FactSage Practical
MSE302

Practical 2. Reaction Module

Basics

Acknowledgements

The teaching team of MSE302 is grateful to:

Professor Mansoor Barati (UofT)

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Reaction Module

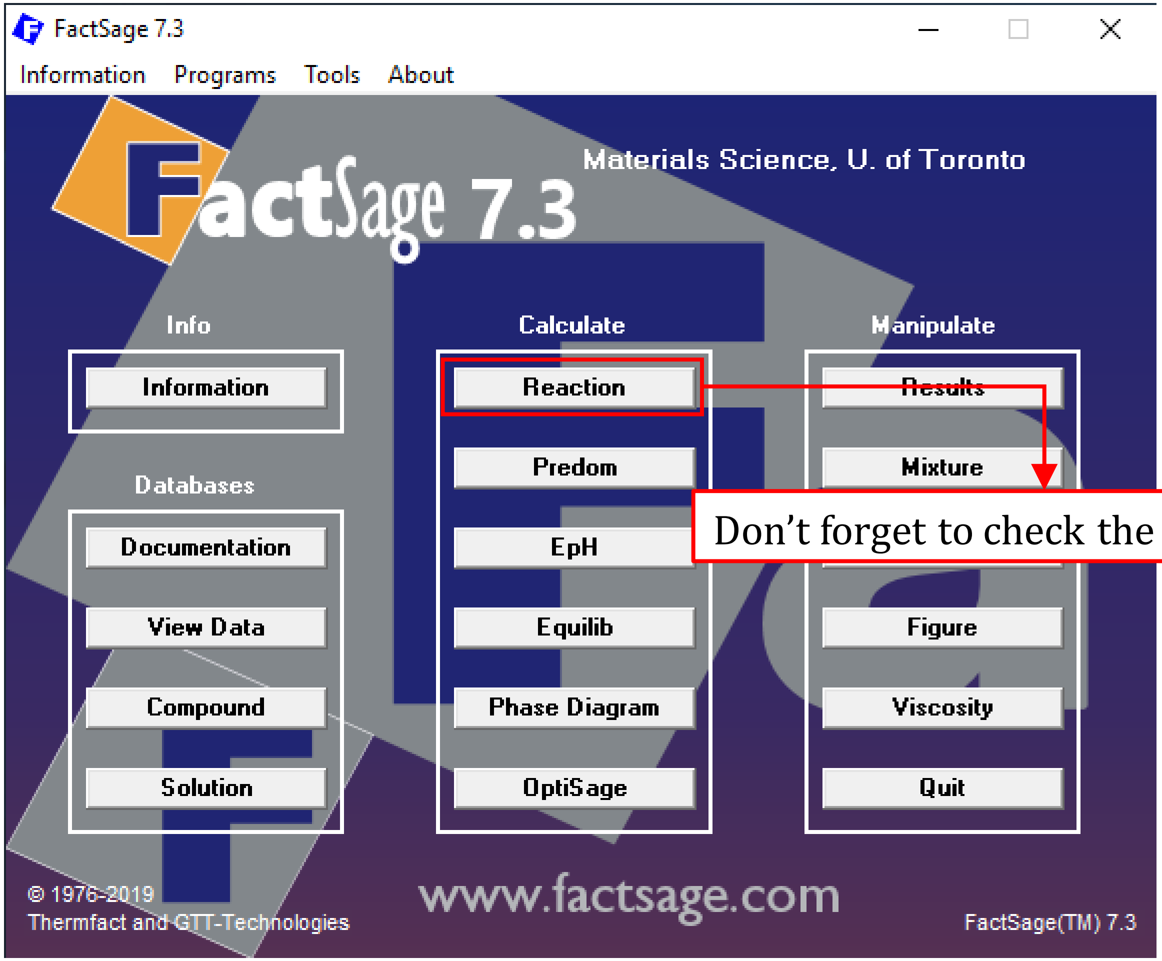
The **Reaction** Module can do the following:

- ✓ **Reaction** calculates the thermodynamic properties of **a species** ($C_{P,i}$, H_i, S_i, V_i, G_i) at given temperature and pressure.
- ✓ **Reaction** calculates the thermodynamic properties of **a mixture of species** (mechanical mixture or solution) (C_P, H, S, V, G) at given temperature and pressure.
- ✓ **Reaction** calculates the thermodynamic properties of **a chemical reaction** ($\Delta_r c_P$, $\Delta_r h$, $\Delta_r s$, $\Delta_r v$, $\Delta_r g$) at given temperature and pressure.

Alert:

- ✓ **Reaction** accesses both compound and solution databases.
- ✓ **Reaction** assumes all gases are ideal and ignores expansivities and compressibilities of solids and liquids.

Reaction Module



Don’t forget to check the Directory!!!

Run the “Reaction” Module

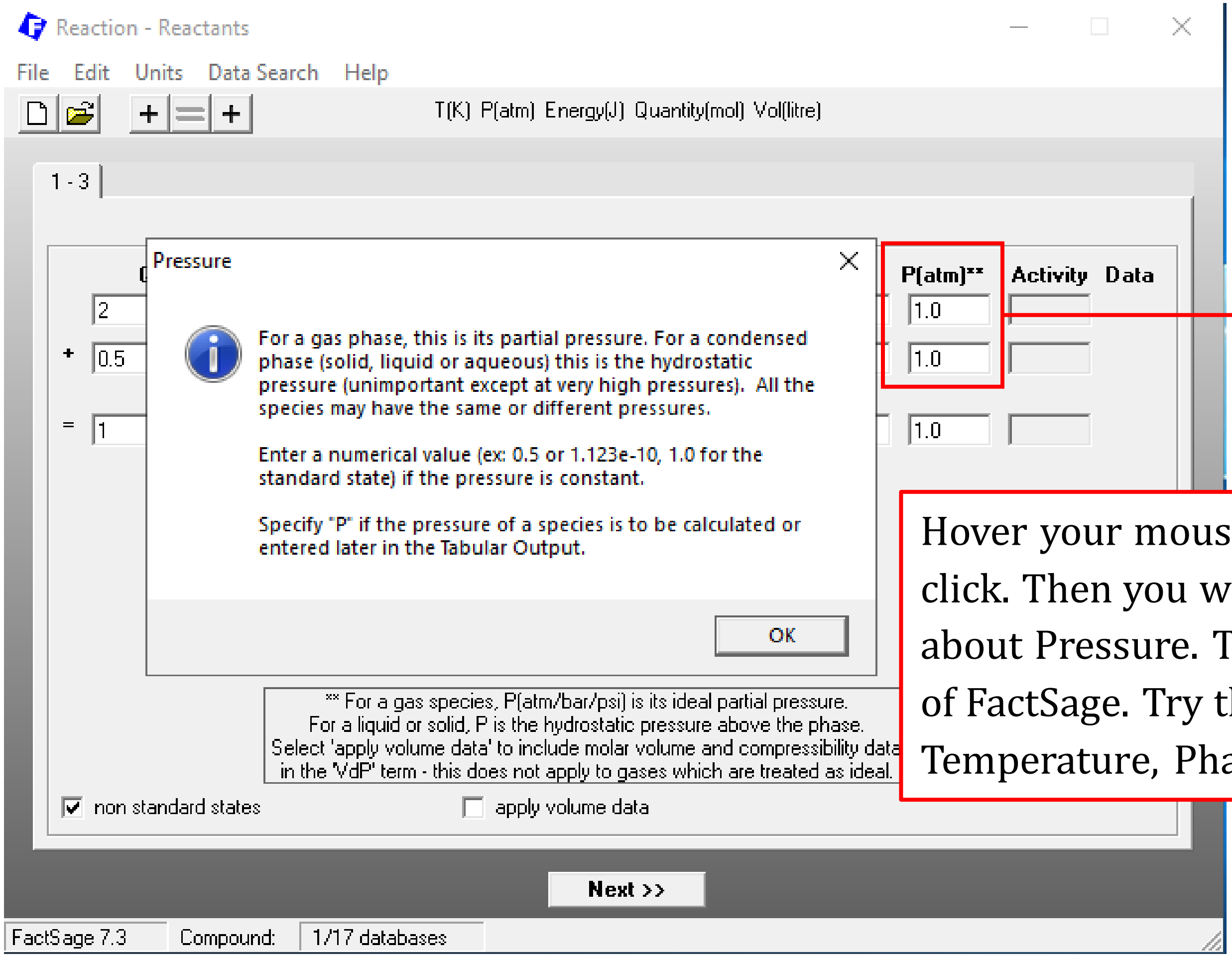
Reaction Module

A Note on **Pressure**:

- ✓ For a gas phase, **Pressure** is its partial pressure.
- ✓ For a condensed phase (solid, liquid or aqueous), **Pressure** is the hydrostatic pressure (unimportant except at very high pressures).
- ✓ All the species may have the same or different pressure.

Reaction Module

A Note on **Pressure**:



2
+ 0.5
= 1

P(atm)**	Activity	Data
1.0		
1.0		
1.0		

Pressure

For a gas phase, this is its partial pressure. For a condensed phase (solid, liquid or aqueous) this is the hydrostatic pressure (unimportant except at very high pressures). All the species may have the same or different pressures.

Enter a numerical value (ex: 0.5 or 1.123e-10, 1.0 for the standard state) if the pressure is constant.

Specify "P" if the pressure of a species is to be calculated or entered later in the Tabular Output.

OK

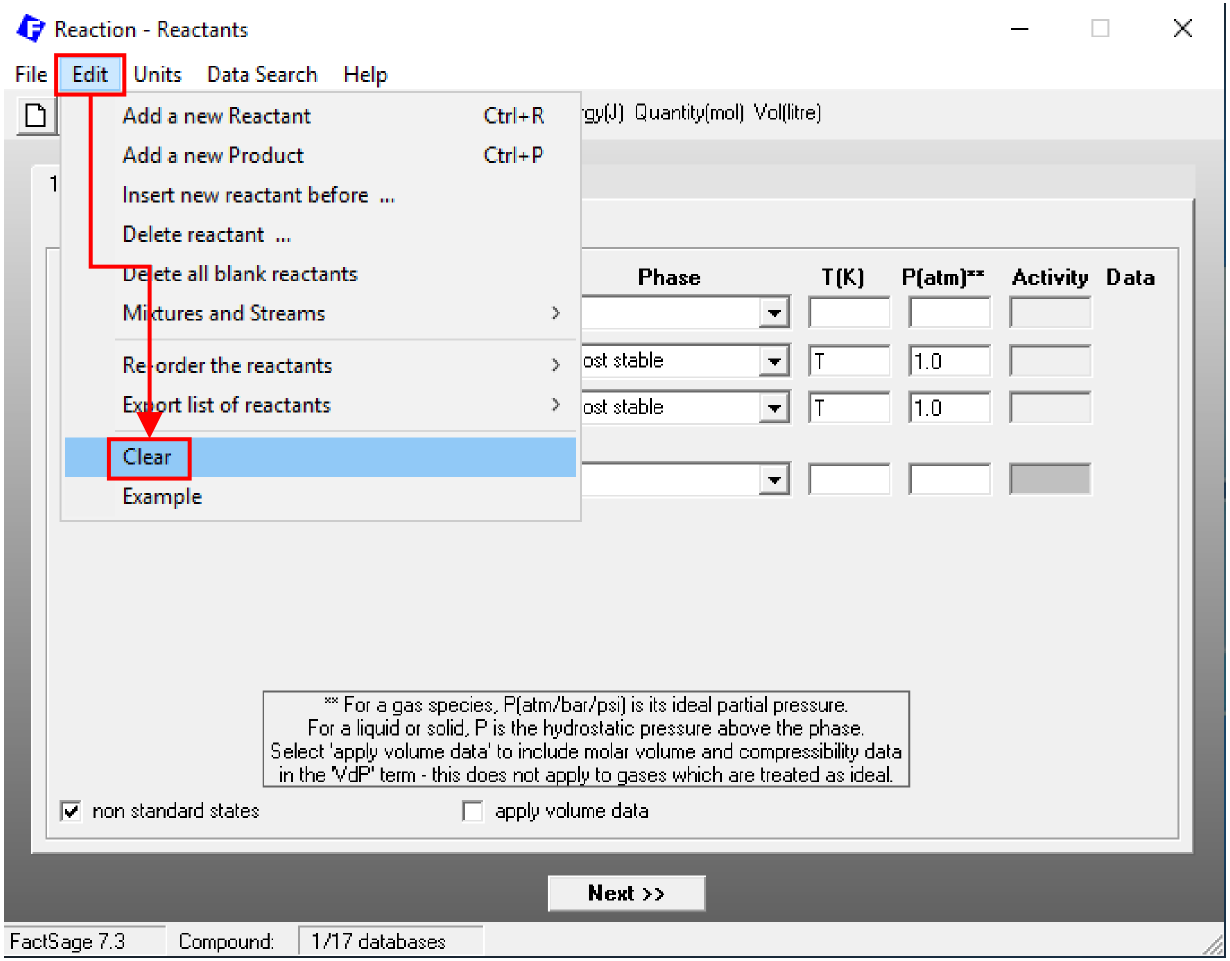
** For a gas species, P(atm/bar/psi) is its ideal partial pressure.
For a liquid or solid, P is the hydrostatic pressure above the phase.
Select 'apply volume data' to include molar volume and compressibility data in the 'VdP' term - this does not apply to gases which are treated as ideal.

☑ non standard states ☐ apply volume data

Hover your mouse near "P(atm)", and right click. Then you will see the explanation about Pressure. This is a very useful feature of FactSage. Try this about Activity and, Temperature, Phase…

Reaction Module

Clear the Reactants:



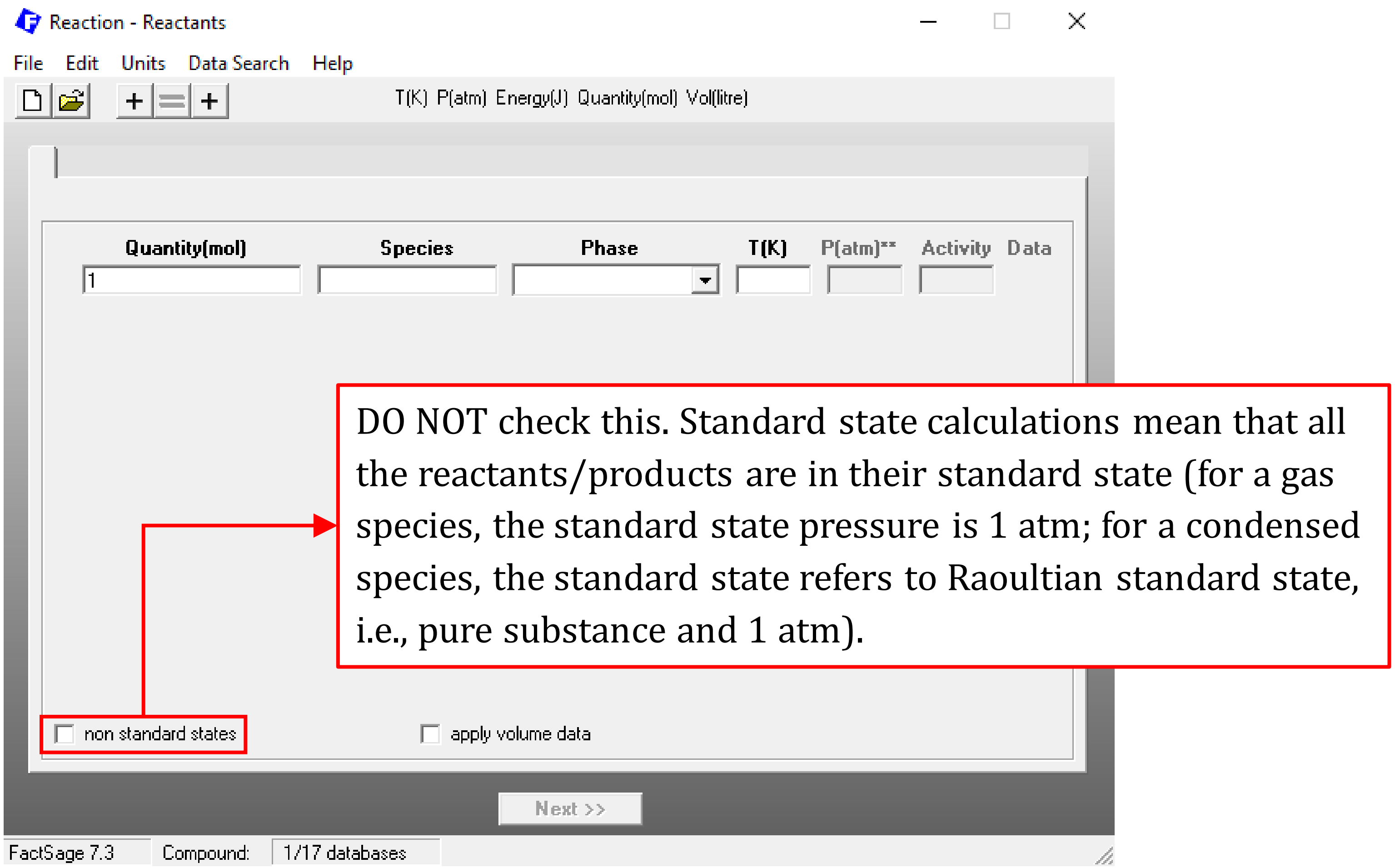
** For a gas species, P(atm/bar/psi) is its ideal partial pressure.
For a liquid or solid, P is the hydrostatic pressure above the phase.
Select 'apply volume data' to include molar volume and compressibility data
in the 'VdP' term - this does not apply to gases which are treated as ideal.

☑ non standard states

☐ apply volume data

Reaction Module

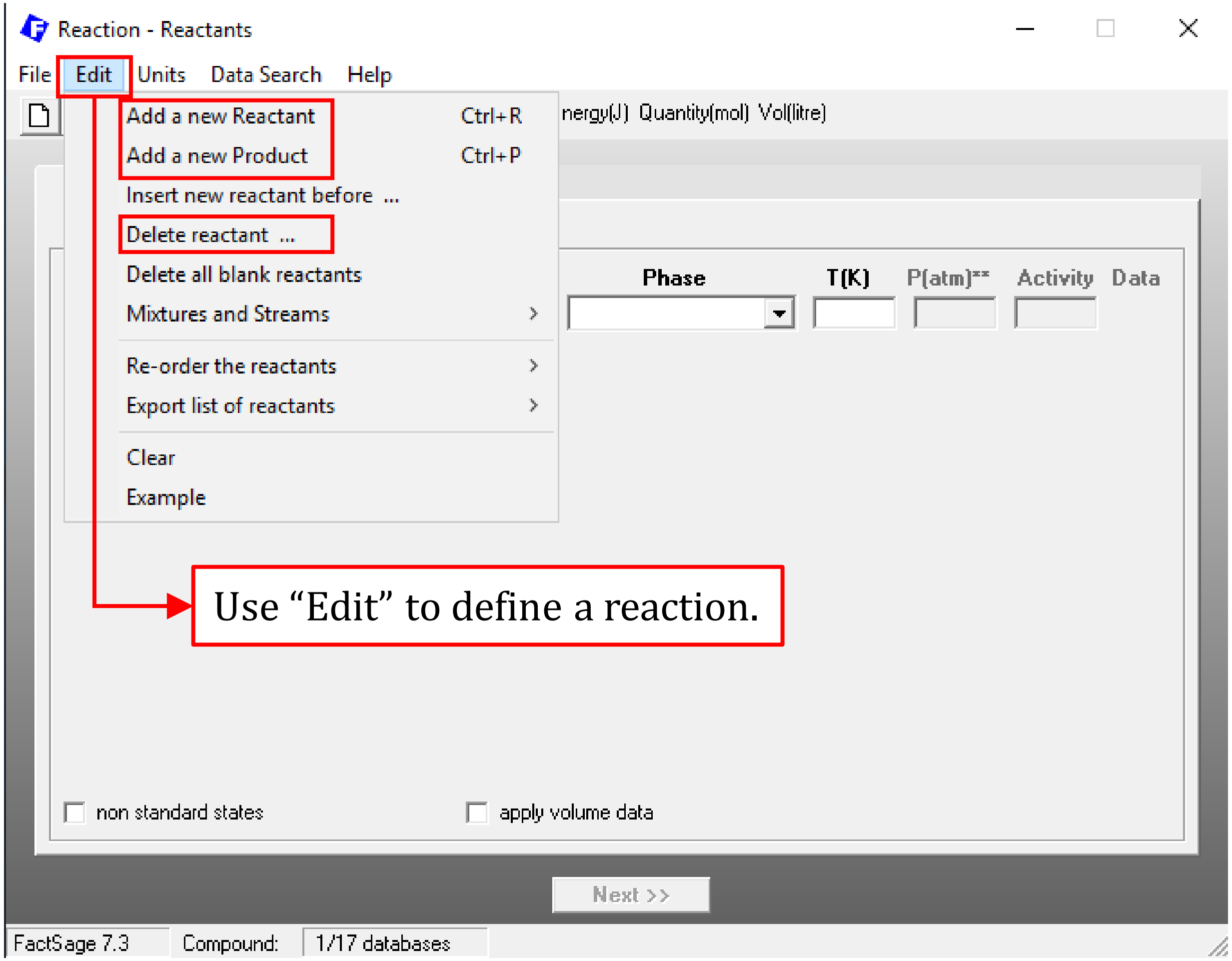
Let us first perform **standard state** calculations.



DO NOT check this. Standard state calculations mean that all the reactants/products are in their standard state (for a gas species, the standard state pressure is 1 atm; for a condensed species, the standard state refers to Raoultian standard state, i.e., pure substance and 1 atm).

Reaction Module

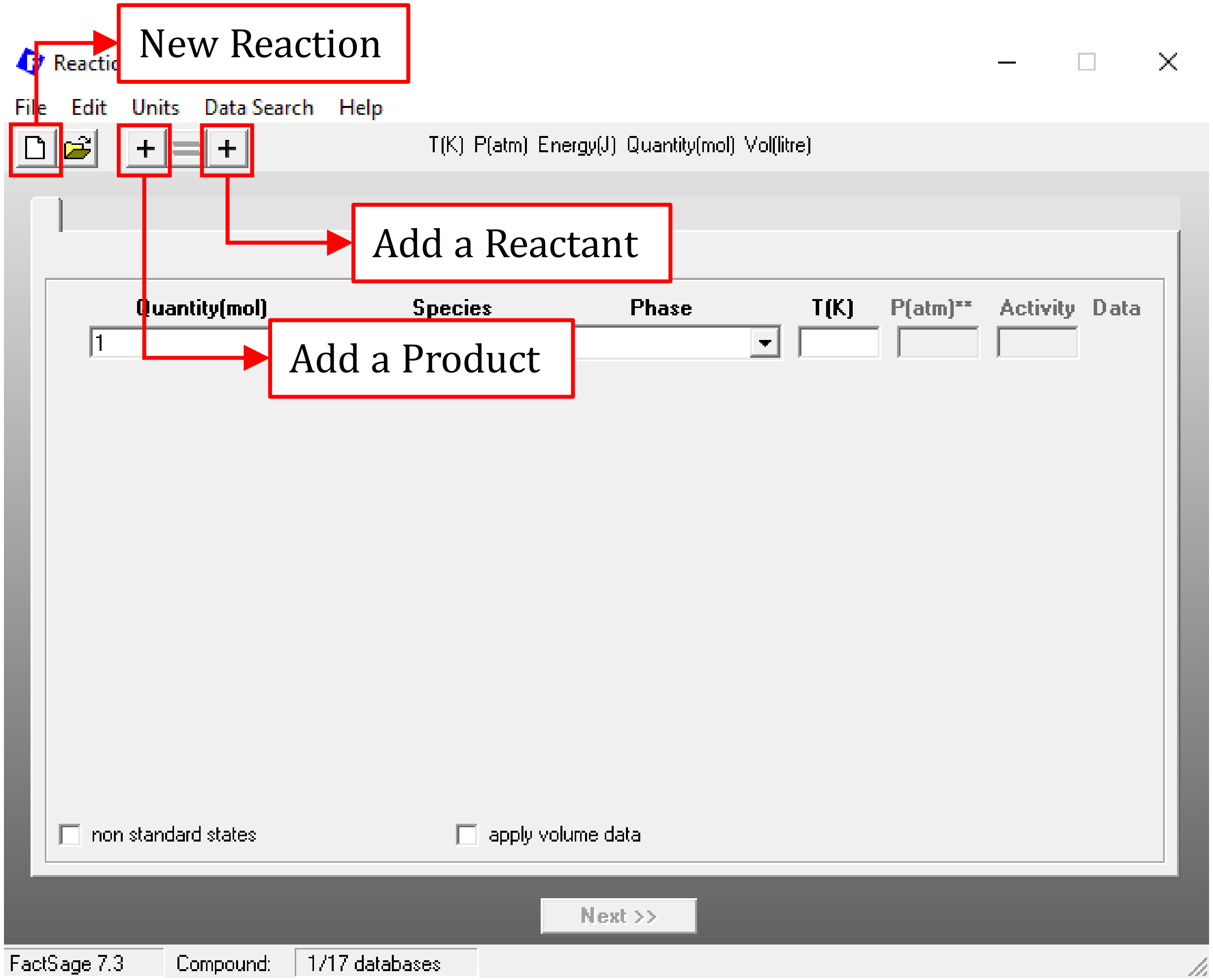
Reactants Window: define a reaction using “Edit”



Use “Edit” to define a reaction.

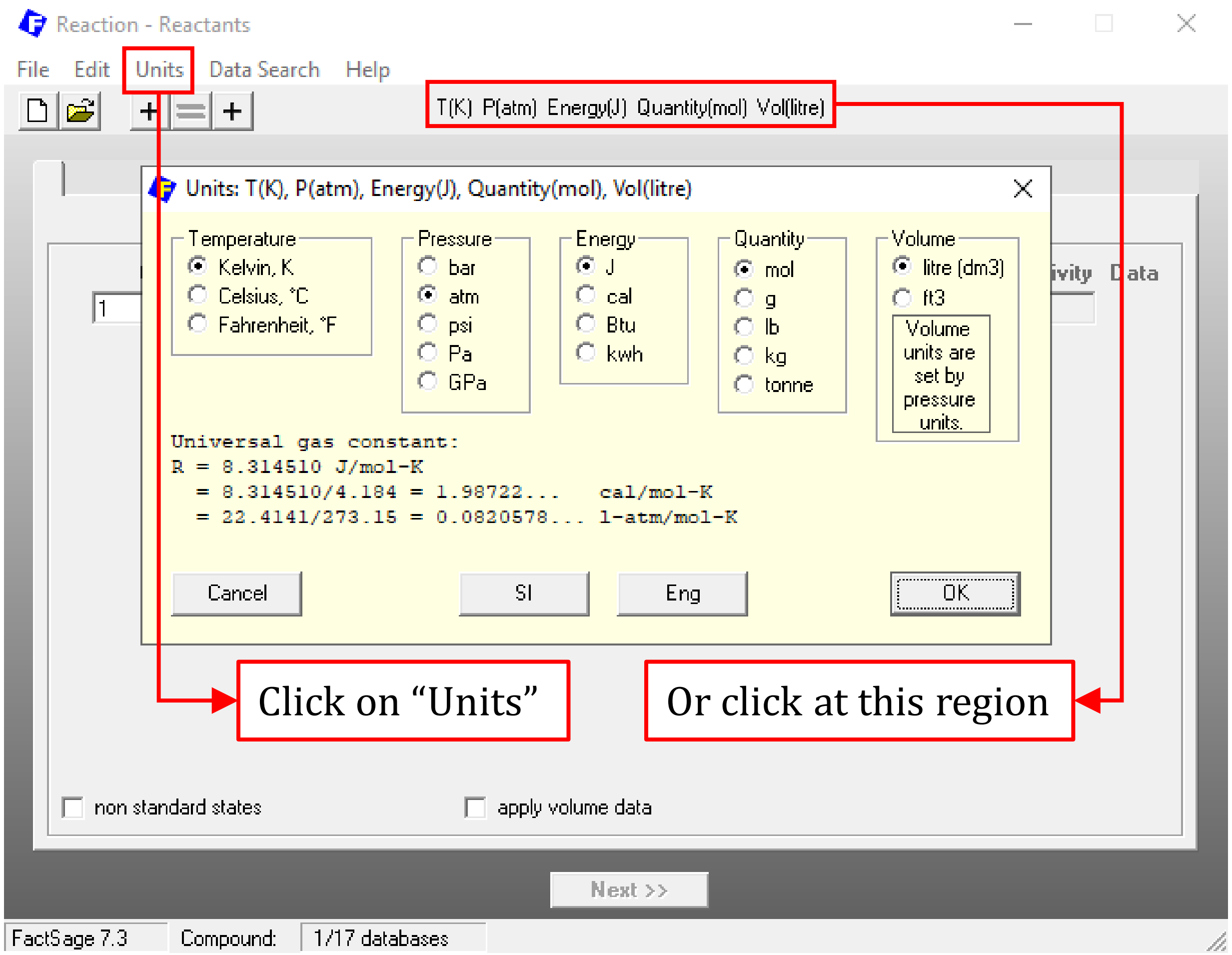
Reaction Module

Reactants Window: define a reaction using “+”



Reaction Module

Reactants Window: set the Units



Units: T(K), P(atm), Energy(J), Quantity(mol), Vol(litre)

Temperature: ● Kelvin, K ○ Celsius, °C ○ Fahrenheit, °F

Pressure: ○ bar ● atm ○ psi ○ Pa ○ GPa

Energy: ● J ○ cal ○ Btu ○ kwh

Quantity: ● mol ○ g ○ lb ○ kg ○ tonne

Volume: ● litre (dm3) ○ ft3

Volume units are set by pressure units.

```
Universal gas constant:
R = 8.314510 J/mol-K
  = 8.314510/4.184 = 1.98722...   cal/mol-K
  = 22.4141/273.15 = 0.0820578... l-atm/mol-K
```

☐ non standard states

☐ apply volume data

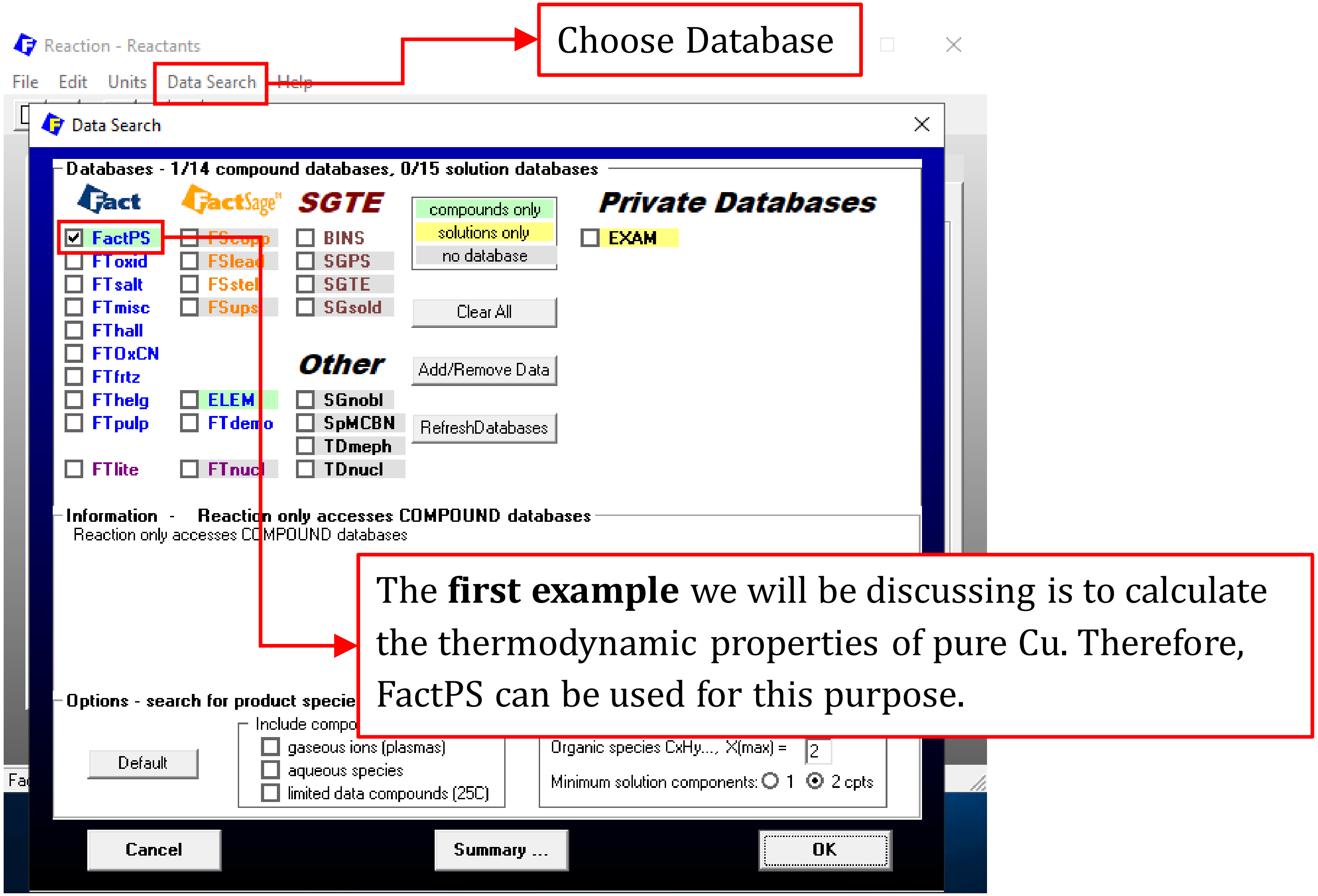
FactSage 7.3 | Compound: | 1/17 databases

Click on “Units”

Or click at this region

Reaction Module: Pure Cu

Reactants Window: choose the database



Databases - 1/14 compound databases, 0/15 solution databases

Fact: ☑ FactPS, ☐ FToxid, ☐ FTsalt, ☐ FTmisc, ☐ FThall, ☐ FTOxCN, ☐ FTfrtz, ☐ FThelg, ☐ FTpulp, ☐ FTlite

FactSage: ☐ FScopp, ☐ FSlead, ☐ FSstel, ☐ FSups, ☐ ELEM, ☐ FTdemo, ☐ FTnucl

SGTE: ☐ BINS, ☐ SGPS, ☐ SGTE, ☐ SGsold

Other: ☐ SGnobl, ☐ SpMCBN, ☐ TDmeph, ☐ TDnucl

compounds only / solutions only / no database

Private Databases: ☐ EXAM

Information - Reaction only accesses COMPOUND databases
Reaction only accesses COMPOUND databases

Options - search for product species

Include compounds
☐ gaseous ions (plasmas)
☐ aqueous species
☐ limited data compounds (25C)

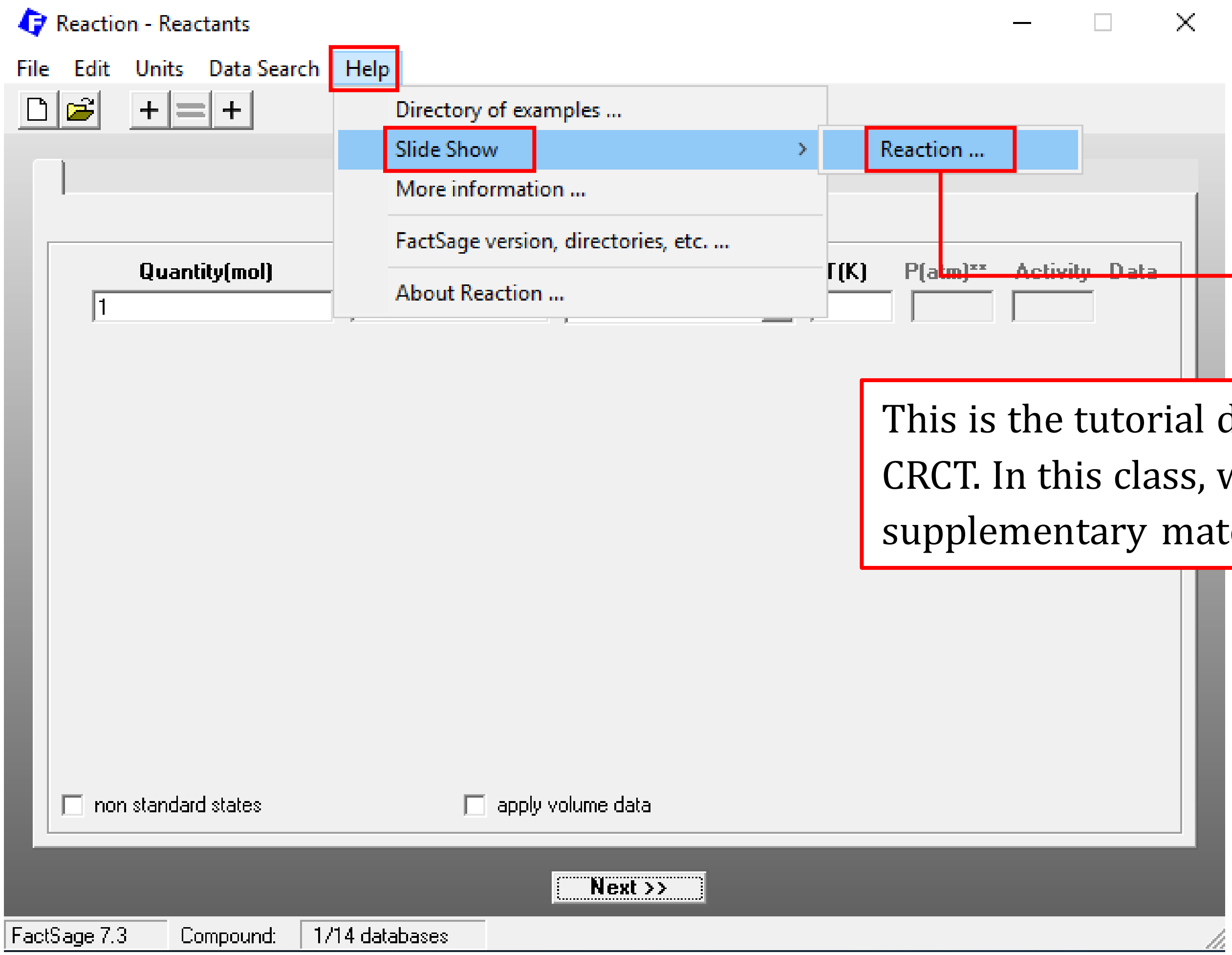
Organic species CxHy..., X(max) = 2

Minimum solution components: ○ 1 ● 2 cpts

The **first example** we will be discussing is to calculate the thermodynamic properties of pure Cu. Therefore, FactPS can be used for this purpose.

