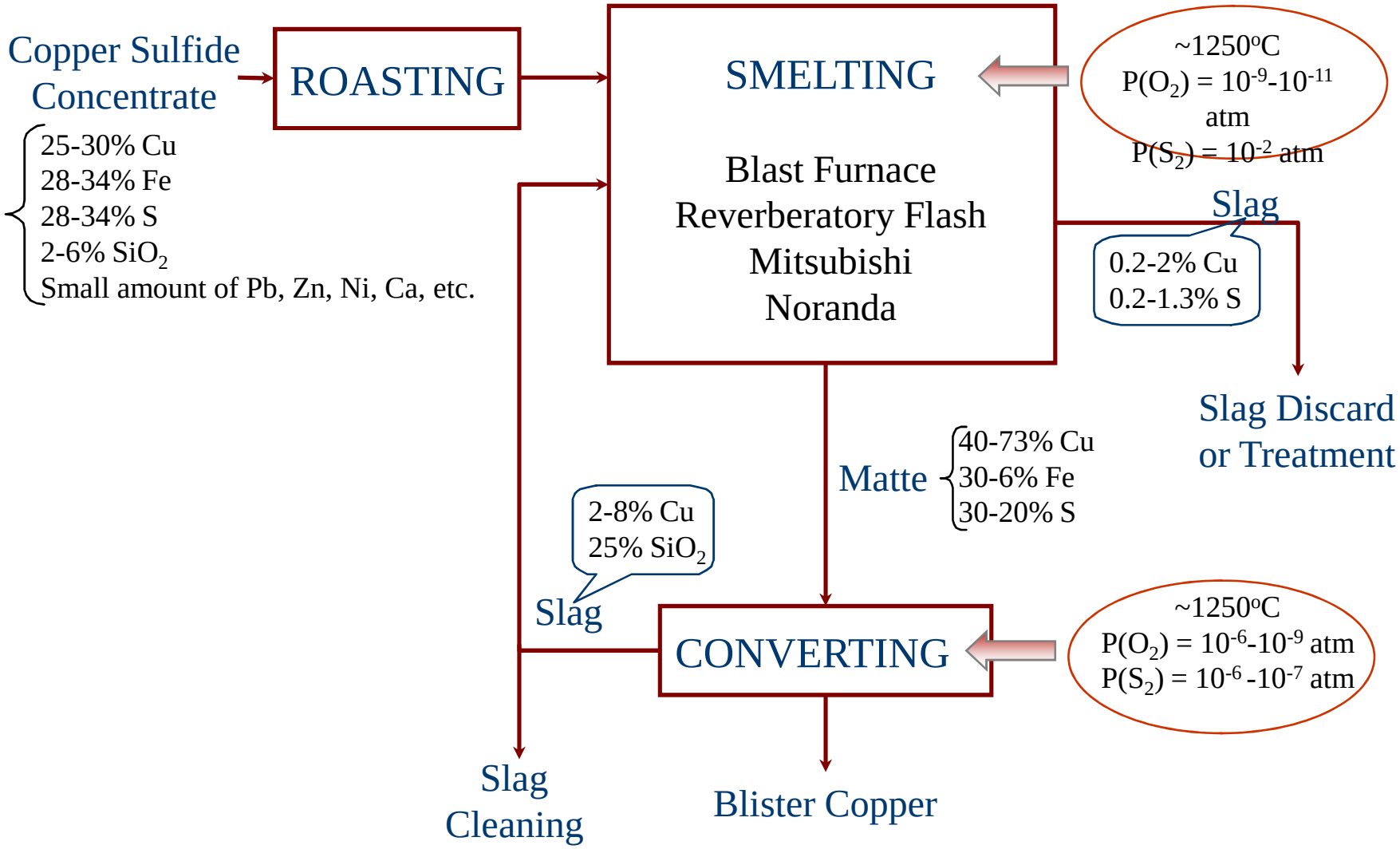
Oxides and Pyrometallurgy

- **Copper Extraction from Sulfide Concentrates**

- **Using Equilib Program**
  - Selection of databases
  - Phase selection
  - ?Slag and ?Monoxide
  - Transition calculation
  - Export of results to Excel and plotting

- **Phase Diagrams of Oxide Systems**
  - In equilibrium with metals
  - At fixed or variable oxygen pressure
  - Being on a join

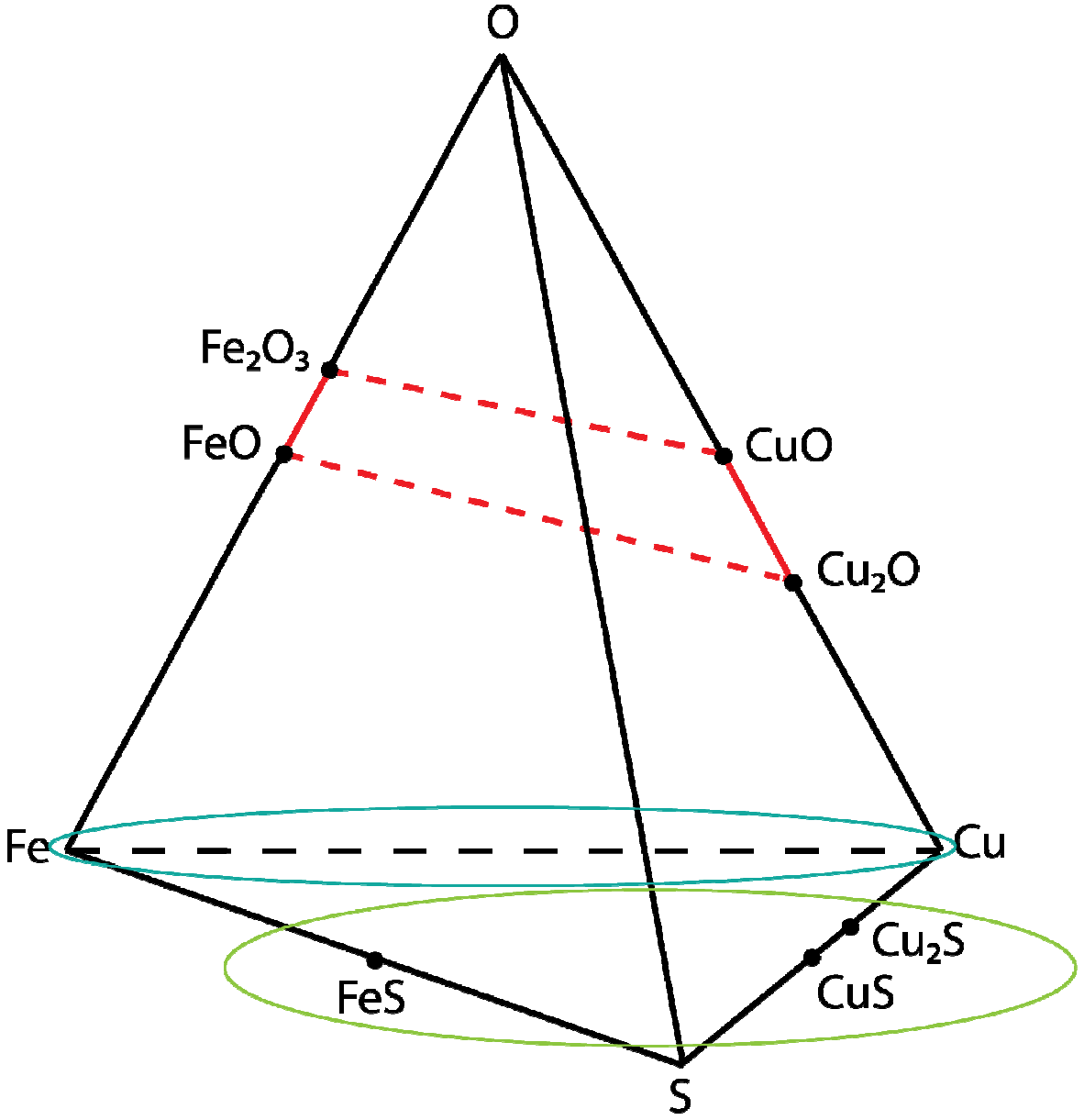
Copper Extraction from Sulfide Concentrates



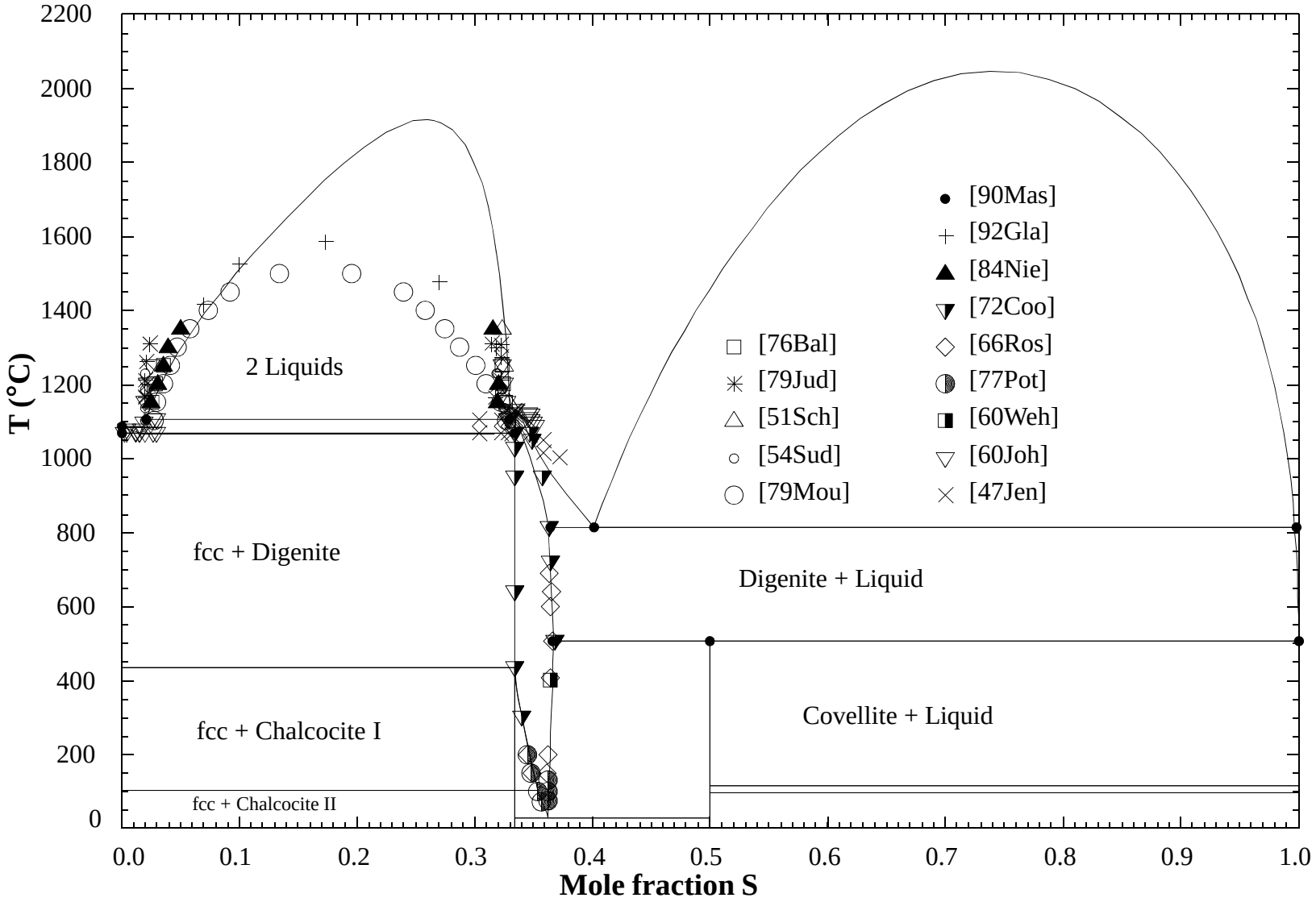
Direct Smelting: Matte/Slag/Cu equilibrium

- **Can all three phases Matte/Slag/Cu be in equilibrium?**
- **Operating variables:**
  - Temperature
  - Oxygen pressure
  - Fe/SiO_2 ratio in the Slag
  - Amount of CaO in the Slag
- **Subjects to examine:**
  - Losses of Cu into Slag
  - Distribution of minor elements, Pb and Zn, among Matte, Slag and Cu
- **Chemical system: Cu-Fe-Si-O-S + Ca-Pb-Zn**
- **Does this task make sense?**
  - At T=const there are 4-2=2 degrees of freedom => fix $P(O_2)$, vary Fe/SiO_2
  - Study the effect of CaO at constant amount of CaO in the Slag
  - Pb(Slag)/Pb(Cu) will approach a constant as the amount of Pb approaches zero

Fe-Cu-O-S System



Cu-S System


2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
T (°C)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Mole fraction S
2 Liquids
fcc + Digenite
Digenite + Liquid
fcc + Chalcocite I
Covellite + Liquid
fcc + Chalcocite II
[90Mas]
[92Gla]
[84Nie]
[72Coo]
[76Bal]
[66Ros]
[79Jud]
[77Pot]
[51Sch]
[60Weh]
[54Sud]
[60Joh]
[79Mou]
[47Jen]

Selection of Databases

FactSage 6.1 - Summary of Databases

Overview of databases

Compound Databases :

FACT53 - FACT 5.3 compound database: — **Gaseous species**

SGPS - SGTE pure substances database

Coupled Compound & Solution Databases :

Fact *Package:*

FToxid - oxide database for slags, glasses, ceramics, refractories — **Slag, Oxides**

FTsalt - salt database
FThall - Hall alumium database
FThelg - aqueous (Helgeson) database

FTmisc - miscealleneous database for sulfides, alloys, etc. — **Matte, Sulfides, Liquid metals**

FTpulp - pulp and paper database (and corrosion and combustion)

Fact *Other databases :*

FTlite - light metal database (formerly FSlite) — **Metal phases**

FactSage™ *Databases:*

V **FScopp** - copper alloy database
V **FSlead** - lead alloy database
FSstel - steel database — **Metal phases**
FSupsi - ultrapure silicon database

SGTE *Databases :*

V **SGnobl** - noble metal database (formerly FSnobl)
SGnucl - nuclear database

SGTE(2007) - alloy database (formerly SGTE (2004)) — **Metal phases**

V **SGsold** - solders database
BINARY - (2004) free alloy database

Other Databases:

TDNucl - Thermodata nuclear database

FTmisc - FACT miscellaneous databases

- the system **S-Fe-Ni-Co-Cr**:

  Liquid sulfide [FTmisc-MAT2] – from pure metal to pure sulfur

  Solid sulfide phases

- the matte smelting system **S-Cu-Fe-Ni-Co-Pb-Zn-As**:

  Liquid matte [FTmisc-MATT] – liquid sulfide, does not extend to pure metal.

  It is designed for calculation of **matte / slag / metal equilibria**

  Consistent with FToxid-SLAG, FTmisc-CuLQ and FTmisc-PbLQ

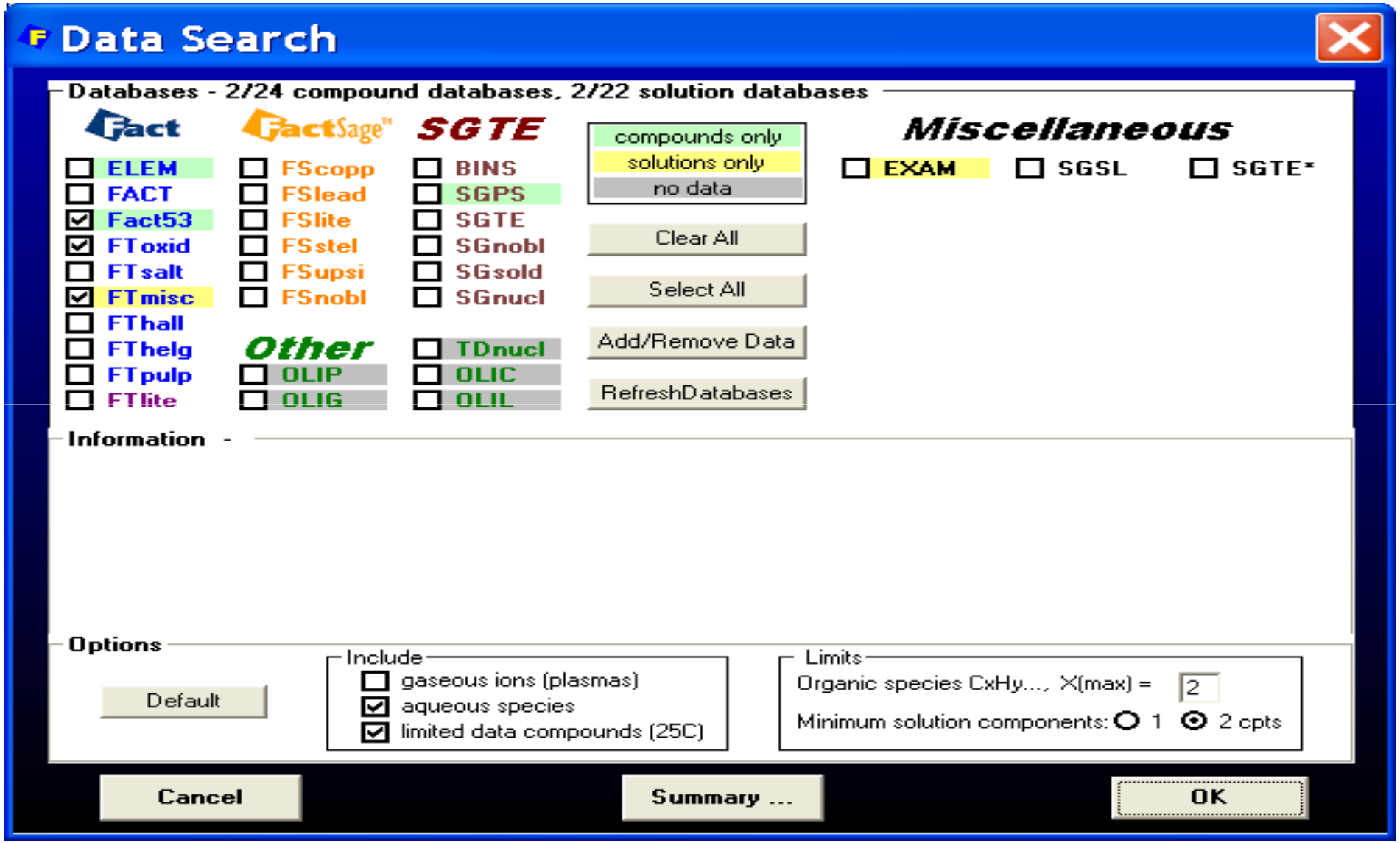
  It is not consistent with solid sulfide phases

- Liquid copper or speiss **[FTmisc-CuLQ]** – **Cu-Pb-Zn-As-Fe-Ni-Au-S-O**

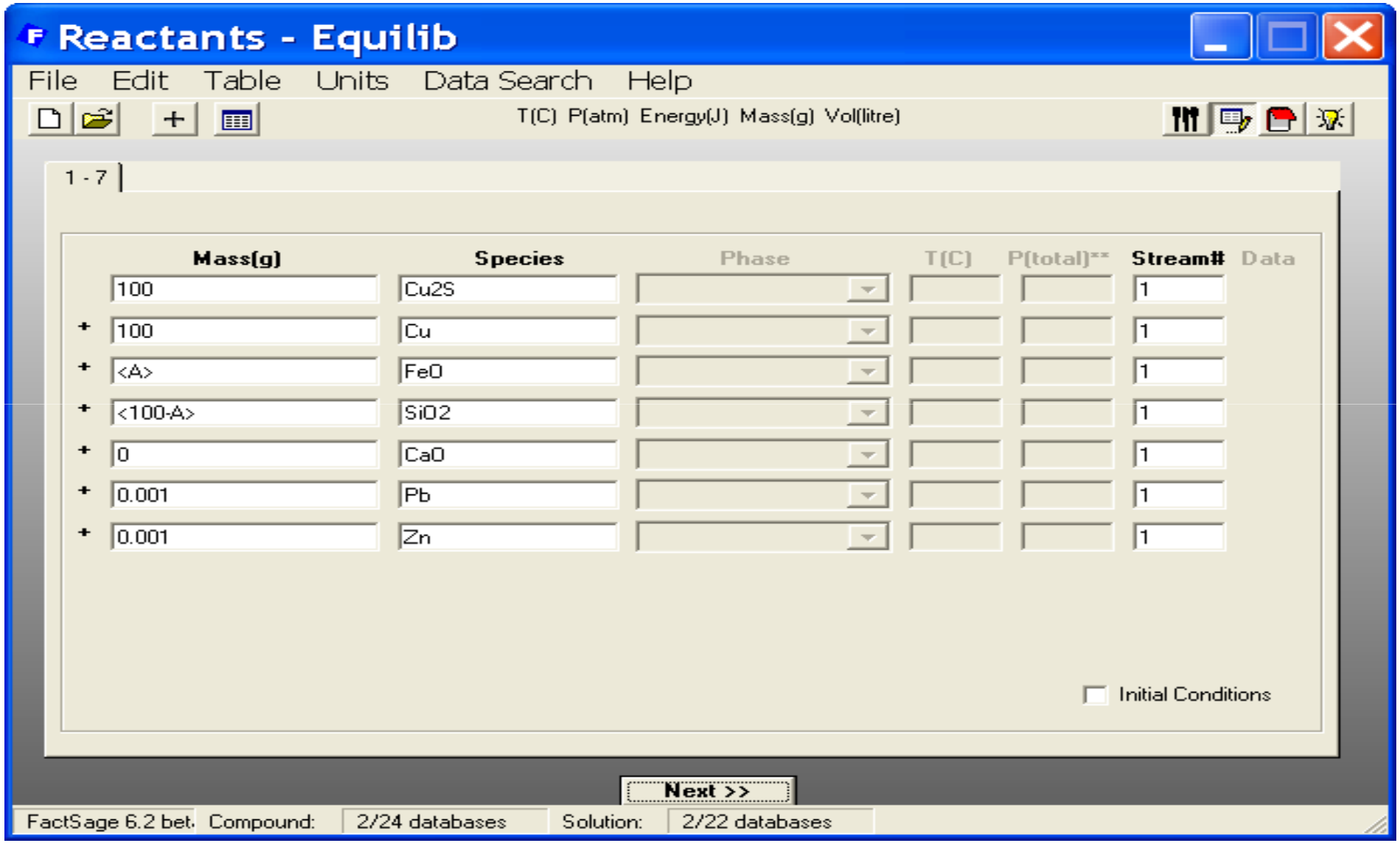
- Liquid Fe **[FTmisc-FeLQ]** with dilute solutes **Al, B, Bi, C, Ca, Ce, Co, Cr, Mg, Mn, Mo, N, Nb, Ni, O, P, Pb, S, Sb, Si, Te, Ti, V, W, Zn, Zr**

- Liquid Pb **[FTmisc-PbLQ]** with dilute solues **Ag, As, Au, Bi, Cu, Fe, Na, O, S, Sb, Sn, Zn**

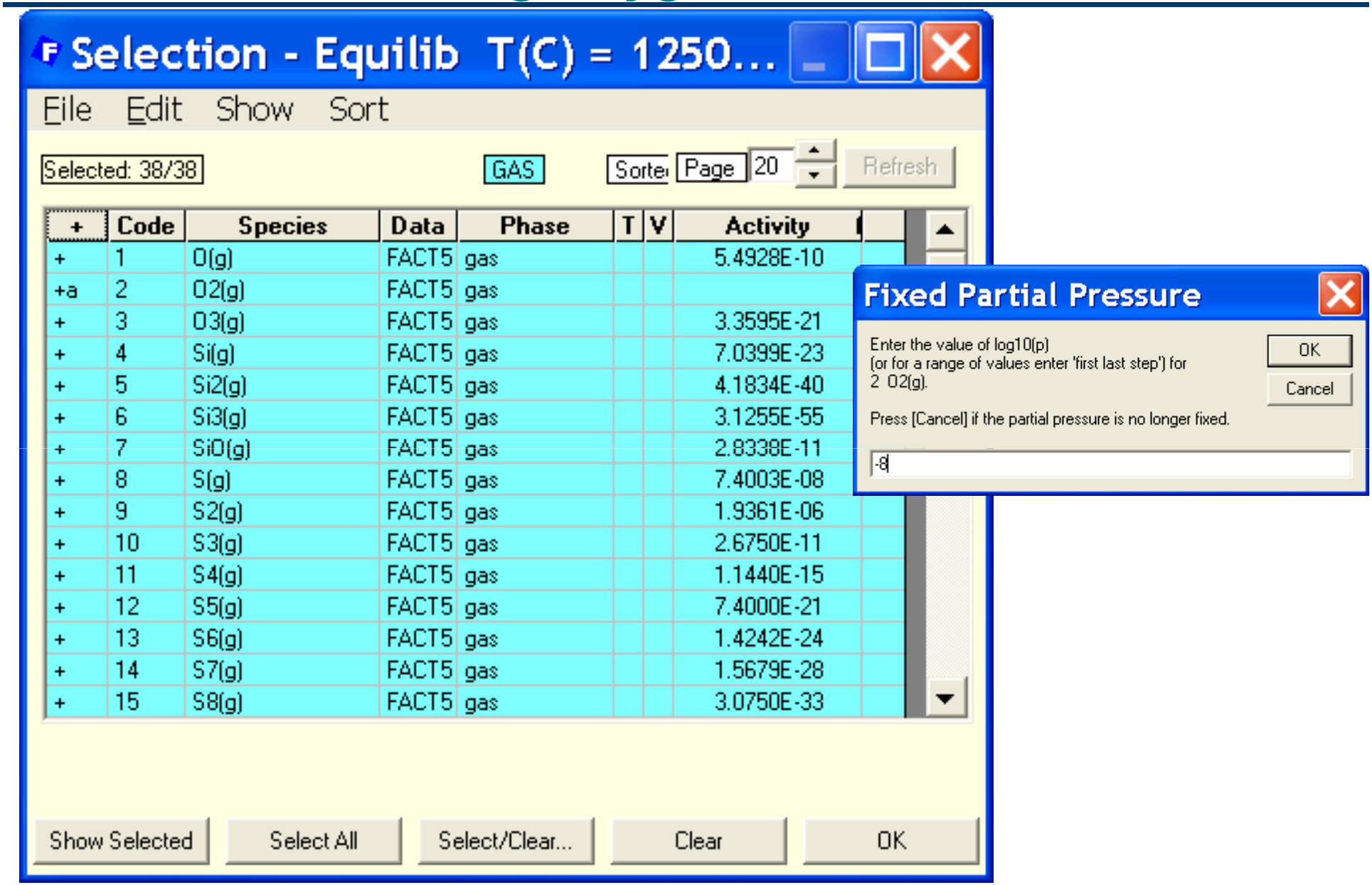
Selection of Databases



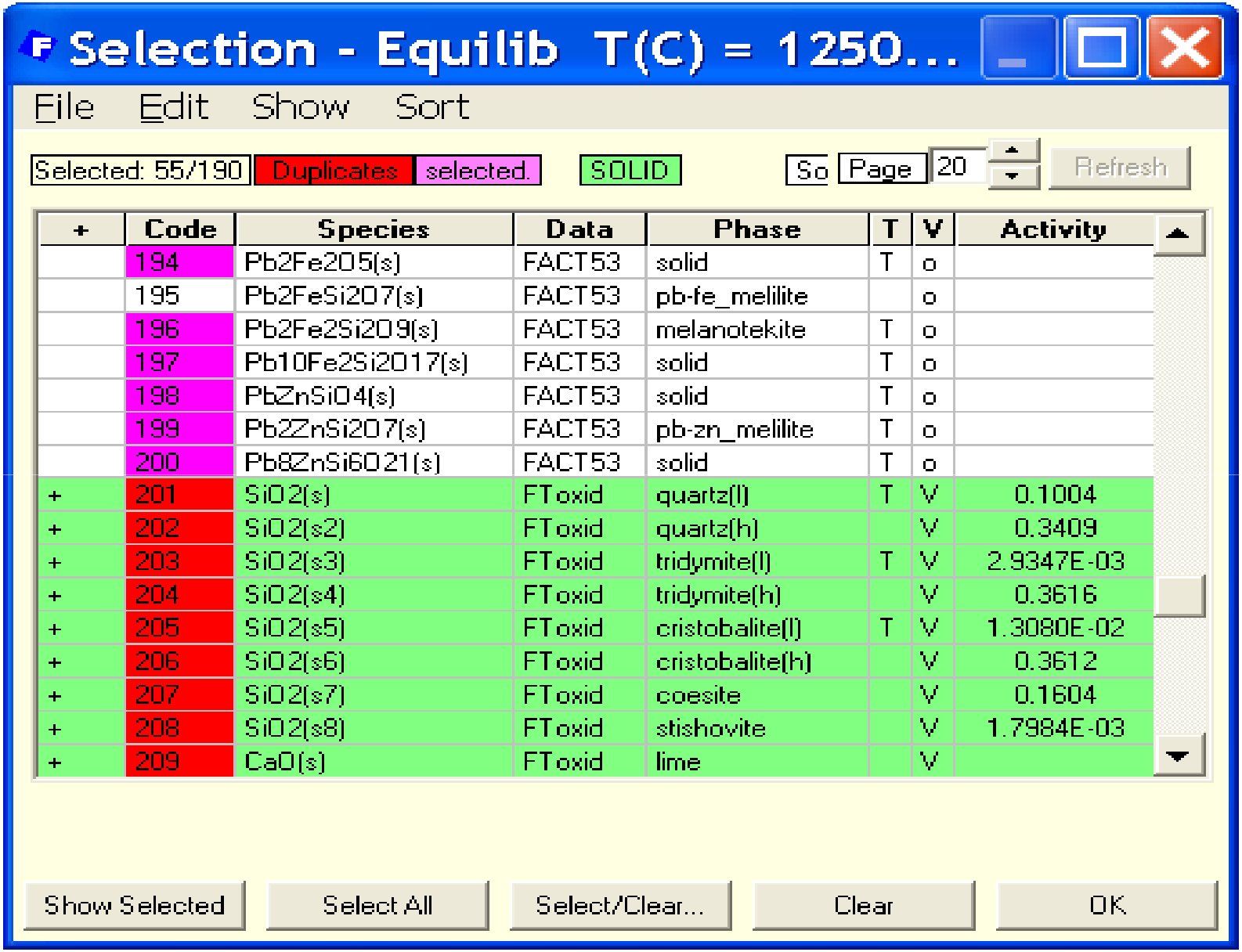
Input for Having Matte + Slag + Cu in Equilibrium



Fixing Oxygen Pressure

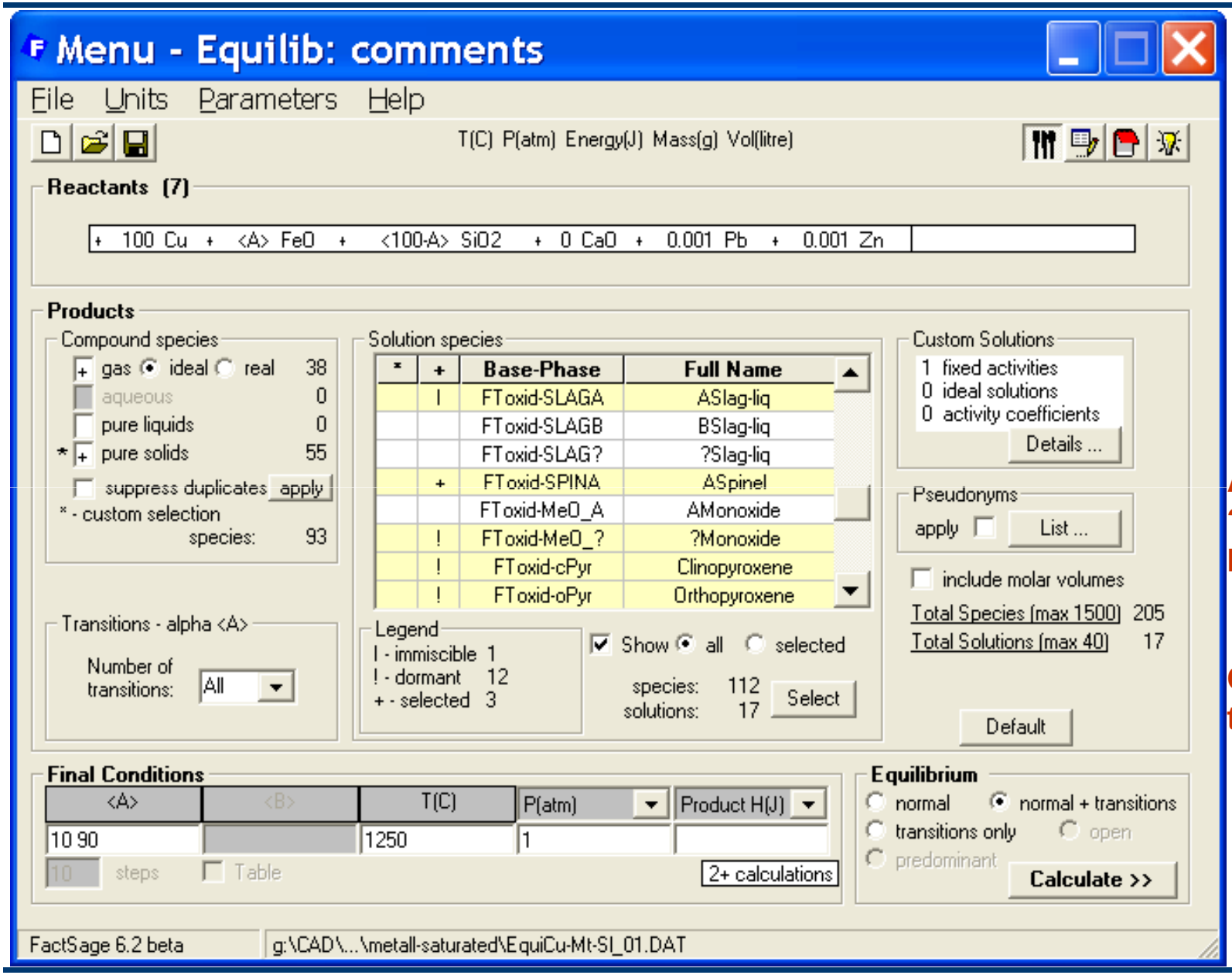


Selection of Stoichiometric Solids from FToxid



+	Code	Species	Data	Phase	T	V	Activity
	194	Pb2Fe2O5(s)	FACT53	solid	T	o	
	195	Pb2FeSi2O7(s)	FACT53	pb-fe_melilite		o	
	196	Pb2Fe2Si2O9(s)	FACT53	melanotekite	T	o	
	197	Pb10Fe2Si2O17(s)	FACT53	solid	T	o	
	198	PbZnSiO4(s)	FACT53	solid	T	o	
	199	Pb2ZnSi2O7(s)	FACT53	pb-zn_melilite	T	o	
	200	Pb8ZnSi6O21(s)	FACT53	solid	T	o	
+	201	SiO2(s)	FToxid	quartz(l)	T	V	0.1004
+	202	SiO2(s2)	FToxid	quartz(h)		V	0.3409
+	203	SiO2(s3)	FToxid	tridymite(l)	T	V	2.9347E-03
+	204	SiO2(s4)	FToxid	tridymite(h)		V	0.3616
+	205	SiO2(s5)	FToxid	cristobalite(l)	T	V	1.3080E-02
+	206	SiO2(s6)	FToxid	cristobalite(h)		V	0.3612
+	207	SiO2(s7)	FToxid	coesite		V	0.1604
+	208	SiO2(s8)	FToxid	stishovite		V	1.7984E-03
+	209	CaO(s)	FToxid	lime		V	

