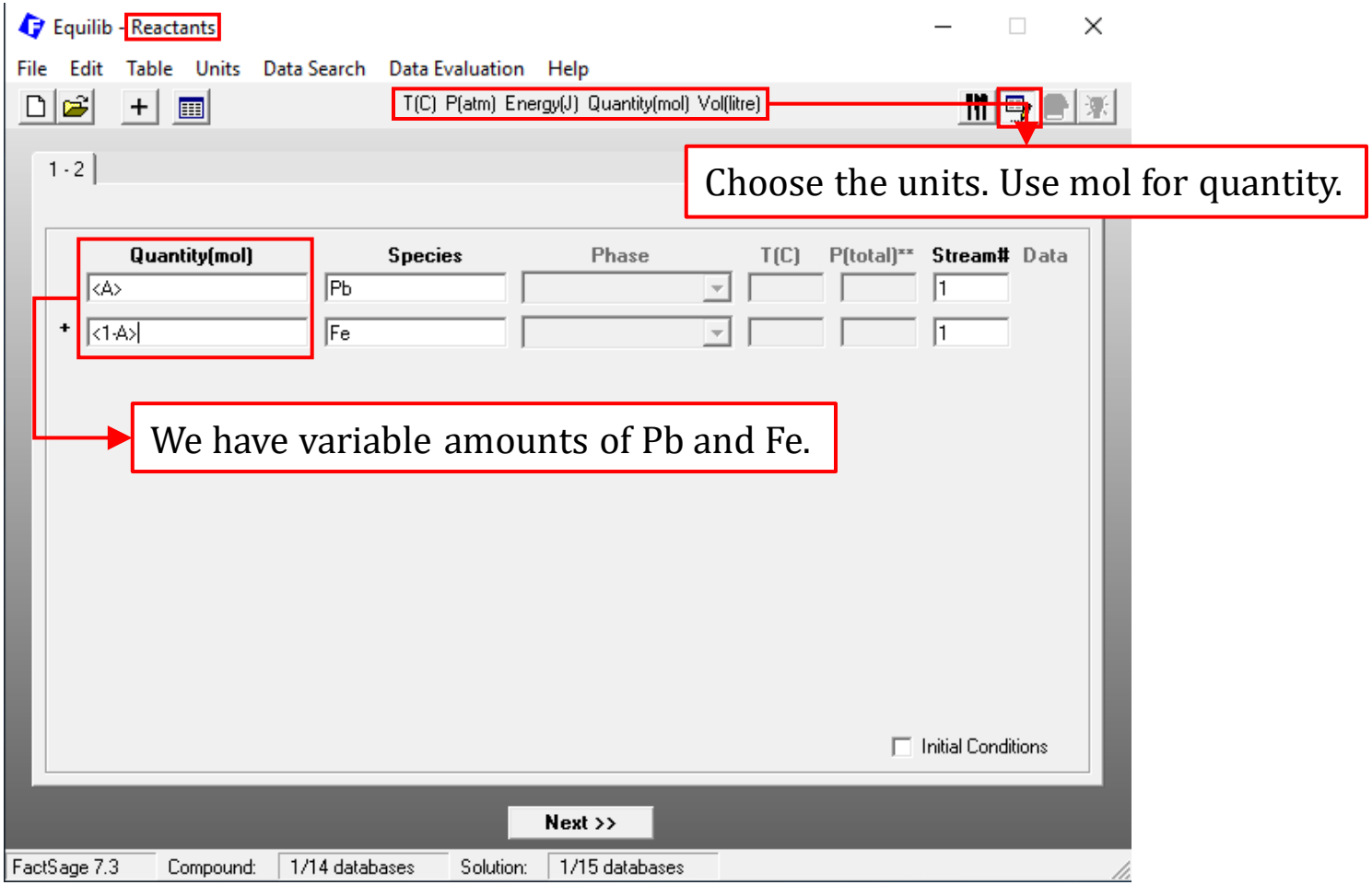
Reactants Window: Database(s)



We use the Documentation Module to find which databases contain the optimized parameters for the Pb-Fe system.
FTlite is selected.