Reaction Module: Pure Cu

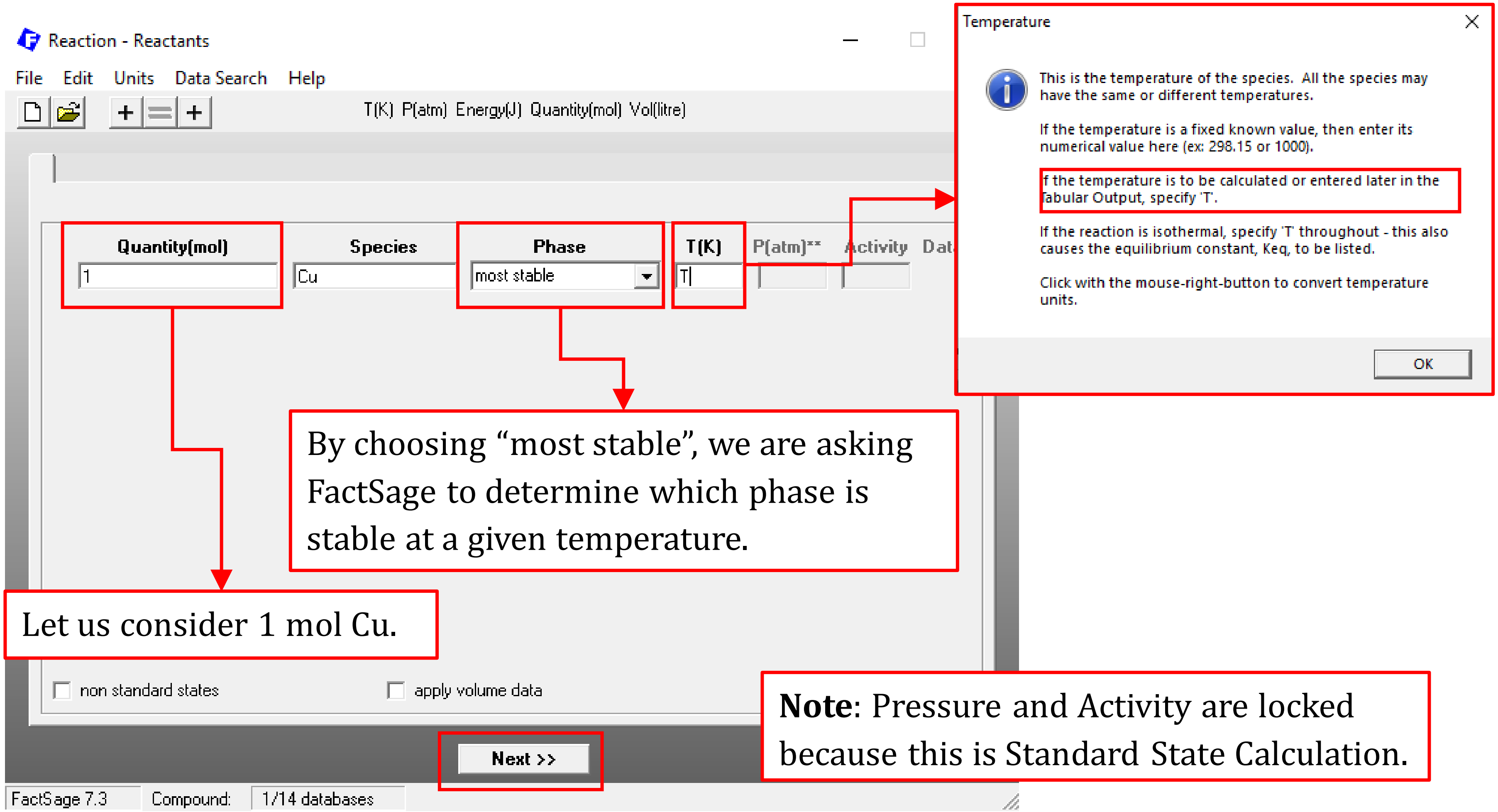
Reactants Window: Help Document



This is the tutorial document provided by CRCT. In this class, we use this as the supplementary material.

Reaction Module: Pure Cu

Reactants Window: Set Reactants (Phase and Temperature)



Quantity(mol)	Species	Phase	T(K)
1	Cu	most stable	T

This is the temperature of the species. All the species may have the same or different temperatures.

If the temperature is a fixed known value, then enter its numerical value here (ex: 298.15 or 1000).

f the temperature is to be calculated or entered later in the Tabular Output, specify 'T'.

If the reaction is isothermal, specify 'T' throughout - this also causes the equilibrium constant, Keq, to be listed.

Click with the mouse-right-button to convert temperature units.

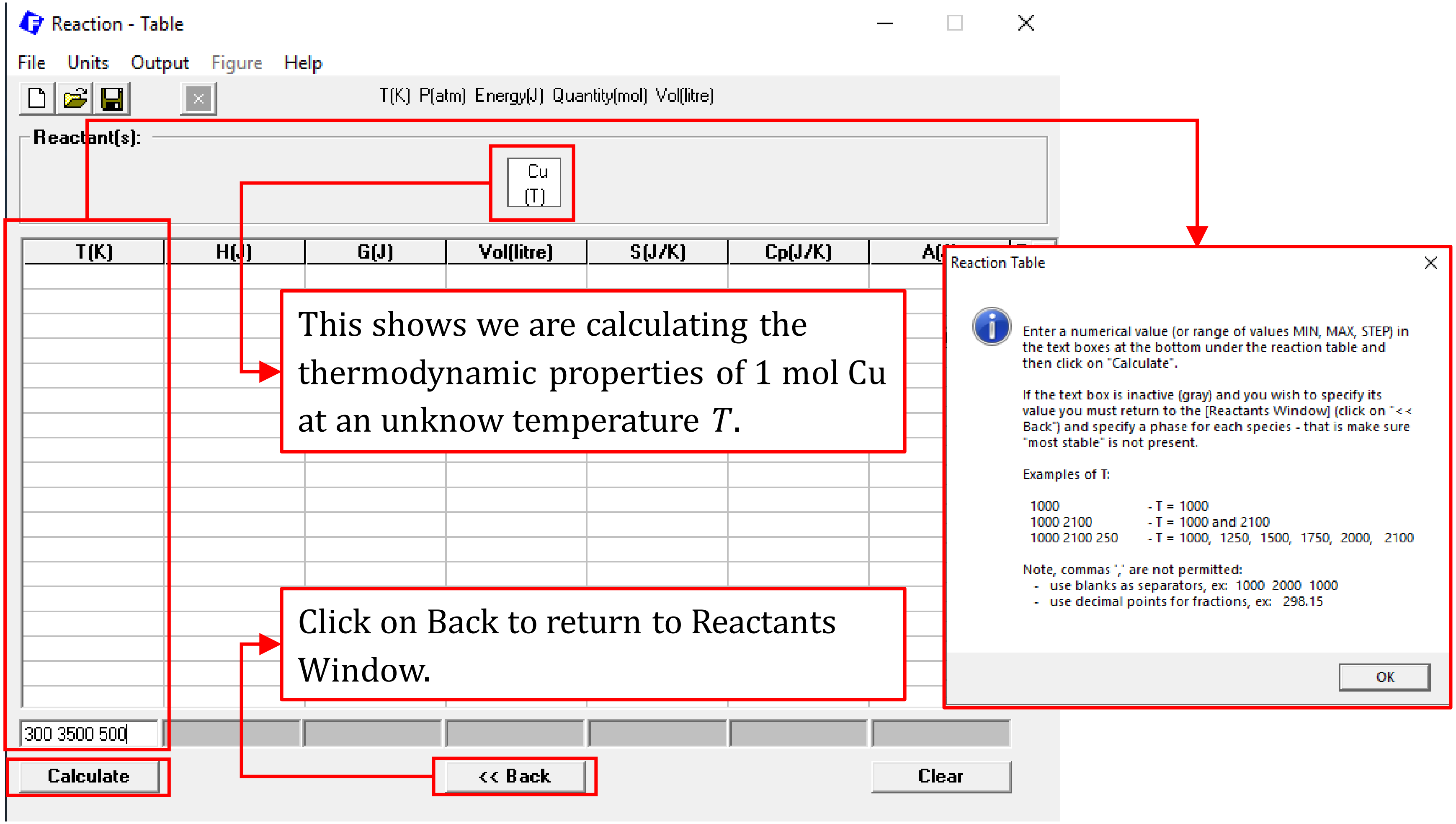
By choosing "most stable", we are asking FactSage to determine which phase is stable at a given temperature.

Let us consider 1 mol Cu.

Note: Pressure and Activity are locked because this is Standard State Calculation.

Reaction Module: Pure Cu

Table Window: Set Conditions



Enter a numerical value (or range of values MIN, MAX, STEP) in the text boxes at the bottom under the reaction table and then click on "Calculate".

If the text box is inactive (gray) and you wish to specify its value you must return to the [Reactants Window] (click on "<< Back") and specify a phase for each species - that is make sure "most stable" is not present.

Examples of T:

1000 - T = 1000
1000 2100 - T = 1000 and 2100
1000 2100 250 - T = 1000, 1250, 1500, 1750, 2000, 2100

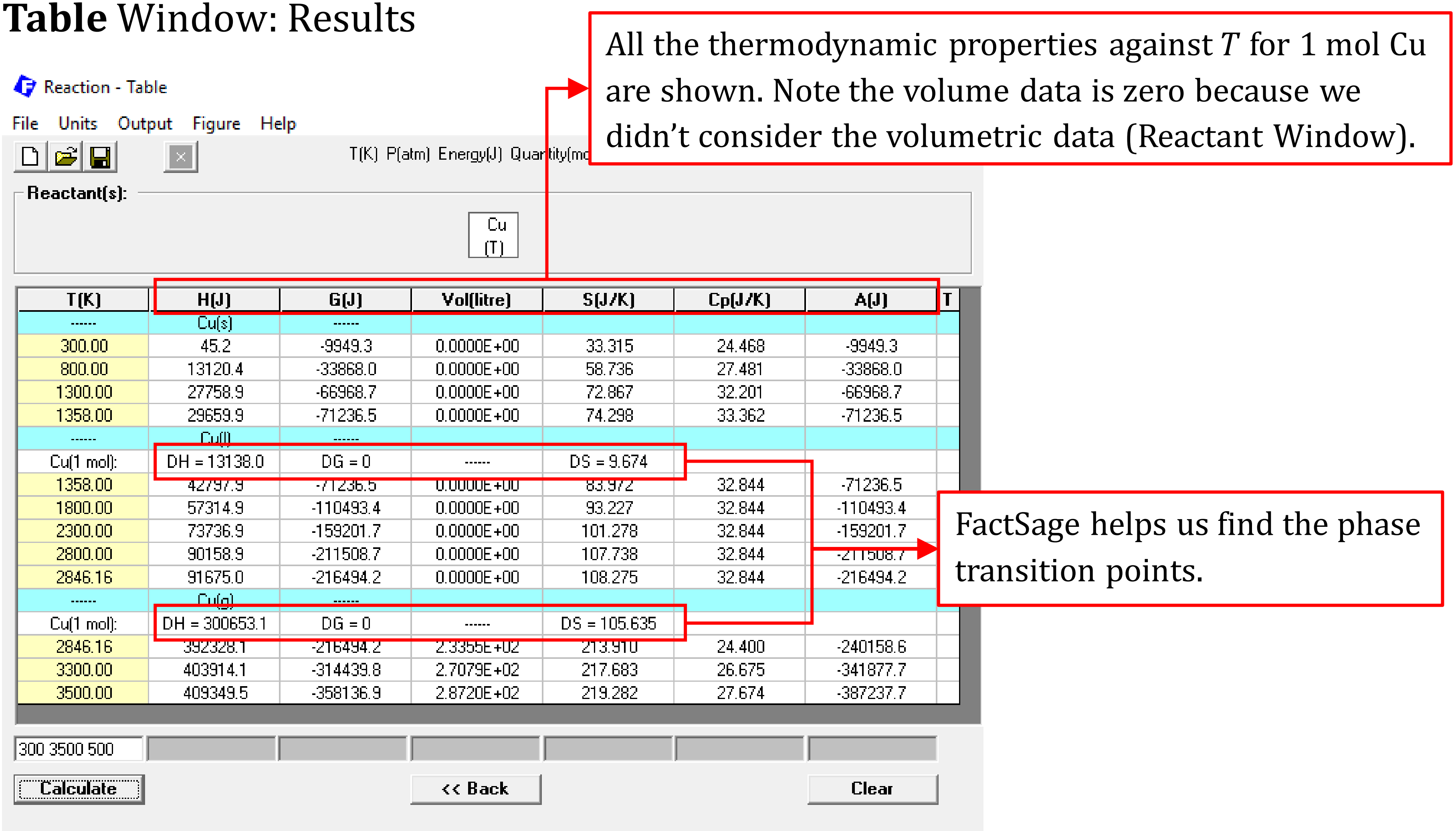
Note, commas ',' are not permitted:
- use blanks as separators, ex: 1000 2000 1000
- use decimal points for fractions, ex: 298.15

This shows we are calculating the thermodynamic properties of 1 mol Cu at an unknow temperature *T*.

Click on Back to return to Reactants Window.

Reaction Module: Pure Cu

Table Window: Results



T(K)	H(J)	G(J)	Vol(litre)	S(J/K)	Cp(J/K)	A(J)	T
------	Cu(s)	------					
300.00	45.2	-9949.3	0.0000E+00	33.315	24.468	-9949.3	
800.00	13120.4	-33868.0	0.0000E+00	58.736	27.481	-33868.0	
1300.00	27758.9	-66968.7	0.0000E+00	72.867	32.201	-66968.7	
1358.00	29659.9	-71236.5	0.0000E+00	74.298	33.362	-71236.5	
------	Cu(l)	------					
Cu(1 mol):	DH = 13138.0	DG = 0	------	DS = 9.674			
1358.00	42797.9	-71236.5	0.0000E+00	83.972	32.844	-71236.5	
1800.00	57314.9	-110493.4	0.0000E+00	93.227	32.844	-110493.4	
2300.00	73736.9	-159201.7	0.0000E+00	101.278	32.844	-159201.7	
2800.00	90158.9	-211508.7	0.0000E+00	107.738	32.844	-211508.7	
2846.16	91675.0	-216494.2	0.0000E+00	108.275	32.844	-216494.2	
------	Cu(g)	------					
Cu(1 mol):	DH = 300653.1	DG = 0	------	DS = 105.635			
2846.16	392328.1	-216494.2	2.3355E+02	213.910	24.400	-240158.6	
3300.00	403914.1	-314439.8	2.7079E+02	217.683	26.675	-341877.7	
3500.00	409349.5	-358136.9	2.8720E+02	219.282	27.674	-387237.7	

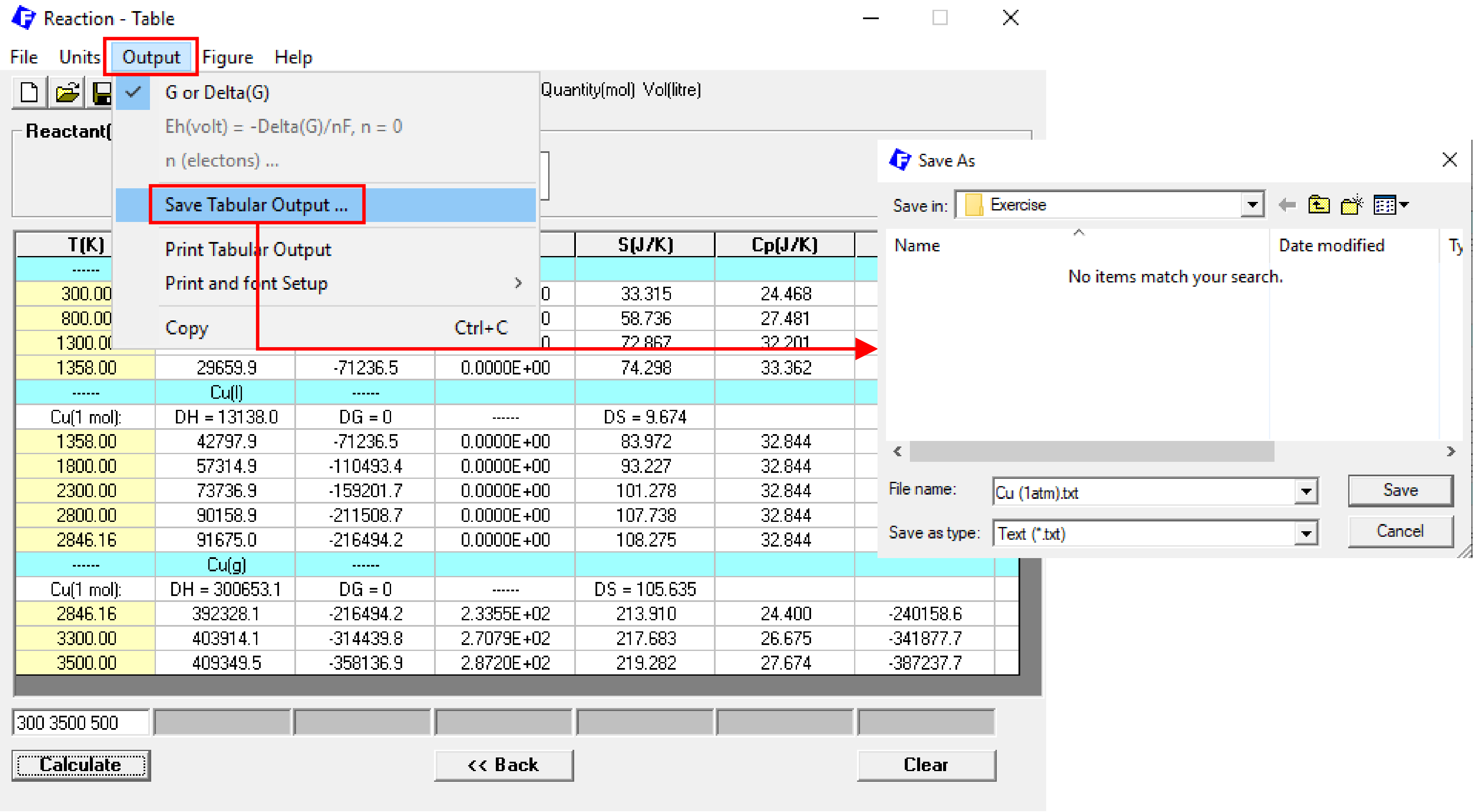
300 3500 500

All the thermodynamic properties against *T* for 1 mol Cu are shown. Note the volume data is zero because we didn't consider the volumetric data (Reactant Window).

FactSage helps us find the phase transition points.

Reaction Module: Pure Cu

Table Window: Output Results



Save in: Exercise

File name: Cu (1atm).txt

Save as type: Text (*.txt)

300 3500 500

T(K)				S(J/K)	Cp(J/K)	

300.00				33.315	24.468	
800.00				58.736	27.481	
1300.00				72.867	32.201	
1358.00	29659.9	-71236.5	0.0000E+00	74.298	33.362	
------	Cu(l)	------				
Cu(1 mol):	DH = 13138.0	DG = 0	------	DS = 9.674		
1358.00	42797.9	-71236.5	0.0000E+00	83.972	32.844	
1800.00	57314.9	-110493.4	0.0000E+00	93.227	32.844	
2300.00	73736.9	-159201.7	0.0000E+00	101.278	32.844	
2800.00	90158.9	-211508.7	0.0000E+00	107.738	32.844	
2846.16	91675.0	-216494.2	0.0000E+00	108.275	32.844	
------	Cu(g)	------				
Cu(1 mol):	DH = 300653.1	DG = 0	------	DS = 105.635		
2846.16	392328.1	-216494.2	2.3355E+02	213.910	24.400	-240158.6
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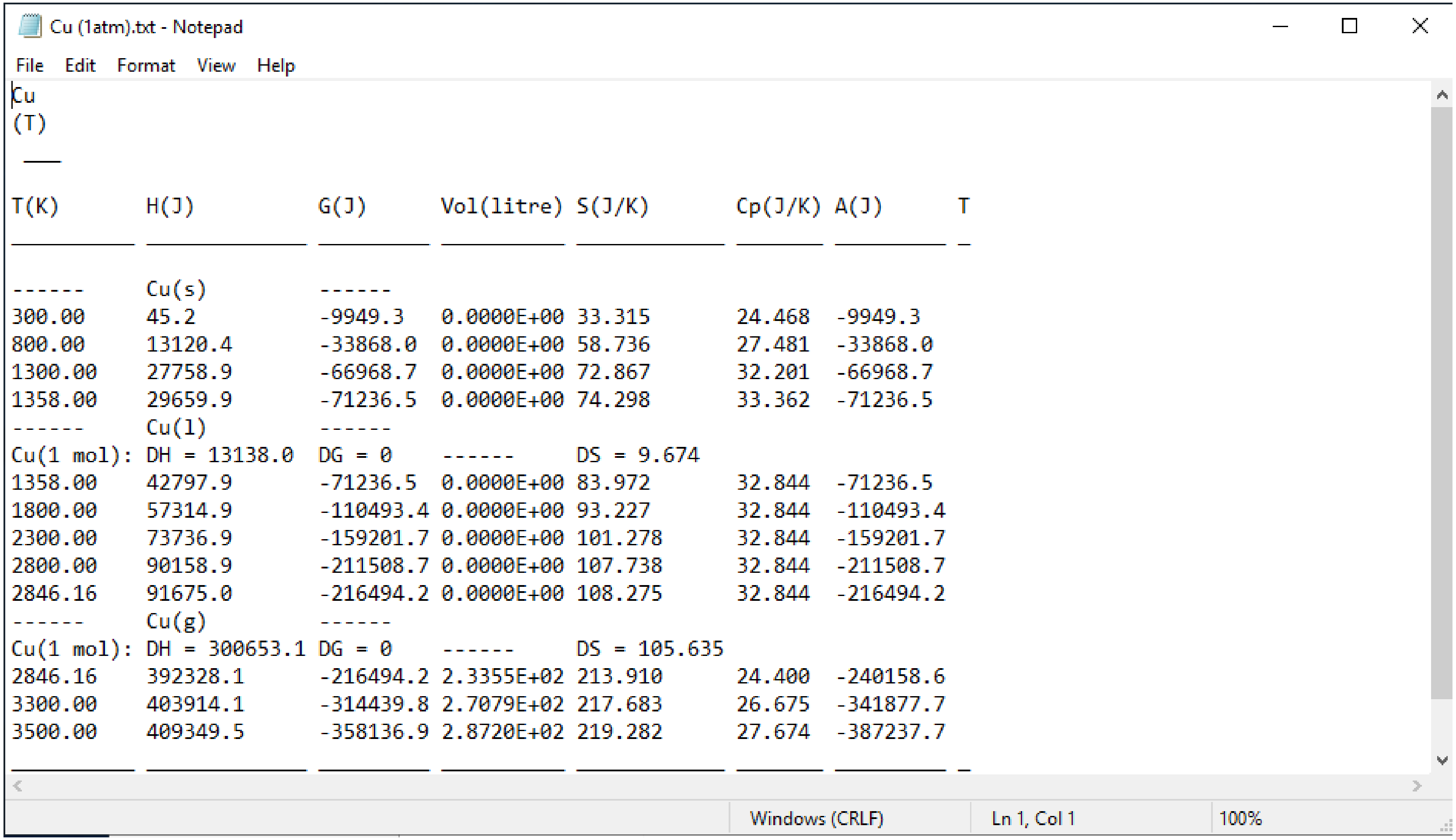
3500.00	409349.5	-358136.9	2.8720E+02	219.282	27.674	-387237.7

Reaction Module: Pure Cu

Table Window: Output Results



```
Cu
(T)
 ___

T(K)       H(J)          G(J)      Vol(litre) S(J/K)       Cp(J/K) A(J)      T
__________ _____________ _________ __________ ____________ _______ _________ _

------     Cu(s)         ------
300.00     45.2          -9949.3   0.0000E+00 33.315       24.468  -9949.3
800.00     13120.4       -33868.0  0.0000E+00 58.736       27.481  -33868.0
1300.00    27758.9       -66968.7  0.0000E+00 72.867       32.201  -66968.7
1358.00    29659.9       -71236.5  0.0000E+00 74.298       33.362  -71236.5
------     Cu(l)         ------
Cu(1 mol): DH = 13138.0  DG = 0    ------     DS = 9.674
1358.00    42797.9       -71236.5  0.0000E+00 83.972       32.844  -71236.5
1800.00    57314.9       -110493.4 0.0000E+00 93.227       32.844  -110493.4
2300.00    73736.9       -159201.7 0.0000E+00 101.278      32.844  -159201.7
2800.00    90158.9       -211508.7 0.0000E+00 107.738      32.844  -211508.7
2846.16    91675.0       -216494.2 0.0000E+00 108.275      32.844  -216494.2
------     Cu(g)         ------
Cu(1 mol): DH = 300653.1 DG = 0    ------     DS = 105.635
2846.16    392328.1      -216494.2 2.3355E+02 213.910      24.400  -240158.6
3300.00    403914.1      -314439.8 2.7079E+02 217.683      26.675  -341877.7
3500.00    409349.5      -358136.9 2.8720E+02 219.282      27.674  -387237.7

__________ _____________ _________ __________ ____________ _______ _________ _
```

Reaction Module: Heating of Cu

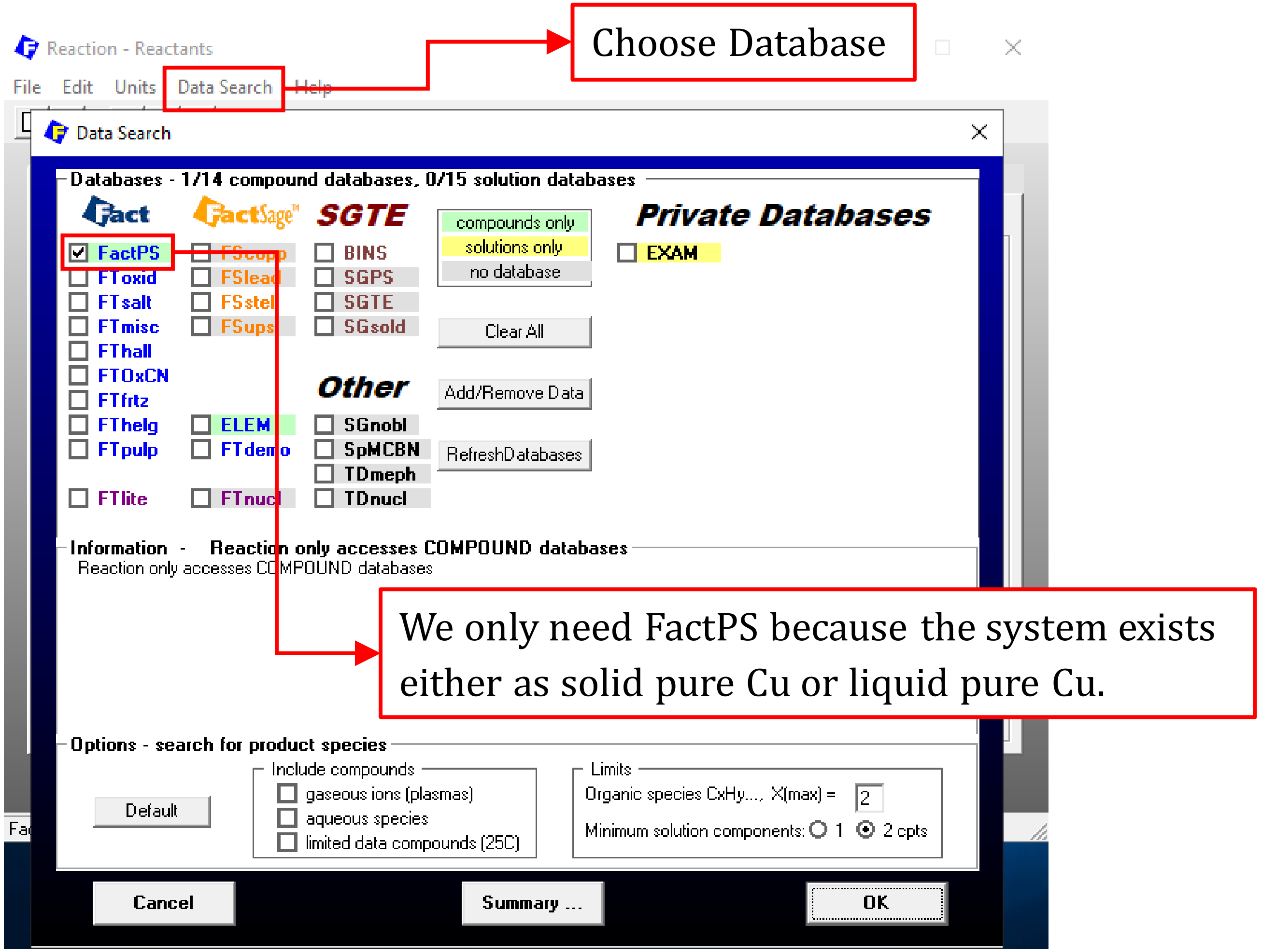
The second example we will be looking at is the heating of Cu from 300 K. This process can be described by the following reaction:

$$\mathrm{Cu}(300\ \mathrm{K}) = \mathrm{Cu}(T)$$

Let us determine the amount of heat (strictly speaking, enthalpy) required to melt 1 mole Cu from 300 K.

Reaction Module: Heating of Cu

Reactants Window: Choose the database



Choose Database

Databases - 1/14 compound databases, 0/15 solution databases

☑ FactPS
☐ FToxid
☐ FTsalt
☐ FTmisc
☐ FThall
☐ FTOxCN
☐ FTfrtz
☐ FThelg
☐ FTpulp
☐ FTlite
☐ FScopp
☐ FSlead
☐ FSstel
☐ FSups
☐ ELEM
☐ FTdemo
☐ FTnucl
☐ BINS
☐ SGPS
☐ SGTE
☐ SGsold
☐ SGnobl
☐ SpMCBN
☐ TDmeph
☐ TDnucl
☐ EXAM

Information - Reaction only accesses COMPOUND databases
Reaction only accesses COMPOUND databases

We only need FactPS because the system exists either as solid pure Cu or liquid pure Cu.

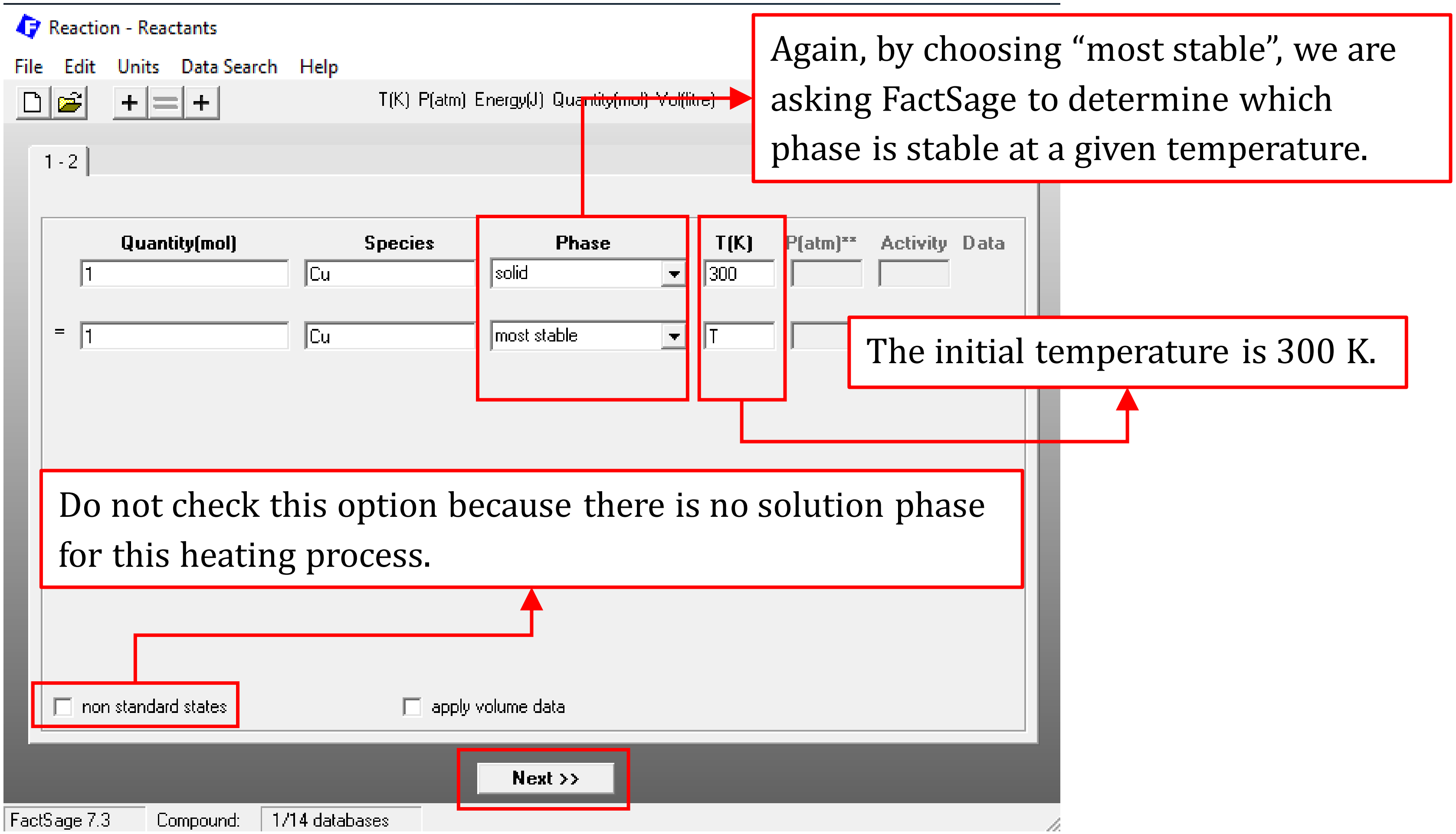
Options - search for product species

Include compounds
☐ gaseous ions (plasmas)
☐ aqueous species
☐ limited data compounds (25C)

Limits
Organic species CxHy...., X(max) = 2
Minimum solution components: ○ 1 ● 2 cpts

Reaction Module: Heating of Cu

Reactants Window: Set Reactants (Phase and Temperature)



Quantity(mol)	Species	Phase	T(K)
1	Cu	solid	300
= 1	Cu	most stable	T

☐ non standard states ☐ apply volume data

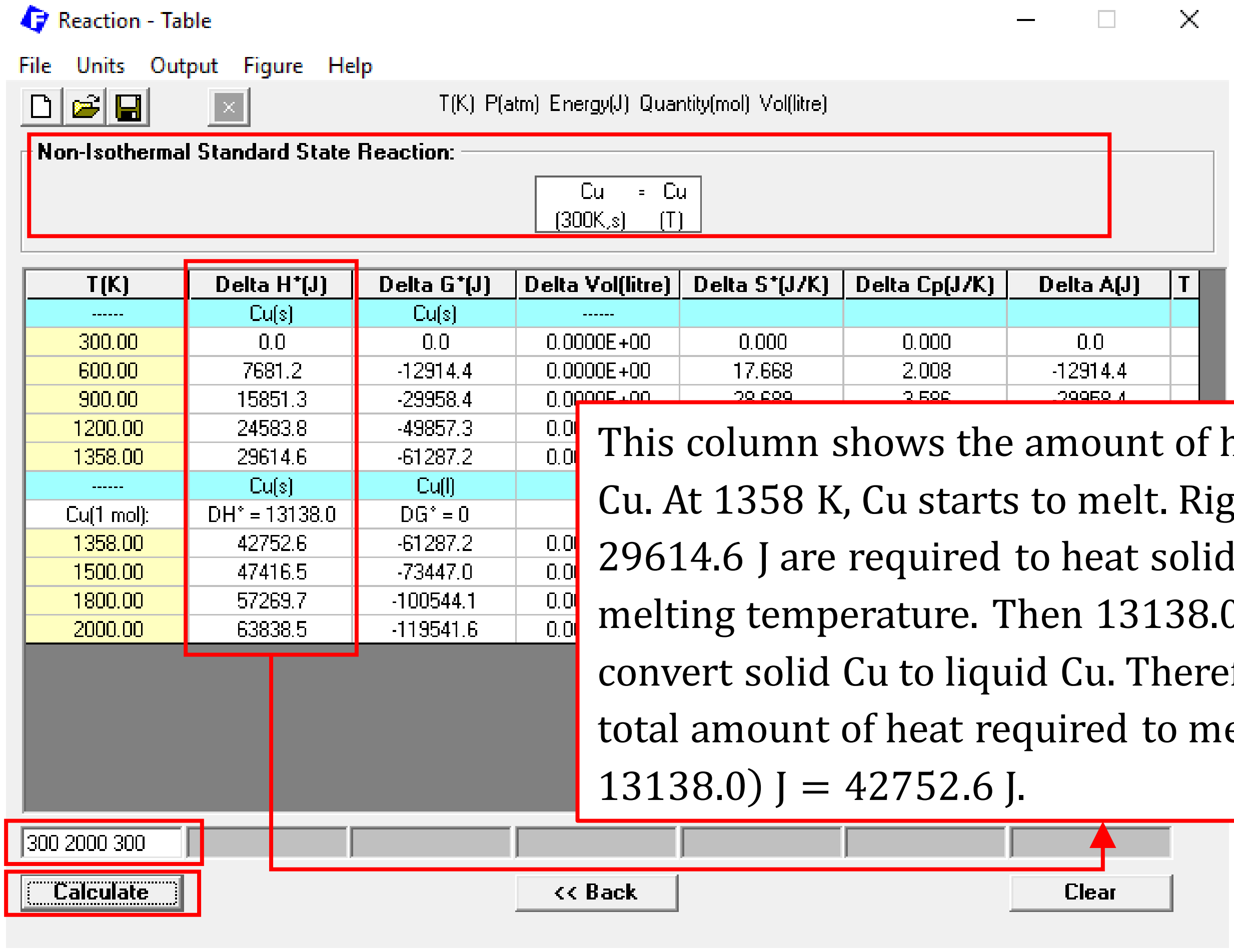
Again, by choosing “most stable”, we are asking FactSage to determine which phase is stable at a given temperature.