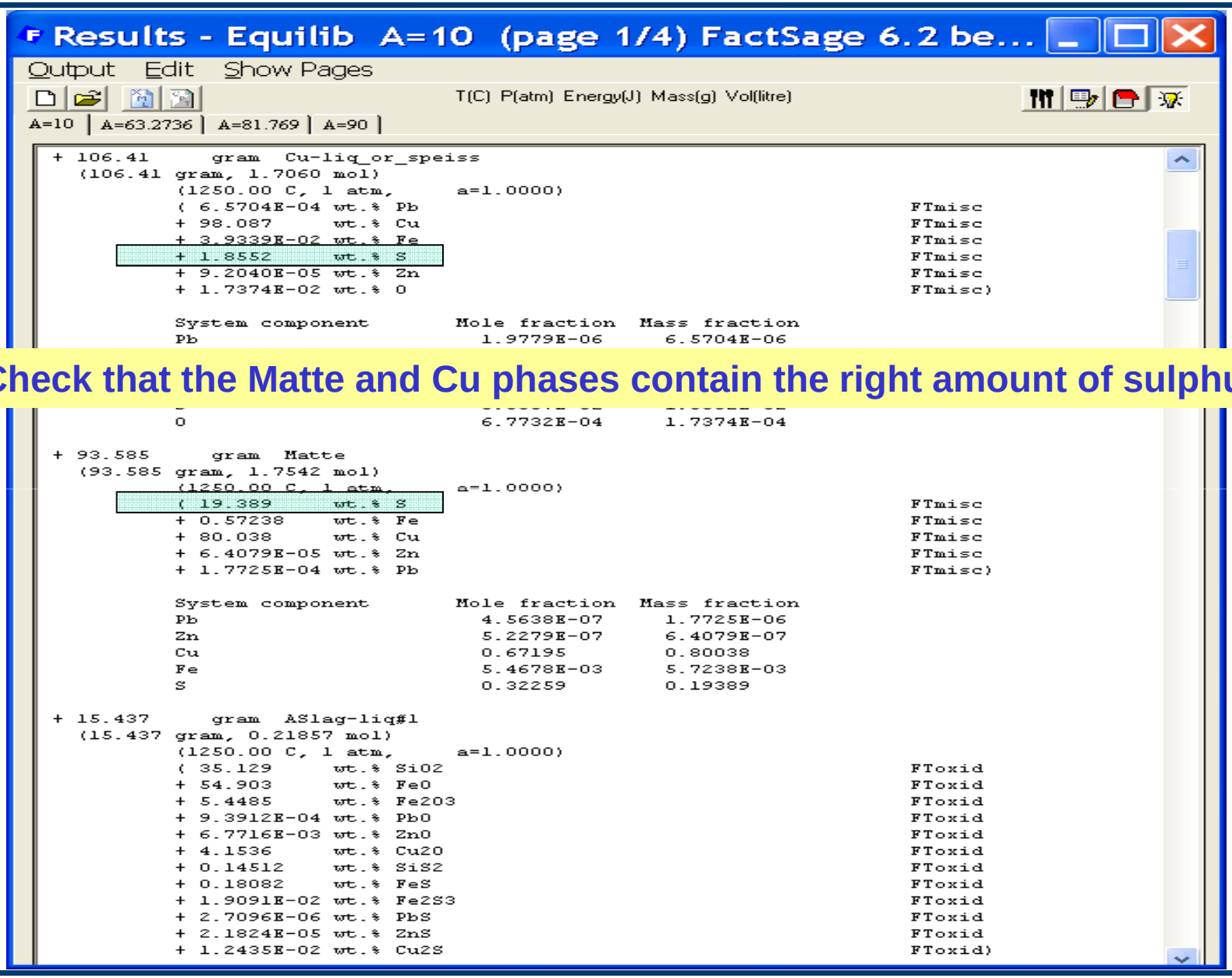
Selection of Solutions



ASlag or ?Slag
?Monoxide
Dormant phases

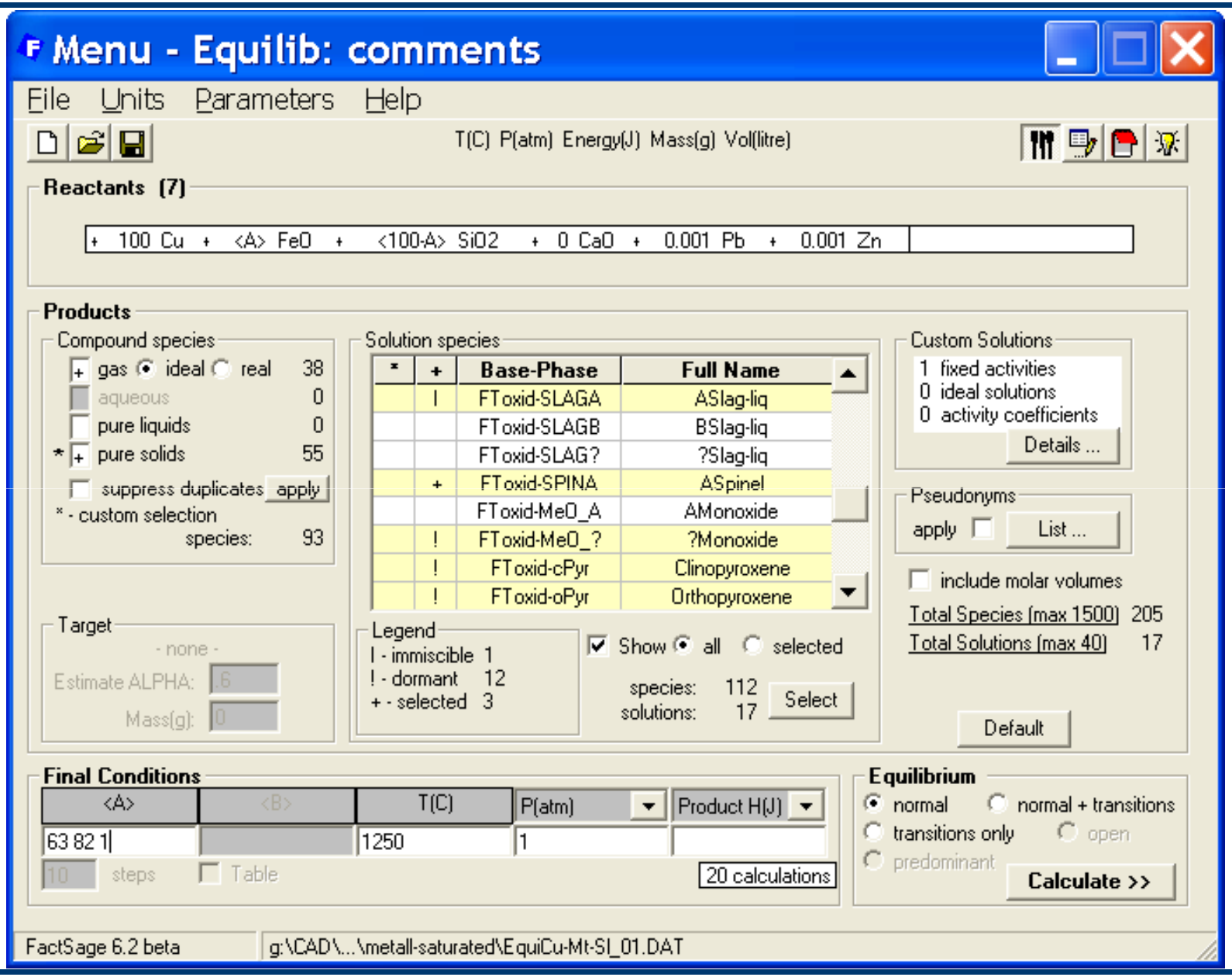
Calculate transitions

Transitions

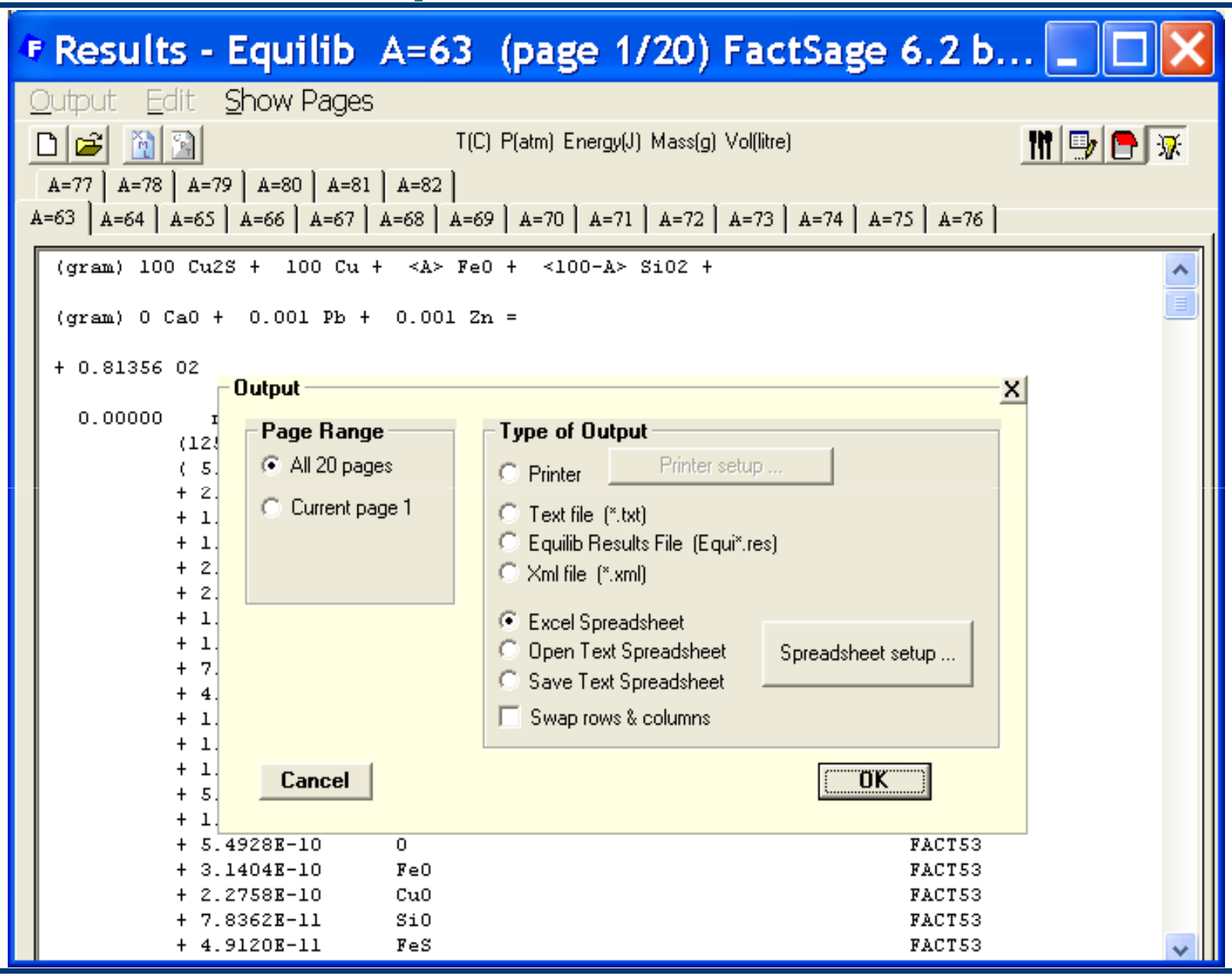


Check that the Matte and Cu phases contain the right amount of sulphur

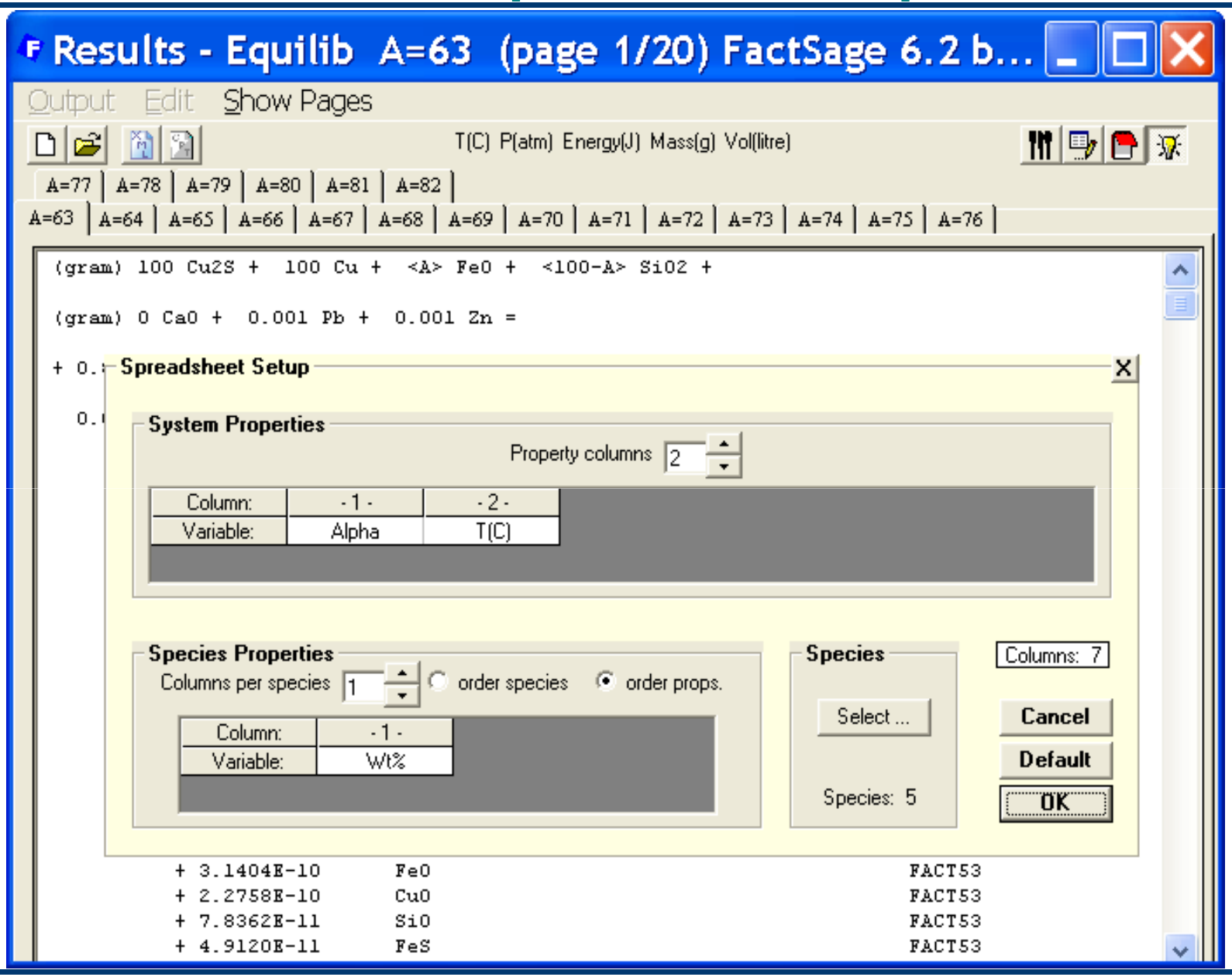
A Series of Calculations



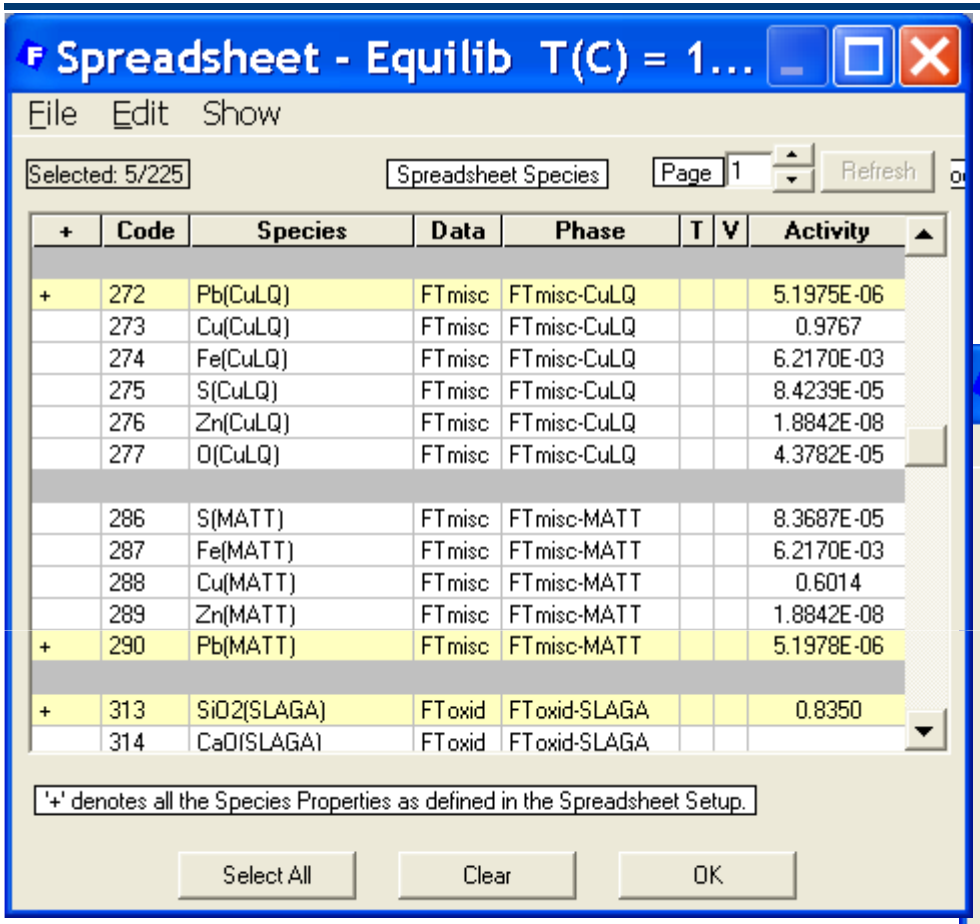
Output Results in Excel

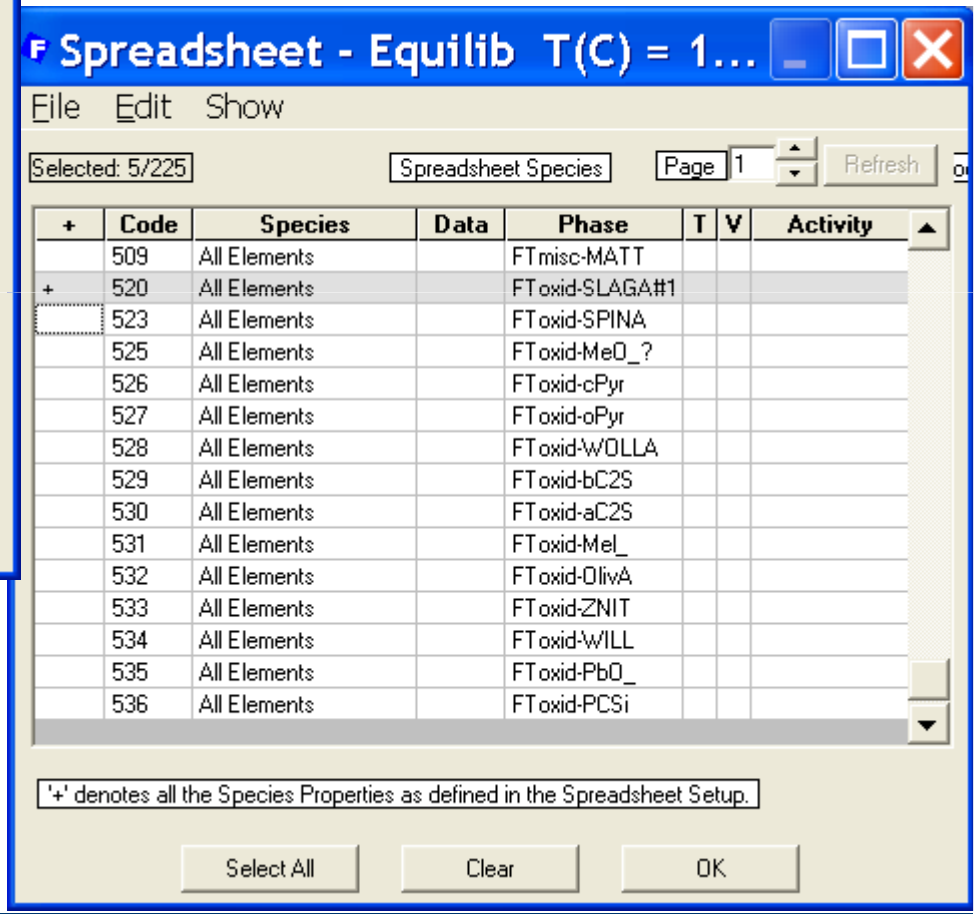


Select Species for Output

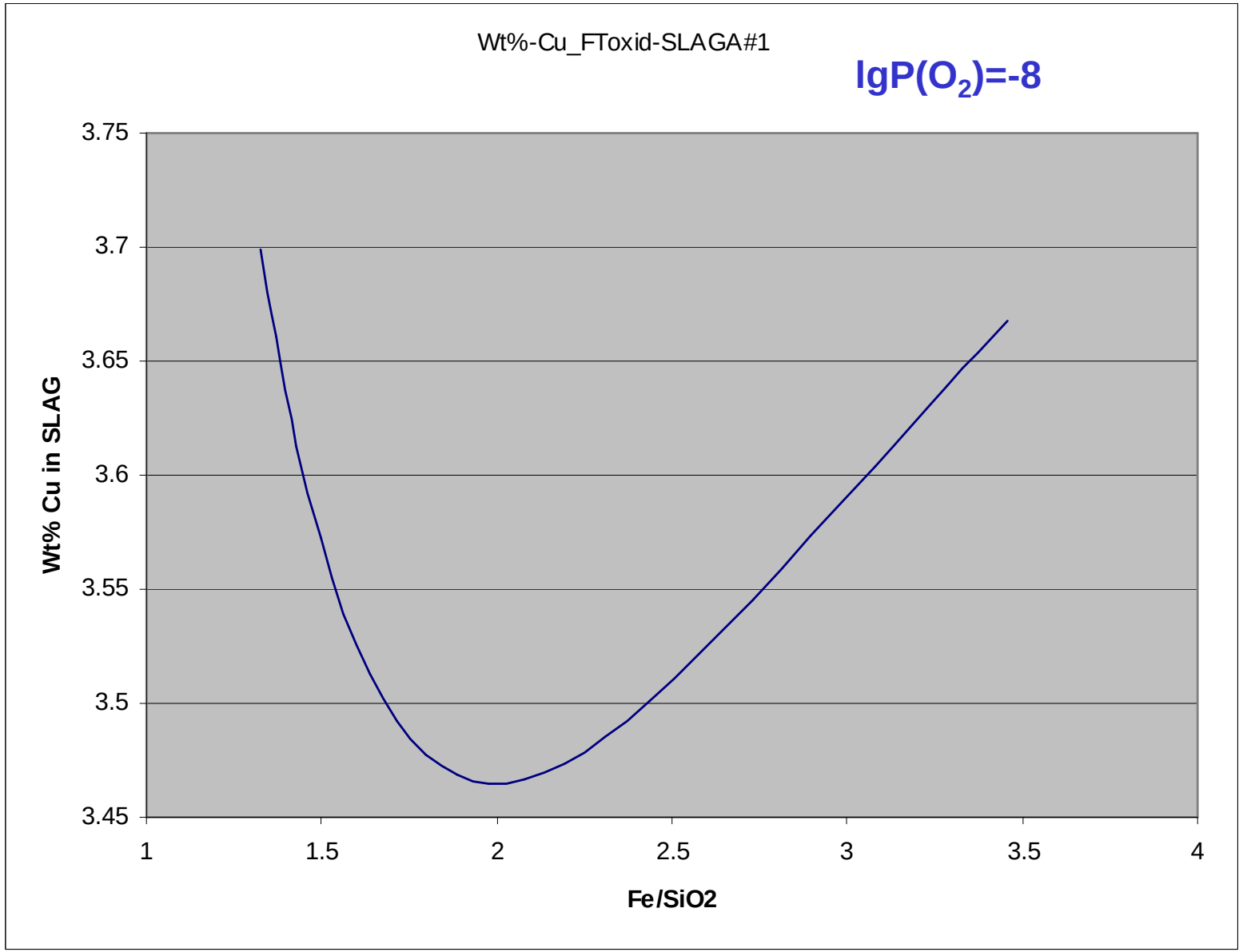


Fe-Zn-Si-O System

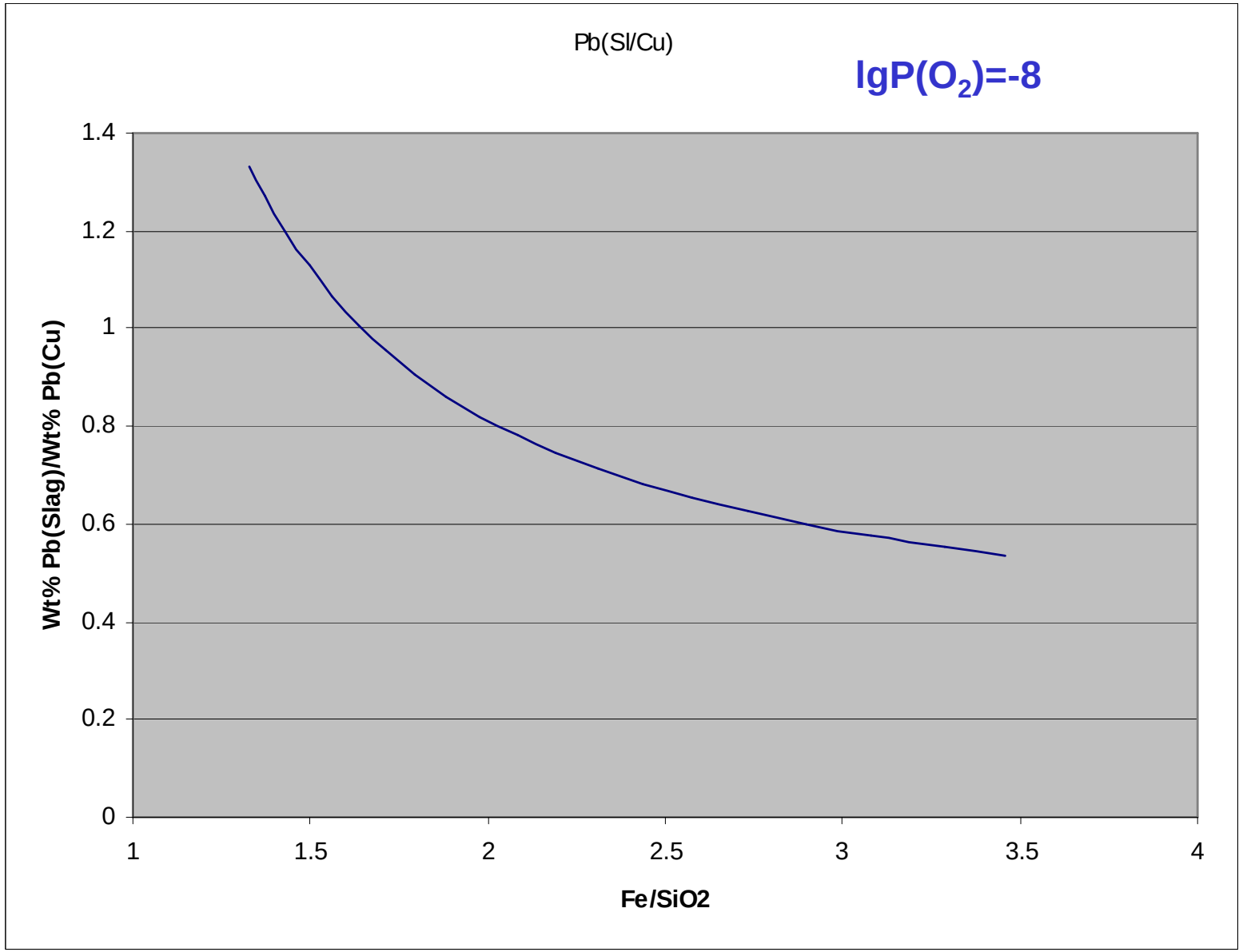




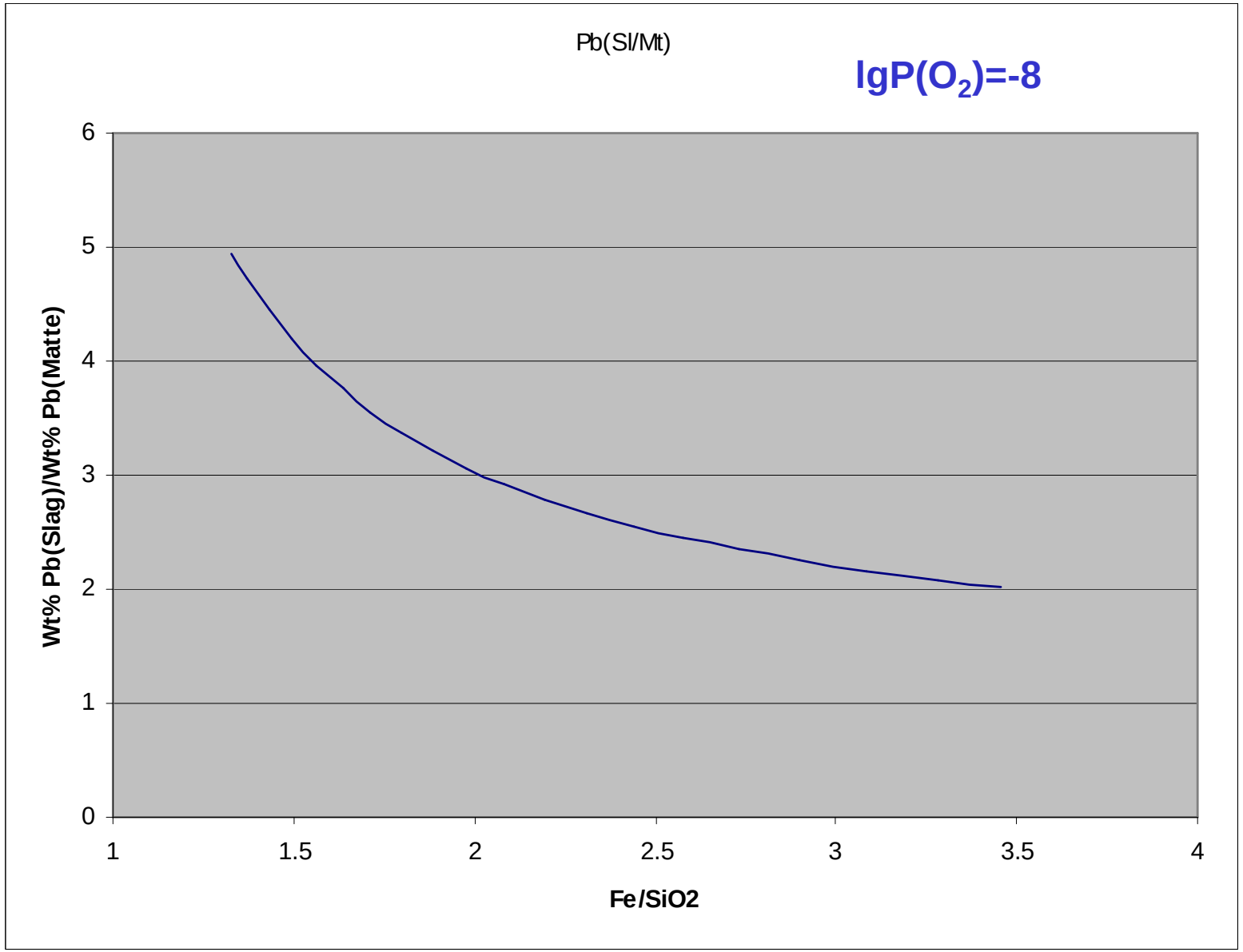
Cu losses to Slag



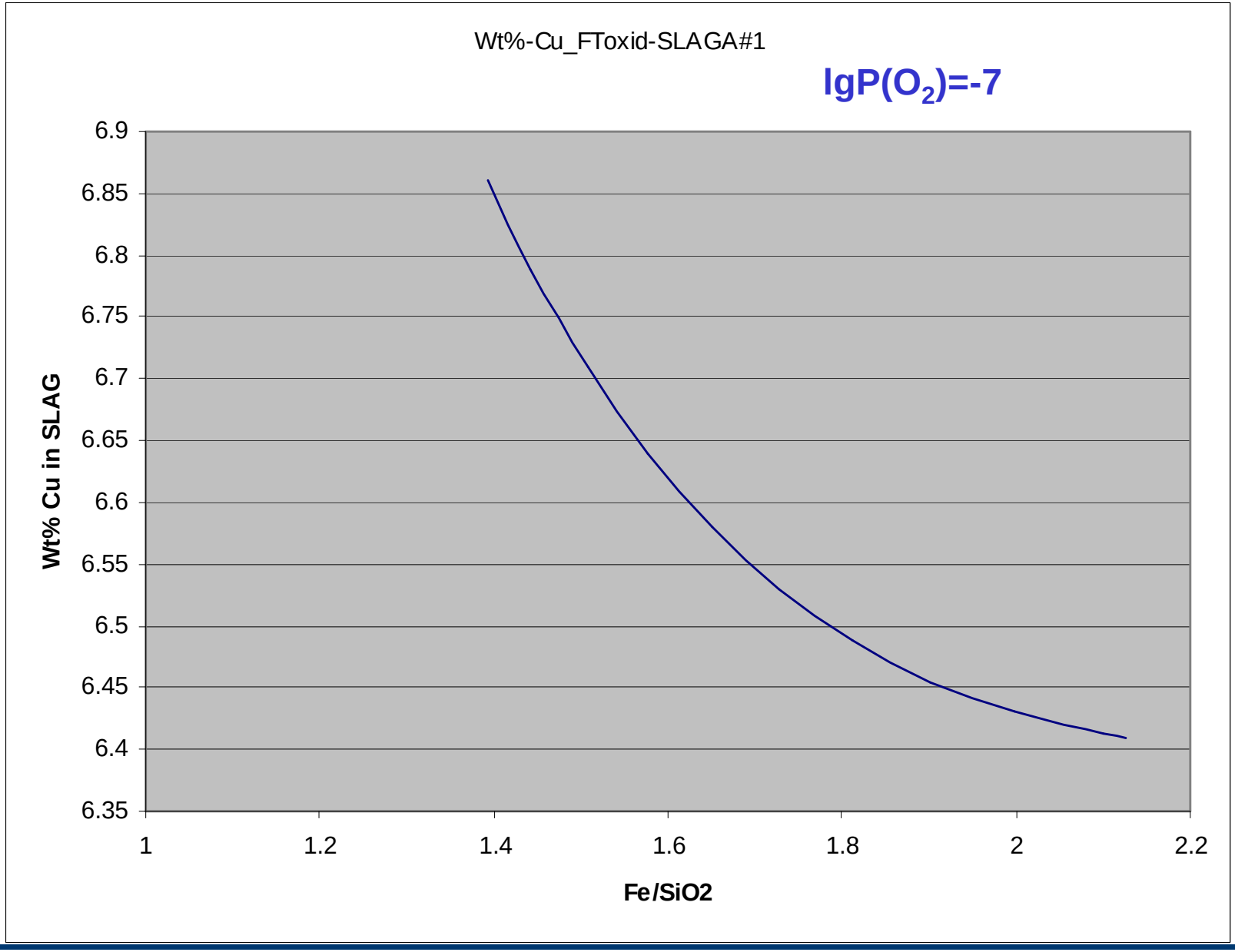
Distribution of Pb between Slag and Cu



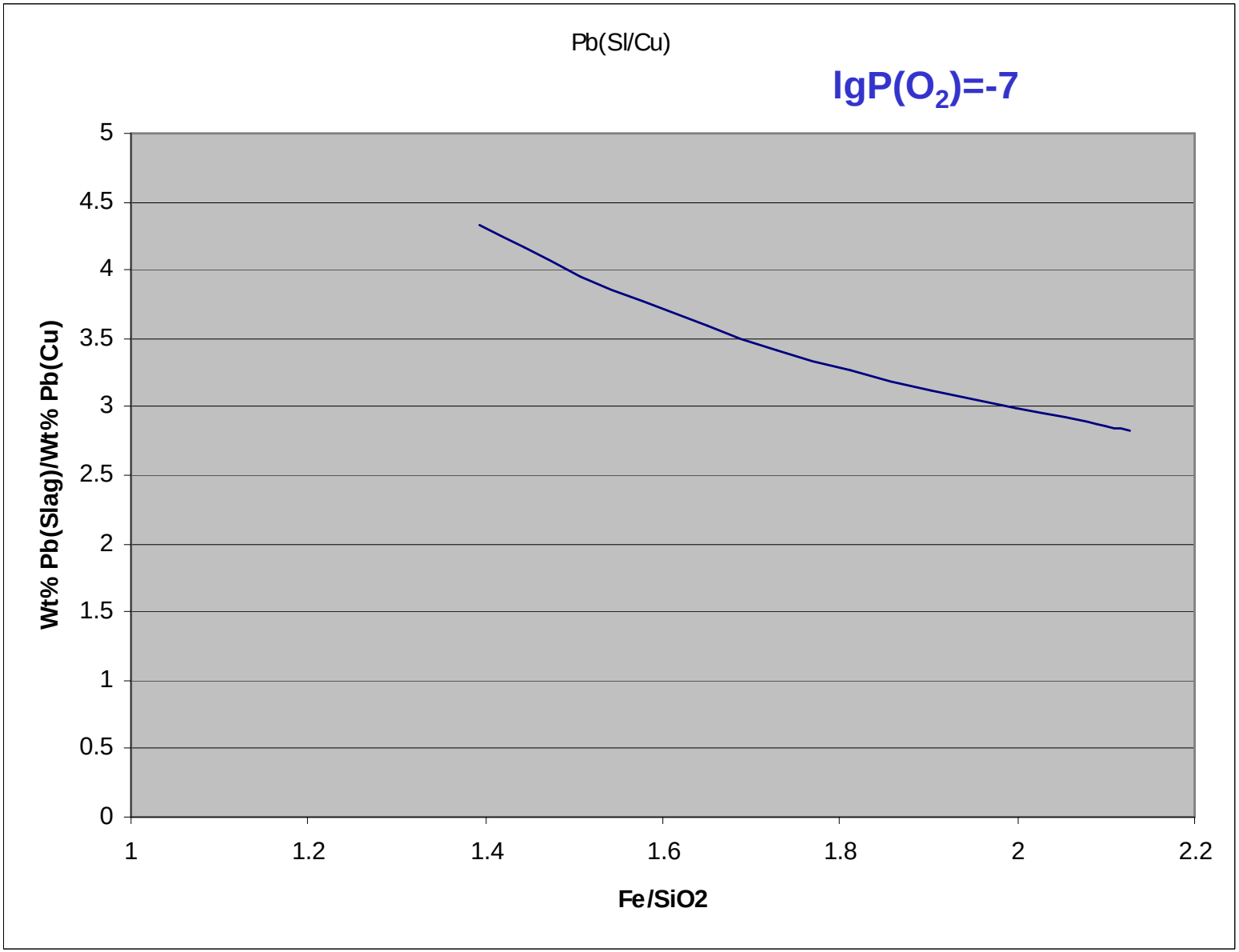
Distribution of Pb between Slag and Matte



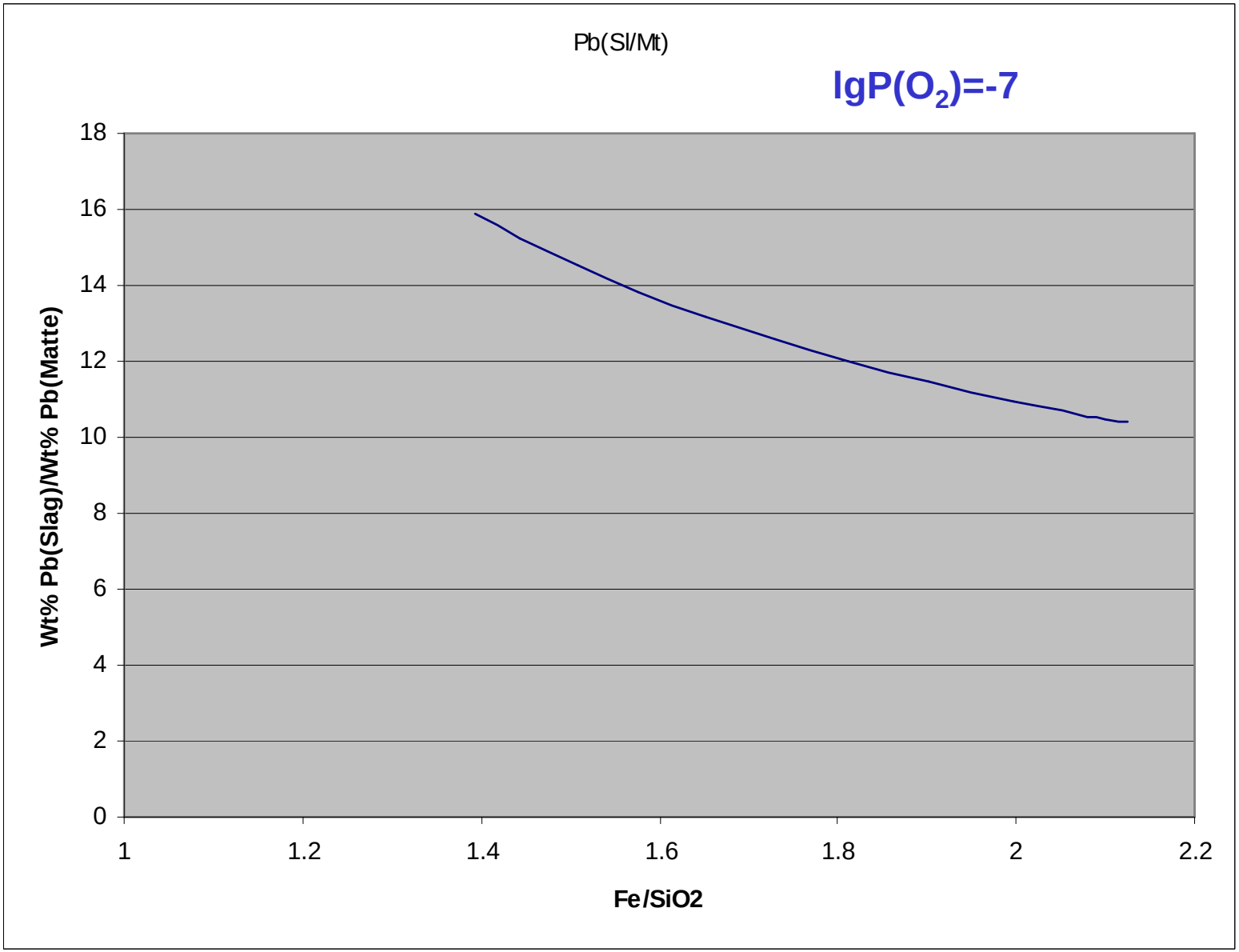
Cu losses to Slag



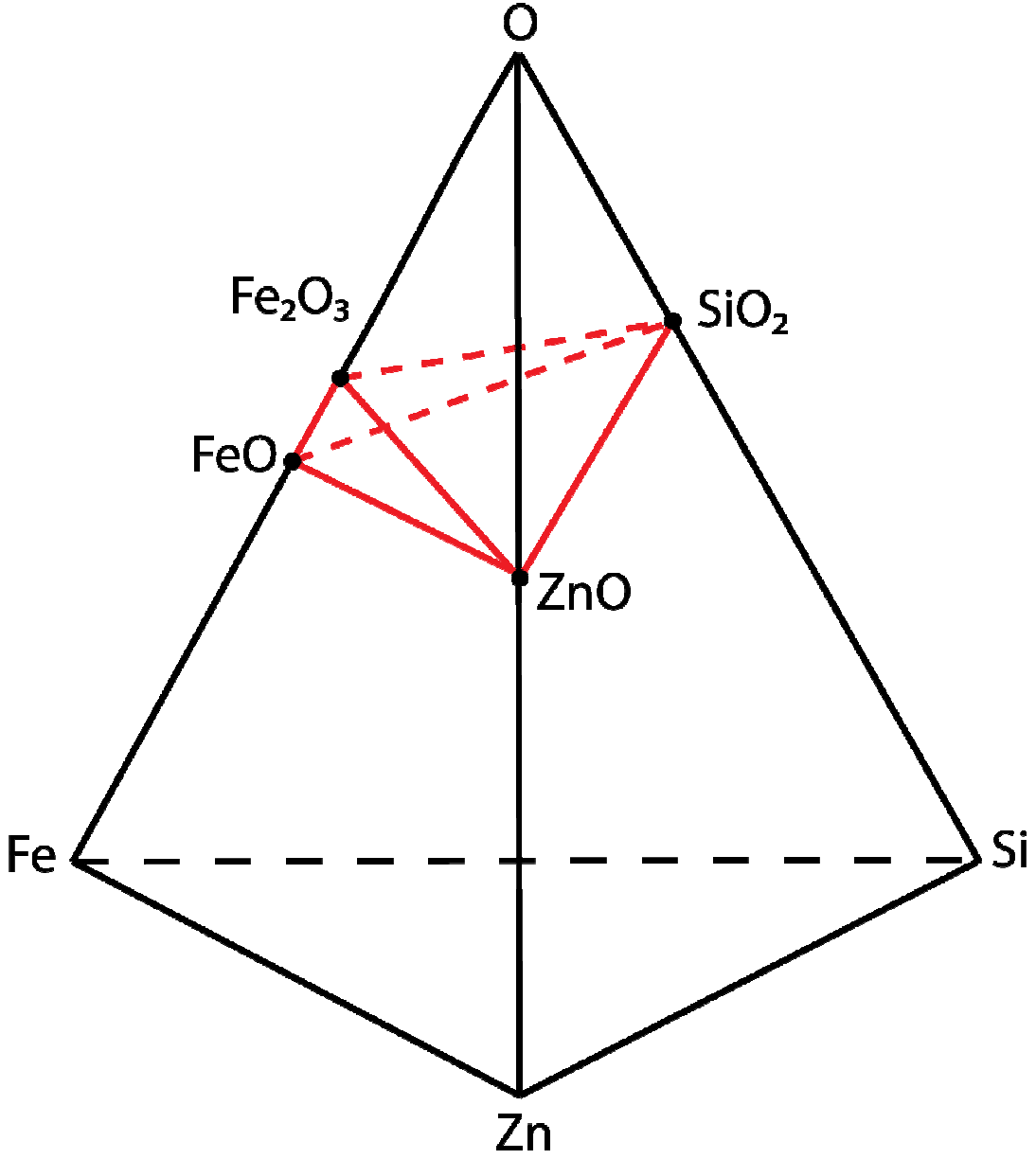
Distribution of Pb between Slag and Cu



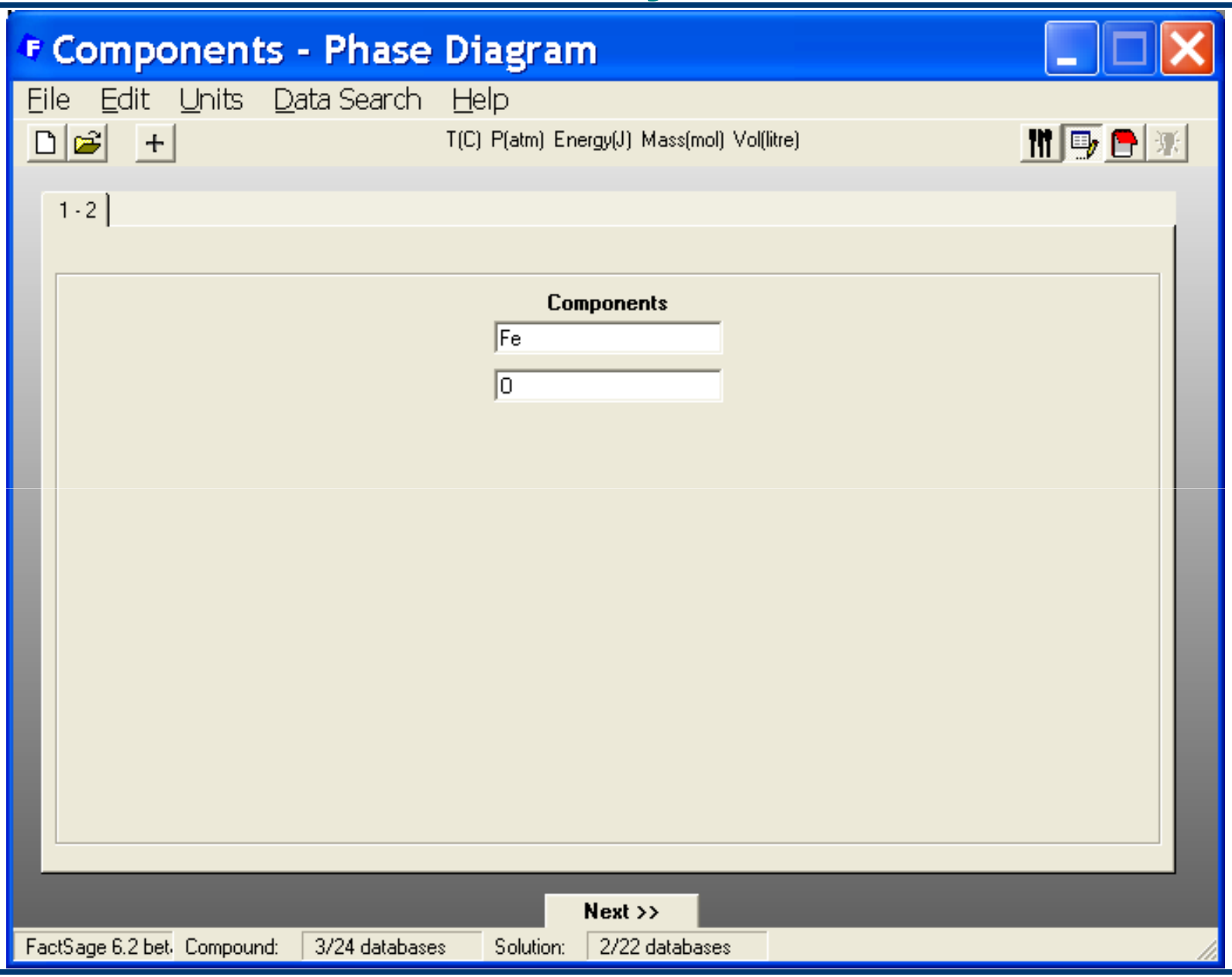
Distribution of Pb between Slag and Matte



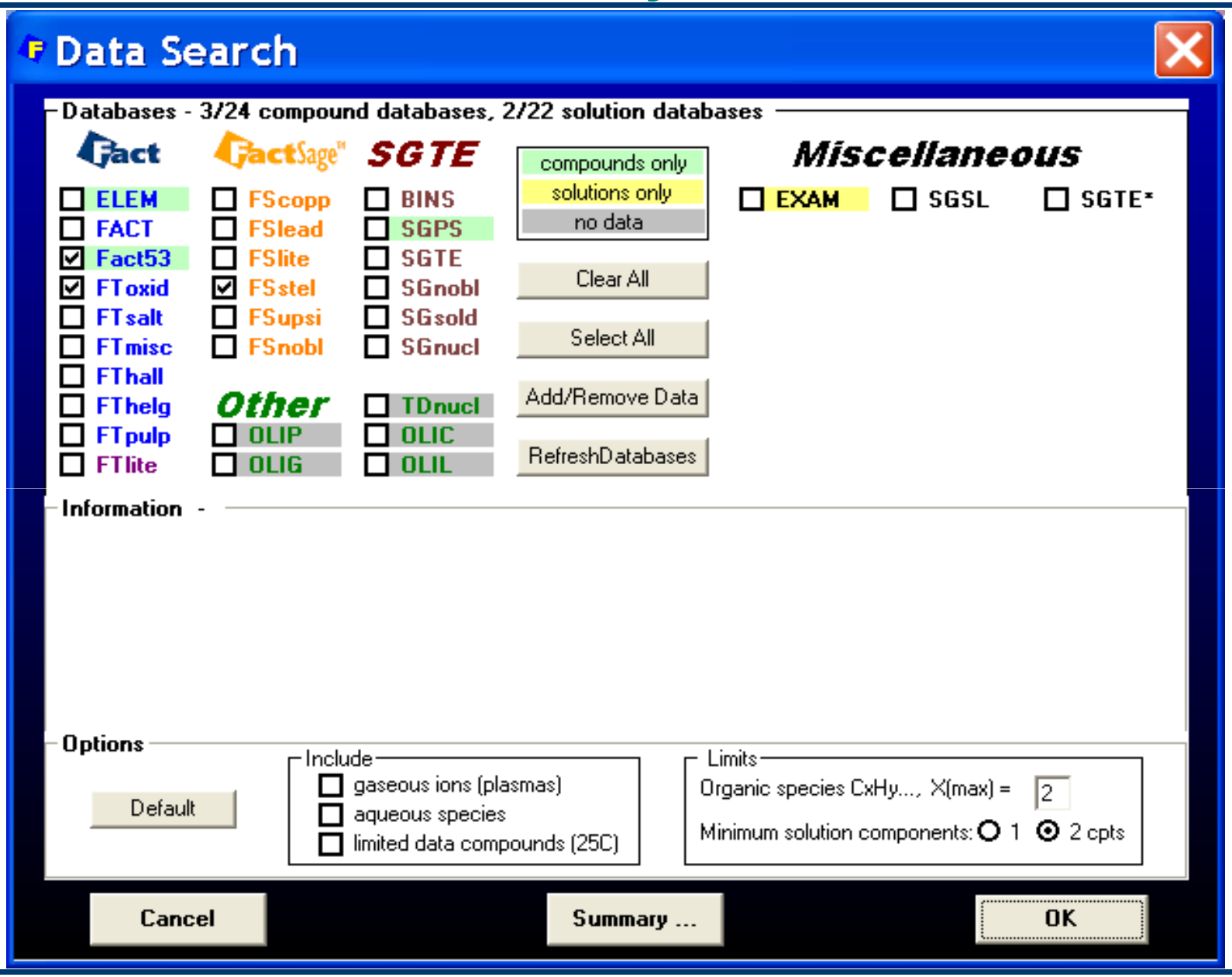
Fe-Zn-Si-O System



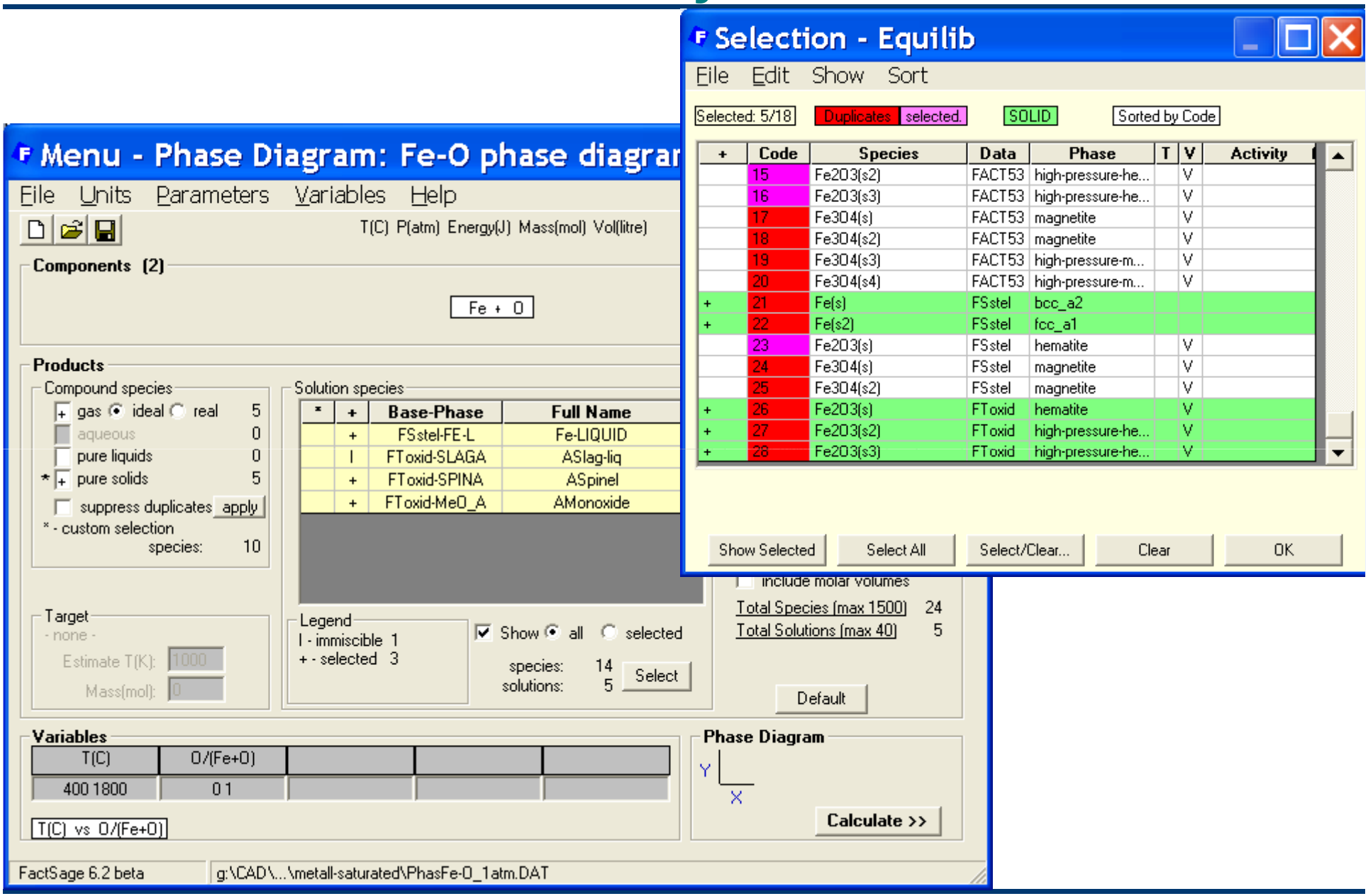
Fe-O System


Components - Phase Diagram
File Edit Units Data Search Help
T(C) P(atm) Energy(J) Mass(mol) Vol(litre)
1 - 2
Components
Fe
O
Next >>
FactSage 6.2 bet
Compound:
3/24 databases
Solution:
2/22 databases

