The *Predom* module

Predom calculates and plots isothermal 1-, 2- and 3-metal predominance area diagrams.

Predom accesses only compound databases.

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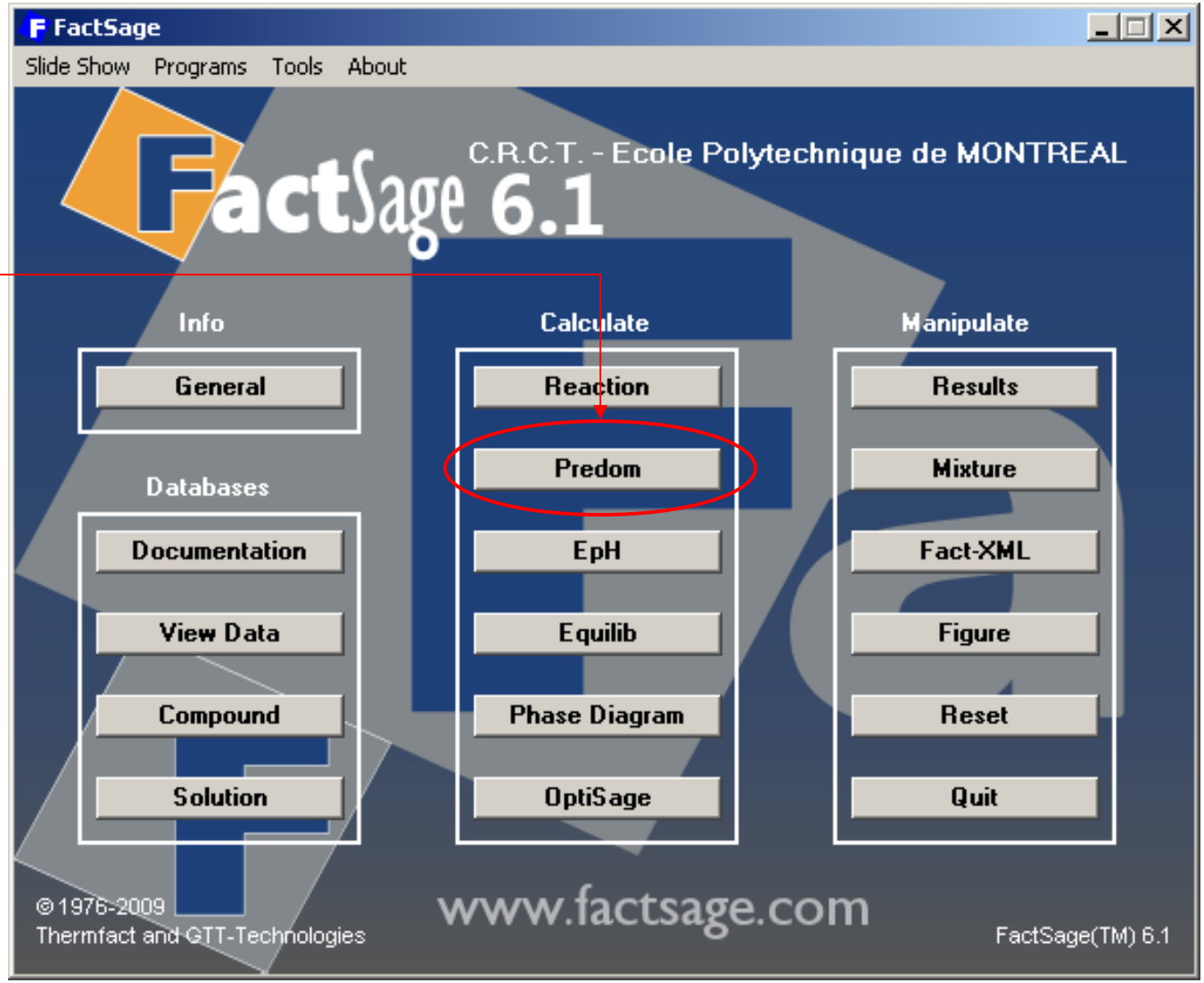
The *Predom* module

Click on ***Predom*** in the main ***FactSage*** window.



Using the *Reaction* program to identify the most probable reaction

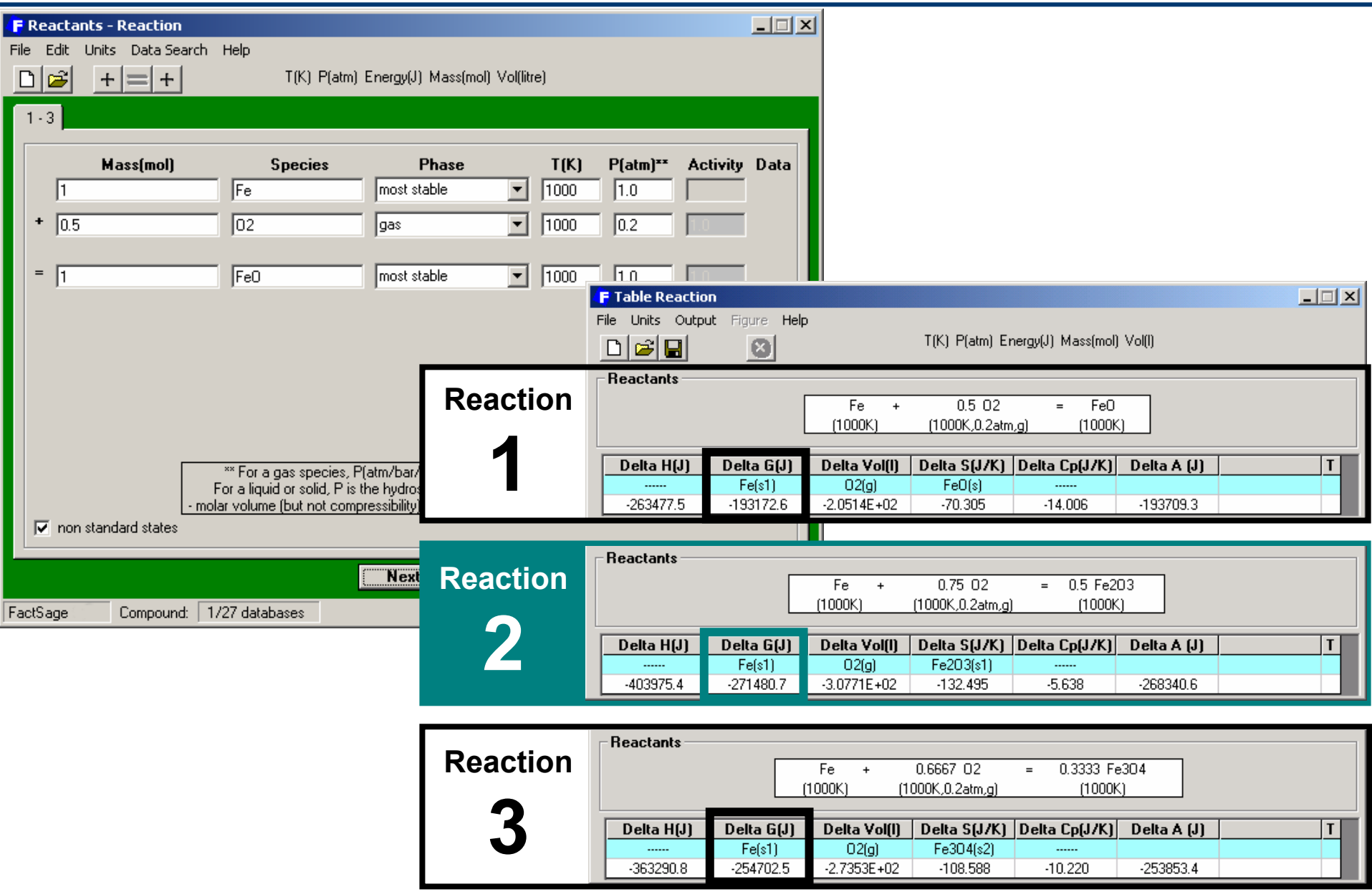
Question: A gas mixture, 80% **SO_2** + 20% **O_2** at **1** atm, is equilibrated with **Fe** at **1000 K**. The possible products are FeO, Fe_2O_3, Fe_3O_4, FeS, FeS_2, $FeSO_4$ and $Fe_2(SO_4)_3$. Which product is the most the stable?

Answer: Although some SO_3(g) forms, for simplicity we will assume that SO_2 and O_2 are at equilibrium: i.e., **P_{SO_2}= 0.8 atm** and **P_{O_2}= 0.2 atm**. In such a case, it can be shown that the equilibrium partial pressure of sulfur is **P_{S_2}= 10^{-29} atm**. Although the value is small, this chemical potential is useful for thermodynamic calculations.

From the ***Reaction*** program, the following values of **ΔG** are calculated:
(note: **1** mol **Fe**(s) reactant in all cases)

1 : Fe(s) + 0.5 O_2 (0.2 atm) = FeO	**ΔG= -193.2 kJ**
2 : Fe(s) + 0.75 O_2 (0.2 atm) = 0.5 Fe_2O_3	**ΔG= -271.5 kJ**
3 : Fe(s) + (2/3) O_2 (0.2 atm) = (1/3) Fe_3O_4	**ΔG= -254.7 kJ**
4 : Fe(s) + 0.5 S_2 (10^{-29} atm) = FeS	**ΔG= 181.6 kJ**
5 : Fe(s) + S_2 (10^{-29} atm) = FeS_2	**ΔG= 454.2 kJ**
6 : Fe(s) + 2 O_2 (0.2 atm) + S_2 (10^{-29} atm) = $FeSO_4$	**ΔG= -266.1 kJ**
7 : Fe(s) + 3 O_2 (0.2 atm) + 0.75 S_2 (10^{-29} atm) = 0.5 $Fe_2(SO_4)_3$	**ΔG= -279.2 kJ**

Reaction program: 7 possible isothermal isobaric reactions and 7 values of ΔG



Predom methodology

Reaction 4

Reactants

Fe (1000K)	+	0.5 S2 (1000K,1E-29atm,g)	=	FeS (1000K)

Delta H(J)	Delta G(J)	Delta Vol(l)	Delta S(J/K)	Delta Cp(J/K)	Delta A (J)		T
------	Fe(s1)	S2(g)	FeS(s3)	------			
-153754.8	181584.6	-4.1029E+30	-335.339	-13.741	181047.4		

Reaction 5

Reactants

Fe (1000K)	+	S2 (1000K,1E-29atm,g)	=	FeS2 (1000K)

Delta H(J)	Delta G(J)	Delta Vol(l)	Delta S(J/K)	Delta Cp(J/K)	Delta A (J)		T
------	Fe(s1)	S2(g)	FeS2(s1)	------			
-297458.5	454223.7	-8.2058E+30	-751.682	-8.904	457843.1		

Reaction 6

Reactants

Fe (1000K)	+	2 O2 (1000K,0.2atm,g)	+	0.5 S2 (1000K,1E-29atm,g)	=	FeSO4 (1000K)

Delta H(J)	Delta G(J)	Delta Vol(l)	Delta S(J/K)	Delta Cp(J/K)	Delta A (J)		T
------	Fe(s1)	O2(g)	S2(g)	FeSO4(s)	------		
-979627.1	-266083.3	-4.1029E+30	-713.544	13.040	-249989.6		

Reaction 7

Reactants

Fe (1000K)	+	3 O2 (1000K,0.2atm,g)	+	0.75 S2 (1000K,1E-29atm,g)	=	0.5 Fe2(SO4)3 (1000K)

Delta H(J)	Delta G(J)	Delta Vol(l)	Delta S(J/K)	Delta Cp(J/K)	Delta A (J)		T
------	Fe(s1)	O2(g)	S2(g)	Fe2(SO4)3(s)	------		
-1373001.6	-279223.8	-6.1543E+30	-1093.778	17.991	-252743.6		

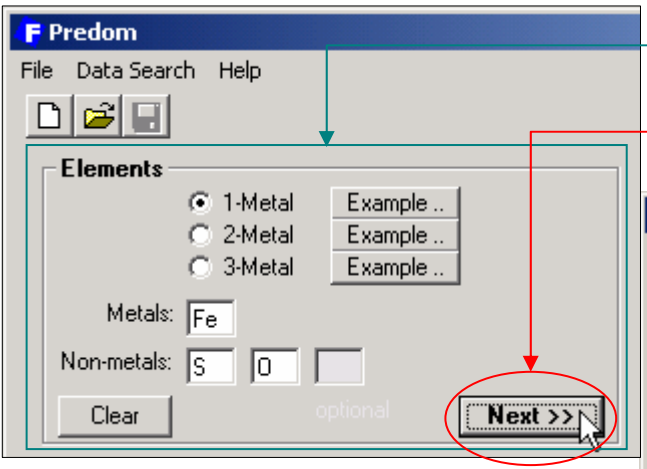
$Fe_2(SO_4)_3$ is the stable product since ΔG is the **most negative**. For example, $FeSO_4$ could not be the most stable since combining reactions 6 and 7, we have:

