The *EpH* module

- ***EpH*** calculates and plots isothermal EpH (Pourbaix) diagrams.
- ***EpH*** accesses only compound databases and treats the aqueous phase as an ideal solution.

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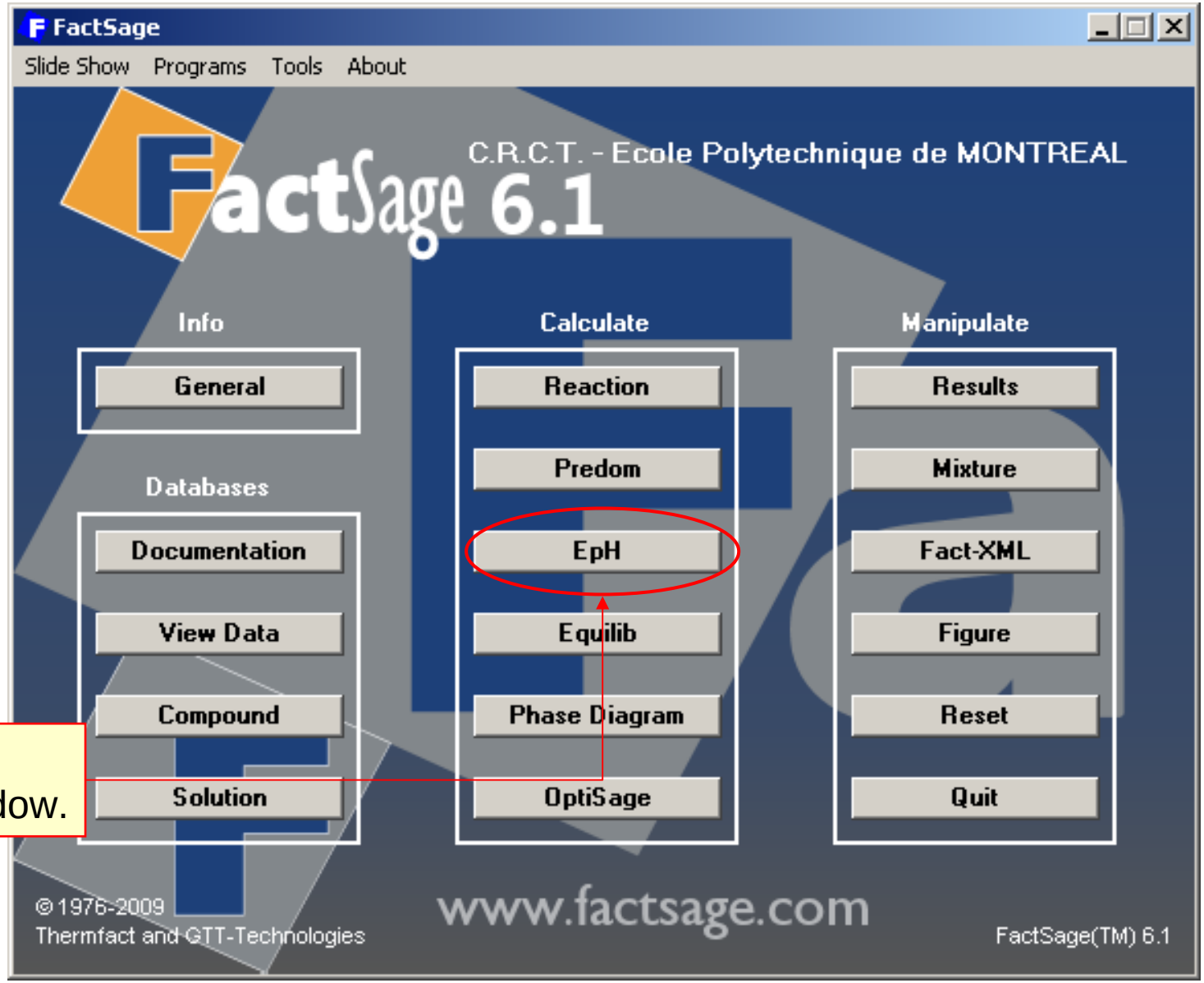
The *EpH* module



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

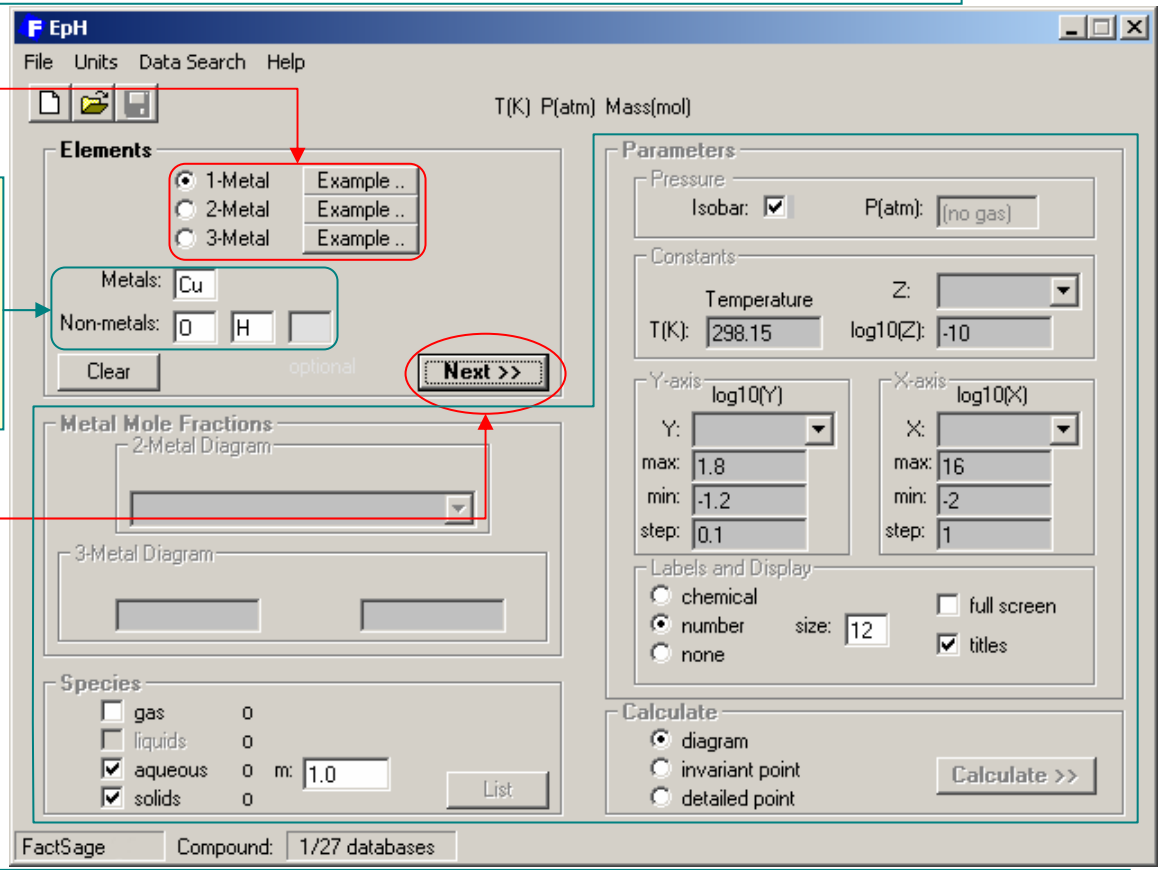
Specifying the Cu-water Eh-pH diagram: the Elements frame

EpH generates redox **potential-pH** (**Pourbaix**) **diagrams** using data from the **compound databases** that include **dilute Henrian solutes**.

1° **Specify** the type of Pourbaix diagram (**1-**, 2- or 3-Metal)

2° **Enter** the elements: **Cu**, **O**, **H** (**O** and **H** are **automatically** entered). **Cu-based species will appear in all domains**.

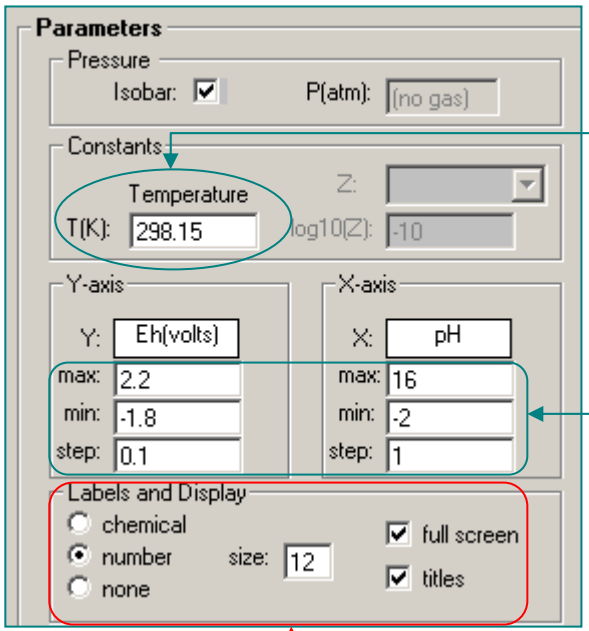
3° **Click** the **Next >>** button to initiate the **data search**.