The initial temperature is 300 K.

Do not check this option because there is no solution phase for this heating process.

Reaction Module: Heating of Cu

Table Window: Set Conditions and Results



Non-Isothermal Standard State Reaction:

Cu (300K,s) = Cu (T)

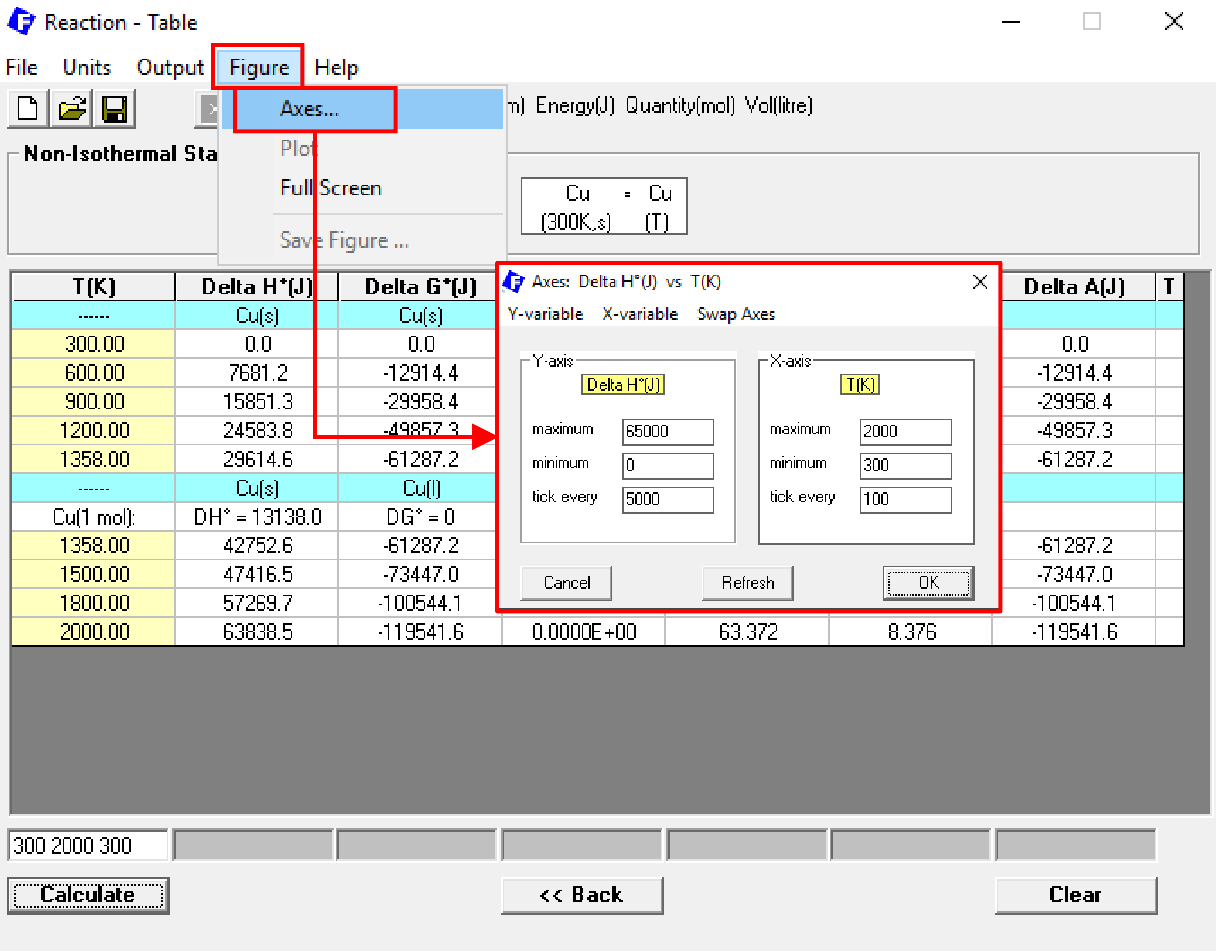
T(K)	Delta H°(J)	Delta G°(J)	Delta Vol(litre)	Delta S°(J/K)	Delta Cp(J/K)	Delta A(J)	T
------	Cu(s)	Cu(s)	------				
300.00	0.0	0.0	0.0000E+00	0.000	0.000	0.0	
600.00	7681.2	-12914.4	0.0000E+00	17.668	2.008	-12914.4	
900.00	15851.3	-29958.4	0.0000E+00				
1200.00	24583.8	-49857.3	0.0				
1358.00	29614.6	-61287.2	0.0				
------	Cu(s)	Cu(l)					
Cu(1 mol):	DH° = 13138.0	DG° = 0					
1358.00	42752.6	-61287.2	0.0				
1500.00	47416.5	-73447.0	0.0				
1800.00	57269.7	-100544.1	0.0				
2000.00	63838.5	-119541.6	0.0				

300 2000 300

This column shows the amount of heat required to heat Cu. At 1358 K, Cu starts to melt. Right before melting, 29614.6 J are required to heat solid Cu from 300 to the melting temperature. Then 13138.0 J are required to convert solid Cu to liquid Cu. Therefore, the minimum total amount of heat required to melt Cu is (29614.6 + 13138.0) J = 42752.6 J.

Reaction Module: Heating of Cu

Table Window: Plot Results



Cu (300K,s) = Cu (T)

T(K)	Delta H°(J)	Delta G°(J)				Delta A(J)	T
------	Cu(s)	Cu(s)					
300.00	0.0	0.0				0.0	
600.00	7681.2	-12914.4				-12914.4	
900.00	15851.3	-29958.4				-29958.4	
1200.00	24583.8	-49857.3				-49857.3	
1358.00	29614.6	-61287.2				-61287.2	
------	Cu(s)	Cu(l)					
Cu(1 mol):	DH° = 13138.0	DG° = 0					
1358.00	42752.6	-61287.2				-61287.2	
1500.00	47416.5	-73447.0				-73447.0	
1800.00	57269.7	-100544.1				-100544.1	
2000.00	63838.5	-119541.6	0.0000E+00	63.372	8.376	-119541.6	

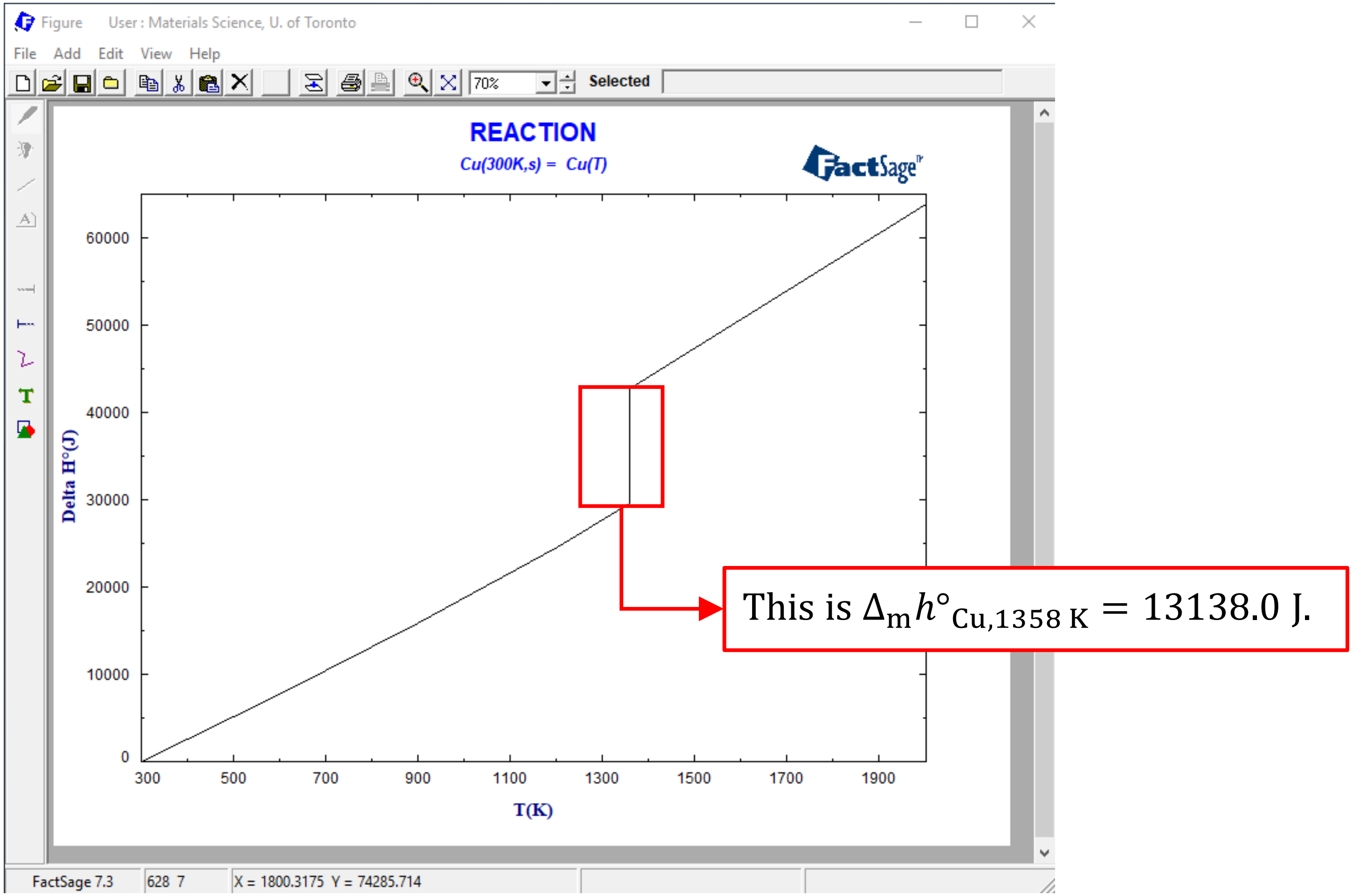
Axes: Delta H°(J) vs T(K)

Y-axis	Delta H°(J)	X-axis	T(K)
maximum	65000	maximum	2000
minimum	0	minimum	300
tick every	5000	tick every	100

300 2000 300

Reaction Module: Heating of Cu

Table Window: Plot Results



This is $\Delta_m h°_{\mathrm{Cu,1358\ K}} = 13138.0$ J.

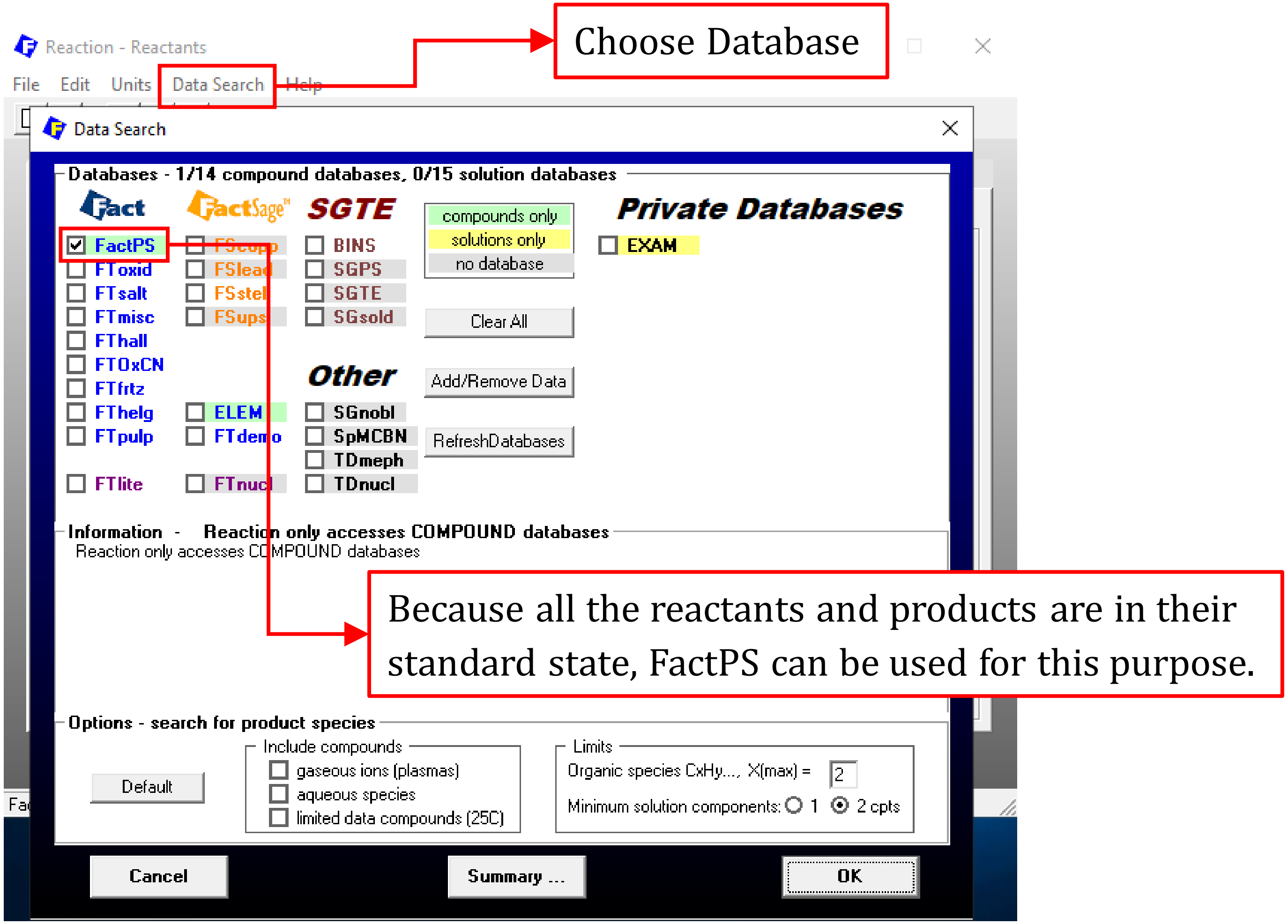
Reaction Module: Oxidation of Cu

The third example we will be discussing is to calculate the thermodynamic properties of the oxidation of Cu by pure oxygen.

First, let us look at the standard state calculation in which all reactants and products are in their standard state.

Reaction Module: Oxidation of Cu

Reactants Window: Choose the database



Databases - 1/14 compound databases, 0/15 solution databases

☑ FactPS

Information - Reaction only accesses COMPOUND databases

Reaction only accesses COMPOUND databases

Organic species CxHy..., X(max) = 2

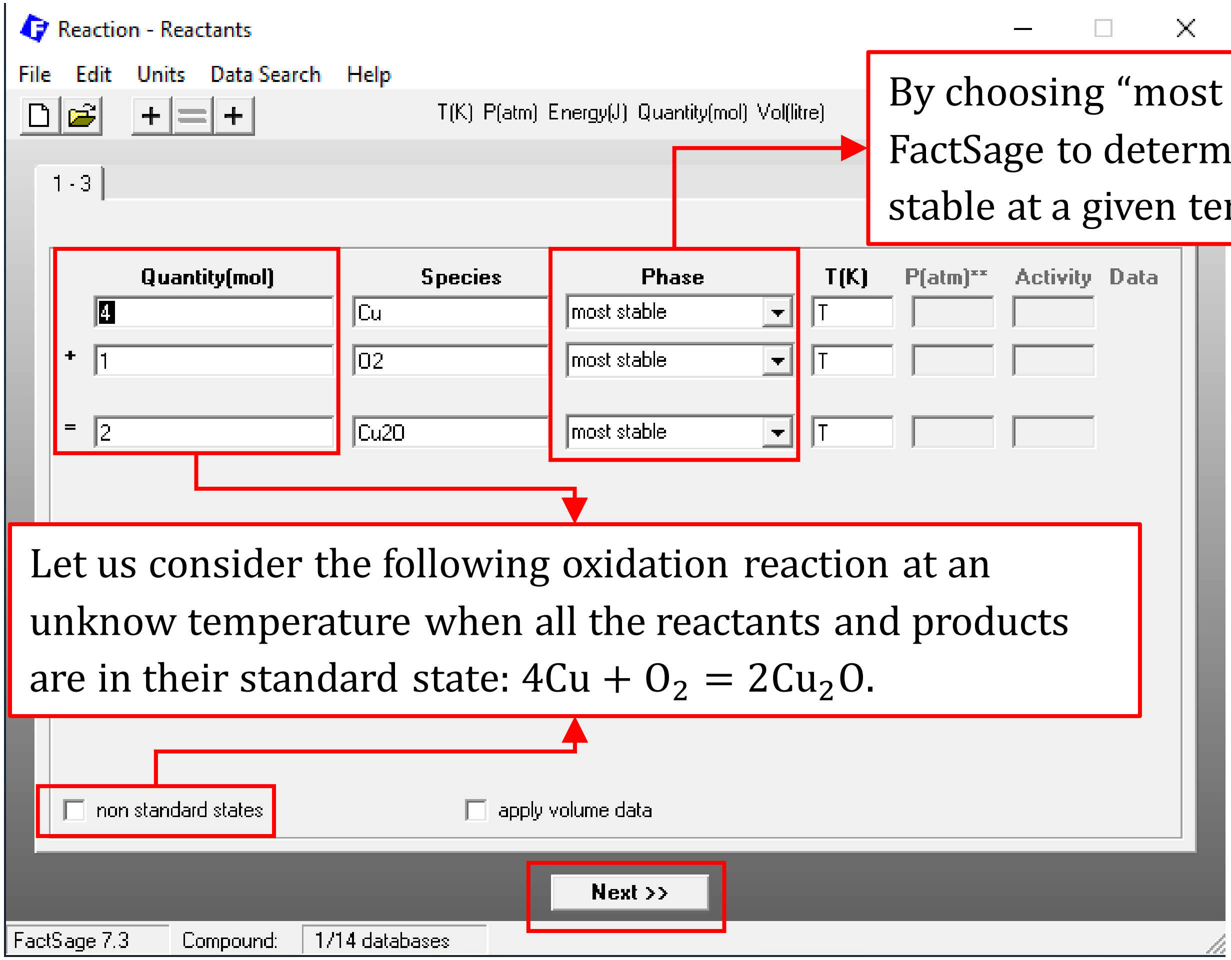
Minimum solution components: ○ 1 ● 2 cpts

Choose Database

Because all the reactants and products are in their standard state, FactPS can be used for this purpose.

Reaction Module: Oxidation of Cu

Reactants Window: Set Reactants (Phase and Temperature)



Quantity(mol)	Species	Phase	T(K)
4	Cu	most stable	T
+ 1	O2	most stable	T
= 2	Cu2O	most stable	T

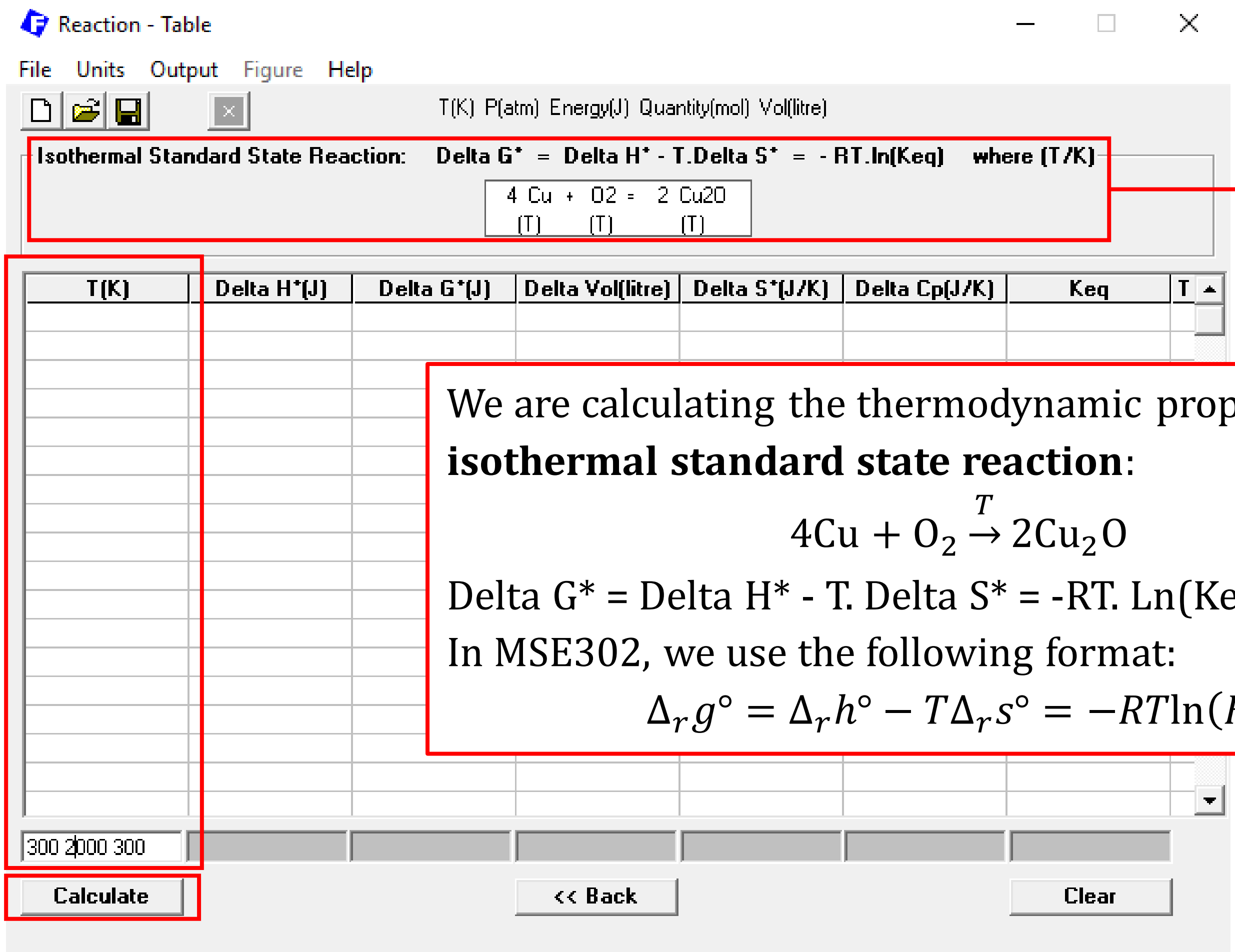
☐ non standard states ☐ apply volume data

By choosing "most stable", we are asking FactSage to determine which phase is stable at a given temperature.

Let us consider the following oxidation reaction at an unknow temperature when all the reactants and products are in their standard state: $4\text{Cu} + \text{O}_2 = 2\text{Cu}_2\text{O}$.

Reaction Module: Oxidation of Cu

Table Window: Set Conditions



Isothermal Standard State Reaction: Delta G° = Delta H° - T.Delta S° = - RT.ln(Keq) where (T/K)

4 Cu + O2 = 2 Cu2O
(T) (T) (T)

300 2000 300

We are calculating the thermodynamic properties for an **isothermal standard state reaction**:

$$4\mathrm{Cu} + \mathrm{O_2} \xrightarrow{T} 2\mathrm{Cu_2O}$$

Delta G* = Delta H* - T. Delta S* = -RT. Ln(Keq)

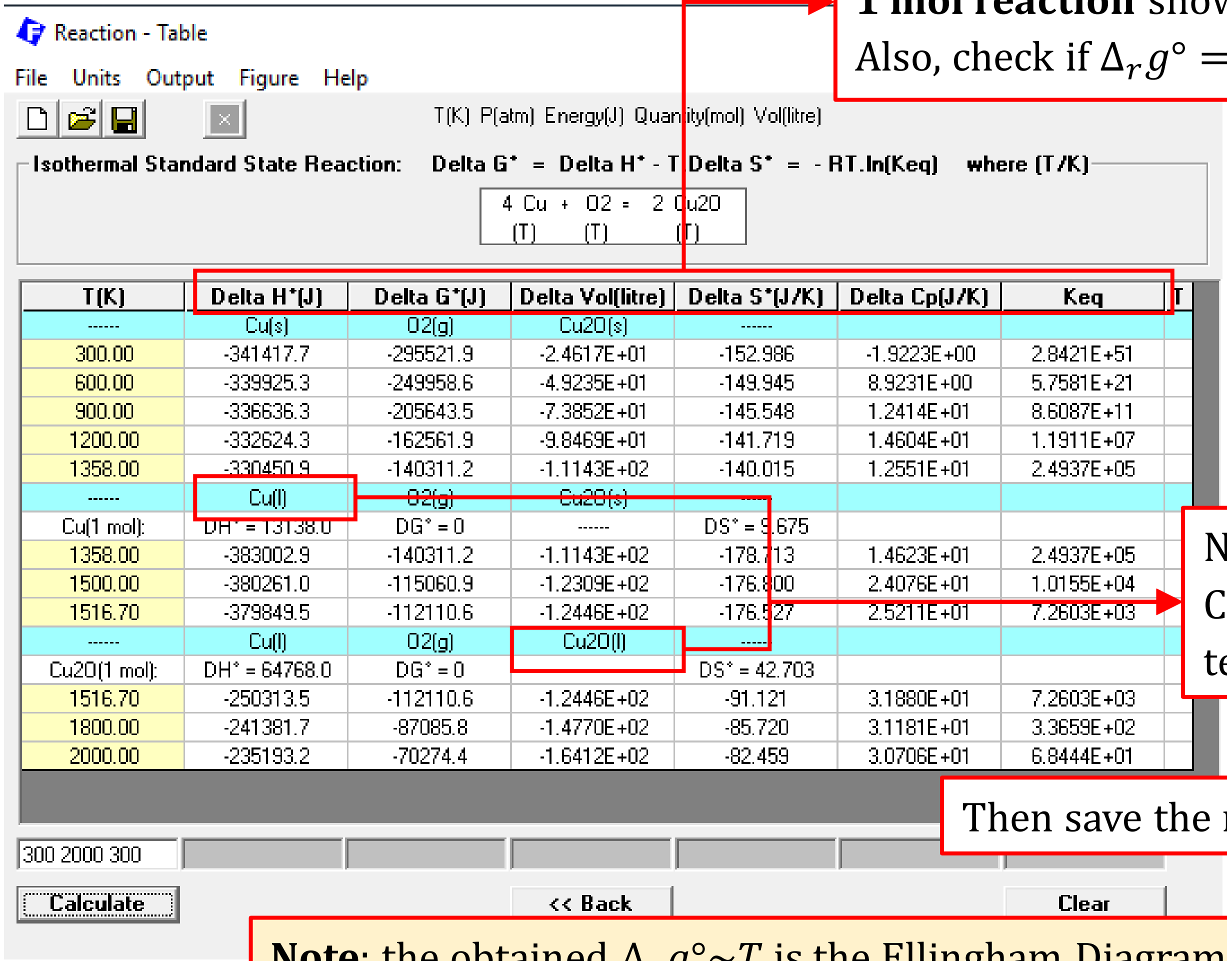
In MSE302, we use the following format:

$$\Delta_r g^\circ = \Delta_r h^\circ - T\Delta_r s^\circ = -RT\ln(K)$$

Reaction Module: Oxidation of Cu

Table Window: Results

All the thermodynamic properties against T for **1 mol reaction** shown below.
Also, check if $\Delta_r g° = \Delta_r h° - T\Delta_r s° = -RT\ln(K)$



Isothermal Standard State Reaction: Delta G° = Delta H° - T Delta S° = - RT.ln(Keq) where (T/K)

4 Cu + O2 = 2 Cu2O
(T) (T) (T)

T(K)	Delta H°(J)	Delta G°(J)	Delta Vol(litre)	Delta S°(J/K)	Delta Cp(J/K)	Keq
------	Cu(s)	O2(g)	Cu2O(s)	------		
300.00	-341417.7	-295521.9	-2.4617E+01	-152.986	-1.9223E+00	2.8421E+51
600.00	-339925.3	-249958.6	-4.9235E+01	-149.945	8.9231E+00	5.7581E+21
900.00	-336636.3	-205643.5	-7.3852E+01	-145.548	1.2414E+01	8.6087E+11
1200.00	-332624.3	-162561.9	-9.8469E+01	-141.719	1.4604E+01	1.1911E+07
1358.00	-330450.9	-140311.2	-1.1143E+02	-140.015	1.2551E+01	2.4937E+05
------	Cu(l)	O2(g)	Cu2O(s)	------		
Cu(1 mol):	DH° = 13138.0	DG° = 0	------	DS° = 9.675		
1358.00	-383002.9	-140311.2	-1.1143E+02	-178.713	1.4623E+01	2.4937E+05
1500.00	-380261.0	-115060.9	-1.2309E+02	-176.800	2.4076E+01	1.0155E+04
1516.70	-379849.5	-112110.6	-1.2446E+02	-176.527	2.5211E+01	7.2603E+03
------	Cu(l)	O2(g)	Cu2O(l)	------		
Cu2O(1 mol):	DH° = 64768.0	DG° = 0		DS° = 42.703		
1516.70	-250313.5	-112110.6	-1.2446E+02	-91.121	3.1880E+01	7.2603E+03
1800.00	-241381.7	-87085.8	-1.4770E+02	-85.720	3.1181E+01	3.3659E+02
2000.00	-235193.2	-70274.4	-1.6412E+02	-82.459	3.0706E+01	6.8444E+01

Note the state change of Cu and Cu_2O (please record these two temperatures).

Then save the results as ".txt"

Note: the obtained $\Delta_r g° \sim T$ is the Ellingham Diagram.

Reaction Module: Oxidation of Cu

Non-standard State Calculation (Part 1)

This time, let us calculate non-standard state reactions. The first scenario is that the oxidation reaction occurs at an unknow temperature when Cu and Cu_2O are pure substance while the partial pressure of O_2 is a variable.

For non-standard state reactions, we **have to specify the state of reactants and products** because defining activity requires the definition of standard state which either is pure solid or pure liquid. From the preceding calculation of the standard state reaction, we have,

$$2\mathrm{Cu}(s) + 0.5\mathrm{O}_2(g) = \mathrm{Cu}_2\mathrm{O}(s); T < 1358\ \mathrm{K}$$

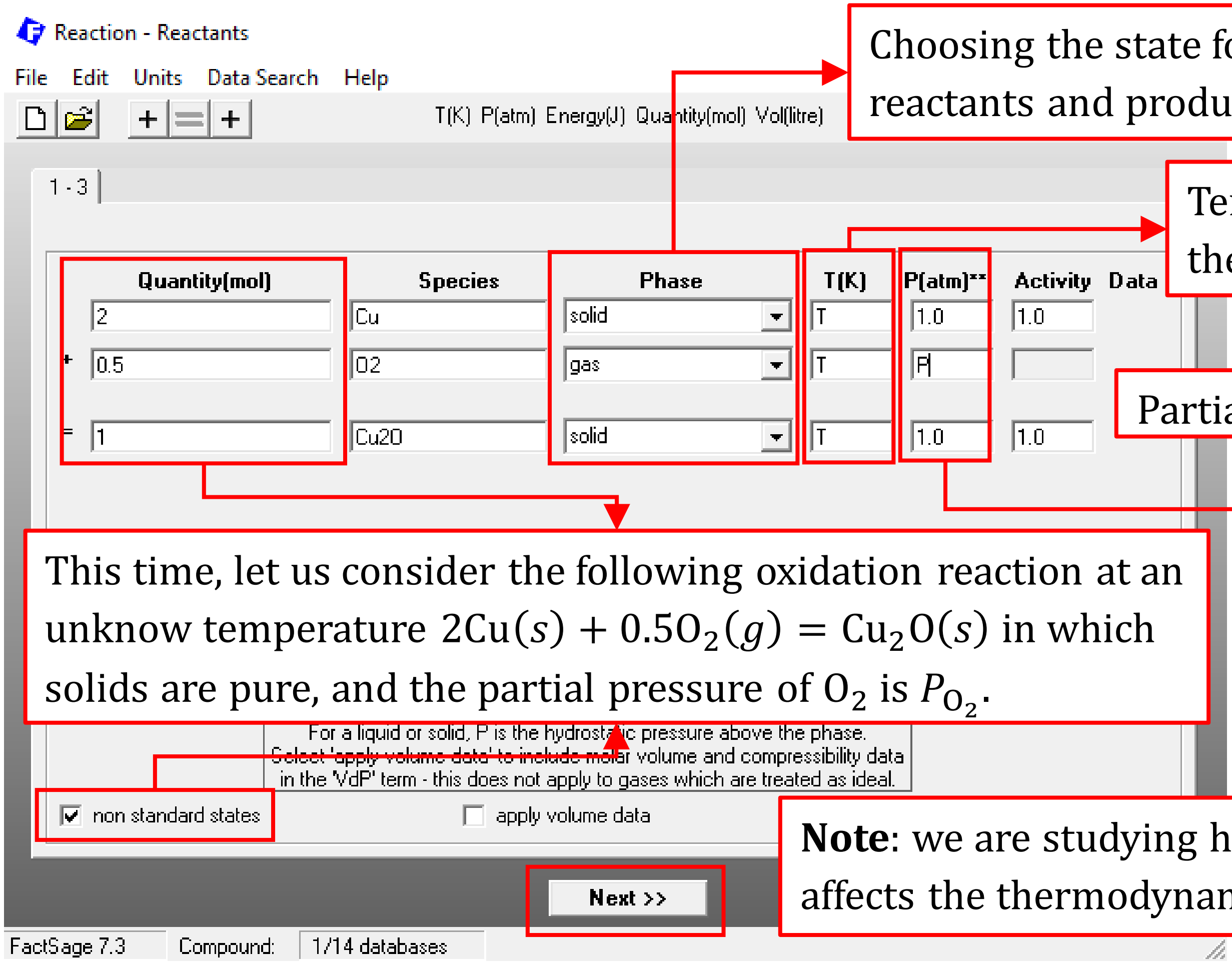
$$2\mathrm{Cu}(l) + 0.5\mathrm{O}_2(g) = \mathrm{Cu}_2\mathrm{O}(s); 1358\ \mathrm{K} < T < 1516.7\ \mathrm{K}$$

$$2\mathrm{Cu}(l) + 0.5\mathrm{O}_2(g) = \mathrm{Cu}_2\mathrm{O}(l);\ T > 1516.7\ \mathrm{K}$$

Therefore, we need to perform 3 calculations for 3 different temperature ranges. Here, we only demonstrate the calculation for the first temperature range.

Reaction Module: Oxidation of Cu

Reactants Window: Set Reactants (Phase and Temperature)



	Quantity(mol)	Species	Phase	T(K)	P(atm)**	Activity	Data
	2	Cu	solid	T	1.0	1.0	
+	0.5	O2	gas	T	P		
=	1	Cu2O	solid	T	1.0	1.0	

For a liquid or solid, P is the hydrostatic pressure above the phase. Select 'apply volume data' to include molar volume and compressibility data in the 'VdP' term - this does not apply to gases which are treated as ideal.

☑ non standard states ☐ apply volume data

Choosing the state for all reactants and products.

Temperature will be specified in the Table Window.