$FeSO_4 + O_2$ (0.2 atm) + 0.25 S_2 (10^{-29}atm) = 0.5 $Fe_2(SO_4)_3$

ΔG = (-279223.8 J) - (-266083.3 J) ≈ -13.1 kJ

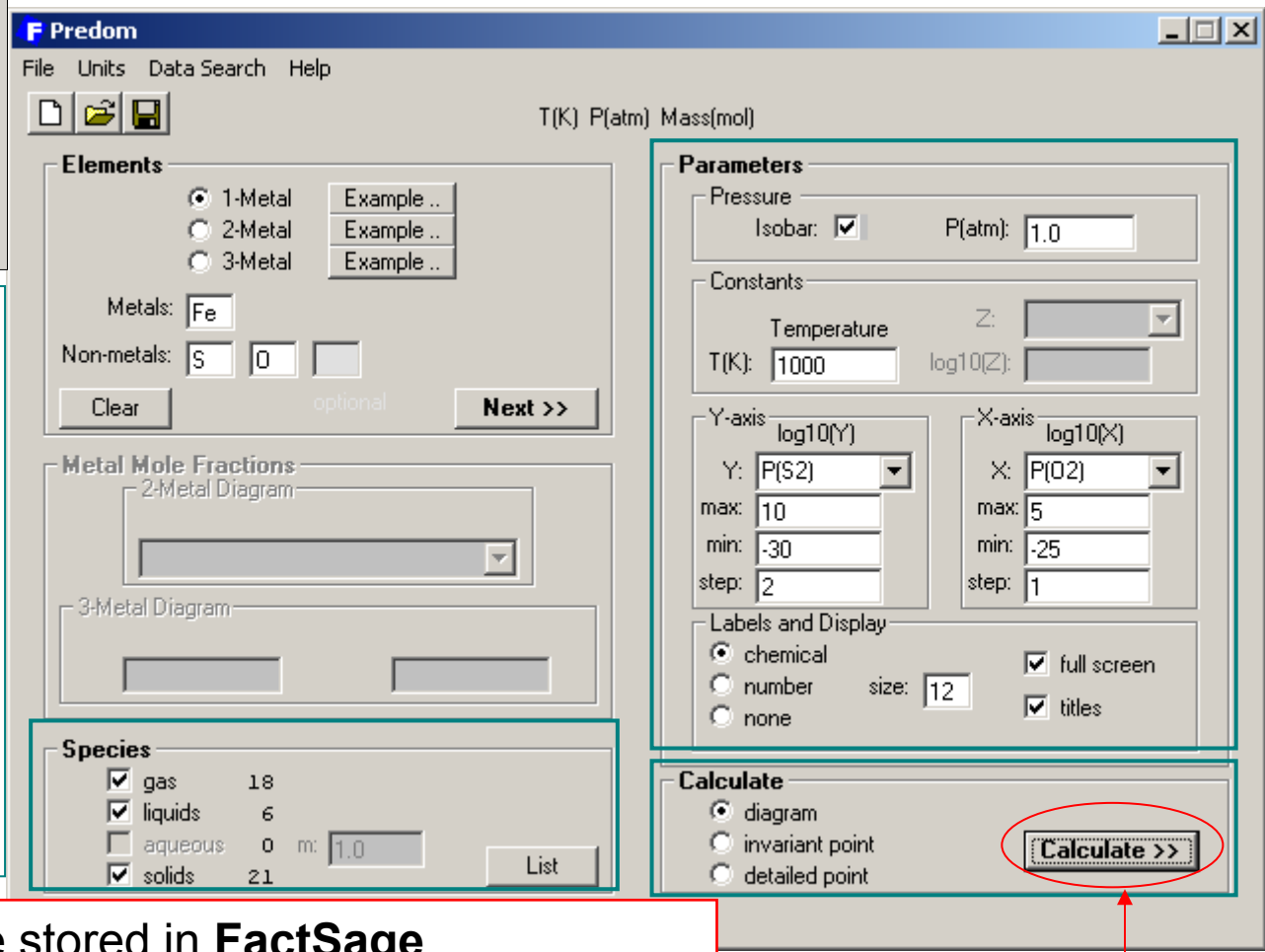
This methodology is used by the ***Predom*** program to locate the domains of stability of each phase as a function of gas potential.

Specifying a classical predominance area diagram: Fe-S_2(g)-O_2(g) at 1000 K



1. Specify the metallic and the non-metallic elements.

2. Press **Next >>** to activate the calculation.

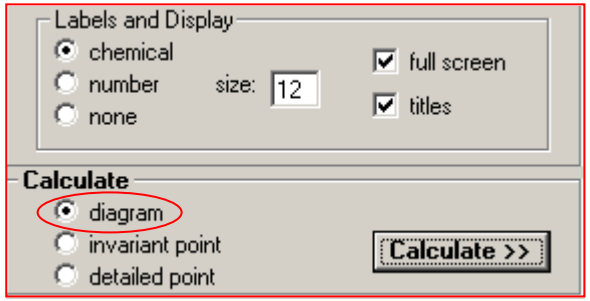


3. Select the variables:
   - **Parameters:**
     - Pressure
     - Constants
     - Axes
     - Labels and Display
   - **Species:** gas, liquids and solids
   - **Calculate:** a diagram

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

4. Press **Calculate >>**

Figure display of the predominance area diagram of **Fe-S_2(g)-O_2(g)** at 1000 K



The arrow is pointing to the $Fe_2(SO_4)_3$ domain where:

$x = \log_{10} P_{O_2} = -0.7333$

→ $P_{O_2} \approx 0.2$ atm

$y = \log_{10} P_{S_2} = -29.01$

→ $P_{S_2} \approx 10^{-29}$ atm

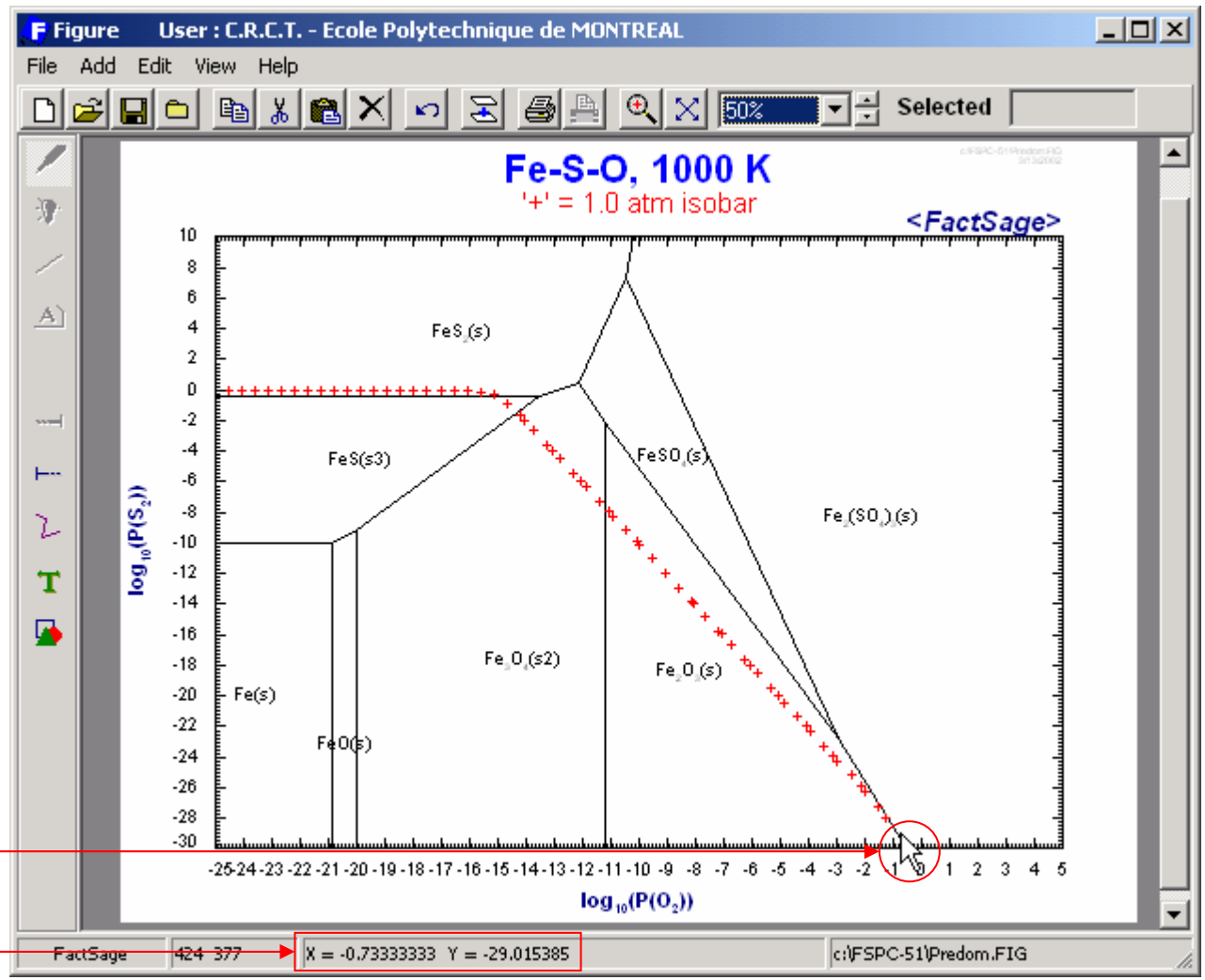
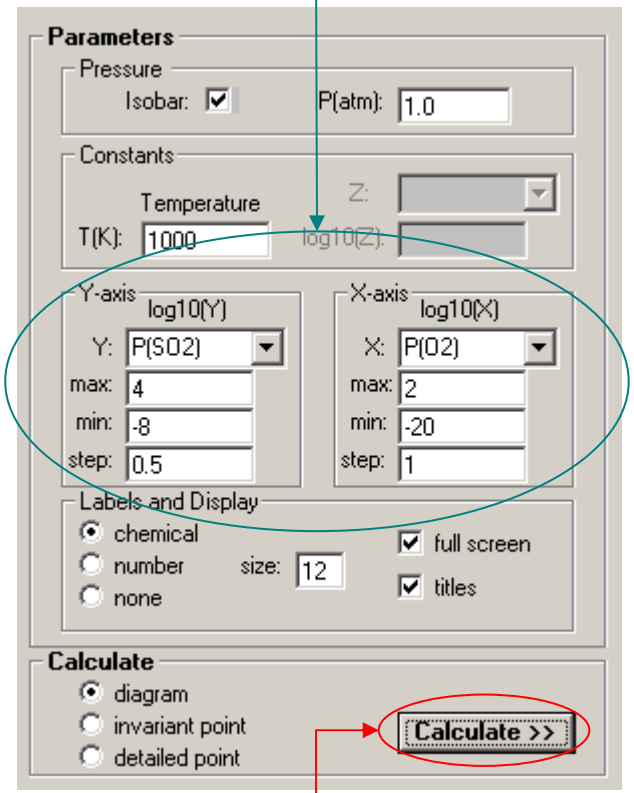