When you **click** the **Next >>** button the pure substances databases are automatically scanned to find all the compounds and henrian solutes formed from the elements. When you make changes in the **Elements** frame it is necessary to **click** the **Next >>** button to **refresh** the system.

Specifying the Cu-water Eh-pH diagram: the Parameters frame

Pressure: The total pressure has no effect upon the ***EpH*** diagram. If you specify a total pressure isobar, this will appear as a series of '**+**'s on the calculated diagram. The total pressure is the sum of partial pressures of all gaseous species and is only computed after the diagram has been calculated. For example, see the **Ti-H-O-F** diagram later on.



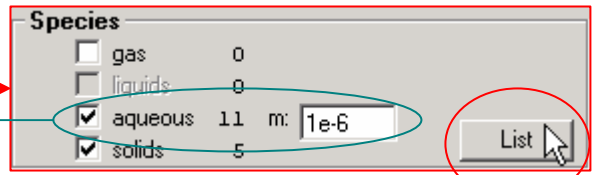
Constants: T = 298.15 K.
For a diagram with a non metallic element other than H and O (Ti-H-O-F for example), it is necessary to specify an additional thermodynamic variable, Z.

Axes: Eh(volts): -1.8 to 2.2, pH: -2 to 16.
The step size determines the axis «ticks» and labels on the diagram and the density of characters '**+**' for the total pressure isobar. A step of **0.1** for the Y-axis and **1** for the X-axis is typical.

Labels and Display: Here you can control the type and size (8 – 20) and type of labels on the calculated diagram.

Specifying the Cu-water Eh-pH diagram: the Species frame

Here you **select** the species to be used in calculation. You may **include** or **exclude** all the **gases**, all the **solids** or all the **liquids**. Unless indicated otherwise, metallic species are assumed to be pure and at unit activity, molality or partial pressure. You can also use the input box "**m:**" to set a common value to all **aqueous** species. For example, **m = 1×10^{-6}**. To **examine** the species or to **add** or **remove** a particular species or **change** its activity, molality or partial pressure, **click** the "**List**" button.



The **concentration** of ions provides the **standard** **Pourbaix** diagram used in **corrosion** application.

List - P(atm), T(K) = 298.15

File Edit Help

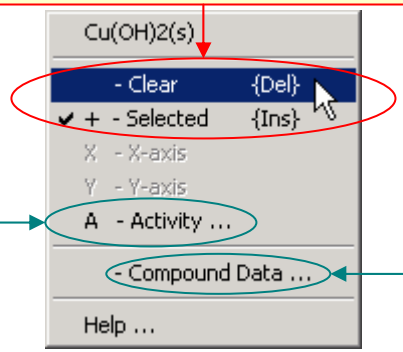
+	Code	A	T	Species	Data	A/P/M	Cp range	G(KJ)	G(Kcal)
				Cu gases:					
	1			Cu(g)	FACT	1.0000E+00	298 - 6000	288.021	68.839
	2			Cu2(g)	FACT	1.0000E+00	298 - 6000	413.308	98.783
	3			CuO(g)	FACT	1.0000E+00	298 - 6000	236.351	56.489
				Cu liquids:					
	4			Cu(l)	FACT	1.0000E+00	298 - 4000	-0.552	-0.132
	5			Cu2O(l)	FACT	1.0000E+00	298 - 2000	-150.740	-36.028
				Cu aqueous species:					
+	6	A		Cu[+]	FACT	1.0000E-06	298 - 573	59.446	14.208
+	7	A		Cu[2+]	FACT	1.0000E-06	298 - 573	94.542	22.596
+	8	A		CuO2[2-]	FACT	1.0000E-06	298 - ****	-183.678	-43.900
+	9	A		HCuO2[-]	FACT	1.0000E-06	298 - ****	-258.571	-61.800
				Cu solids:					
+	10			Cu(s)	FACT	1.0000E+00	298 - 2001	-9.888	-2.363
+	11			CuO(s)	FACT	1.0000E+00	298 - 2000	-168.762	-40.335
+	12			Cu2O(s)	FACT	1.0000E+00	298 - 2000	-198.244	-47.381
+	13			Cu(OH)2(s)	FACT	1.0000E+00	298 - 1500	-482.675	-115.362
				Other gases:					
	14			H(g)	FACT		298 - 6000	183.829	43.936
	15			H2(g)	FACT		298 - 6000	-38.930	-9.304
	16			O(g)	FACT		298 - 6000	201.186	48.085
	17			O2(g)	FACT		298 - 6000	-61.132	-14.611
	18			O3(g)	FACT		298 - 6000	71.469	17.082

Specifying the Cu-water Eh-pH diagram: the List window

We **suppress** species 13: **$Cu(OH)_2$** in order to compare the calculated diagram with one published in the «**Atlas of Electrochemical Equilibria in Aqueous Solution**» (M. Pourbaix, Pergammon Press, 1966)

Click in the **+** to **remove** species **13**. You can also **right-click** on the «+» column to access an extended menu and **select clear**.

+	Code	A	T	Species	Data	A/P/M	Cp range	G(KJ)	G(Kcal)
				Cu gases:					
	1			Cu(g)	FACT	1.0000E+00	298 - 6000	288.021	68.839
	2			Cu2(g)	FACT	1.0000E+00	298 - 6000	413.308	98.783
	3			CuO(g)	FACT	1.0000E+00	298 - 6000	236.351	56.489
				Cu liquids:					
	4			Cu(l)	FACT	1.0000E+00	298 - 4000	-0.552	-0.132
	5			Cu2O(l)	FACT	1.0000E+00	298 - 2000	-150.740	-36.028
				Cu aqueous species:					
+	6	A		Cu[+]	FACT	1.0000E-06	298 - 573	59.446	14.208
+	7	A		Cu[2+]	FACT	1.0000E-06	298 - 573	94.542	22.596
+	8	A		CuO2[2-]	FACT	1.0000E-06	298 - *****	-183.678	-43.900
+	9	A		HCuO2[-]	FACT	1.0000E-06	298 - *****	-258.571	-61.800
				Cu solids:					
+	10			Cu(s)	FACT	1.0000E+00	298 - 2001	-9.888	-2.363
+	11			CuO(s)	FACT	1.0000E+00	298 - 2000	-168.762	-40.335
+	12			Cu2O(s)	FACT	1.0000E+00	298 - 2000	-198.244	-47.381
	13			Cu(OH)2(s)	FACT	1.0000E+00	298 - 1500	-482.675	-115.362
				Other gases:					
	14			H(g)	FACT		298 - 6000	183.829	43.936
	15			H2(g)	FACT		298 - 6000	-38.930	-9.304
	16			O(g)	FACT		298 - 6000	201.186	48.085
	17			O2(g)	FACT		298 - 6000	-61.132	-14.611
	18			O3(g)	FACT		298 - 6000	71.469	17.082
	19			OH(g)	FACT		298 - 6000	-15.753	-3.765
	20			H2O(g)	FACT		298 - 6000	-298.102	-71.248
	21			HO2(g)	FACT		298 - 6000	-66.183	-15.818
							298 - 1500	-205.540	-49.125
							298 - 500	-306.686	-73.300
							298 - 431	-219.984	-52.577
							298 - 500	0.000	0.000
+	26	A		H2(aq)	FACT		289 - 573	-21.399	-5.114
+	27	A		O2(aq)	FACT		298 - 400	-44.773	-10.701
+	28	A		OH[-]	FACT		298 - 573	-226.744	-54.193
+	29	A		HO2[-]	FACT		298 - 573	-167.358	-39.999
+	30	A		HOOH(aq)	FACT		298 - 473	-234.122	-55.956
+	31	A		e[-](aq)	ELEM		298 - 6000	-19.465	-4.652
				Other solids:					
+	32		T	H2O(s)	FACT		250 - 273	-306.093	-73.158