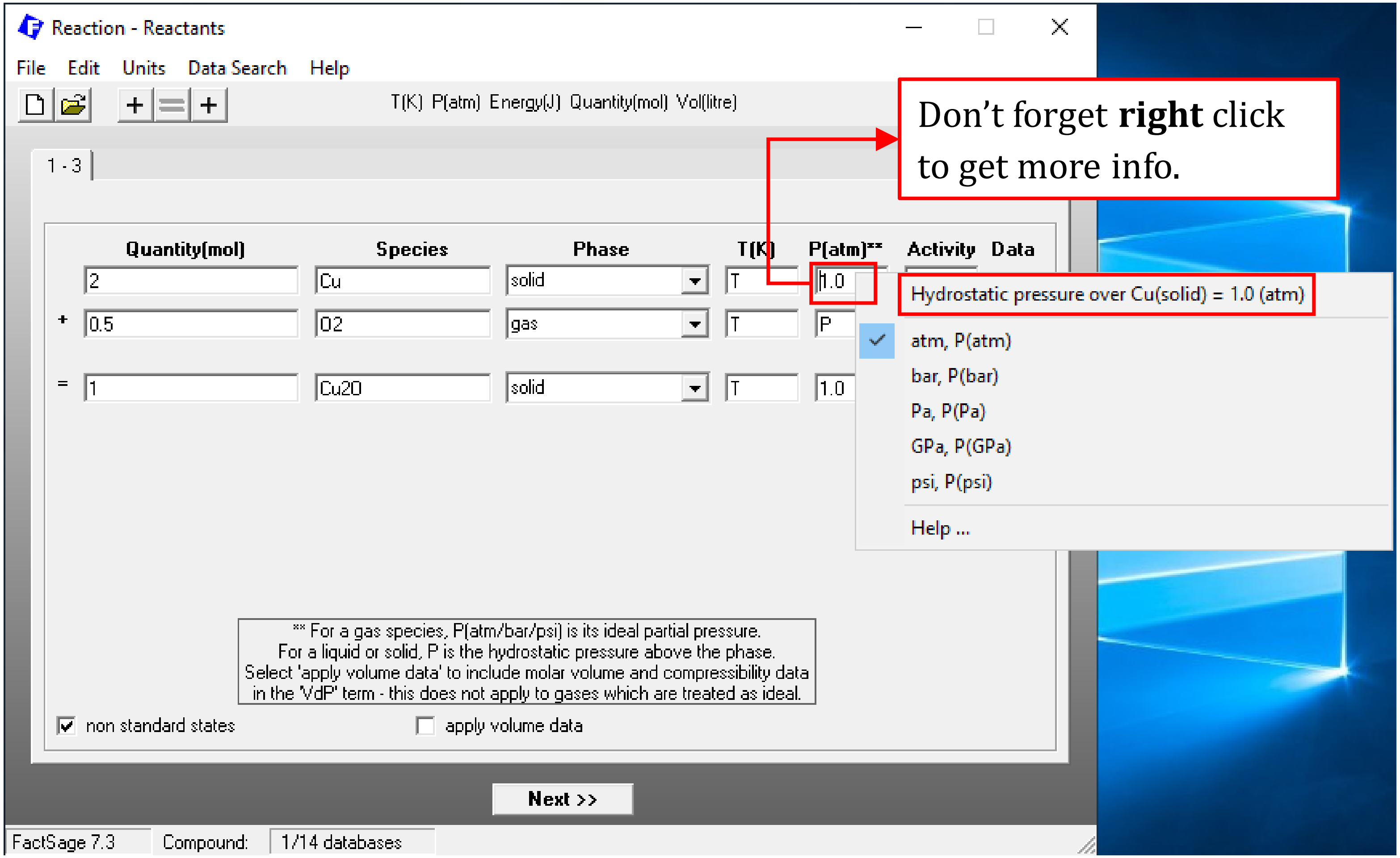
Partial pressure of O_2 is set as P.

This time, let us consider the following oxidation reaction at an unknow temperature $2Cu(s) + 0.5O_2(g) = Cu_2O(s)$ in which solids are pure, and the partial pressure of O_2 is P_{O_2}.

Note: we are studying how partial pressure of O_2 affects the thermodynamics of the oxidation of Cu.

Reaction Module: Oxidation of Cu

Reactants Window: Set Reactants (Phase and Temperature)



	Quantity(mol)	Species	Phase	T(K)	P(atm)**
	2	Cu	solid	T	1.0
+	0.5	O2	gas	T	P
=	1	Cu2O	solid	T	1.0

Hydrostatic pressure over Cu(solid) = 1.0 (atm)

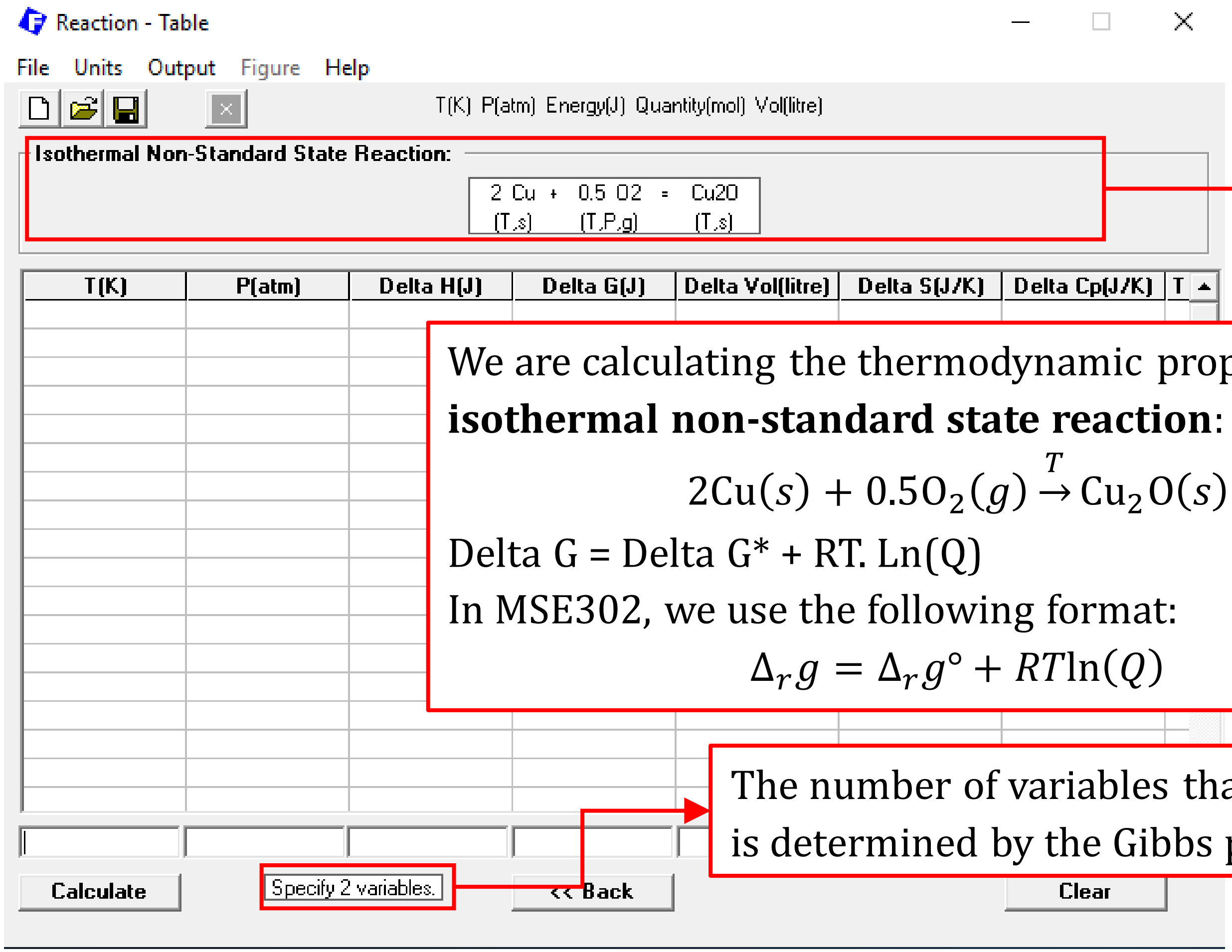
** For a gas species, P(atm/bar/psi) is its ideal partial pressure.
For a liquid or solid, P is the hydrostatic pressure above the phase.
Select 'apply volume data' to include molar volume and compressibility data in the 'VdP' term - this does not apply to gases which are treated as ideal.

☑ non standard states ☐ apply volume data

Don't forget **right** click to get more info.

Reaction Module: Oxidation of Cu

Table Window: Set Conditions



Isothermal Non-Standard State Reaction:

2 Cu	+	0.5 O2	=	Cu2O
(T,s)		(T,P,g)		(T,s)

T(K)	P(atm)	Delta H(J)	Delta G(J)	Delta Vol(litre)	Delta S(J/K)	Delta Cp(J/K)	T

Specify 2 variables.

We are calculating the thermodynamic properties for an **isothermal non-standard state reaction**:

$$2\mathrm{Cu}(s) + 0.5\mathrm{O}_2(g) \xrightarrow{T} \mathrm{Cu}_2\mathrm{O}(s)$$

Delta G = Delta G* + RT. Ln(Q)

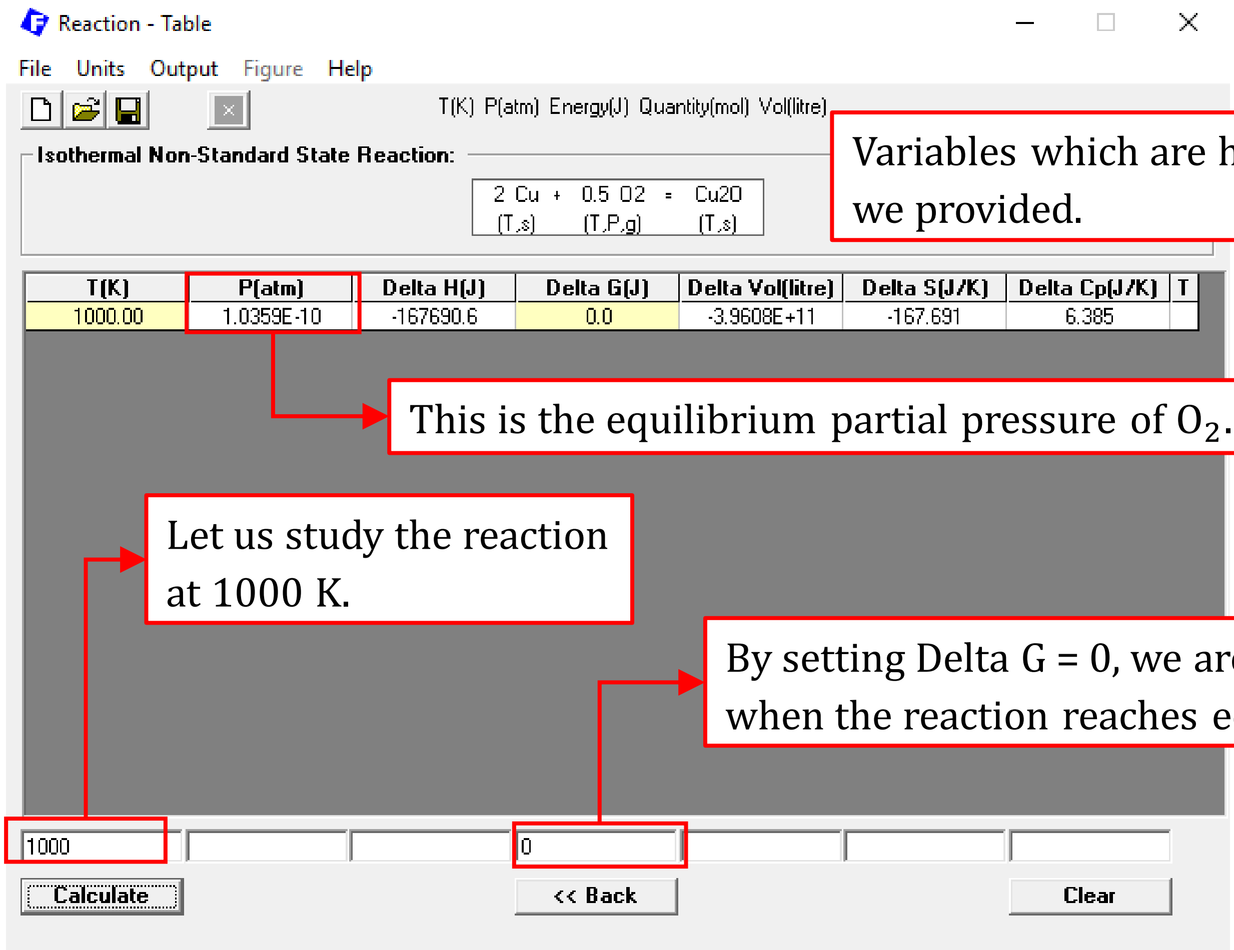
In MSE302, we use the following format:

$$\Delta_r g = \Delta_r g^\circ + RT\ln(Q)$$

The number of variables that need to be specified is determined by the Gibbs phase rule.

Reaction Module: Oxidation of Cu

Table Window: Results



Isothermal Non-Standard State Reaction:

$2\ Cu\ (T,s) + 0.5\ O2\ (T,P,g) = Cu2O\ (T,s)$

T(K)	P(atm)	Delta H(J)	Delta G(J)	Delta Vol(litre)	Delta S(J/K)	Delta Cp(J/K)	T
1000.00	1.0359E-10	-167690.6	0.0	-3.9608E+11	-167.691	6.385	

1000			0			

Variables which are highlighted are the conditions we provided.

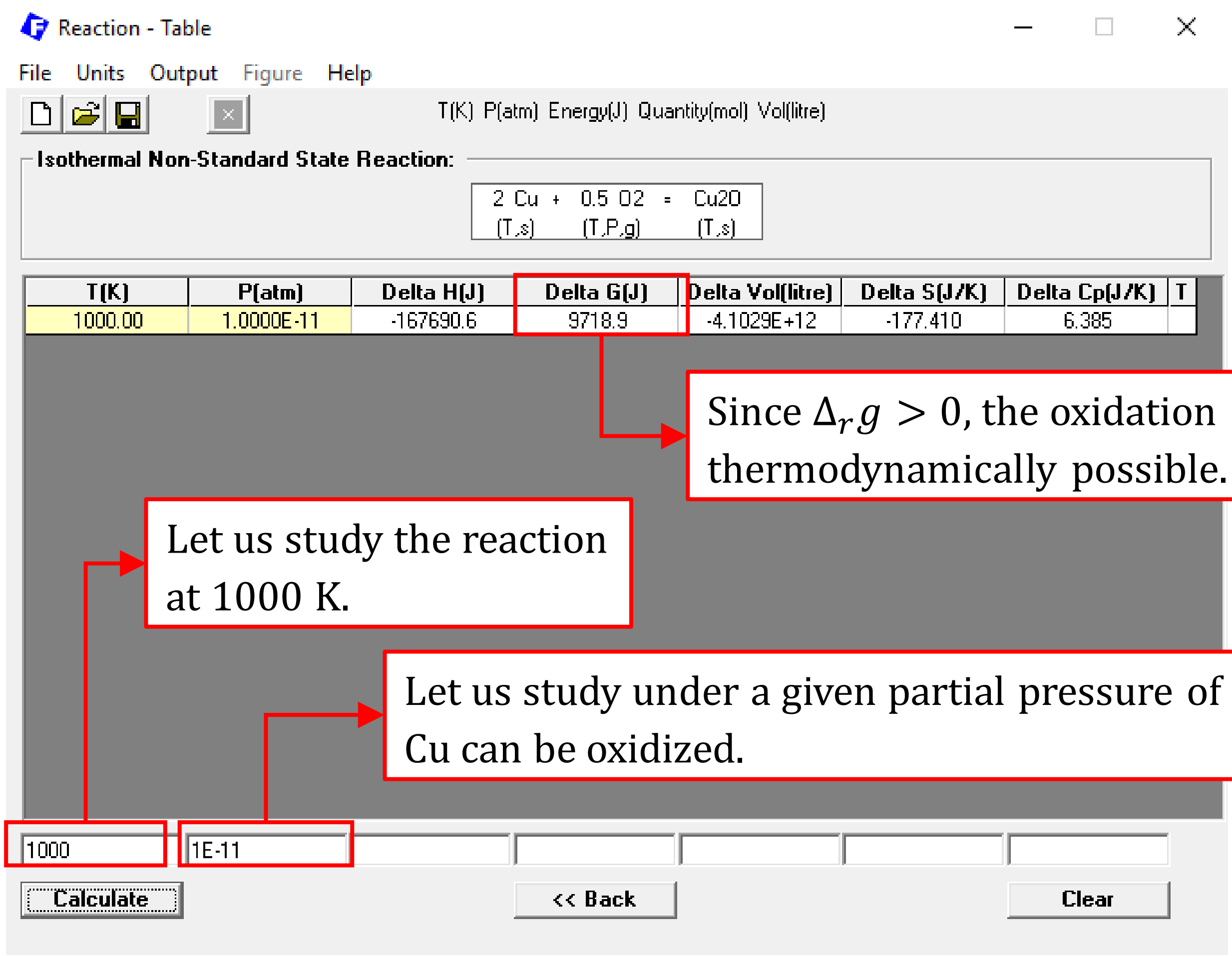
This is the equilibrium partial pressure of O_2.

Let us study the reaction at 1000 K.

By setting Delta G = 0, we are performing the calculation when the reaction reaches equilibrium.

Reaction Module: Oxidation of Cu

Table Window: Results



Isothermal Non-Standard State Reaction:

2 Cu	+	0.5 O2	=	Cu2O
(T,s)		(T,P,g)		(T,s)

T(K)	P(atm)	Delta H(J)	Delta G(J)	Delta Vol(litre)	Delta S(J/K)	Delta Cp(J/K)	T
1000.00	1.0000E-11	-167690.6	9718.9	-4.1029E+12	-177.410	6.385	

T(K): 1000

P(atm): 1E-11

Since $\Delta_r g > 0$, the oxidation is not thermodynamically possible.

Let us study the reaction at 1000 K.

Let us study under a given partial pressure of O_2, if pure Cu can be oxidized.

Reaction Module: Oxidation of Cu

Non-standard State Calculation (Part 2)

Now let us consider the removal of impurity Cu from a gold bath by blowing pure oxygen at 1 atm. The operation temperature is 1400 K, and the product is pure $\mathrm{Cu_2O}$.

The above reaction can be described as:

$$2\mathrm{Cu}(l, \text{solute in liquid Au}) + 0.5\mathrm{O_2}(g, 1\ \text{atm}) = \mathrm{Cu_2O}(s)$$

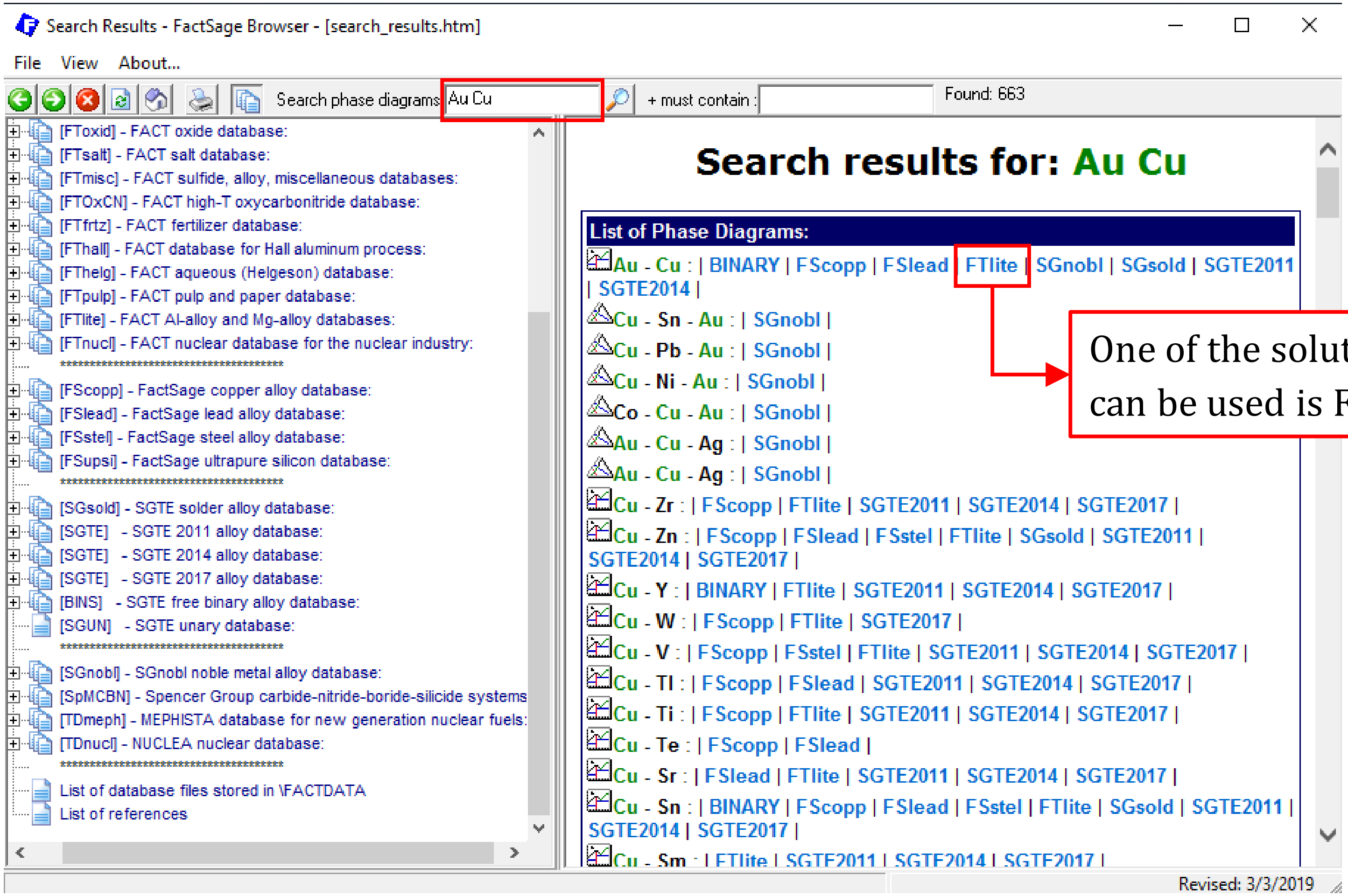
To study the equilibrium of this reaction, we use $\Delta_r g$.

$$\Delta_r g = \Delta_r g^\circ + RT\ln\left(\frac{\left(a_{\mathrm{Cu_2O}}^{(s2)}\right)^1}{\left(a_{\mathrm{Cu}}^{(l)}\right)^2\left(P_{\mathrm{O_2}}\right)^{0.5}}\right) \text{ where } a_{\mathrm{Cu_2O}}^{(s2)} = 1 \text{ and } P_{\mathrm{O_2}} = 1$$

$a_{\mathrm{Cu}}^{(l)}$ depends on the liquid Au-Cu model. Therefore, we need to choose a solution database in which the Au-Cu system has been optimized (using Documentation or View Data).

Reaction Module: Oxidation of Cu

Documentation: determine which **solution** database for the Au-Cu system



Search Results - FactSage Browser - [search_results.htm]

File View About...

Search phase diagrams: Au Cu

+ must contain :

Found: 663

[FToxid] - FACT oxide database:
[FTsalt] - FACT salt database:
[FTmisc] - FACT sulfide, alloy, miscellaneous databases:
[FTOxCN] - FACT high-T oxycarbonitride database:
[FTfrtz] - FACT fertilizer database:
[FThall] - FACT database for Hall aluminum process:
[FThelg] - FACT aqueous (Helgeson) database:
[FTpulp] - FACT pulp and paper database:
[FTlite] - FACT Al-alloy and Mg-alloy databases:
[FTnucl] - FACT nuclear database for the nuclear industry:
****
[FScopp] - FactSage copper alloy database:
[FSlead] - FactSage lead alloy database:
[FSstel] - FactSage steel alloy database:
[FSupsi] - FactSage ultrapure silicon database:
****
[SGsold] - SGTE solder alloy database:
[SGTE] - SGTE 2011 alloy database:
[SGTE] - SGTE 2014 alloy database:
[SGTE] - SGTE 2017 alloy database:
[BINS] - SGTE free binary alloy database:
[SGUN] - SGTE unary database:
****
[SGnobl] - SGnobl noble metal alloy database:
[SpMCBN] - Spencer Group carbide-nitride-boride-silicide systems
[TDmeph] - MEPHISTA database for new generation nuclear fuels:
[TDnucl] - NUCLEA nuclear database:
****
List of database files stored in \FACTDATA
List of references

Search results for: Au Cu

List of Phase Diagrams:

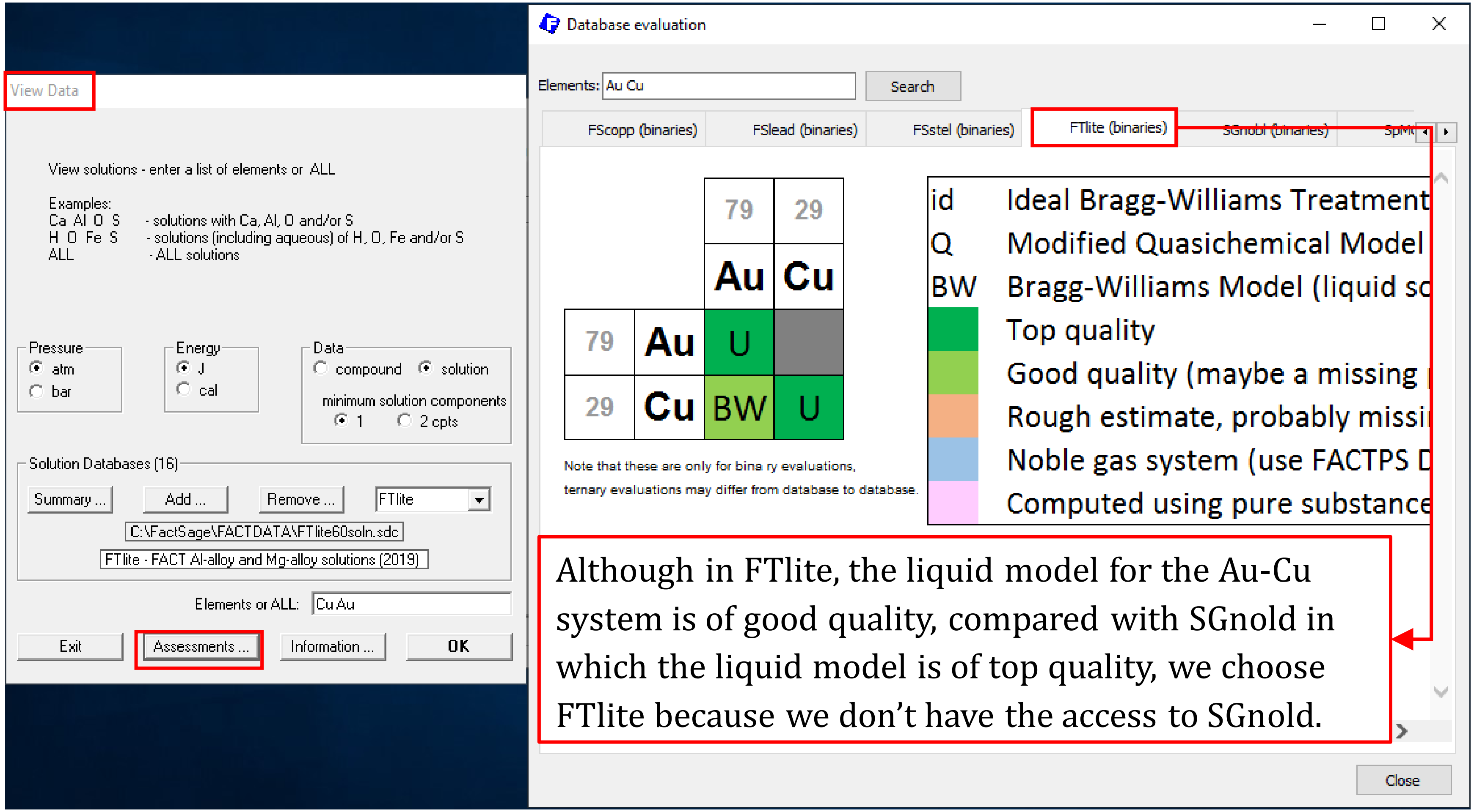
Au - Cu : | BINARY | FScopp | FSlead | FTlite | SGnobl | SGsold | SGTE2011 | SGTE2014 |
Cu - Sn - Au : | SGnobl |
Cu - Pb - Au : | SGnobl |
Cu - Ni - Au : | SGnobl |
Co - Cu - Au : | SGnobl |
Au - Cu - Ag : | SGnobl |
Au - Cu - Ag : | SGnobl |
Cu - Zr : | FScopp | FTlite | SGTE2011 | SGTE2014 | SGTE2017 |
Cu - Zn : | FScopp | FSlead | FSstel | FTlite | SGsold | SGTE2011 | SGTE2014 | SGTE2017 |
Cu - Y : | BINARY | FTlite | SGTE2011 | SGTE2014 | SGTE2017 |
Cu - W : | FScopp | FTlite | SGTE2017 |
Cu - V : | FScopp | FSstel | FTlite | SGTE2011 | SGTE2014 | SGTE2017 |
Cu - Tl : | FScopp | FSlead | SGTE2011 | SGTE2014 | SGTE2017 |
Cu - Ti : | FScopp | FTlite | SGTE2011 | SGTE2014 | SGTE2017 |
Cu - Te : | FScopp | FSlead |
Cu - Sr : | FSlead | FTlite | SGTE2011 | SGTE2014 | SGTE2017 |
Cu - Sn : | BINARY | FScopp | FSlead | FSstel | FTlite | SGsold | SGTE2011 | SGTE2014 | SGTE2017 |
Cu - Sm : | FTlite | SGTE2011 | SGTE2014 | SGTE2017 |

Revised: 3/3/2019

One of the solution databases can be used is FTlite.

Reaction Module: Oxidation of Cu

View Data: determine which **solution** database for the Au-Cu system



View solutions - enter a list of elements or ALL

Examples:
Ca Al O S - solutions with Ca, Al, O and/or S
H O Fe S - solutions (including aqueous) of H, O, Fe and/or S
ALL - ALL solutions

Pressure: ● atm ○ bar

Energy: ● J ○ cal

Data: ○ compound ● solution

minimum solution components: ● 1 ○ 2 cpts

Solution Databases (16): FTlite

C:\FactSage\FACTDATA\FTlite60soln.sdc

FTlite - FACT Al-alloy and Mg-alloy solutions (2019)

Elements or ALL: Cu Au

Elements: Au Cu

		79	29
		Au	Cu
79	Au	U	
29	Cu	BW	U

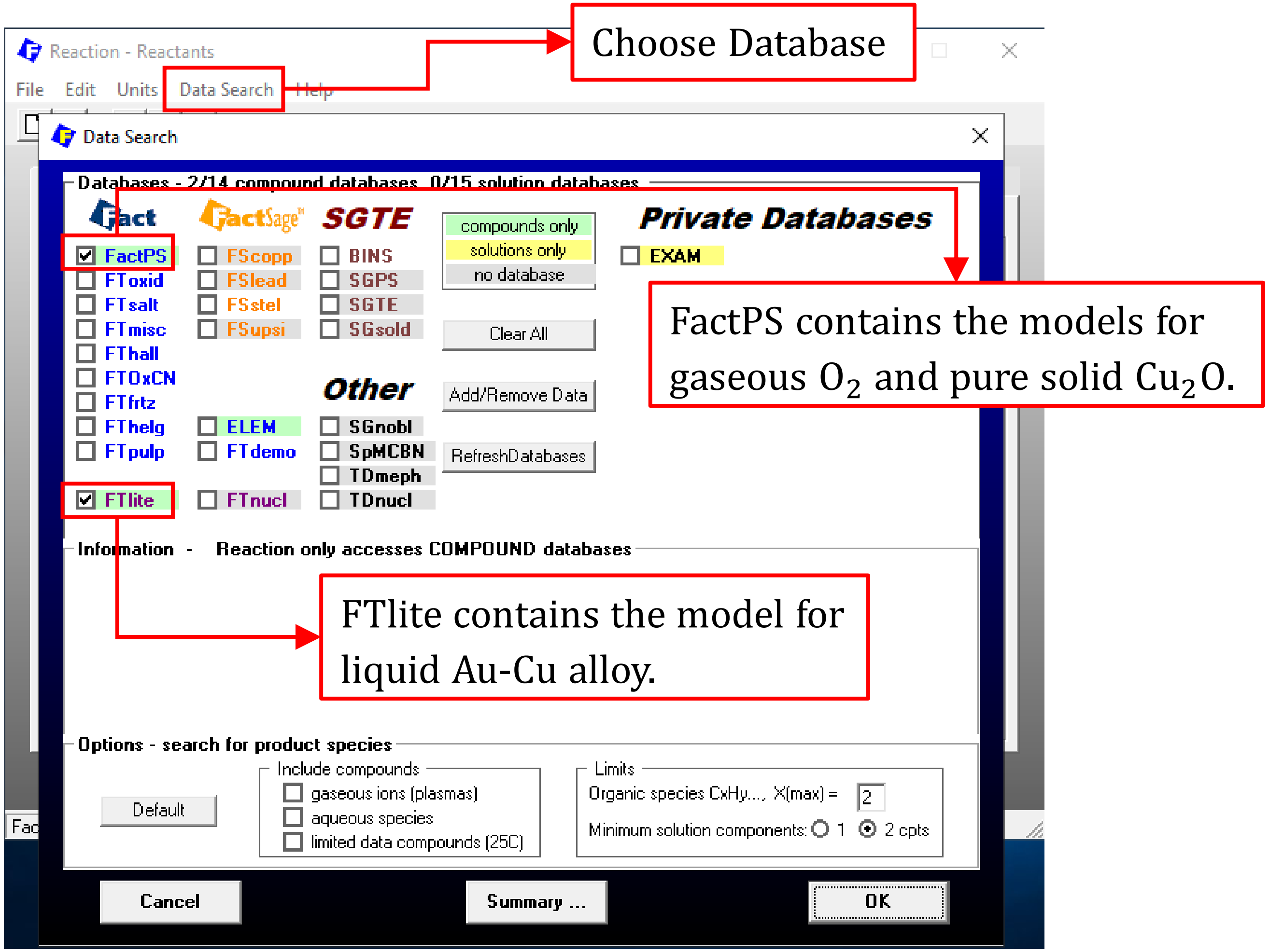
Note that these are only for binary evaluations, ternary evaluations may differ from database to database.

id	Ideal Bragg-Williams Treatment
Q	Modified Quasichemical Model
BW	Bragg-Williams Model (liquid so
🟩	Top quality
🟩	Good quality (maybe a missing
🟧	Rough estimate, probably missi
🟦	Noble gas system (use FACTPS D
🟪	Computed using pure substance

Although in FTlite, the liquid model for the Au-Cu system is of good quality, compared with SGnold in which the liquid model is of top quality, we choose FTlite because we don't have the access to SGnold.

Reaction Module: Oxidation of Cu

Reactants Window: Choose the database



Choose Database

FactPS contains the models for gaseous O_2 and pure solid Cu_2O.

FTlite contains the model for liquid Au-Cu alloy.

Databases - 2/14 compound databases 0/15 solution databases

☑ FactPS
☐ FToxid
☐ FTsalt
☐ FTmisc
☐ FThall
☐ FTOxCN
☐ FTfrtz
☐ FThelg
☐ FTpulp
☑ FTlite

☐ FScopp
☐ FSlead
☐ FSstel
☐ FSupsi
☐ ELEM
☐ FTdemo
☐ FTnucl

☐ BINS
☐ SGPS
☐ SGTE
☐ SGsold
☐ SGnobl
☐ SpMCBN
☐ TDmeph
☐ TDnucl

☐ EXAM

Information - Reaction only accesses COMPOUND databases

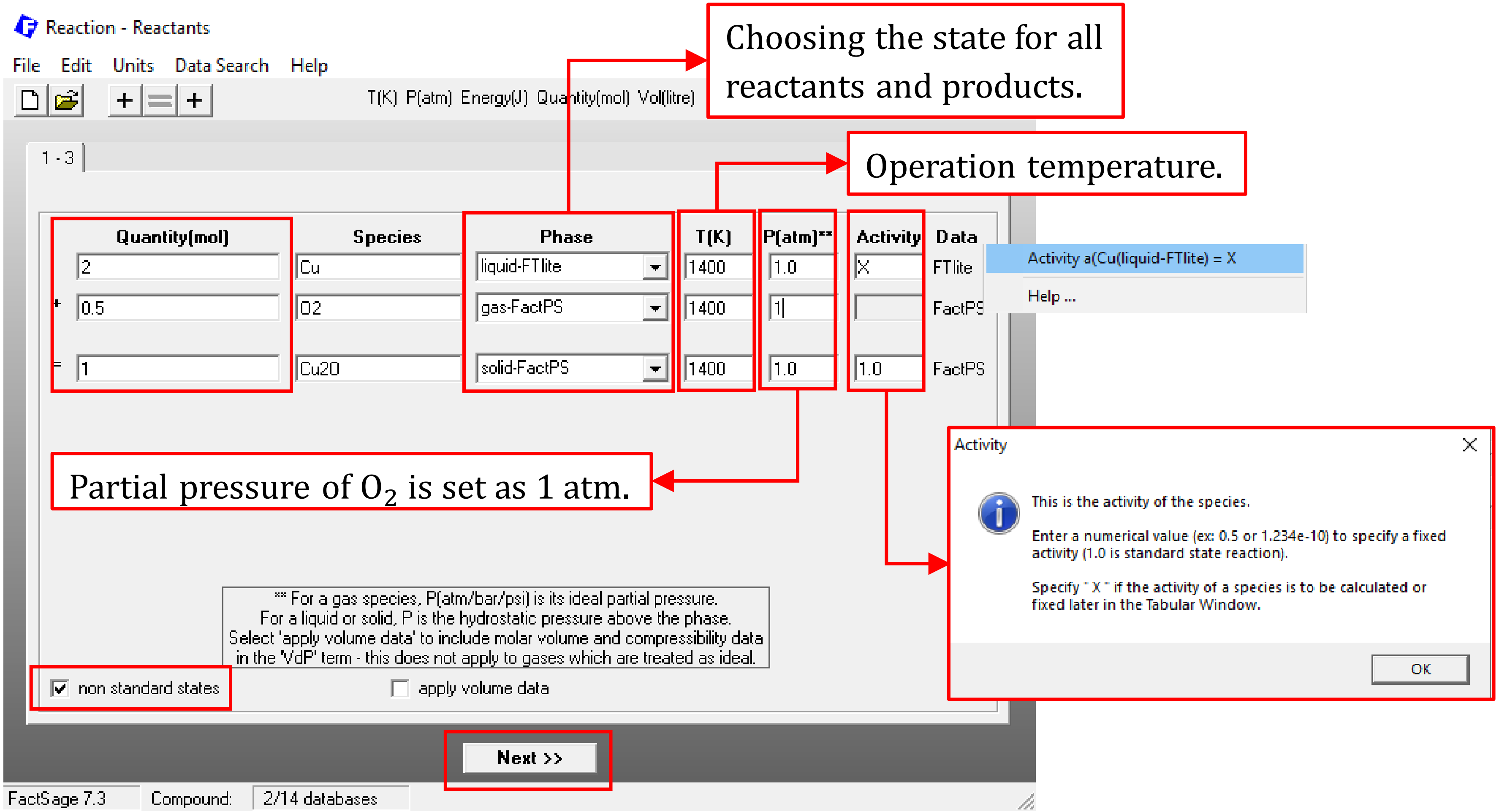
Options - search for product species

Include compounds
☐ gaseous ions (plasmas)
☐ aqueous species
☐ limited data compounds (25C)

Limits
Organic species CxHy...., X(max) = 2
Minimum solution components: ○ 1 ● 2 cpts

Reaction Module: Oxidation of Cu

Reactants Window: Set Reactants (Phase and Temperature)



Choosing the state for all reactants and products.