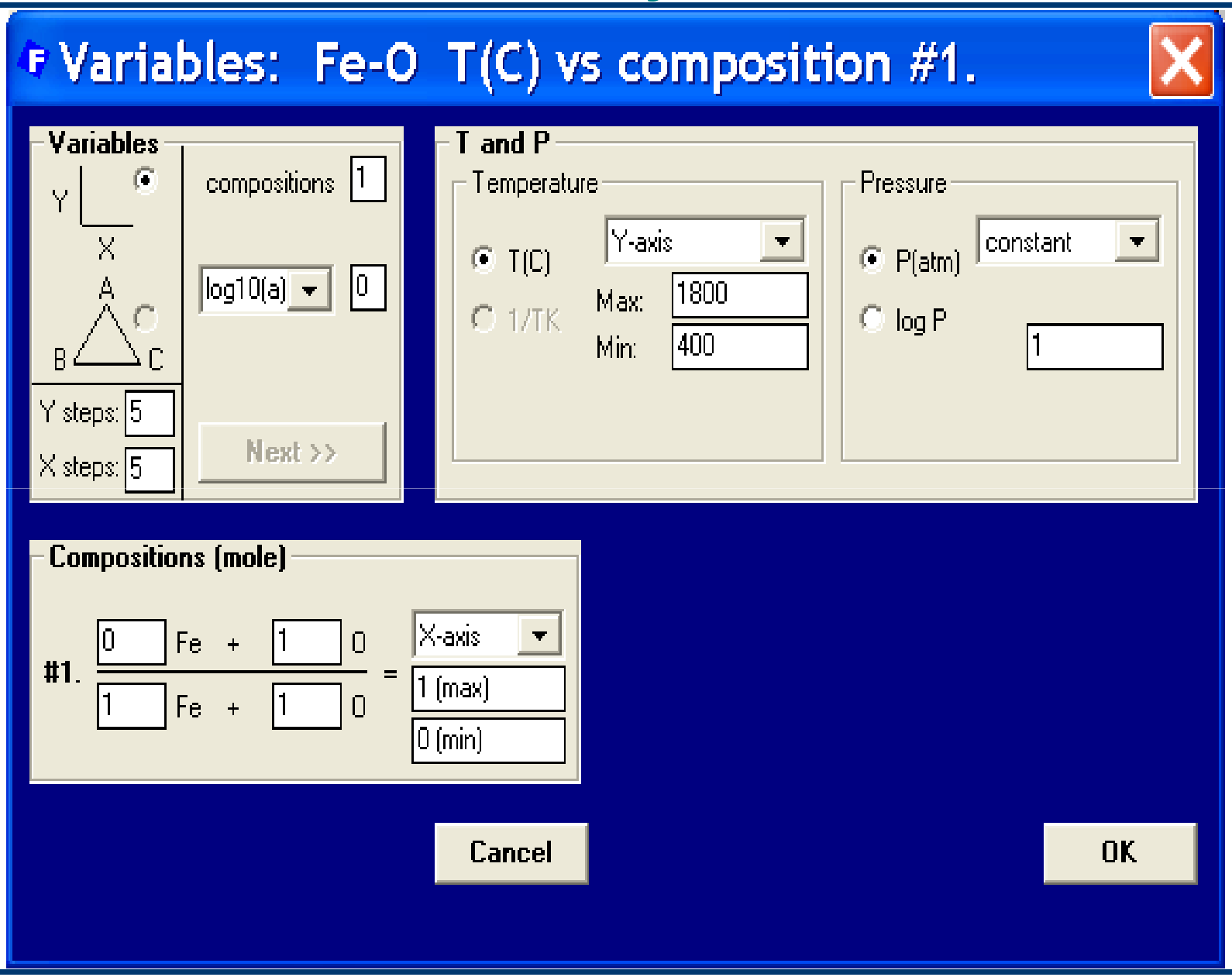
Fe-O System


Data Search
Databases - 3/24 compound databases, 2/22 solution databases
Fact
FactSage
SGTE
ELEM
FACT
Fact53
FToxid
FTsalt
FTmisc
FThall
FThelg
FTpulp
FTlite
FScopp
FSlead
FSlite
FSstel
FSupsi
FSnobl
BINS
SGPS
SGTE
SGnobl
SGsold
SGnucl
Other
TDnucl
OLIP
OLIC
OLIG
OLIL
compounds only
solutions only
no data
Clear All
Select All
Add/Remove Data
RefreshDatabases
Miscellaneous
EXAM
SGSL
SGTE*
Information -
Options
Default
Include
gaseous ions (plasmas)
aqueous species
limited data compounds (25C)
Limits
Organic species CxHy..., X(max) =
2
Minimum solution components:
1
2 cpts
Cancel
Summary ...
OK

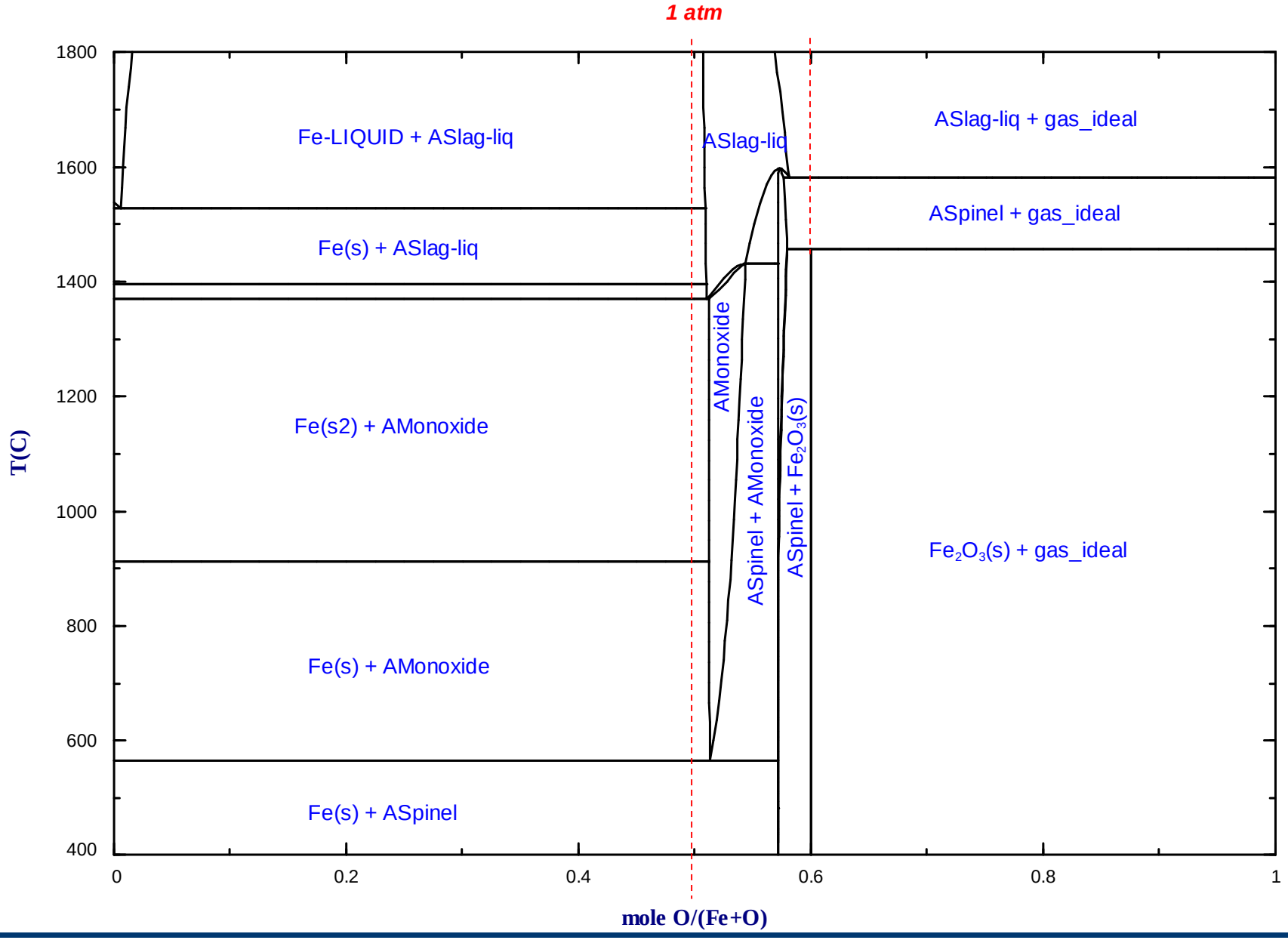
Fe-O System


Selection - Equilib
File Edit Show Sort
Selected: 5/18
Duplicates selected.
SOLID
Sorted by Code
+ Code Species Data Phase T V Activity
15 Fe2O3(s2) FACT53 high-pressure-he... V
16 Fe2O3(s3) FACT53 high-pressure-he... V
17 Fe3O4(s) FACT53 magnetite V
18 Fe3O4(s2) FACT53 magnetite V
19 Fe3O4(s3) FACT53 high-pressure-m... V
20 Fe3O4(s4) FACT53 high-pressure-m... V
+ 21 Fe(s) FSstel bcc_a2
+ 22 Fe(s2) FSstel fcc_a1
23 Fe2O3(s) FSstel hematite V
24 Fe3O4(s) FSstel magnetite V
25 Fe3O4(s2) FSstel magnetite V
+ 26 Fe2O3(s) FToxid hematite V
+ 27 Fe2O3(s2) FToxid high-pressure-he... V
+ 28 Fe2O3(s3) FToxid high-pressure-he... V
Show Selected
Select All
Select/Clear...
Clear
OK
Menu - Phase Diagram: Fe-O phase diagram
File Units Parameters Variables Help
T(C) P(atm) Energy(J) Mass(mol) Vol(litre)
Components (2)
Fe + O
Products
Compound species
gas ideal real 5
aqueous 0
pure liquids 0
pure solids 5
suppress duplicates apply
* - custom selection species: 10
Solution species
* + Base-Phase Full Name
+ FSstel-FE-L Fe-LIQUID
I FToxid-SLAGA ASlag-liq
+ FToxid-SPINA ASpinel
+ FToxid-MeO_A AMonoxide
Target
- none -
Estimate T(K): 1000
Mass(mol): 0
Legend
I - immiscible 1
+ - selected 3
Show all selected
species: 14
solutions: 5
Select
Include molar volumes
Total Species (max 1500) 24
Total Solutions (max 40) 5
Default
Variables
T(C) O/(Fe+O)
400 1800 0 1
T(C) vs O/(Fe+O)
Phase Diagram
Y
X
Calculate >>
FactSage 6.2 beta
g:\CAD\...\metall-saturated\PhasFe-O_1atm.DAT

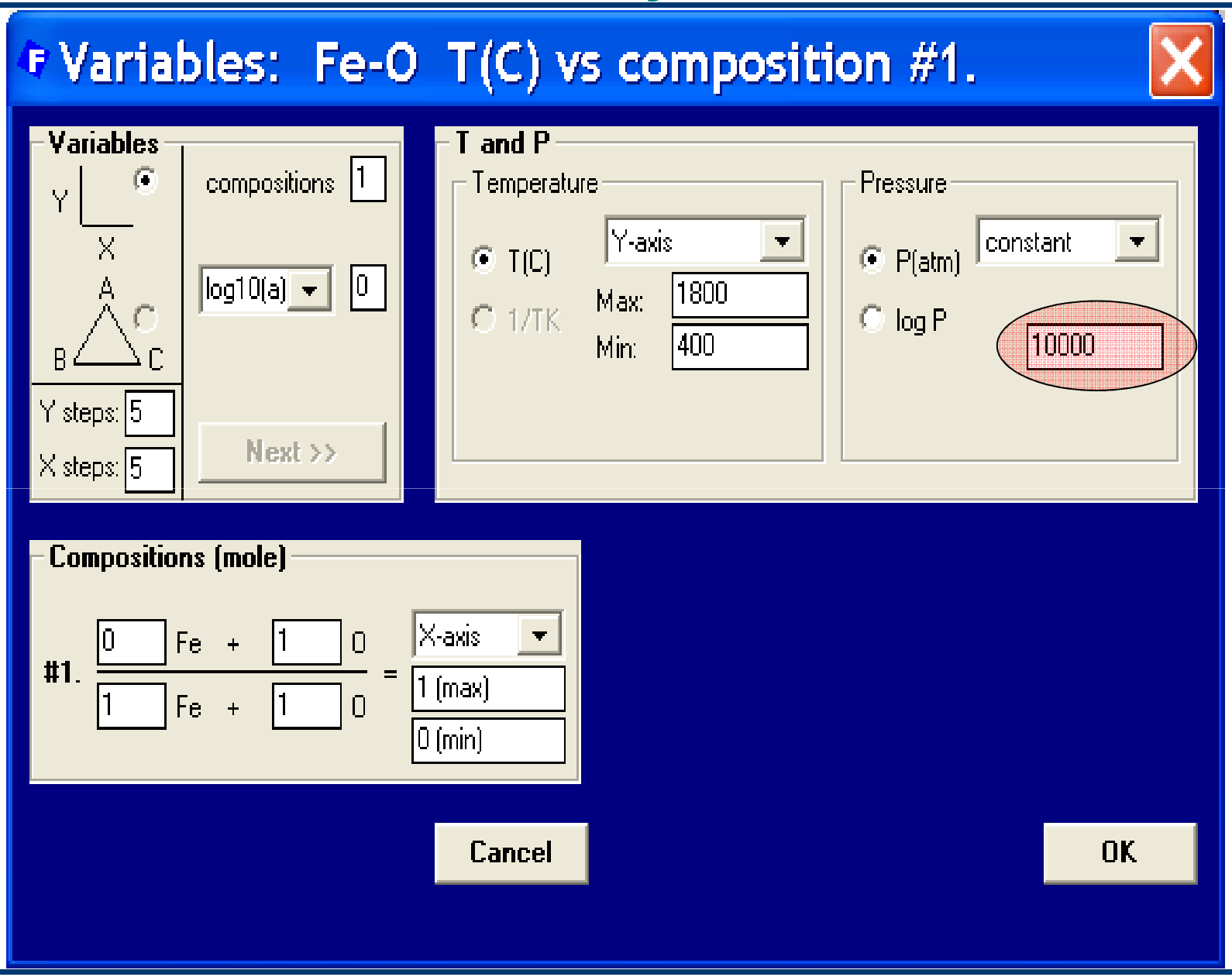
Fe-O System


Variables: Fe-O T(C) vs composition #1.
Variables
Y
X
A
B
C
compositions
1
log10(a)
0
Y steps:
5
X steps:
5
Next >>
T and P
Temperature
T(C)
1/TK
Y-axis
Max:
1800
Min:
400
Pressure
P(atm)
log P
constant
1
Compositions (mole)
#1.
0
Fe
+
1
O
1
Fe
+
1
O
=
X-axis
1 (max)
0 (min)
Cancel
OK

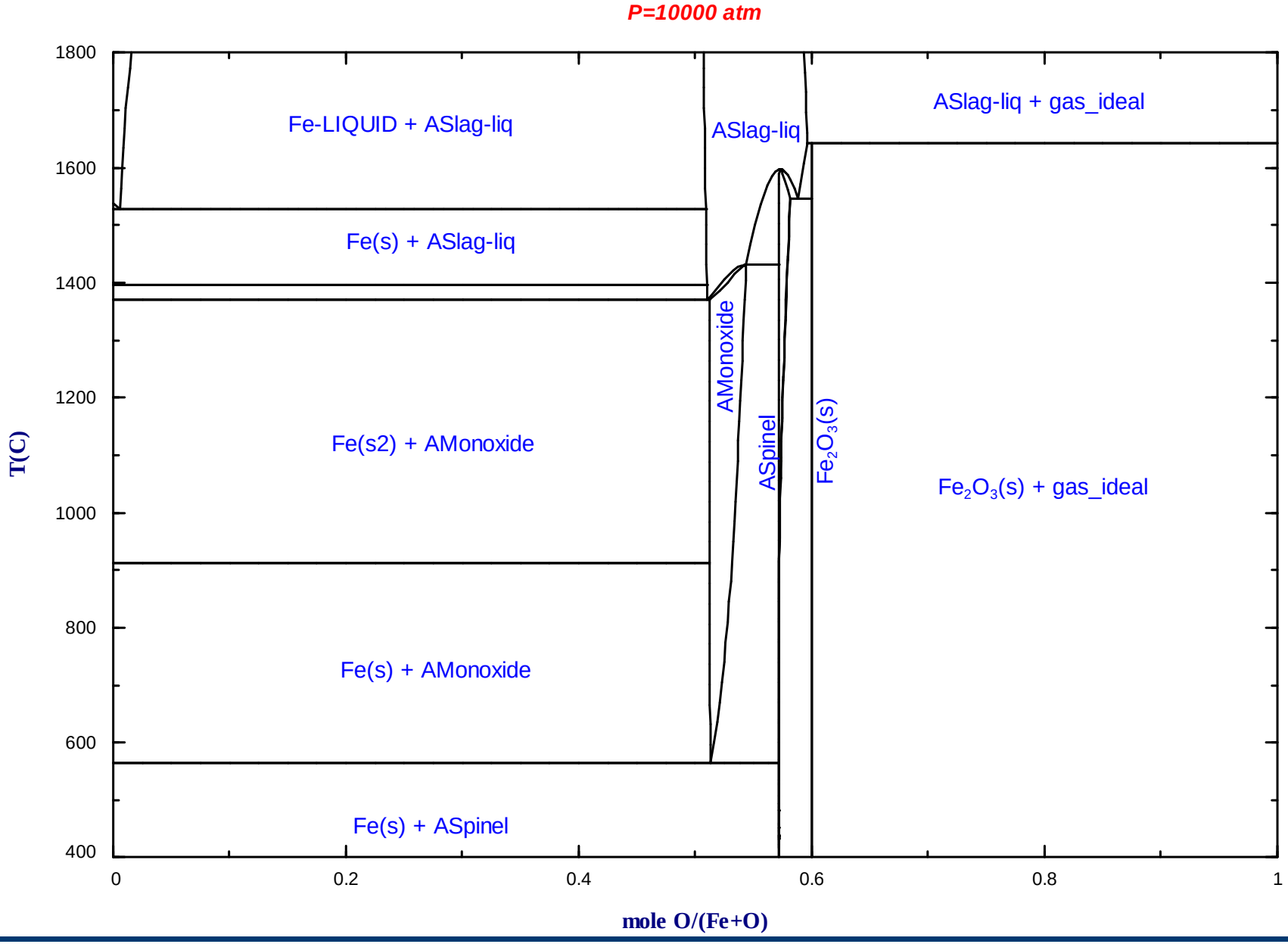
Fe-O System


1 atm
1800
1600
1400
1200
1000
800
600
400
T(C)
0
0.2
0.4
0.6
0.8
1
mole O/(Fe+O)
Fe-LIQUID + ASlag-liq
ASlag-liq
ASlag-liq + gas_ideal
ASpinel + gas_ideal
Fe(s) + ASlag-liq
AMonoxide
ASpinel + AMonoxide
ASpinel + Fe2O3(s)
Fe(s2) + AMonoxide
Fe2O3(s) + gas_ideal
Fe(s) + AMonoxide
Fe(s) + ASpinel

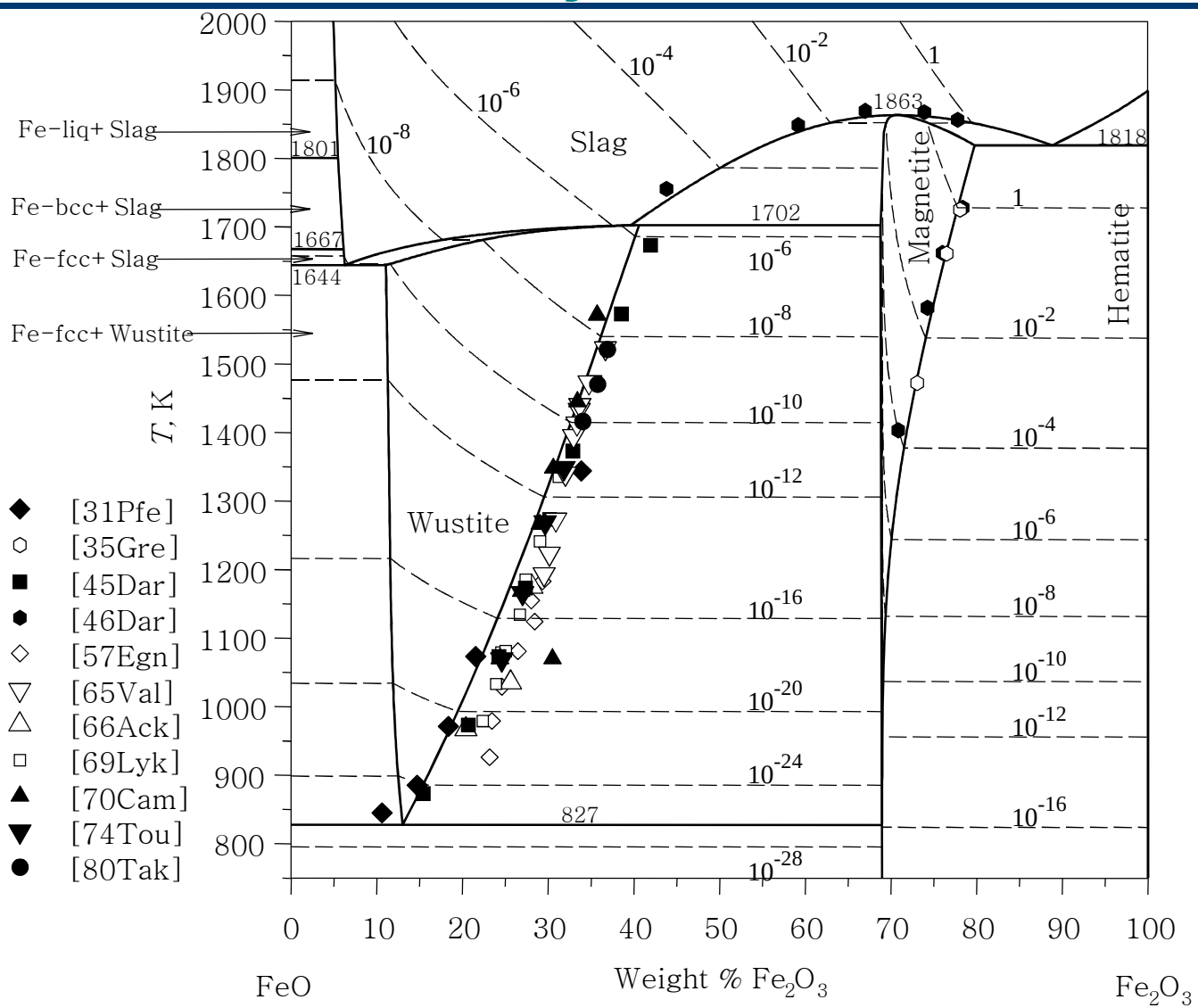
Fe-O System


Variables: Fe-O T(C) vs composition #1.
Variables
Y
X
A
B
C
compositions
1
log10(a)
0
Y steps:
5
X steps:
5
Next >>
T and P
Temperature
T(C)
1/TK
Y-axis
Max:
1800
Min:
400
Pressure
P(atm)
log P
constant
10000
Compositions (mole)
#1.
0
Fe
+
1
O
1
Fe
+
1
O
=
X-axis
1 (max)
0 (min)
Cancel
OK

Fe-O System

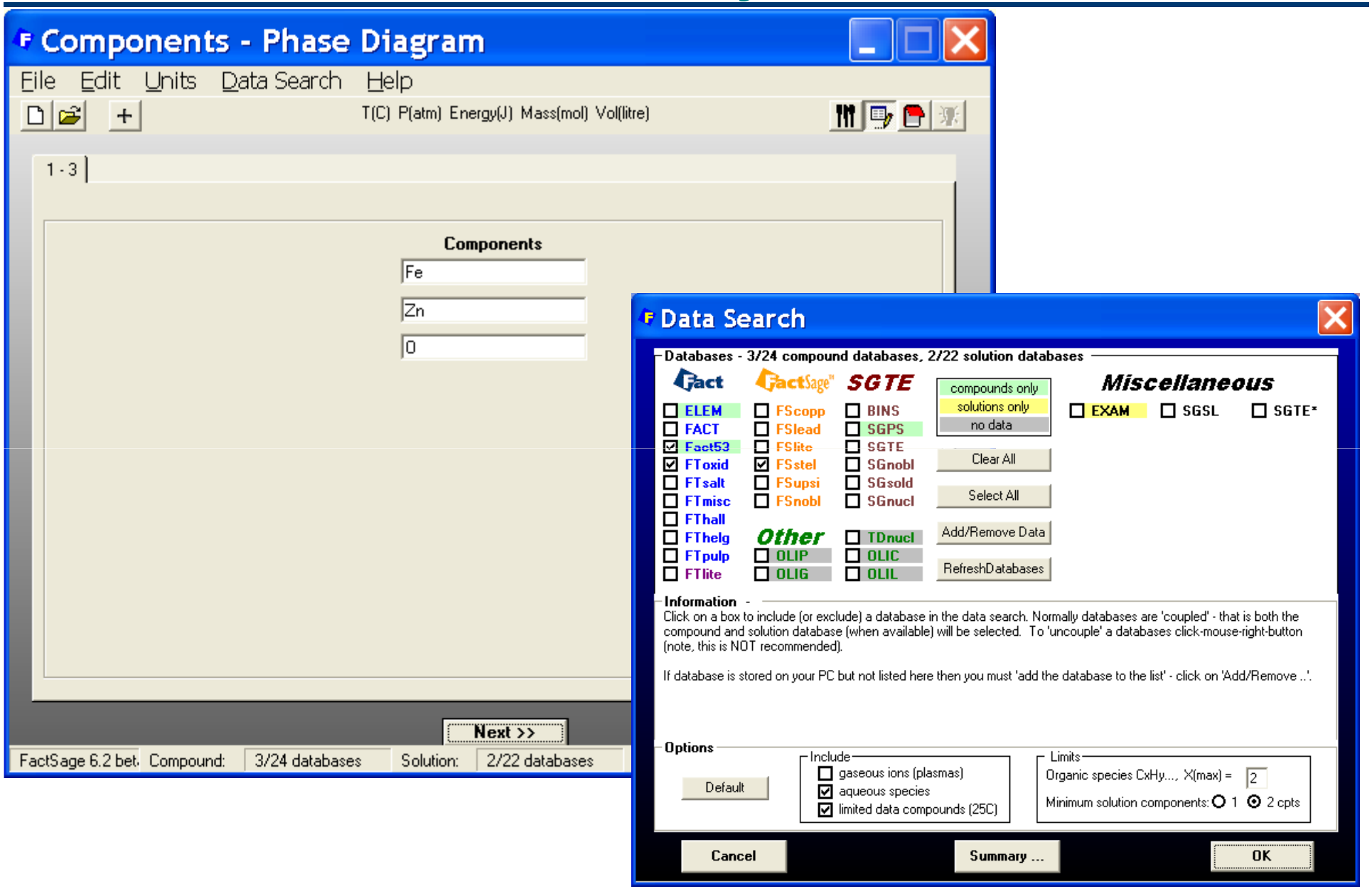

P=10000 atm
1800
1600
1400
1200
1000
800
600
400
T(C)
0
0.2
0.4
0.6
0.8
1
mole O/(Fe+O)
Fe-LIQUID + ASlag-liq
ASlag-liq
ASlag-liq + gas_ideal
Fe(s) + ASlag-liq
AMonoxide
ASpinel
Fe2O3(s)
Fe(s2) + AMonoxide
Fe2O3(s) + gas_ideal
Fe(s) + AMonoxide
Fe(s) + ASpinel

Fe-O System

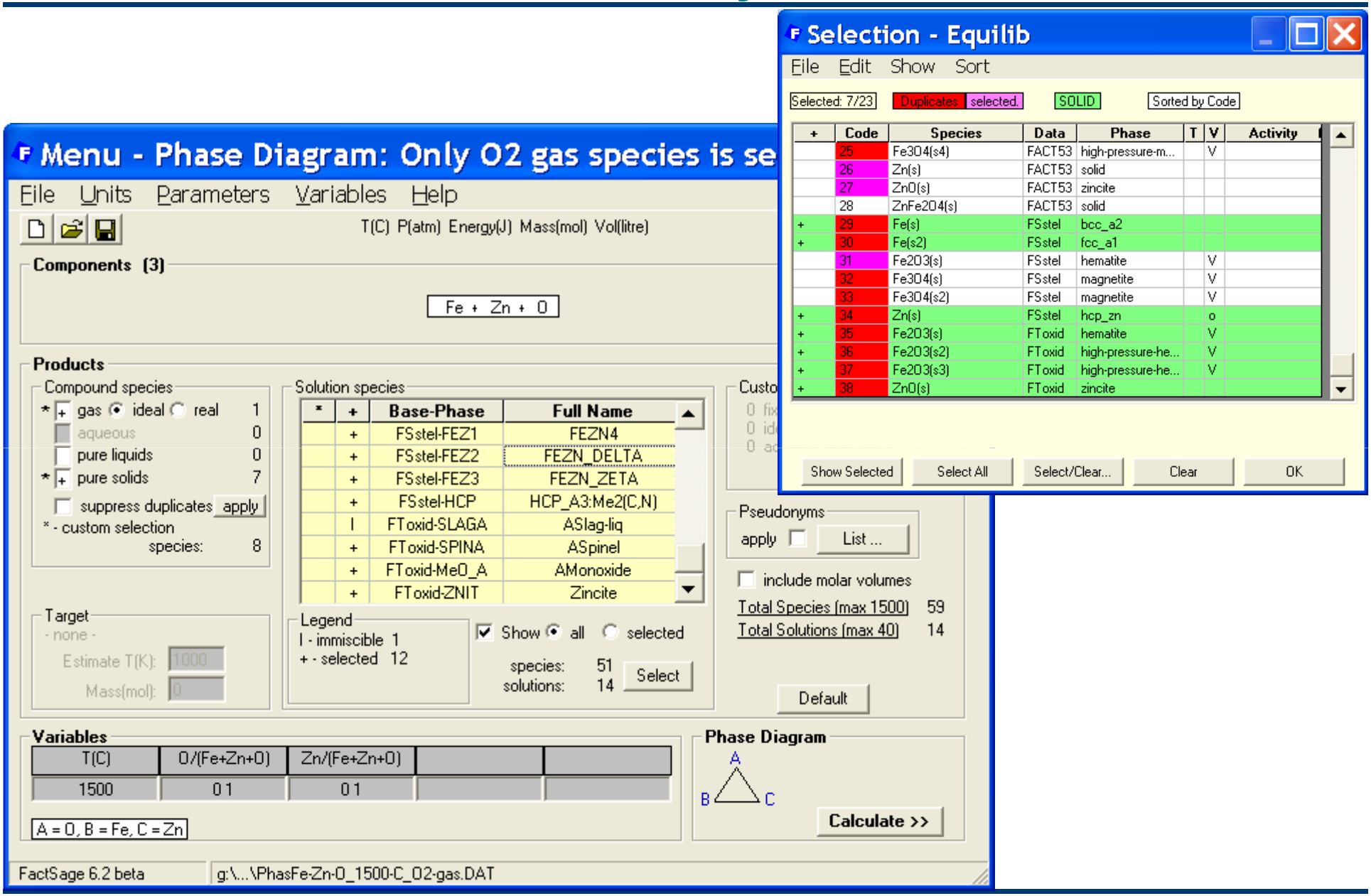


FeO-Fe_2O_3 phase diagram: experimental points and calculated lines. Dashed lines are oxygen isobars (atm).

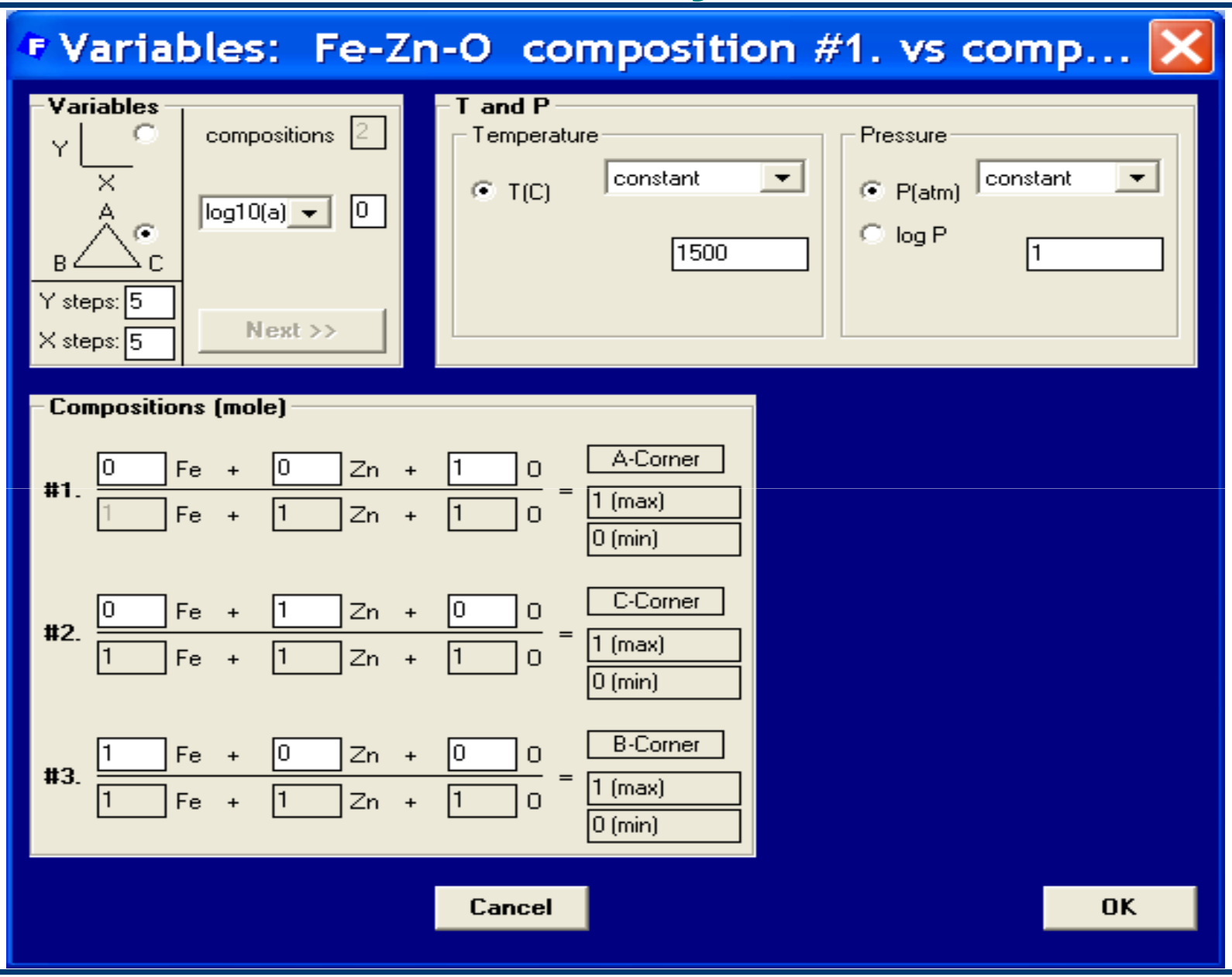
Fe-Zn-O System



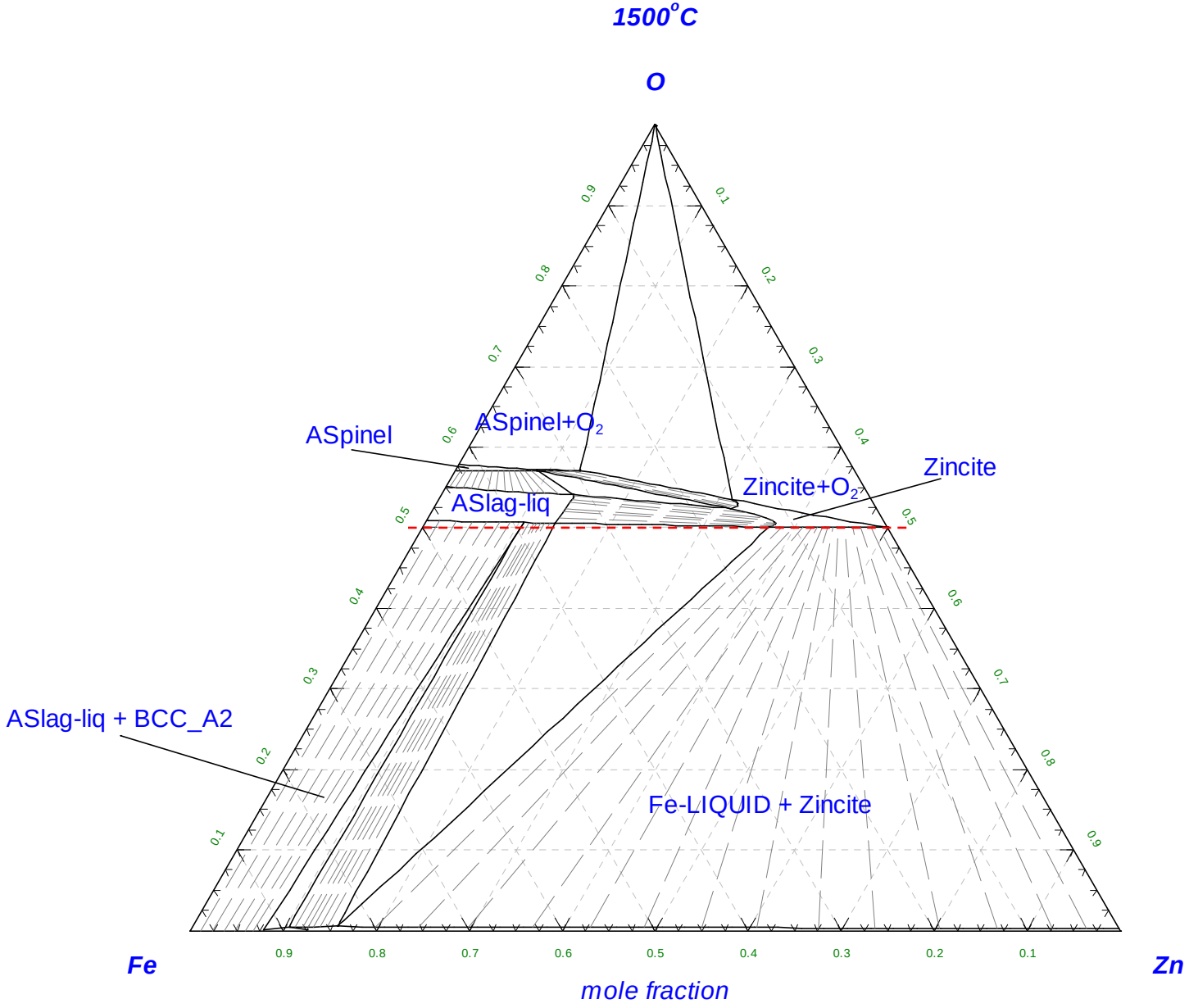
Fe-Zn-O System



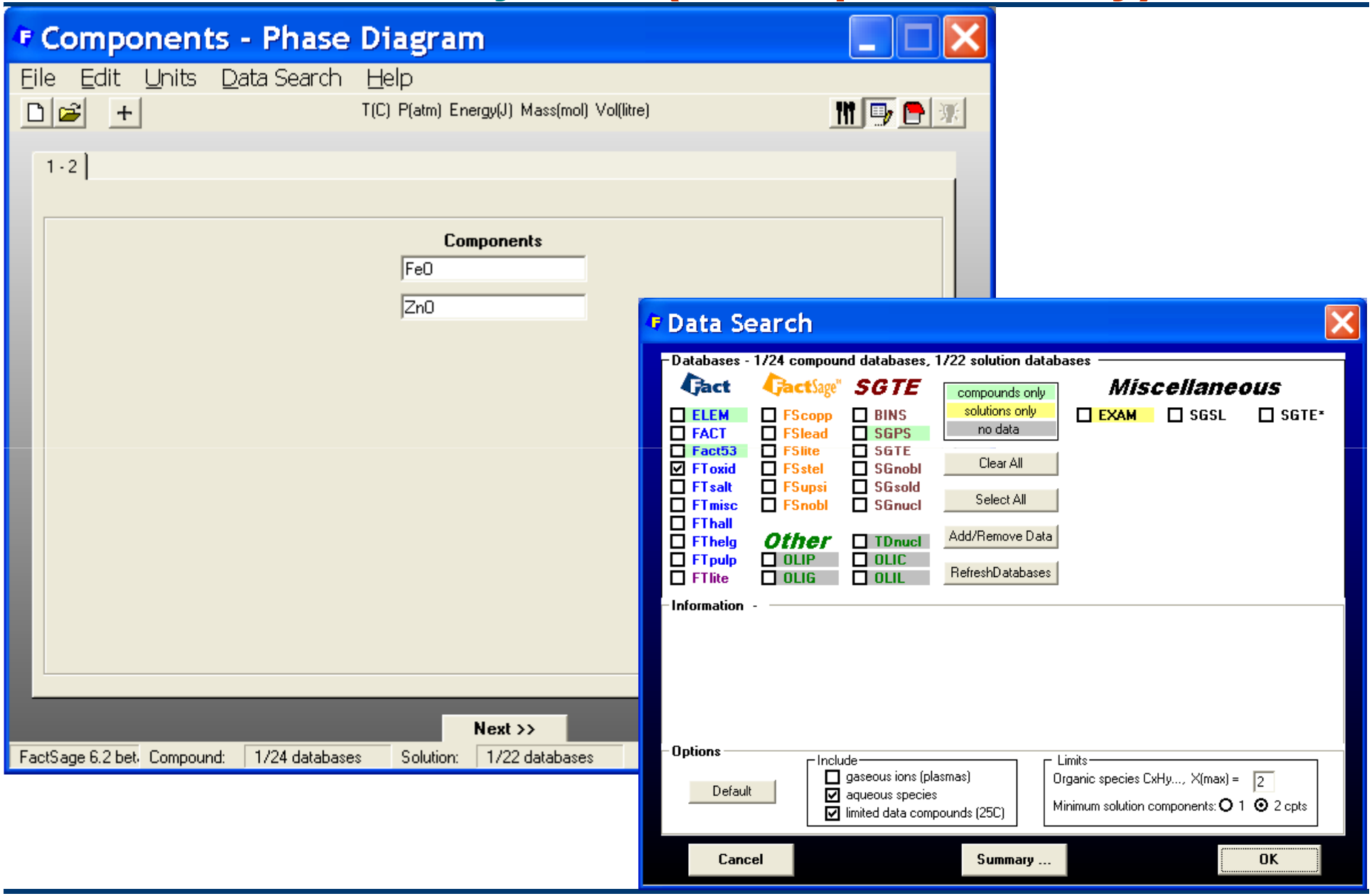
Fe-Zn-O System



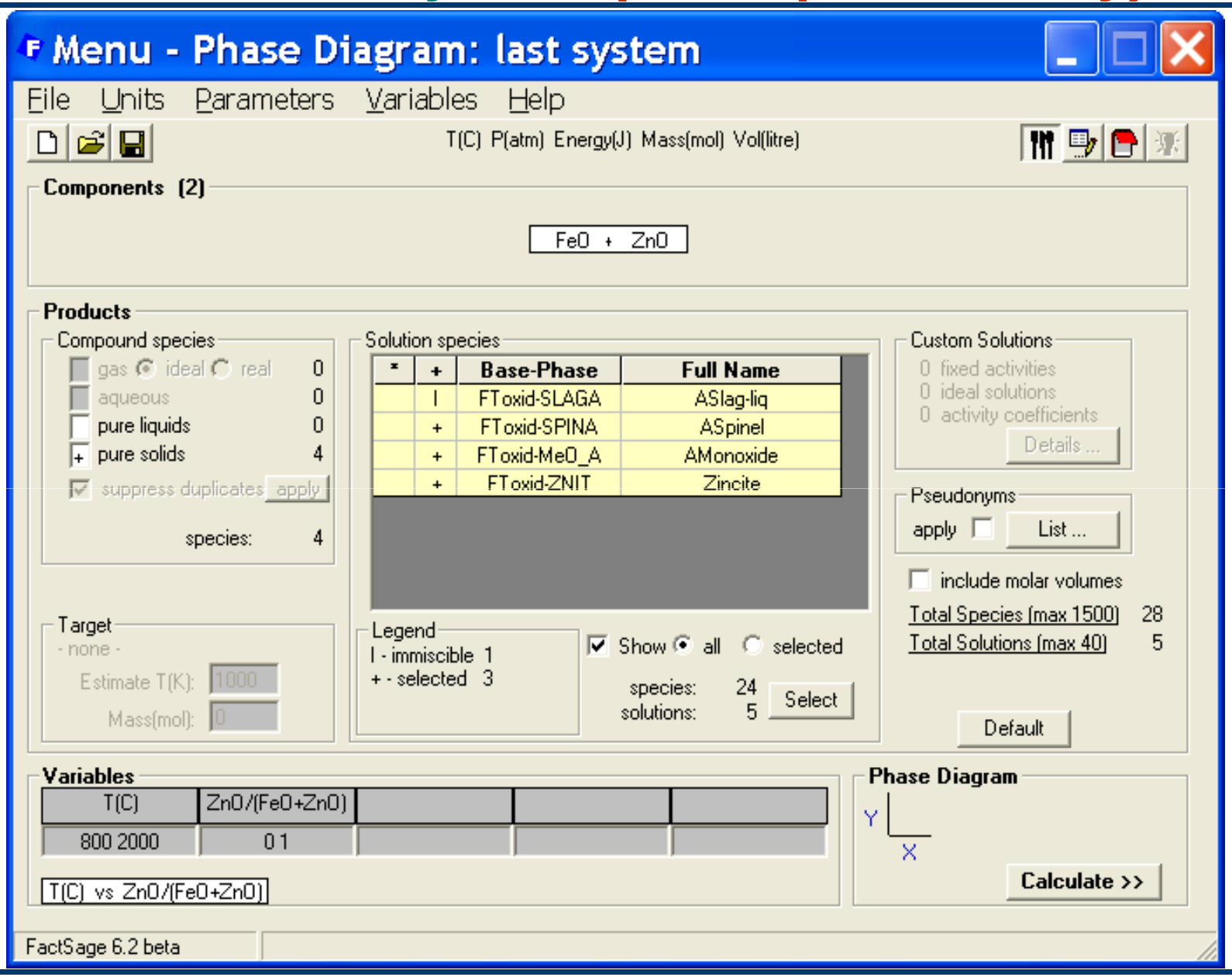
Fe-Zn-O System



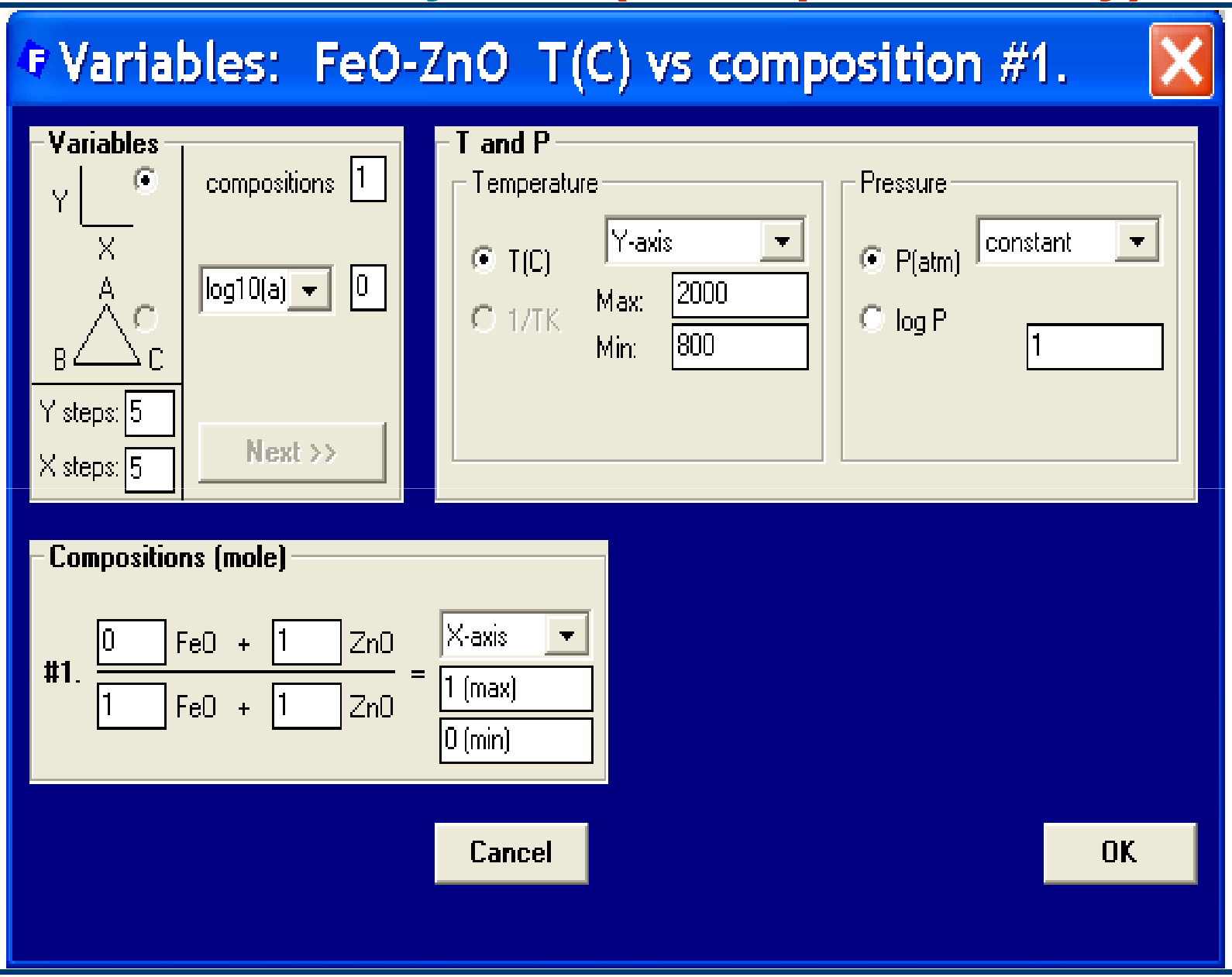
FeO-ZnO System (oxide phases only)