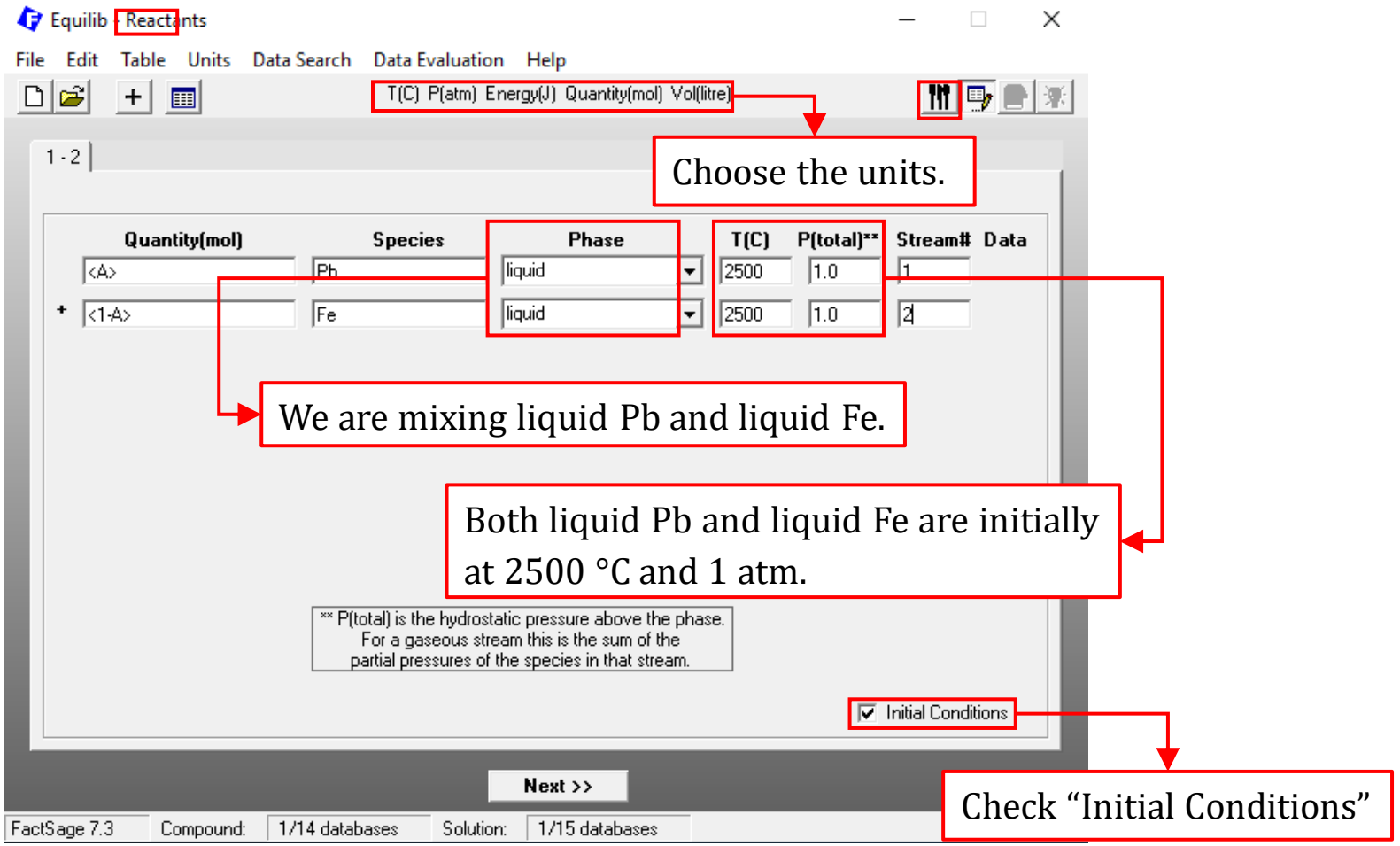
Equilib Module: Mixing Properties

Reactants Window: Choose Units and Input the Quantity of Species



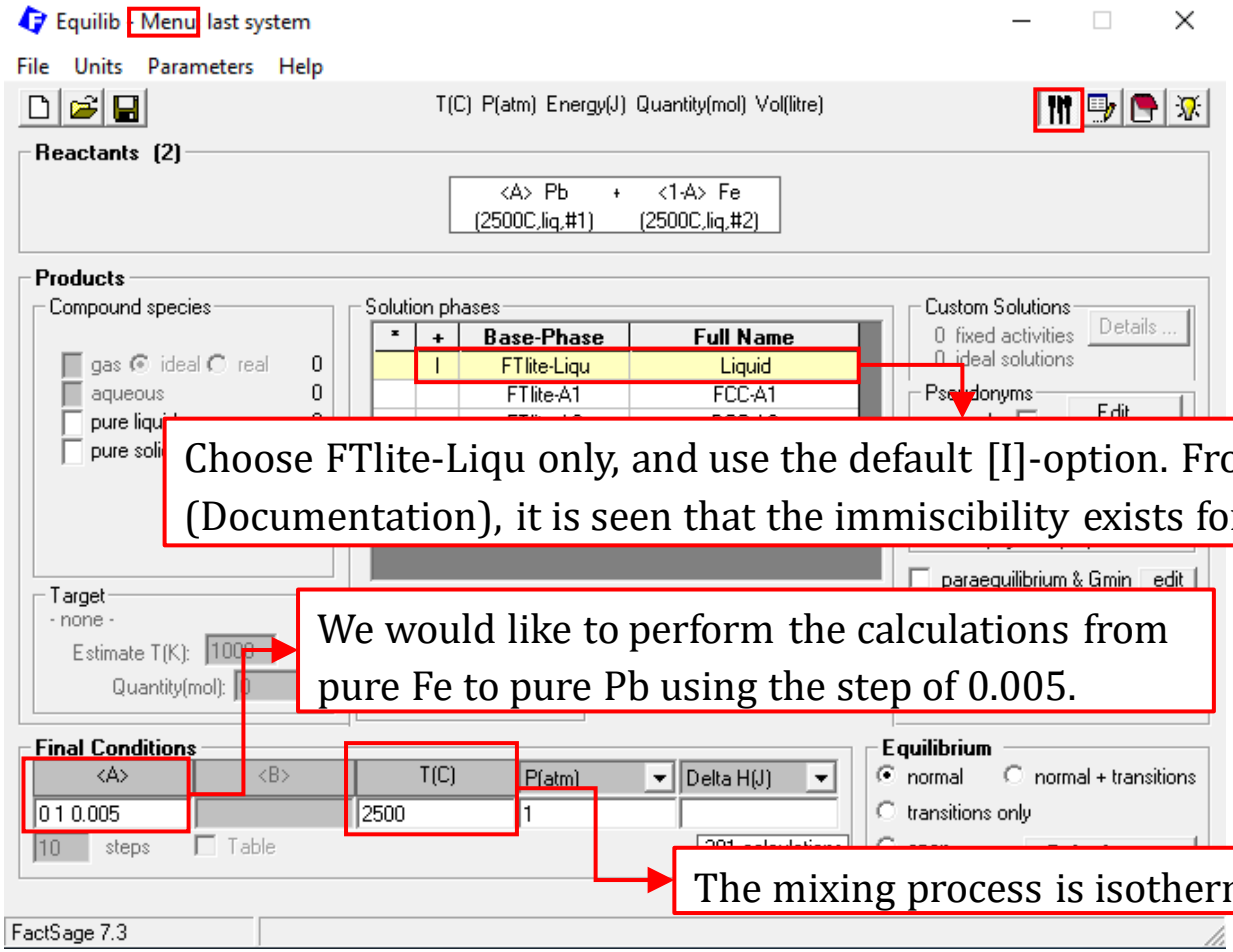
Equilib Module: Mixing Properties

Reactants Window: Specify the Initial Conditions



Equilib Module: Mixing Properties