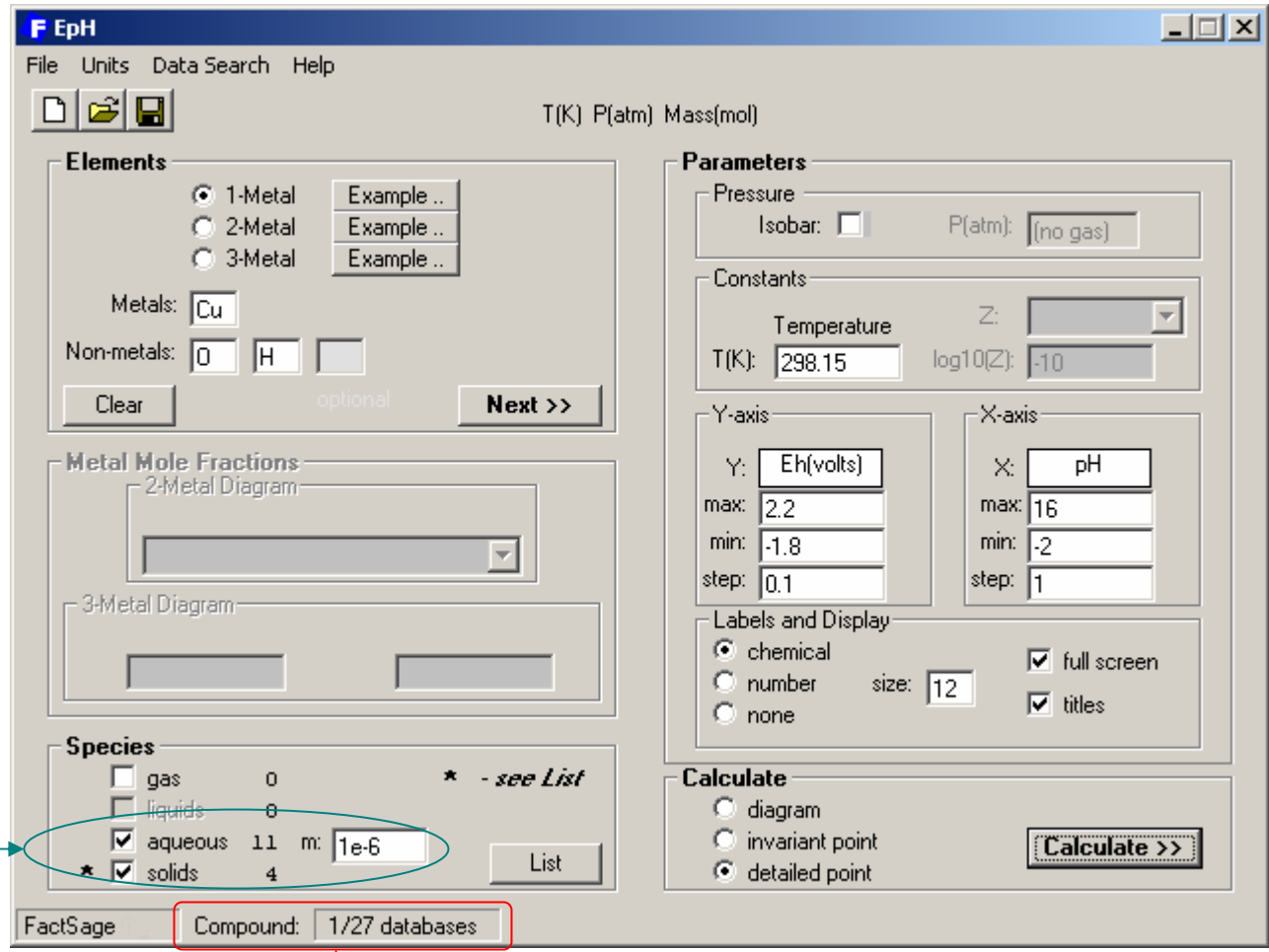


Select – Compound Data… or **double-click** on the species to **view** it's compound data.

You can **select** A – Activity… or **double-click** in the A/P/M column to **change** the activity (partial pressure or molality) of a species.

Specifying the Cu-water Eh-pH diagram: Compound selection

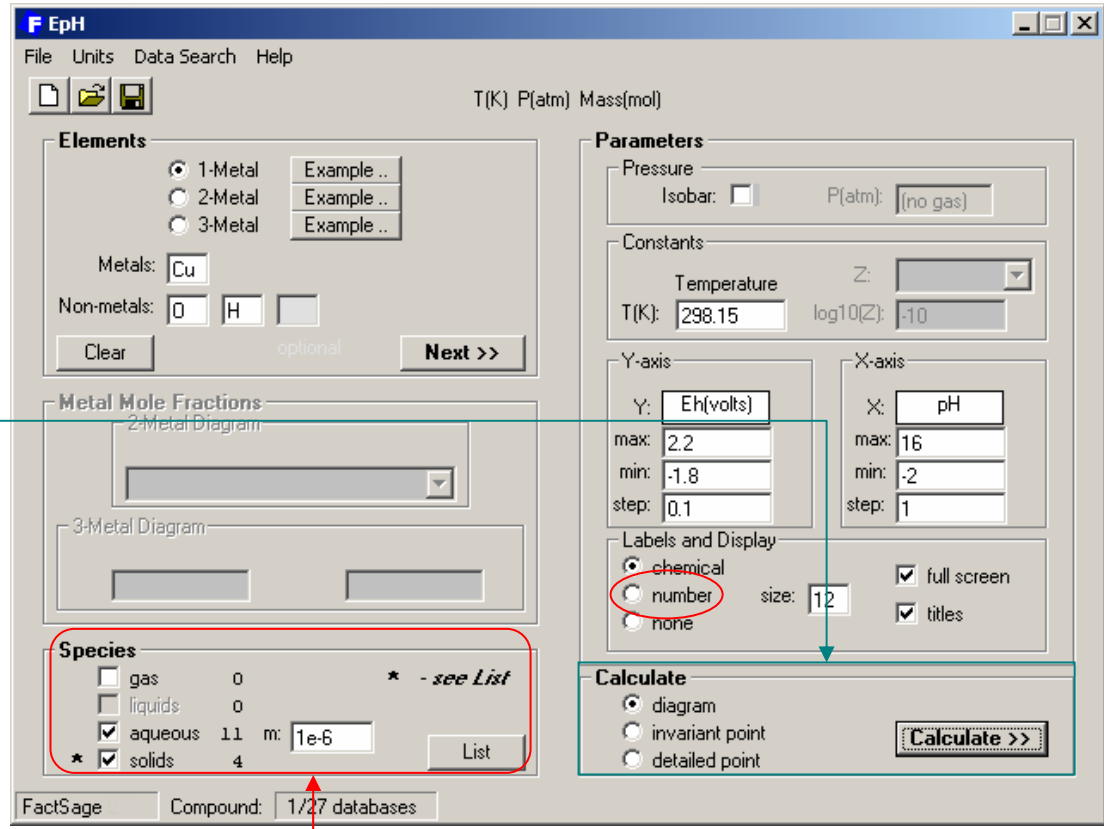
11 aqueous species and **4 solids** species were selected from the ***FACT*** **compound** database containing **Cu**, **O** and/or **H**.



Here, only the ***FACT*** **compound** database is included.
See section 9 for **inclusion** or **exclusion** of a **database**.

Specifying the Cu-water Eh-pH diagram: the Calculate frame

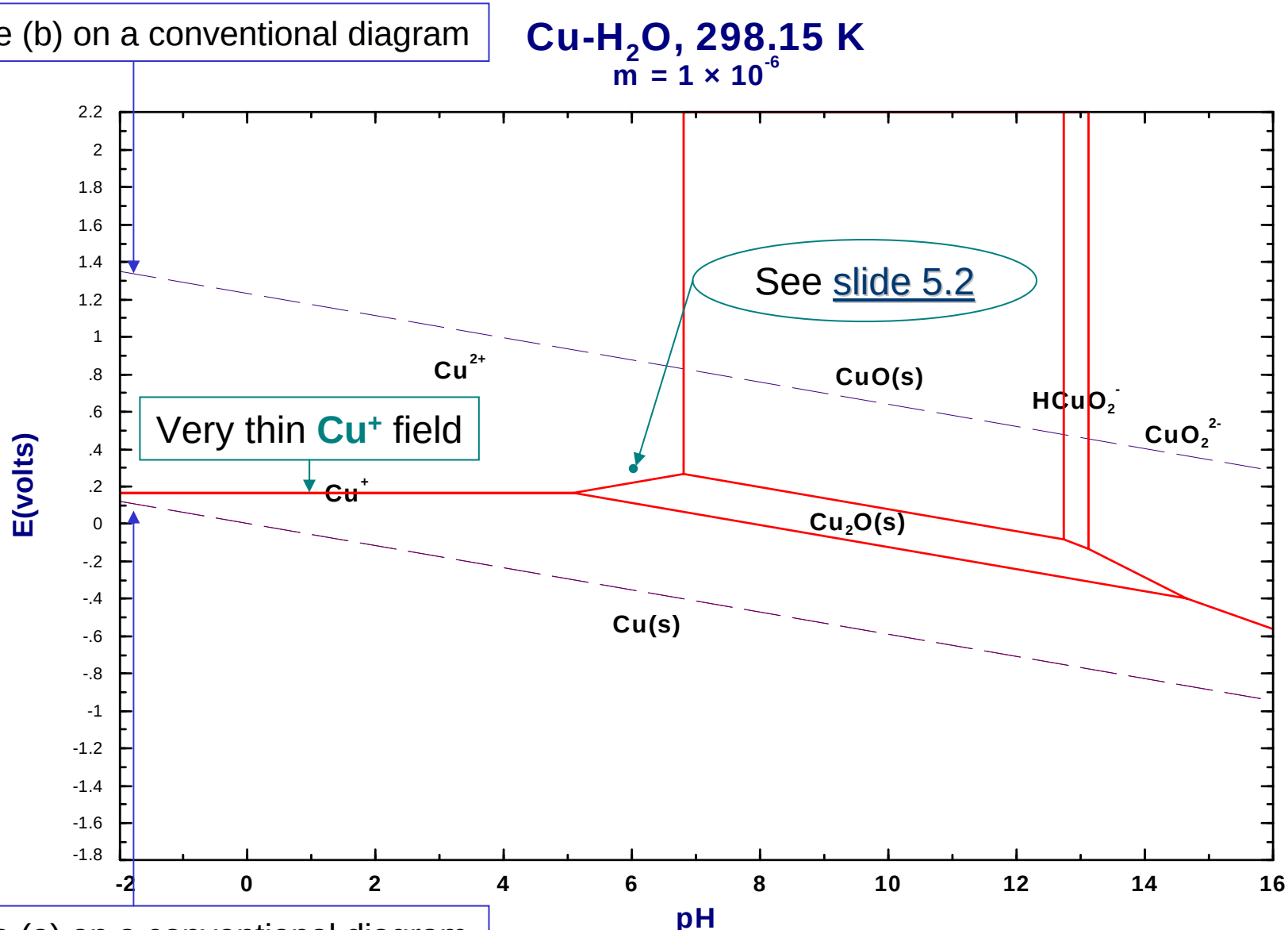
- **Diagram:**
  This calculates and plots the diagram.
- **Invariant Point:**
  This gives the precise position of the triple points where three domains meet.
- **Detailed Point:**
  This enables you to display the equilibrium activity or partial pressure of all species at a specified coordinate on the diagram.