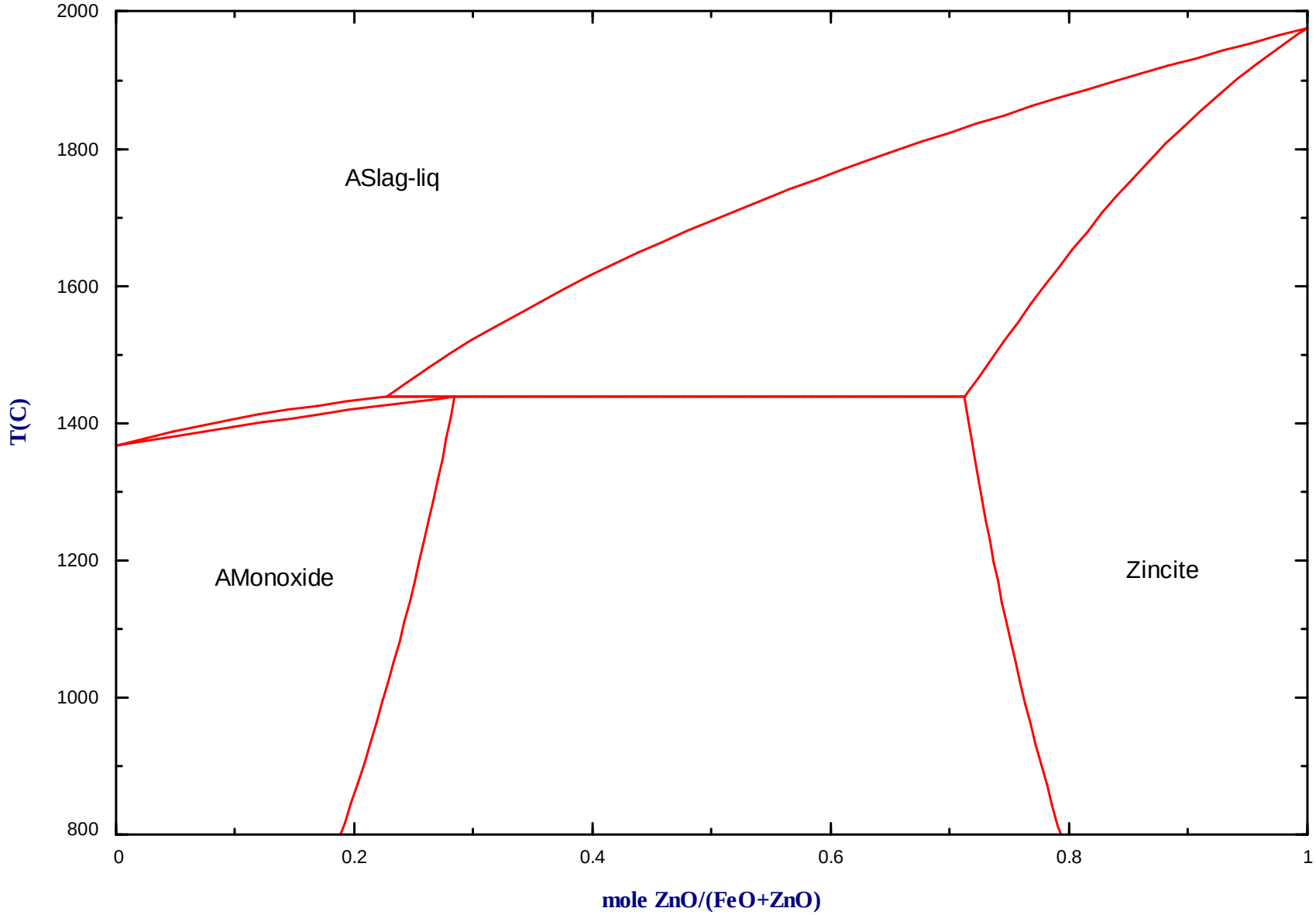
FeO-ZnO System (oxide phases only)



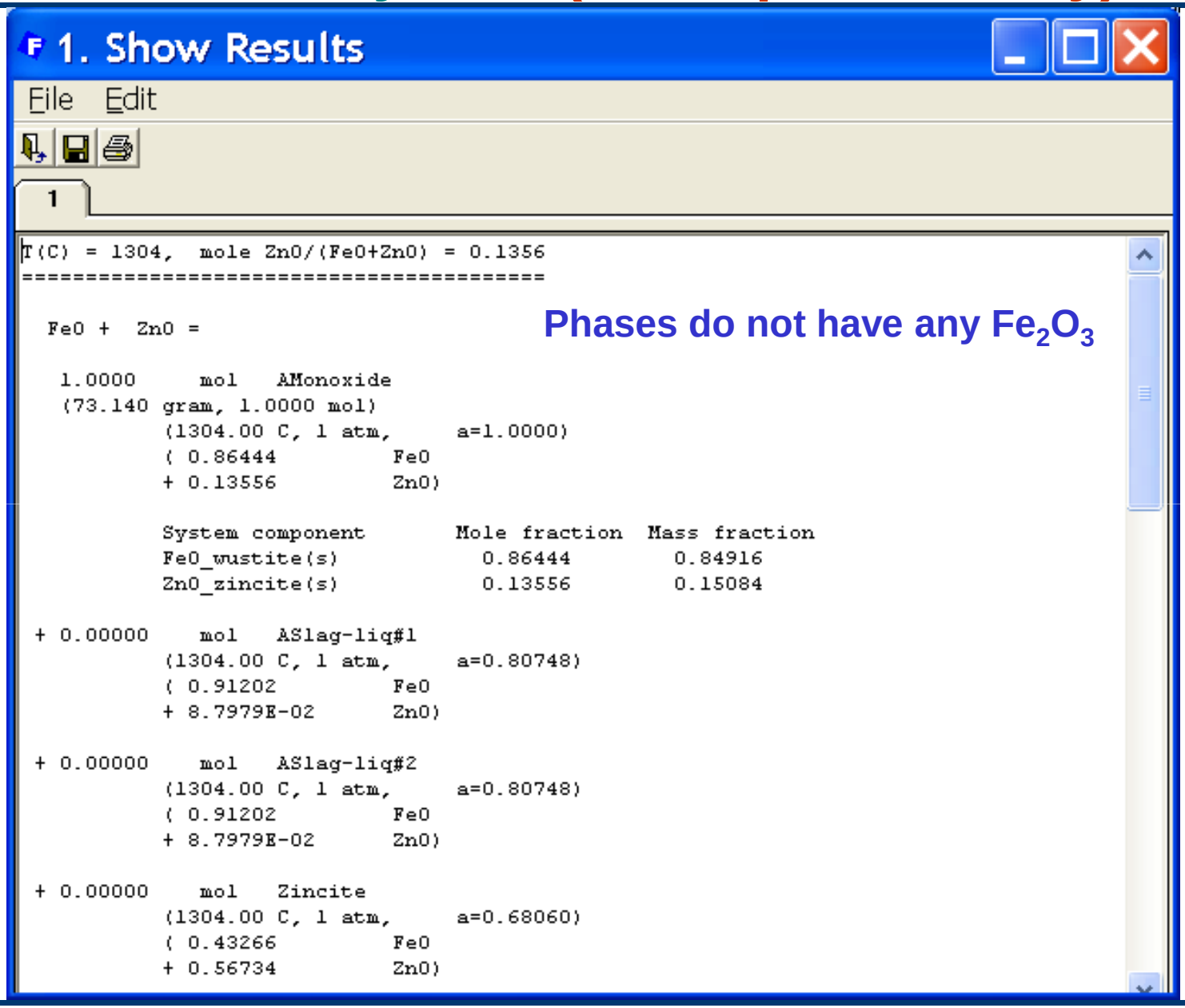
FeO-ZnO System (oxide phases only)



FeO-ZnO System (oxide phases only)

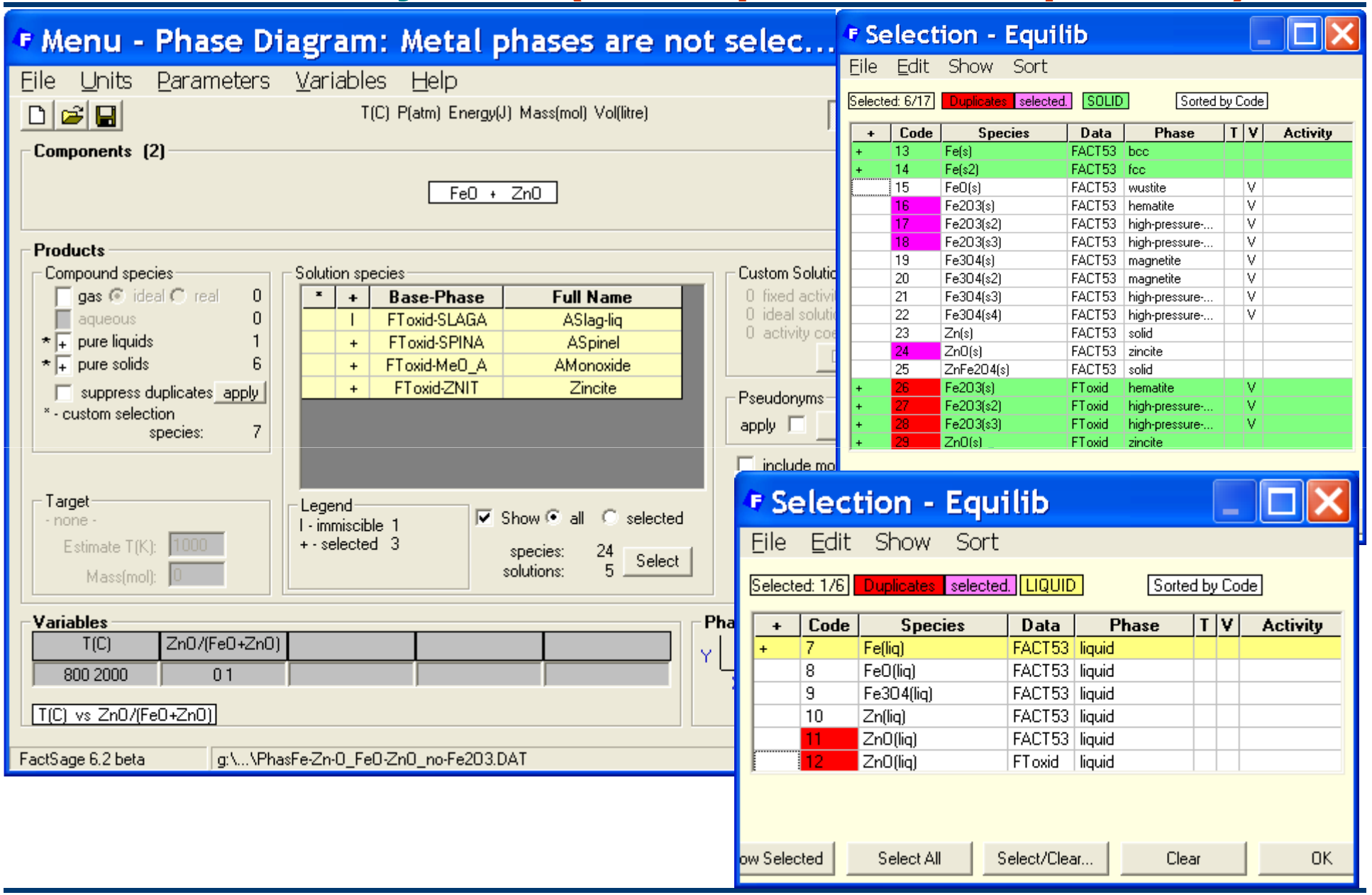


FeO-ZnO System (oxide phases only)

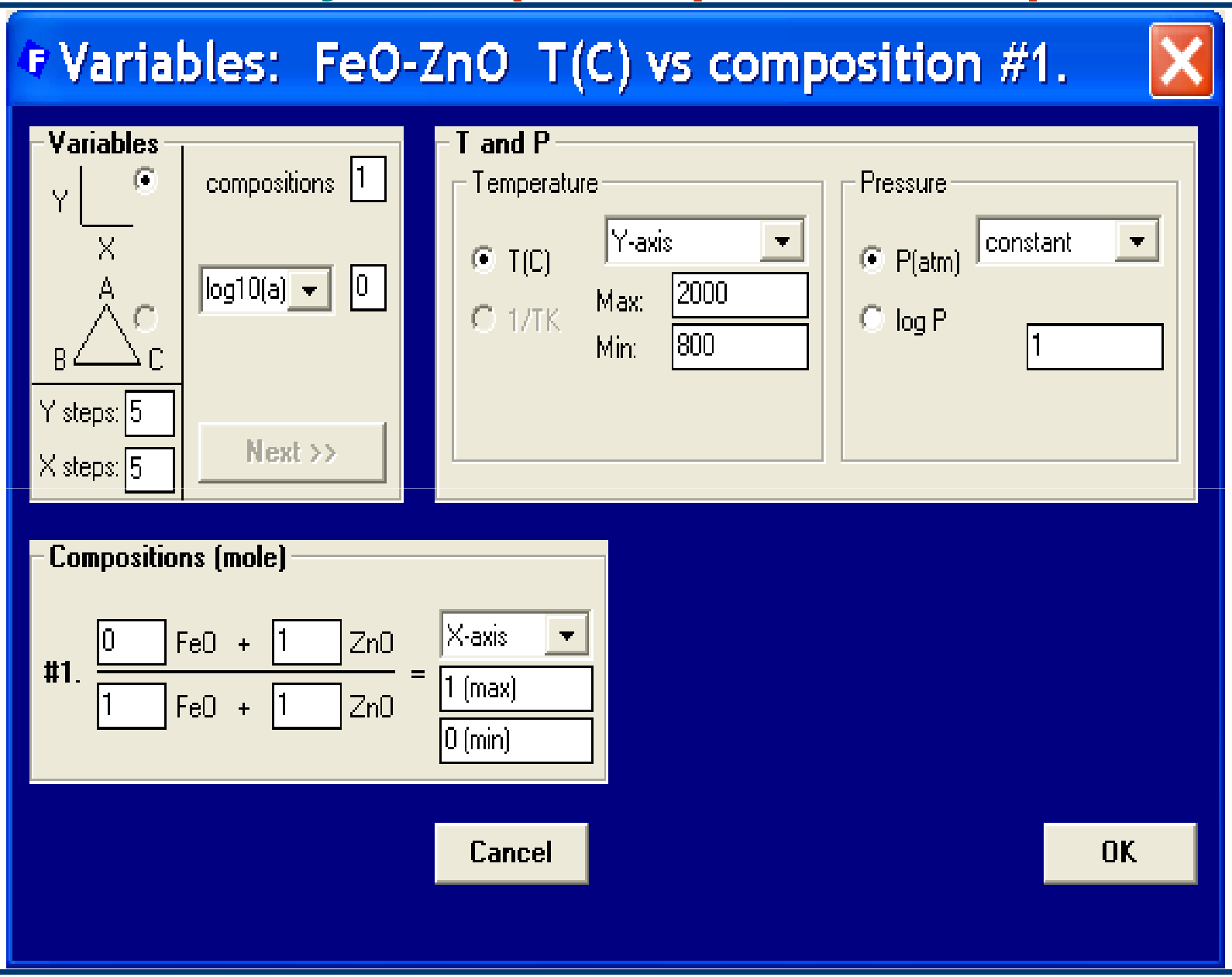


Phases do not have any Fe_2O_3

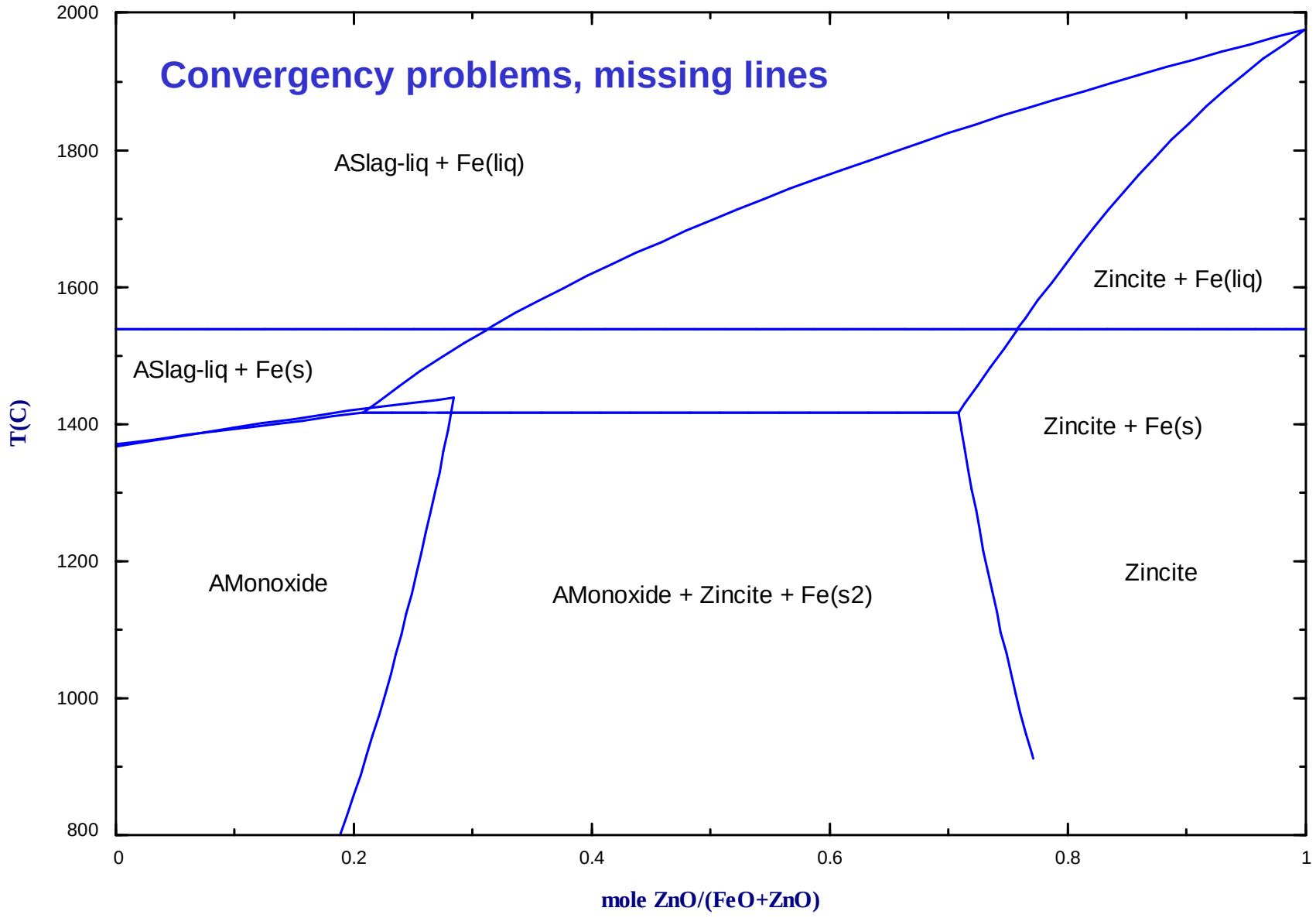
FeO-ZnO System (oxide phases and pure Fe)



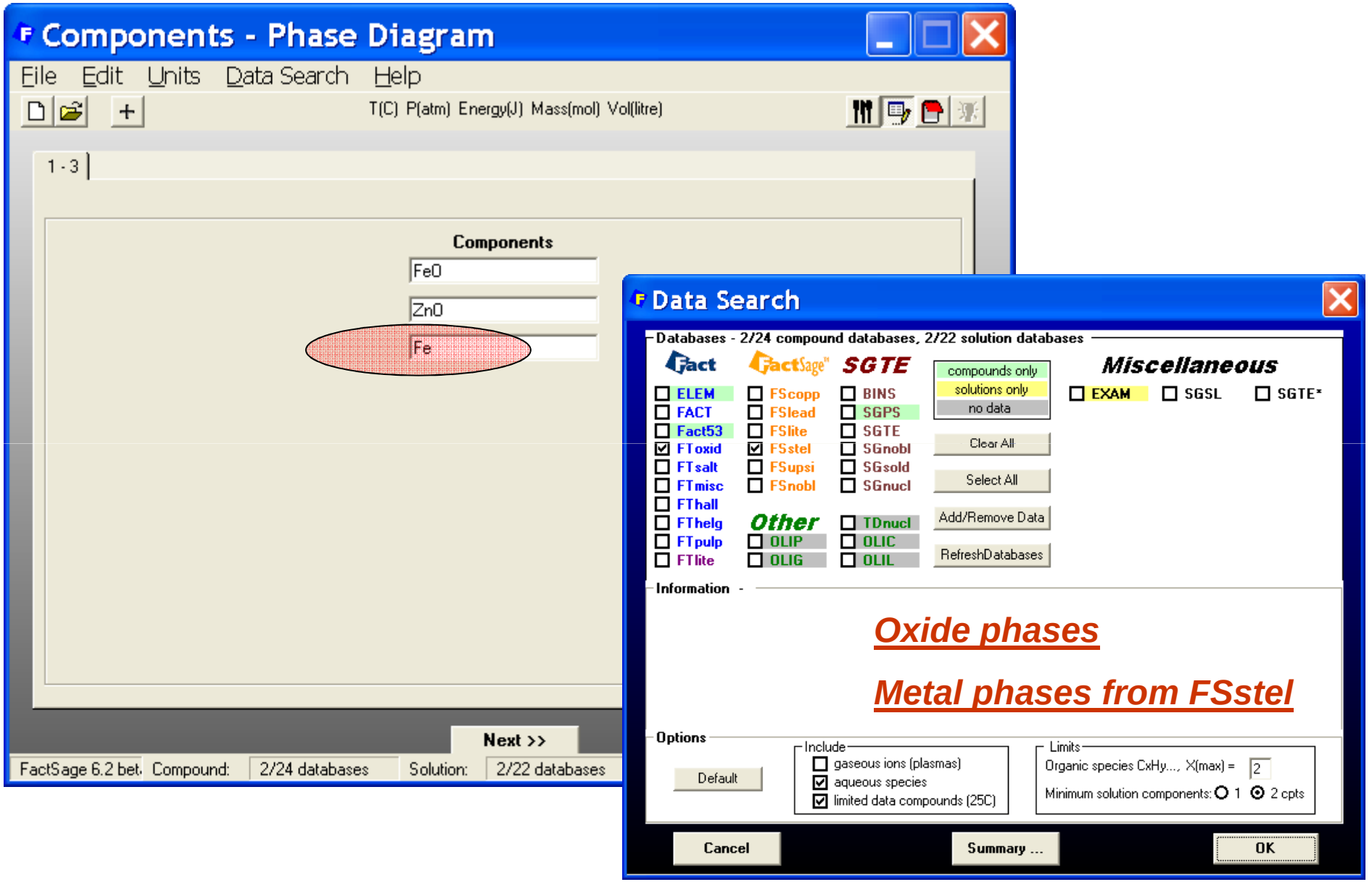
FeO-ZnO System (oxide phases and pure Fe)



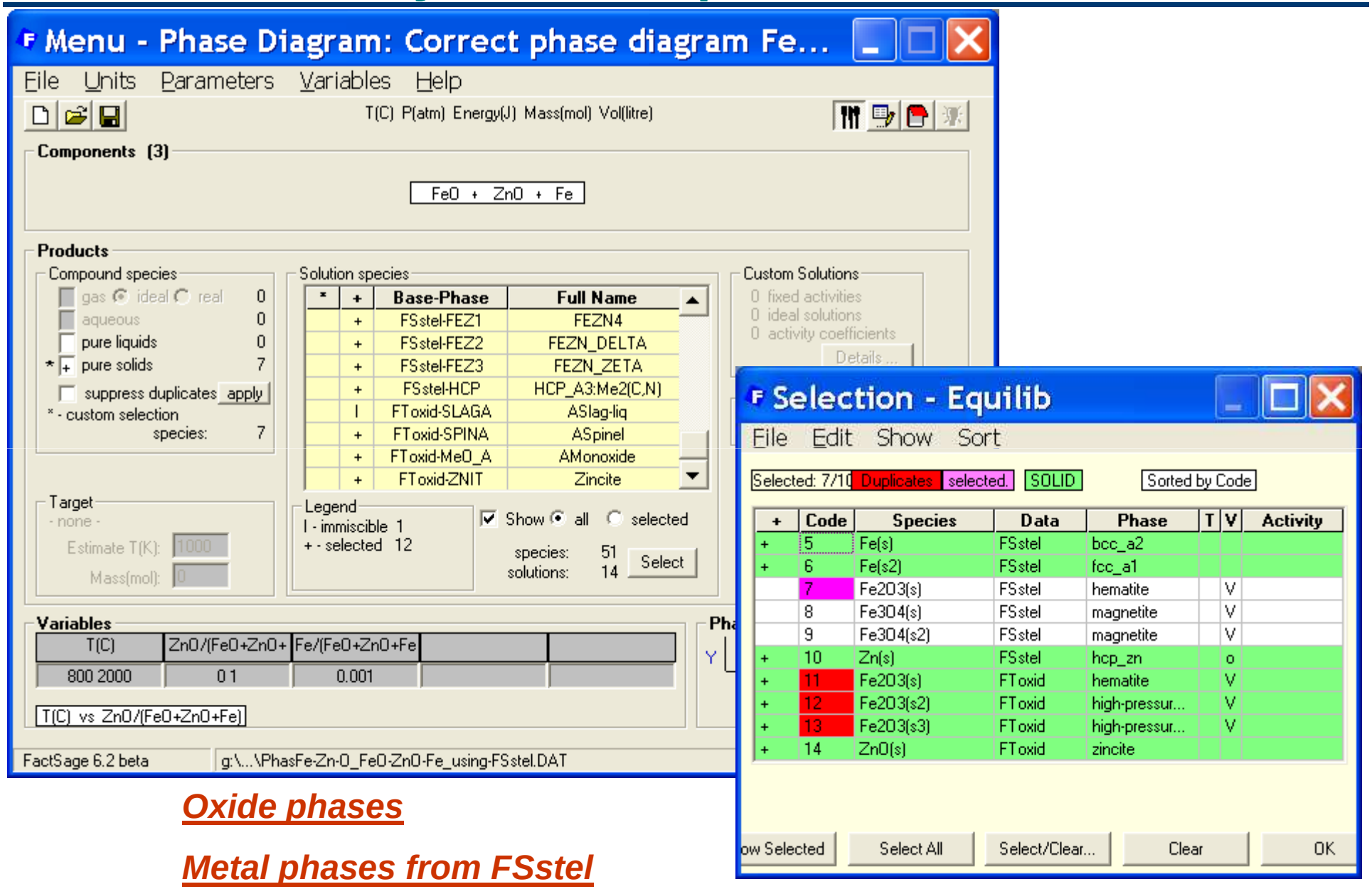
FeO-ZnO System (oxide phases and pure Fe)



FeO-ZnO System in Equilibrium with Metals



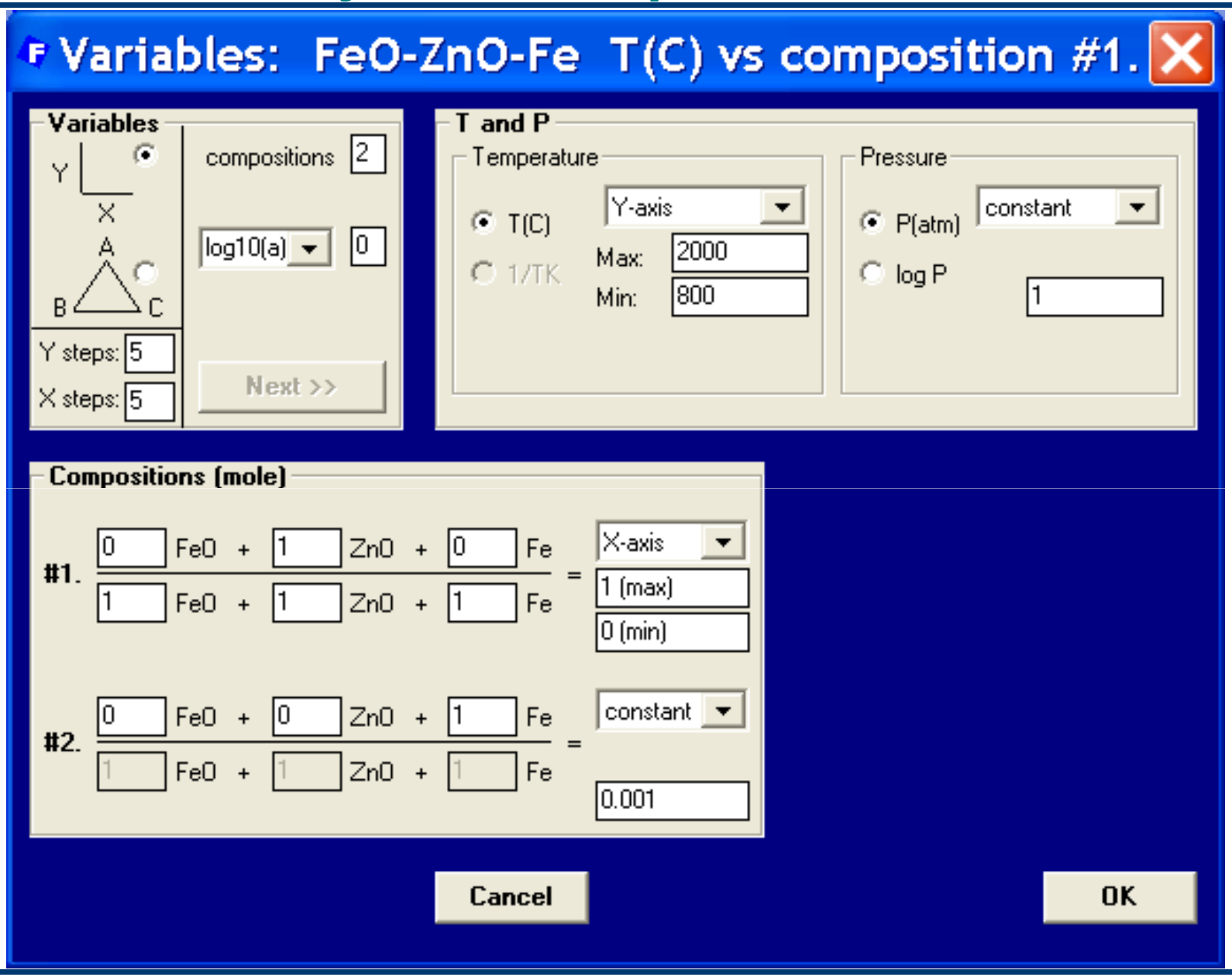
FeO-ZnO System in Equilibrium with Metals



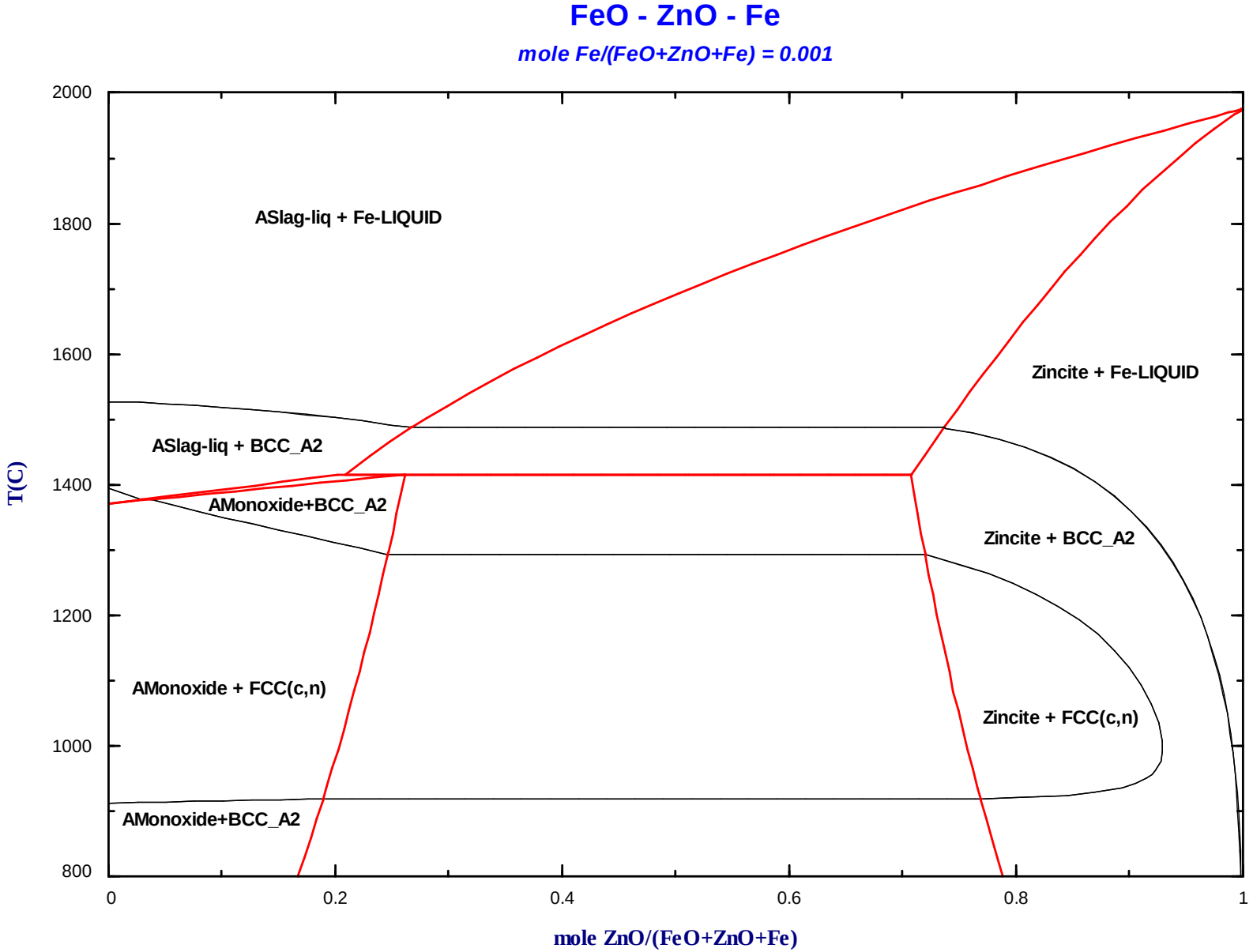
Oxide phases

Metal phases from FSstel

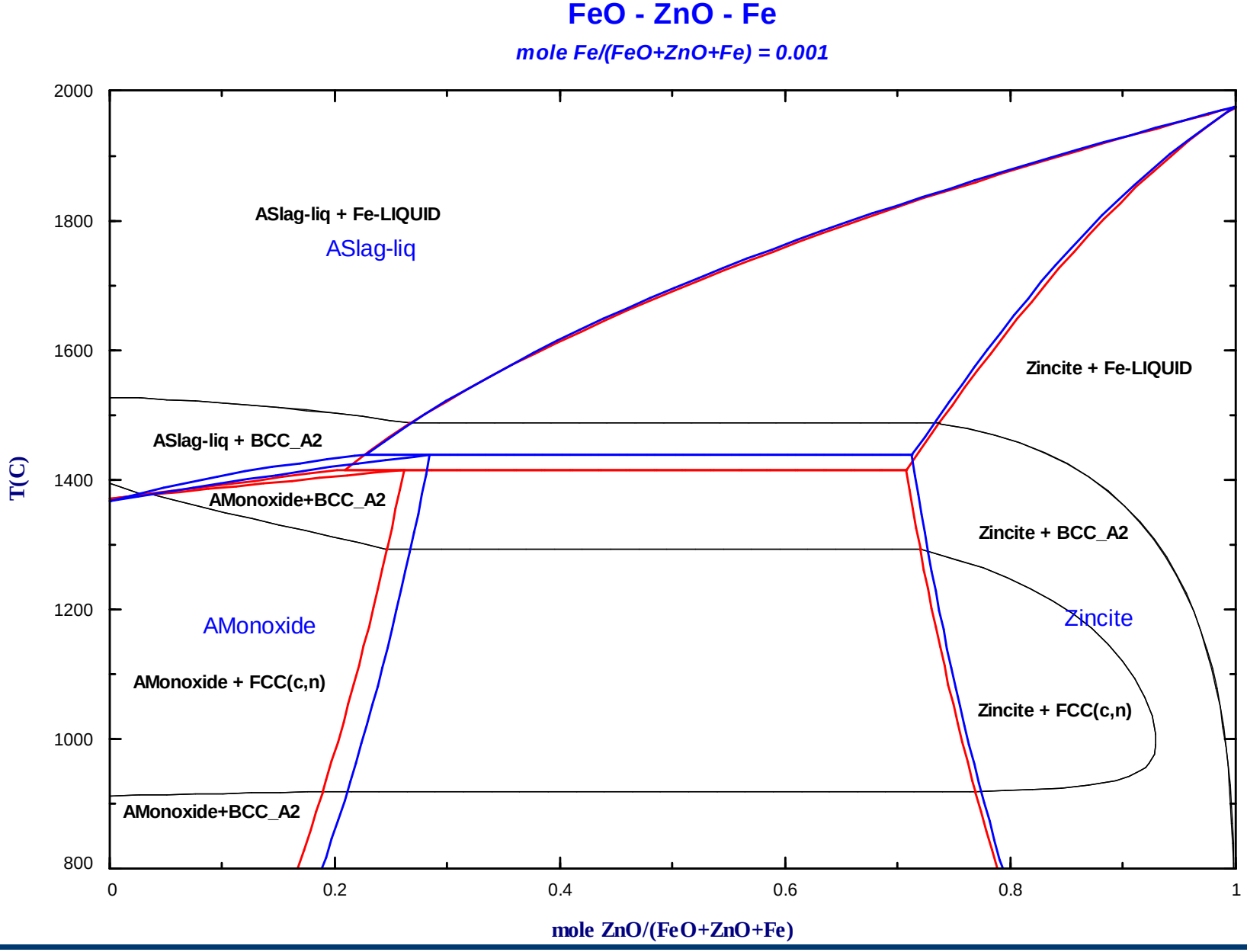
FeO-ZnO System in Equilibrium with Metals



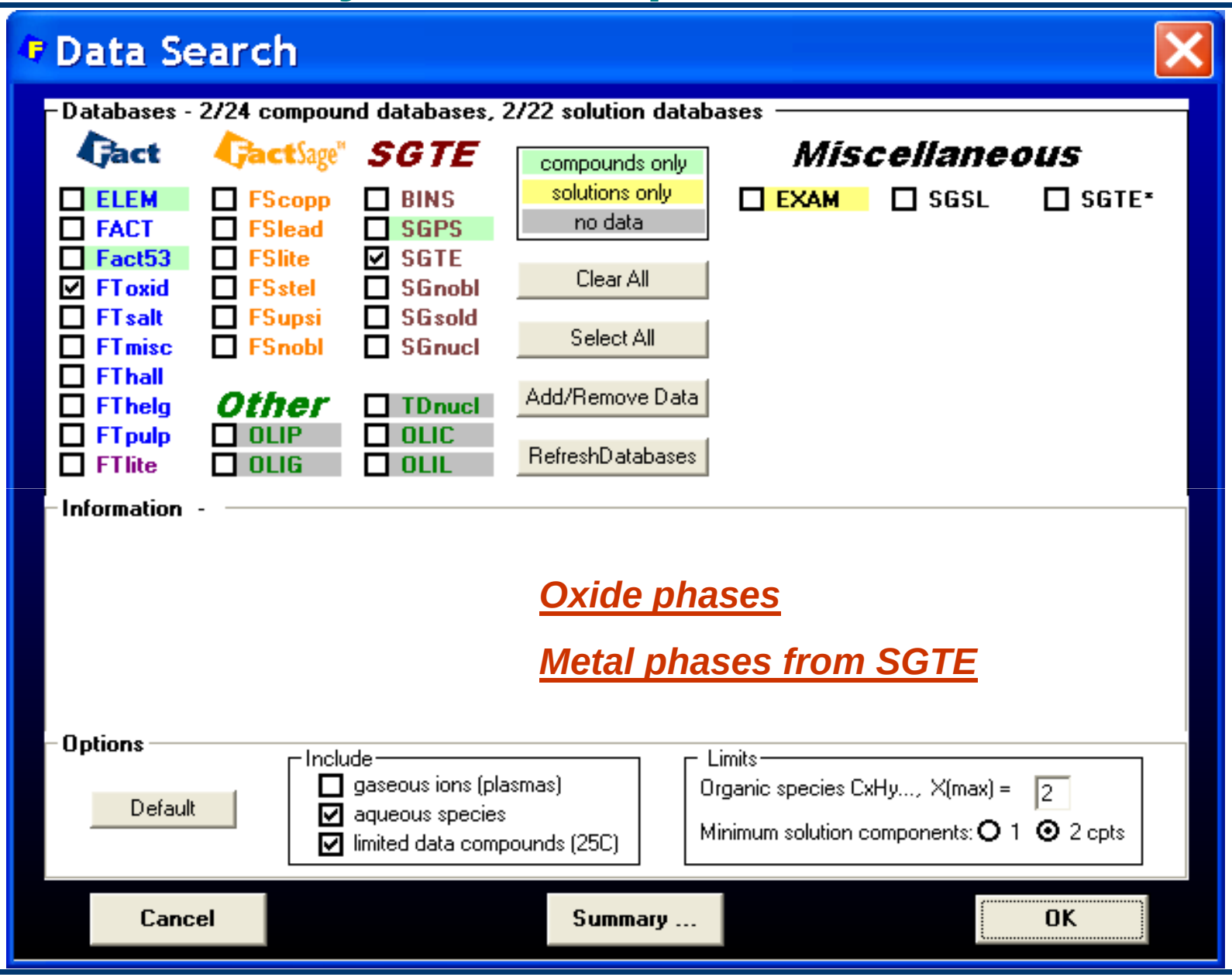
FeO-ZnO System in Equilibrium with Metals