Menu Window: Select Products and Define Final Conditions



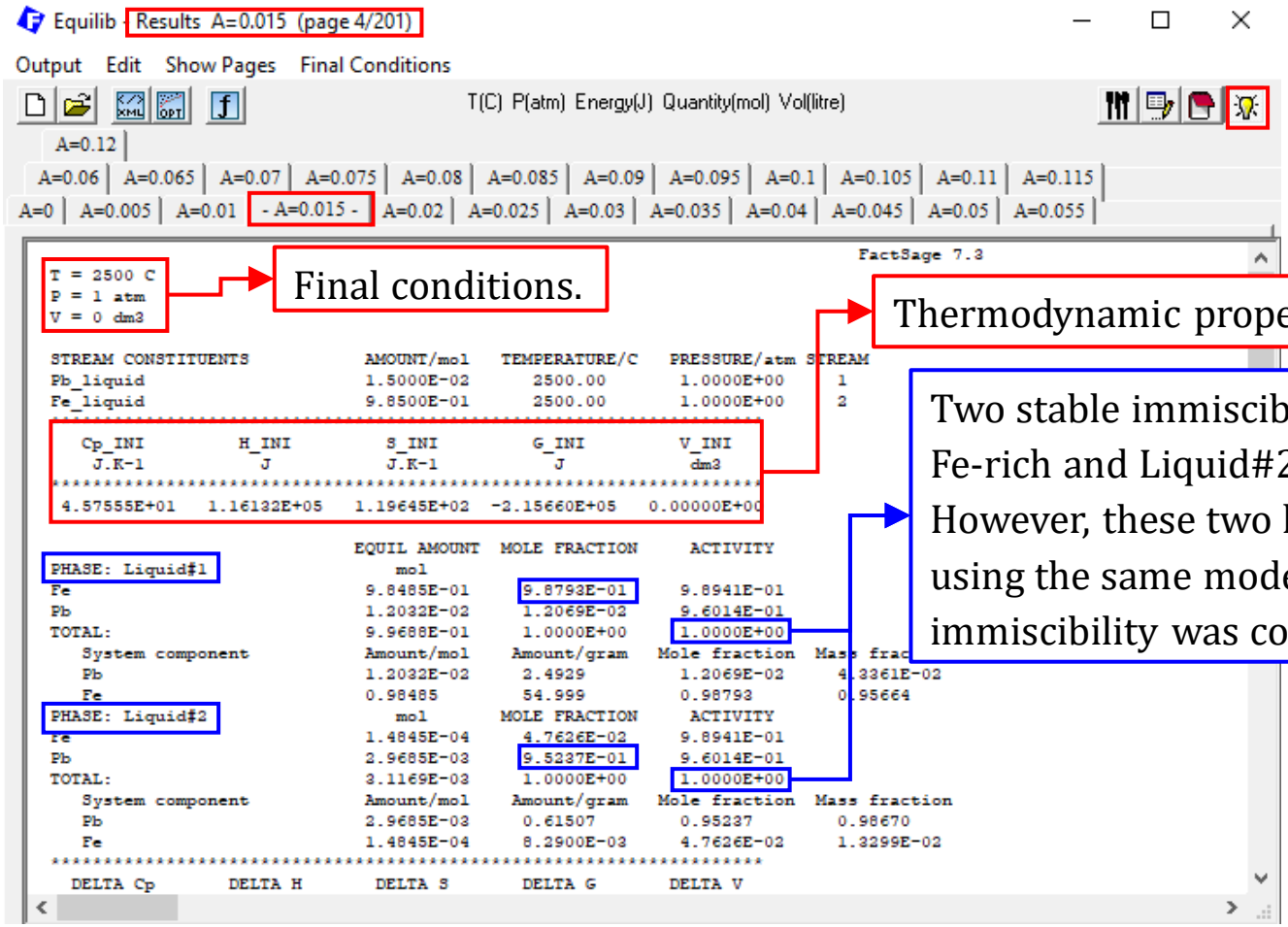
Choose FTlite-Liqu only, and use the default [I]-option. From the Pb-Fe phase diagram (Documentation), it is seen that the immiscibility exists for liquid Pb and liquid Fe.