Note the **custom** (*) **selection** of **solid** species.

Cu-H_2O Eh-pH diagram: Graphical Output

O_2 (1 atm) line (b) on a conventional diagram



H_2 (1 atm) line (a) on a conventional diagram

Published **Pourbaix** diagram for **Cu-H_2O**

Lines for **m = 1 × 10^{-6}** are highlighted in red.

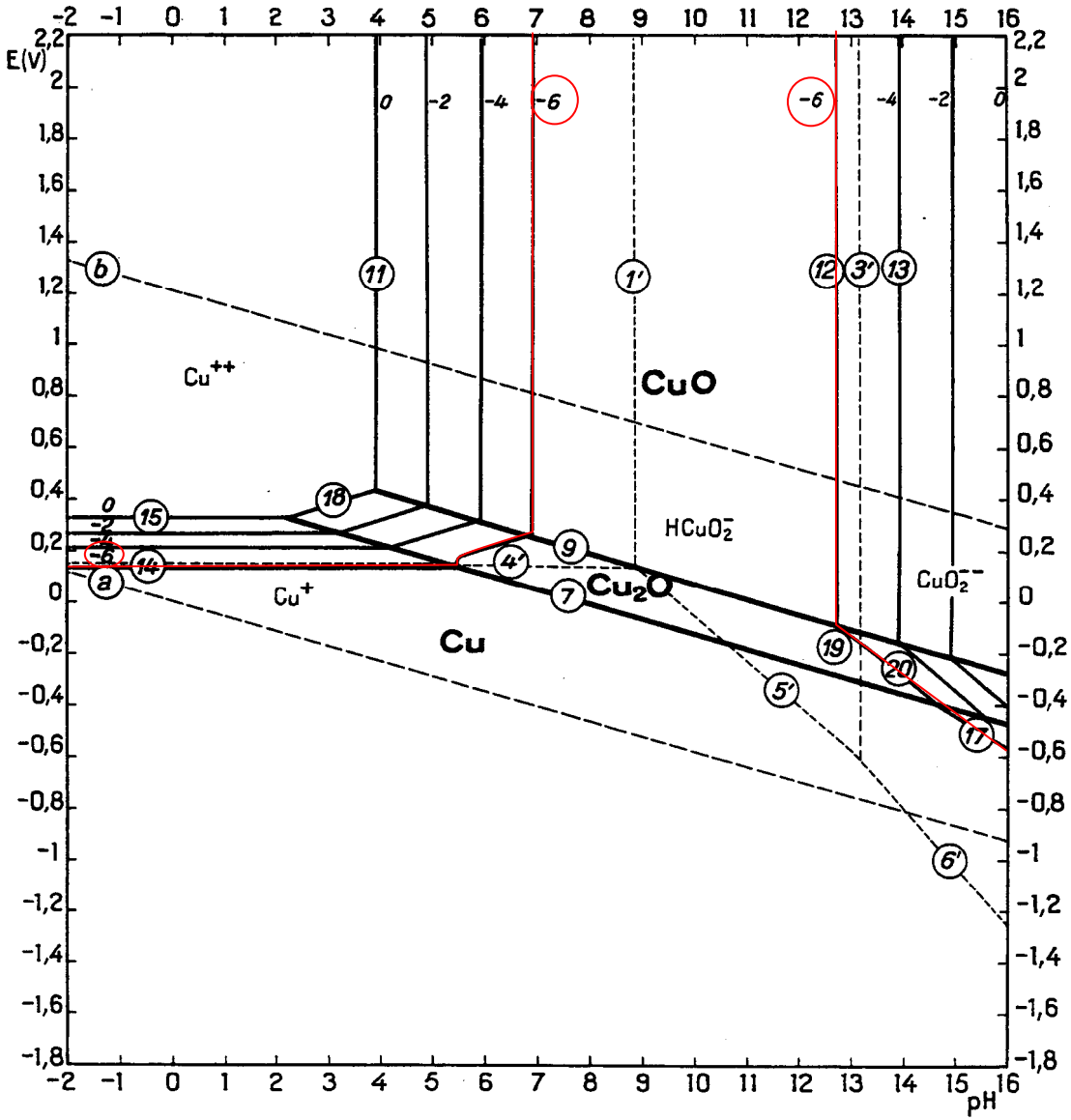
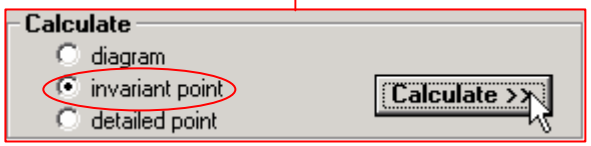


FIG. 1. Potential–pH equilibrium diagram for the system copper–water, at 25°C.
[Considering the solid substances Cu, Cu_2O and CuO. $Cu(OH)_2$ is not considered.]

Cu-H_2O Eh-pH diagram: Computation of invariant points



Invariant Points - E(volts), pH, T(K) = 298.15

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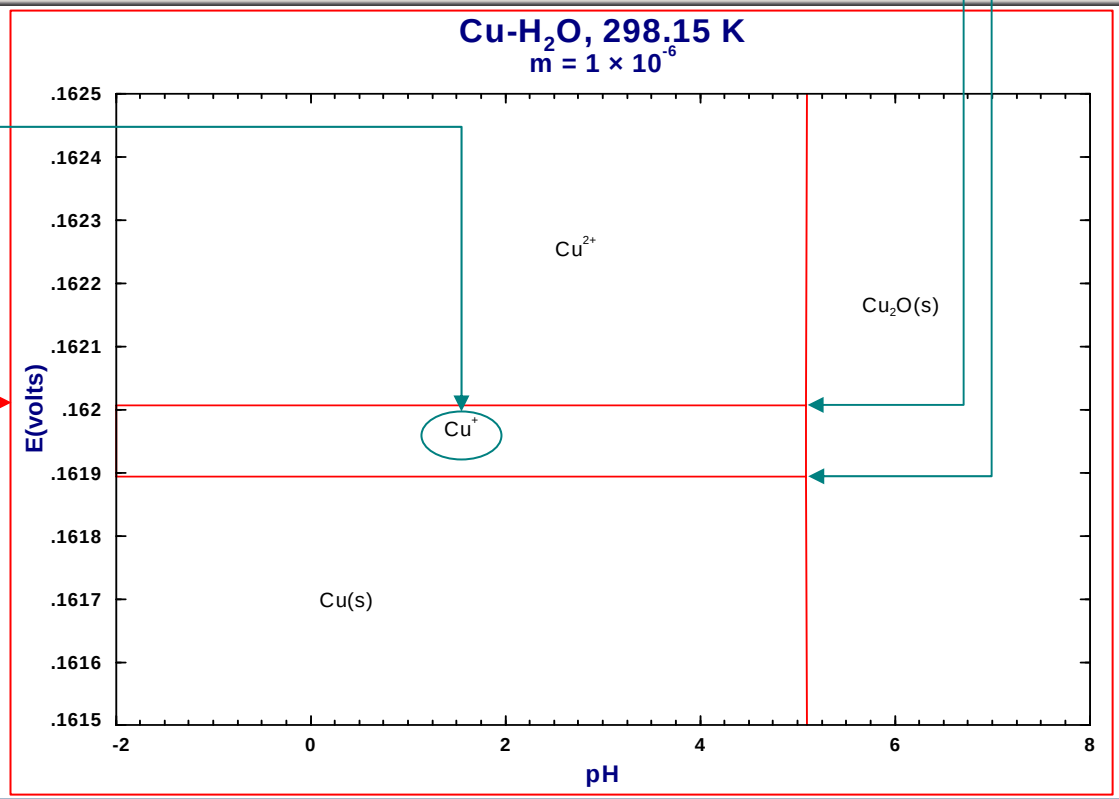
E(volts)	pH		Species A		Species B		Species C
0.1619	5.0847	10	Cu[s]	6	Cu[+]	12	Cu2O[s]
-0.4036	14.6431	10	Cu[s]	8	CuO2[2-]	12	Cu2O[s]
0.1620	5.0847	6	Cu[+]	7	Cu[2+]	12	Cu2O[s]
0.2635	6.8000	7	Cu[2+]	11	CuO[s]	12	Cu2O[s]
-0.0875	12.7328	11	CuO[s]	12	Cu2O[s]	9	HCuO2[-]
-0.1334	13.1207	8	CuO2[2-]	12	Cu2O[s]	9	HCuO2[-]

A very thin Cu^+ field indeed!