Operation temperature.

Partial pressure of O_2 is set as 1 atm.

	Quantity(mol)	Species	Phase	T(K)	P(atm)**	Activity	Data
	2	Cu	liquid-FTlite	1400	1.0	X	FTlite
+	0.5	O2	gas-FactPS	1400	1		FactPS
=	1	Cu2O	solid-FactPS	1400	1.0	1.0	FactPS

Activity a(Cu(liquid-FTlite) = X
Help ...

** For a gas species, P(atm/bar/psi) is its ideal partial pressure.
For a liquid or solid, P is the hydrostatic pressure above the phase.
Select 'apply volume data' to include molar volume and compressibility data in the 'VdP' term - this does not apply to gases which are treated as ideal.

☑ non standard states
☐ apply volume data

Activity

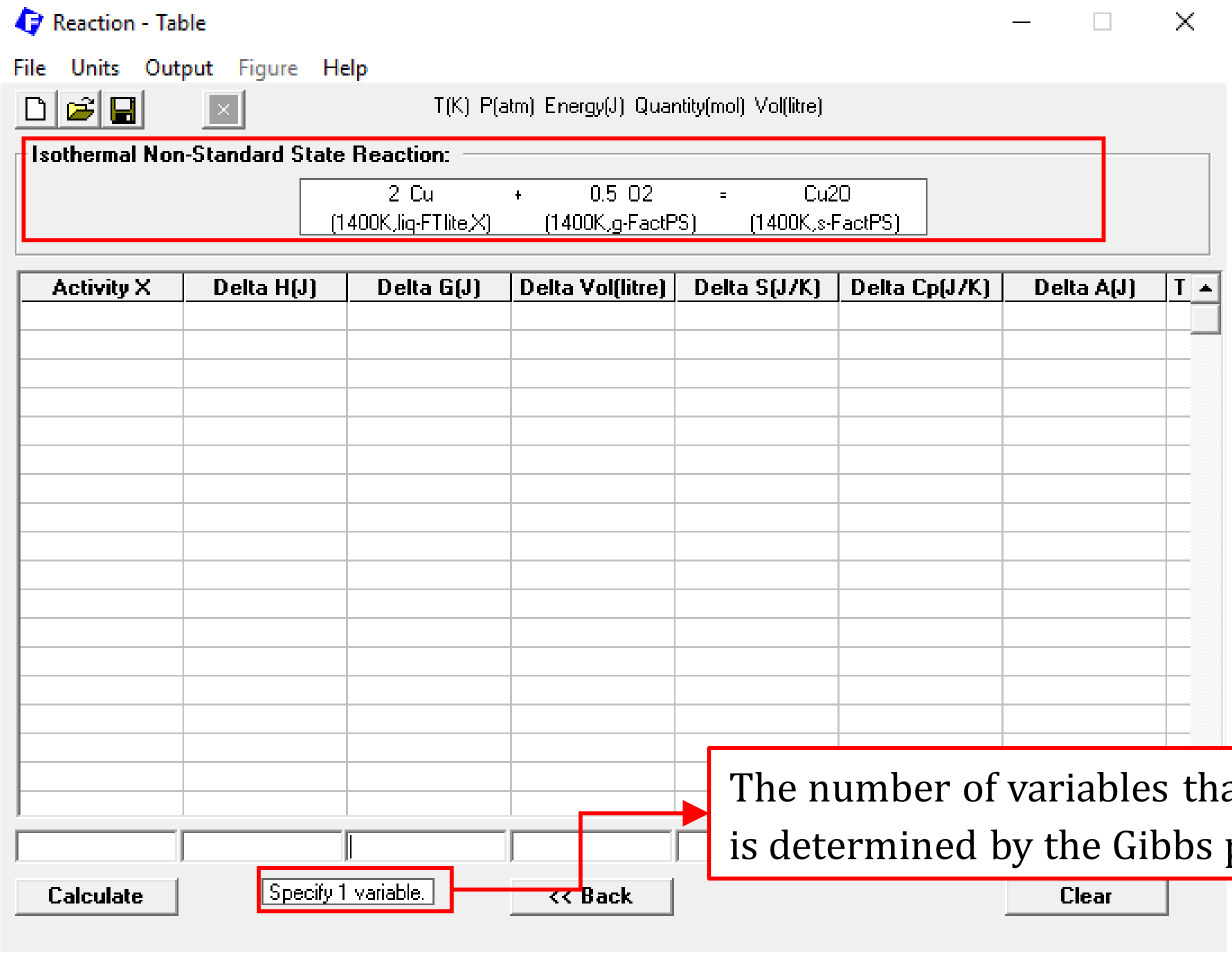
This is the activity of the species.

Enter a numerical value (ex: 0.5 or 1.234e-10) to specify a fixed activity (1.0 is standard state reaction).

Specify " X " if the activity of a species is to be calculated or fixed later in the Tabular Window.

Reaction Module: Oxidation of Cu

Table Window: Set Conditions



Isothermal Non-Standard State Reaction:

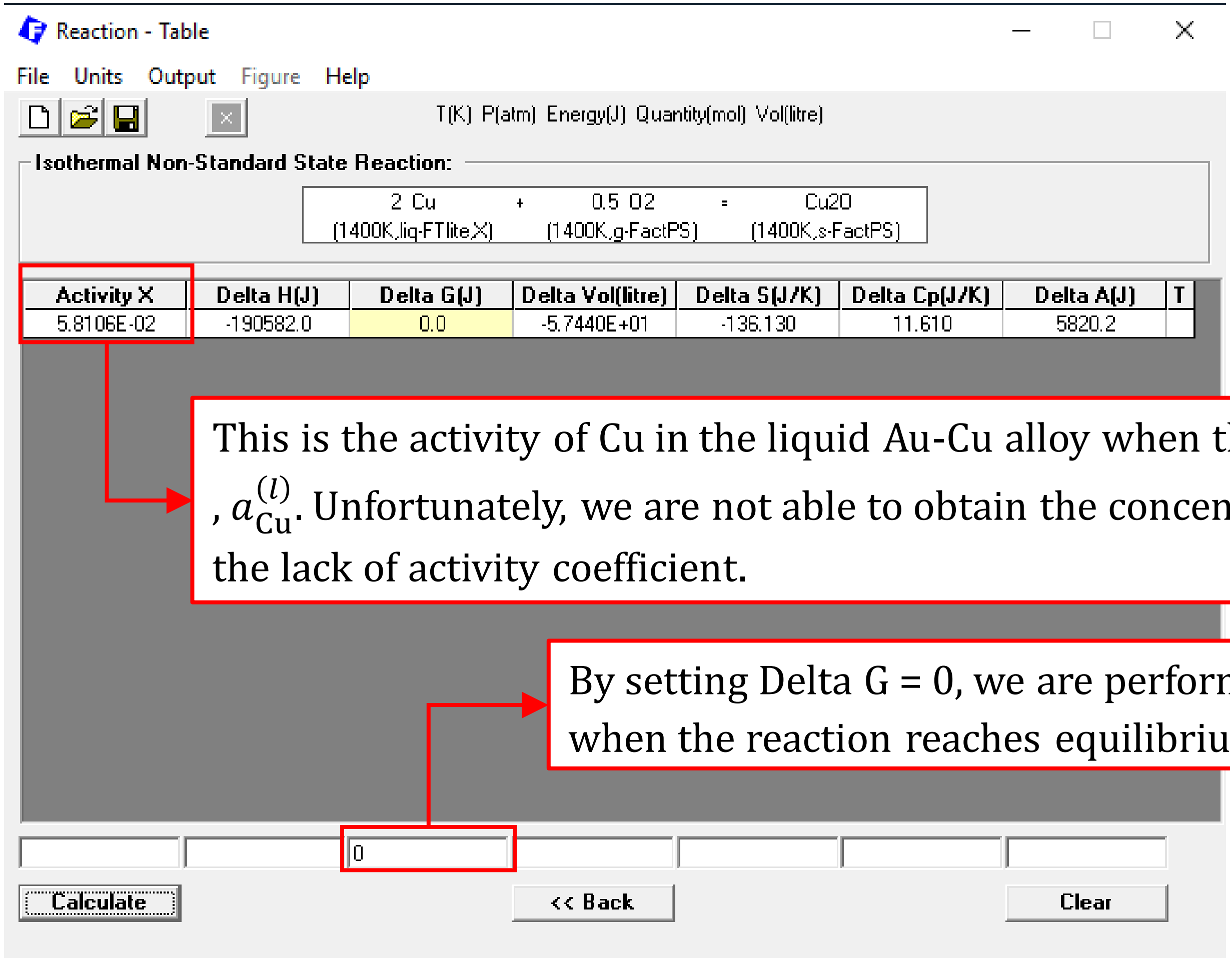
2 Cu (1400K,liq-FTlite,X) + 0.5 O2 (1400K,g-FactPS) = Cu2O (1400K,s-FactPS)

Specify 1 variable.

The number of variables that need to be specified is determined by the Gibbs phase rule.

Reaction Module: Oxidation of Cu

Table Window: Results



2 Cu	+	0.5 O2	=	Cu2O
(1400K,liq-FTlite,X)		(1400K,g-FactPS)		(1400K,s-FactPS)

Activity X	Delta H(J)	Delta G(J)	Delta Vol(litre)	Delta S(J/K)	Delta Cp(J/K)	Delta A(J)	T
5.8106E-02	-190582.0	0.0	-5.7440E+01	-136.130	11.610	5820.2	

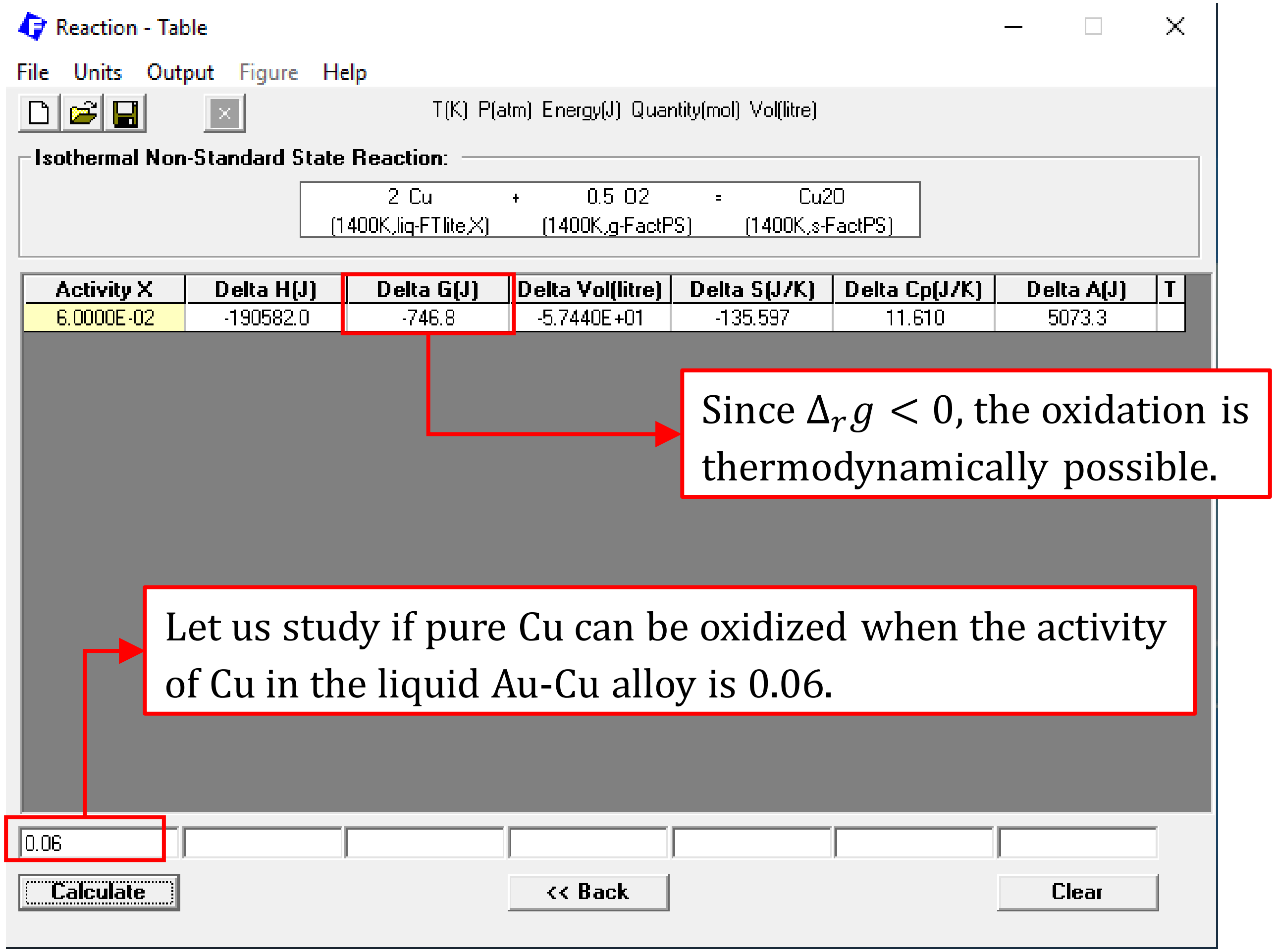
Delta G(J) input: 0

This is the activity of Cu in the liquid Au-Cu alloy when the system reaches equilibrium , $a_{\mathrm{Cu}}^{(l)}$. Unfortunately, we are not able to obtain the concentration of Cu, $X_{\mathrm{Cu}}^{(l)}$ because of the lack of activity coefficient.

By setting Delta G = 0, we are performing the calculation when the reaction reaches equilibrium.

Reaction Module: Oxidation of Cu

Table Window: Results



Isothermal Non-Standard State Reaction:

2 Cu	+	0.5 O2	=	Cu2O
(1400K,liq-FTlite,X)		(1400K,g-FactPS)		(1400K,s-FactPS)

Activity X	Delta H(J)	Delta G(J)	Delta Vol(litre)	Delta S(J/K)	Delta Cp(J/K)	Delta A(J)	T
6.0000E-02	-190582.0	-746.8	-5.7440E+01	-135.597	11.610	5073.3	

0.06

Since $\Delta_r g < 0$, the oxidation is thermodynamically possible.

Let us study if pure Cu can be oxidized when the activity of Cu in the liquid Au-Cu alloy is 0.06.

Reaction Module: Oxidation of Cu

Non-standard State Calculation (Part 3)

The third part of non-standard state calculation is to include a slag phase. That is, instead of forming pure solid Cu_2O, a liquid slag consisting of SiO_2 and Cu_2O is in contact with the gold bath.

In this case, the activity of Cu_2O in the liquid slag should be used, and FToxid contains the model for the liquid SiO_2-Cu_2O slag.

The set up would be very similar to the previous calculation, except for Cu_2O of which the activity must be used.

In-Class Exercise

Question 1.

Solve Question 1 and 2 from the first problem set using the Reaction Module.

Question 2.

Carry out the following calculations using the View Data and/or Reaction Module (not identical, since you will need to tailor conditions to your particular metal) on one or as many metals as you wish from the following list:

Nickel, Chromium, Lead, Iron, Manganese, Vanadium, Magnesium, Zinc,
Titanium, Sodium, Cobalt.

(1) Create a data table for the most stable species of the M over a suitable temperature range.

(2) Find the available solution phases the Metal-Fe-S system.

(3) Create a data Table for the reaction between Metal, oxygen, and the lowest oxide. The maximum temperature should be at least 2000 K, or as appropriate.

In-Class Exercise

(4a) Create a data Table for the above oxidation reaction for at least five different conditions at equilibrium (always isothermal and always at equilibrium). For example, you could choose to calculate T in three runs with different defined X and P. Then you could calculate X at defined P and T, and then P at defined X and T.

(4b) Next, assume that the reaction needs some super-saturation to nucleate the oxide, so set Delta G = Delta G^o/100 (which will be a negative number) and find the P_{O_2} needed compared to one of your above equilibrium conditions. Include this result in your data Table and add a written comment.

(5) Create a plot showing the Enthalpy required to heat Metal up to and beyond the boiling point (or as close as you can get).

Note: you should annotate all your five sheets by hand as appropriate - to make everything clear to the reader.

FactSage Practical
MSE302

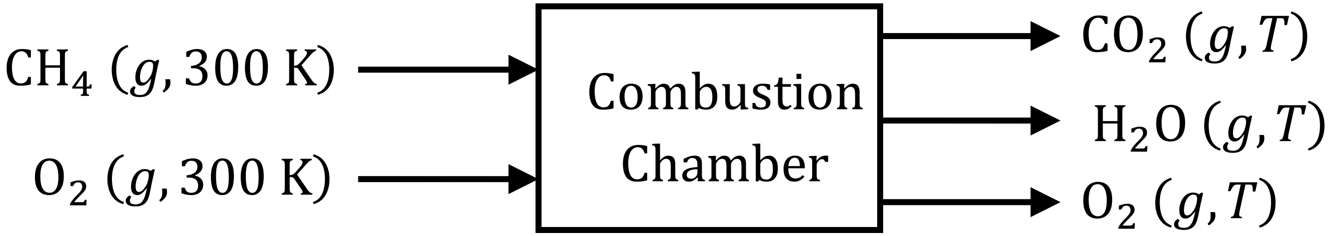
Practical 2. Reaction Module

Advanced Applications

Application 1: Combustion of Methane

The first application is the combustion of gaseous methane in the pressure of **excess oxygen**. In this case, the combustion products would be CO_2, H_2O and unused O_2 (note: because of the excess of O_2, no CO would form).

Consider the following combustion process.



$CH_4\ (g, 300\ \mathrm{K})$

$O_2\ (g, 300\ \mathrm{K})$

Combustion Chamber

$CO_2\ (g, T)$

$H_2O\ (g, T)$

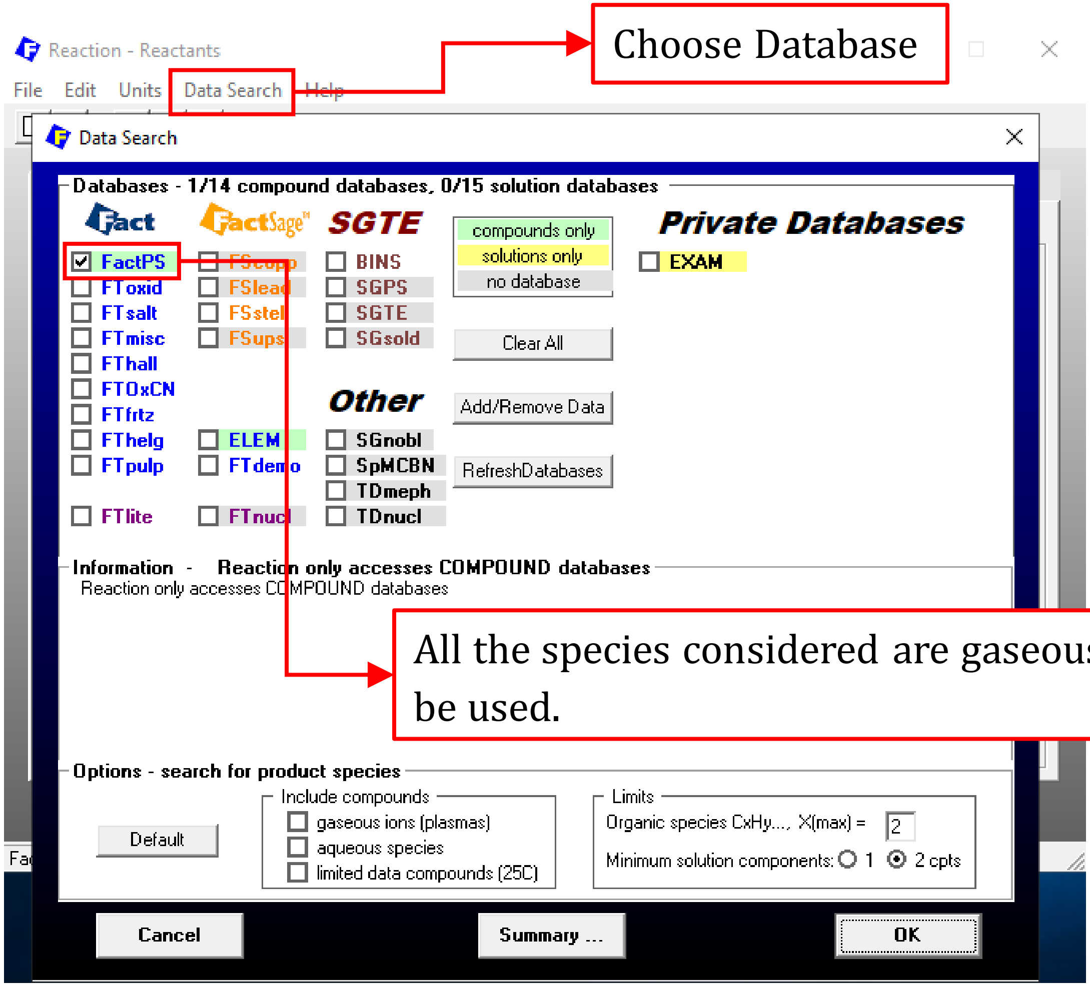
$O_2\ (g, T)$

Let us calculate the adiabatic flame temperature (AFT) in the Reaction Module, and how AFT is affected by the excess ratio of oxygen.

Note: we assume the gas phase behaves ideally, and thus standard state calculations could be performed when calculating enthalpy change associated with the combustion process.

Application 1: Combustion of Methane

Reactants Window: Choose the database



Databases - 1/14 compound databases, 0/15 solution databases

☑ FactPS

Information - Reaction only accesses COMPOUND databases

Reaction only accesses COMPOUND databases

Options - search for product species

Include compounds
☐ gaseous ions (plasmas)
☐ aqueous species
☐ limited data compounds (25C)

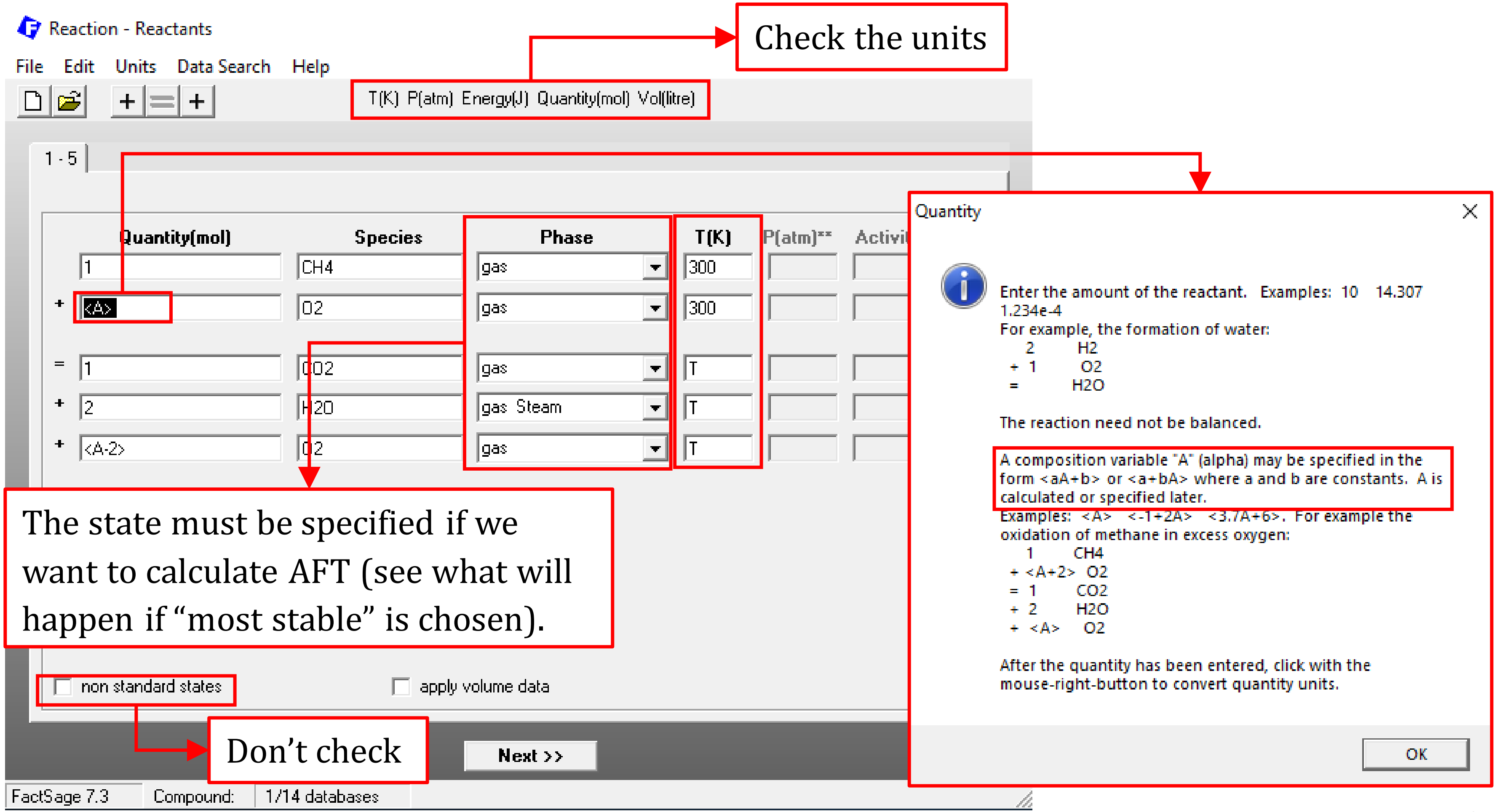
Limits
Organic species CxHy...., X(max) = 2
Minimum solution components: ○ 1 ● 2 cpts

Choose Database

All the species considered are gaseous. FactPS should be used.

Application 1: Combustion of Methane

Reactants Window: Set Reactants (Phase and Temperature)



	Quantity(mol)	Species	Phase	T(K)	P(atm)**	Activi
	1	CH4	gas	300		
+	<A>	O2	gas	300		
=	1	CO2	gas	T		
+	2	H2O	gas Steam	T		
+	<A-2>	O2	gas	T		

☐ non standard states

Enter the amount of the reactant. Examples: 10 14.307 1.234e-4

For example, the formation of water:

```
   2      H2
 + 1      O2
 =        H2O
```

The reaction need not be balanced.

A composition variable "A" (alpha) may be specified in the form <aA+b> or <a+bA> where a and b are constants. A is calculated or specified later.

Examples: <A> <-1+2A> <3.7A+6>. For example the oxidation of methane in excess oxygen:

```
   1      CH4
 + <A+2>  O2
 = 1      CO2
 + 2      H2O
 + <A>    O2
```

After the quantity has been entered, click with the mouse-right-button to convert quantity units.

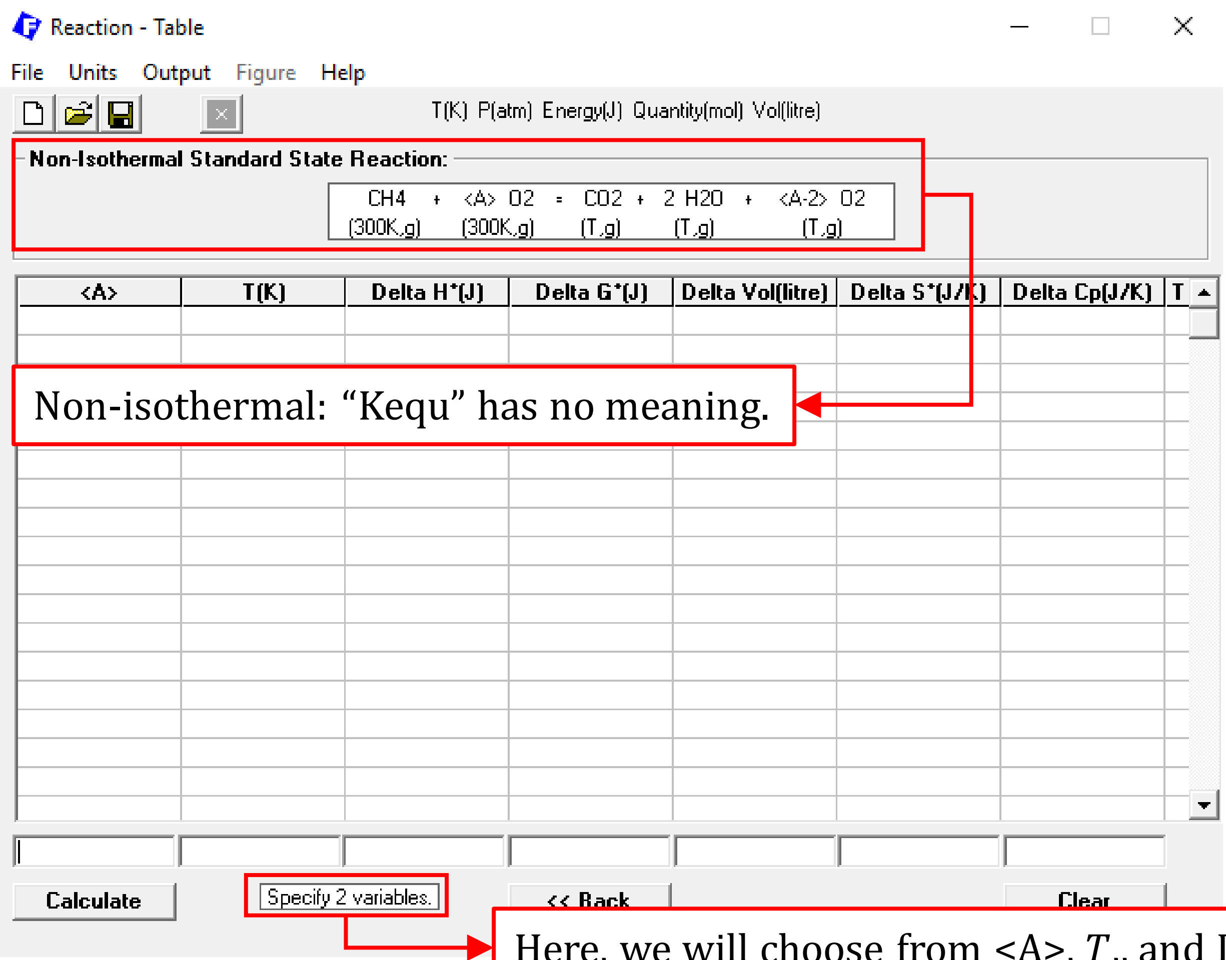
Check the units

The state must be specified if we want to calculate AFT (see what will happen if "most stable" is chosen).

Don't check

Application 1: Combustion of Methane

Reactants Window: Set Conditions



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

Non-Isothermal Standard State Reaction:

CH4	+	<A> O2	=	CO2	+	2 H2O	+	<A-2> O2
(300K,g)		(300K,g)		(T,g)		(T,g)		(T,g)

<A>	T(K)	Delta H°(J)	Delta G°(J)	Delta Vol(litre)	Delta S°(J/K)	Delta Cp(J/K)	T

Specify 2 variables.

Non-isothermal: “Kequ” has no meaning.

Here, we will choose from <A>, T,, and Delta H*

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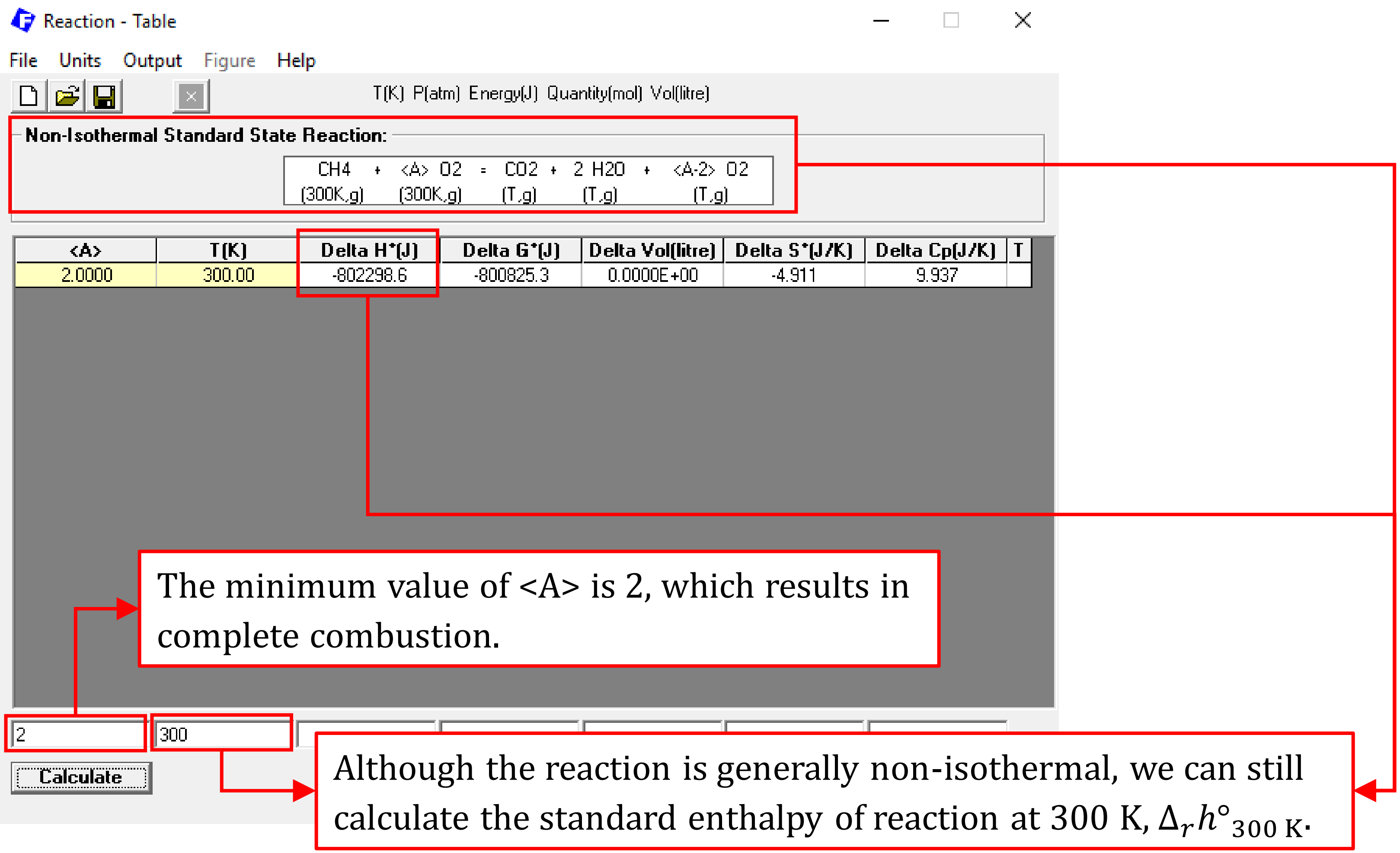
Reactants Window: Results



Non-Isothermal Standard State Reaction:

CH_4 (300K,g) + <A> O_2 (300K,g) = CO_2 (T,g) + 2 H_2O (T,g) + <A-2> O_2 (T,g)

<A>	T(K)	Delta H°(J)	Delta G°(J)	Delta Vol(litre)	Delta S°(J/K)	Delta Cp(J/K)	T
2.0000	300.00	-802298.6	-800825.3	0.0000E+00	-4.911	9.937	

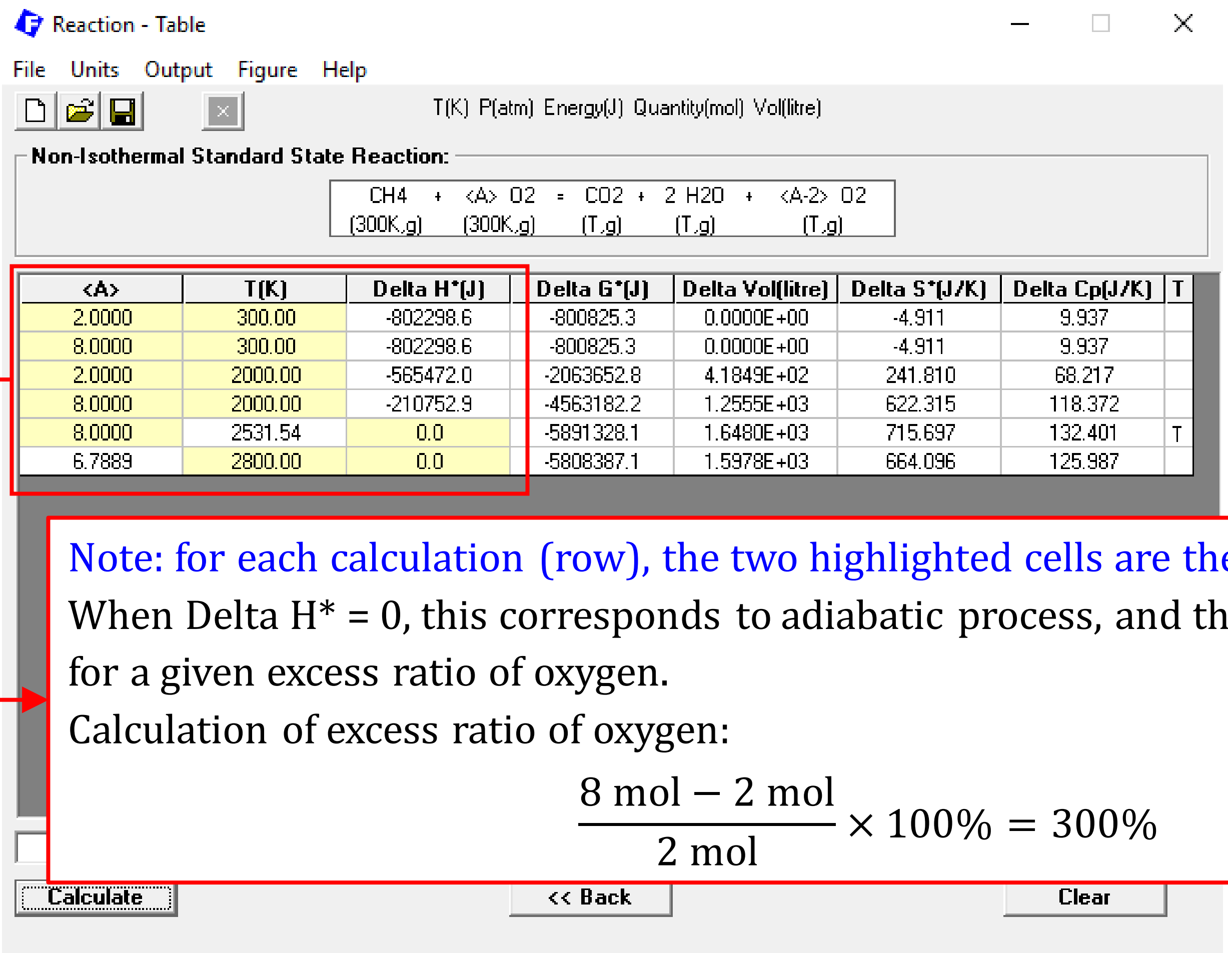
2	300					

The minimum value of <A> is 2, which results in complete combustion.