We would like to perform the calculations from pure Fe to pure Pb using the step of 0.005.

The mixing process is isothermal.

Equilib Module: Mixing Properties

Results



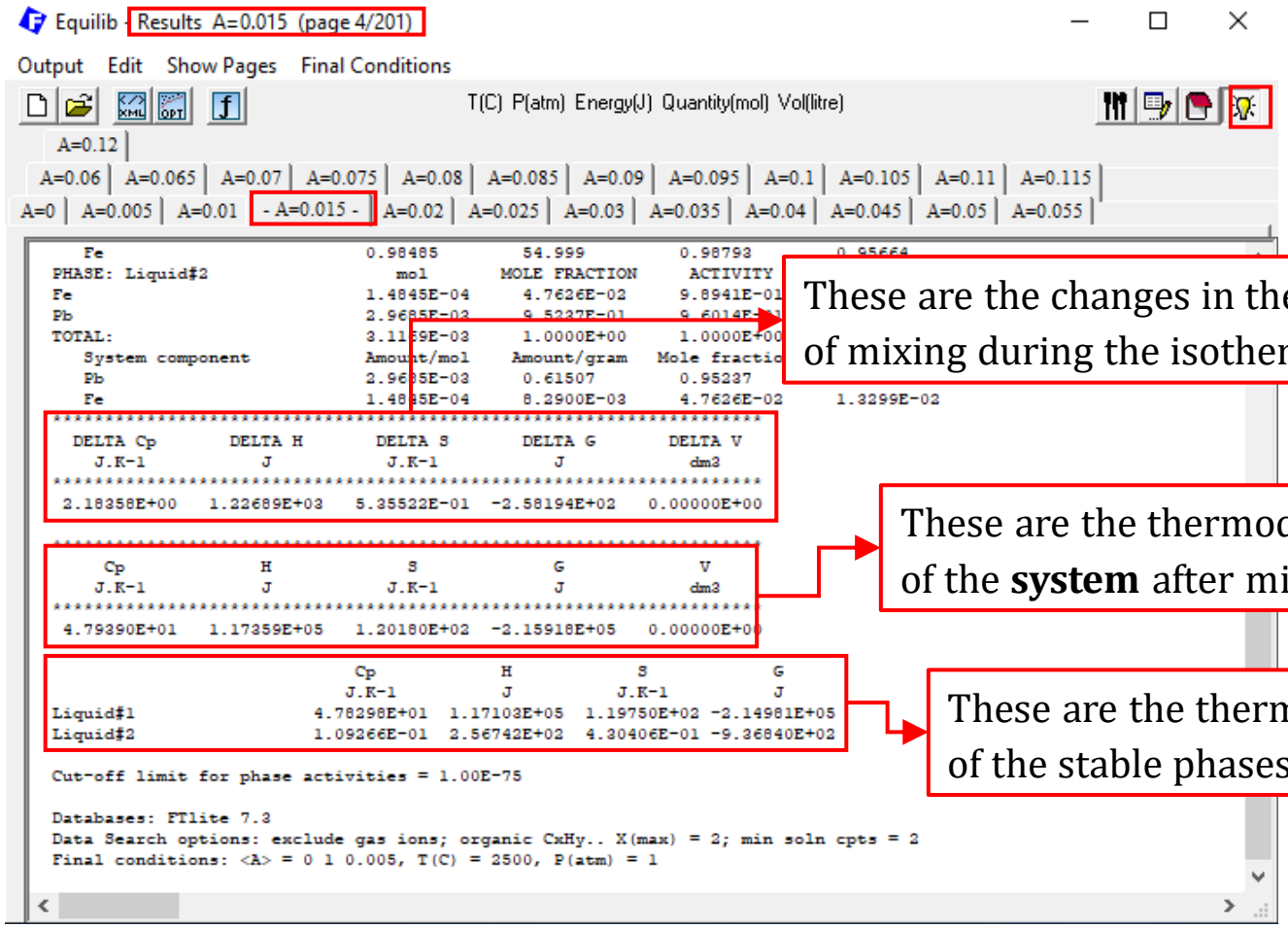
Final conditions.

Thermodynamic properties before mixing.

Two stable immiscible liquids: Liquid#1 is Fe-rich and Liquid#2 is Pb rich.
However, these two liquids are described using the same model, but the possibility of immiscibility was considered.