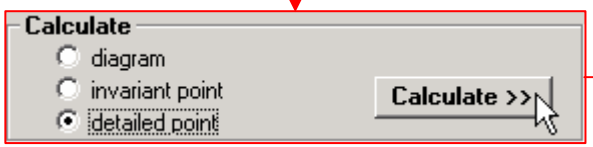
Enlargement of the previous diagram



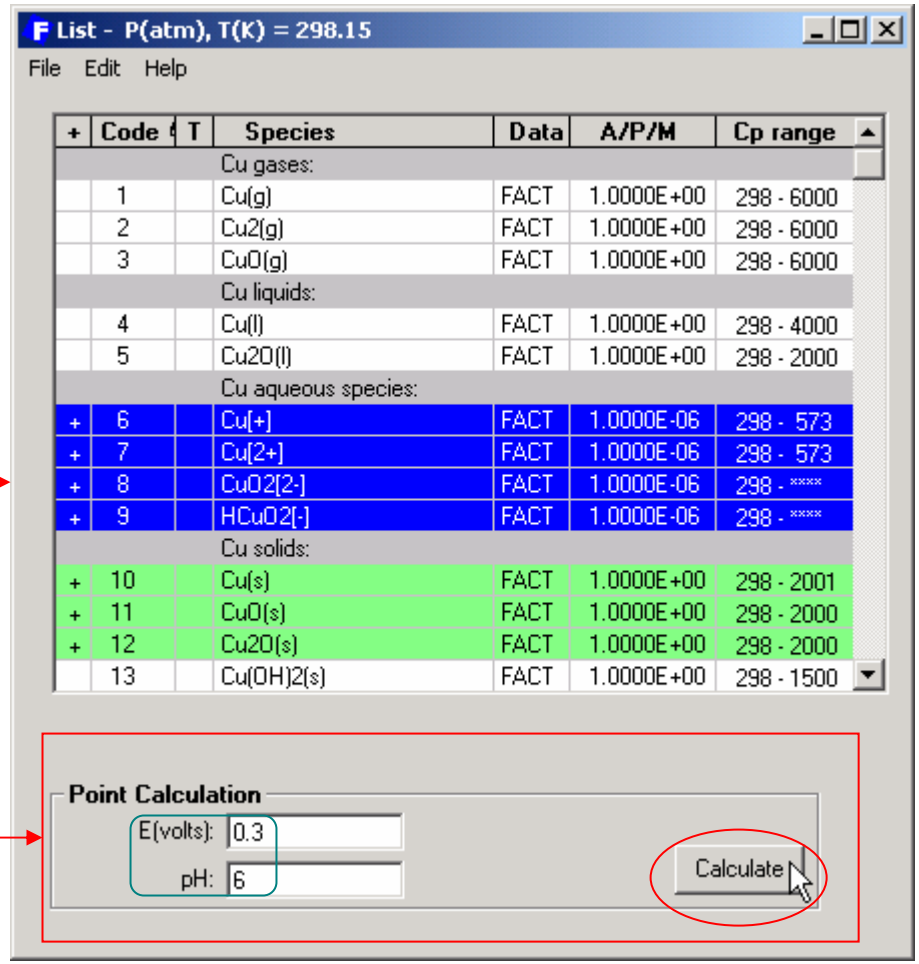
Cu-H_2O Eh-pH diagram: Detailed Point Calculation

The point calculation gives activities and ideal concentrations for all metal-element containing species at the specified coordinate, E(volts), pH.

1° Select detailed point in the Calculate frame to open a Point Calculation dialog box.

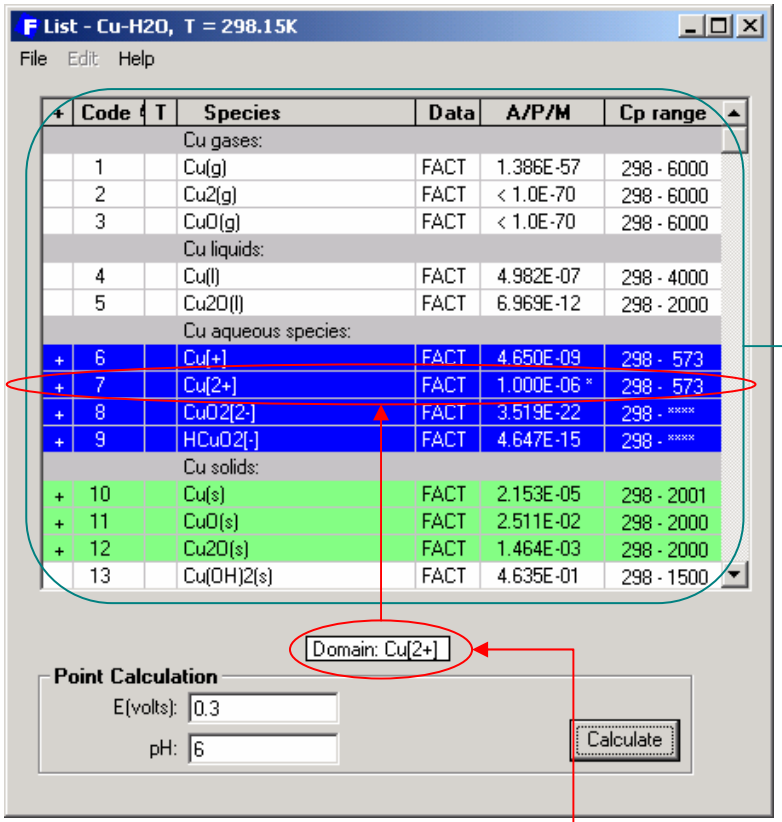


2° Enter the coordinate of interest and press the Calculate button.



The specified coordinate is in the domain of Cu^{2+} set at 10^{-6} (the green dot on slide 4.2).

$Cu\text{-}H_2O$ Eh-pH diagram: Detailed Point Calculation – Output



+	Code	T	Species	Data	A/P/M	Cp range
			Cu gases:			
	1		Cu(g)	FACT	1.386E-57	298 - 6000
	2		Cu2(g)	FACT	< 1.0E-70	298 - 6000
	3		CuO(g)	FACT	< 1.0E-70	298 - 6000
			Cu liquids:			
	4		Cu(l)	FACT	4.982E-07	298 - 4000
	5		Cu2O(l)	FACT	6.969E-12	298 - 2000
			Cu aqueous species:			
+	6		Cu[+]	FACT	4.650E-09	298 - 573
+	7		Cu[2+]	FACT	1.000E-06 *	298 - 573
+	8		CuO2[2-]	FACT	3.519E-22	298 - *****
+	9		HCuO2[-]	FACT	4.647E-15	298 - *****
			Cu solids:			
+	10		Cu(s)	FACT	2.153E-05	298 - 2001
+	11		CuO(s)	FACT	2.511E-02	298 - 2000
+	12		Cu2O(s)	FACT	1.464E-03	298 - 2000
	13		Cu(OH)2(s)	FACT	4.635E-01	298 - 1500
			Other gases:			
	14		H(g)	FACT	2.059E-47	298 - 6000
	15		H2(g)	FACT	7.210E-23	298 - 6000
	16		O(g)	FACT	9.714E-61	298 - 6000
	17		O2(g)	FACT	1.502E-39	298 - 6000
	18		O3(g)	FACT	< 1.0E-70	298 - 6000
	19		OH(g)	FACT	3.252E-37	298 - 6000
	20		H2O(g)	FACT	3.135E-02	298 - 6000
	21		HOO(g)	FACT	3.808E-53	298 - 6000
	22		HOOH(g)	FACT	3.263E-43	298 - 1500
			Other liquids:			
	23		H2O(l)	FACT	1.000E+00	298 - 500
	24		HOOH(l)	FACT	1.107E-40	298 - 431
			Other aqueous species:			
+	25		H[+]	FACT	1.000E-06	298 - 500
+	26		H2(aq)	FACT	6.120E-26	289 - 573
+	27		O2(aq)	FACT	2.045E-42	298 - 400
+	28		OH[-]	FACT	9.883E-09	298 - 573
+	29		HO2[-]	FACT	6.675E-44	298 - 573
+	30		HOOH(aq)	FACT	3.318E-38	298 - 473
+	31		e[-](aq)	ELEM	8.491E-06	298 - 6000
			Other solids:			
+	32	T	H2O(s)	FACT	7.872E-01	250 - 273

Cu^{2+} is the stable species and its activity must be equal to the molality **m** specified for the aqueous species (here **1×10^{-6}**) – the activities of the other Cu-bearing species are less than 1.0 for the solids and than $m = 1 \times 10^{-6}$ in our case for the other aqueous species. The further the field of a species is from the specified coordinate the lower its activity.