Although the reaction is generally non-isothermal, we can still calculate the standard enthalpy of reaction at 300 K, $\Delta_r h°_{300\ \mathrm{K}}$.

Application 1: Combustion of Methane

Reactants Window: Results



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

Non-Isothermal Standard State Reaction:

CH4 + <A> O2 = CO2 + 2 H2O + <A-2> O2
(300K,g) (300K,g) (T,g) (T,g) (T,g)

<A>	T(K)	Delta H*(J)	Delta G*(J)	Delta Vol(litre)	Delta S*(J/K)	Delta Cp(J/K)	T
2.0000	300.00	-802298.6	-800825.3	0.0000E+00	-4.911	9.937	
8.0000	300.00	-802298.6	-800825.3	0.0000E+00	-4.911	9.937	
2.0000	2000.00	-565472.0	-2063652.8	4.1849E+02	241.810	68.217	
8.0000	2000.00	-210752.9	-4563182.2	1.2555E+03	622.315	118.372	
8.0000	2531.54	0.0	-5891328.1	1.6480E+03	715.697	132.401	T
6.7889	2800.00	0.0	-5808387.1	1.5978E+03	664.096	125.987	

Note: for each calculation (row), the two highlighted cells are the variables specified.

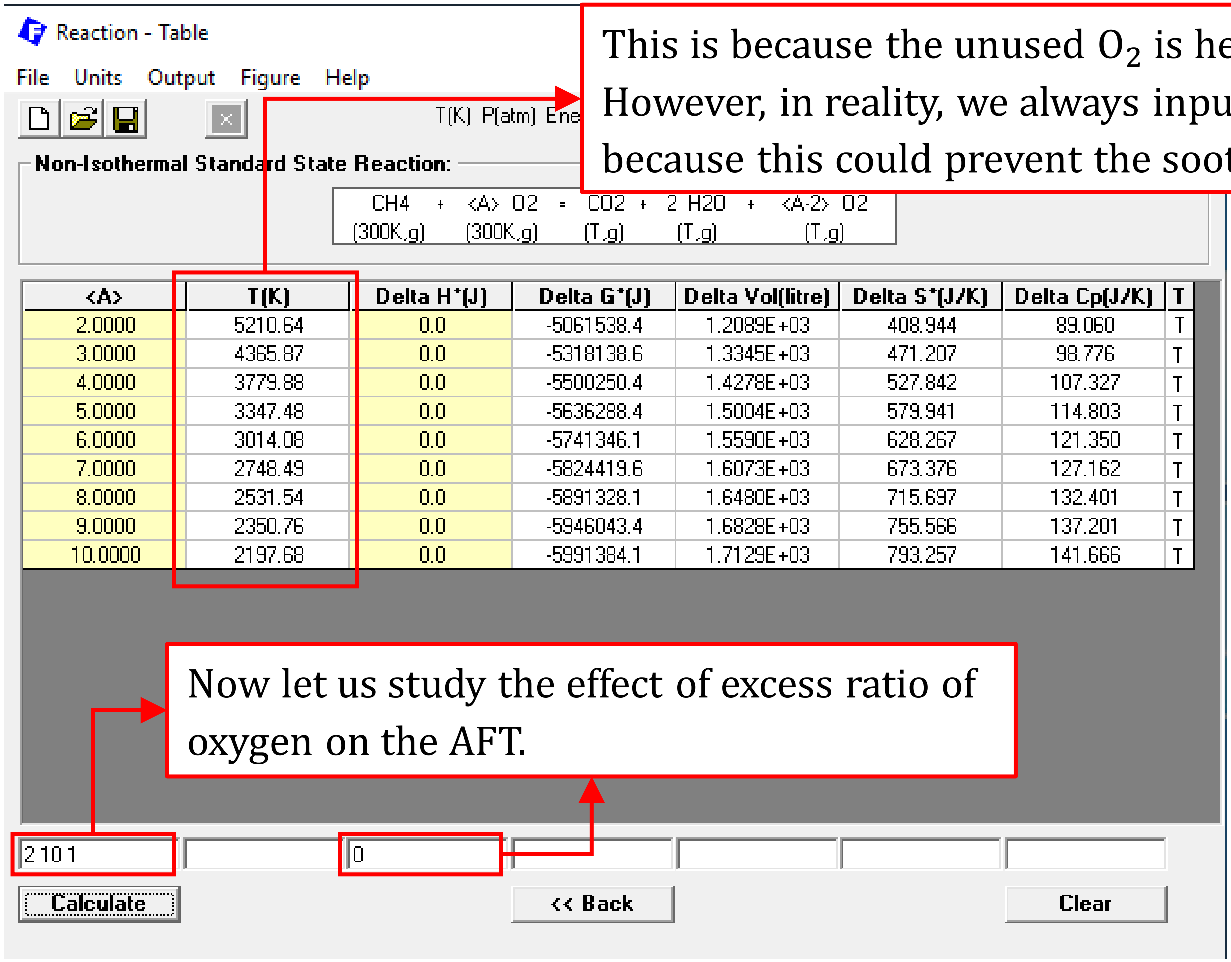
When Delta H* = 0, this corresponds to adiabatic process, and the AFT can be calculated for a given excess ratio of oxygen.

Calculation of excess ratio of oxygen:

$$\frac{8\ \text{mol} - 2\ \text{mol}}{2\ \text{mol}} \times 100\% = 300\%$$

Application 1: Combustion of Methane

Reactants Window: Results



This is because the unused O_2 is heated up from 300 K to AFT. However, in reality, we always input excess amount of oxygen because this could prevent the soot formation.

Non-Isothermal Standard State Reaction:

CH_4 (300K,g) + <A> O_2 (300K,g) = CO_2 (T,g) + 2 H_2O (T,g) + <A-2> O_2 (T,g)

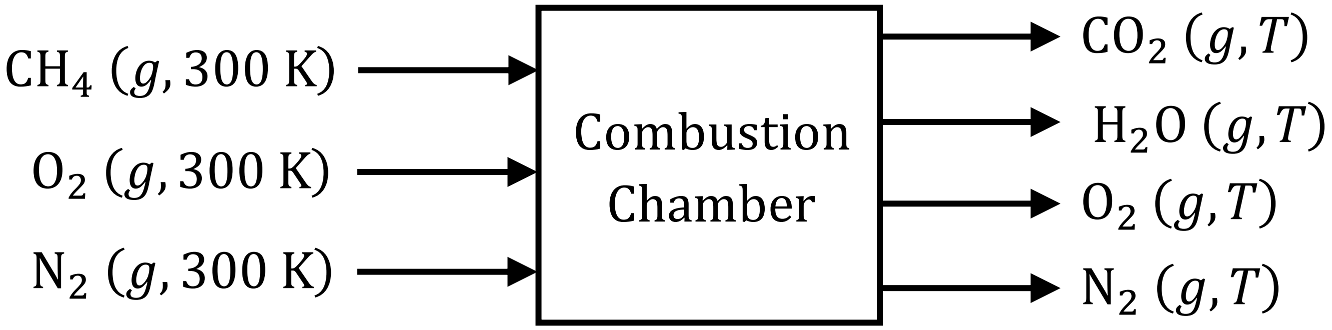
<A>	T(K)	Delta H°(J)	Delta G°(J)	Delta Vol(litre)	Delta S°(J/K)	Delta Cp(J/K)	T
2.0000	5210.64	0.0	-5061538.4	1.2089E+03	408.944	89.060	T
3.0000	4365.87	0.0	-5318138.6	1.3345E+03	471.207	98.776	T
4.0000	3779.88	0.0	-5500250.4	1.4278E+03	527.842	107.327	T
5.0000	3347.48	0.0	-5636288.4	1.5004E+03	579.941	114.803	T
6.0000	3014.08	0.0	-5741346.1	1.5590E+03	628.267	121.350	T
7.0000	2748.49	0.0	-5824419.6	1.6073E+03	673.376	127.162	T
8.0000	2531.54	0.0	-5891328.1	1.6480E+03	715.697	132.401	T
9.0000	2350.76	0.0	-5946043.4	1.6828E+03	755.566	137.201	T
10.0000	2197.68	0.0	-5991384.1	1.7129E+03	793.257	141.666	T

Now let us study the effect of excess ratio of oxygen on the AFT.

2 10 1		0

Application 1: Combustion of Methane

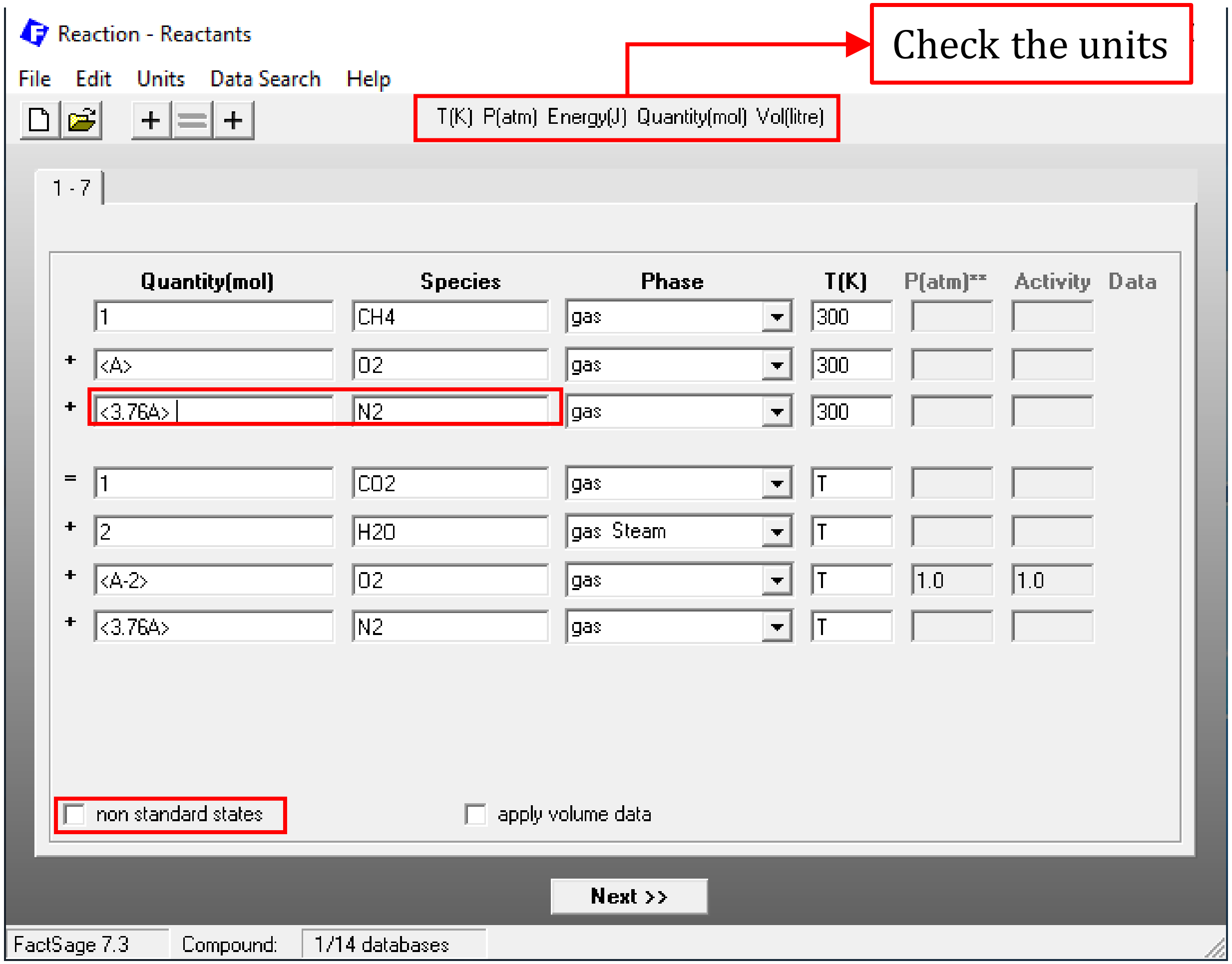
We can also calculate the AFT for a burner that uses air instead of pure oxygen. In this case, equivalent amounts of nitrogen accompanying oxygen should be entered in the reaction.



Note: since the air composition (mole fraction) can be approximated as "0.79 N_2 + 0.21 O_2", for every mole of O_2 input, there are 3.76 mol N_2.

Application 1: Combustion of Methane

Reactants Window: Set Reactants (Phase and Temperature)



Check the units

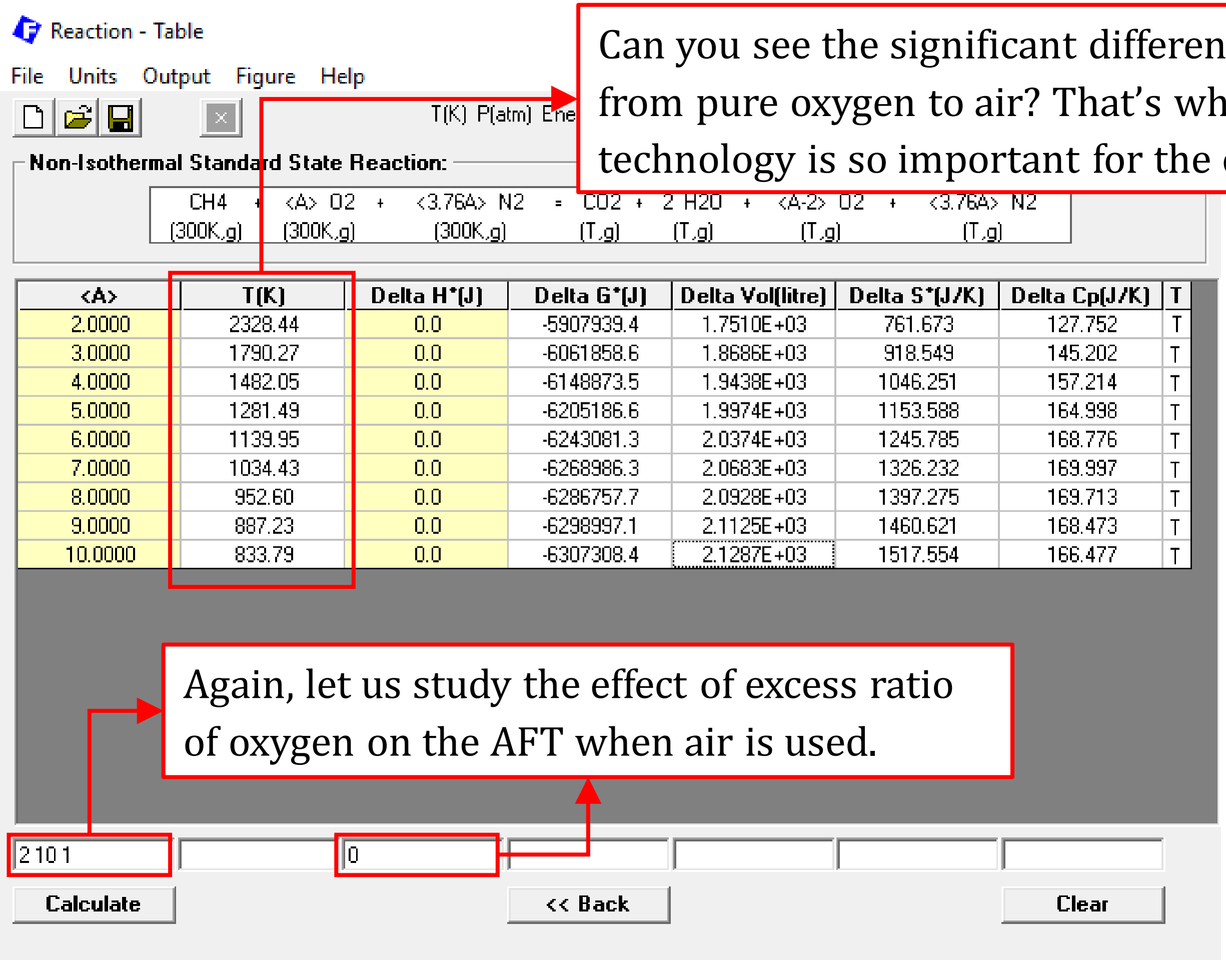
T(K) P(atm) Energy(J) Quantity(mol) Vol(litre)

	Quantity(mol)	Species	Phase	T(K)	P(atm)**	Activity	Data
	1	CH4	gas	300			
+	<A>	O2	gas	300			
+	<3.76A>	N2	gas	300			
=	1	CO2	gas	T			
+	2	H2O	gas Steam	T			
+	<A-2>	O2	gas	T	1.0	1.0	
+	<3.76A>	N2	gas	T			

☐ non standard states ☐ apply volume data

Application 1: Combustion of Methane

Reactants Window: Results



Non-Isothermal Standard State Reaction:

CH4 (300K,g) + <A> O2 (300K,g) + <3.76A> N2 (300K,g) = CO2 (T,g) + 2 H2O (T,g) + <A-2> O2 (T,g) + <3.76A> N2 (T,g)

<A>	T(K)	Delta H°(J)	Delta G°(J)	Delta Vol(litre)	Delta S°(J/K)	Delta Cp(J/K)	T
2.0000	2328.44	0.0	-5907939.4	1.7510E+03	761.673	127.752	T
3.0000	1790.27	0.0	-6061858.6	1.8686E+03	918.549	145.202	T
4.0000	1482.05	0.0	-6148873.5	1.9438E+03	1046.251	157.214	T
5.0000	1281.49	0.0	-6205186.6	1.9974E+03	1153.588	164.998	T
6.0000	1139.95	0.0	-6243081.3	2.0374E+03	1245.785	168.776	T
7.0000	1034.43	0.0	-6268986.3	2.0683E+03	1326.232	169.997	T
8.0000	952.60	0.0	-6286757.7	2.0928E+03	1397.275	169.713	T
9.0000	887.23	0.0	-6298997.1	2.1125E+03	1460.621	168.473	T
10.0000	833.79	0.0	-6307308.4	2.1287E+03	1517.554	166.477	T

2 10 1		0				

Can you see the significant difference in the AFT when we switch from pure oxygen to air? That’s why the oxygen-enrichment technology is so important for the combustion process.

Again, let us study the effect of excess ratio of oxygen on the AFT when air is used.

Application 2: Pidgeon Process

Magnesium can be produced by reducing MgO with ferrosilicon at low pressures and in the solid state. This is called the Pidgeon Process and was developed by UofT MSE's Professor Pidgeon in Canada in WWII to produce much-needed magnesium metal then. The essential reaction can be described as:

$$\mathrm{MgO}(s) + \mathrm{Si}(s) = \mathrm{Mg}(g) + \mathrm{SiO_2}(s)$$

By controlling the system's pressure, solid charge composition (which affects the activity of SiO_2), etc., the above reduction can be shifted to improve the productivity of Mg.

The flowsheet of the Pidgeon Process is shown on the next slide.

Application 2: Pidgeon Process

Flowsheet of the Pidgeon Process (Schematic)

Dolomite

Calcination

Pulverization

Ferrosilicon
75% Si

Pulverization

Mixing

$MgO \cdot CaO + Si(Fe) + CaF_2$

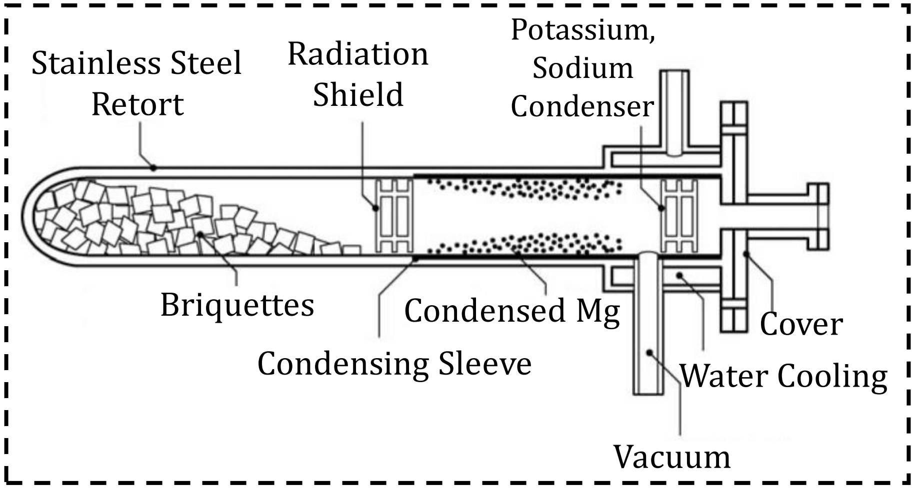
Briquetting

~1200 °C

Spent Briquettes
$(Ca_2SiO_4 + Fe)$

Magnesium
Crown (Mg)

Lloyd M. Pidgeon
(1943~1969 UofT
MSE Chair)



Kipouros and Sadoway, The Chemistry and Electrochemistry of Magnesium Production.

Application 2: Pidgeon Process

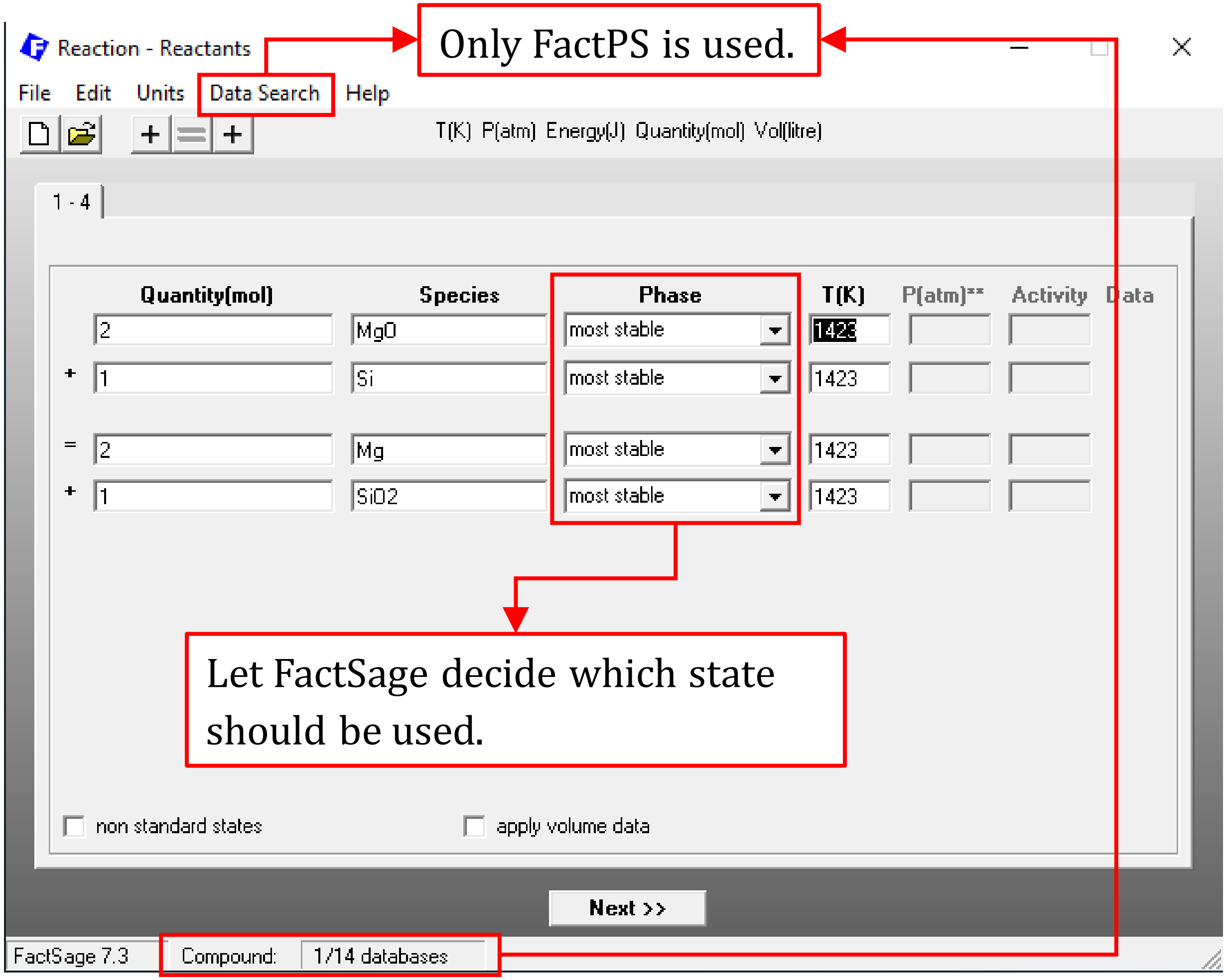
For the purpose of illustration, let us assume that **pure solid MgO** (not $MgO \cdot CaO$) and **pure solid Si** (not ferrosilicon) are charged into the Pidgeon reactor. Then, the simplified Pidgeon process can be described as:

$$2\mathrm{MgO}(s) + \mathrm{Si}(s) = 2\mathrm{Mg}(g) + \mathrm{SiO_2}(s)$$

First, let us study the **standard-state reaction** using the Reaction Module. The temperature is 1423 K.

Application 2: Pidgeon Process

Standard-state Calculation:



Only FactPS is used.

	Quantity(mol)	Species	Phase	T(K)	P(atm)**	Activity	Data
	2	MgO	most stable	1423			
+	1	Si	most stable	1423			
=	2	Mg	most stable	1423			
+	1	SiO2	most stable	1423			

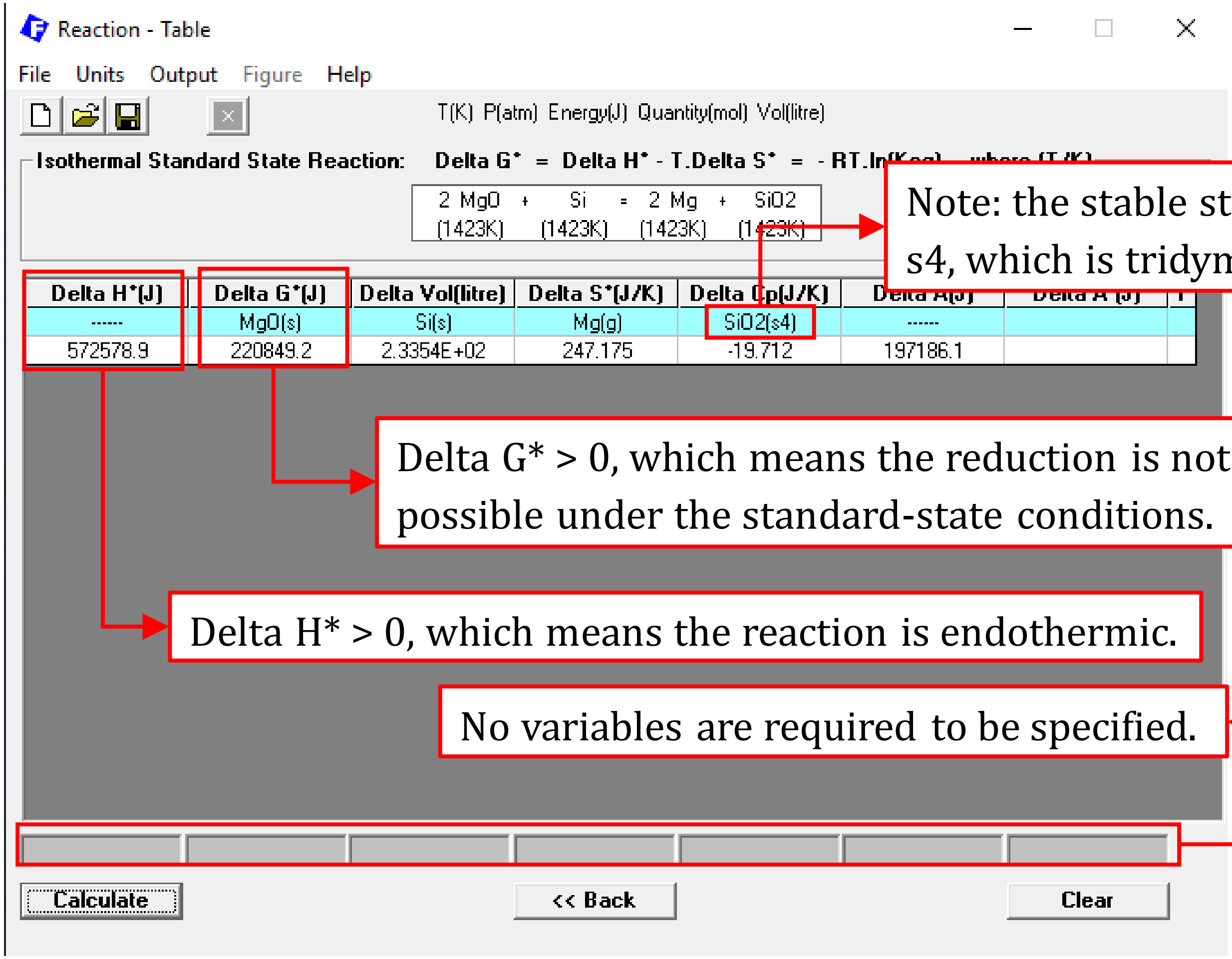
☐ non standard states ☐ apply volume data

Compound: 1/14 databases

Let FactSage decide which state should be used.

Application 2: Pidgeon Process

Standard-state Calculation:



Isothermal Standard State Reaction: Delta G° = Delta H° - T.Delta S° = - RT.ln(Keq) where (T/K)

2 MgO	+	Si	=	2 Mg	+	SiO2
(1423K)		(1423K)		(1423K)		(1423K)

Delta H°(J)	Delta G°(J)	Delta Vol(litre)	Delta S°(J/K)	Delta Cp(J/K)	Delta A(J)	Delta A (J)	T
------	MgO(s)	Si(s)	Mg(g)	SiO2(s4)	------		
572578.9	220849.2	2.3354E+02	247.175	-19.712	197186.1		

Note: the stable structure of SiO_2 at 1423 K is s4, which is tridymite (View Data Module)

Delta G* > 0, which means the reduction is not possible under the standard-state conditions.

Delta H* > 0, which means the reaction is endothermic.

No variables are required to be specified.

Application 2: Pidgeon Process

Now, let us go back to the reaction and assume that all reactants/products are not necessarily in their standard state:

$$2\text{MgO}(s1) + \text{Si}(s2) = 2\text{Mg}(g) + \text{SiO}_2(s3)$$

To study the direction of this reaction, $\Delta_r g$ should be used:

$$\Delta_r g = \Delta_r g^\circ + RT\ln \frac{\left(P_{\text{Mg}(g)}\right)^2 \times \left(a_{\text{SiO}_2}^{(s3)}\right)}{\left(a_{\text{MgO}}^{(s1)}\right)^2 \times \left(a_{\text{Si}}^{(s2)}\right)}$$

Clearly, to drive this rection to the right, we can consider the following.

1. Increase the reaction temperature (because the reaction is endothermic).

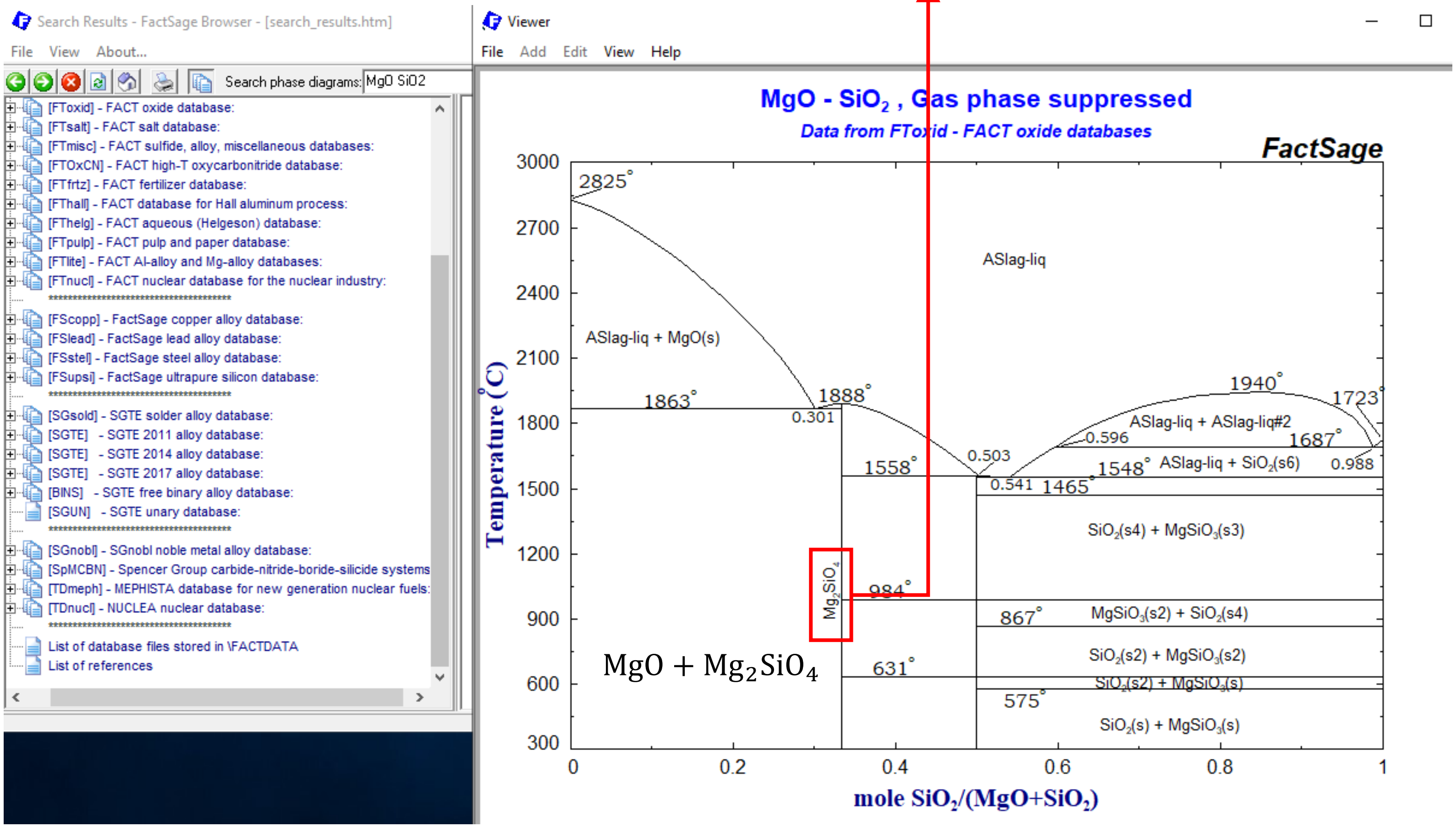
2. Reduce a_{SiO_2} by fluxing.

3. Reduce$P_{\text{Mg}(g)}$ by employing vacuum.

Note: you probably know the Le Chatelier principle, and its mathematical basis is the expression of $\Delta_r g$.

Application 2: Pidgeon Process

a_{SiO_2}: from the MgO-SiO_2 phase diagram, it is seen that MgO(s) and SiO_2(s) cannot coexist because they react to form $\boxed{(MgO)_2 \cdot SiO_2}$.



Search phase diagrams: MgO SiO2

[FToxid] - FACT oxide database:
[FTsalt] - FACT salt database:
[FTmisc] - FACT sulfide, alloy, miscellaneous databases:
[FTOxCN] - FACT high-T oxycarbonitride database:
[FTfrtz] - FACT fertilizer database:
[FThall] - FACT database for Hall aluminum process:
[FThelg] - FACT aqueous (Helgeson) database:
[FTpulp] - FACT pulp and paper database:
[FTlite] - FACT Al-alloy and Mg-alloy databases:
[FTnucl] - FACT nuclear database for the nuclear industry:
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[FScopp] - FactSage copper alloy database:
[FSlead] - FactSage lead alloy database:
[FSstel] - FactSage steel alloy database:
[FSupsi] - FactSage ultrapure silicon database:
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[SGsold] - SGTE solder alloy database:
[SGTE] - SGTE 2011 alloy database:
[SGTE] - SGTE 2014 alloy database:
[SGTE] - SGTE 2017 alloy database:
[BINS] - SGTE free binary alloy database:
[SGUN] - SGTE unary database:
****
[SGnobl] - SGnobl noble metal alloy database:
[SpMCBN] - Spencer Group carbide-nitride-boride-silicide systems
[TDmeph] - MEPHISTA database for new generation nuclear fuels:
[TDnucl] - NUCLEA nuclear database:
****
List of database files stored in \FACTDATA
List of references

Application 2: Pidgeon Process

$a_{\mathrm{SiO_2}}$: from the MgO-SiO_2 phase diagram, it is seen that MgO(s) and SiO_2(s) cannot coexist because they react to form $(MgO)_2 \cdot SiO_2$ or Mg_2SiO_4, known as forsterite.