Equilib Module: Mixing Properties

Results (Cont'd)



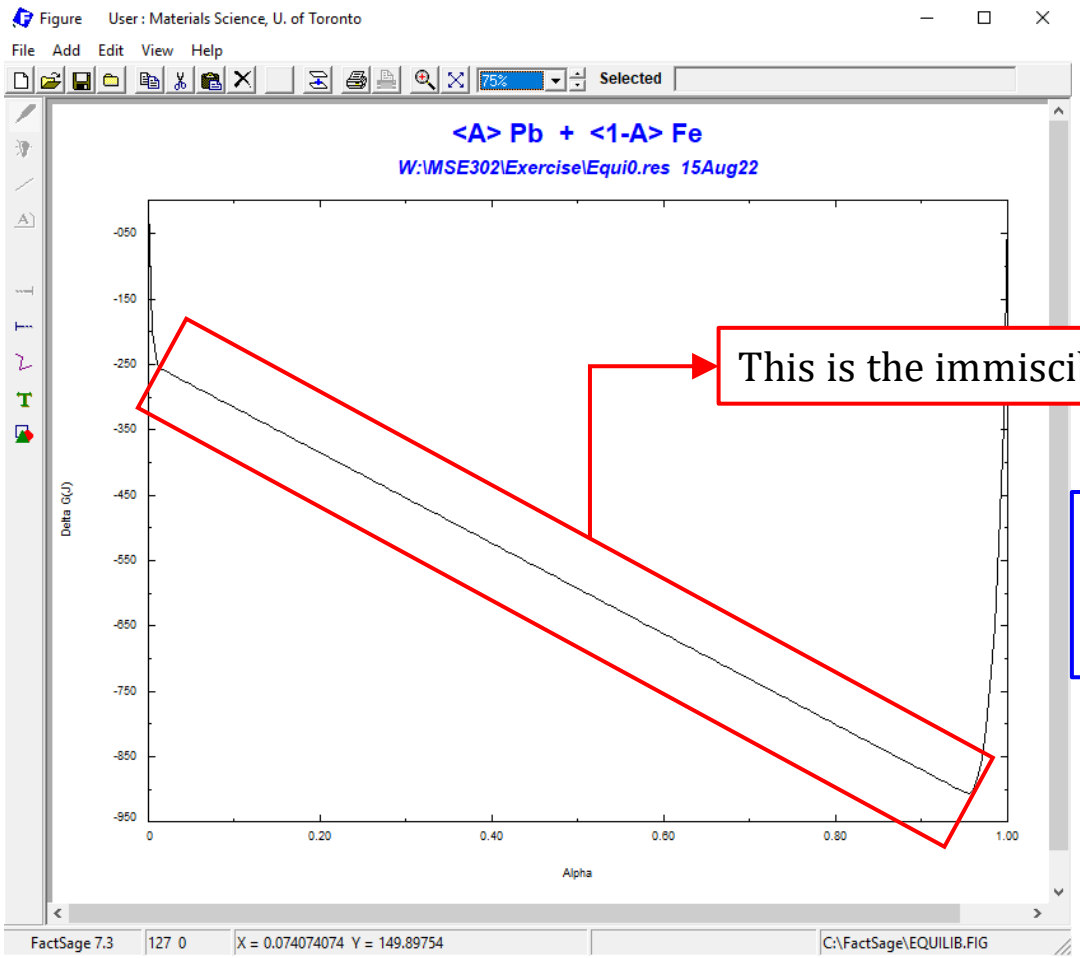
These are the changes in thermodynamic properties of mixing during the isothermal mixing.

These are the thermodynamic properties of the **system** after mixing.

These are the thermodynamic properties of the stable phases after mixing.