One-metal Eh-pH diagram with four elements: Ti-O-H-F

Specifying the Eh-pH diagram for: **Ti-O-H-F** at 298.15 K and m [F^-] = 0.1 (i.e. $\log_{10}$ (m [F^-]) = -1).

1° Enter the elements. This is a **1-metal Ti** system with **O**, **H** and **F** as non-metallic elements.

2° Press Next to search the compound databases.

3° To Calculate an isobar, **Check** Isobar and **enter** a value (**here, 0.05 atm**).

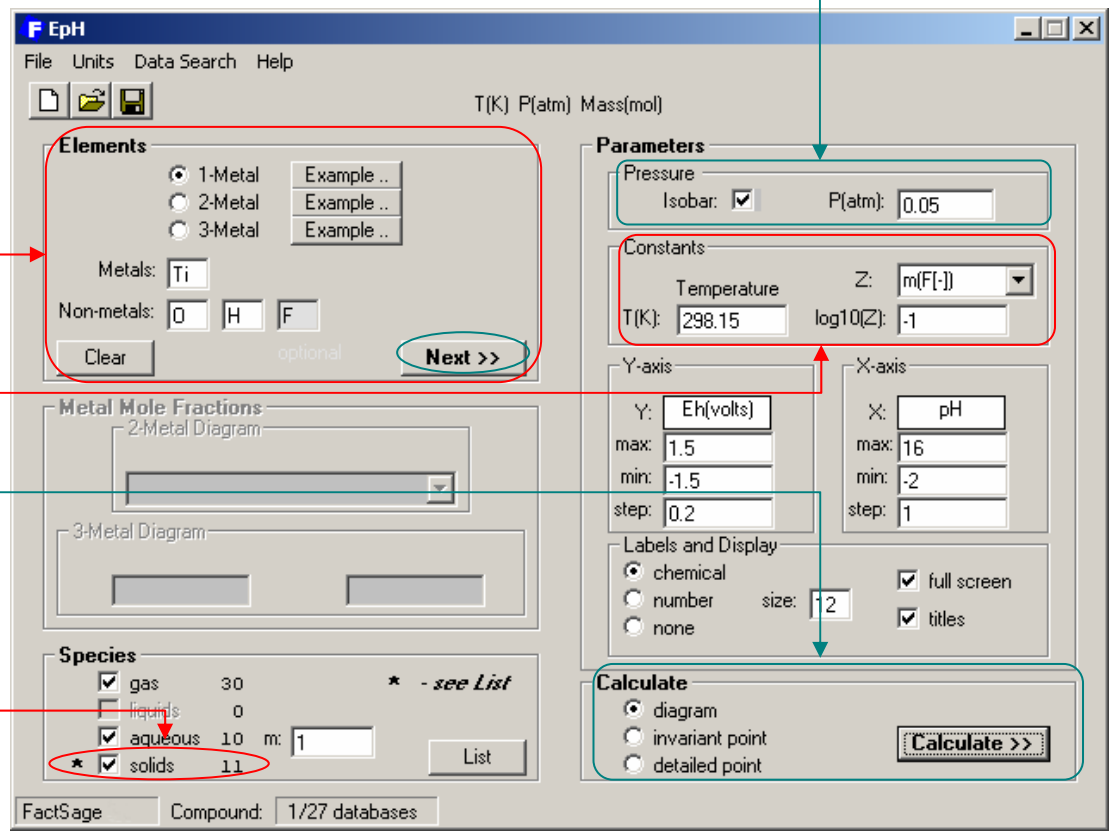
Note: to activate the Pressure frame, select gaseous species in the Species frame.

4° You must **enter 2** constants.

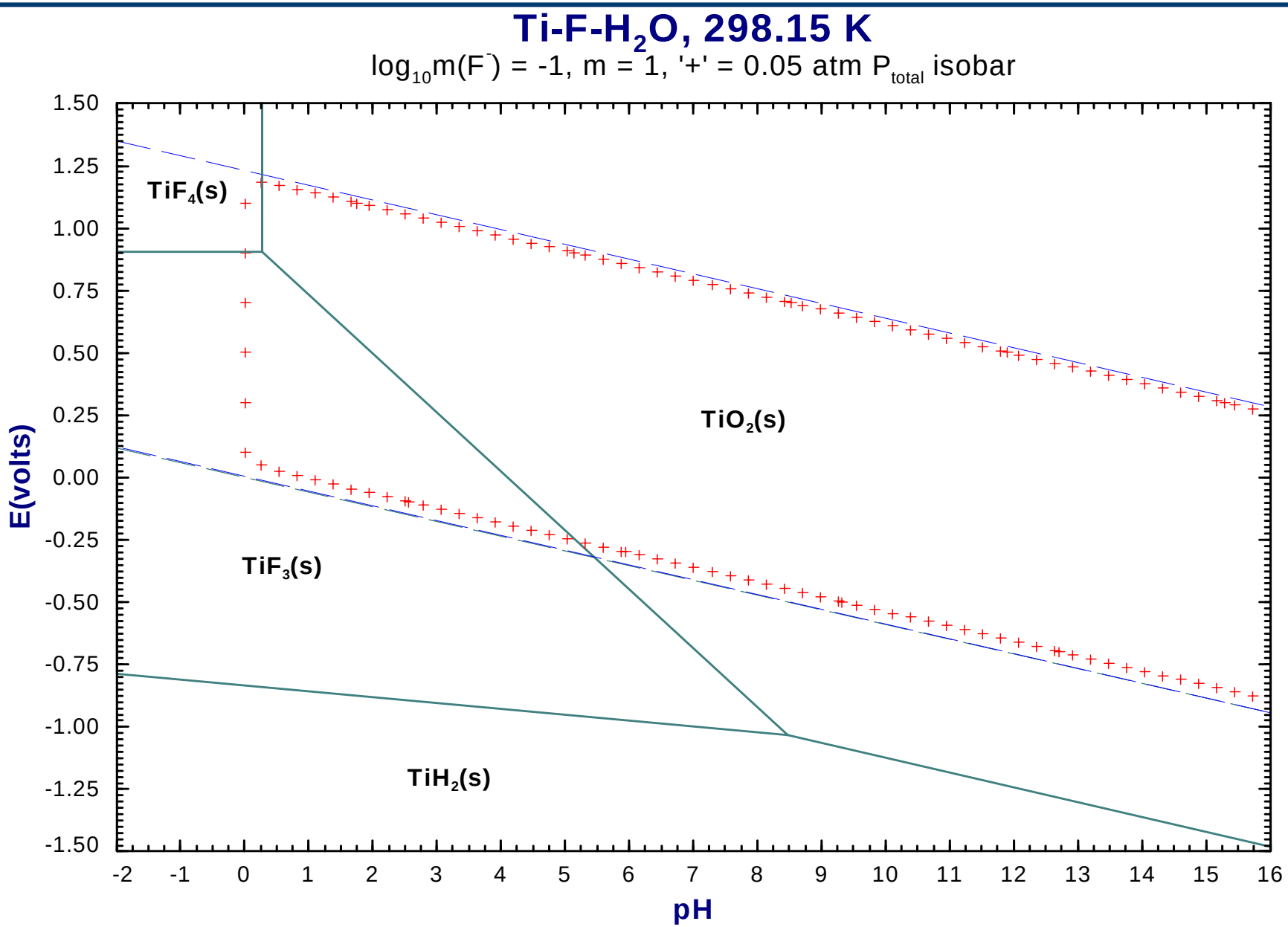
- **T = 298.15 K**
- **Z = m [F^-] = 10^{-1}**

5° Select the type of calculation and press **Calculate**.

Note: For diagram clarity, we remove all solid titanium oxides Ti_xO_y with x > 1 and y > 2.



One-metal Eh-pH diagram with four elements: Output



Two-metal Pourbaix diagram for Cu-As – formation of mixed oxides

We calculate the diagram in the usual manner except we specify two metal elements **Cu** and **As** since we wish to study the formation of mixed oxides.