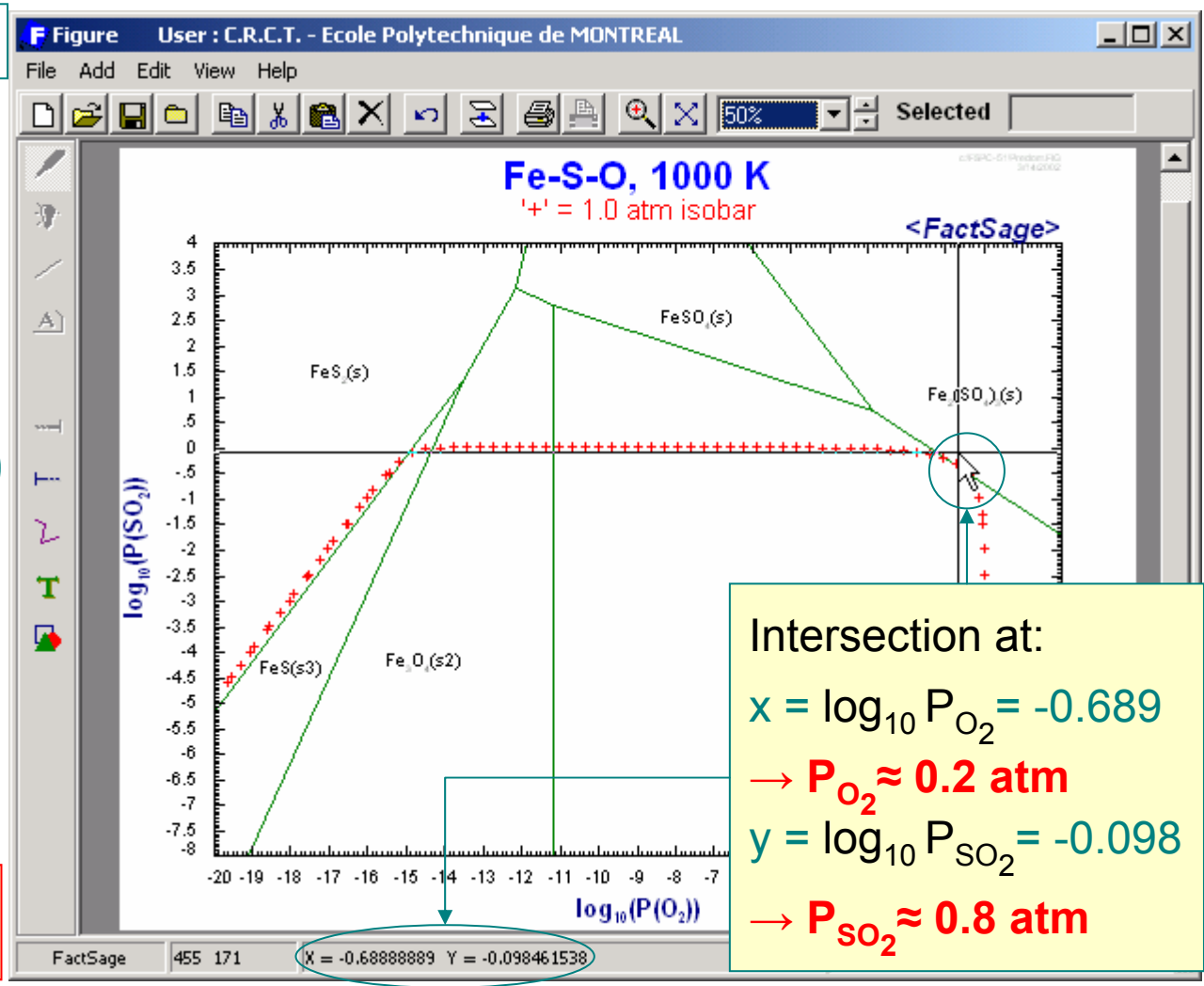
Figure creates a predominance diagram that can be edited, manipulated and stored in a variety of ways.

Revised *Predom* diagram displayed in *Figure* for Fe-SO_2(g)-O_2(g) at 1000 K

Changing the X and Y axes.



And **Calculate >>…**
a revised ***Predom* diagram**.



Intersection at:

$x = \log_{10} P_{O_2} = -0.689$

→ **$P_{O_2} \approx 0.2$ atm**

$y = \log_{10} P_{SO_2} = -0.098$

→ **$P_{SO_2} \approx 0.8$ atm**

Note: The **Fe-S_2(g)-O_2(g)** diagram (previous page) and the **Fe-SO_2(g)-O_2(g)** diagram (here) are topologically equivalent, i.e. the same combination of species coexists at the invariant points.

Invariant points of Fe-SO_2(g)-O_2(g) at 1000 K.

Calculate
- diagram
- invariant point
- detailed point

Calculate >>

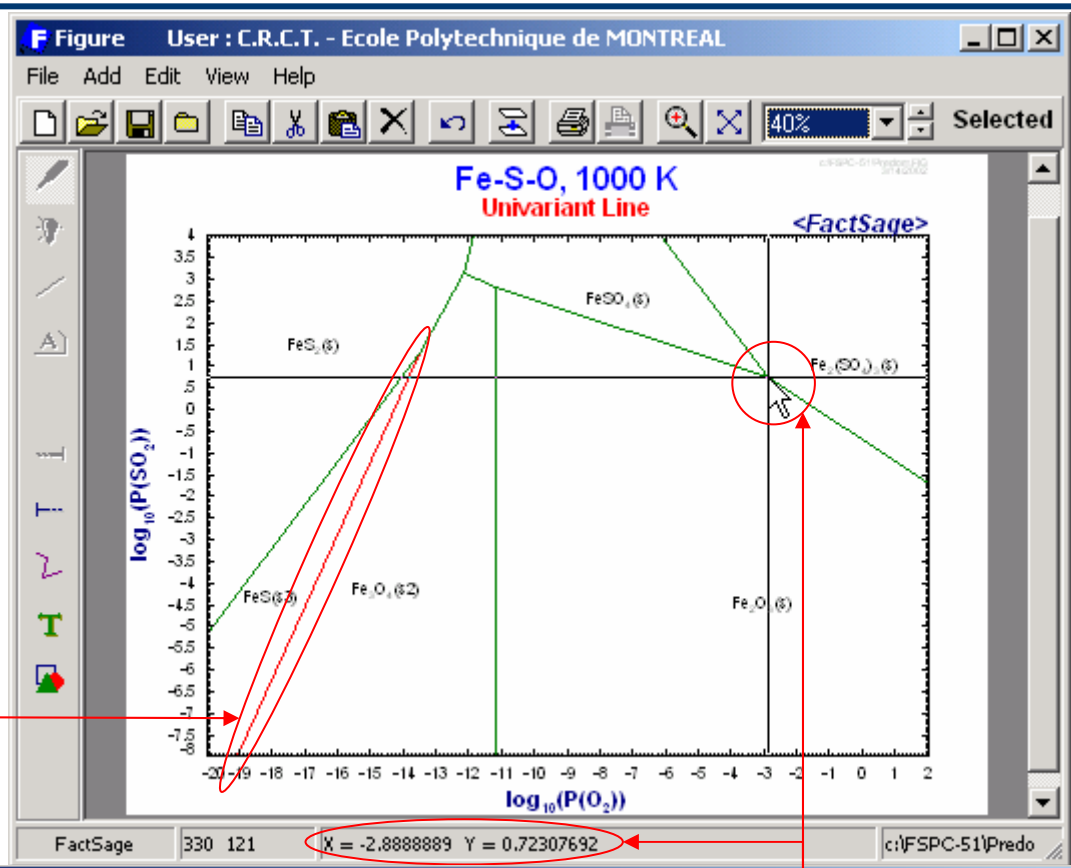
Phase Rule:

F = C - P + 2

F : degrees of freedom
C : number of components
P : number of phases

Univariant line (/):
FeS/Fe_3O_4/gas. From the phase rule, F = 2. Hence, at 1000 K only one of SO_2 or O_2 can be fixed.

At the arrow, C = 3 (Fe,S,O) and P = 4 (3 solids and 1 gas); hence F = 1. At 1000 K, the system is invariant. (Note that the total pressure is not specified.)



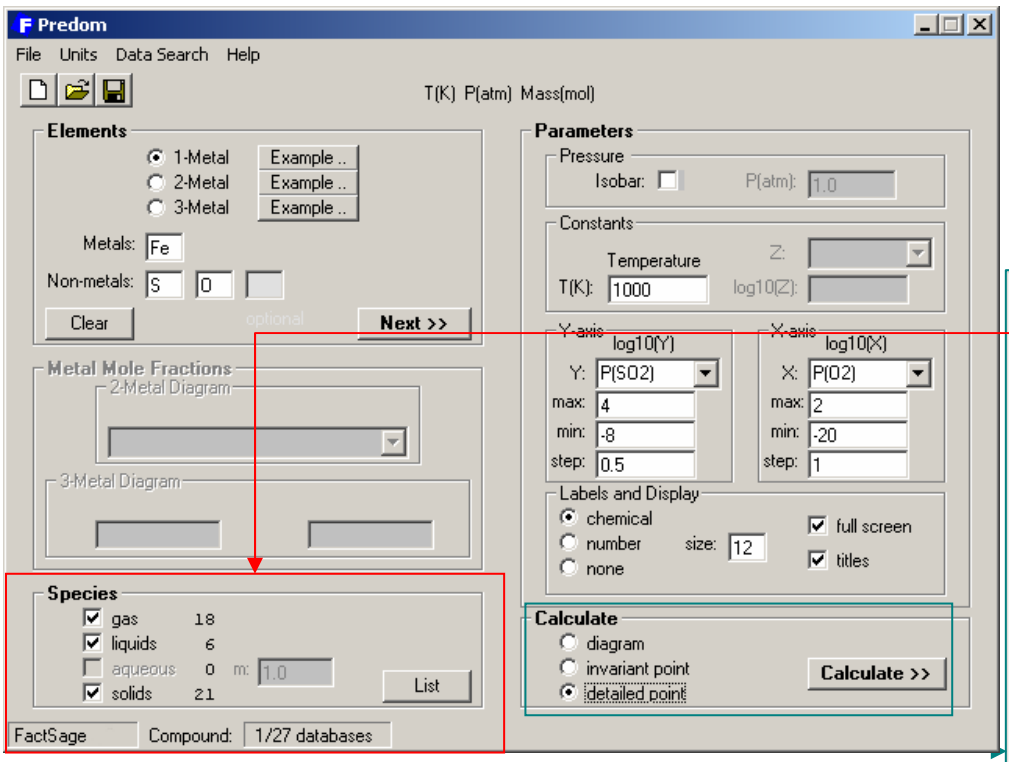
Invariant Points - P(atm), Y = P(SO2), X = P(O2), T(K) = 1000

File Edit

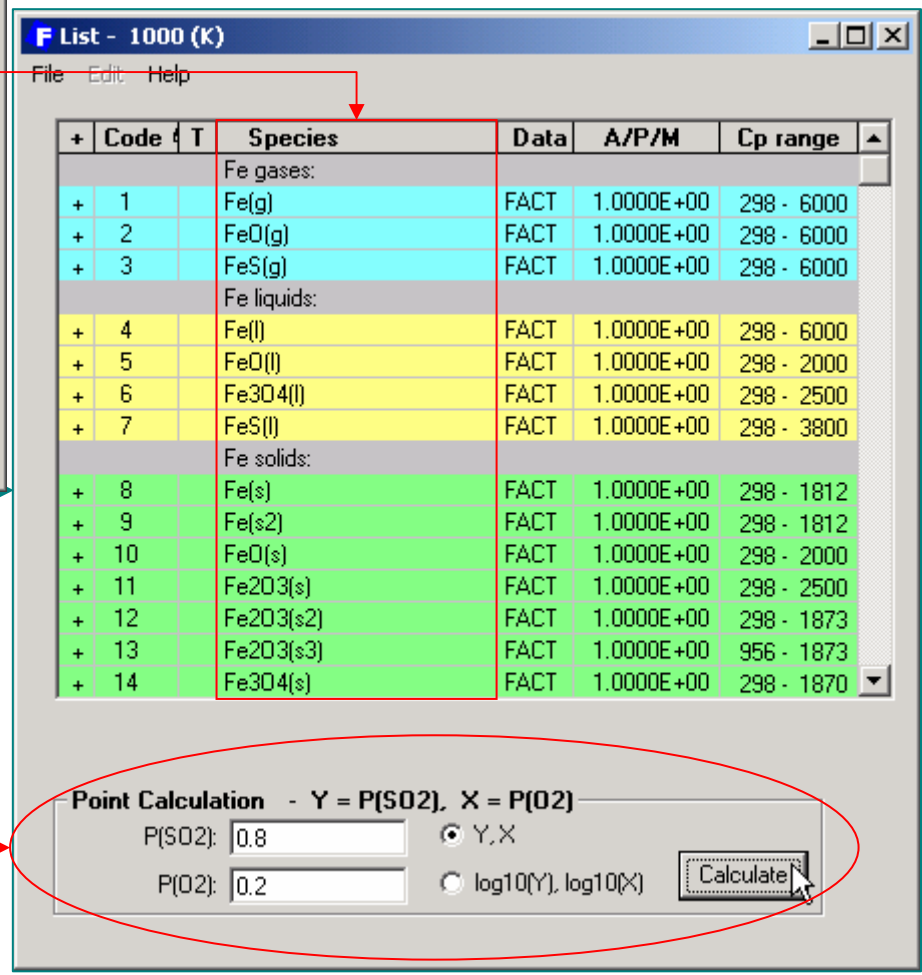
log10(X), log10(Y) X, Y

log10(Y)	log10(X)		Species A		Species B		Species C
-10.8102	-20.8786	8	Fe(s)	10	FeO(s)	20	FeS(s3)
-9.4910	-19.9991	10	FeO(s)	15	Fe3O4(s2)	20	FeS(s3)
2.7908	-11.1933	11	Fe2O3(s)	15	Fe3O4(s2)	24	FeSO4(s)
0.7191	-2.9064	11	Fe2O3(s)	24	FeSO4(s)	25	Fe2(SO4)3(s)
1.2992	-13.5250	15	Fe3O4(s2)	20	FeS(s3)	21	FeS2(s)
3.1143	-12.1637	15	Fe3O4(s2)	21	FeS2(s)	24	FeSO4(s)
8.2608	-10.4482	21	FeS2(s)	24	FeSO4(s)	25	Fe2(SO4)3(s)

Detailed point calculation at P_{SO_2}=0.8 atm and P_{O_2}=0.2 atm for **Fe-SO_2(g)-O_2**(g) at 1000K



18 gas species, 6 liquid species and 21 solids species (total: 46 species) in the ***FACT*** compound database containing **Fe**, **S** and/or **O**.