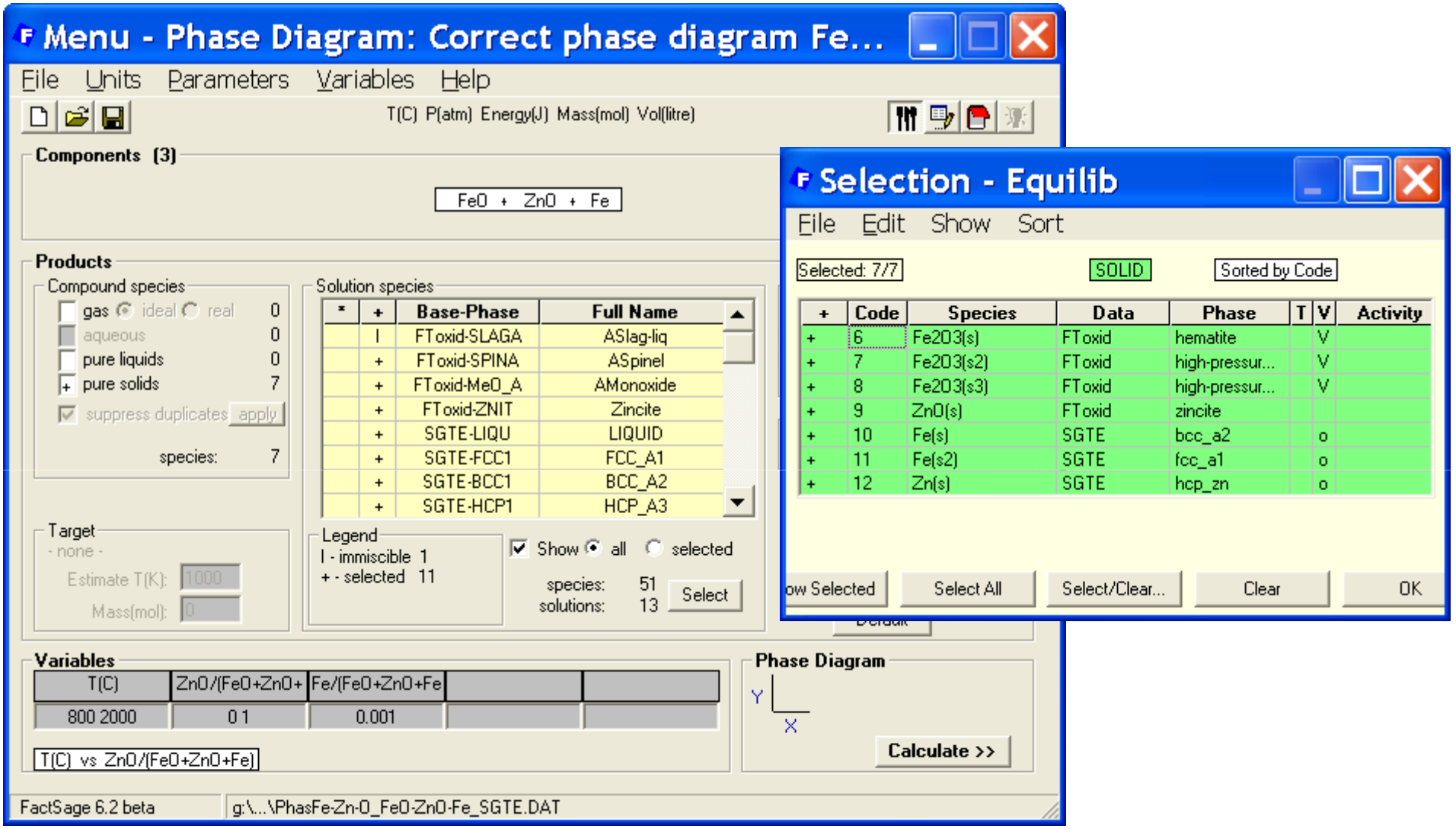
FeO-ZnO in Equilibrium with Metals vs FeO-ZnO



FeO-ZnO System in Equilibrium with Metals



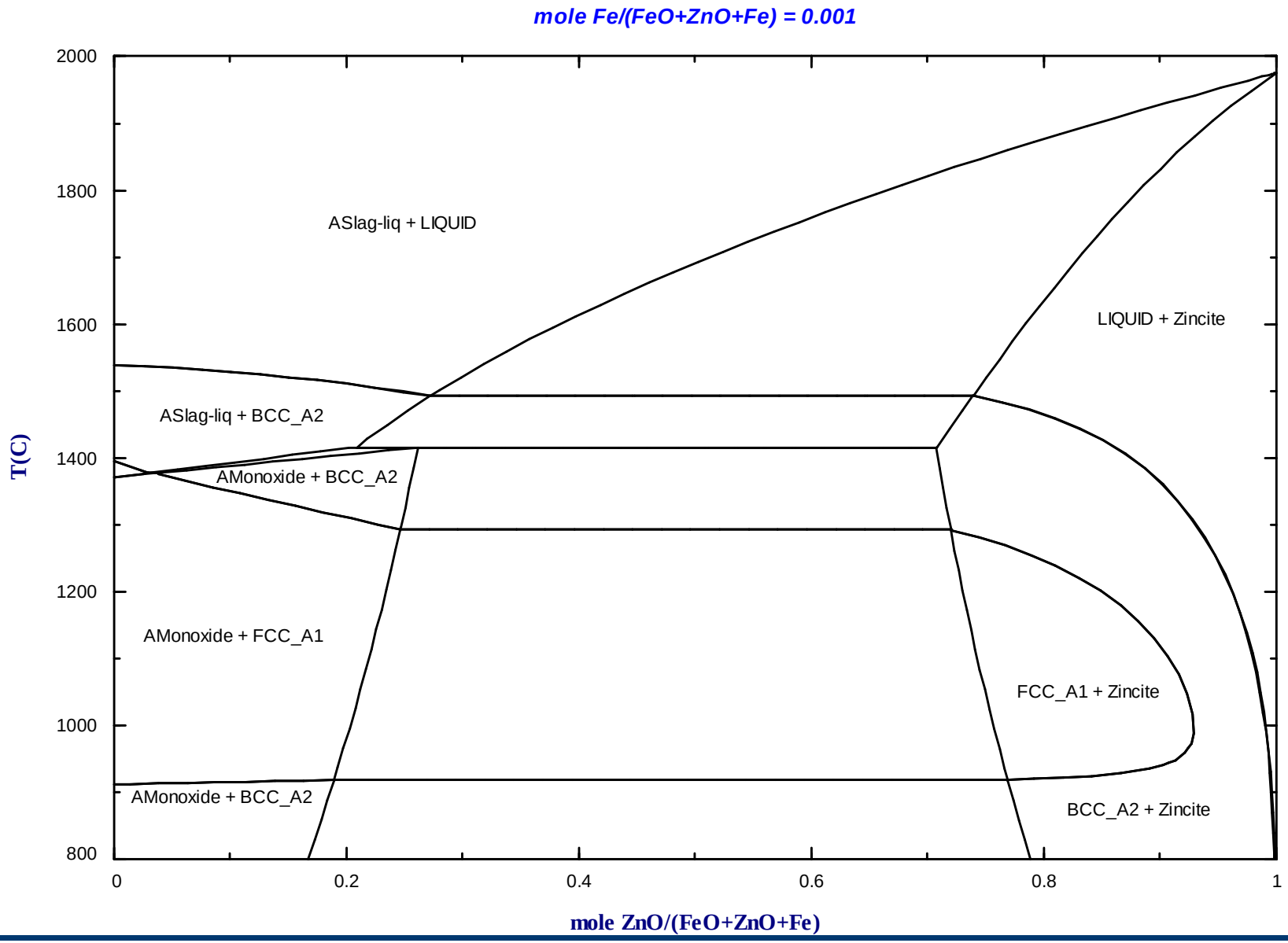
FeO-ZnO System in Equilibrium with Metals



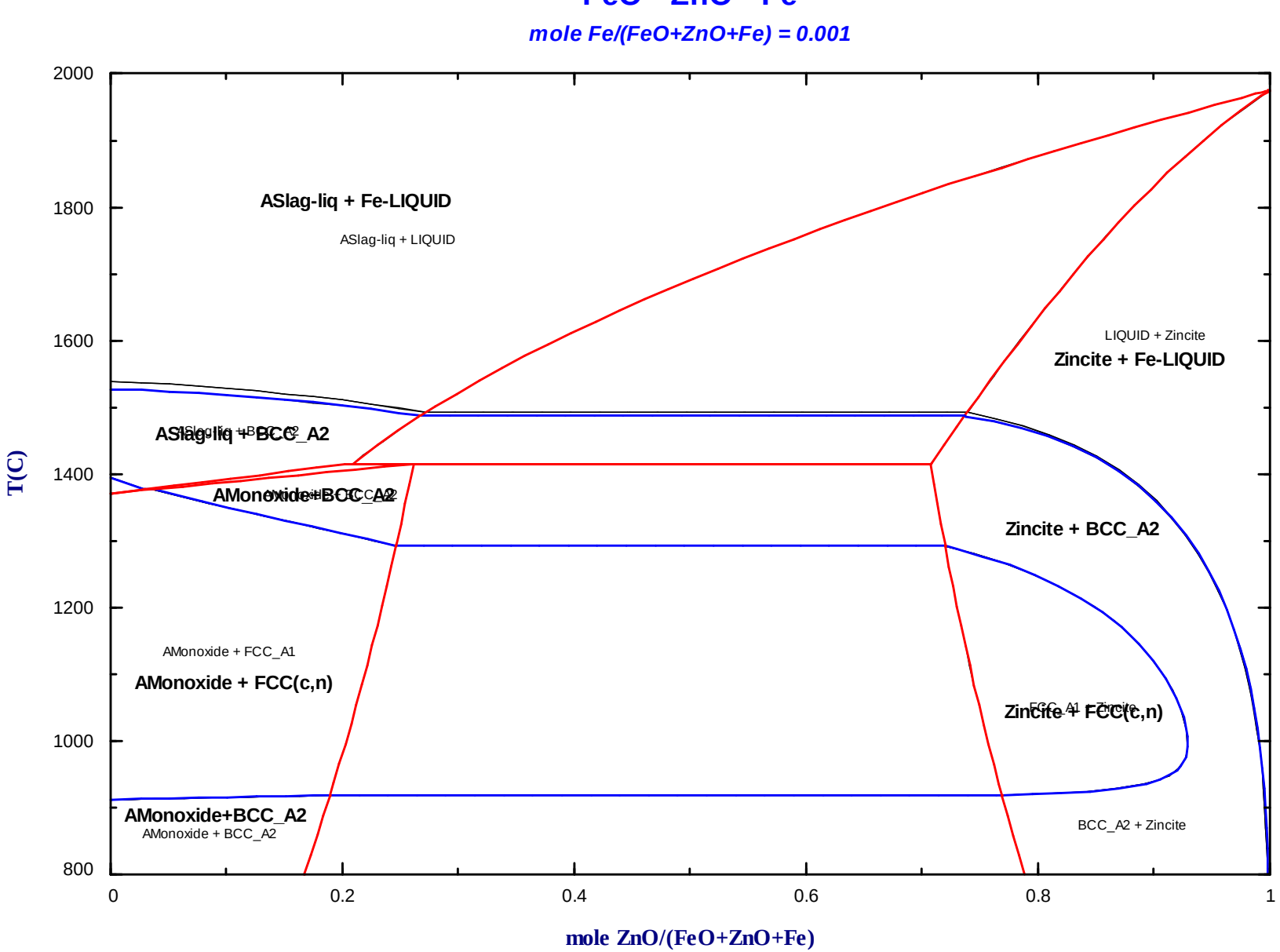
Oxide phases

Metal phases from SGTE

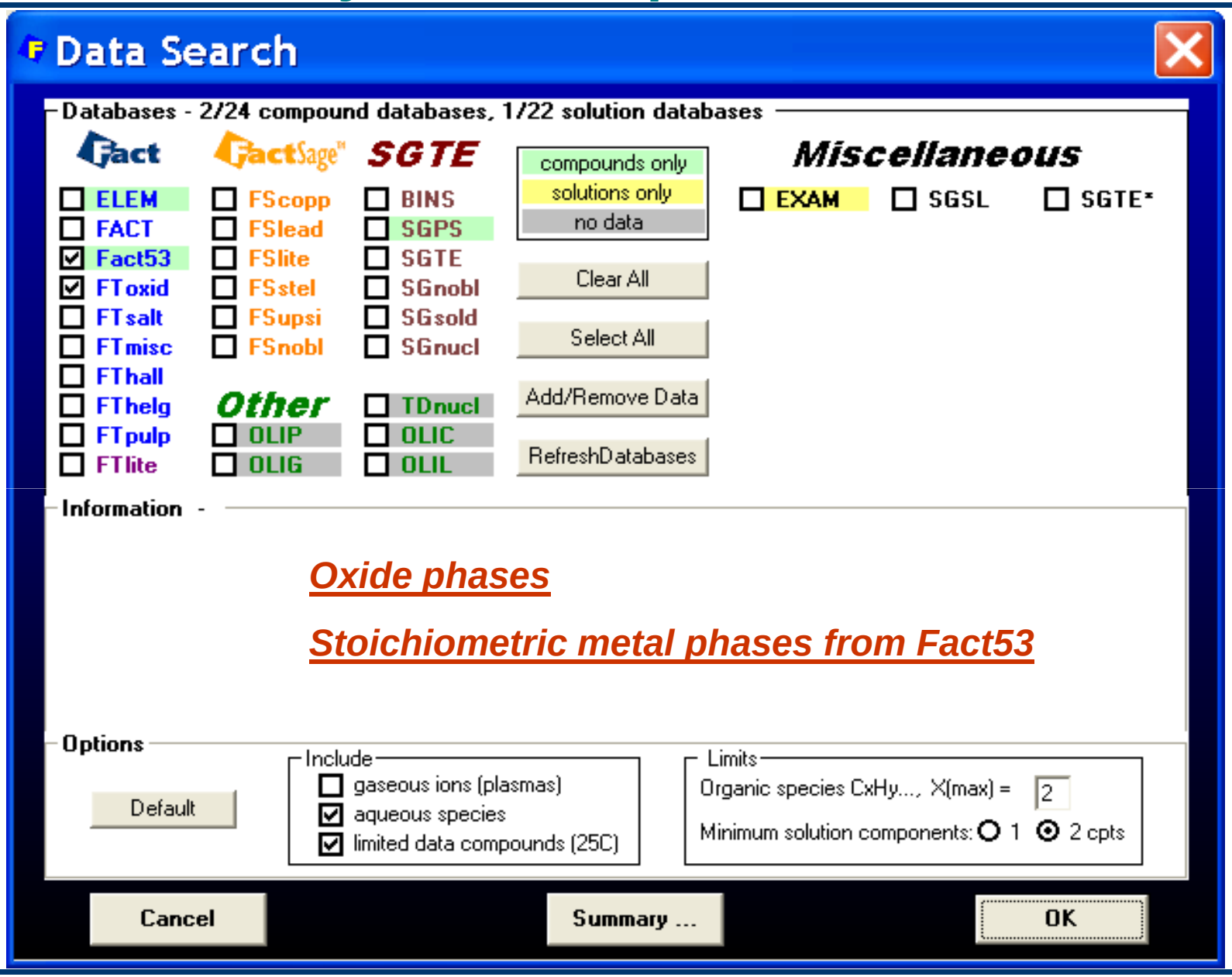
FeO-ZnO System in Equilibrium with Metals



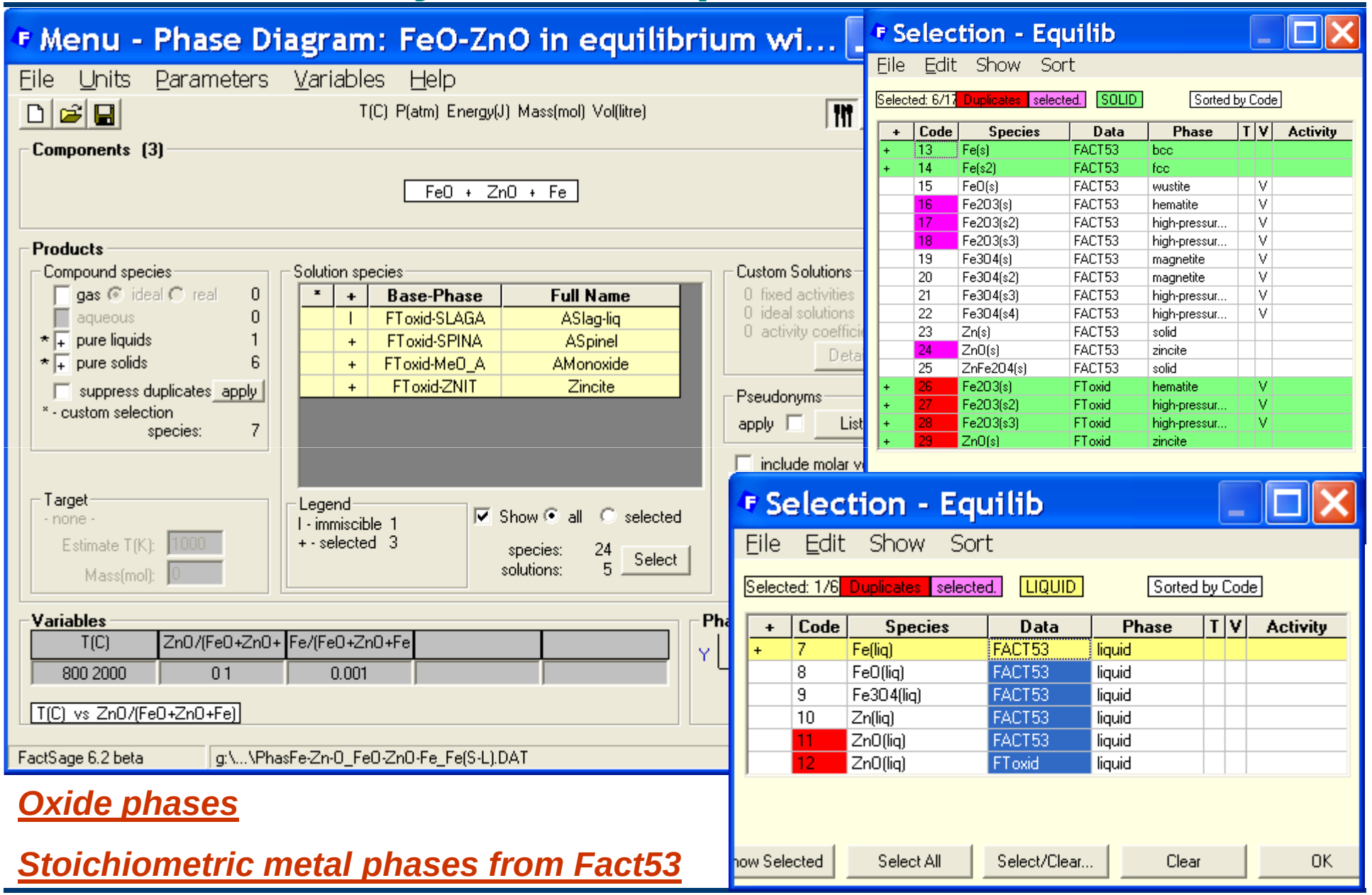
FeO-ZnO in Equilibrium with Metals (FSstel vs SGTE)



FeO-ZnO System in Equilibrium with Metals



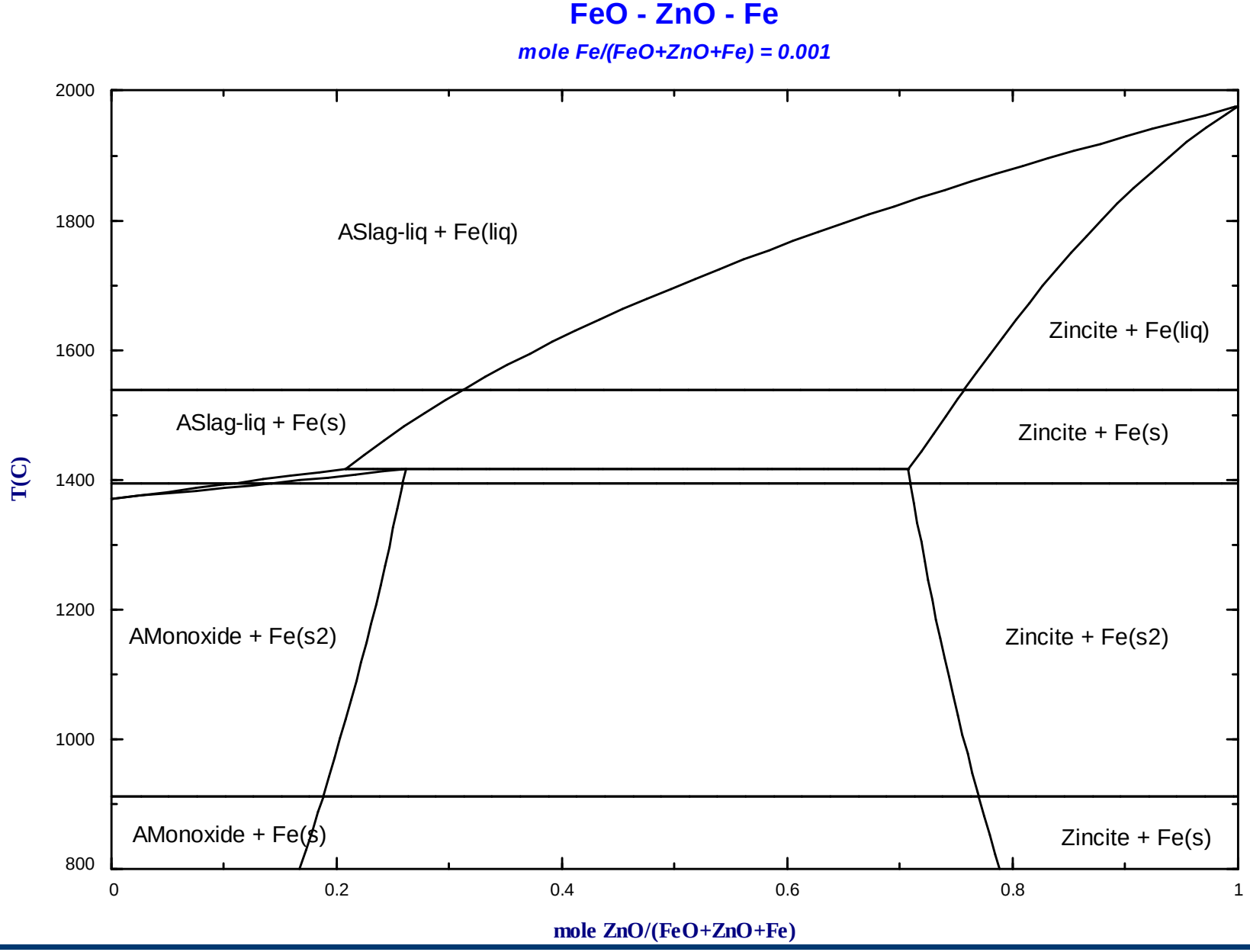
FeO-ZnO System in Equilibrium with Metals



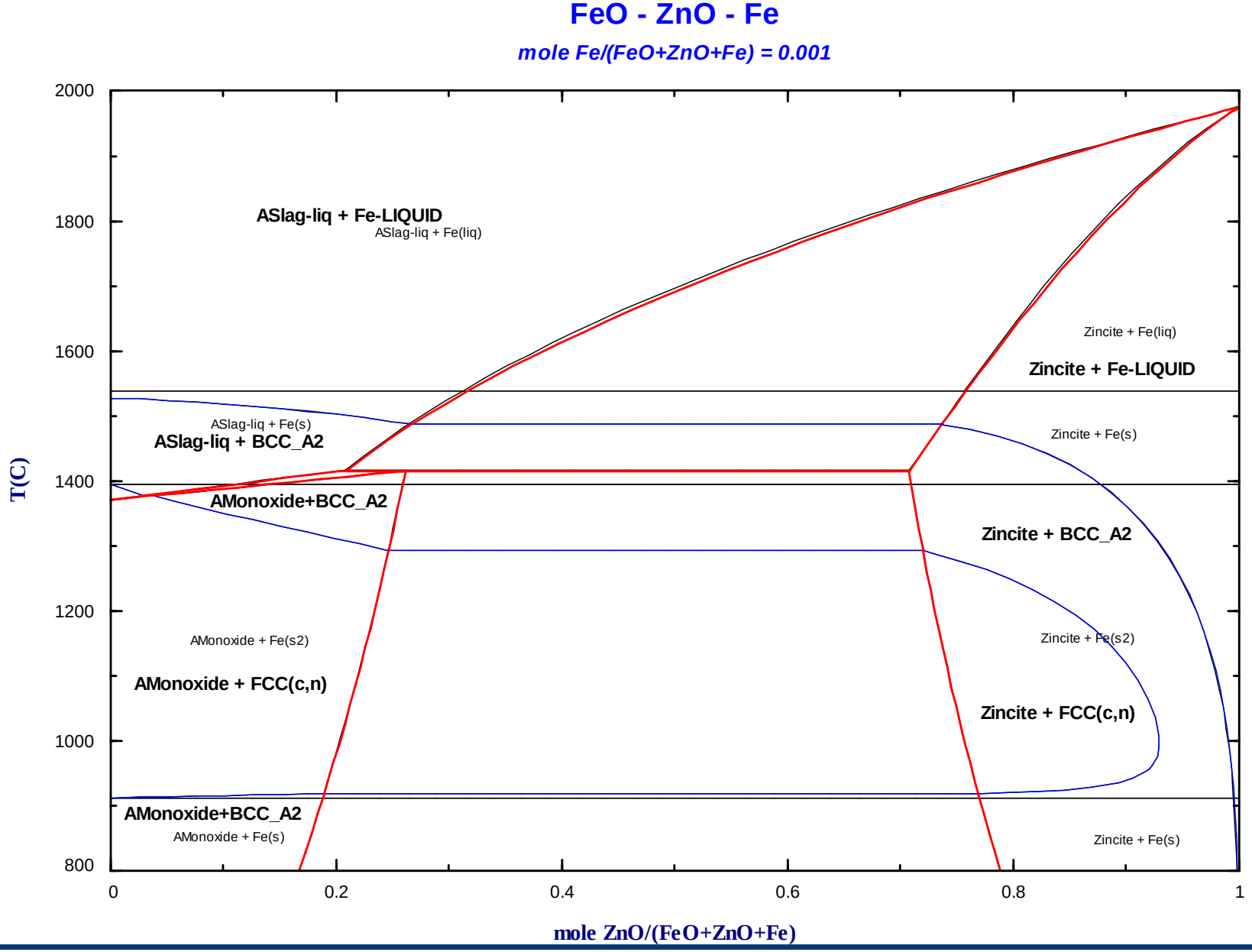
Oxide phases

Stoichiometric metal phases from Fact53

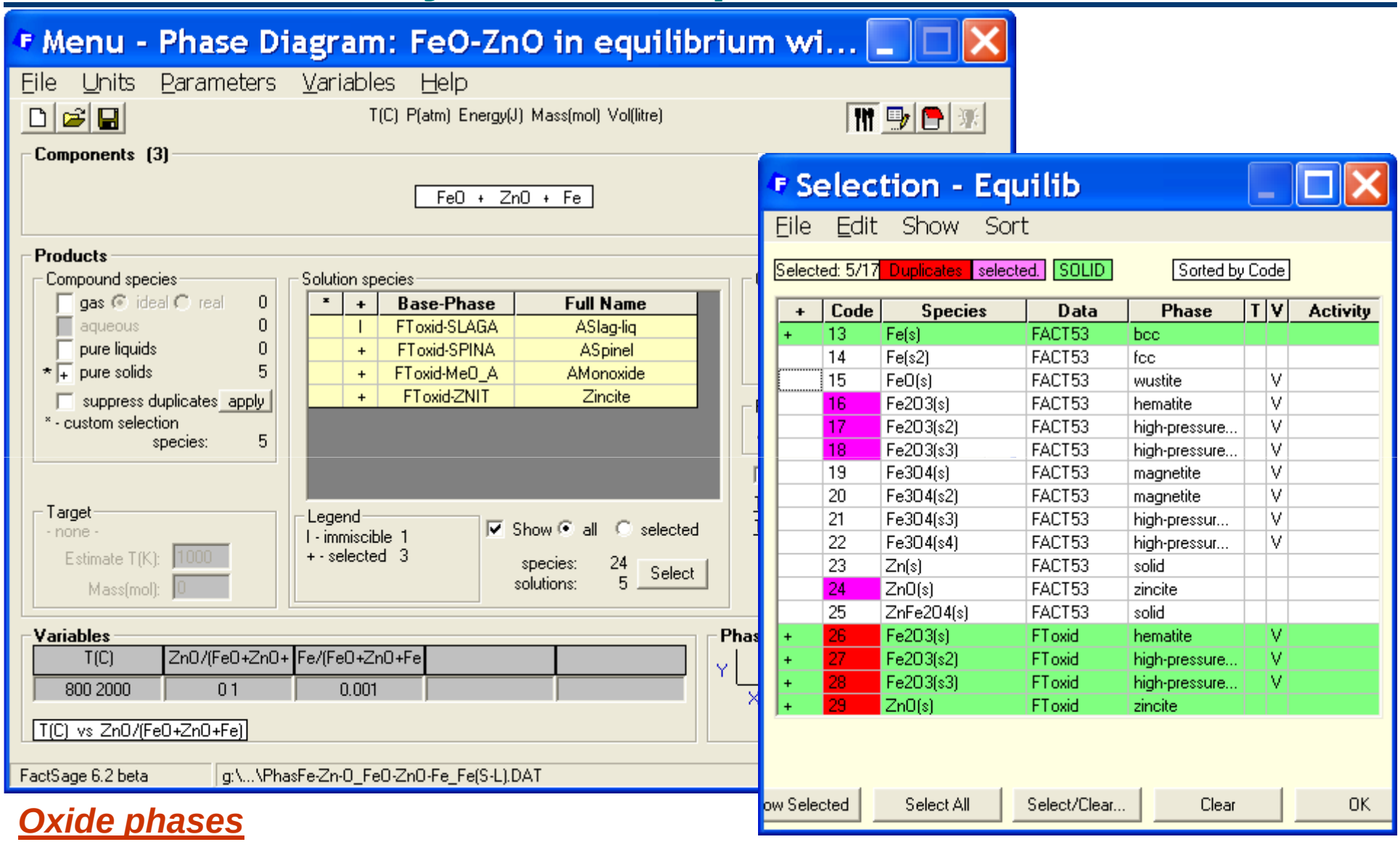
FeO-ZnO System in Equilibrium with Metals



FeO-ZnO in Equilibrium with Metals: FSstel vs pure Fe



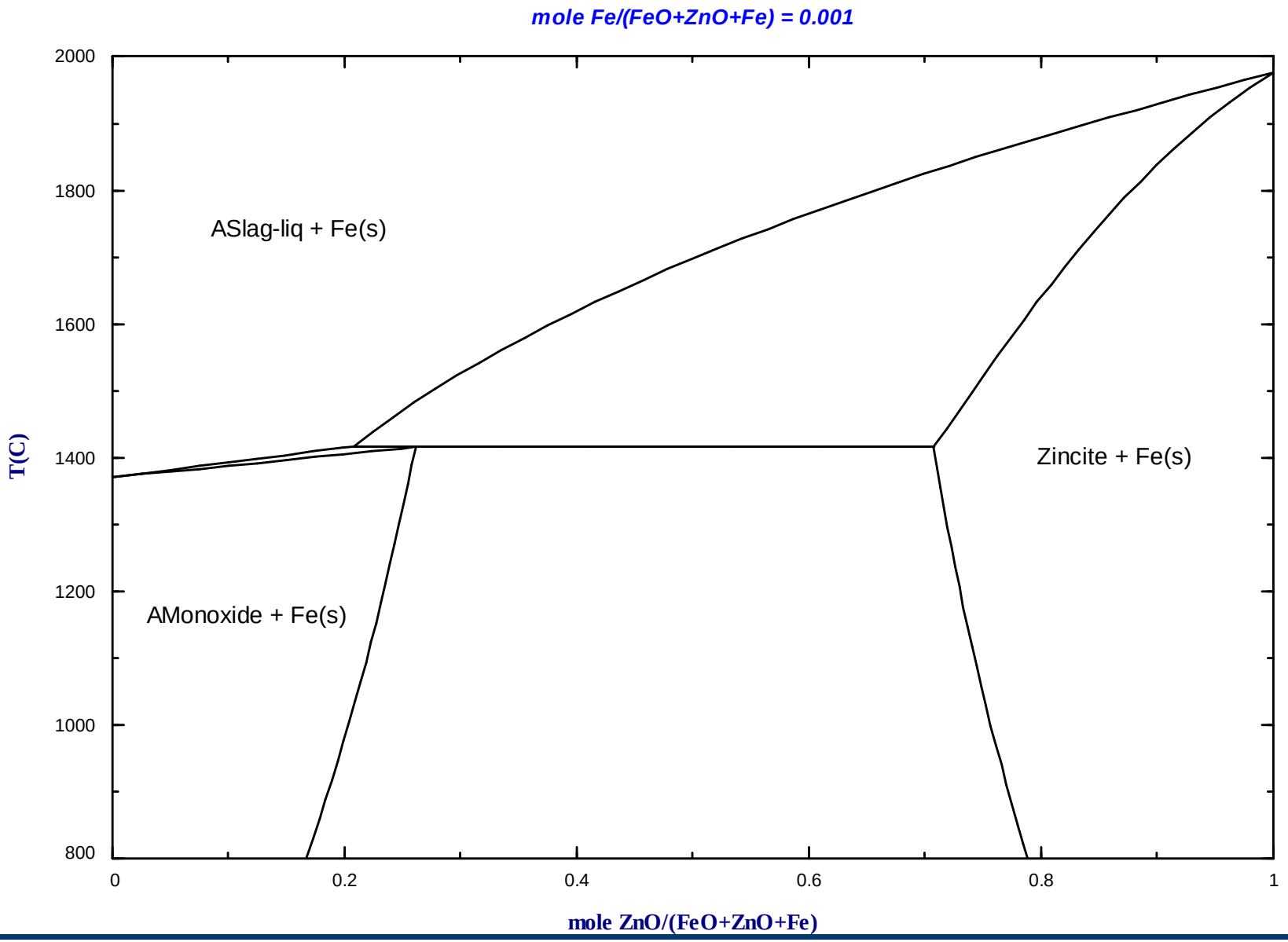
FeO-ZnO System in Equilibrium with Metals



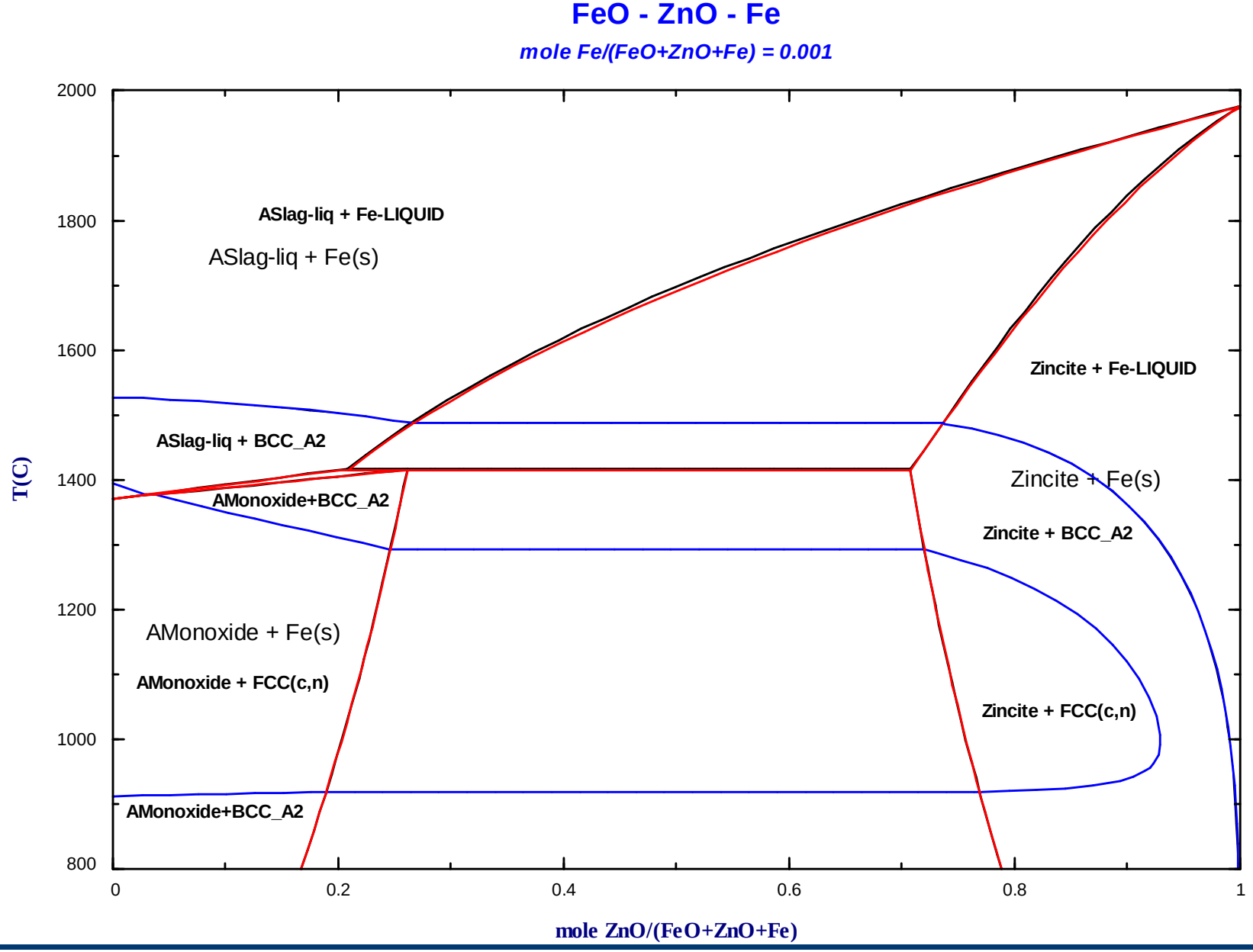
Oxide phases

Only one metal phase, Fe(s), from Fact53

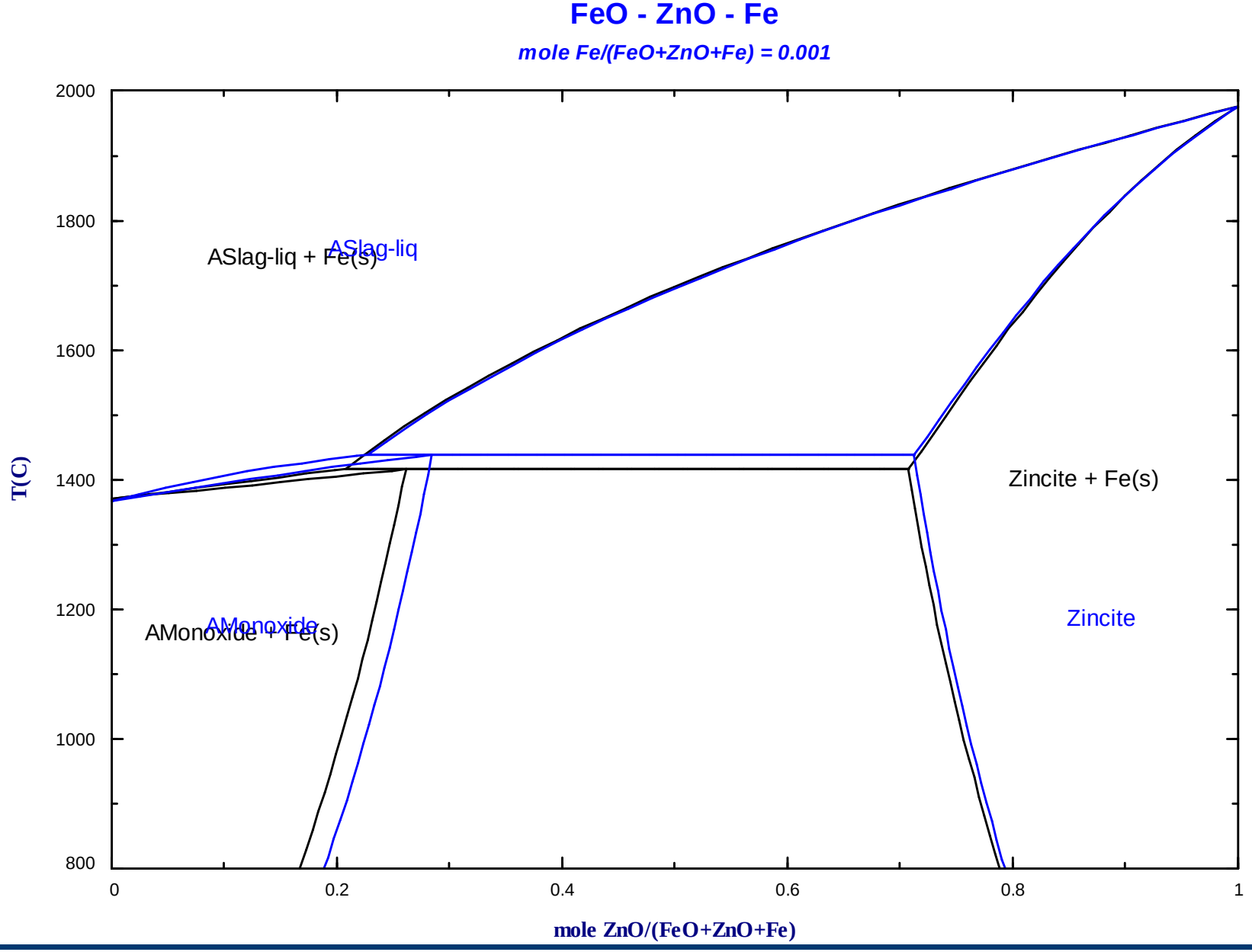
FeO-ZnO System in Equilibrium with Metals



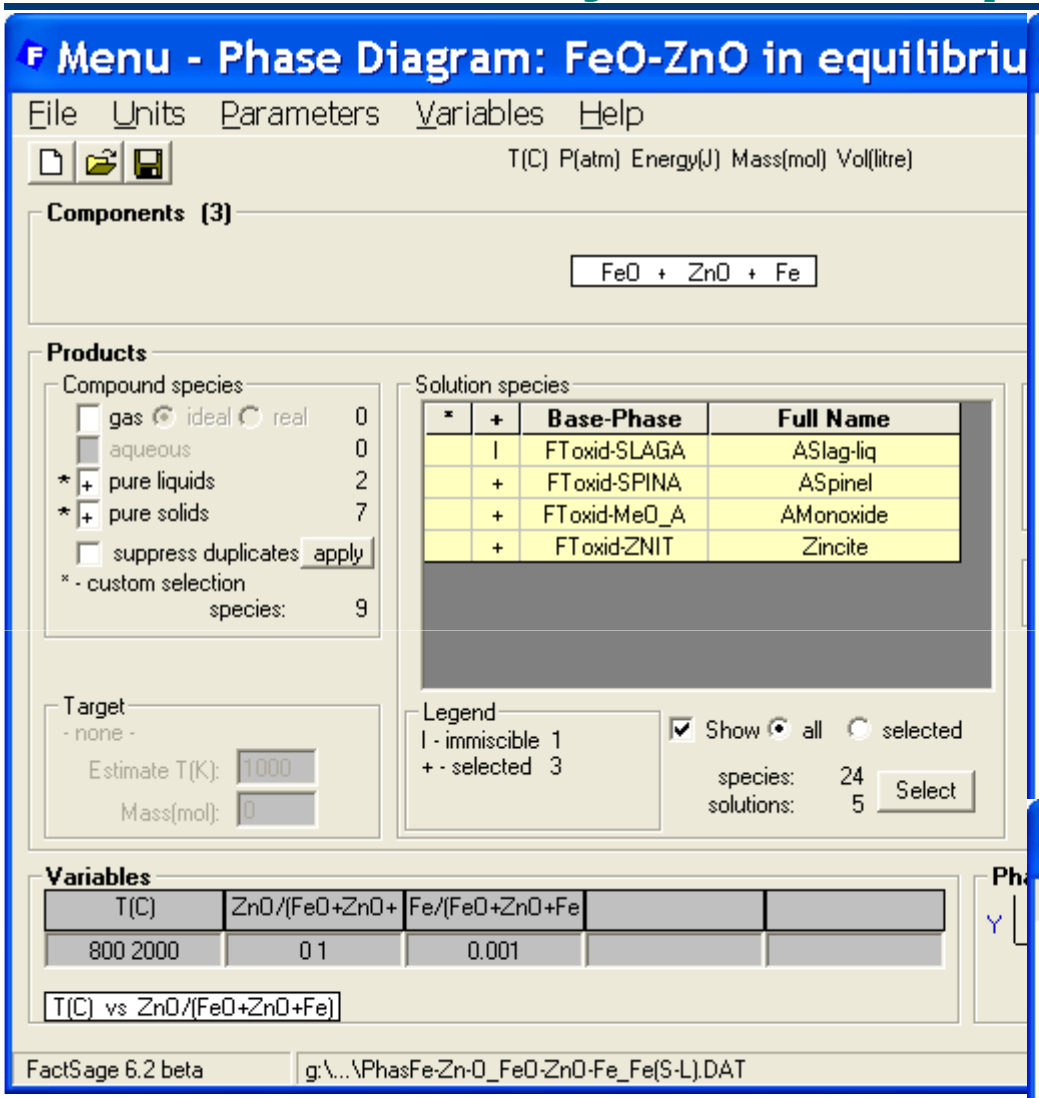
FeO-ZnO in Equilibrium with Metals: FSstel vs Fe(s)