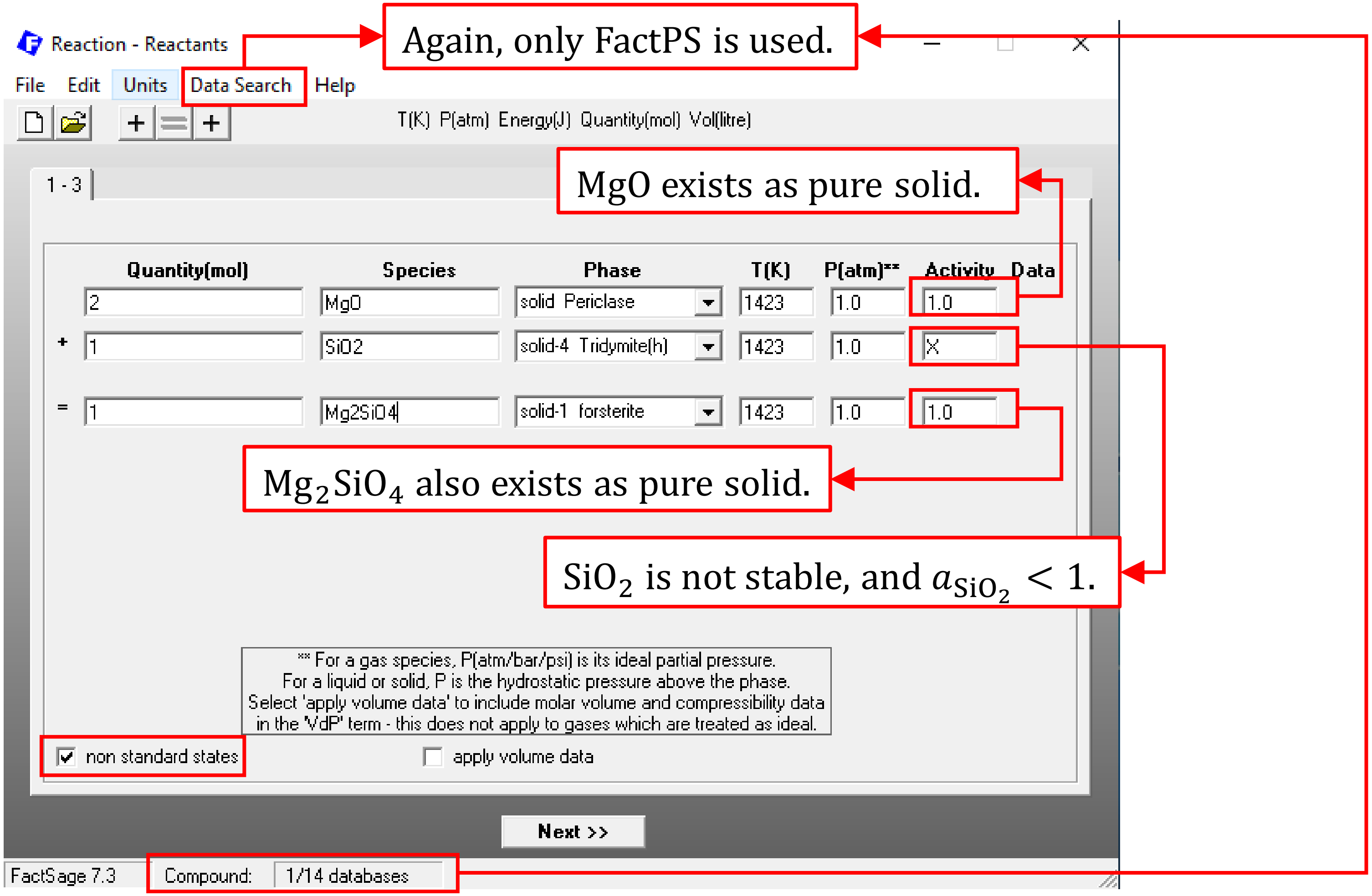
The MgO-SiO_2 phase diagram indicates that given excess MgO(s) in the Pidgeon reactor, the formed SiO_2(s) will react with MgO(s) to form $(MgO)_2 \cdot SiO_2$, and thus, $a_{\mathrm{SiO_2}}^{(s3)} < 1$. In other words, SiO_2(s) is not stable.

The next page shows the calculation of $a_{\mathrm{SiO_2}}$ for a system consisting of MgO(s) and Mg_2SiO_4(s). You can also consider $a_{\mathrm{SiO_2}}$ as the activity of solid SiO_2 when it exists as solid $(MgO)_2 \cdot SiO_2$. To do this, the following reaction which contains SiO_2(s) is considered.

$$2\mathrm{MgO(s)} + \mathrm{SiO_2(s)} = \mathrm{Mg_2SiO_4(s)}$$

Application 2: Pidgeon Process

Calculation of a_{SiO_2}:



Reaction - Reactants

	Quantity(mol)	Species	Phase	T(K)	P(atm)**	Activity	Data
	2	MgO	solid Periclase	1423	1.0	1.0	
+	1	SiO2	solid-4 Tridymite(h)	1423	1.0	X	
=	1	Mg2SiO4	solid-1 forsterite	1423	1.0	1.0	

** For a gas species, P(atm/bar/psi) is its ideal partial pressure.
For a liquid or solid, P is the hydrostatic pressure above the phase.
Select 'apply volume data' to include molar volume and compressibility data
in the 'VdP' term - this does not apply to gases which are treated as ideal.

☑ non standard states ☐ apply volume data

FactSage 7.3 | Compound: | 1/14 databases

Again, only FactPS is used.

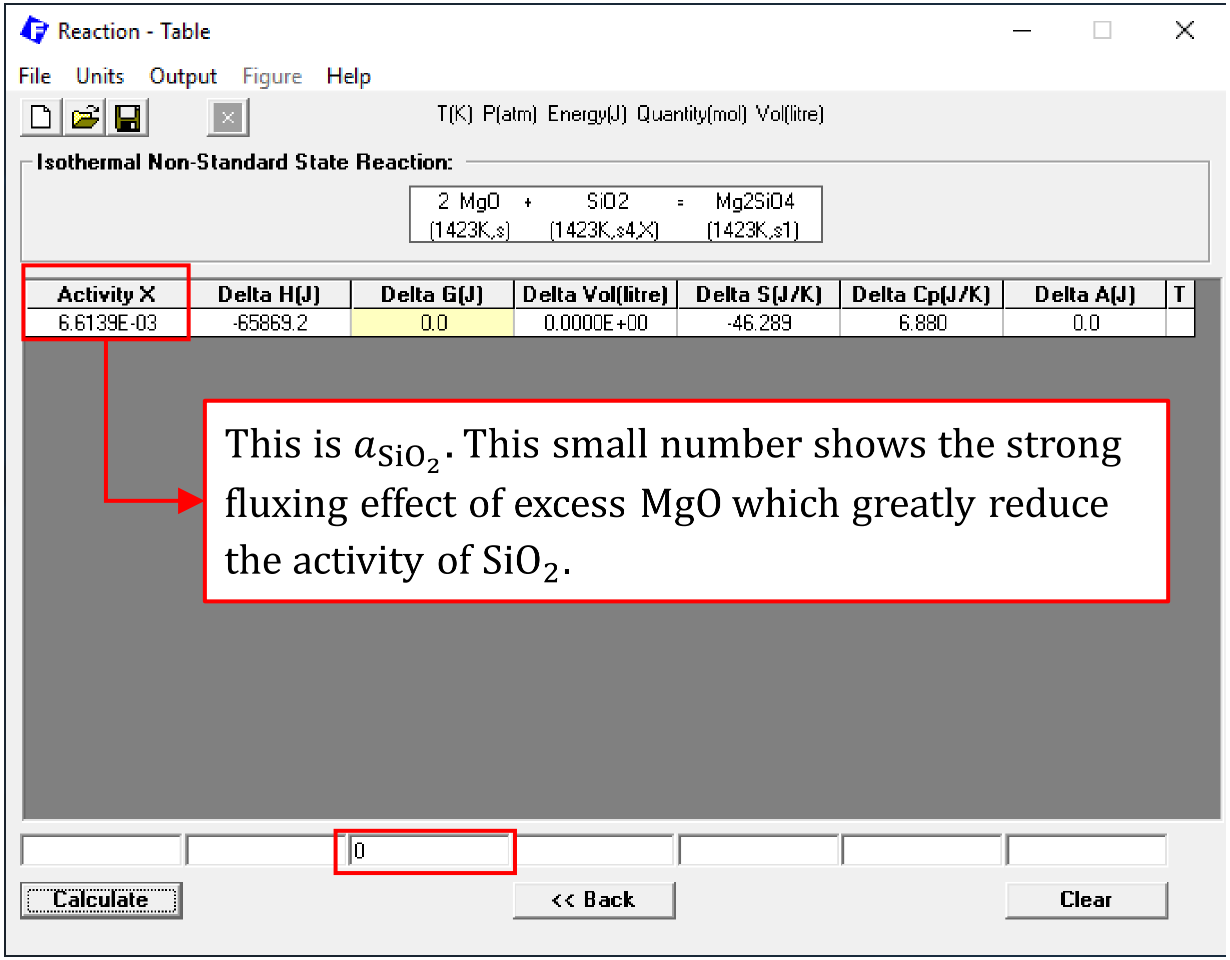
MgO exists as pure solid.

Mg_2SiO_4 also exists as pure solid.

SiO_2 is not stable, and $a_{SiO_2} < 1$.

Application 2: Pidgeon Process

Calculation of a_{SiO_2}:



Isothermal Non-Standard State Reaction:

2 MgO	+	SiO2	=	Mg2SiO4
(1423K,s)		(1423K,s4,X)		(1423K,s1)

Activity X	Delta H(J)	Delta G(J)	Delta Vol(litre)	Delta S(J/K)	Delta Cp(J/K)	Delta A(J)	T
6.6139E-03	-65869.2	0.0	0.0000E+00	-46.289	6.880	0.0	

		0				

This is a_{SiO_2}. This small number shows the strong fluxing effect of excess MgO which greatly reduce the activity of SiO_2.

Application 2: Pidgeon Process

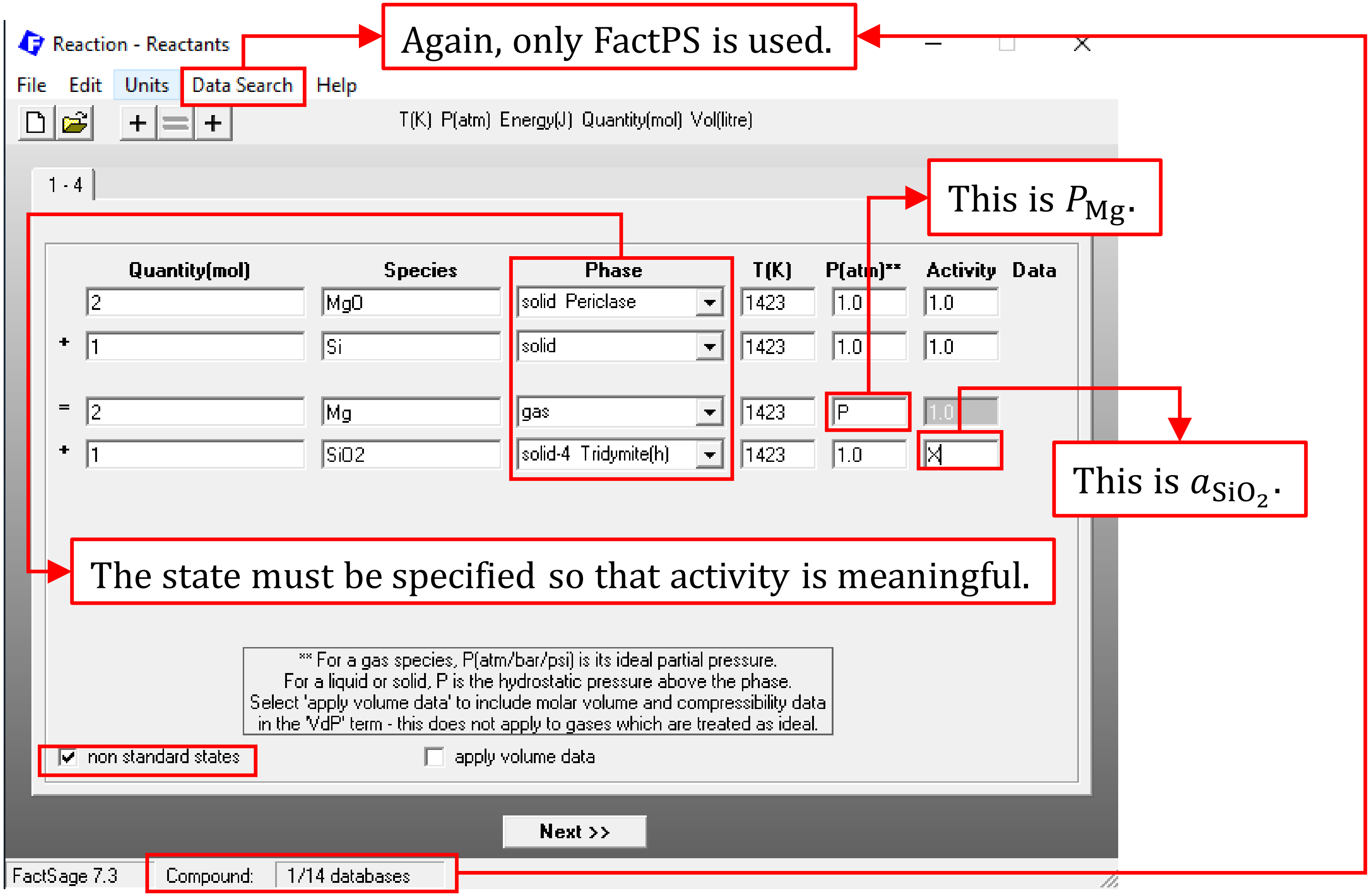
Also, in our simplified Pidgen Process:

$a_{\mathrm{MgO}}^{(s1)}$: because MgO exists as a pure solid,$a_{\mathrm{MgO}}^{(s1)} = 1.$

$a_{\mathrm{Si}}^{(s2)}$: because Si exists as a pure solid,$a_{\mathrm{Si}}^{(s2)} = 1.$

Application 2: Pidgeon Process

Non Standard-state Calculation: Calculate the equilibrium, i.e., $\Delta_r g = 0$



Again, only FactPS is used.

This is P_{Mg}.

This is a_{SiO_2}.

The state must be specified so that activity is meaningful.

	Quantity(mol)	Species	Phase	T(K)	P(atm)**	Activity	Data
	2	MgO	solid Periclase	1423	1.0	1.0	
+	1	Si	solid	1423	1.0	1.0	
=	2	Mg	gas	1423	P	1.0	
+	1	SiO2	solid-4 Tridymite(h)	1423	1.0	X	

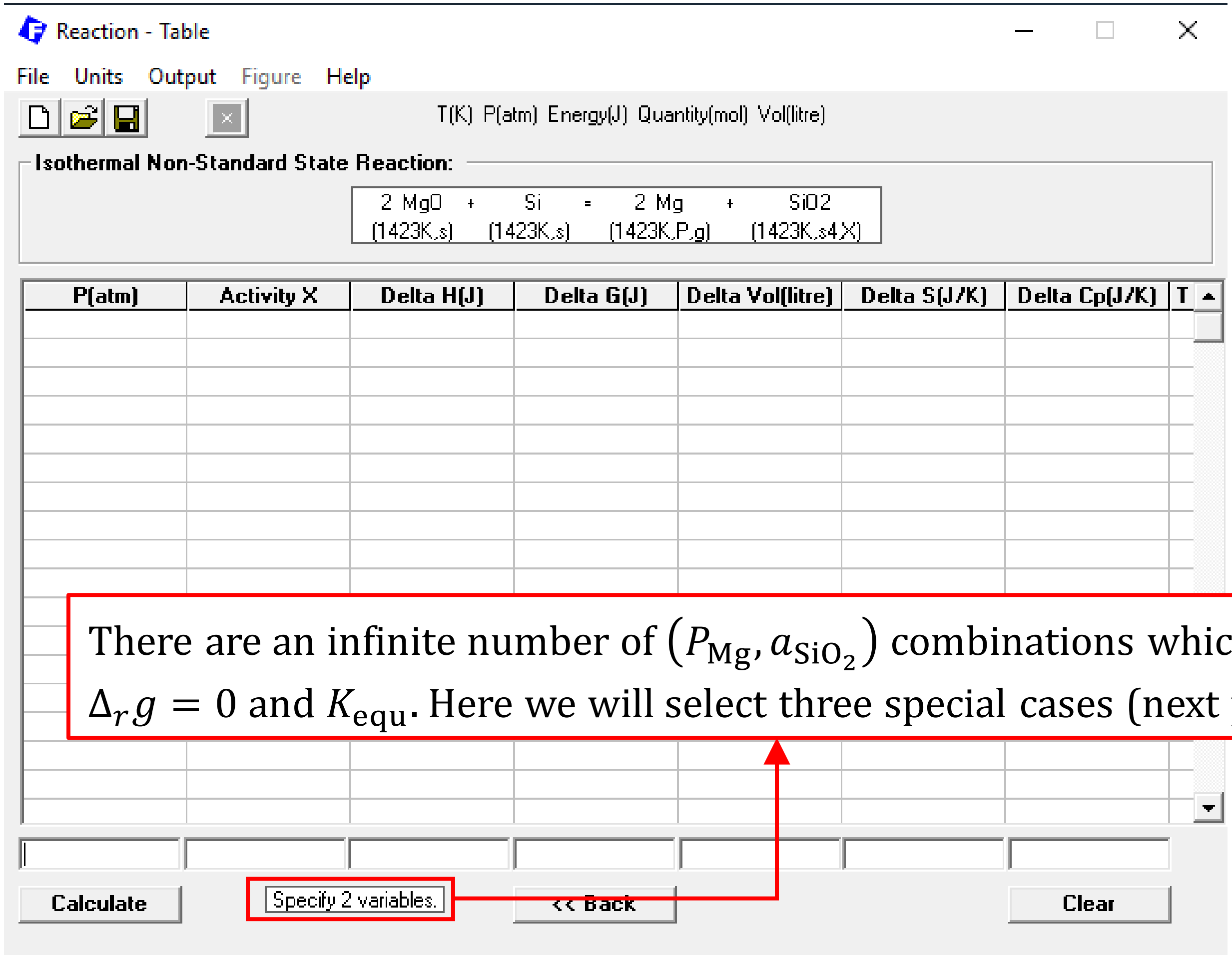
** For a gas species, P(atm/bar/psi) is its ideal partial pressure.
For a liquid or solid, P is the hydrostatic pressure above the phase.
Select 'apply volume data' to include molar volume and compressibility data in the 'VdP' term - this does not apply to gases which are treated as ideal.

☑ non standard states ☐ apply volume data

Compound: 1/14 databases

Application 2: Pidgeon Process

Non Standard-state Calculation: Calculate the equilibrium, i.e., $\Delta_r g = 0$

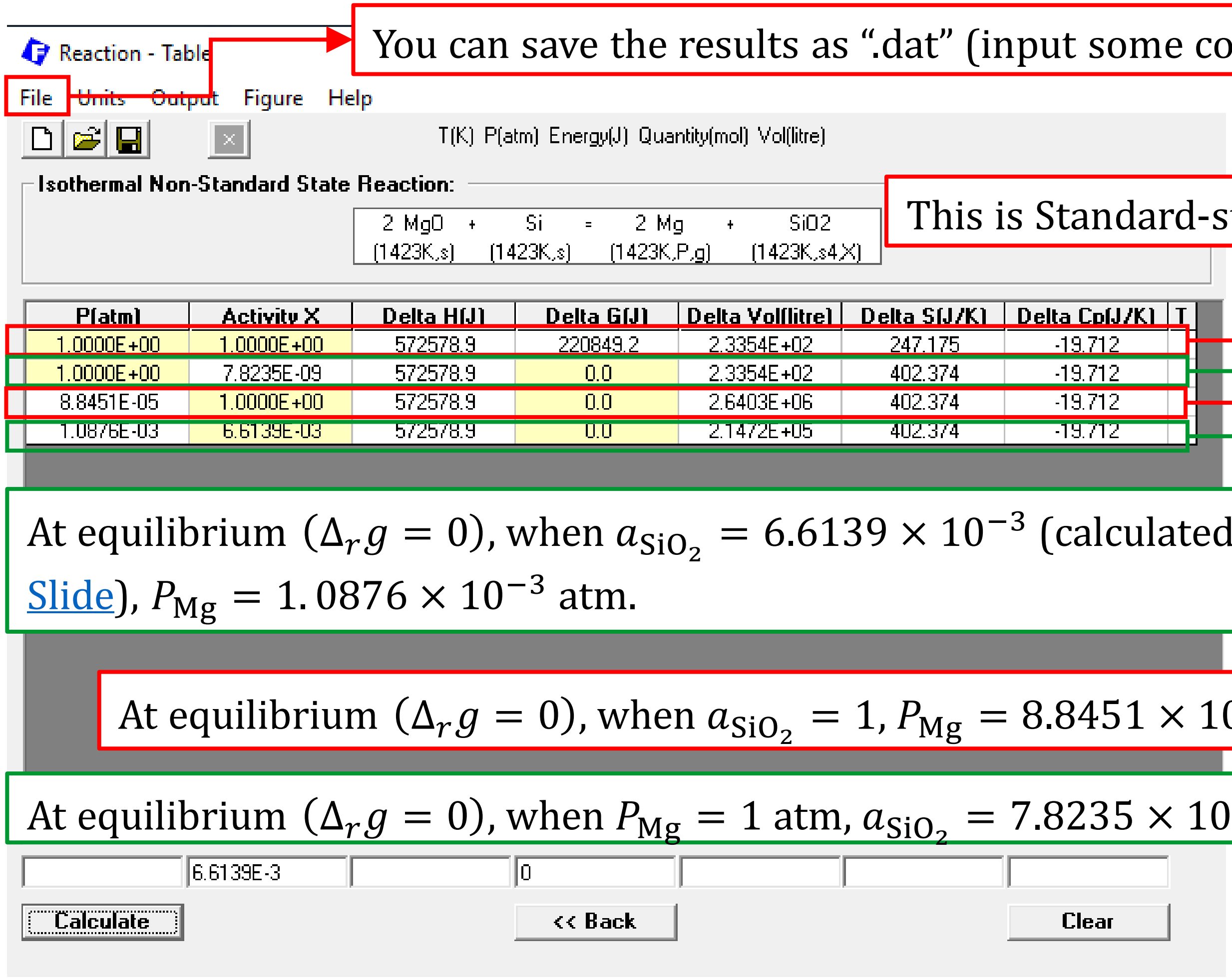


2 MgO + Si = 2 Mg + SiO2
(1423K,s) (1423K,s) (1423K,P,g) (1423K,s4,X)

There are an infinite number of $\left(P_{\mathrm{Mg}}, a_{\mathrm{SiO_2}}\right)$ combinations which could give $\Delta_r g = 0$ and K_{equ}. Here we will select three special cases (next page).

Application 2: Pidgeon Process

Non Standard-state Calculation: Calculate the equilibrium, i.e., $\Delta_r g = 0$



You can save the results as ".dat" (input some comments).

Isothermal Non-Standard State Reaction:

2 MgO	+	Si	=	2 Mg	+	SiO2
(1423K,s)		(1423K,s)		(1423K,P,g)		(1423K,s4,X)

This is Standard-state calculation.

P(atm)	Activity X	Delta H(J)	Delta G(J)	Delta Vol(litre)	Delta S(J/K)	Delta Cp(J/K)	T
1.0000E+00	1.0000E+00	572578.9	220849.2	2.3354E+02	247.175	-19.712	
1.0000E+00	7.8235E-09	572578.9	0.0	2.3354E+02	402.374	-19.712	
8.8451E-05	1.0000E+00	572578.9	0.0	2.6403E+06	402.374	-19.712	
1.0876E-03	6.6139E-03	572578.9	0.0	2.1472E+05	402.374	-19.712	

At equilibrium ($\Delta_r g = 0$), when $a_{\mathrm{SiO_2}} = 6.6139 \times 10^{-3}$ (calculated in Slide), $P_{\mathrm{Mg}} = 1.0876 \times 10^{-3}$ atm.

At equilibrium ($\Delta_r g = 0$), when $a_{\mathrm{SiO_2}} = 1$, $P_{\mathrm{Mg}} = 8.8451 \times 10^{-5}$ atm.

At equilibrium ($\Delta_r g = 0$), when $P_{\mathrm{Mg}} = 1$ atm, $a_{\mathrm{SiO_2}} = 7.8235 \times 10^{-9}$.

	6.6139E-3		0			

Application 2: Pidgeon Process

The above calculation verified that the magnesium production at a certain temperature can be enhanced by:

1. Reduce the total pressure ($< 1.0876 \times 10^{-3}$ atm).

2. Reduce a_{SiO_2} by fluxing – this is done automatically due to the formation of $Mg_2SiO_4(s)$, and the presence of CaO can reduce a_{SiO_2} further.

Application 2: Pidgeon Process

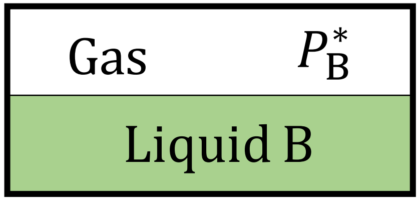
Another way of studying this simplified Pidgeon process is to write the reaction as:

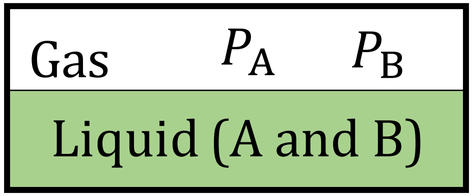
$$4\mathrm{MgO}(s) + \mathrm{Si}(s) = 2\mathrm{Mg}(g) + \mathrm{Mg_2SiO_4}(s)$$

In doing so, we don't need to consider the unstable phase – solid $\mathrm{SiO_2}$. Please perform the equilibrium calculations using this reaction.

Application 3: Vapor Pressure of Lead

Recall from Chapter 4.1 that for any **condensed** phase, there is a vapor pressure above it.

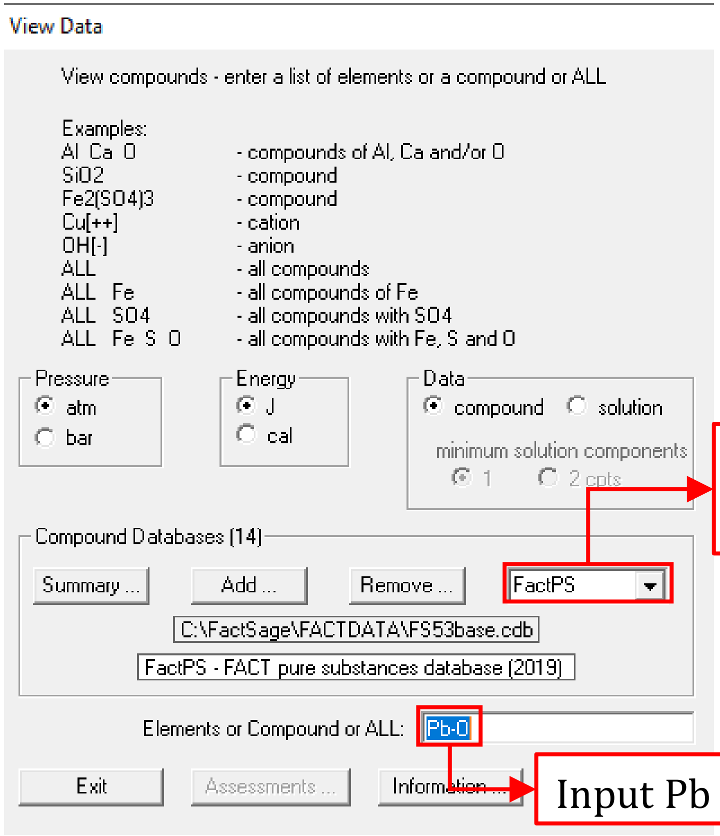




Say we are interested in the vapor pressure of lead above a lead-based solder bath (Sn-Pb) so that we can determine the safety precautions for the workers. Assume we have already known that **the activity of lead** in a eutectic solder is around 0.5 relative to the pure liquid ($a_{\mathrm{Pb}}^{(\mathrm{solder})} = 0.5$). The solder temperatures of interest are from 480~530 K (207~257 °C).

Application 3: Vapor Pressure of Lead

Gaseous Species of Lead. First, let us use the View Data Module to find what gaseous species of lead are modeled in the FactSage databases.



View Data

View compounds - enter a list of elements or a compound or ALL

Examples:

Al Ca O	- compounds of Al, Ca and/or O
SiO2	- compound
Fe2(SO4)3	- compound
Cu[++]	- cation
OH[-]	- anion
ALL	- all compounds
ALL Fe	- all compounds of Fe
ALL SO4	- all compounds with SO4
ALL Fe S O	- all compounds with Fe, S and O

Pressure: ● atm ○ bar

Energy: ● J ○ cal

Data: ● compound ○ solution

minimum solution components: ● 1 ○ 2 cpts

Compound Databases (14)

FactPS

C:\FactSage\FACTDATA\FS53base.cdb

FactPS - FACT pure substances database (2019)

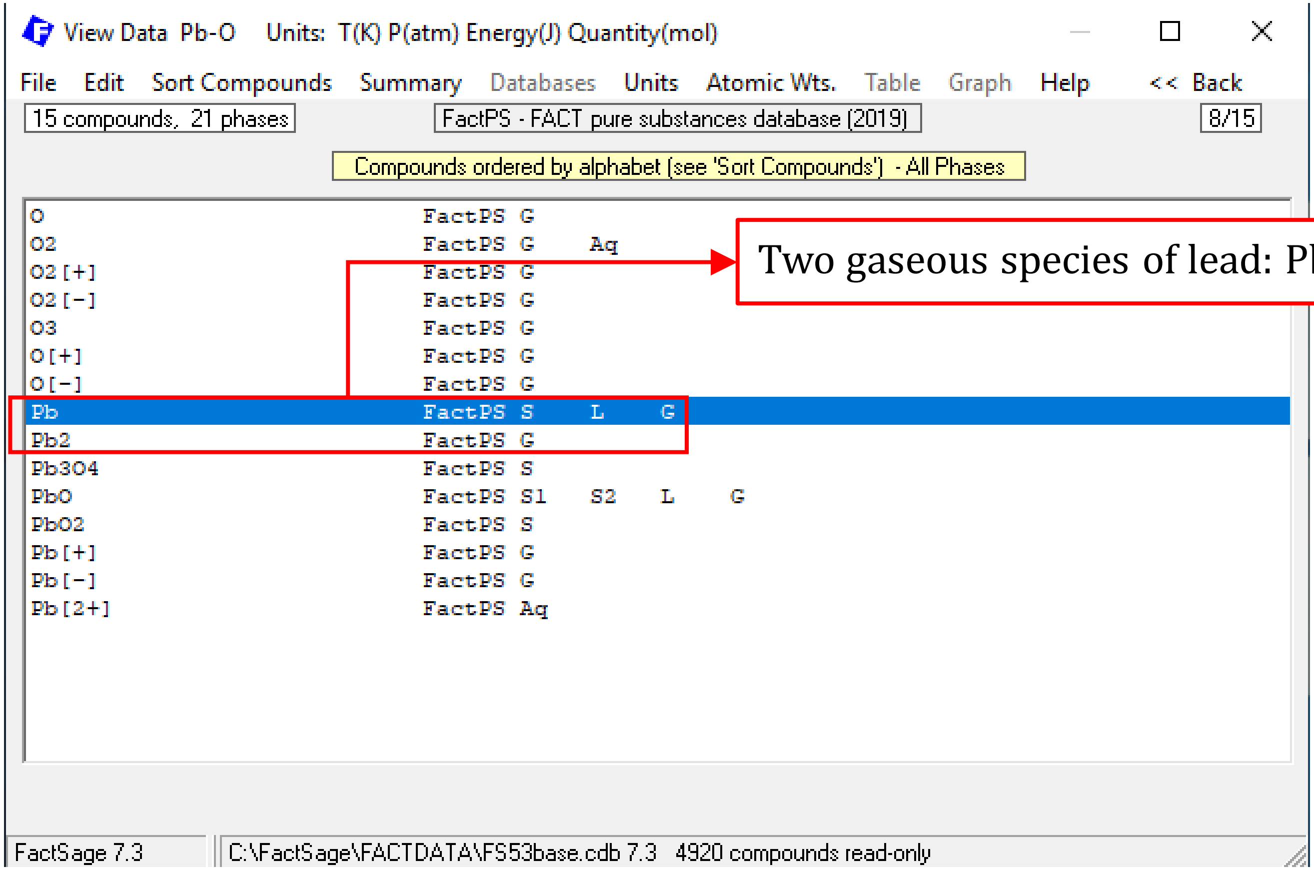
Elements or Compound or ALL: Pb-O

Choose FactPS which contains the models of most gaseous species.

Input Pb and another element, for example, Pb-O.

Application 3: Vapor Pressure of Lead

Gaseous Species of Lead. First, let us use the View Data Module to find what gaseous species of lead are modeled in the FactSage databases.



15 compounds, 21 phases

FactPS - FACT pure substances database (2019)

8/15

Compounds ordered by alphabet (see 'Sort Compounds') - All Phases

```
O                            FactPS G
O2                           FactPS G    Aq
O2[+]                        FactPS G
O2[-]                        FactPS G
O3                           FactPS G
O[+]                         FactPS G
O[-]                         FactPS G
Pb                           FactPS S    L    G
Pb2                          FactPS G
Pb3O4                        FactPS S
PbO                          FactPS S1   S2   L    G
PbO2                         FactPS S
Pb[+]                        FactPS G
Pb[-]                        FactPS G
Pb[2+]                       FactPS Aq
```

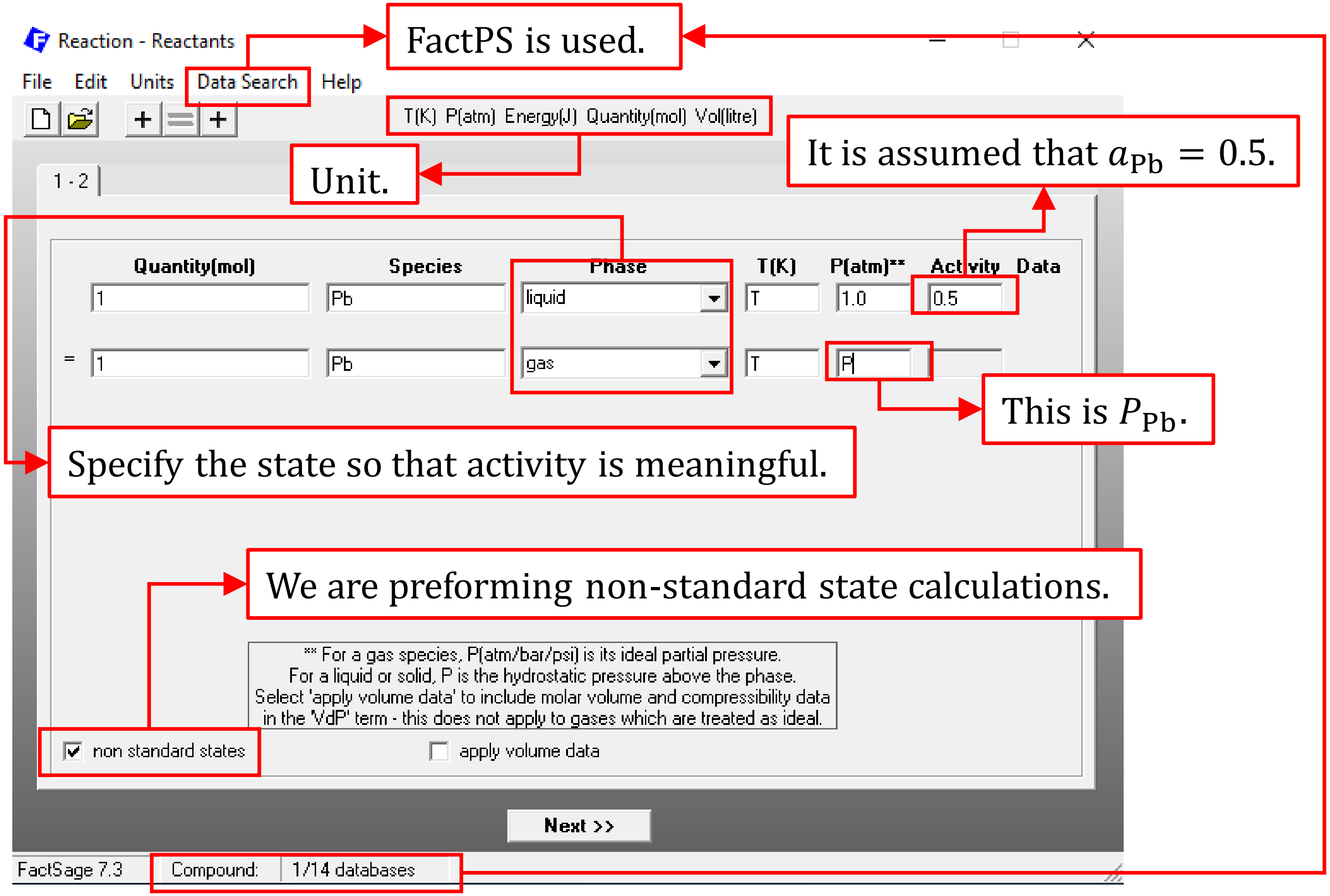
FactSage 7.3

C:\FactSage\FACTDATA\FS53base.cdb 7.3 4920 compounds read-only

Two gaseous species of lead: Pb and Pb_2.