+	Code	T	Species	Data	A/P/M	Cp range
			Fe gases:			
+	1		Fe(g)	FACT	1.0000E+00	298 - 6000
+	2		FeO(g)	FACT	1.0000E+00	298 - 6000
+	3		FeS(g)	FACT	1.0000E+00	298 - 6000
			Fe liquids:			
+	4		Fe(l)	FACT	1.0000E+00	298 - 6000
+	5		FeO(l)	FACT	1.0000E+00	298 - 2000
+	6		Fe3O4(l)	FACT	1.0000E+00	298 - 2500
+	7		FeS(l)	FACT	1.0000E+00	298 - 3800
			Fe solids:			
+	8		Fe(s)	FACT	1.0000E+00	298 - 1812
+	9		Fe(s2)	FACT	1.0000E+00	298 - 1812
+	10		FeO(s)	FACT	1.0000E+00	298 - 2000
+	11		Fe2O3(s)	FACT	1.0000E+00	298 - 2500
+	12		Fe2O3(s2)	FACT	1.0000E+00	298 - 1873
+	13		Fe2O3(s3)	FACT	1.0000E+00	956 - 1873
+	14		Fe3O4(s)	FACT	1.0000E+00	298 - 1870

Click on **Data Search** to include or exclude a database in the search. Here, only the ***FACT*** compound database is included.

Point calculation data entry:
P_{SO_2}= 0.8 atm, P_{O_2}= 0.2 atm

Detailed point calculation at P_{SO_2}=0.8 atm and P_{O_2}=0.2 atm for **Fe-SO_2(g)-O_2**(g) at 1000K

$Fe_2(SO_4)_3$(s) is the stable species:
unit activity, C_p values **not** extrapolated

A/P/M: **A**ctivity/**P**artial pressure/**M**olality

«T» indicates **extrapolated data**

F List - Fe-S-O, T = 1000 (K)

File Edit Help

+	Code	T	Species	Data	A/P/M	Cp range
			Fe gases:			
+	1		Fe(g)	FACT	5.137E-29	298 - 6000
+	2		FeO(g)	FACT	3.004E-23	298 - 6000
+	3		FeS(g)	FACT	2.528E-40	298 - 6000
			Fe liquids:			
+	4		Fe(l)	FACT	1.144E-15	298 - 6000
+	5		FeO(l)	FACT	6.901E-06	298 - 2000
+	6		Fe3O4(l)	FACT	5.325E-08	298 - 2500
+	7		FeS(l)	FACT	2.396E-25	298 - 3800
			Fe solids:			
+	8		Fe(s)	FACT	2.440E-15	298 - 1812
+	9		Fe(s2)	FACT	2.343E-15	298 - 1812
+	10		FeO(s)	FACT	3.001E-05	298 - 2000
+	11		Fe2O3(s)	FACT	1.370E-01	298 - 2500
+	12		Fe2O3(s2)	FACT	1.388E-05	298 - 1873
+	13		Fe2O3(s3)	FACT	1.398E-05	956 - 1873
+	14		Fe3O4(s)	FACT	1.167E-04	298 - 1870

Total pressure in gas phase =1.651E+00 atm.

Domain: Fe2(SO4)3(s)

Point Calculation - Y = P(SO2), X = P(O2)

P(SO2): 0.8 Y,X

P(O2): 0.2 log10(Y), log10(X) Calculate

+	Code	T	Species	Data	A/P/M	Cp range
+	15		Fe3O4(s2)	FACT	1.207E-04	848 - 2500
+	16		Fe3O4(s3)	FACT	5.554E-12	298 - 1870
+	17		Fe3O4(s4)	FACT	5.743E-12	848 - 2500
+	18		FeS(s)			
+	19		FeS(s2)			
+	20		FeS(s3)			
+	21		FeS2(s)			
+	22		FeS2(s2)			
+	23	T	Fe7S8(s)	FACT	< 1.0E-70	295 - 300
+	24		FeSO4(s)	FACT	2.015E-01	298 - 2000
+	25		Fe2(SO4)3(s)	FACT	1.000E+00 *	298 - 2000
			Other gases:			
+	26		O(g)	FACT	6.990E-11	298 - 6000
X	27		O2(g)	FACT	2.000E-01	298 - 6000
+	28		O3(g)	FACT	7.828E-13	298 - 6000
+	29		S(g)	FACT	2.304E-23	298 - 2300
+	30		S2(g)	FACT	1.090E-29	298 - 6000
+	31		S3(g)	FACT	2.870E-45	298 - 6000
+	32		S4(g)	FACT	2.787E-60	298 - 6000
+	33		S5(g)	FACT	< 1.0E-70	298 - 6000
+	34		S6(g)	FACT	< 1.0E-70	298 - 6000
+	35		S7(g)	FACT	< 1.0E-70	298 - 6000
+	36		S8(g)	FACT	< 1.0E-70	298 - 6000
+	37		SO(g)	FACT	3.405E-12	298 - 6000
Y	38		SO2(g)	FACT	8.000E-01	298 - 6000
+	39		SO3(g)	FACT	6.511E-01	298 - 6000
+	40		SSO(g)	FACT	1.016E-23	298 - 6000
			Other liquids:			
+	41		S(l)	FACT	1.422E-15	298 - 1500
+	42	T	SO3(l)	FACT	1.437E-05	298 - 311
			Other solids:			
+	43	T	S(s)	FACT		298 - 801
+	44	T	S(s2)	FACT	7.627E-16	298 - 801
+	45	T	SO3(s)	FACT	3.157E-07	298 - 301

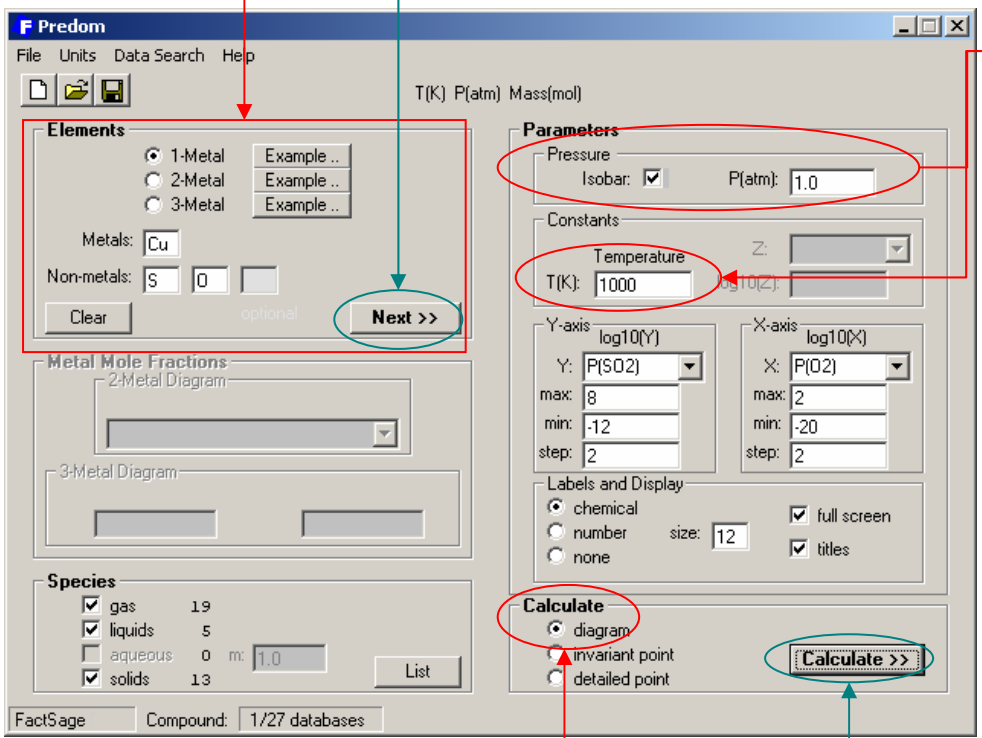
Mainly SO_2 (0.8 atm), O_2 (0.2 atm) and SO_3 (0.65 atm, see code 39).

Predom diagram for Cu-SO_2(g)-O_2(g) at 1000 K

1. Specify the metallic elements (**Cu**) and the non-metallic elements (**S** and **O**) in the **Elements** frame.

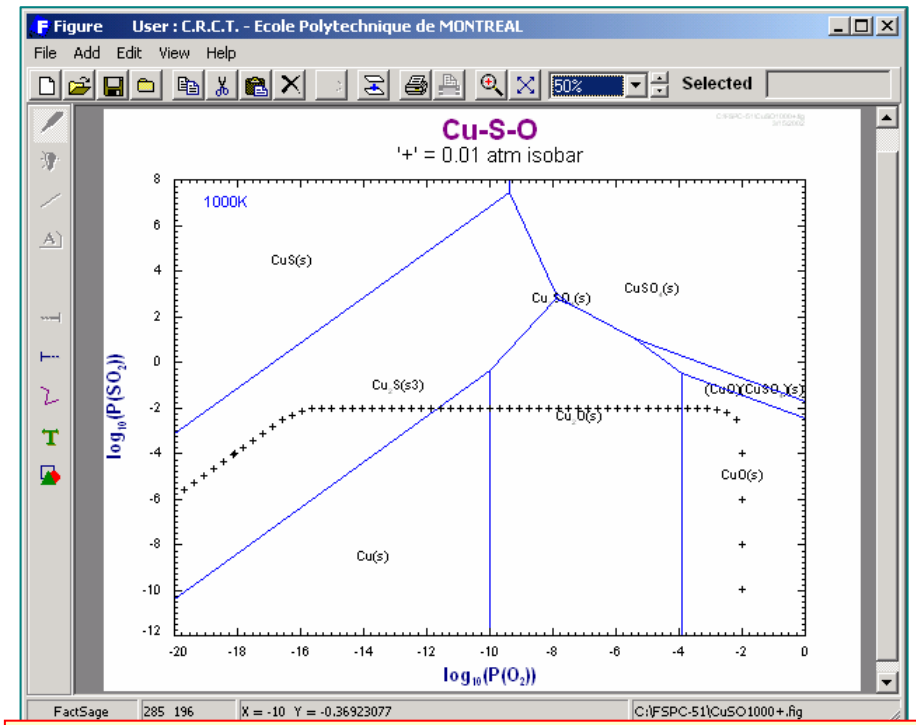
2. Press **Next >>** to search through the selected Compound database(s) (here, ***FACT***) and activate the calculation.