Equilib Module: Mixing Properties

Results: Make Plots $\Delta_{mix}g_{2500\,°C} \sim X_{Pb}$

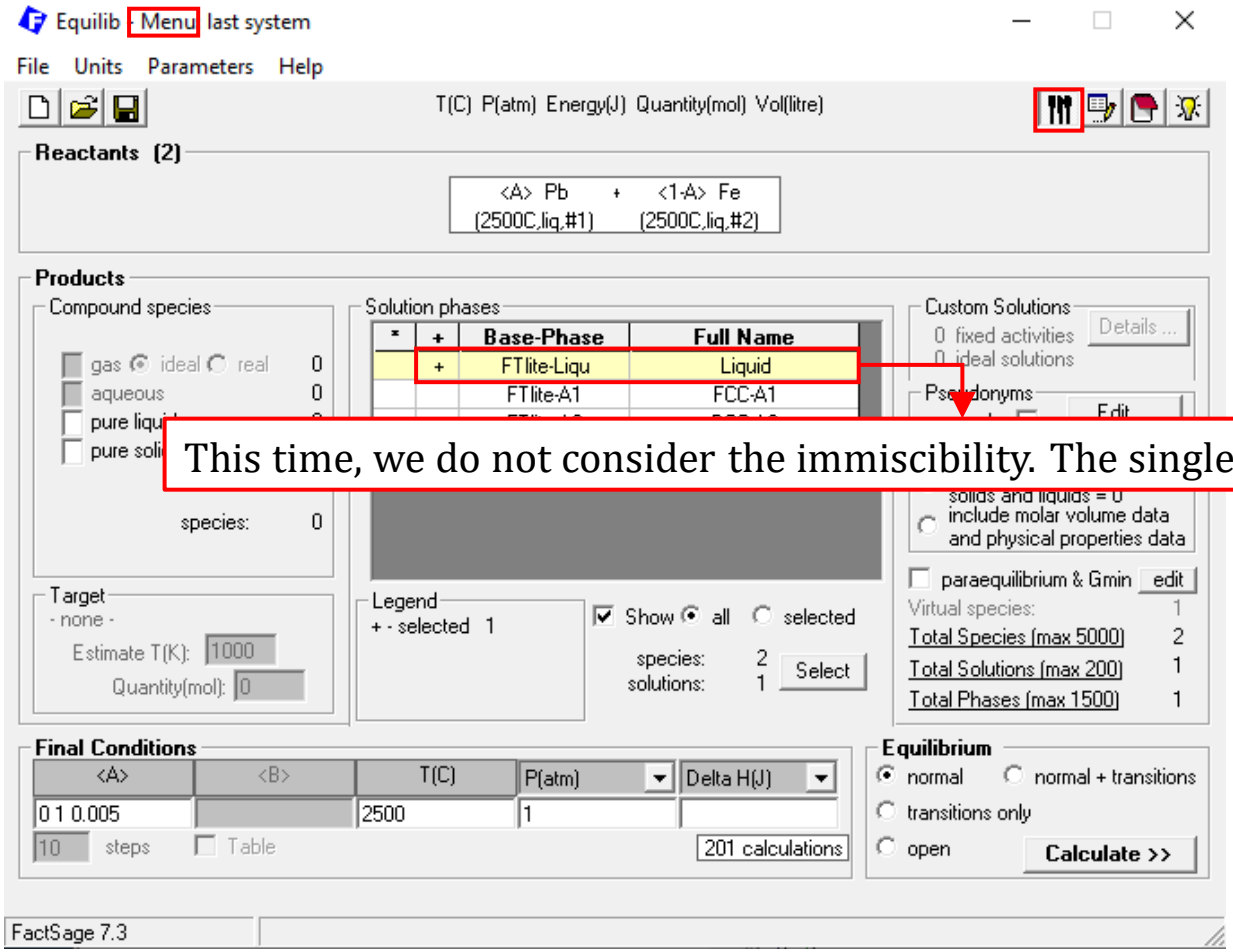


This is the immiscibility region.

You might ask, what if liquid Pb and liquid Fe are completely miscible and form a single liquid solution?

Equilib Module: Mixing Properties

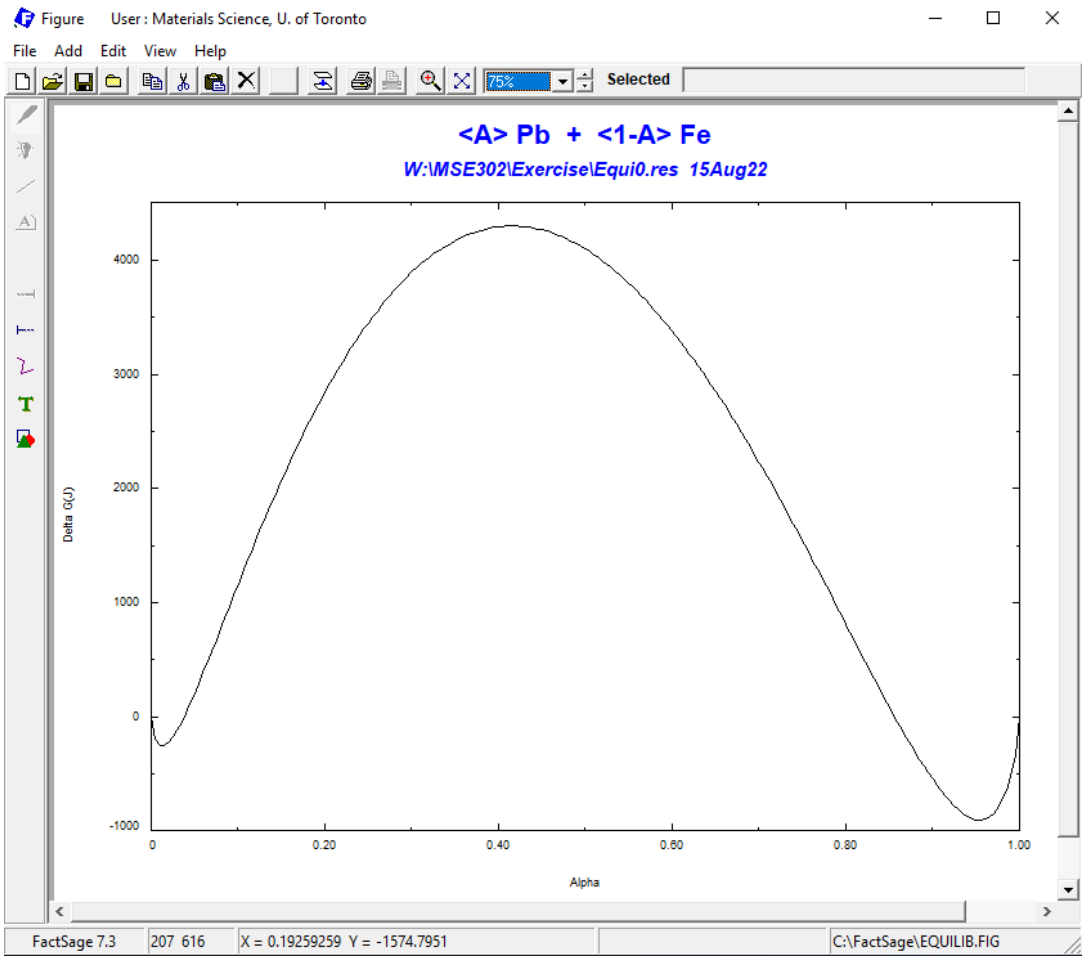
Menu Window: Select Products and Define Final Conditions



This time, we do not consider the immiscibility. The single-phase setting is chosen.