Application 3: Vapor Pressure of Lead

Lead Monomer Vapor Pressure.



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

	Quantity(mol)	Species	Phase	T(K)	P(atm)**	Activity	Data
	1	Pb	liquid	T	1.0	0.5	
=	1	Pb	gas	T	P		

** For a gas species, P(atm/bar/psi) is its ideal partial pressure.
For a liquid or solid, P is the hydrostatic pressure above the phase.
Select 'apply volume data' to include molar volume and compressibility data
in the 'VdP' term - this does not apply to gases which are treated as ideal.

☑ non standard states

☐ apply volume data

FactSage 7.3 | Compound: | 1/14 databases

FactPS is used.

Unit.

It is assumed that $a_{\mathrm{Pb}} = 0.5$.

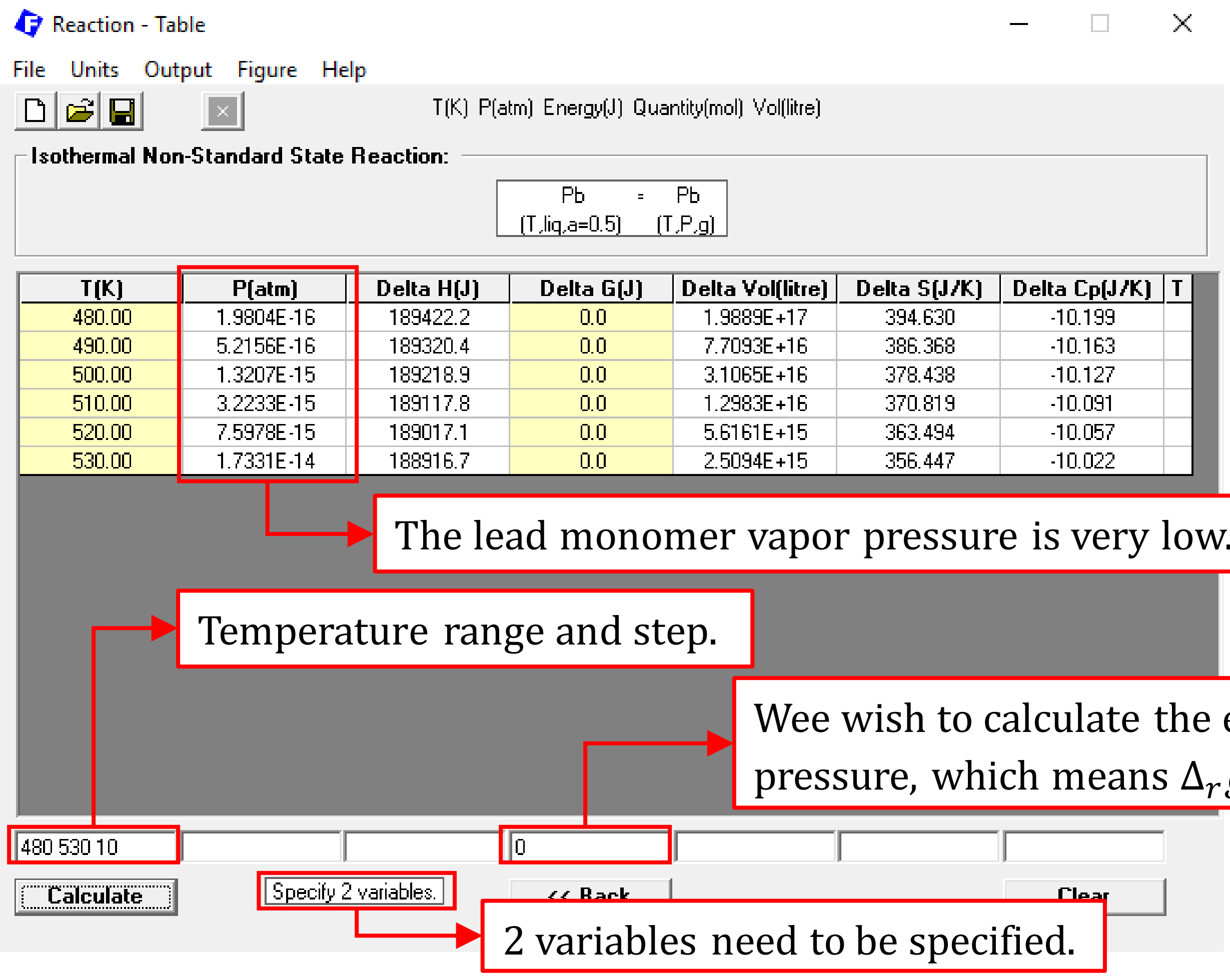
This is P_{Pb}.

Specify the state so that activity is meaningful.

We are preforming non-standard state calculations.

Application 3: Vapor Pressure of Lead

Lead Monomer Vapor Pressure.



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

Isothermal Non-Standard State Reaction:

Pb (T,liq,a=0.5) = Pb (T,P,g)

T(K)	P(atm)	Delta H(J)	Delta G(J)	Delta Vol(litre)	Delta S(J/K)	Delta Cp(J/K)	T
480.00	1.9804E-16	189422.2	0.0	1.9889E+17	394.630	-10.199	
490.00	5.2156E-16	189320.4	0.0	7.7093E+16	386.368	-10.163	
500.00	1.3207E-15	189218.9	0.0	3.1065E+16	378.438	-10.127	
510.00	3.2233E-15	189117.8	0.0	1.2983E+16	370.819	-10.091	
520.00	7.5978E-15	189017.1	0.0	5.6161E+15	363.494	-10.057	
530.00	1.7331E-14	188916.7	0.0	2.5094E+15	356.447	-10.022	

T(K): 480 530 10

Delta G(J): 0

Specify 2 variables.

The lead monomer vapor pressure is very low.

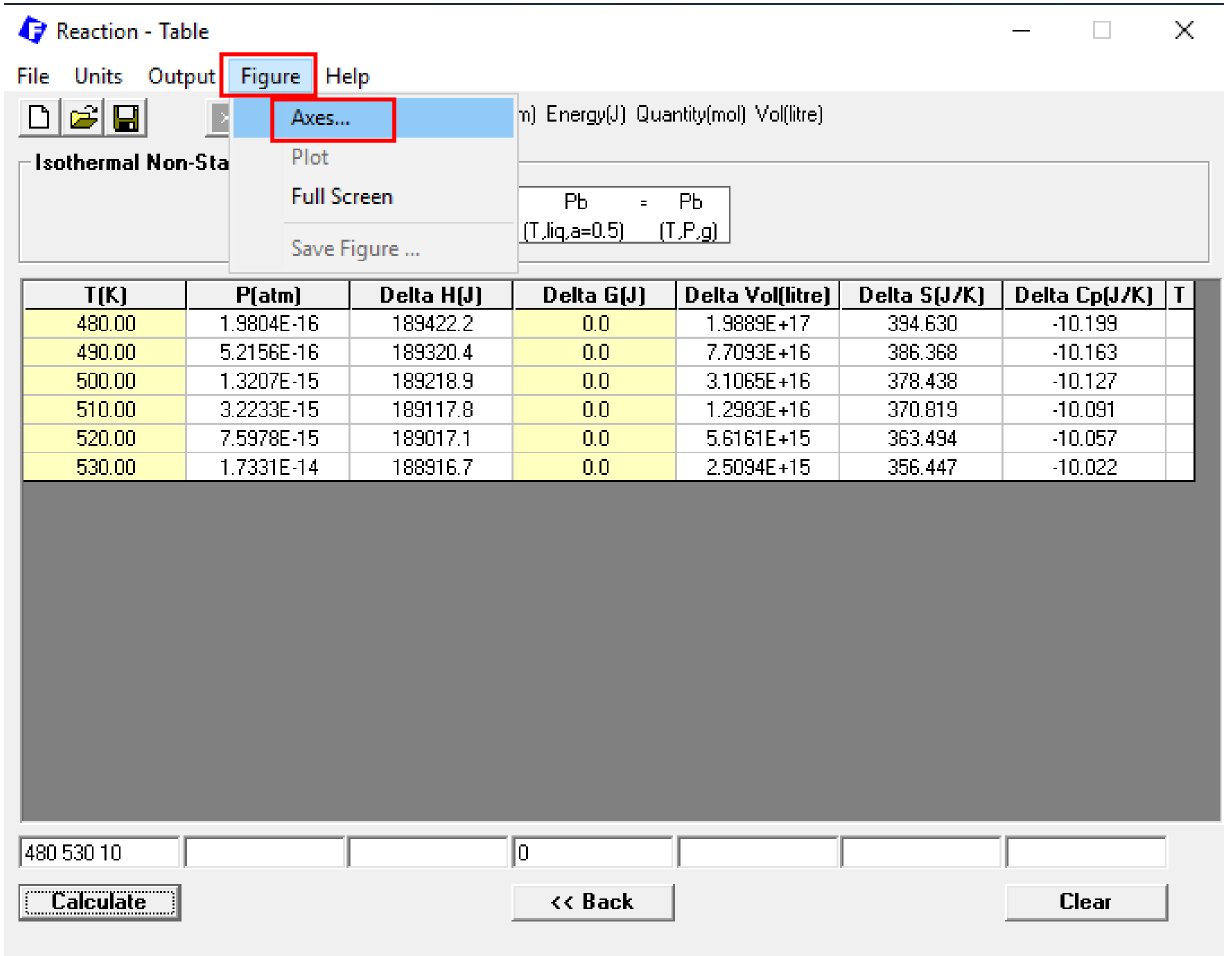
Temperature range and step.

Wee wish to calculate the equilibrium vapor pressure, which means $\Delta_r g = 0$

2 variables need to be specified.

Application 3: Vapor Pressure of Lead

Lead Monomer Vapor Pressure: plot the data.



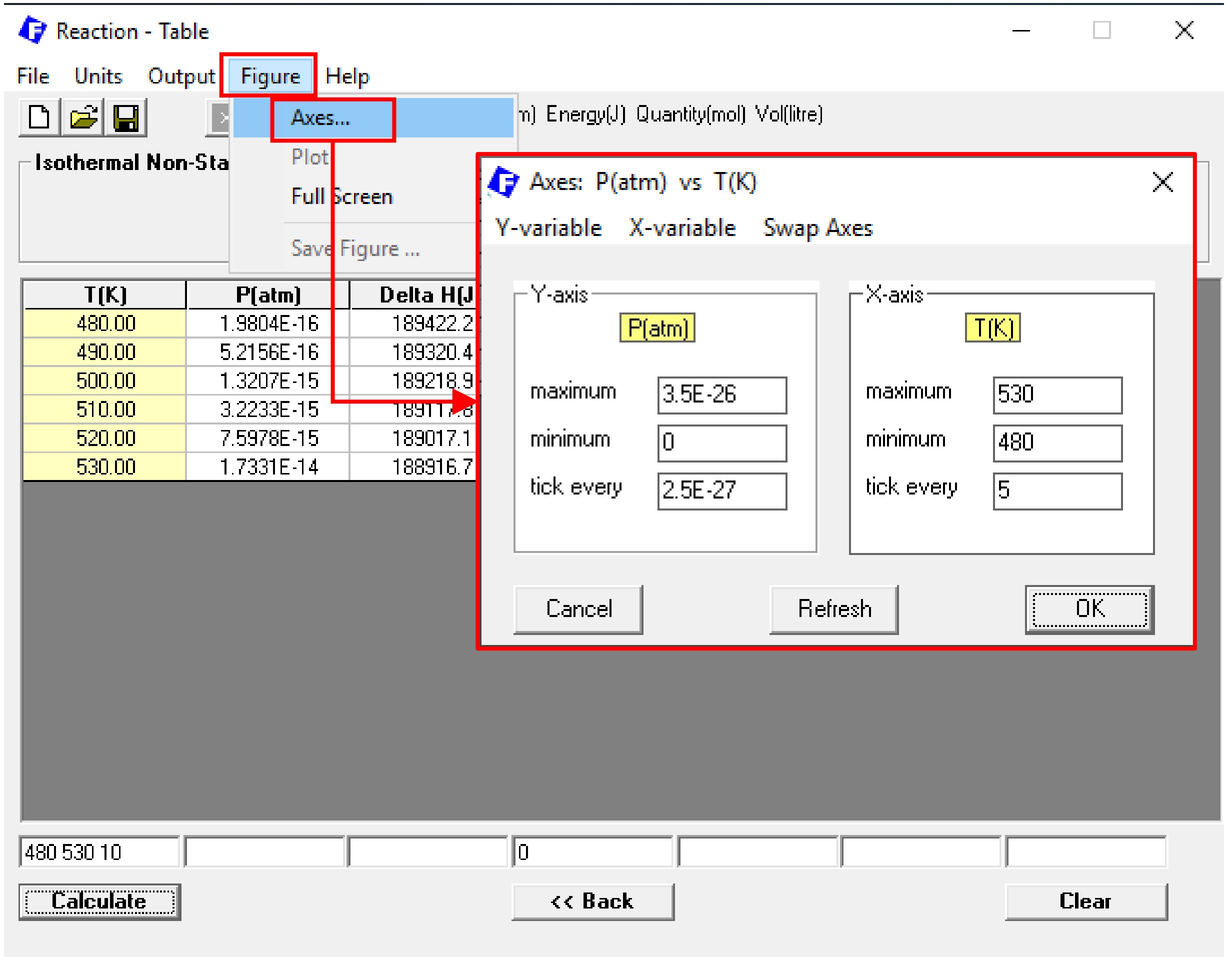
Pb (T,liq,a=0.5) = Pb (T,P,g)

T(K)	P(atm)	Delta H(J)	Delta G(J)	Delta Vol(litre)	Delta S(J/K)	Delta Cp(J/K)	T
480.00	1.9804E-16	189422.2	0.0	1.9889E+17	394.630	-10.199	
490.00	5.2156E-16	189320.4	0.0	7.7093E+16	386.368	-10.163	
500.00	1.3207E-15	189218.9	0.0	3.1065E+16	378.438	-10.127	
510.00	3.2233E-15	189117.8	0.0	1.2983E+16	370.819	-10.091	
520.00	7.5978E-15	189017.1	0.0	5.6161E+15	363.494	-10.057	
530.00	1.7331E-14	188916.7	0.0	2.5094E+15	356.447	-10.022	

T(K)	P(atm)	Delta H(J)	Delta G(J)	Delta Vol(litre)	Delta S(J/K)	Delta Cp(J/K)
480 530 10			0			

Application 3: Vapor Pressure of Lead

Lead Monomer Vapor Pressure: plot the data.



T(K)	P(atm)	Delta H(J
480.00	1.9804E-16	189422.2
490.00	5.2156E-16	189320.4
500.00	1.3207E-15	189218.9
510.00	3.2233E-15	189117.8
520.00	7.5978E-15	189017.1
530.00	1.7331E-14	188916.7

Y-axis P(atm)

maximum 3.5E-26

minimum 0

tick every 2.5E-27

X-axis T(K)

maximum 530

minimum 480

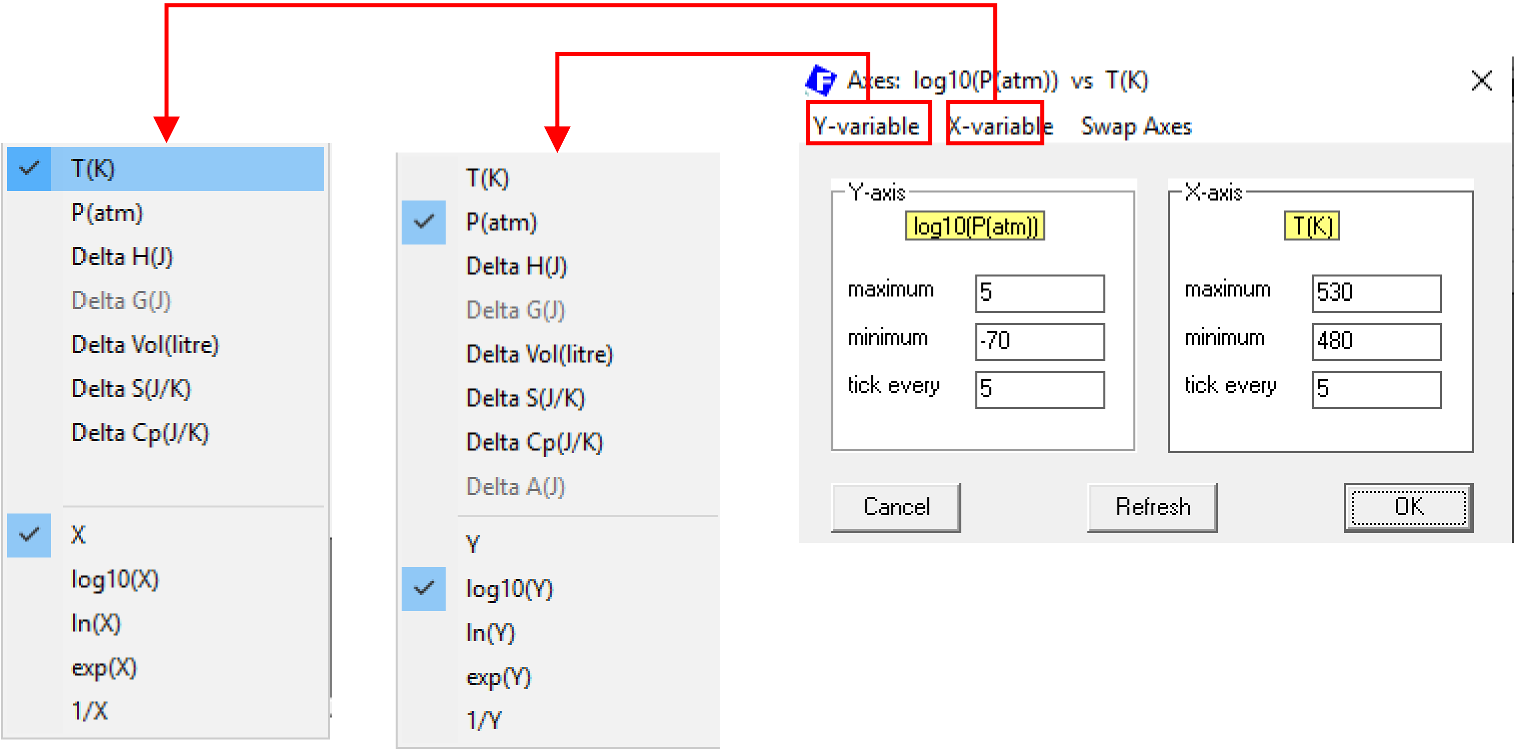
tick every 5

480 530 10

0

Application 3: Vapor Pressure of Lead

Lead Monomer Vapor Pressure: plot the data.



Axes: log10(P(atm)) vs T(K)

Y-axis

log10(P(atm))

maximum 5

minimum -70

tick every 5

X-axis

T(K)

maximum 530

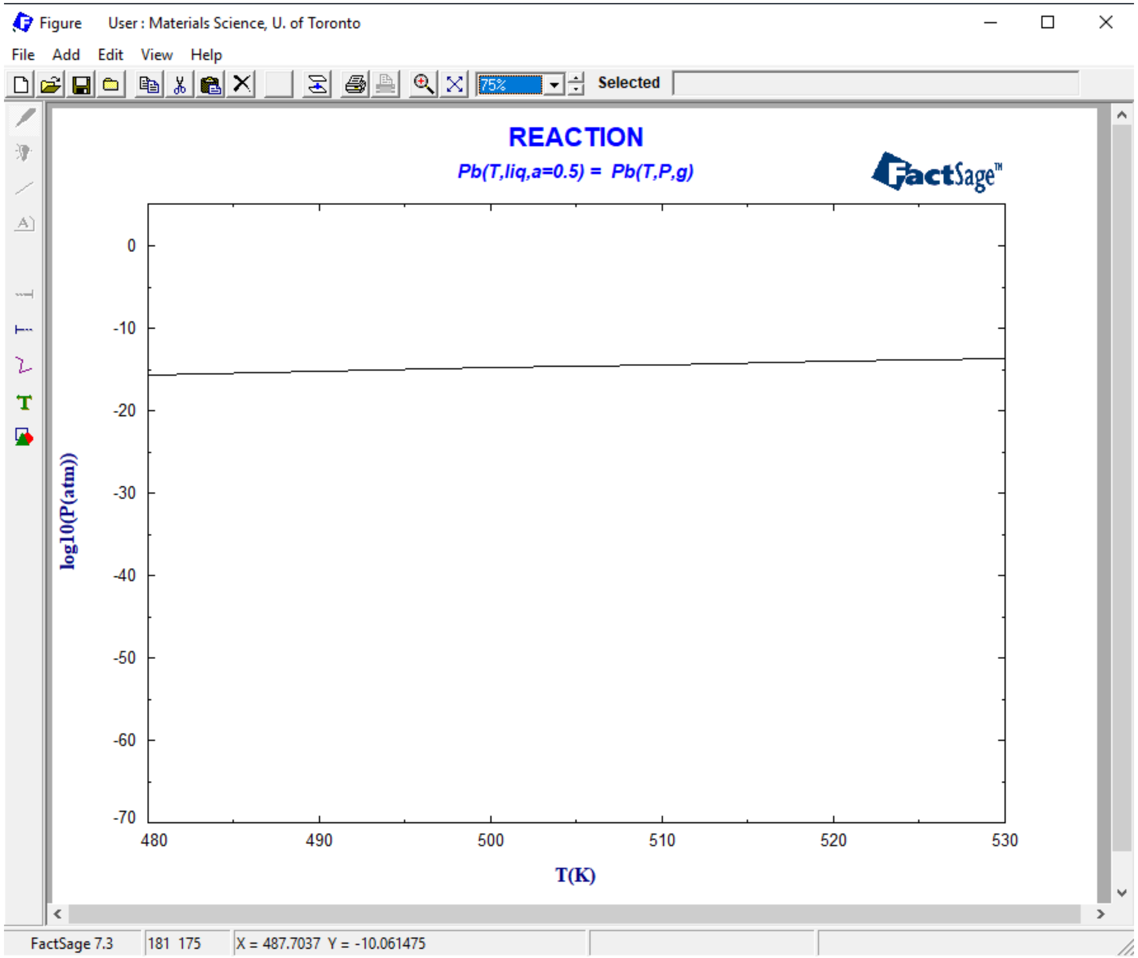
minimum 480

tick every 5

You can choose the variable of axes and their format.

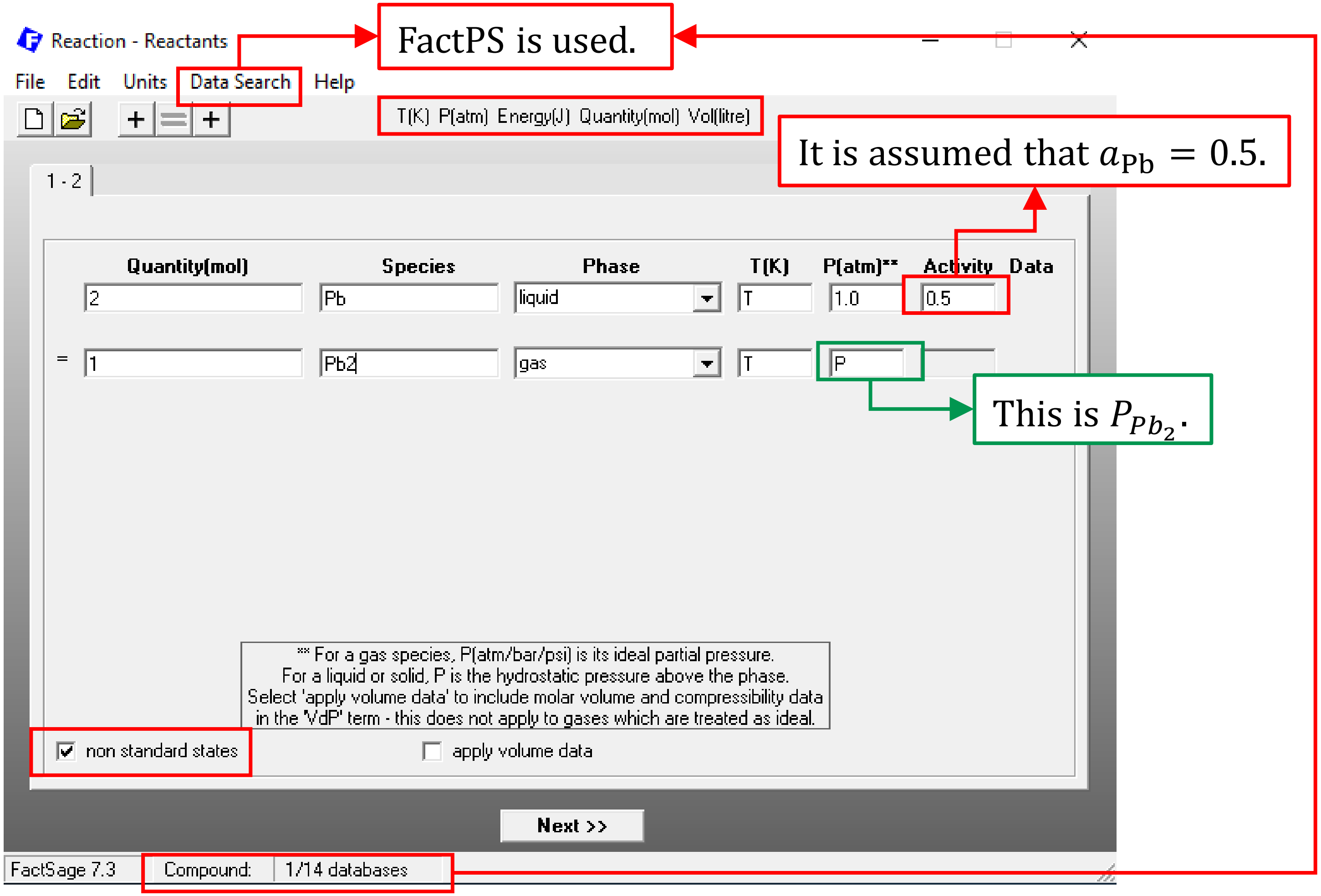
Application 3: Vapor Pressure of Lead

Lead Monomer Vapor Pressure: plot the data.



Application 3: Vapor Pressure of Lead

Lead Dimer Vapor Pressure.



FactPS is used.

It is assumed that $a_{\mathrm{Pb}} = 0.5$.

This is P_{Pb_2}.

	Quantity(mol)	Species	Phase	T(K)	P(atm)**	Activity	Data
	2	Pb	liquid	T	1.0	0.5	
=	1	Pb2	gas	T	P		

** For a gas species, P(atm/bar/psi) is its ideal partial pressure.
For a liquid or solid, P is the hydrostatic pressure above the phase.
Select 'apply volume data' to include molar volume and compressibility data in the 'VdP' term - this does not apply to gases which are treated as ideal.

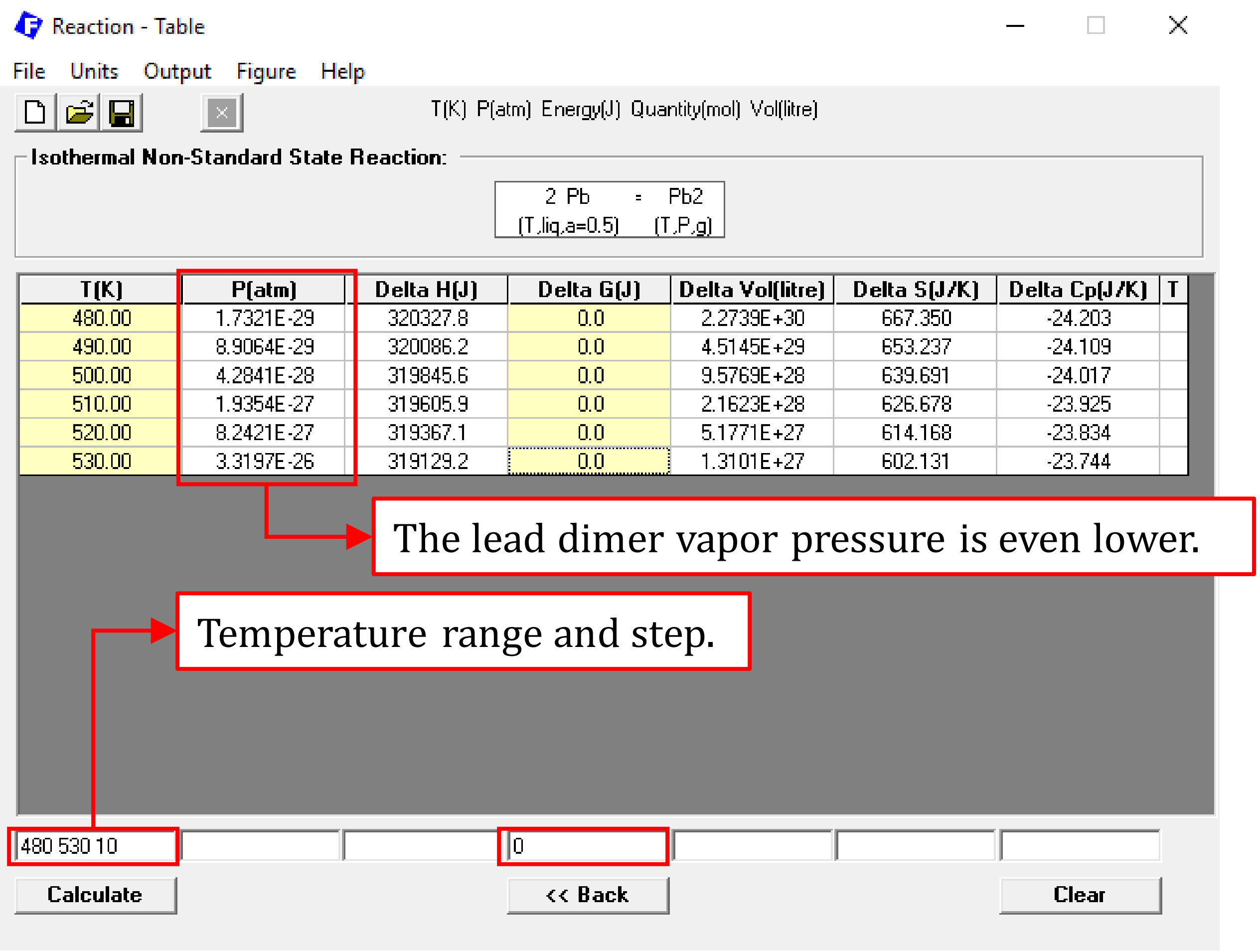
☑ non standard states

☐ apply volume data

Compound: 1/14 databases

Application 3: Vapor Pressure of Lead

Lead Dimer Vapor Pressure.



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

Isothermal Non-Standard State Reaction:

$2\ Pb\ (T,liq,a=0.5) = Pb2\ (T,P,g)$

T(K)	P(atm)	Delta H(J)	Delta G(J)	Delta Vol(litre)	Delta S(J/K)	Delta Cp(J/K)	T
480.00	1.7321E-29	320327.8	0.0	2.2739E+30	667.350	-24.203	
490.00	8.9064E-29	320086.2	0.0	4.5145E+29	653.237	-24.109	
500.00	4.2841E-28	319845.6	0.0	9.5769E+28	639.691	-24.017	
510.00	1.9354E-27	319605.9	0.0	2.1623E+28	626.678	-23.925	
520.00	8.2421E-27	319367.1	0.0	5.1771E+27	614.168	-23.834	
530.00	3.3197E-26	319129.2	0.0	1.3101E+27	602.131	-23.744	

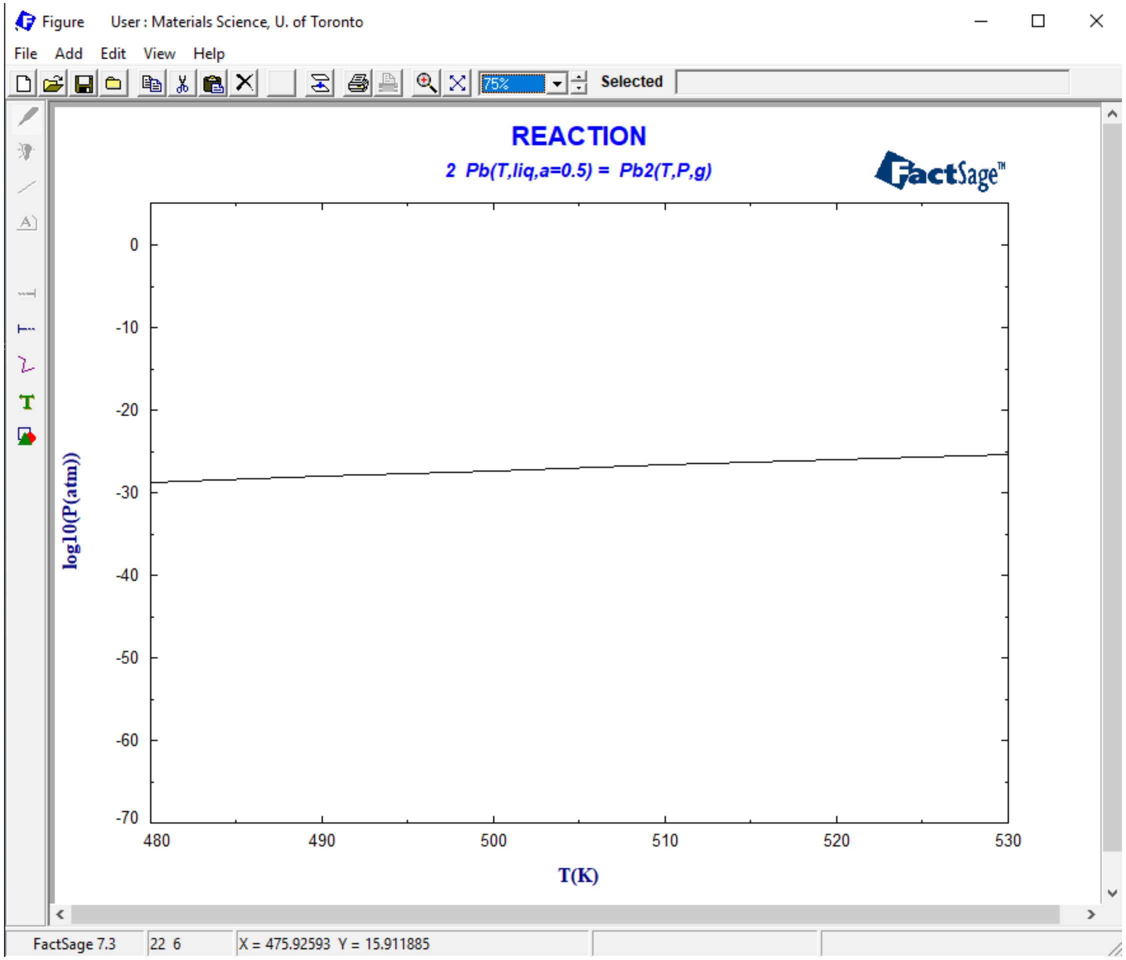
480 530 10			0			

The lead dimer vapor pressure is even lower.

Temperature range and step.

Application 3: Vapor Pressure of Lead

Lead Dimer Vapor Pressure: plot the data



X = 475.92593 Y = 15.911885

In-Class Exercise

Question 1.

Plot the “liquidus line” for **ideal** nickel alloys.

Tip: perform the equilibrium calculation for the melting reaction $\mathrm{Ni}(s) = \mathrm{Ni}(l)$ and note $\mathrm{Ni}(s)$ is pure solid whereas $\mathrm{Ni}(l)$ is in the solution state, i.e., $a_{\mathrm{Ni}} < 1$ relative to pure liquid Ni.

(You can find help from the supplementary materials: “02 FACTSage_Raction Module_Supplementary”)

Question 2.

Calculate the AFT for combustion of propane (C_3H_8) in air (0 to 100% excess air – meaning from stoichiometric air to twice as much).

In-Class Exercise

Question 3.

In each case below, is the metal recovery possible from the slag and what is the effect of temperature?

Note: for reduction by Fe, the FeO activity in the oxide melt will be assumed to be 0.4; and for reduction by Si, the SiO_2 activity will be 0.3. Activities in molten alloys and slags are relative to pure liquid (i.e., Raoultian pure substance standard state). If no data for liquid oxide, then choose solid.

(3a) Treatment of arc furnace dust. Look at the reduction of ZnO, initially with an activity of 0.1, by solid iron scrap. Temperature range is 1200~1600 °C. The zinc must come off as vapor at 1 atm (partial pressure of zinc).

(3b) Recovery of cobalt from scrap superalloys. Look at the reduction of CoO initially with an activity of 0.01 in a molten slag, by iron scrap. The cobalt will form as a liquid in a molten alloy and should have an activity of 0.2. Temperature range is 1500~1700 °C.

In-Class Exercise

Question 3.

(3c) Recovery of cadmium from "NiCad" battery scrap. Look at the reduction of CdO, initially with an activity of 0.002 in a molten slag, by solid iron scrap. Temperature range is 1200~1600 °C. The cadmium must come off as vapor at 1 atm (partial pressure of cadmium).

Question 4.

Look at the vapor species for a metal (Fe, Ni, Zn, etc.) using the View Data Module. Then use the Reaction Module to plot $\log(P)$ vs. $1/T$ (K) for the **monomer** species above the pure liquid. Choose Y-axis numbers between 10 and 0.0001 initially [$\log(P)$ between 1 and -4] and use that to help you find the appropriate temperature range. (Choose one metal)