3. Specifying an isobar, **P = 0.01 atm**, at **T = 1000 K**.



4. Select diagram

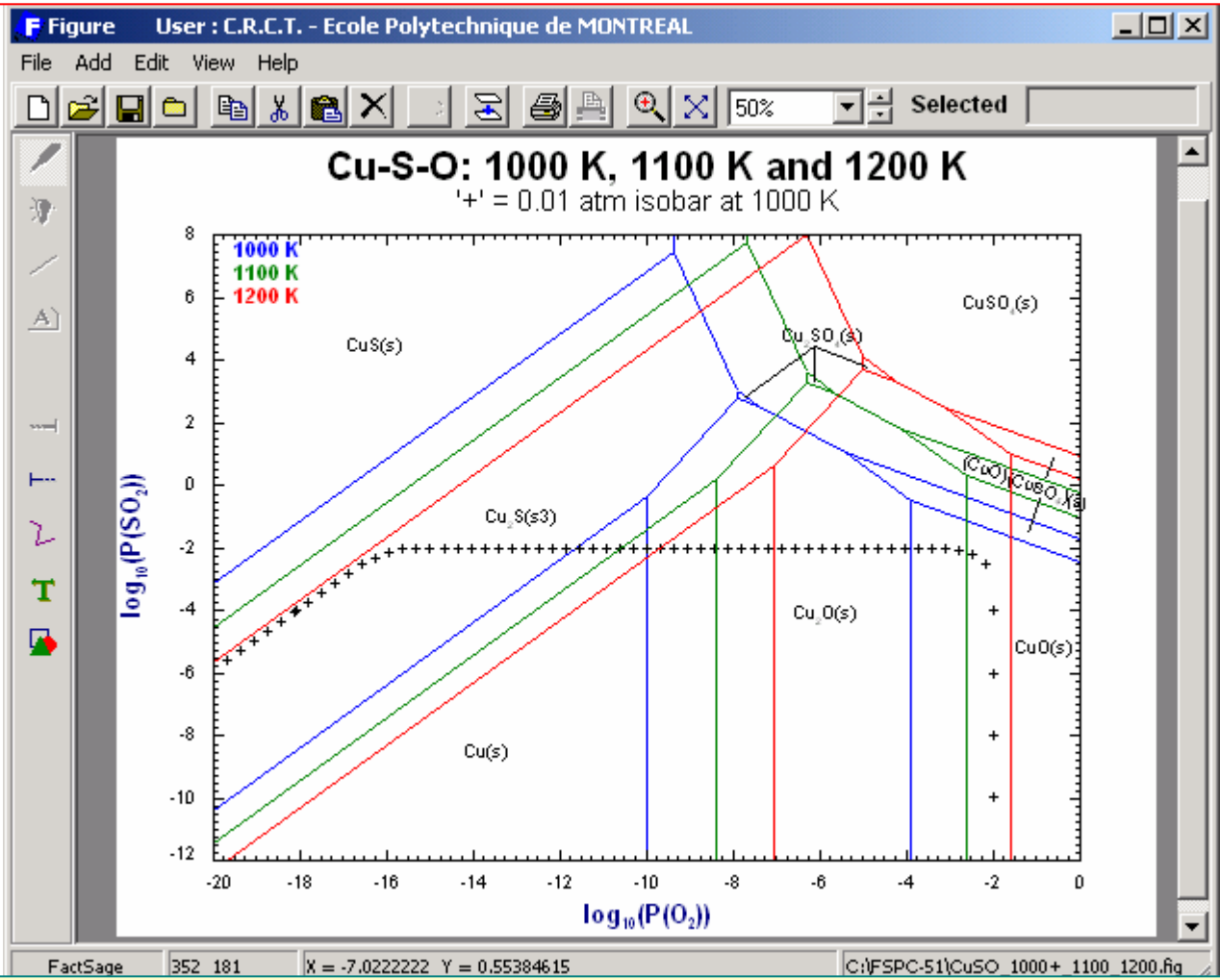
5. Press **Calculate>>**



6. In ***Figure***, edit the diagram and save it.

Figure: Superimposed ***Predom*** diagrams for Cu-SO_2(g)-O_2(g) at 1000, 1100 and 1200 K

7. Repeat steps 3 (but uncheck the isobar checkbox), 5 and 6 for **T=1100 K** and **1200 K**



8. Use the superimpose figure function in the **Figure** program to edit this predominance area diagram at **1000 K**, **1100 K** and **1200 K**.

One-metal predominance diagram with four elements: Fe-S-O-Cl

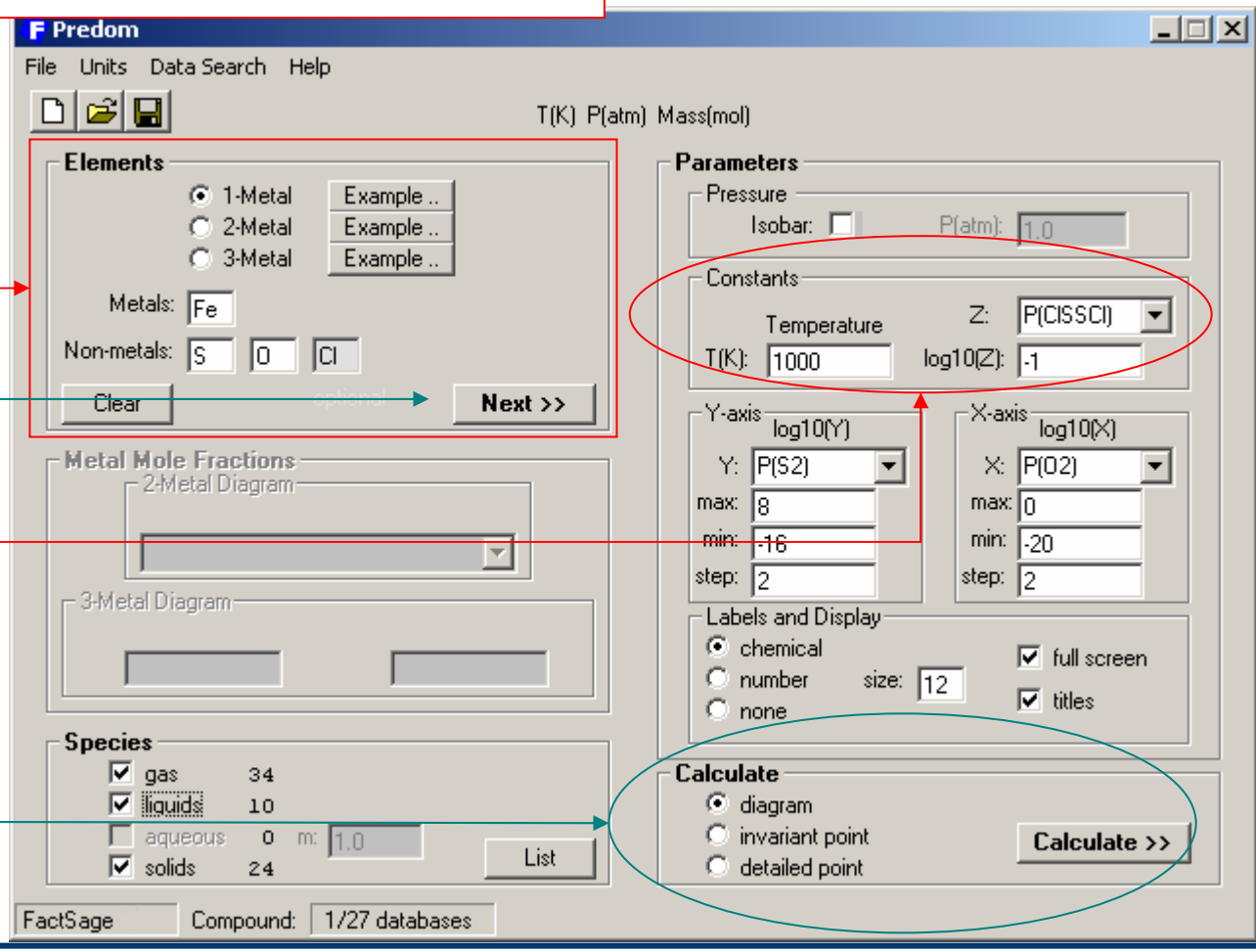
Specifying the isothermal predominance area diagram for: Fe-S_2(g)-O_2(g)- S_2Cl_2(g) at 1000 K and $P_{S_2Cl_2}$= 0.1 atm

1. Enter the elements. This is a **one-metal Fe** system with **S**, **O** and **Cl** non-metallic elements.

2. Press **Next >>**.

3. Note: you must enter **2** constants.
   - **T = 1000 K**
   - **Z = $P_{S_2Cl_2}$= 10^{-1} atm**

4. Select what you wish to calculate and press **Calculate>>**.



Invariant points table and predominance diagram for Fe-S_2(g)-O_2(g)-S_2Cl_2(g)

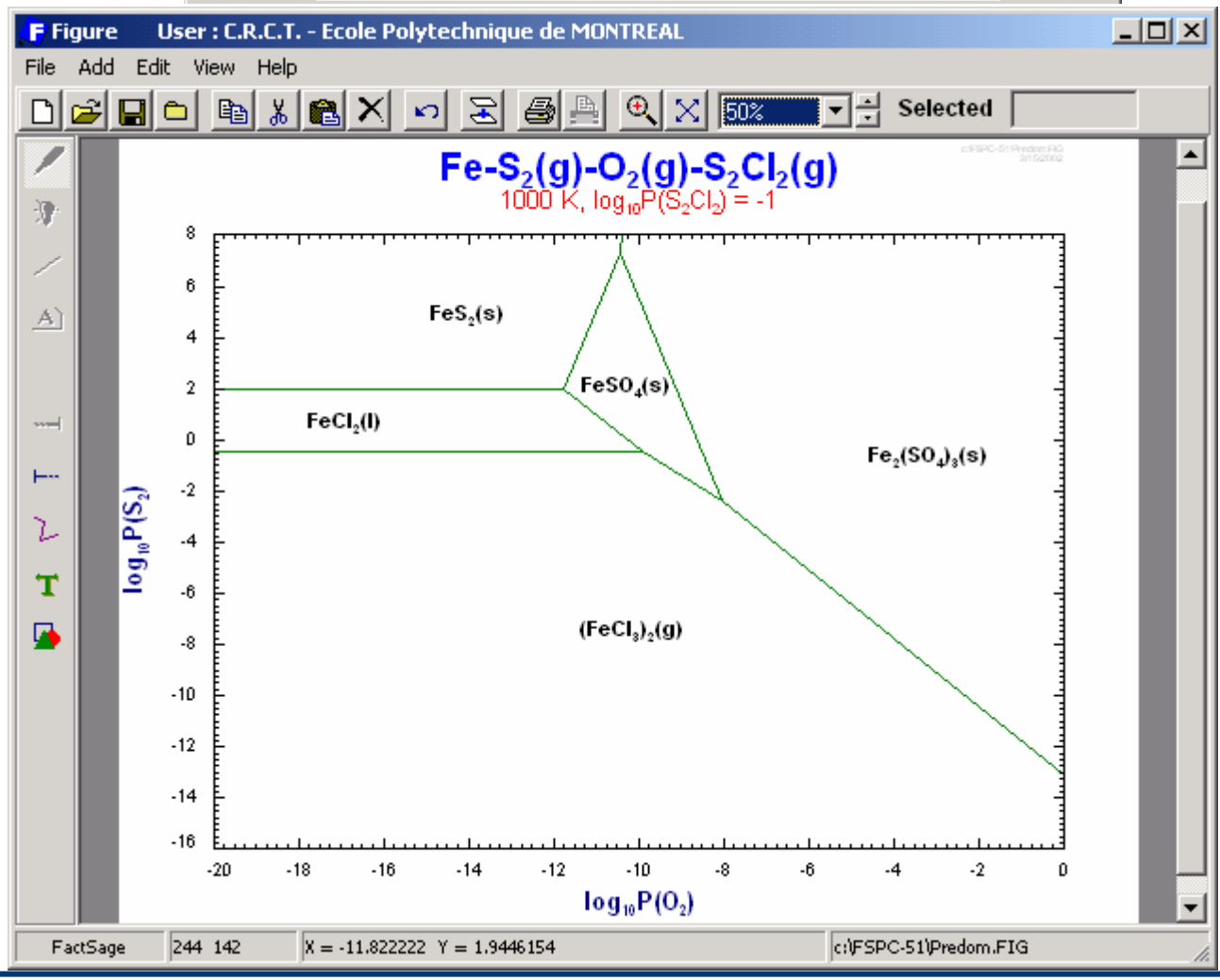
Application:
Chlorination of FeS

Invariant Points - Y = P(S2), X = P(O2), T = 1000 (K).