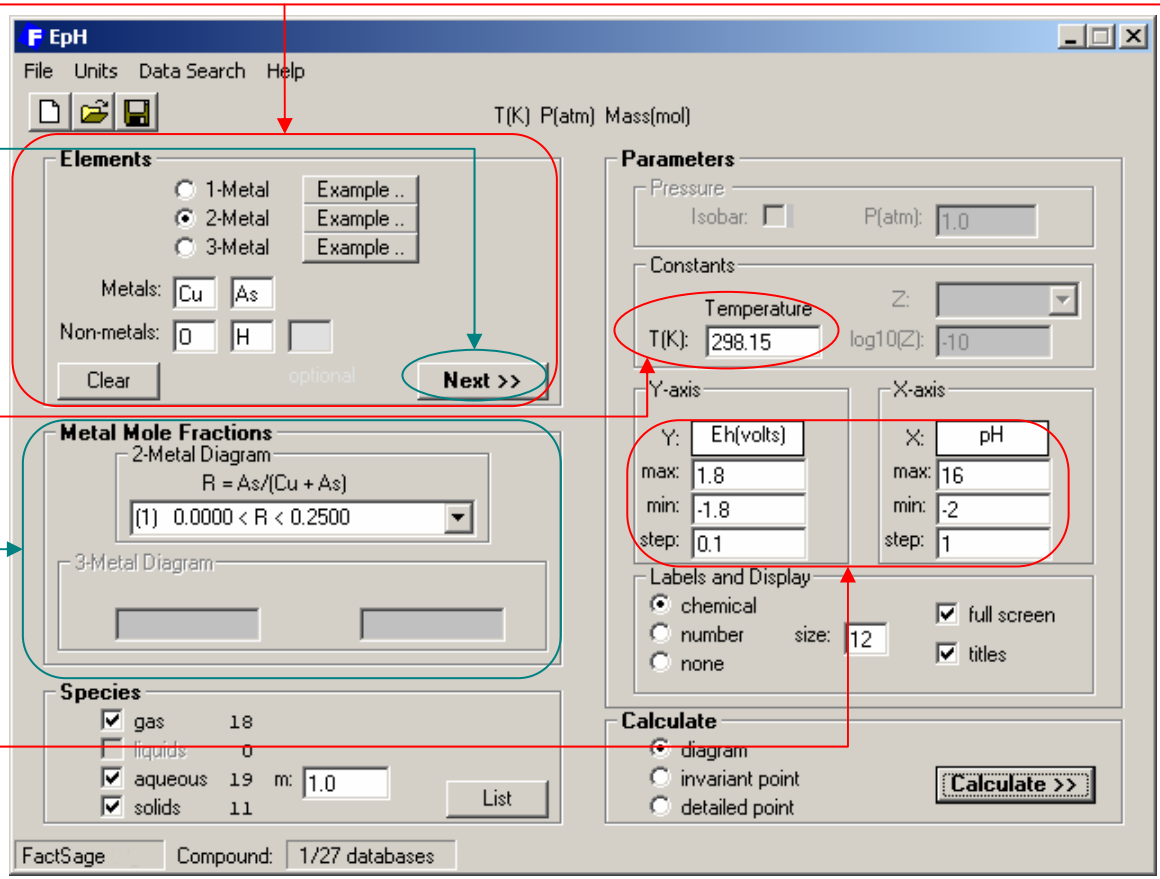
1° Enter the elements. This is a **2-metal Cu-As** system with **O** and **H** as non-metallic elements. **We wish to see if Cu and As form intermediate compounds. Each domain will contain a Cu-bearing and an As-bearing species.**

2° Press Next to search the compound databases.

3° Enter the temperature: **T = 298.15 K**

Note that the **Metal Mole Fractions frame** is **enabled**.

4° Enter the limits of the axes.

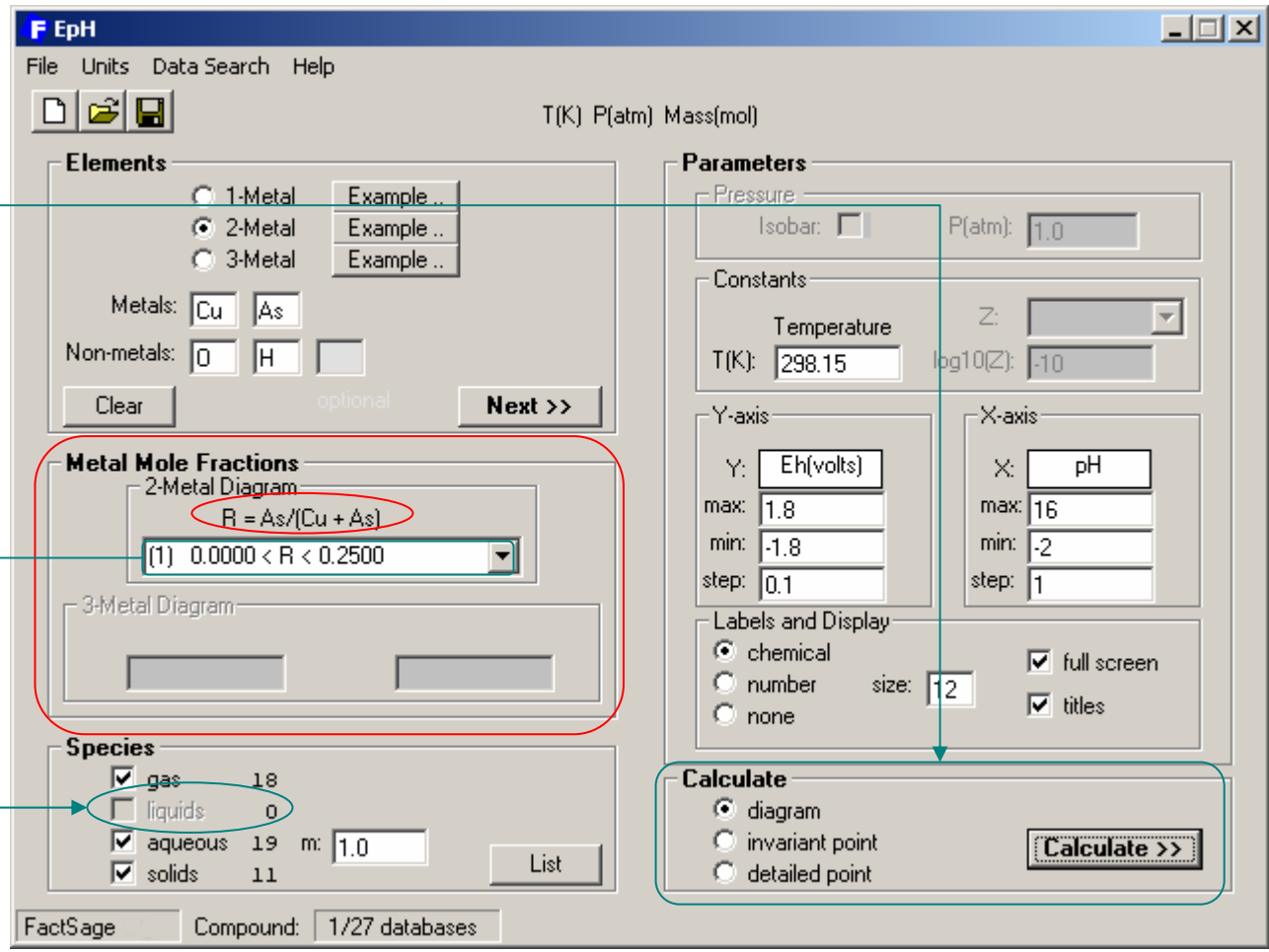


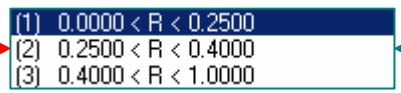
The Cu-As-water Eh-pH diagram: the **Metal Mole Fraction** frame

The values 0.25 and 0.40 are the **As/(Cu+As)** compositions of the Cu-As intermediate compounds. For example, $Cu_3(AsO_4)_2$ has a R value of 0.40 and Cu_3As has R = 0.25

5° Select the range of atomic ratio **R = As/(Cu+As)**. **A Cu-rich-alloy is assigned**.

6° Select diagram and press Calculate.