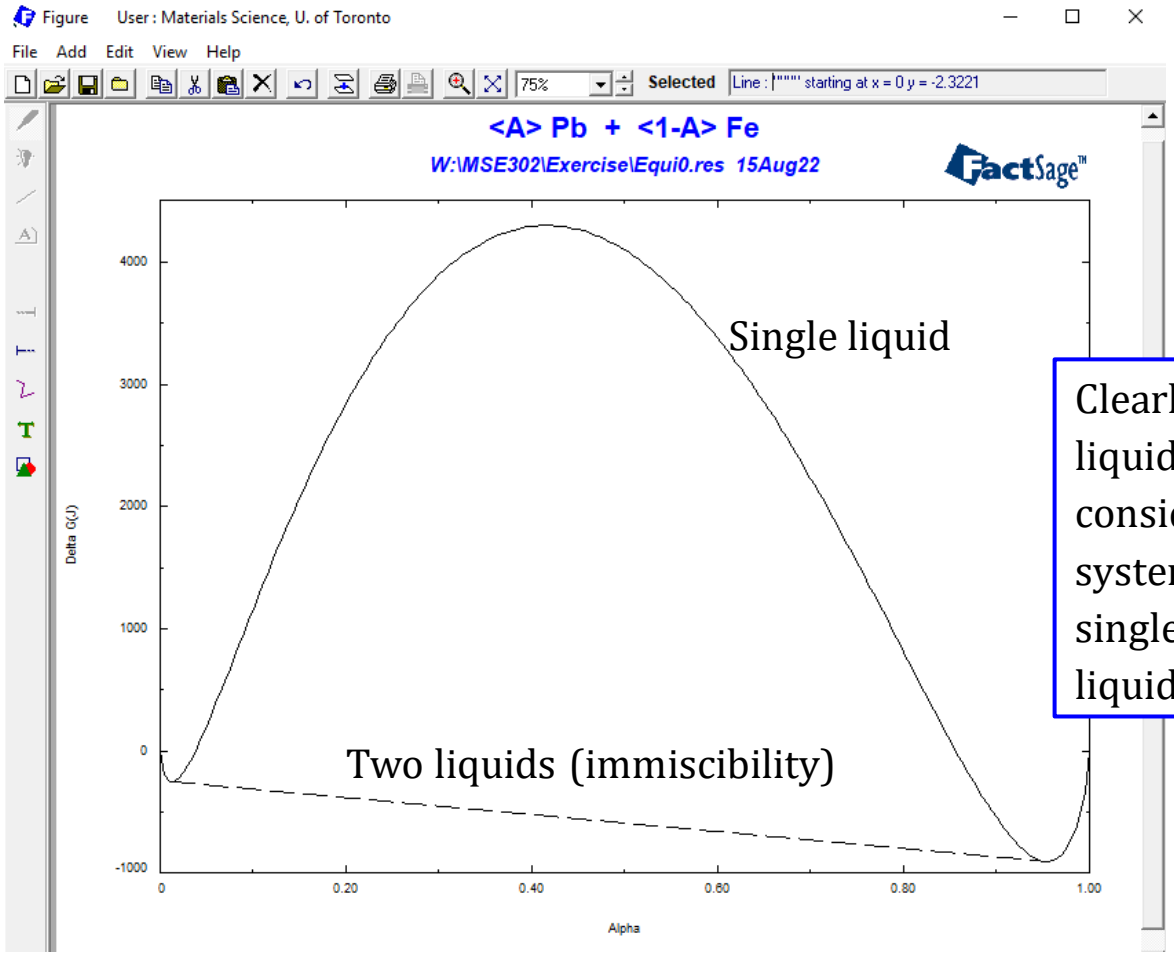
Equilib Module: Mixing Properties

Results: Make Plots $\Delta_{mix}g_{2500\,°C} \sim X_{Pb}$



Equilib Module: Mixing Properties

Results: Use the Figure Module to superimpose the two figures



Clearly, if the system exists as two liquids, that is, immiscibility is considered, the Gibbs energy of the system would be much lower than if single liquid exists. Therefore, two liquids are more stable.

Equilib Module: Mixing Properties

Results

Use the [I]-option for FTlite-Liqu, please plot other mixing properties

$$\Delta_{\text{mix}} h_{2500\,^{\circ}\text{C}} \sim X_{\text{Pb}} \text{ and } \Delta_{\text{mix}} s_{2500\,^{\circ}\text{C}} \sim X_{\text{Pb}}.$$

Then, please go back to the Menu Window, and save the solution properties for FTlite-Liqu.

(It is also recommended that you use Fact-XML to plot all the solution properties)

Equilib Module: General Tips

Some general tips for the Equilib Module are summarized in a Q&A format

Q1: How to perform calculations when the mass of the reactant changes?