File Edit

log10[Y]	log10[X]		Species		Species		Species
7.251	-10.448	28	FeS2(s)	31	FeSO4(s)	32	Fe2(SO4)3(s)
1.940	-11.776	28	FeS2(s)	31	FeSO4(s)	13	FeCl2(l)
-2.424	-8.029	31	FeSO4(s)	32	Fe2(SO4)3(s)	8	(FeCl3)2(g)
-0.528	-9.925	31	FeSO4(s)	13	FeCl2(l)	8	(FeCl3)2(g)

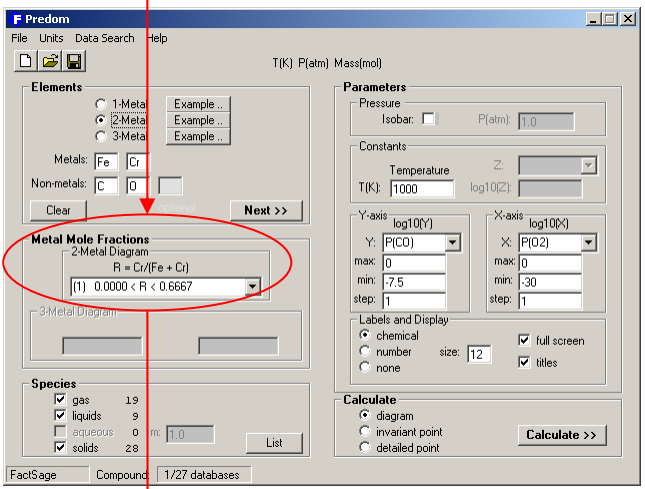
At **1000 K** and
$P_{S_2Cl_2}$ = 0.1 atm

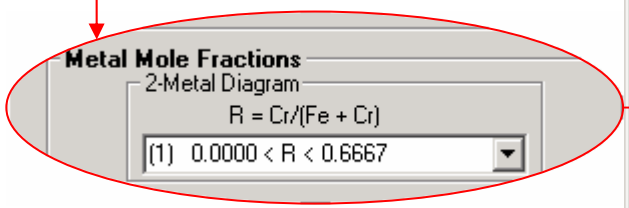


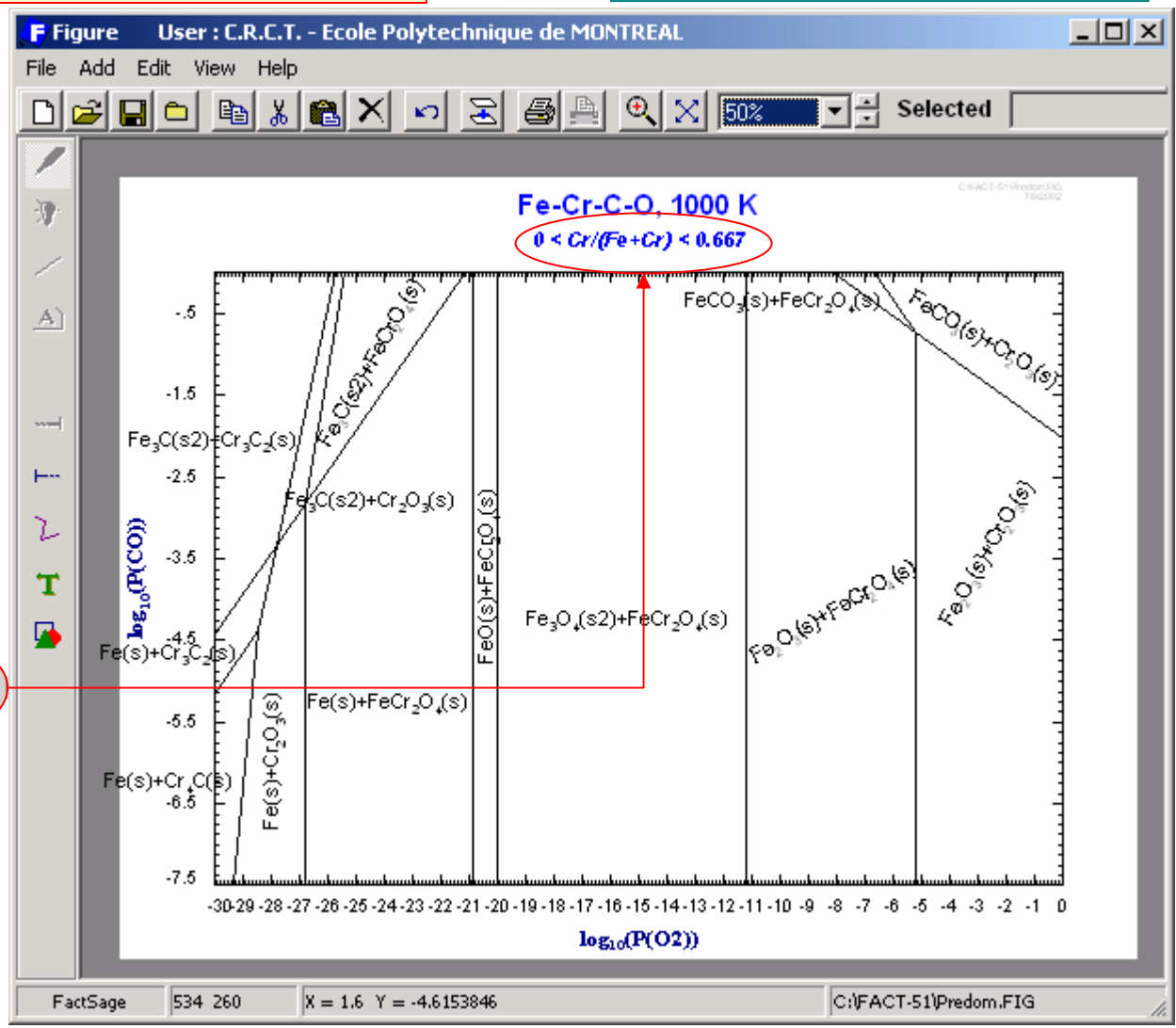
Two-metal predominance diagram with four elements: Fe-Cr-C-O

Fe-rich side of the iron-chronium 2-metal predominance area diagram

Application:
Passivity of Fe-Cr alloys



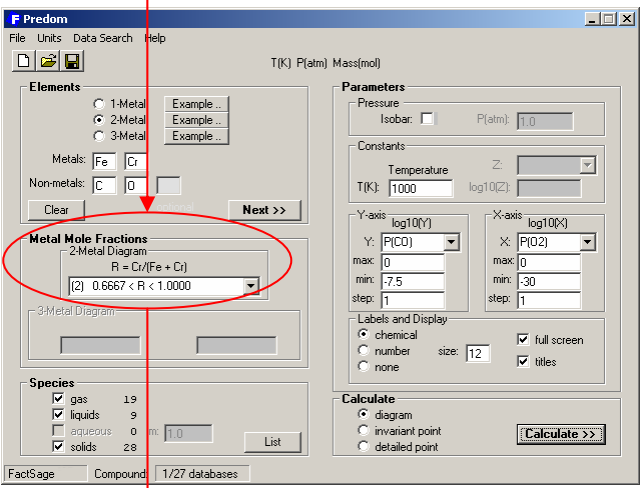


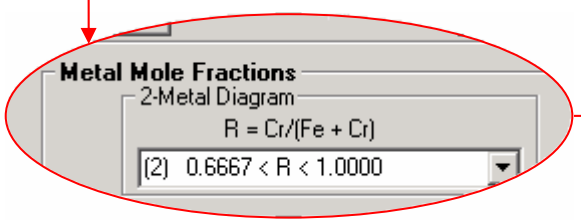


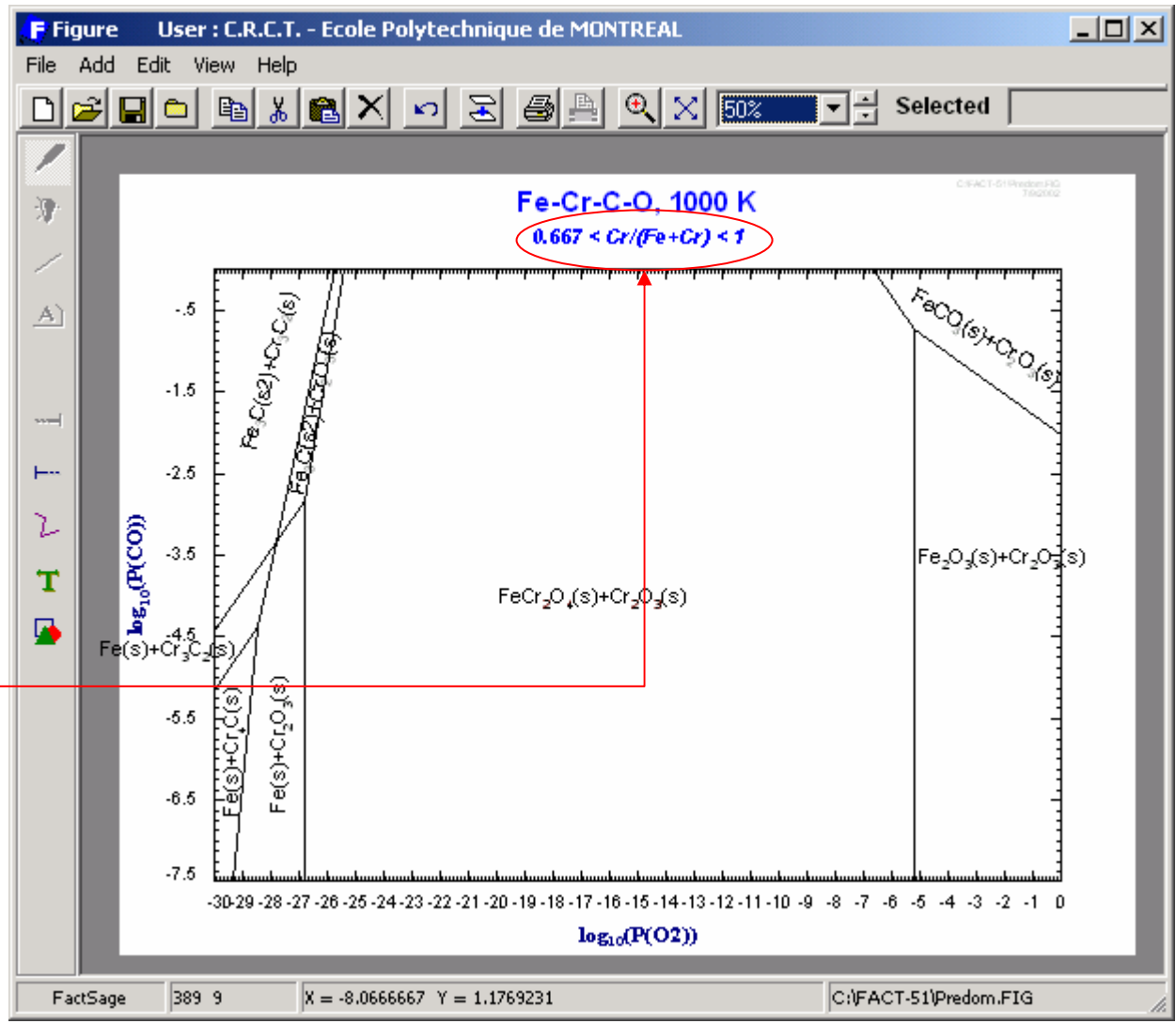
Two-metal predominance diagram with four elements: Fe-Cr-C-O