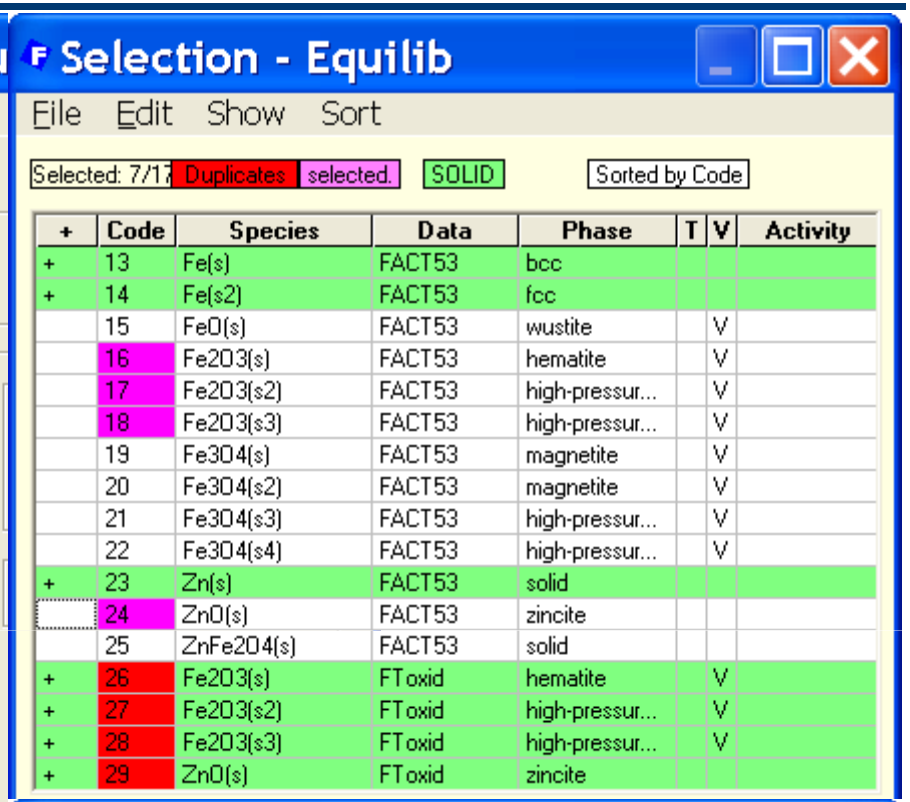


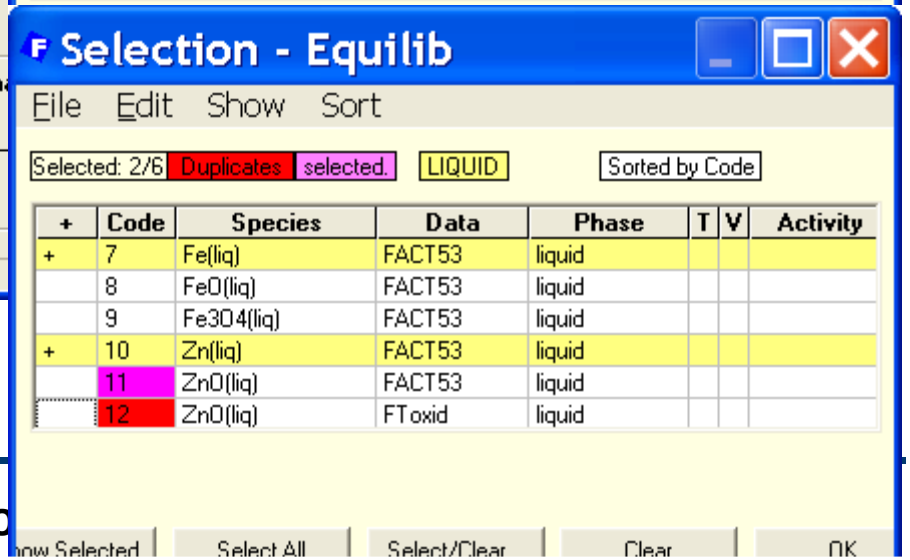
FeO-ZnO in Equilibrium with Fe(s) vs FeO-ZnO



FeO-ZnO System in Equilibrium with Metals



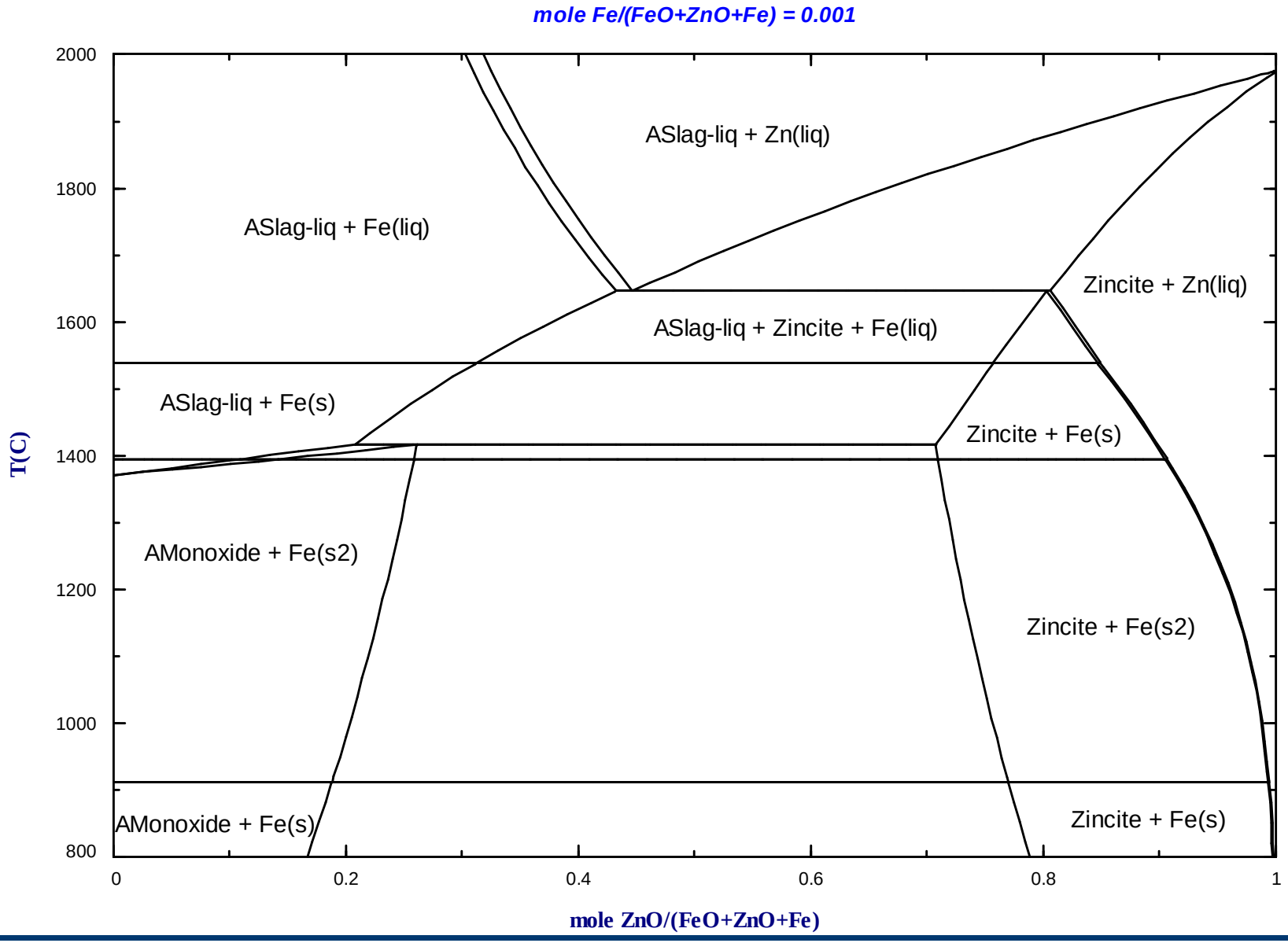




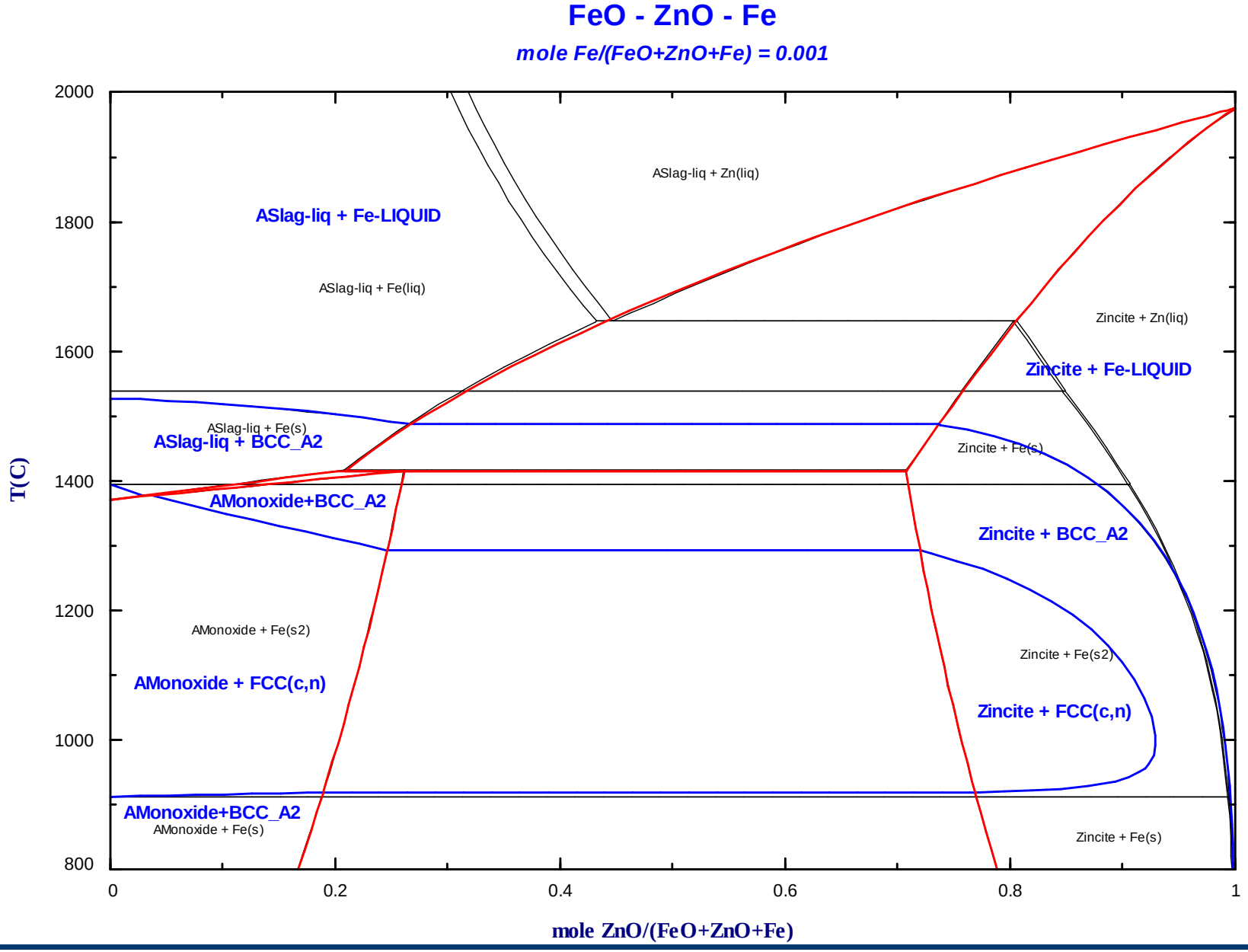
Oxide phases

Pure Fe and Zn (sol. and liq.) from Fact53

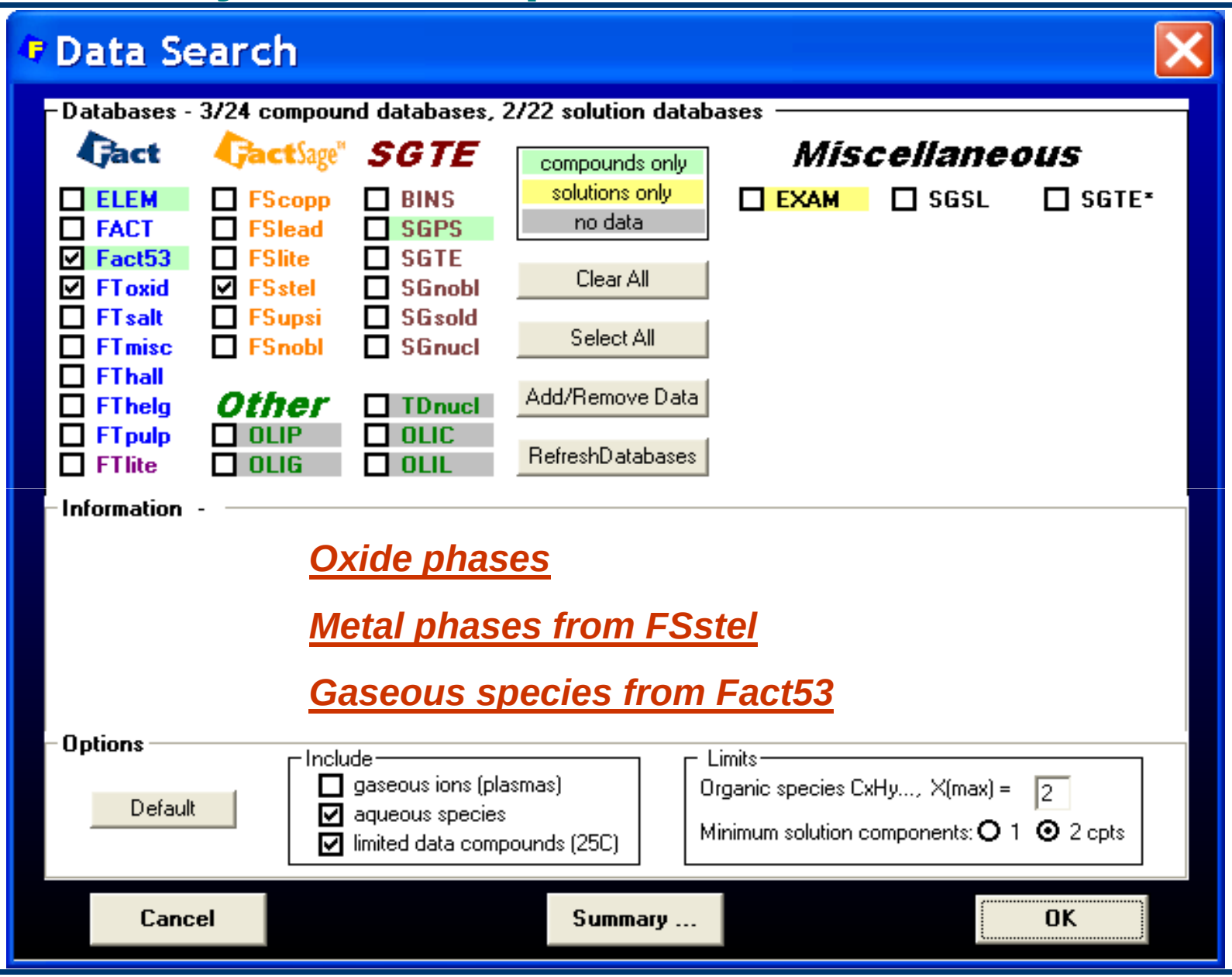
FeO-ZnO System in Equilibrium with Metals



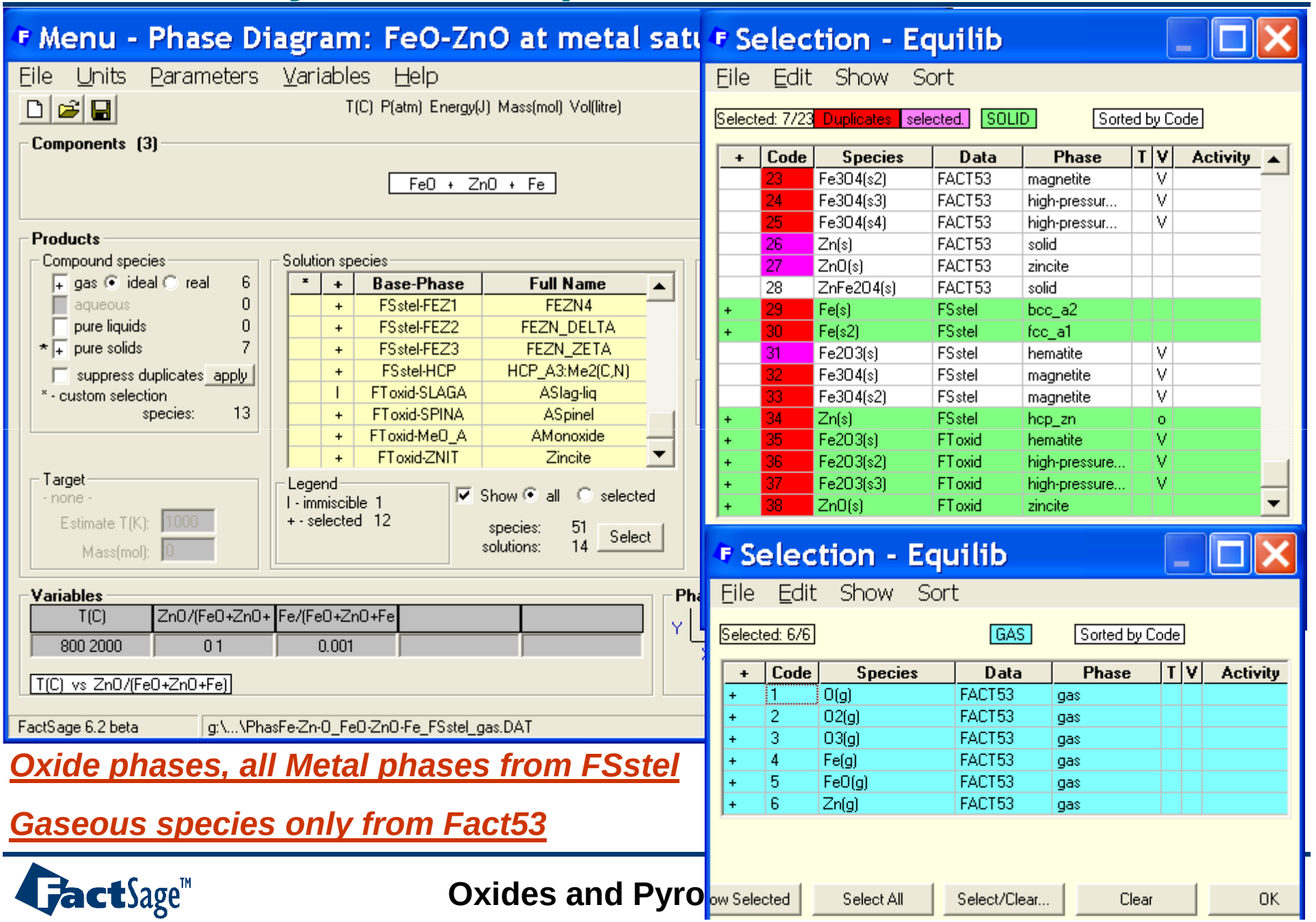
FeO-ZnO in Equilibrium with Fe & Zn (s,l) vs FSstel



FeO-ZnO System in Equilibrium with Metals and Gas



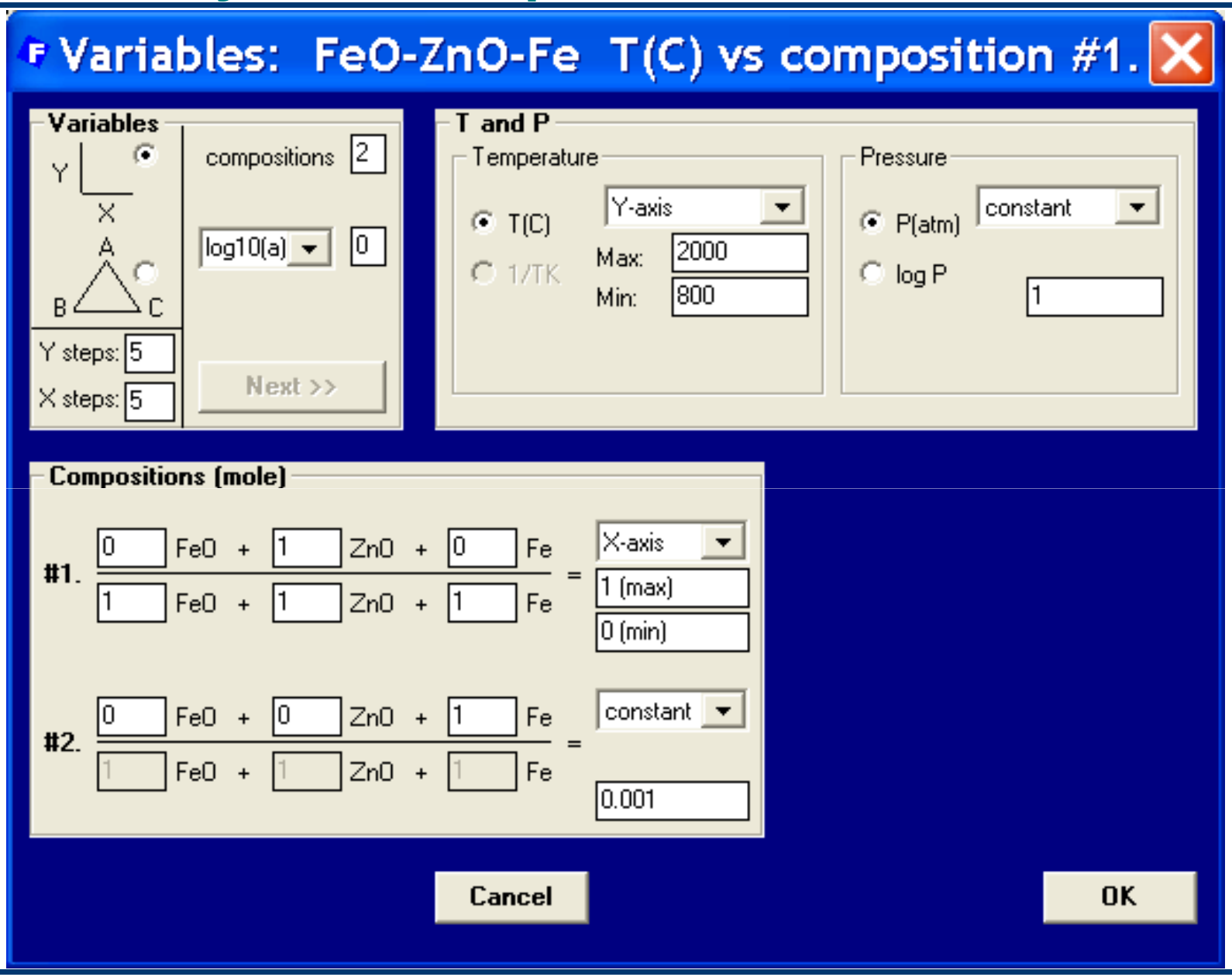
FeO-ZnO System in Equilibrium with Metals and Gas



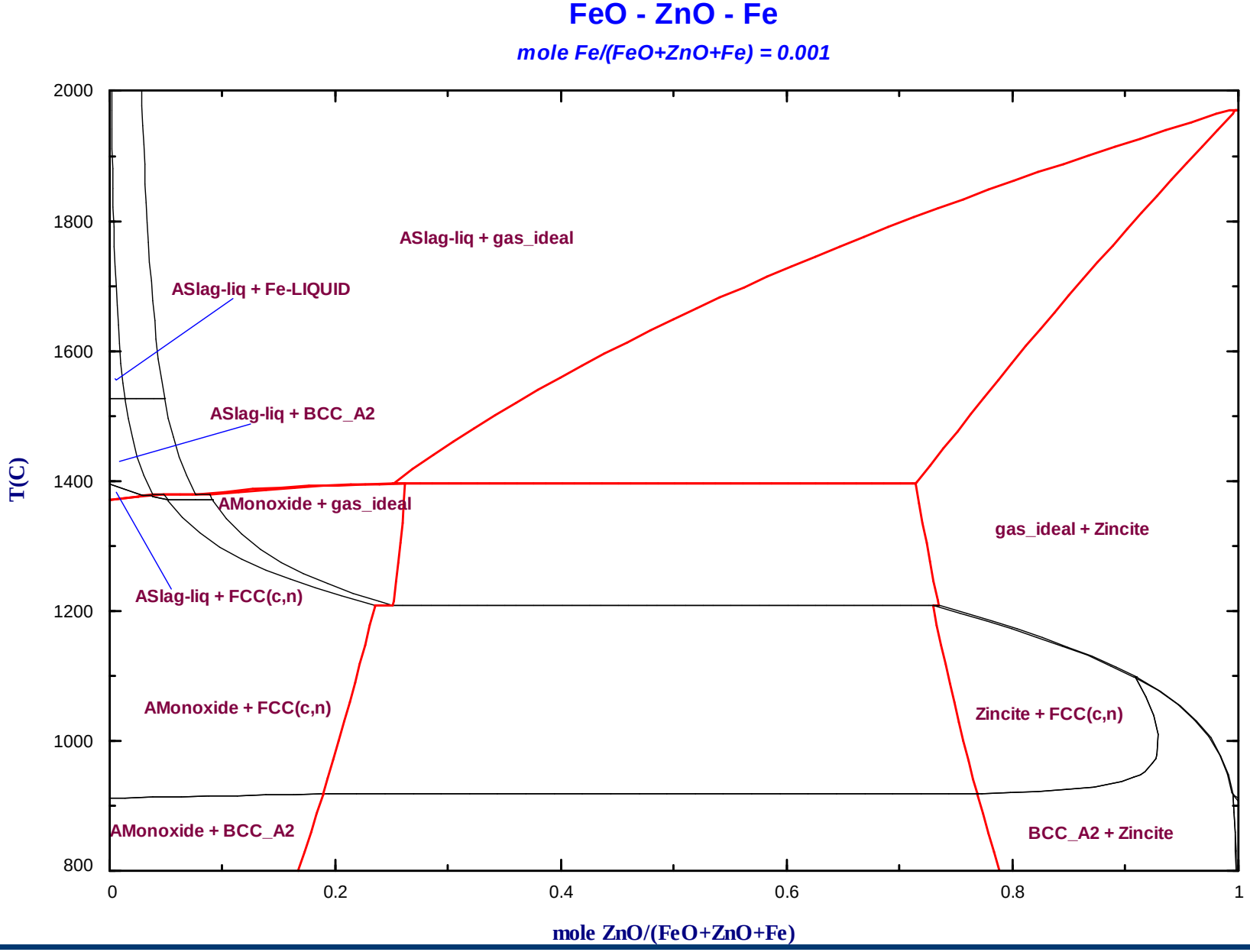
Oxide phases, all Metal phases from FSstel

Gaseous species only from Fact53

FeO-ZnO System in Equilibrium with Metals and Gas

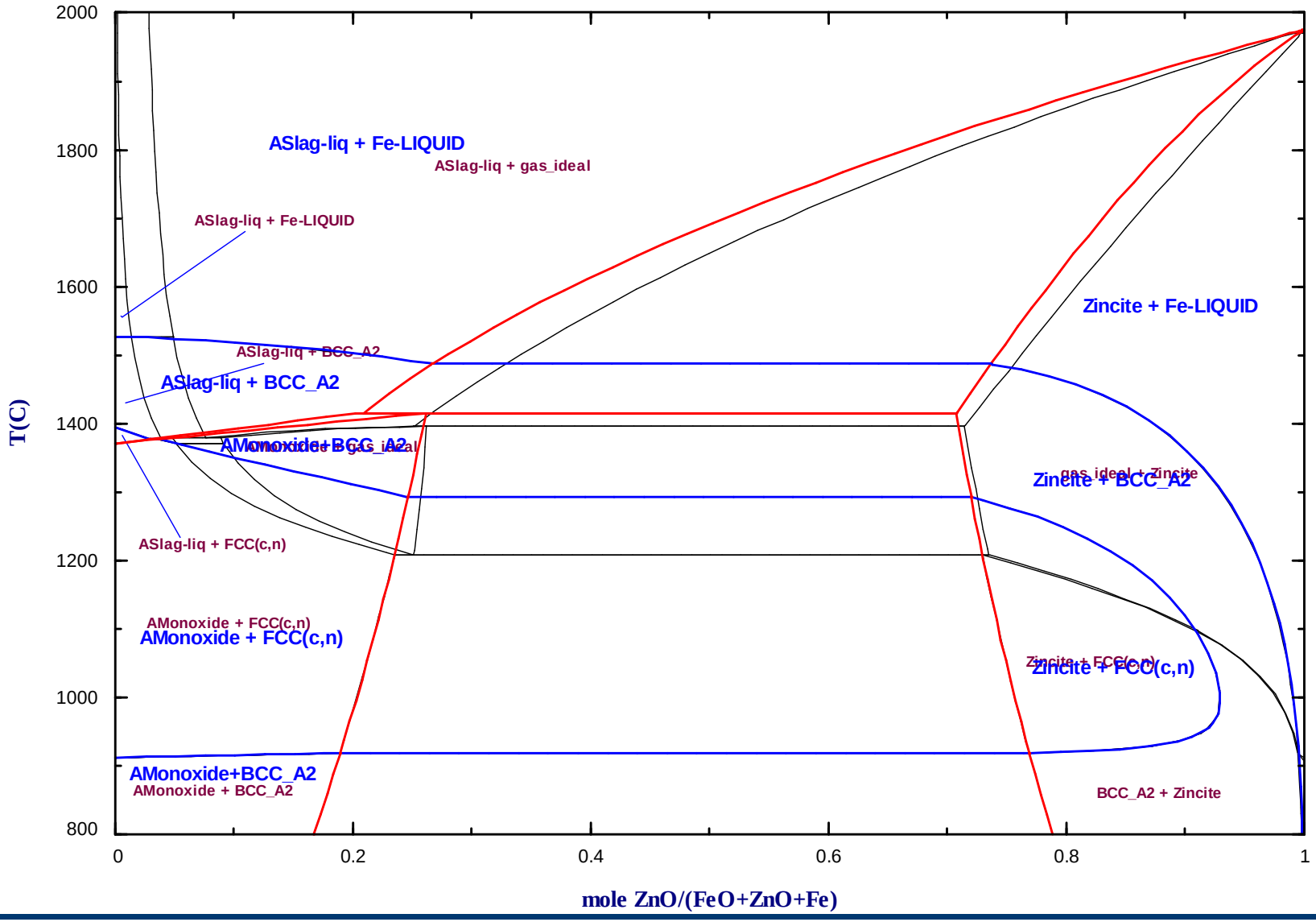


FeO-ZnO System in Equilibrium with Metals and Gas

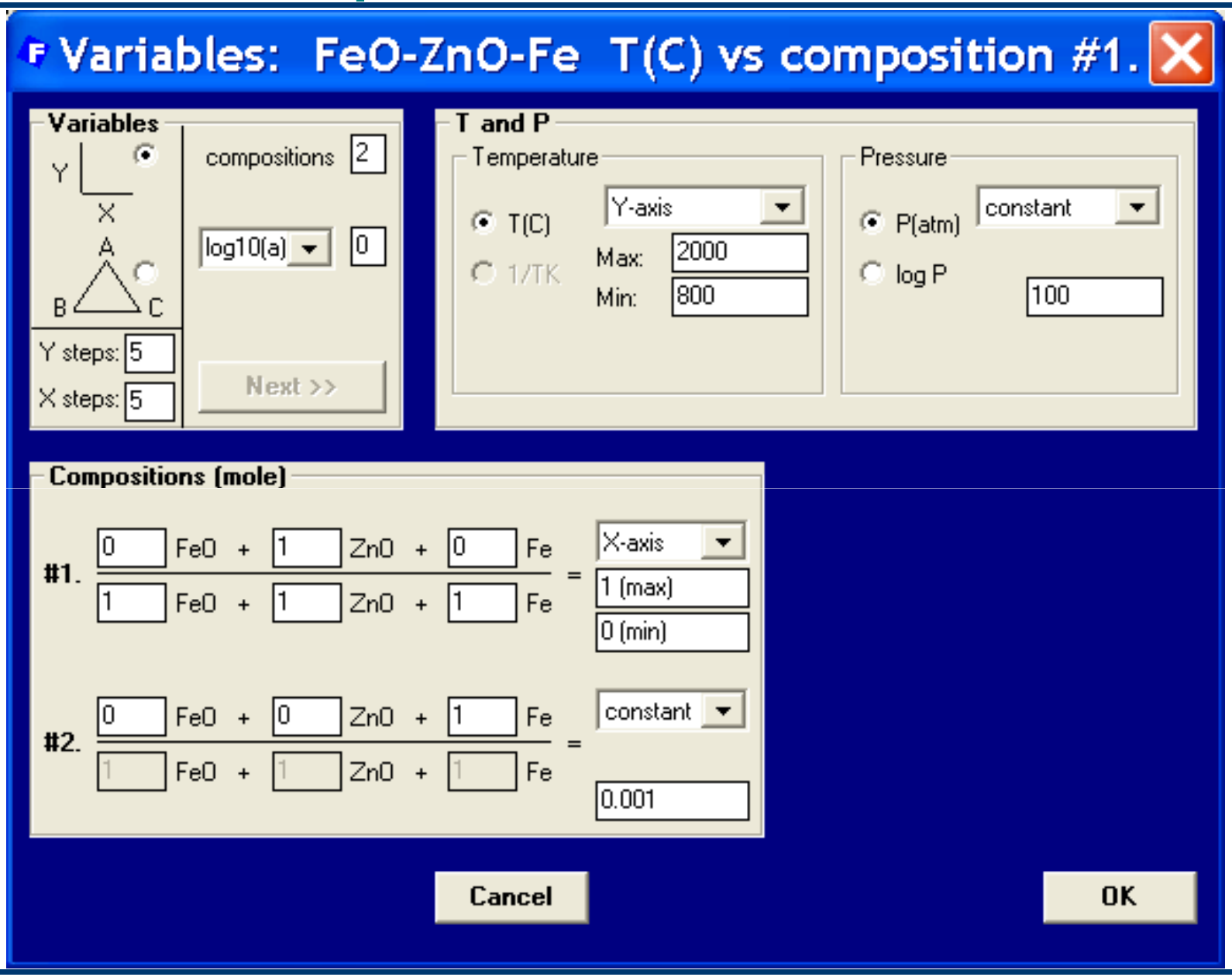


FeO-ZnO System in Equilibrium with Metals and Gas

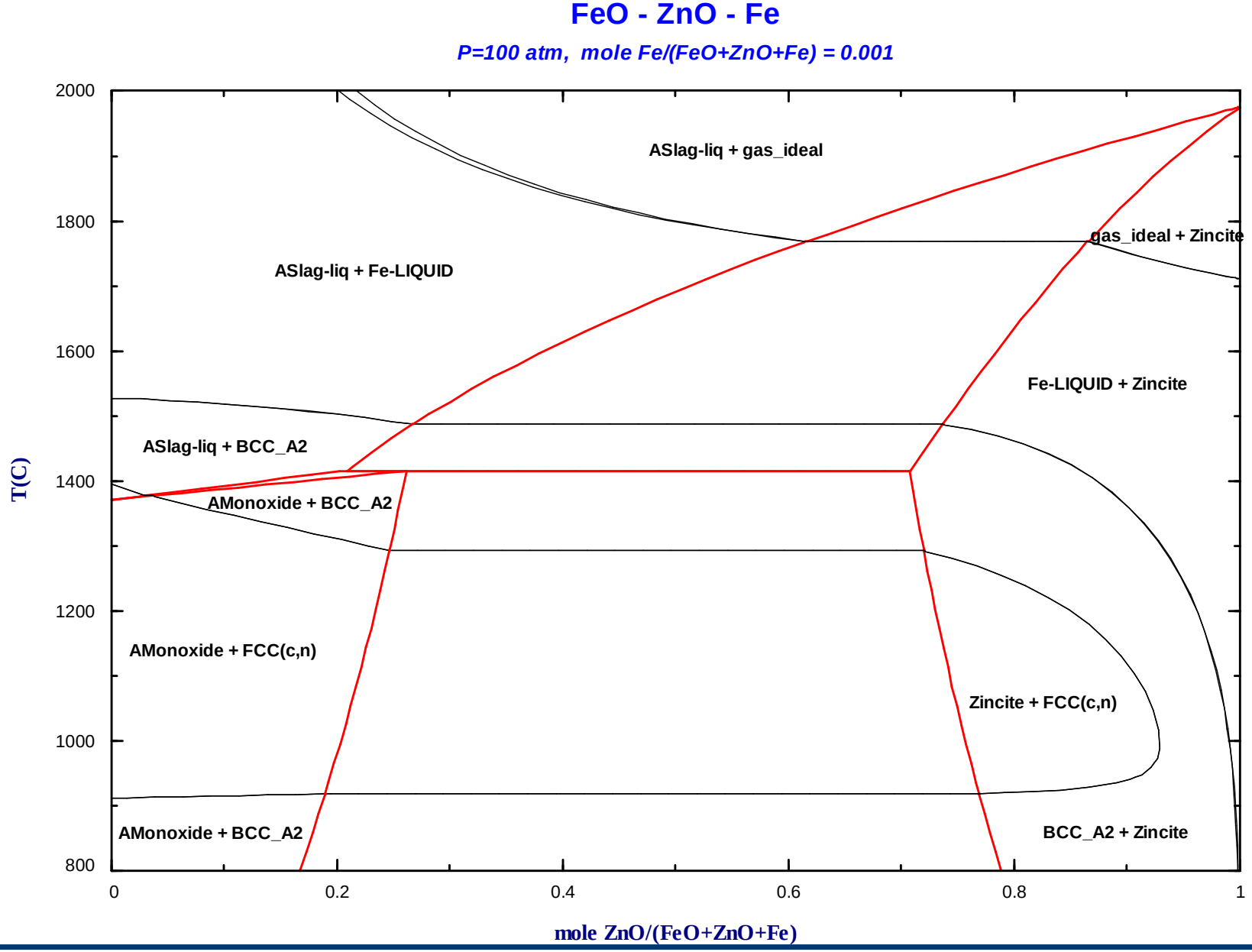
Red and blue curves are calculated without gas



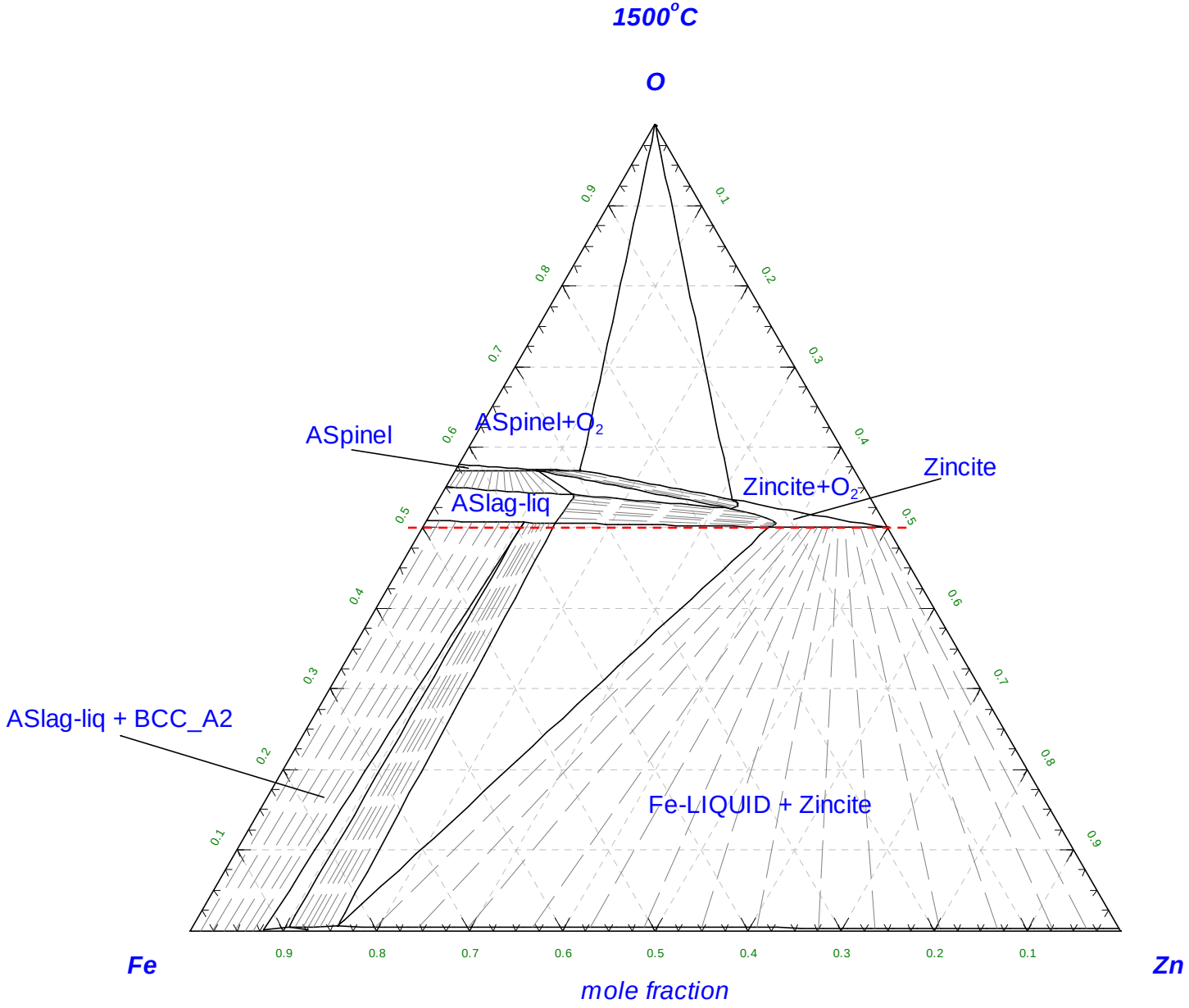
FeO-ZnO in Equilibrium with Metals at P=100 atm



FeO-ZnO in Equilibrium with Metals at P=100 atm



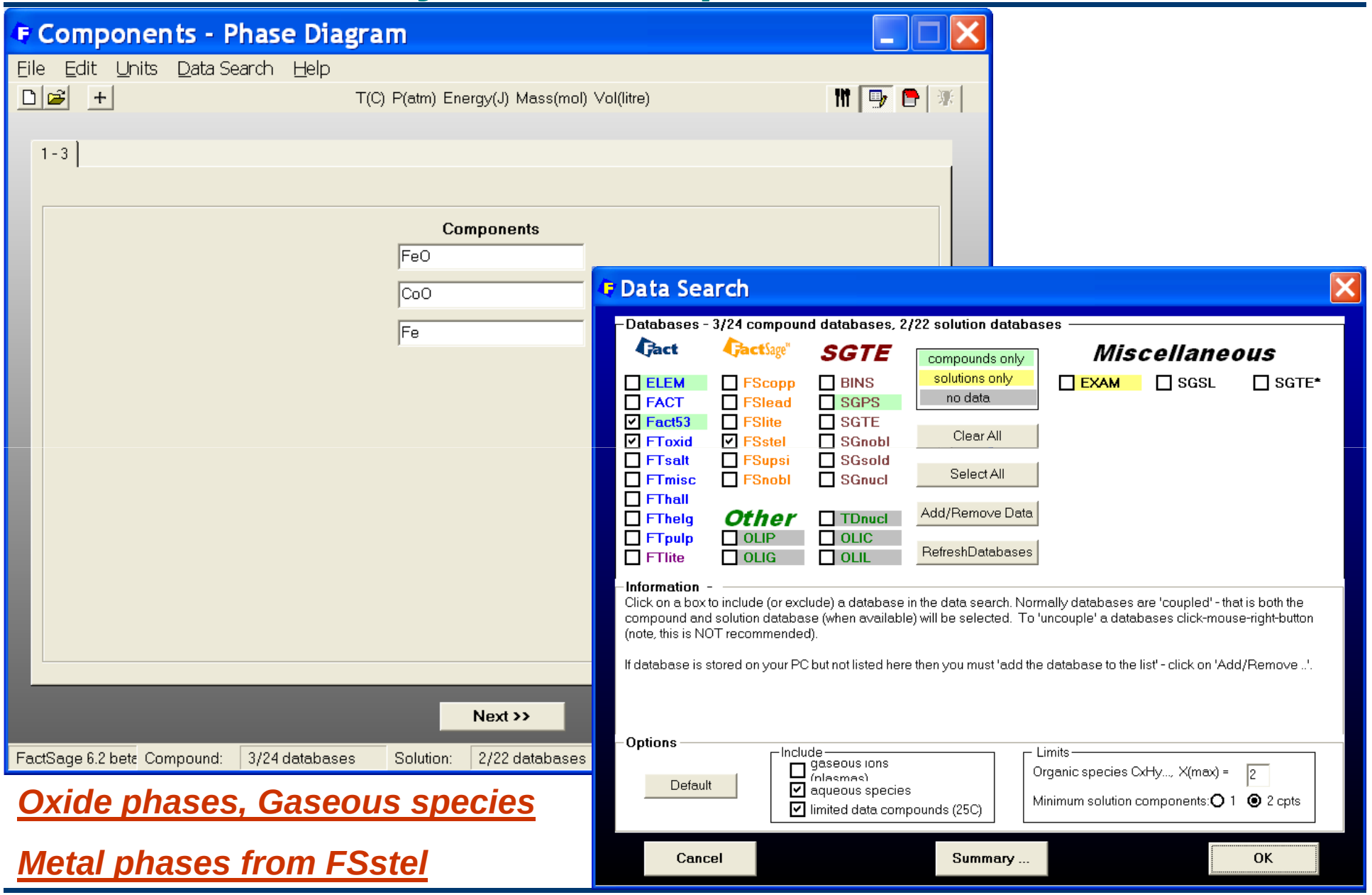
Fe-Zn-O System



Oxide Phase Diagrams under Reducing Conditions

- Metal phases must be selected
- Step a bit off an oxide section towards metals
- FSstel is needed to see the ***right metal phases*** in equilibrium
- Metal phases often have only a minor effect on ***oxide phase boundaries***
- If you do not have FSstel or SGTE database for metal phases, select metals from Fact53
- Do not forget the gas phase

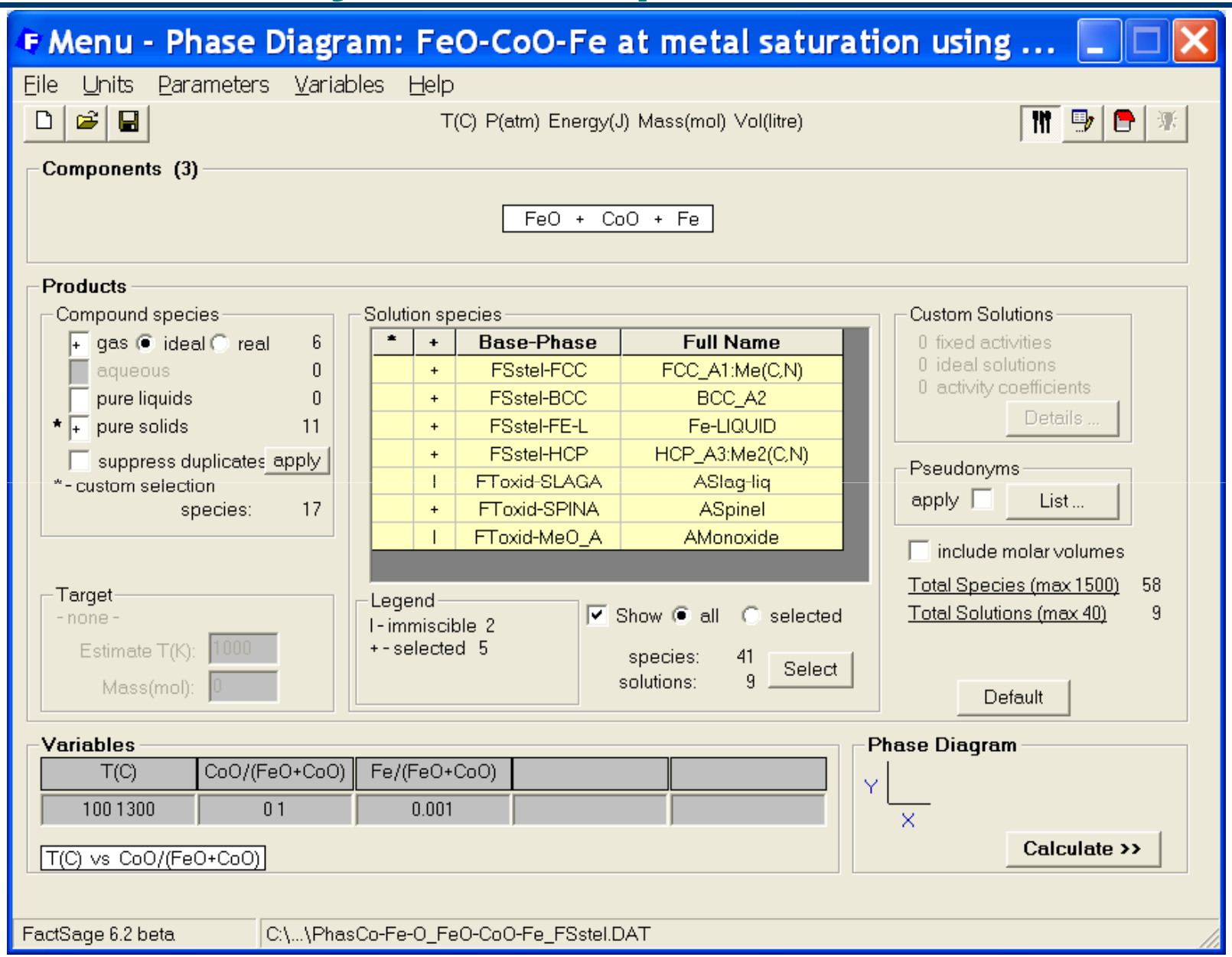
FeO-CoO System in Equilibrium with Metals