A1: You can use <A> or <aA + b> or <a + bA> where “a” and “b” are constants and <A> (alpha) is a variable to represent the quantities of the reactants.

Q2: How to calculate the adiabatic flame temperature?

A2: After inputting the initial temperature, you can leave the final temperature blank, and set 0 for the Enthalpy change .

Q3: I saw in the FToxid database, the slag is modeled as SLAGA, SLAGB, SLAG?, which one should I select?.

A3: On the Menu window, right click on FToxid-SLAGA, FToxid-SLAGB, FToxid-SLAG?, and then check the phase information. You should find the description which details the elements that are considered in the phase model, and then choose the model which contains the elements of interest.

Equilib Module: General Tips

Some general tips for the Equilib Module are summarized in a Q&A format

Q4: I want to perform some calculations about high-temperature treatment of solid wastes (slag, fly ash, mine tailings, municipal solid wastes…)?

A4: Sine the solid wastes are mostly high-order systems, trial-and-error calculations are required to find the optimal phase selection. If the molten oxide slag is expected, "FToxid-SLAG?" can be used for preliminary calculations; if you are interested in the chlorine behavior, you should select the FTsalt database.

Q5: How to control the oxygen partial pressure?

A5: You need to use the FactPS database. Right click on the gas (Compound species on the Menu Window), then right click on the "+" column of O_2 to set the activity which is numerally identical to partial pressure of O_2 in the ideal gas mixture. The oxygen input amount will be automatically calculated.

Equilib Module: General Tips

Some general tips for the Equilib Module are summarized in a Q&A format

Q6: How to calculate the equilibrium composition of slag by specifying the activity of the slag components?

A6: Right click on the FToxid-SLAGA, and use the [C]-option. This will permit us to specify the activity of the slag component.

Q7: How to determine the solidus temperature and liquidus temperature?

A7: Right click on the liquid phase (e.g., FTlite-Liqu), and use the [P]-option for the calculation of liquidus temperature and [F]-option for the calculation of solidus temperature. Also, you need to leave the temperature (Final Conditions) blank. However, for a complicated system, these two temperatures may not be obtained by this approach. In this case, it is suggested to activate the "normal + transitions" option, and generate the graph to find these two temperatures (We will discuss this in the advanced applications).

Equilib Module: General Tips

Some general tips for the Equilib Module are summarized in a Q&A format

Q8: What should I do if the solution model does not contain the species I want to calculate? For example, TiO_2 is not included in the FToxid-SLAG.

A8: If the amount of the species is low, we can consider using the dilute solution model. Instructions can be found in the help file (Select/Slide Show/Advanced Features).

Q9: Based on the information shown in the Documentation Module, the system I am investigating has not been optimized by any of the available FactSage databases? What should I do?

A9: Please consider building a private database for the system of interest using the assessment papers that have been published.

Equilib Module: General Tips

Some general tips for the Equilib Module are summarized in a Q&A format

Q10: I want to analyze a system containing metastable phases, for example, Fe-C system. What should I do?

A10: Do not select $C(s)$ (Graphite), but select $Fe_3C(s)$ (Cementite), and then perform the calculation.

Q11: I am experiencing "Abort" issue (no solution) even though it is a simple problem?

A11: You can try to add a small amount of argon (e.g., 1E-6) to the list of reactants.

In-Class Exercise

Question 1. Use the Equilib Module to solve the following questions.

(1) 1 mole of H_2O becomes a gas mixture at 2500 °C and 1 atm. Calculate the equilibrium partial pressure of H_2 in the gas mixture.

(2) For a gas mixture containing 2 mole of H_2O, 0.79 mole of N_2, and 0.21 mole of O_2, calculate at 25 °C and 1 atm the equilibrium partial pressure of H_2O.

(c) Heating of LVDS 3 ($NaHCO_3$) results in the formation of Na_2CO_3, CO_2, and H_2O, find the minimum temperature for this reaction.

(d) Find the Enthalpy for 1 mole of H_2O (s), 1 mole of H_2O (l), and 1 mole of H_2O (g) when the temperature is 150 °C and the pressure is 1 atm.

(e) Find the composition and temperature of the system when 10 J of energy is supplied to 1 gram of water at 25 °C.

(f) Calculate the final temperature when 1 gram of ice (0 °C) and 2 gram of hot water (90 °C) are mixed. Assume no heat exchange with the surroundings.

In-Class Exercise

Question 2. Mixing Properties

(1) Use FTlite database to calculate the Al-Mg phase diagram. $T(℃) \sim X_{\mathrm{Mg}}$

(2) From the diagram, you should see that at 800 °C, the system exists as liquid over the entire composition range, i.e., X_{Mg} varies from 0 to 1. Calculate and plot for the liquid phase $\Delta_{\mathrm{mix}} g_{800\,℃} \sim X_{\mathrm{Mg}}$ and $\Delta_{\mathrm{mix}} h_{800\,℃} \sim X_{\mathrm{Mg}}$.

(3) From the diagram, you should see that at 500 °C, the system may exists as two coexisting phases or single phase over the entire composition range. Calculate and plot the molar Gibbs energy of the system when X_{Mg} varies from 0 to 1.