Cr-rich side of the iron-chronium 2-metal predominance area diagram

Application:
Passivity of Fe-Cr alloys



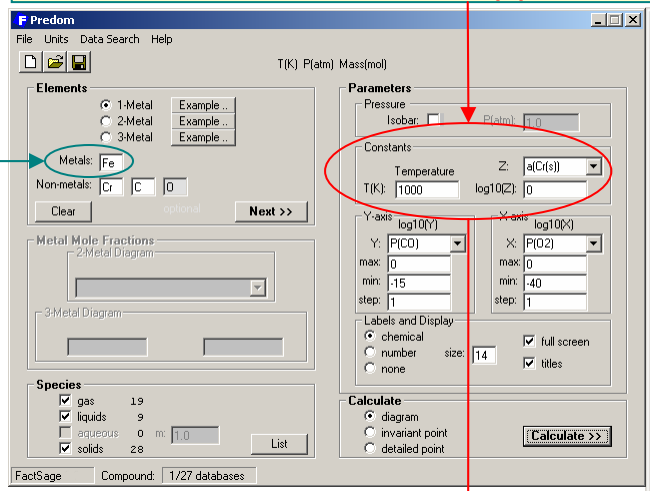


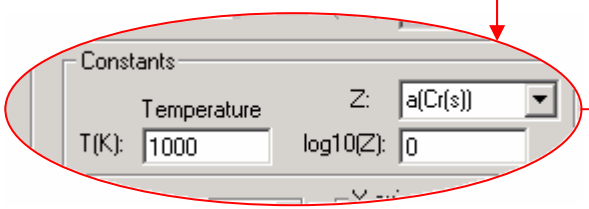


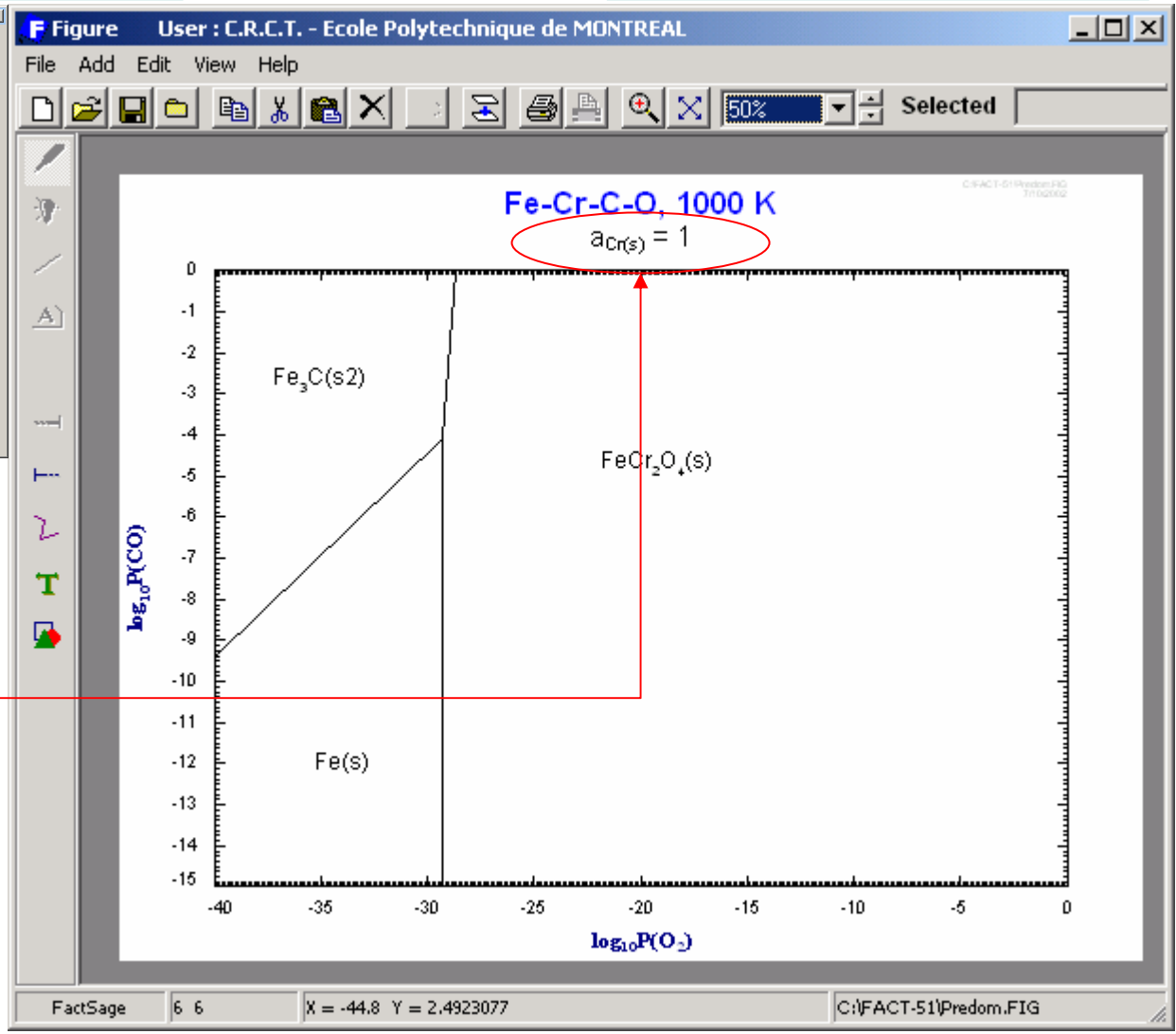
One-metal predominance diagram with four elements: Fe-Cr-C-O

Fe-Cr-C-O with Fe as the 1-metal element, $a_{Cr(s)} = 1$

Application:
Passivity of Fe-Cr alloys



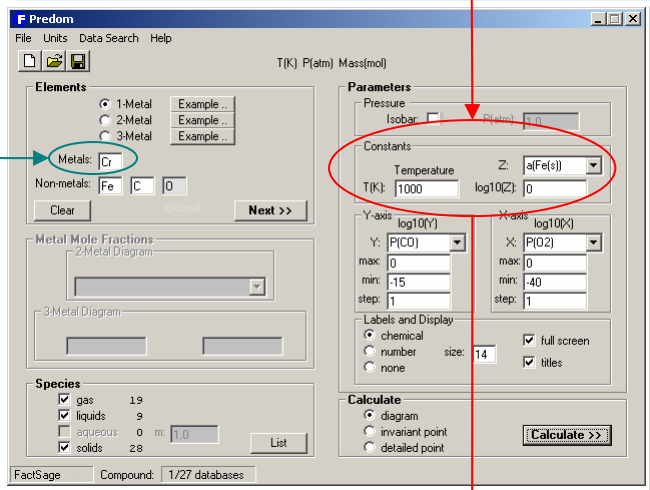


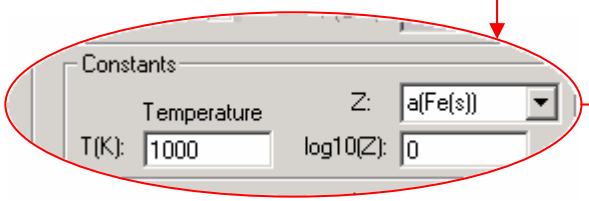


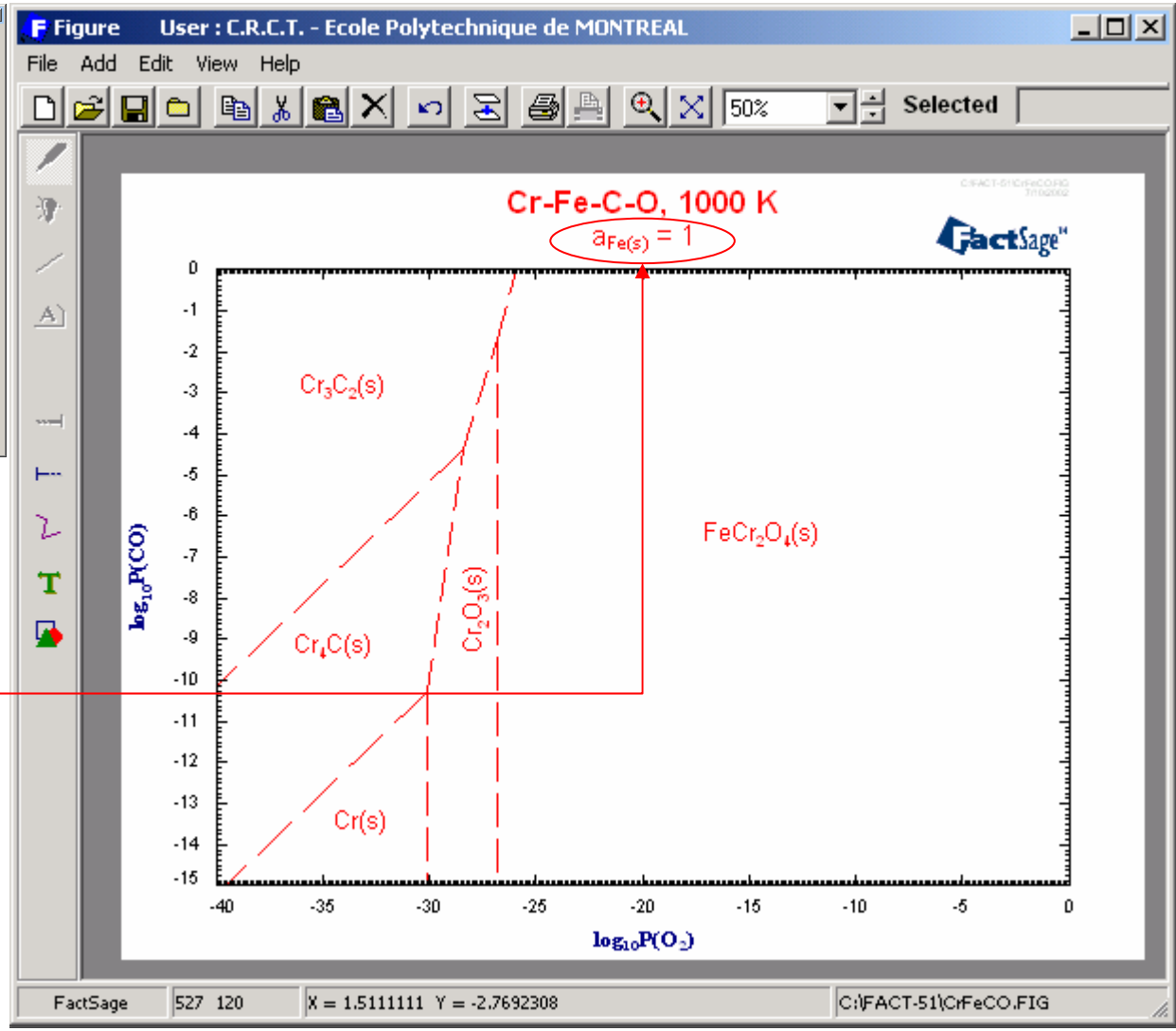
One-metal predominance diagram with four elements: Cr-Fe-C-O