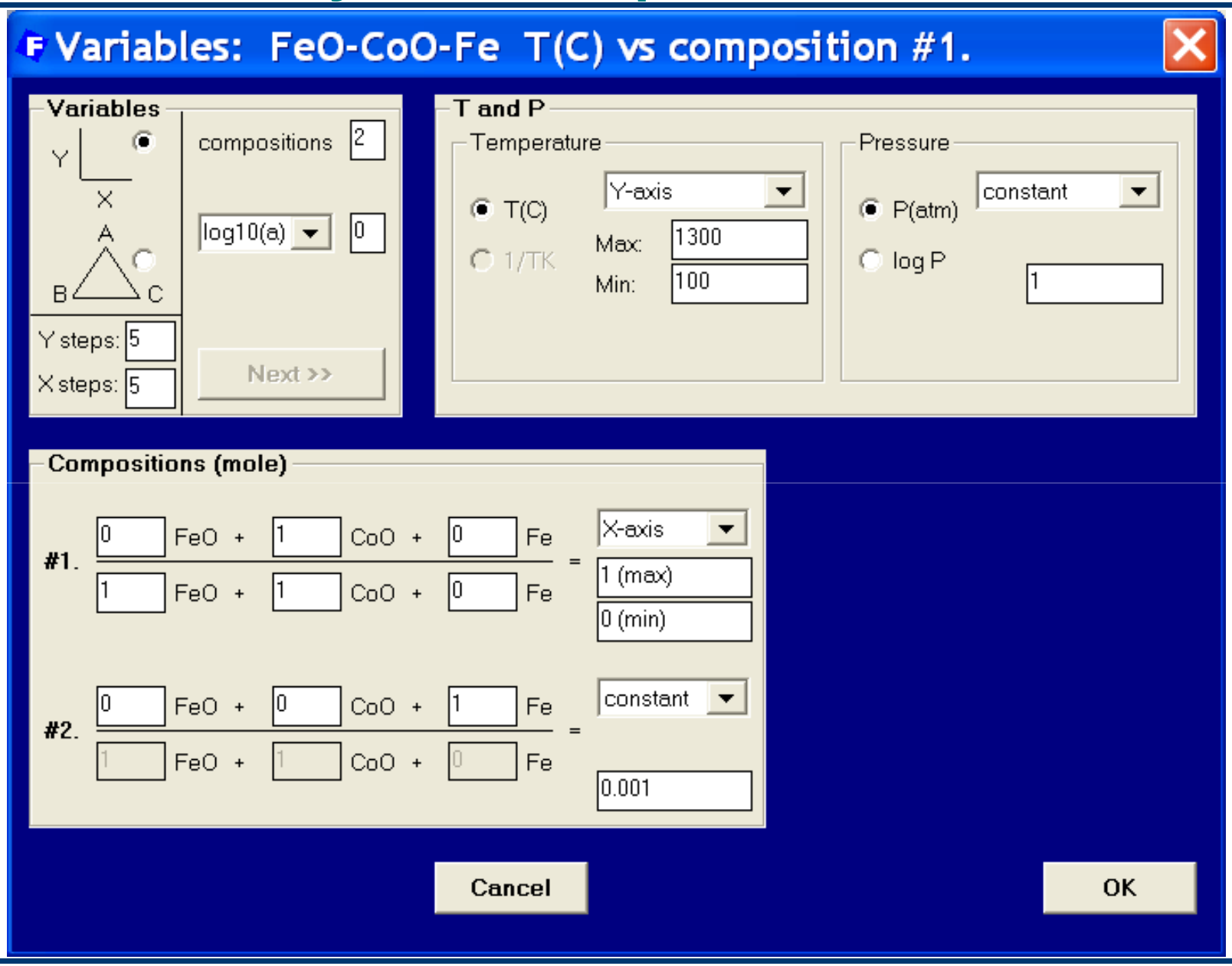
Oxide phases, Gaseous species

Metal phases from FSstel

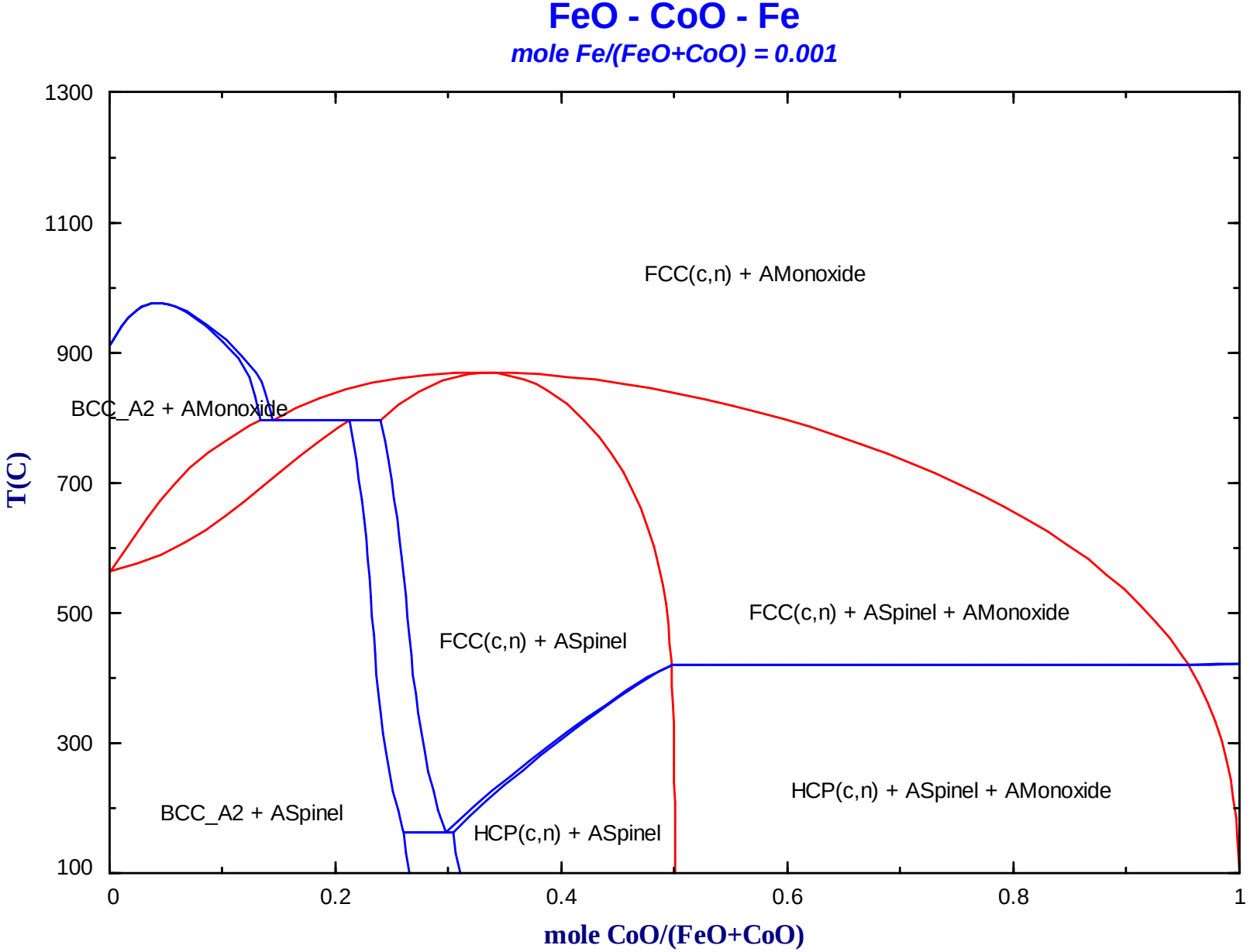
FeO-CoO System in Equilibrium with Metals



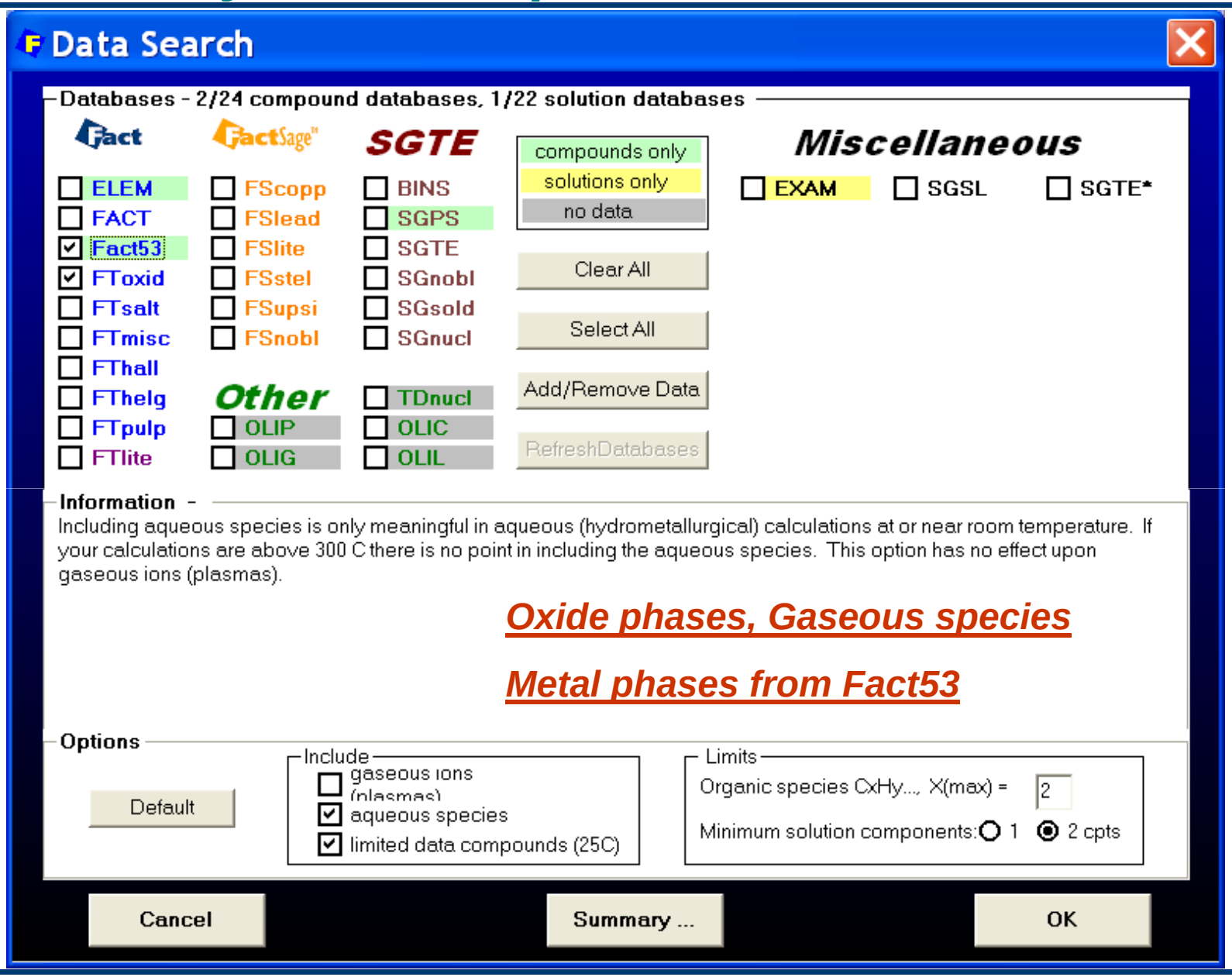
FeO-CoO System in Equilibrium with Metals



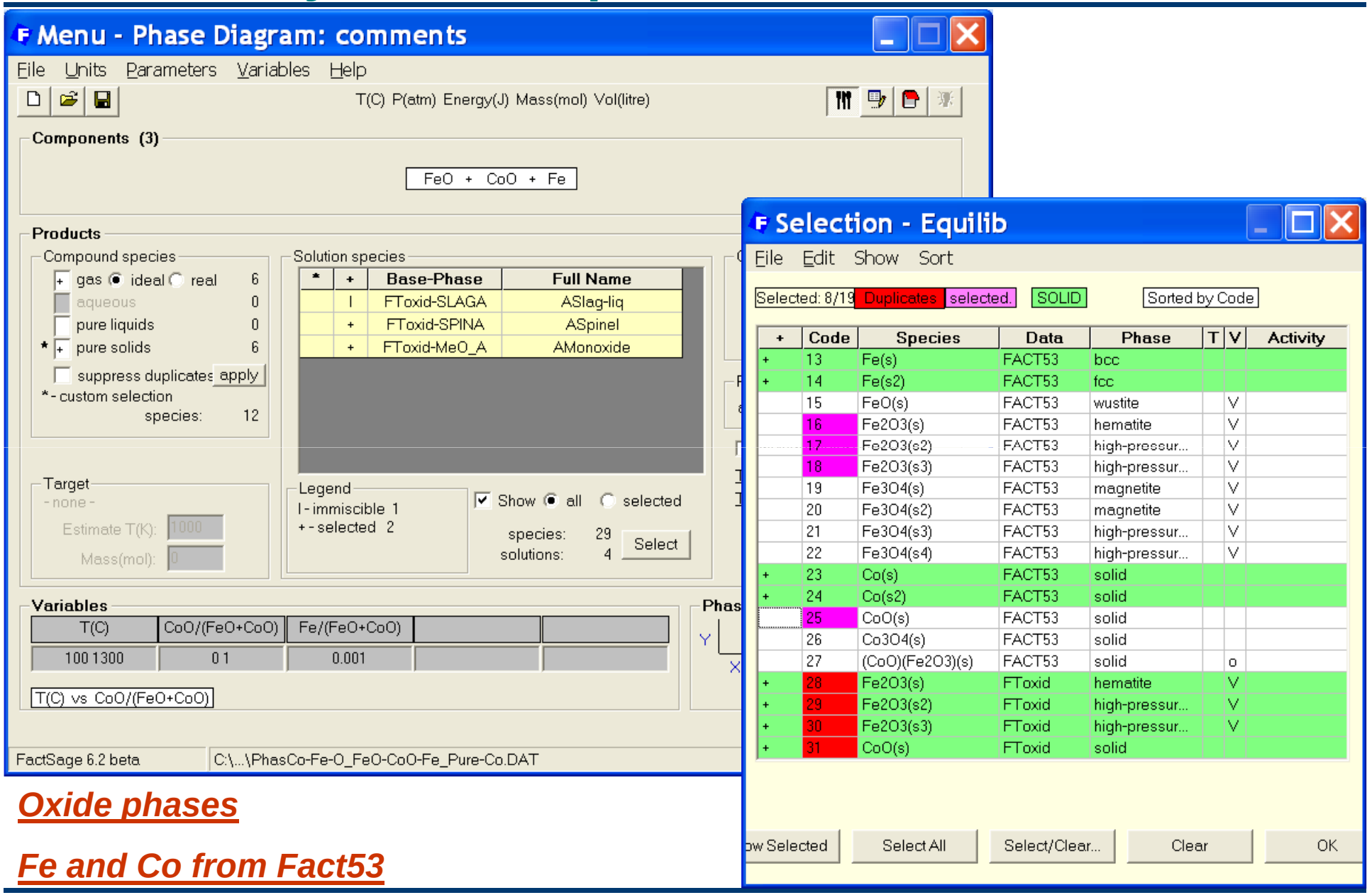
FeO-CoO System in Equilibrium with Metals



FeO-CoO System in Equilibrium with Pure Fe and Co



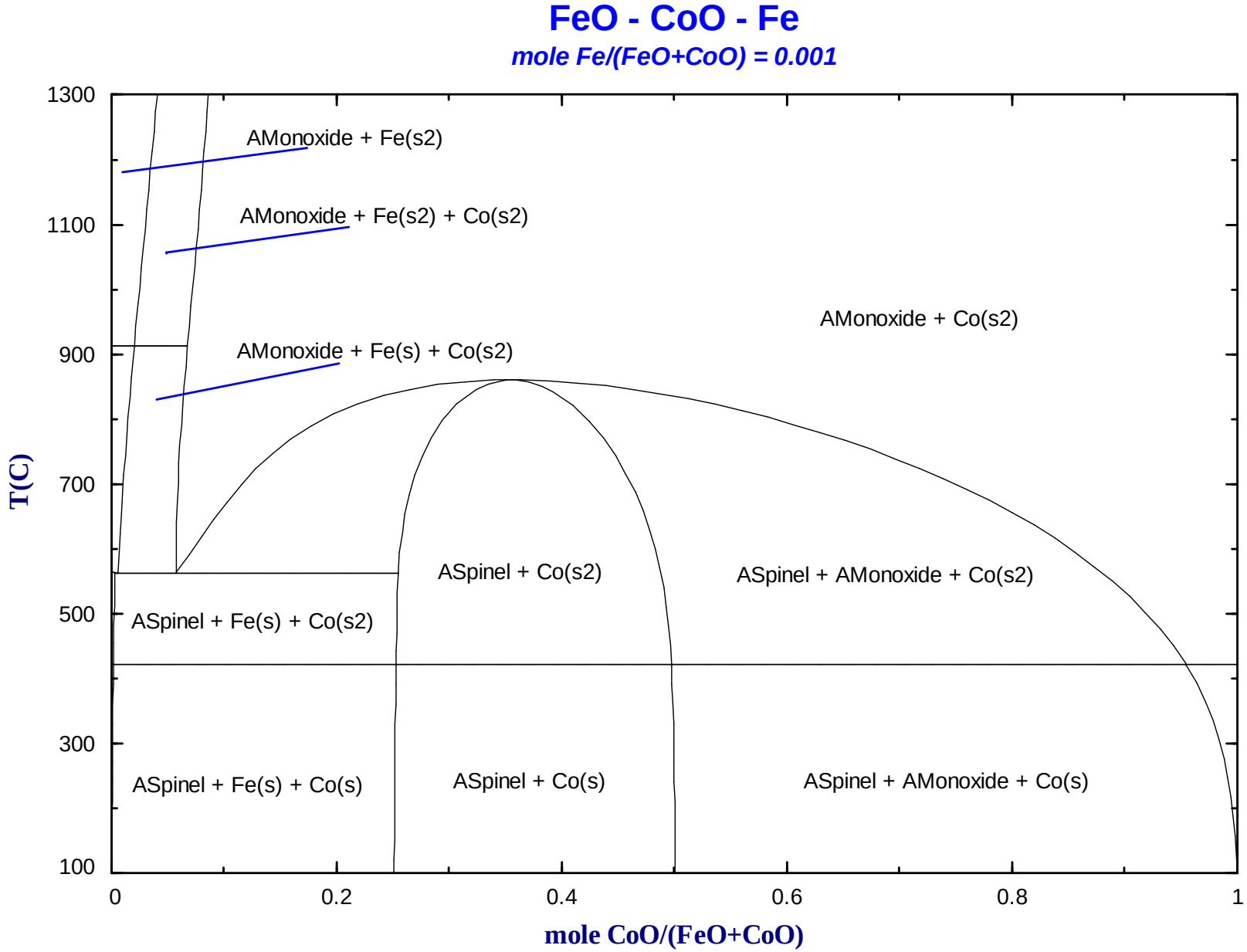
FeO-CoO System in Equilibrium with Pure Fe and Co



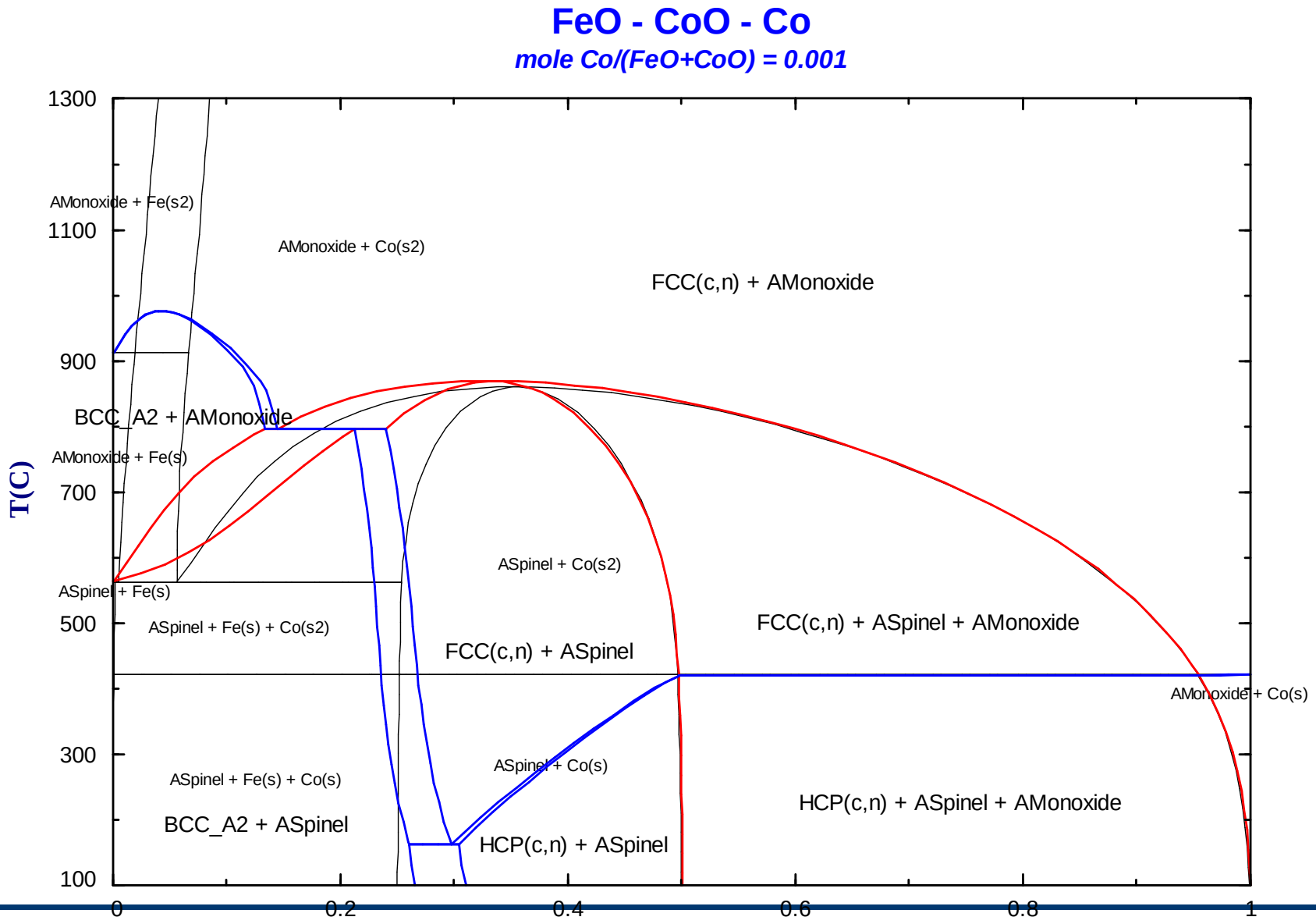
Oxide phases

Fe and Co from Fact53

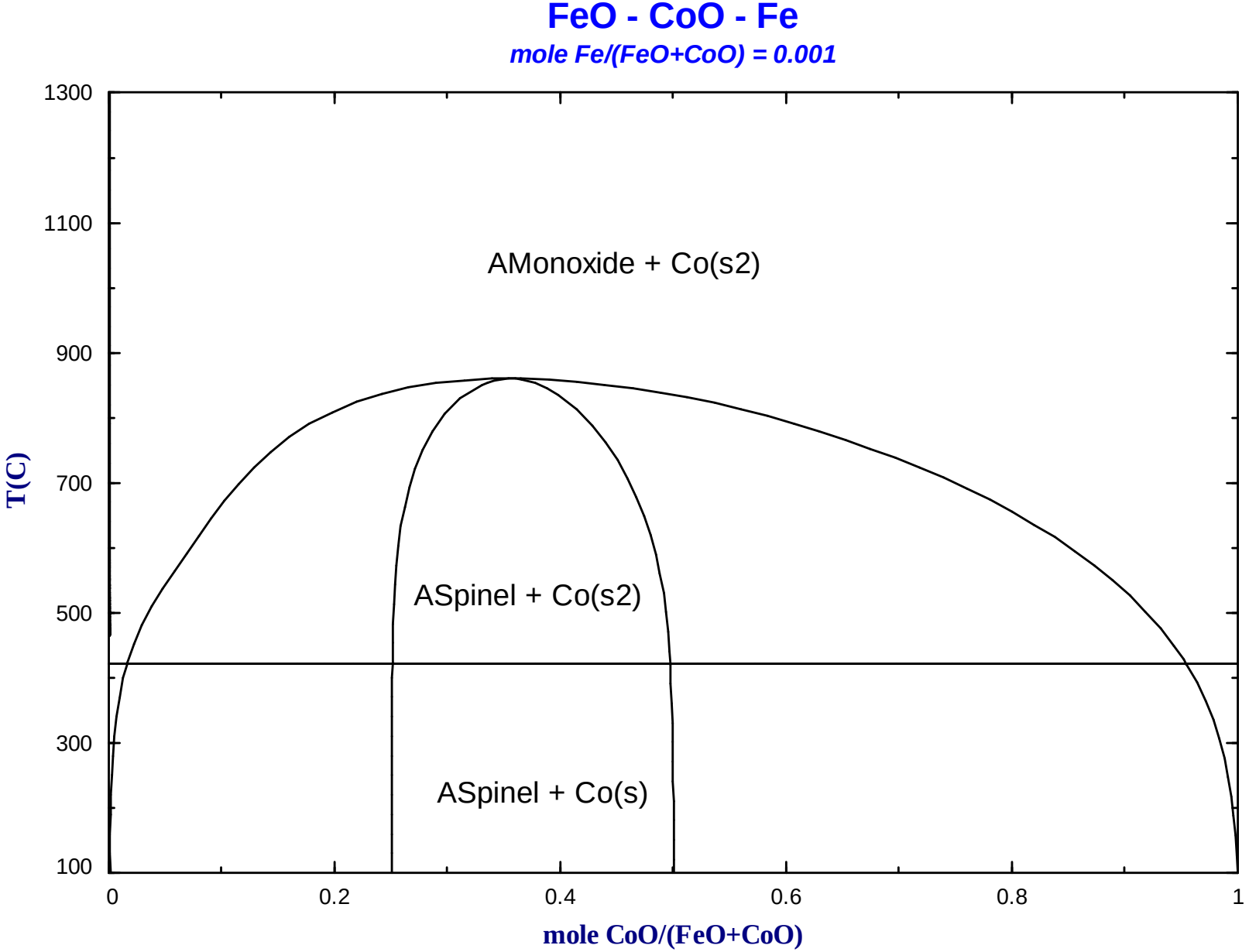
FeO-CoO System in Equilibrium with Pure Fe and Co



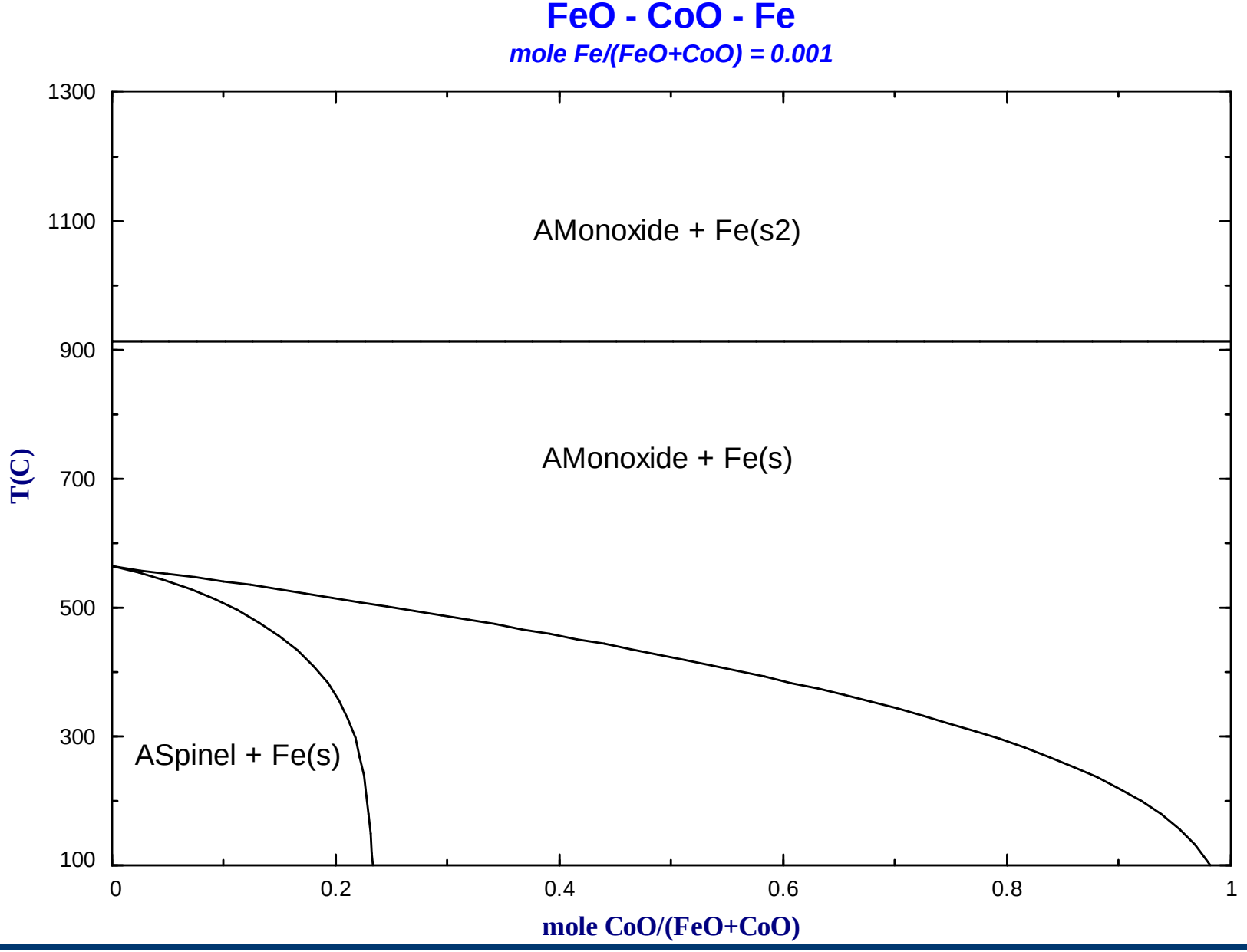
FeO-CoO in Equilibrium with Fe and Co vs FSstel



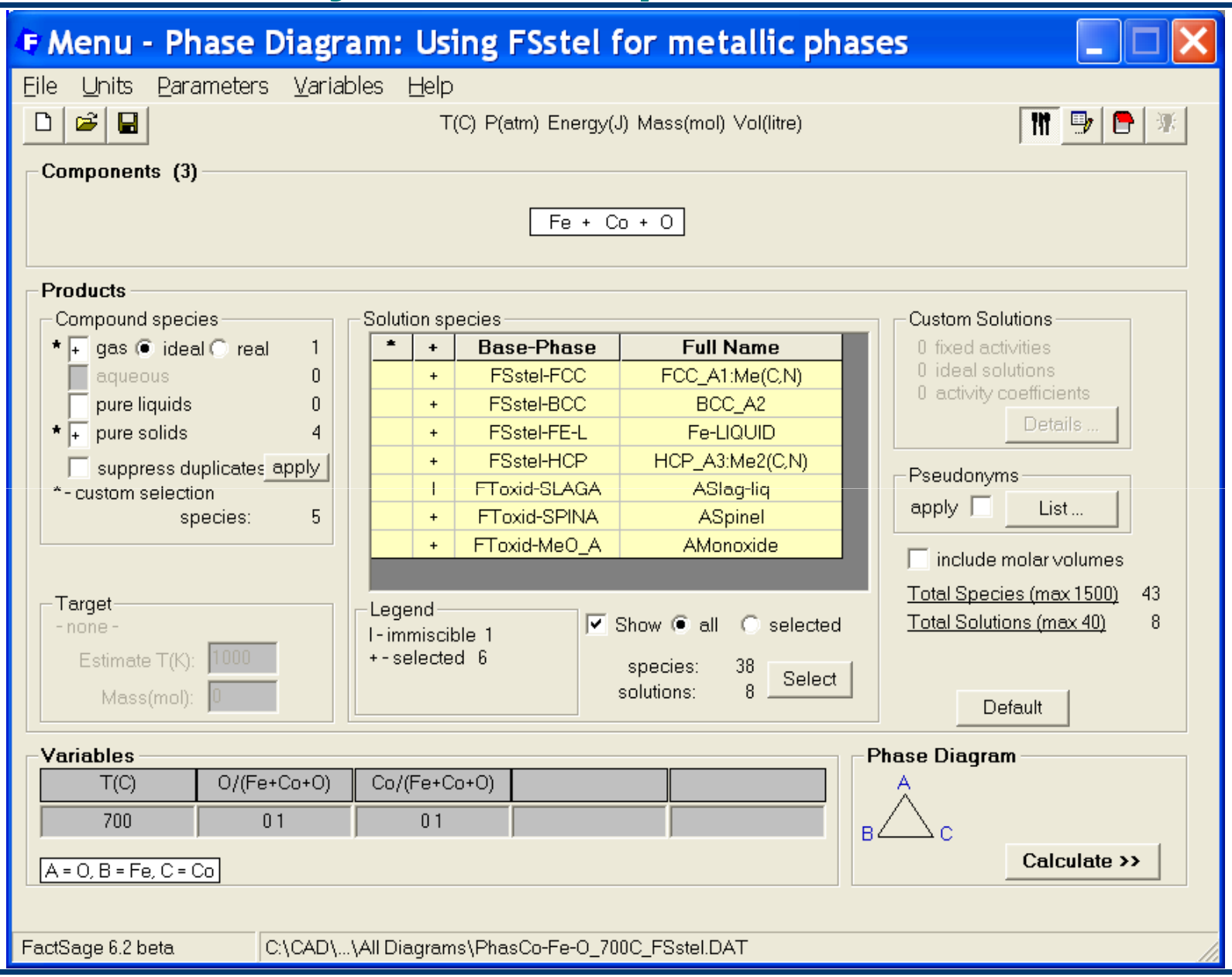
FeO-CoO System in Equilibrium with Pure Co



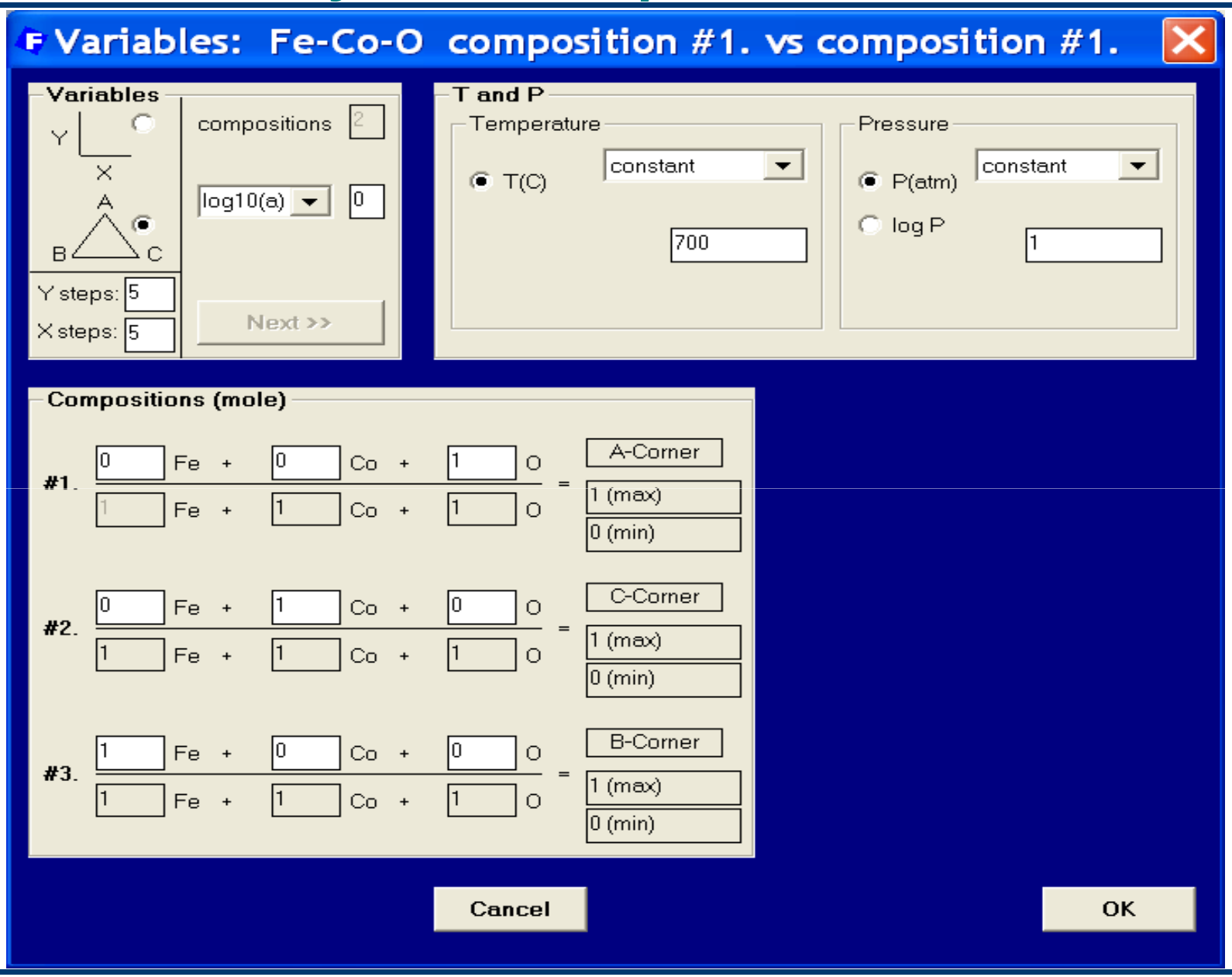
FeO-CoO System in Equilibrium with Pure Fe



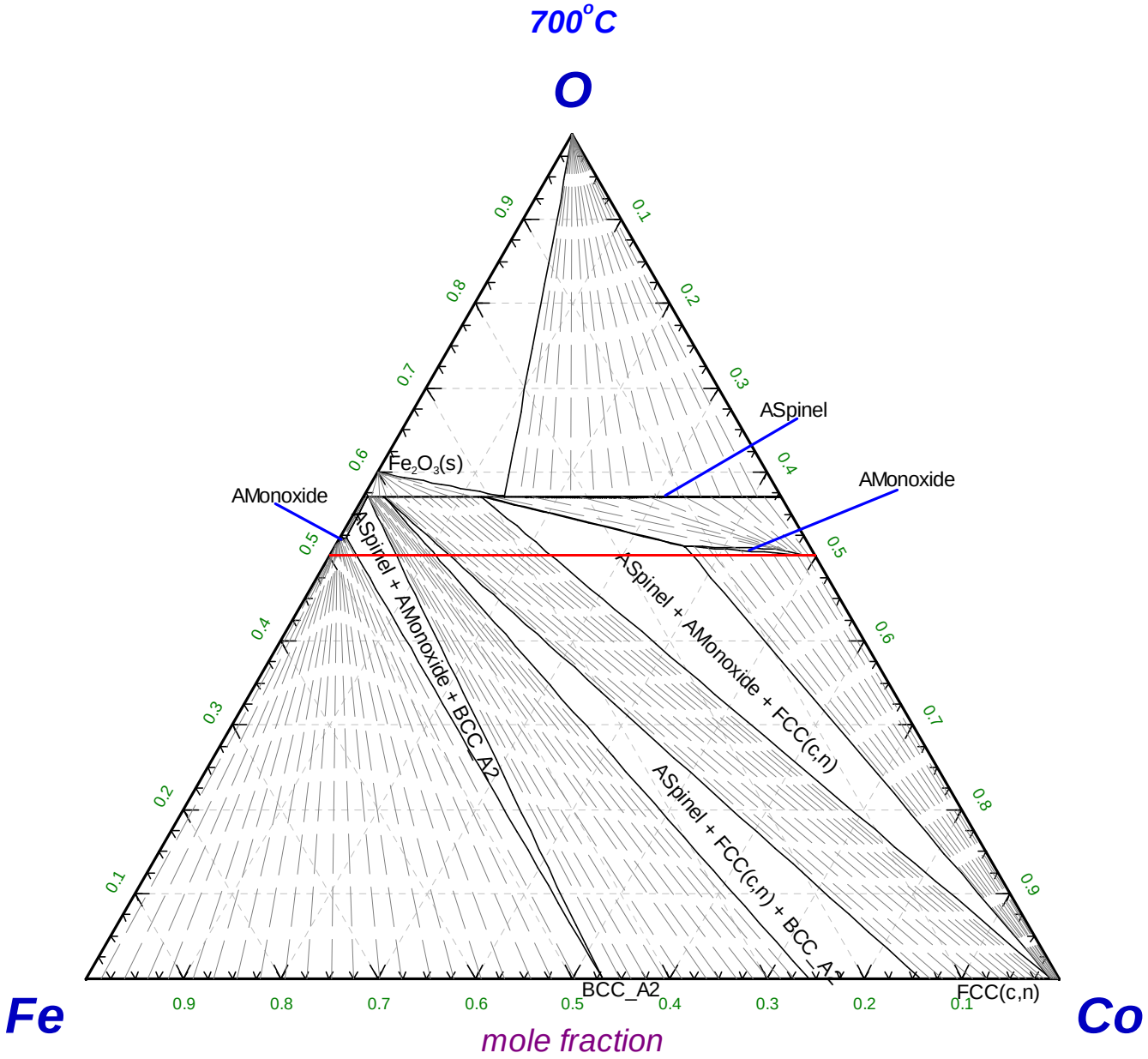
Fe-Co-O System in Equilibrium with Metals



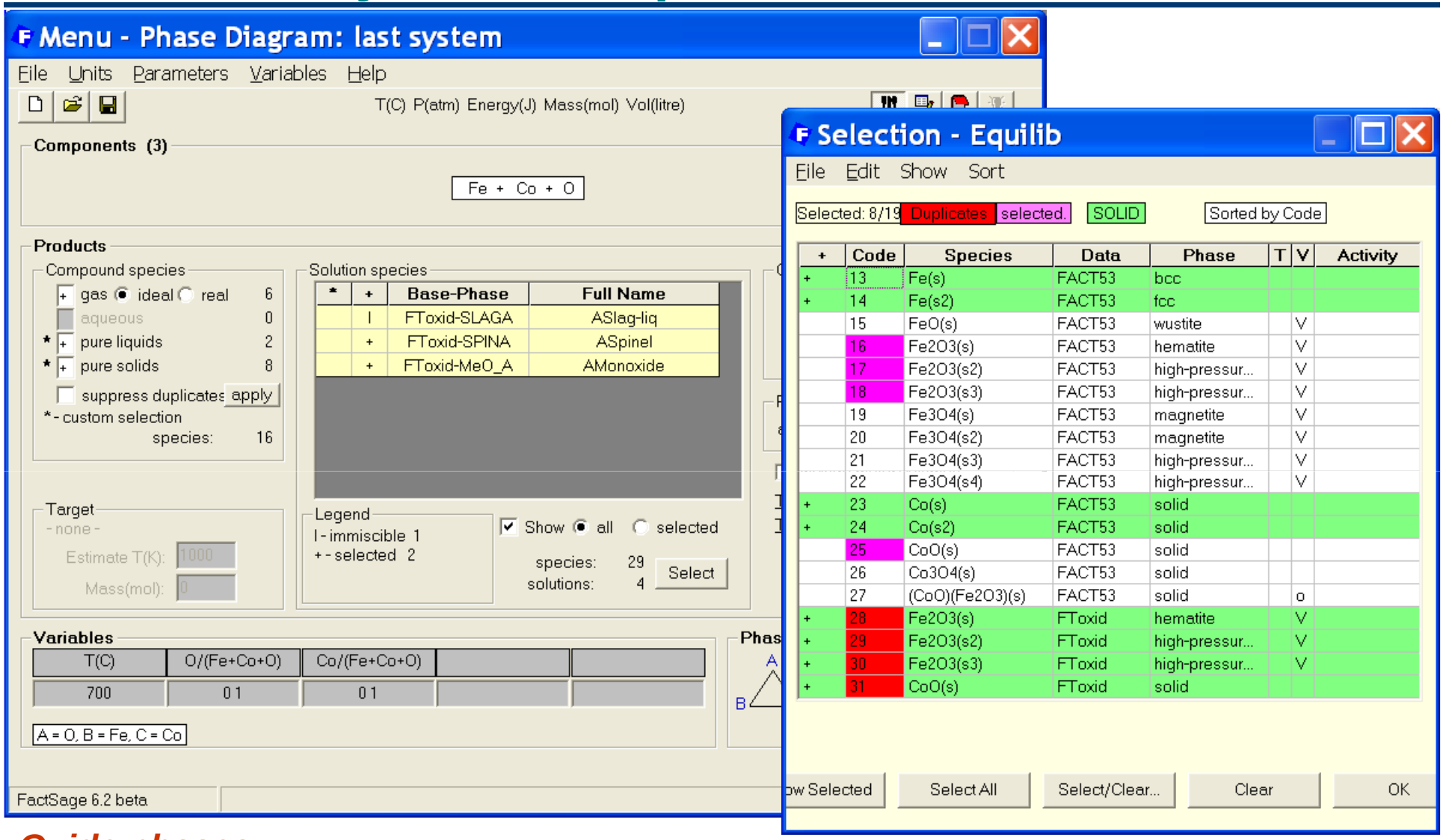
Fe-Co-O System in Equilibrium with Metals



Fe-Co-O System in Equilibrium with Metals



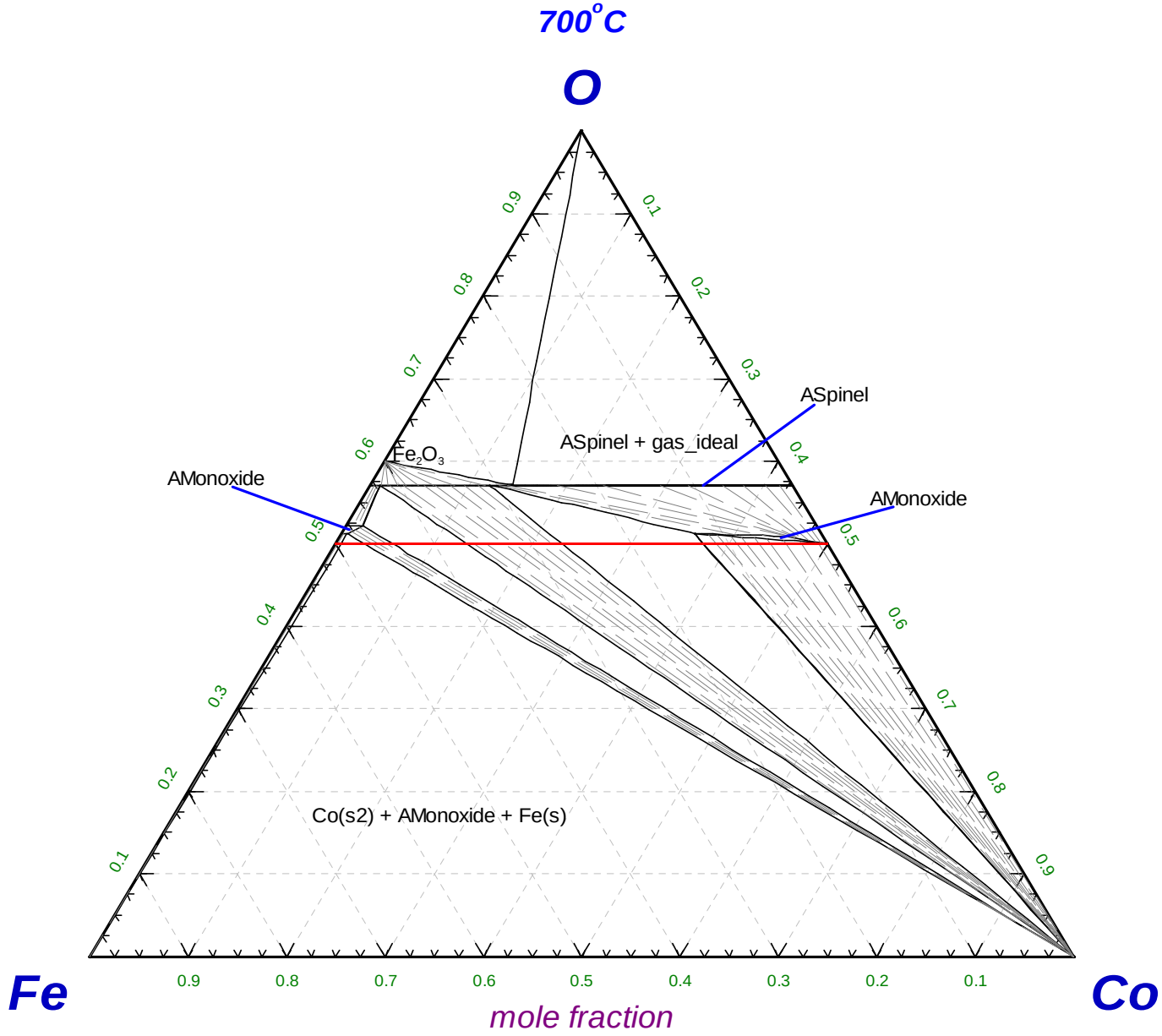
Fe-Co-O System in Equilibrium with Pure Metals



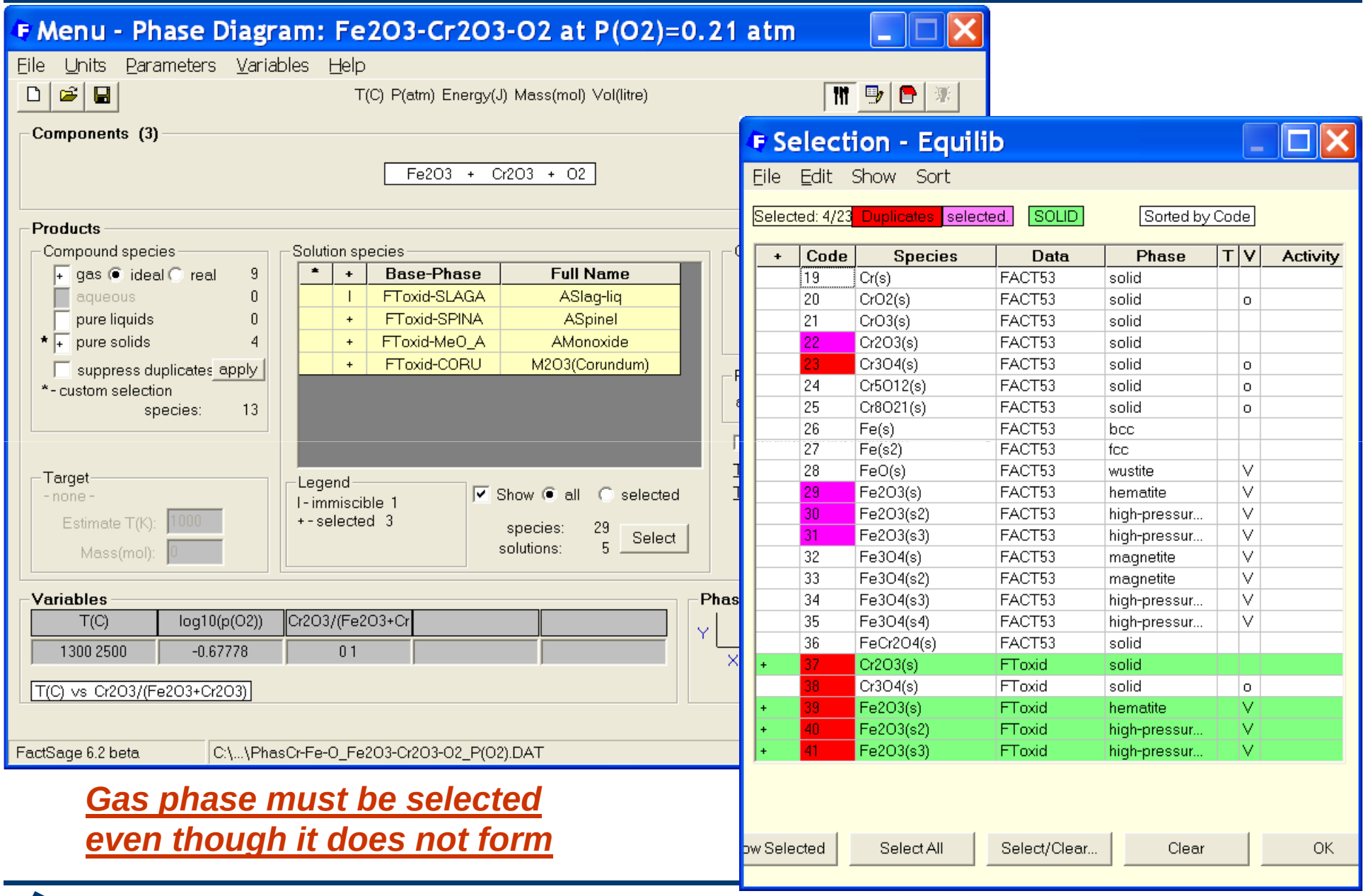
Oxide phases

Fe and Co from Fact53

Fe-Co-O System in Equilibrium with Pure Metals

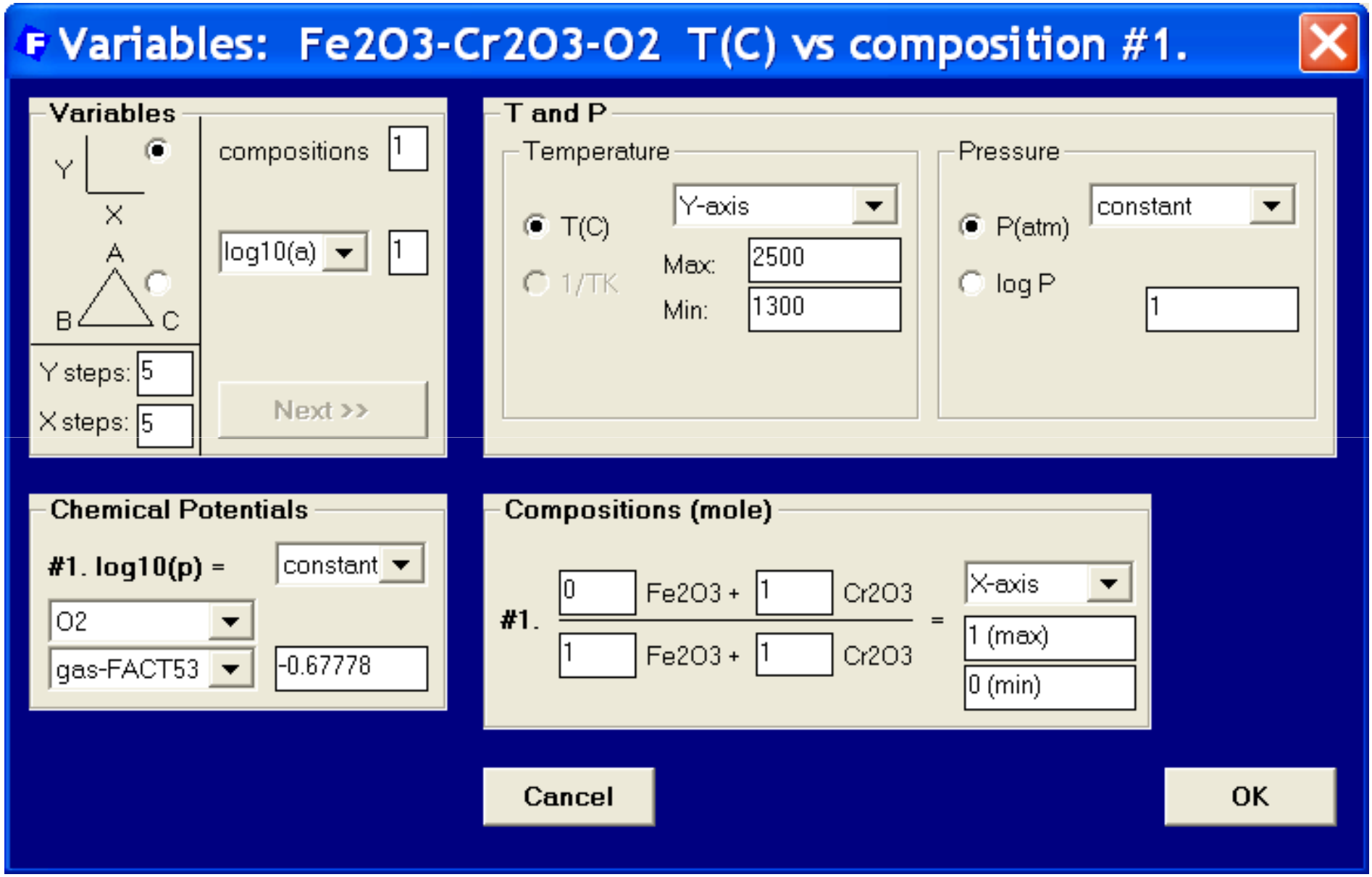


Fe_2O_3-Cr_2O_3 System in Equilibrium with Air

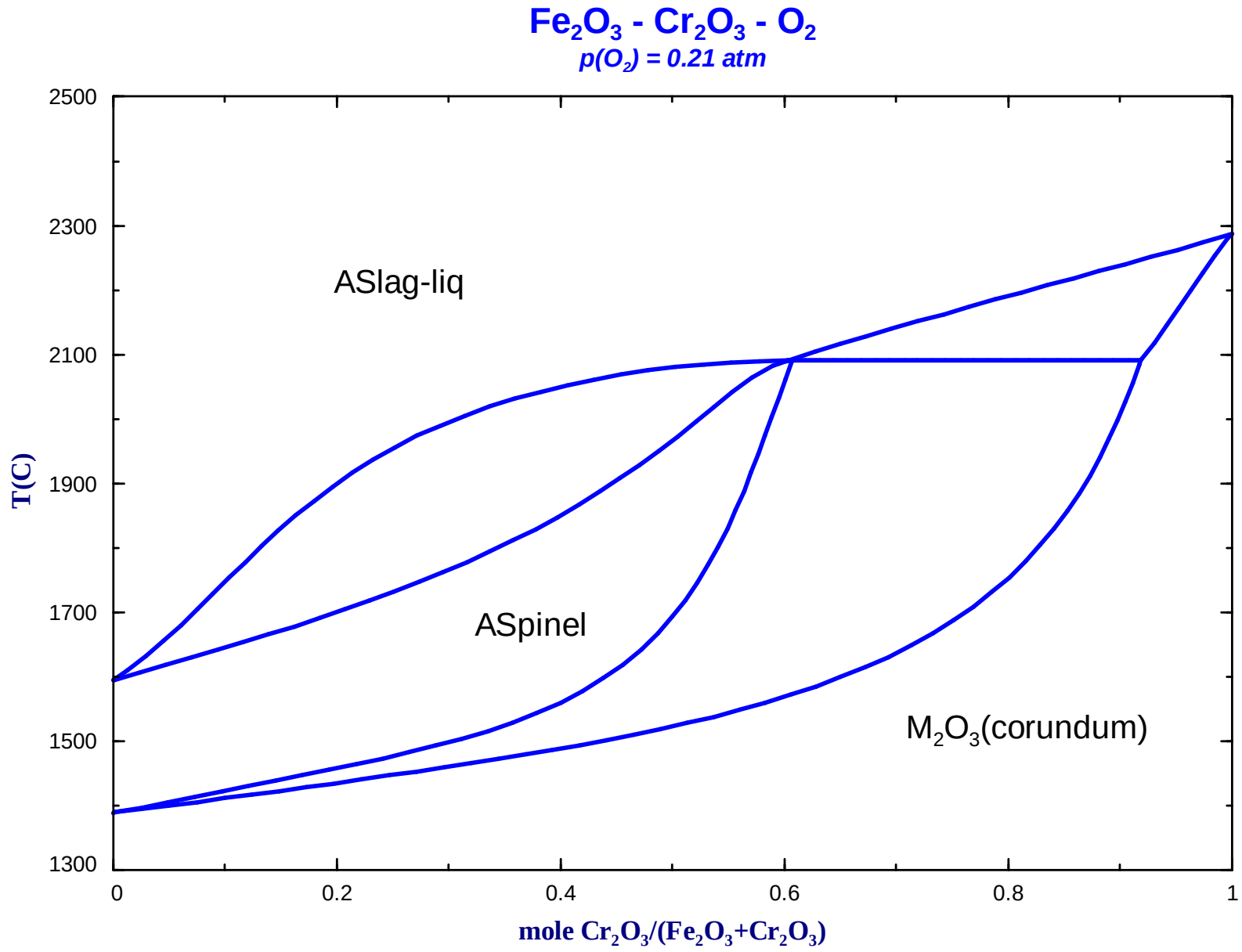


Gas phase must be selected even though it does not form

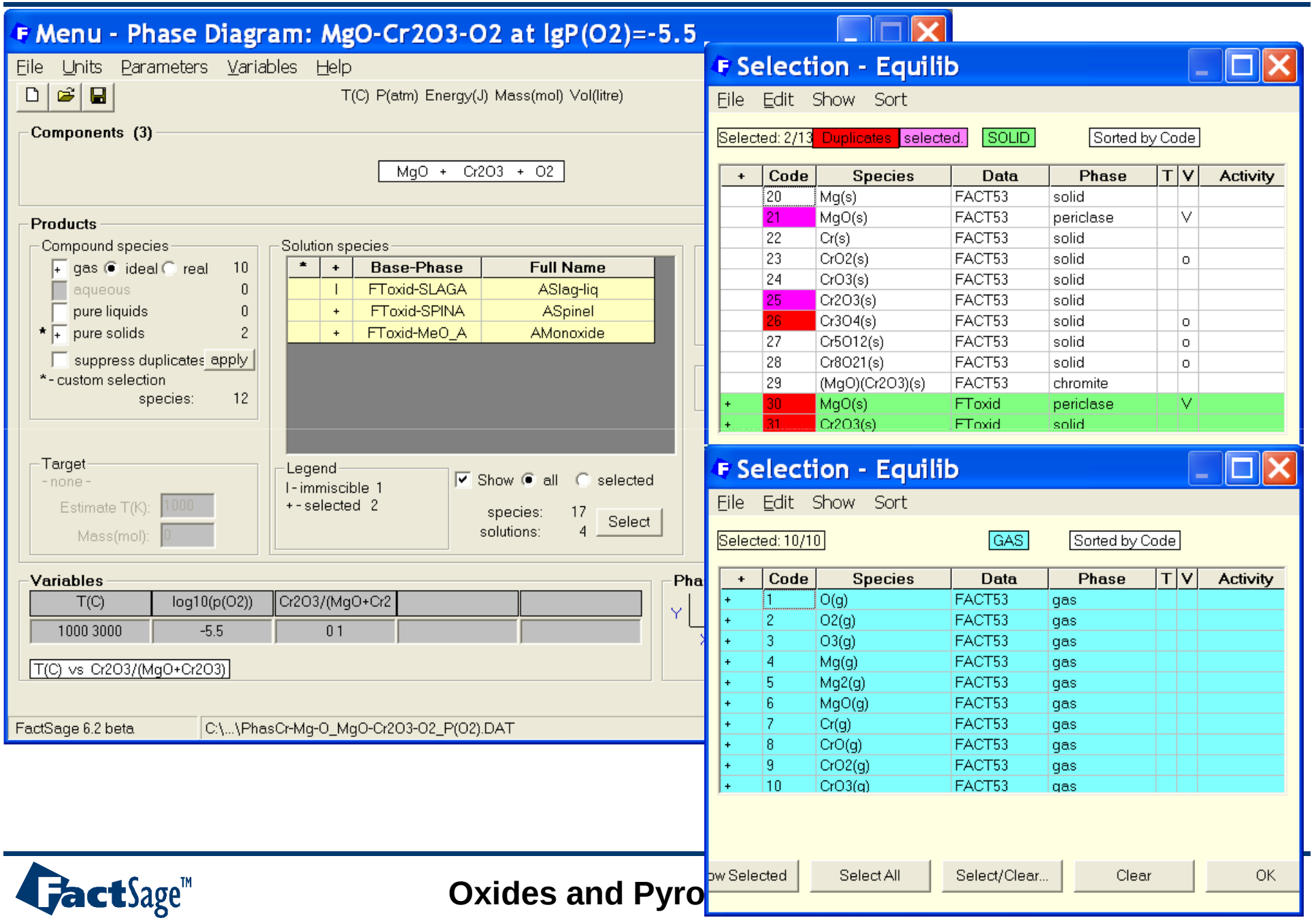
Fe_2O_3-Cr_2O_3 System in Equilibrium with Air



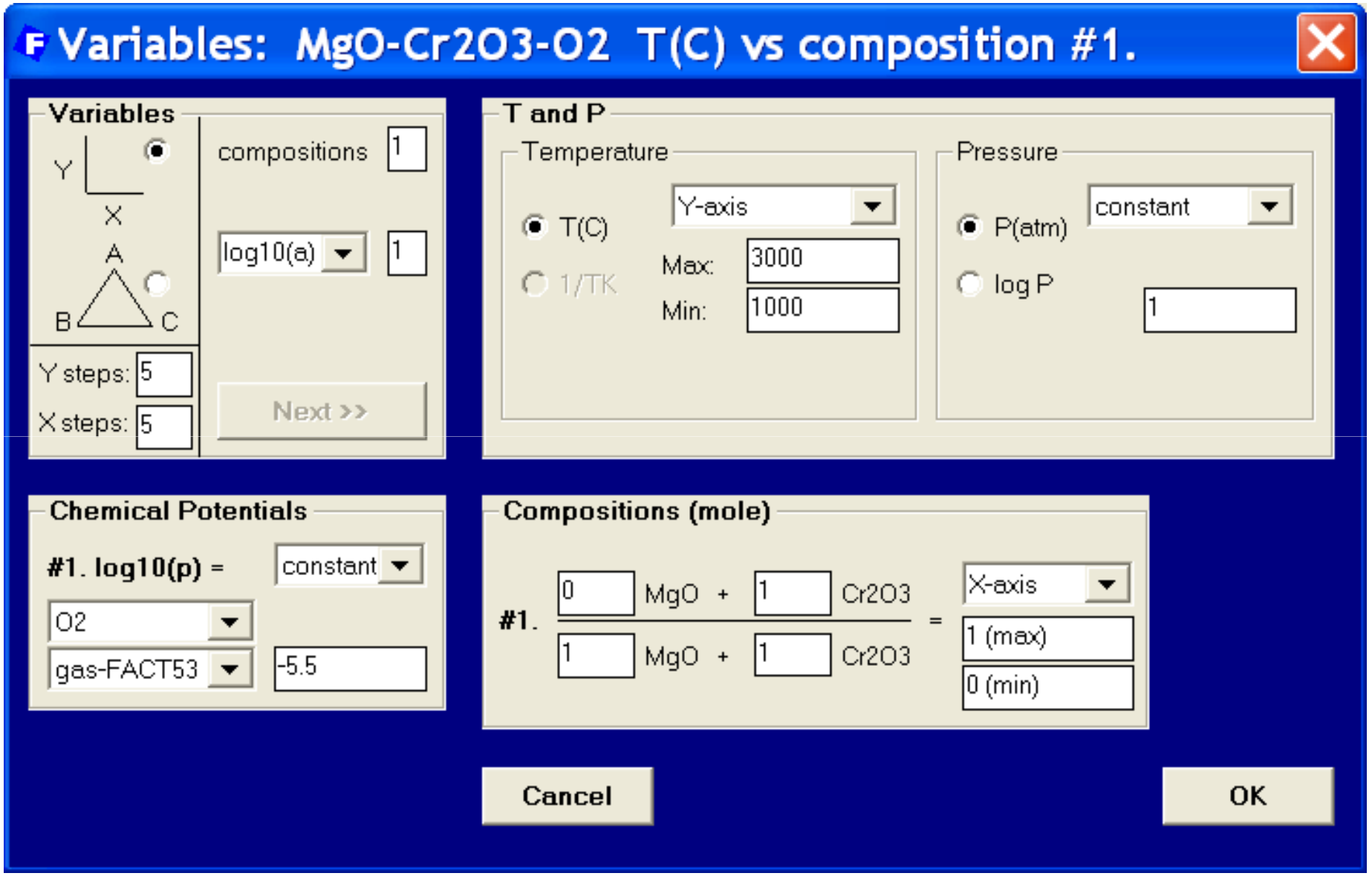
Fe_2O_3-Cr_2O_3 System in Equilibrium with Air



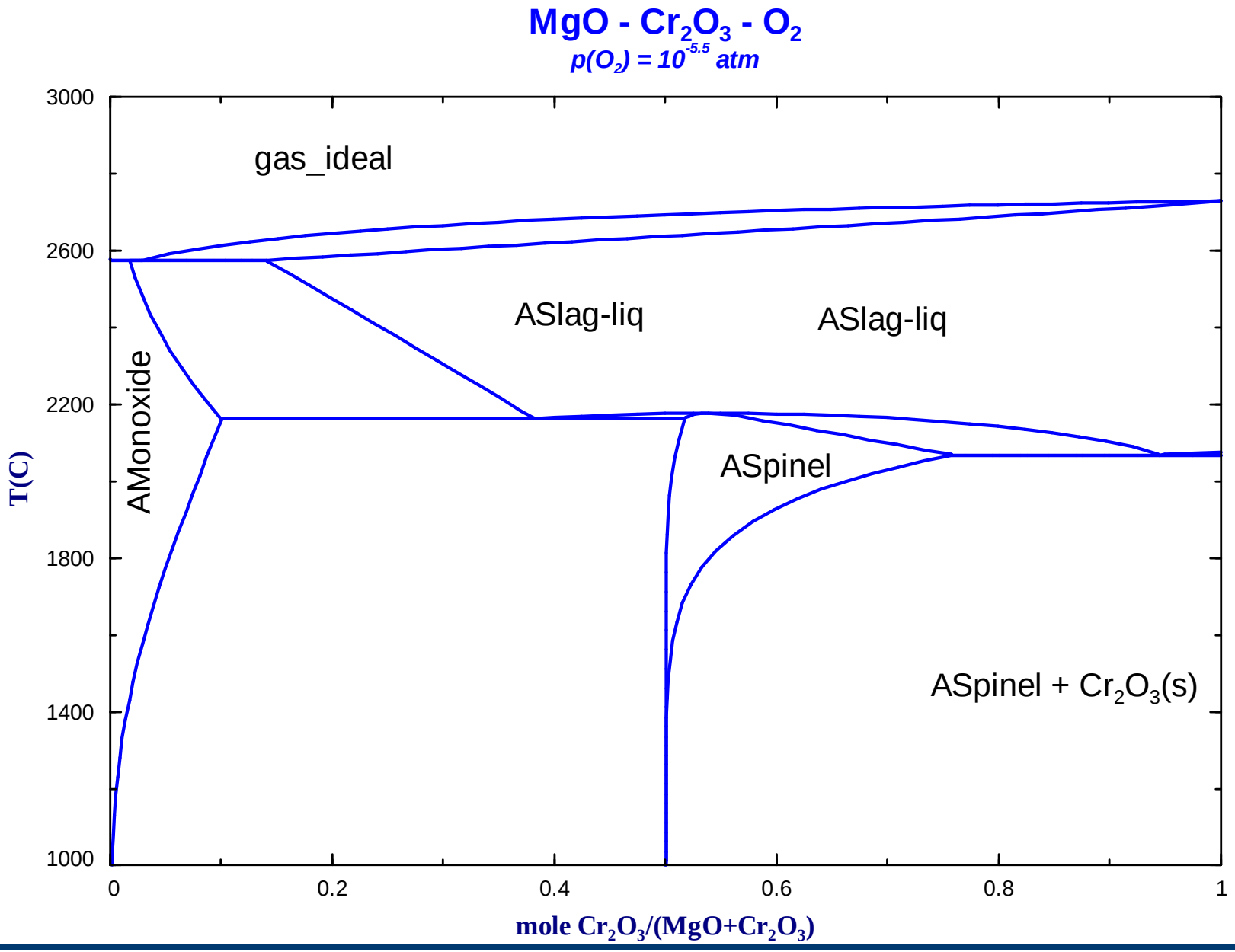
$MgO\text{-}Cr_2O_3$ System at $P(O_2)=10^{-5.5}$ atm



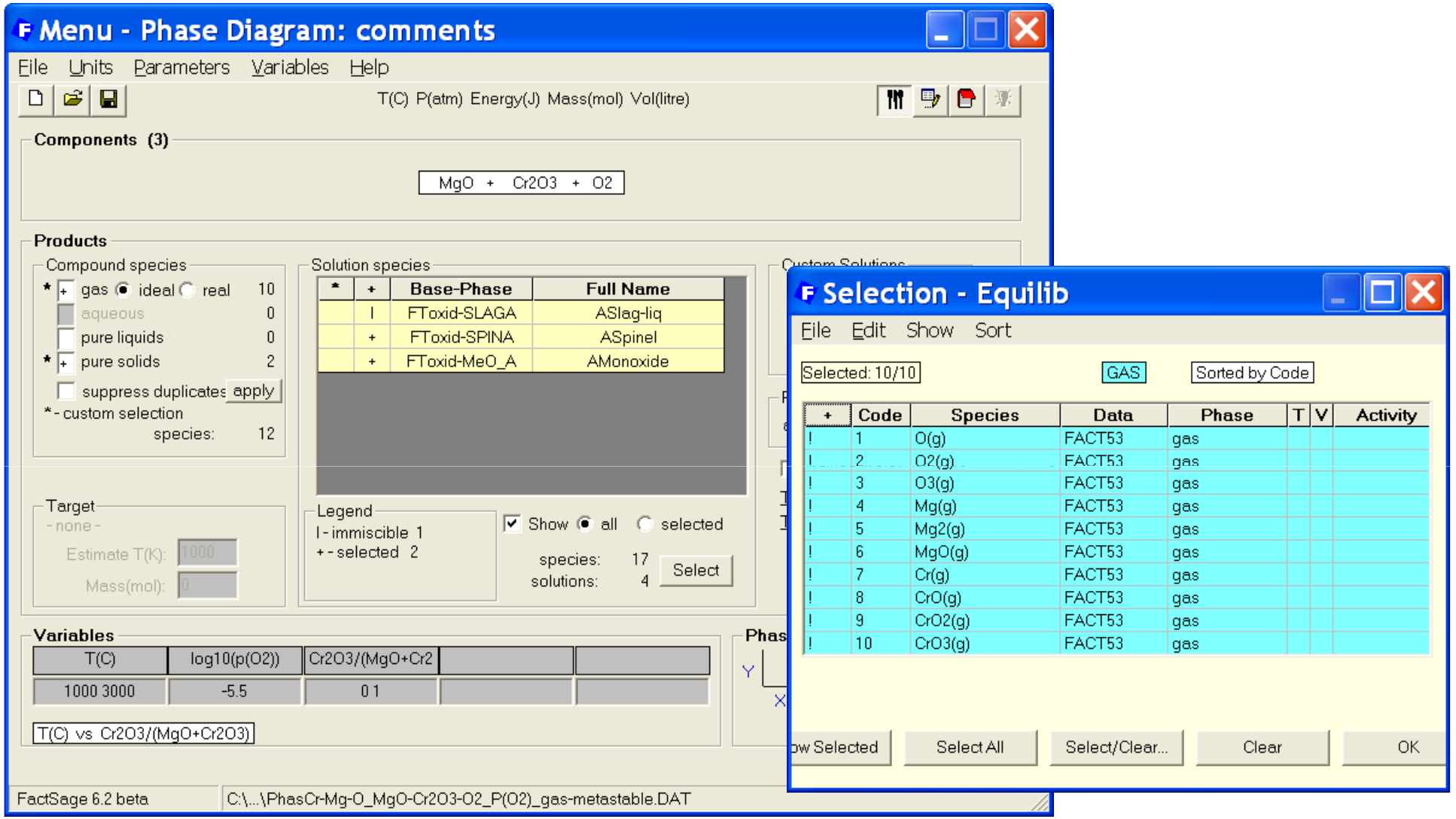
$MgO\text{-}Cr_2O_3$ System at $P(O_2)=10^{-5.5}$ atm



$MgO\text{-}Cr_2O_3$ System at $P(O_2)=10^{-5.5}$ atm

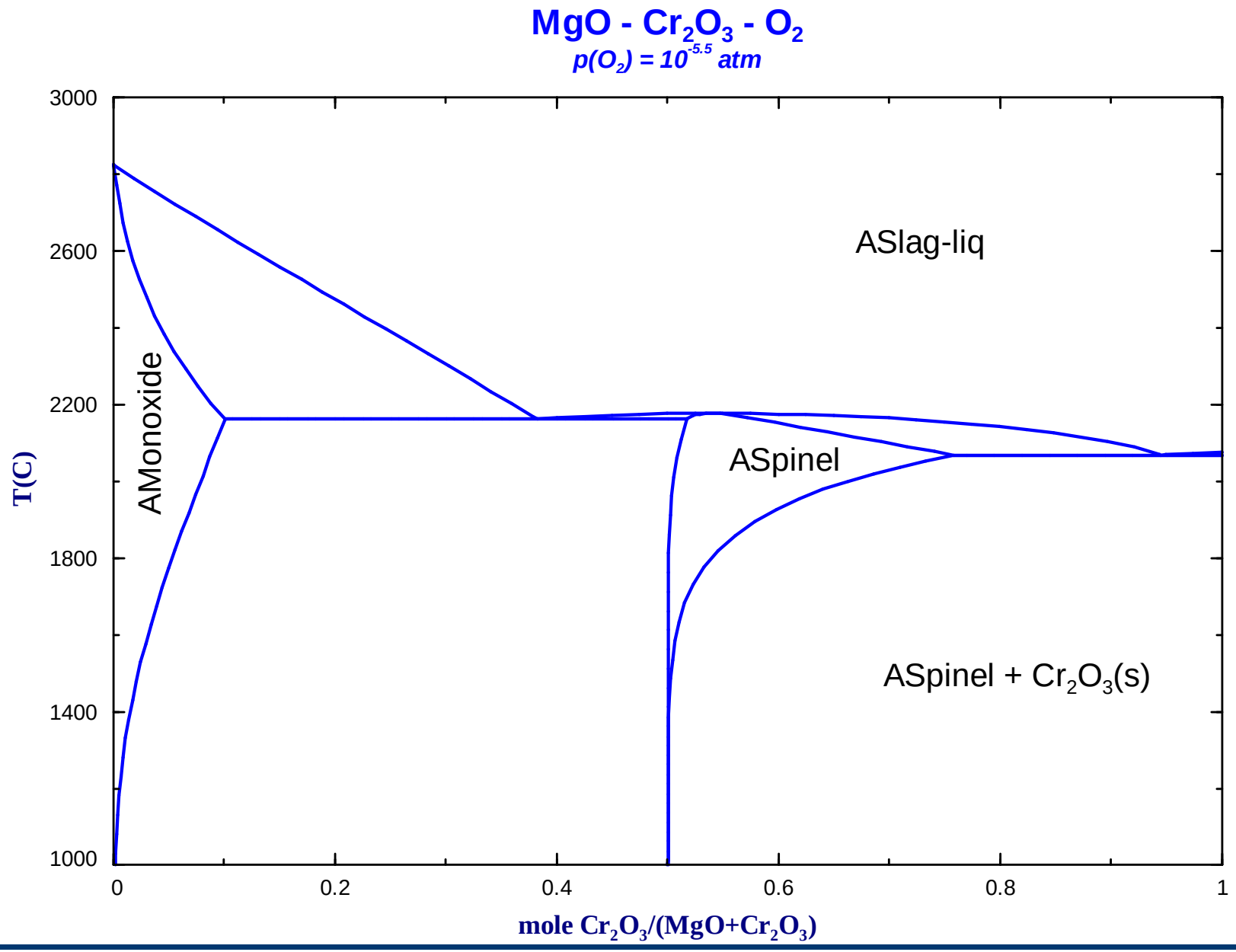


$MgO\text{-}Cr_2O_3$ System at $P(O_2)=10^{-5.5}$ atm

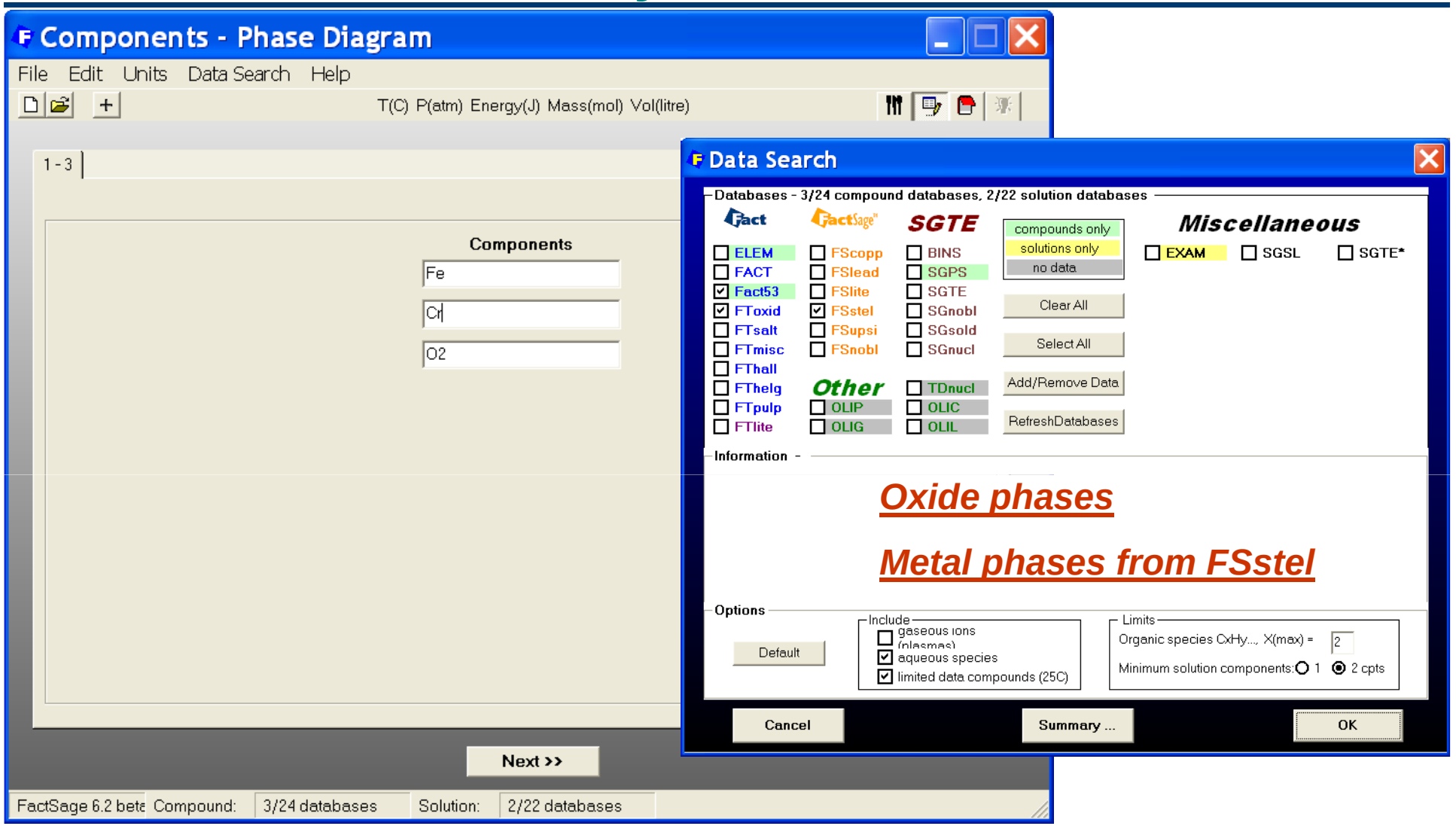


Gas phase must be selected, but it can be made dormant

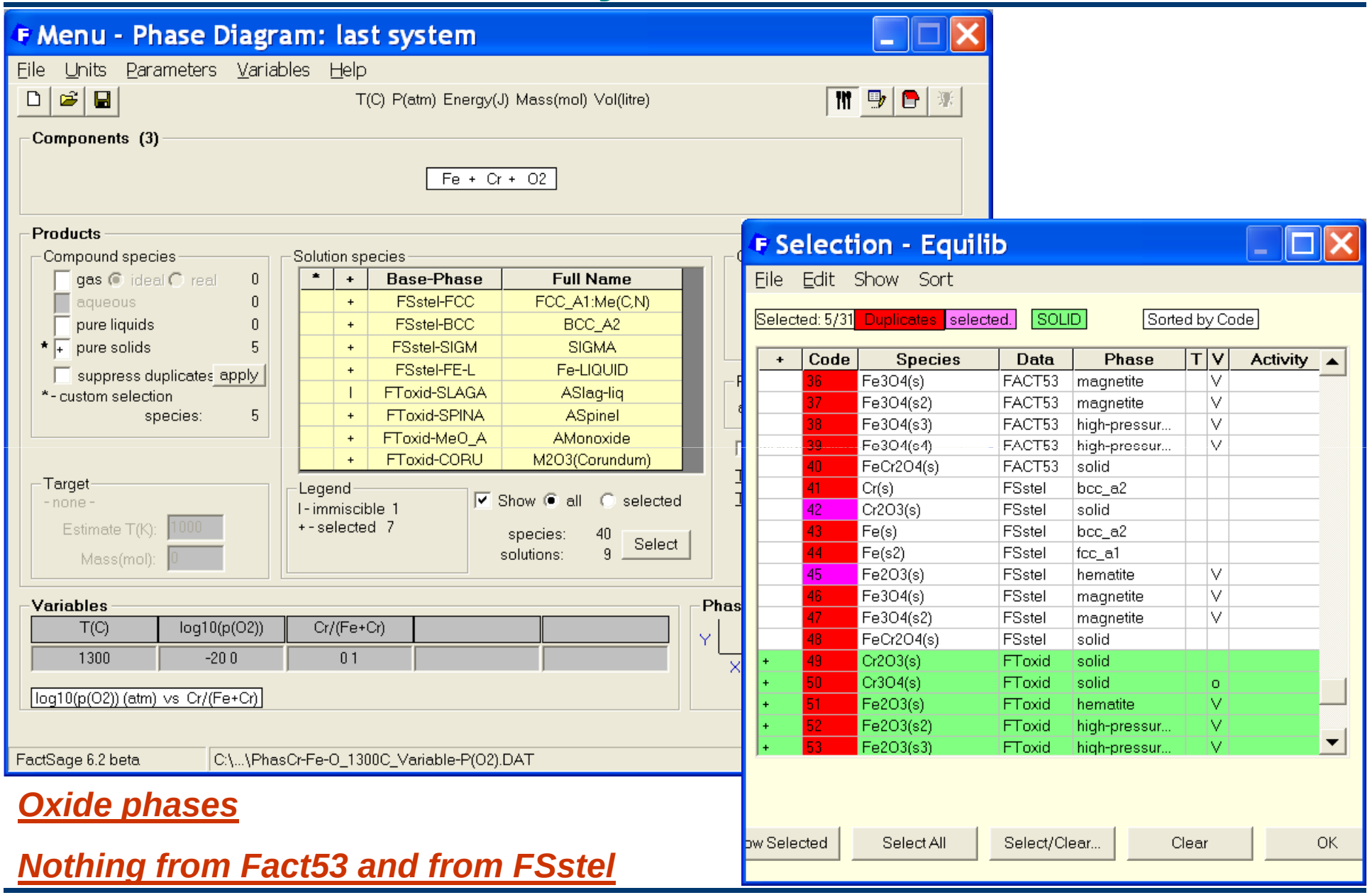
MgO-Cr_2O_3 System at $P(O_2)=10^{-5.5}$ atm, Dormant Gas



Fe-Cr-O System at 1300 ℃



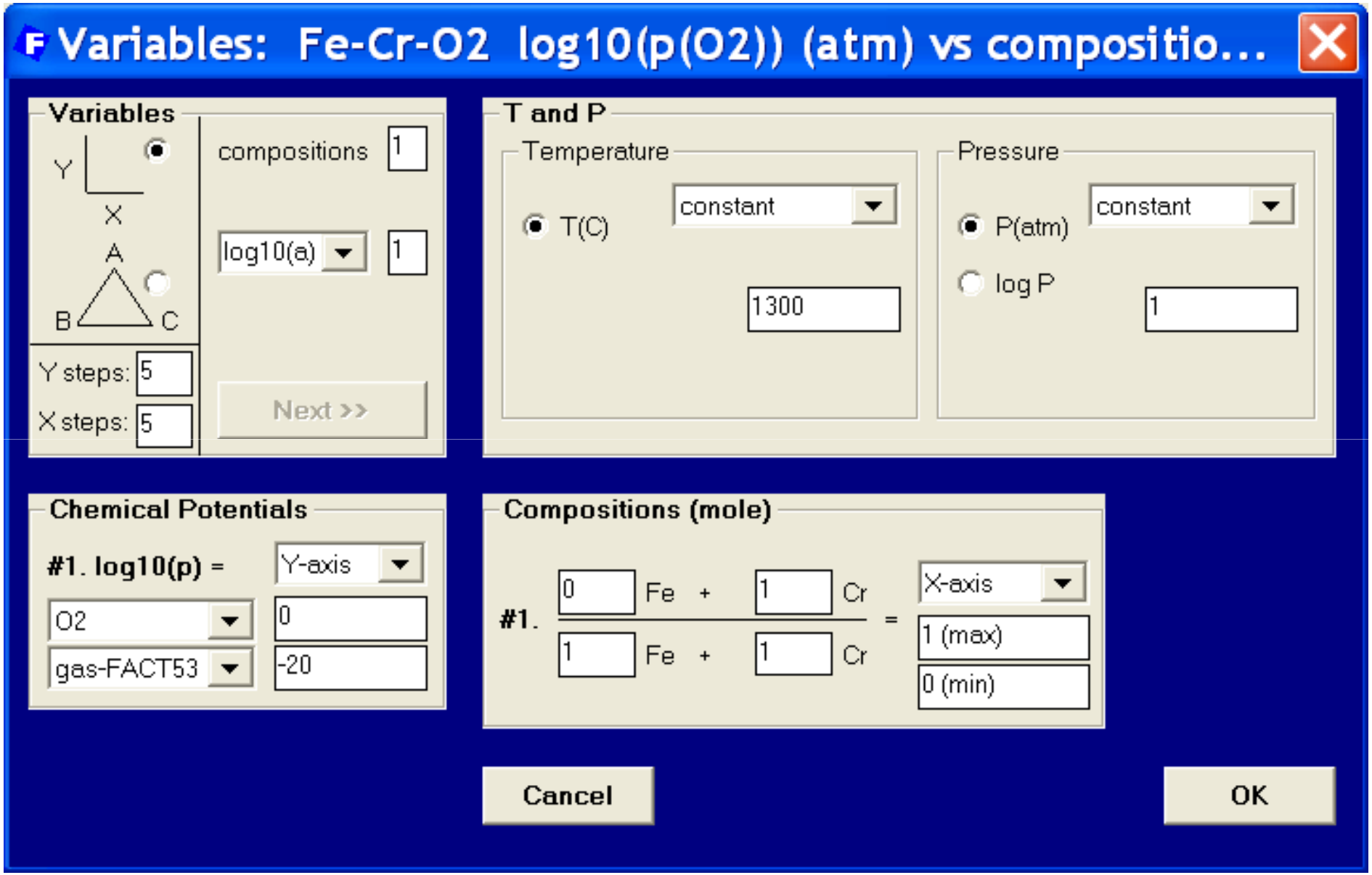
Fe-Cr-O System at 1300 ℃



Oxide phases

Nothing from Fact53 and from FSstel

Fe-Cr-O System at 1300 ℃



Fe-Cr-O System at 1300 ℃