Cr-Fe-C-O with Cr as the 1-metal element, $a_{Fe(s)} = 1$

Application:
Passivity of Fe-Cr alloys

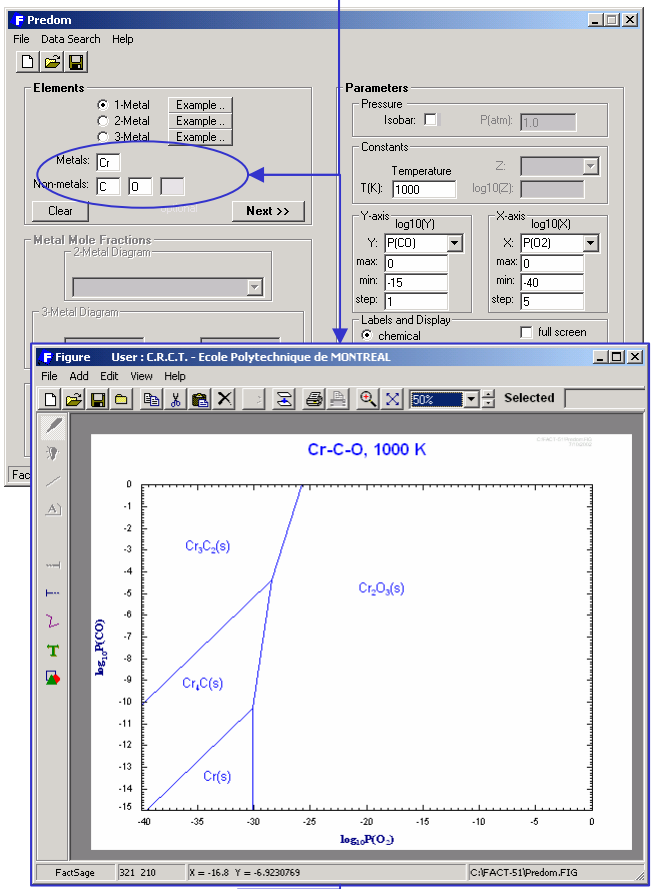


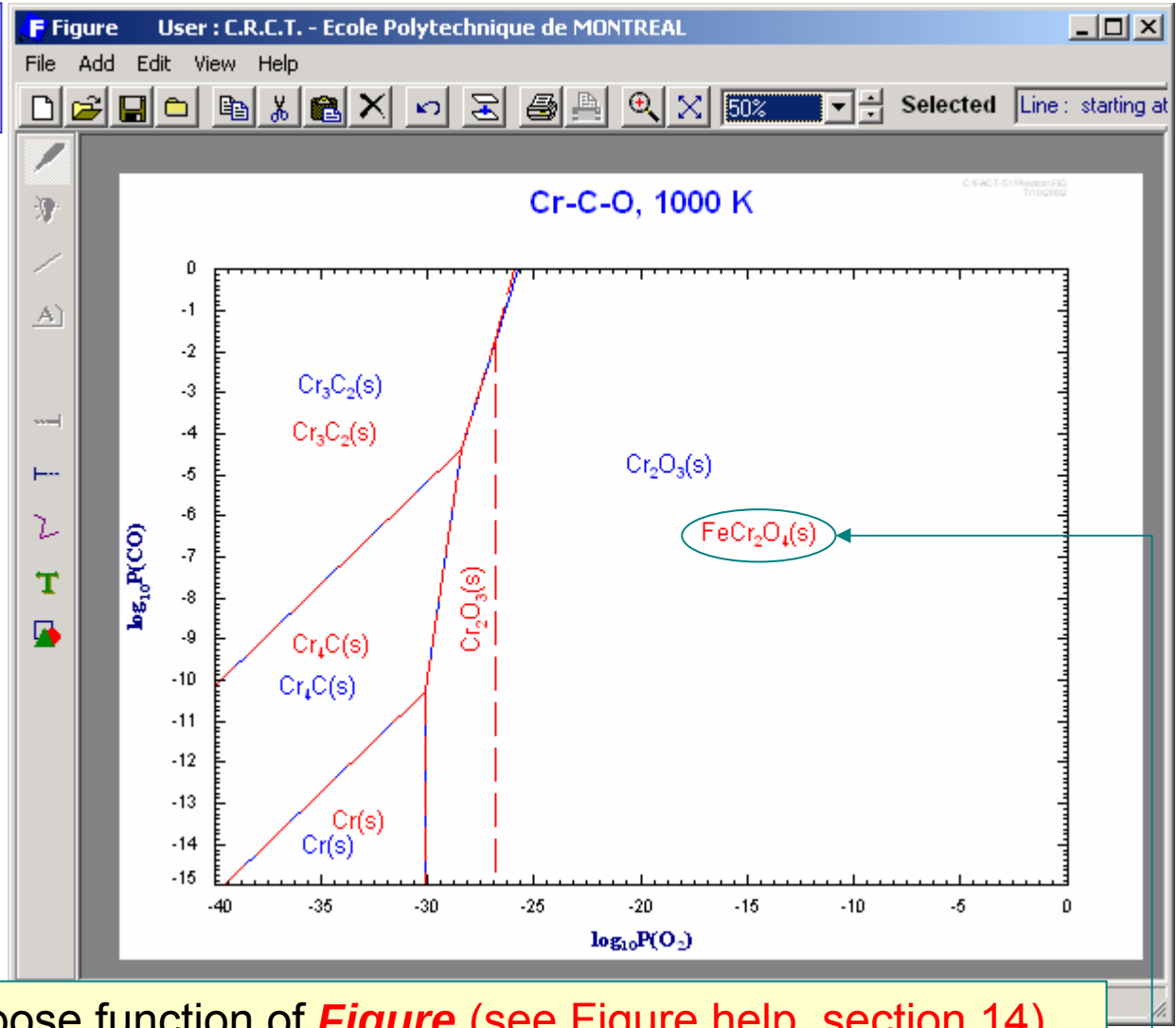




Chromium-Carbon-Oxygen Predominance Diagram

Application:
Decarburization of Chromium





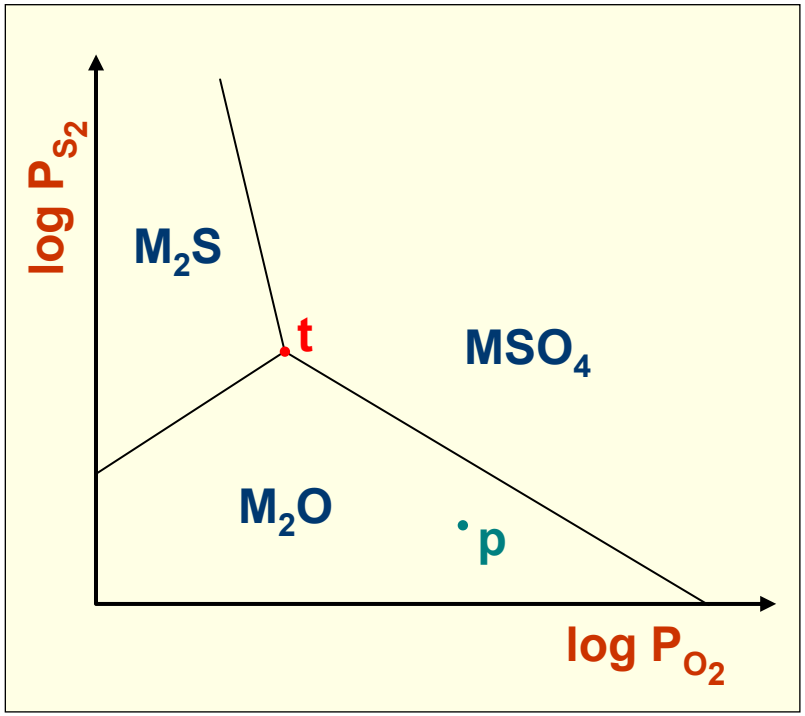
Use of the surimpose function of ***Figure*** (see Figure help, section 14) makes it easy to compare the **Cr-Fe-C-O** diagram (previous slide) with this **Cr-C-O** diagram to show the role of Fe in the formation of $FeCr_2O_4$

The following five slides give a detailed explanation on the stoichiometric relationships of the reactions that govern the phase boundaries in a predominance area diagram.

In principle there is no limitation in this approach as to the number of system components. However, there is one major restriction in the entire approach of using stoichiometric reactions: it is not suited for the treatment of systems with solution phases.

Basic computational procedure in the construction of a predominance diagram

Isothermal predominance diagram establishes at each **log P_{S_2}** and **log P_{O_2}** a particular compound **MS_aO_b** with the lowest **ΔG** of formation (based on 1 mole of M).



$$M + \frac{a}{2}S_2 + \frac{b}{2}O_2 \rightarrow MS_aO_b$$

$$\Delta G_{MS_aO_b} = \Delta G^o_{MS_aO_b} + RT \ln \left(\frac{a_{MS_aO_b}}{a_M \cdot P_{S_2}^{\frac{a}{2}} \cdot P_{O_2}^{\frac{b}{2}}} \right)$$

At point **p**, **ΔG** (for formation) of **M_2O** is most negative (per mole of M).
At point **t**, **ΔG** (for formation) of **M_2O**, **M_2S** and **MSO_4** are equally negative.

Notes:

- It is not necessary to identify possible equilibria among phases by this method.
- The user may set **$a_{MS_aO_b}$** or **$P_{MS_aO_b}$** to other than 1 for some species. Useful especially when **MS_aO_b** is a gaseous species.

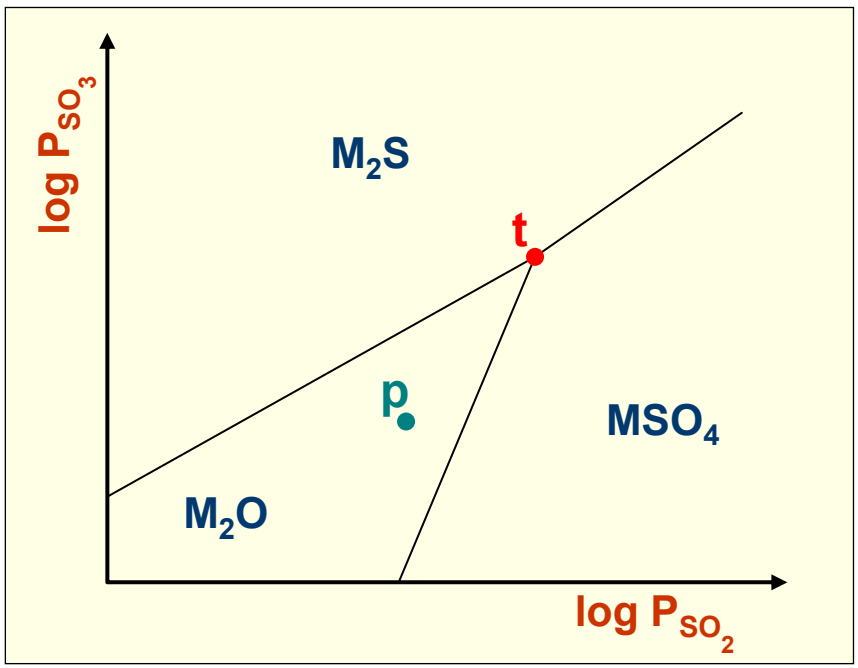
Compounds as species represented on axes

Use of species other than elements for partial pressure associated with the axes. Select S-O species with different ratios of S/O for each axis. For example SO_2 and SO_3:

$$SO_2 + \tfrac{1}{2}O_2 \leftrightarrow SO_3$$

$$3SO_2 \leftrightarrow 2SO_3 + \tfrac{1}{2}S_2$$

At any coordinate, **p**, on the diagram, the partial pressure or chemical potential of elemental species O_2 or S_2 may be determined. The basic algorithm on the previous page can now be applied:

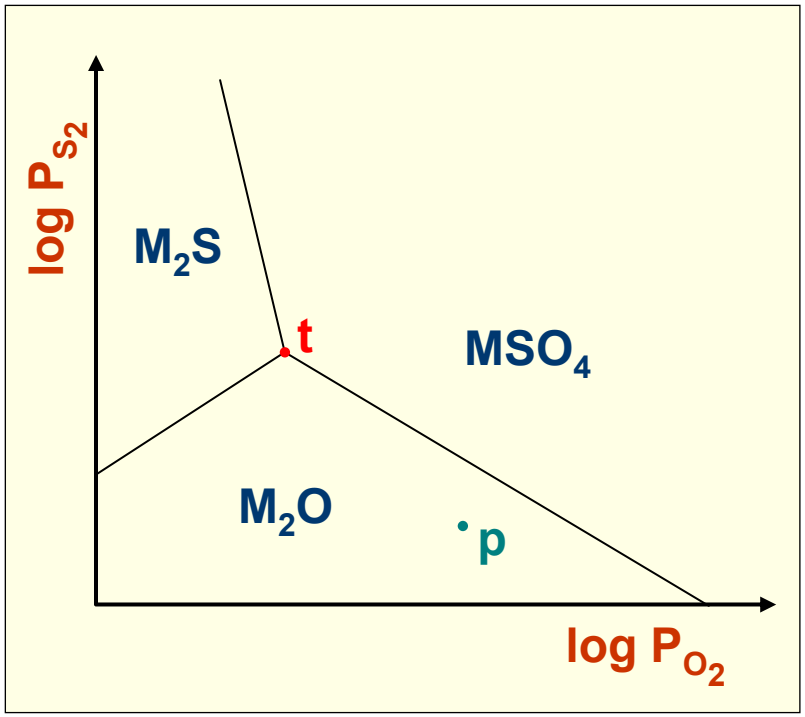


Notes:

- Species on axes must not contain the base element **M**
- Combination of species at triple point is independent of choice of S/O species for axes

Point calculation

At any particular point such as p in a known domain activity of M can be determined.



$$M + \tfrac{a}{2}S_2 + \tfrac{b}{2}O_2 \rightarrow MS_aO_b$$

Insert a_M from above into equation below

$$\Delta G = RT \ln\left(\frac{a_{MS_aO_b}}{a_M \cdot P_{S_2}^{\frac{a}{2}} \cdot P_{O_2}^{\frac{b}{2}}}\right)$$

To find the activity of each MS_aO_b: $M + \tfrac{a}{2}S_2 + \tfrac{b}{2}O_2 \leftrightarrow MS_aO_b$

Activities and partial pressures of base-element-containing species at any point in the diagram. The activity of the particular species MS_aO_b identifying that domain is the set value (usually 1).

More than 3 Elements Involved in Diagram

2 ways to proceed:

a) Fix additional chemical potentials (eg. P_{Cl_2})

Formulate formation reactions to construct the predominance area diagram shown in ***Predom*** 15 as follows:

$$M + \frac{a}{2}S_2 + \frac{b}{2}O_2 + \frac{c}{2}Cl_2 \rightarrow M_1S_aO_bCl_c$$

One can specify P_{Cl_2} for entire diagram, or as in ***Predom*** 15, specify partial pressure or activity of any Cl-S-O species (eg. S_2Cl_2)

$$S_2(g) + Cl_2(g) \leftrightarrow S_2Cl_2(g)$$

By this equilibrium, one can find Cl_2 for any S_2 partial pressure

b) Introduce an additional base element (eg. N)

$$(1-r)M + rN + \tfrac{a}{2}S_2 + \tfrac{b}{2}O_2 \rightarrow gM_wN_xS_cO_d + hM_yN_zS_eO_f$$

Base elements (specify range in which r may be found)

Combination of two M and N containing compounds which satisfy the mass balances with non negative values for g and h for a specified value of r

Note: In the case of a **two base element** diagram each domain is **doubly labelled**. In the special case of there being no compounds containing both M and N, the two base element diagram may be regarded simply as the superimposition of the two one base element diagrams for M and N.