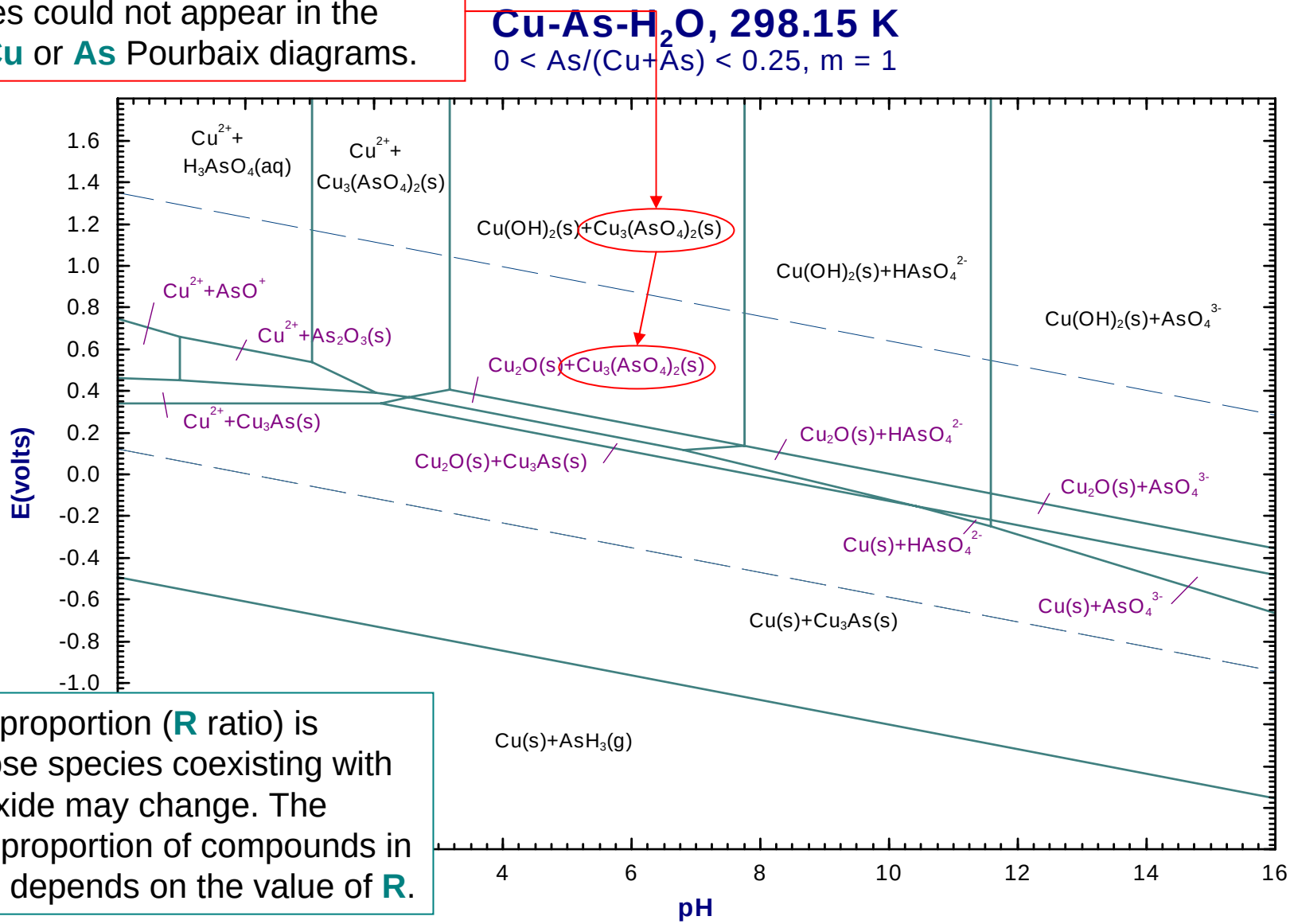




Note that the **all liquid (non-aqueous) base metal species are suppressed**.

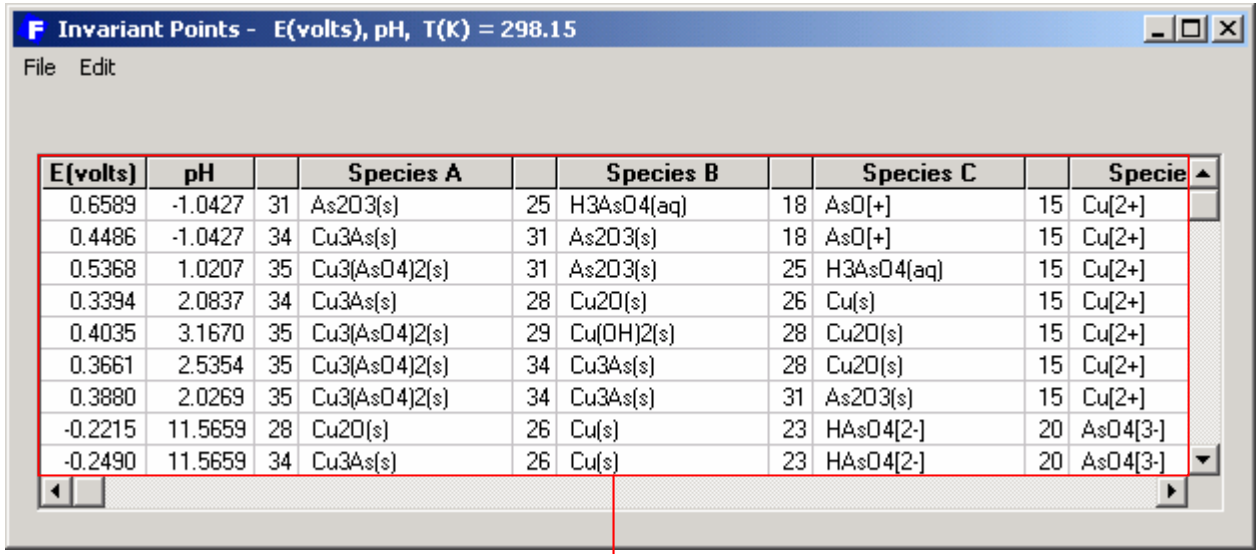
The Cu-As-water Eh-pH diagram: graphical output

The mixed oxide **$Cu_3(AsO_4)_2(s)$** is shown – this species could not appear in the one-metal **Cu** or **As** Pourbaix diagrams.



If the **Cu/As** proportion (**R** ratio) is changed, those species coexisting with the double oxide may change. The actual molar proportion of compounds in each domain depends on the value of **R**.

The Cu-As-water Eh-pH diagram: **invariant points**

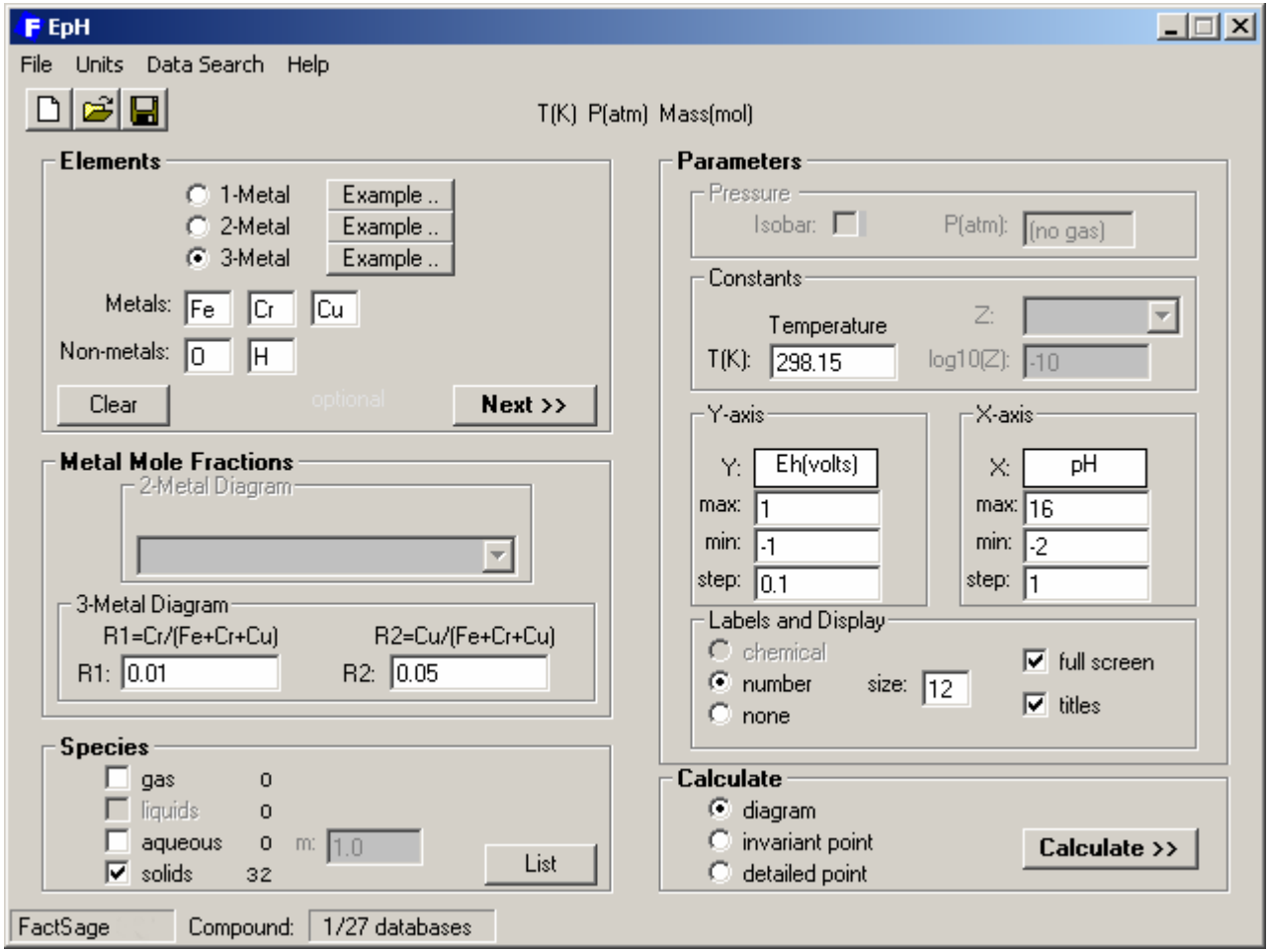


E(volts)	pH		Species A		Species B		Species C		Specie
0.6589	-1.0427	31	As2O3(s)	25	H3AsO4(aq)	18	AsO[+]	15	Cu[2+]
0.4486	-1.0427	34	Cu3As(s)	31	As2O3(s)	18	AsO[+]	15	Cu[2+]
0.5368	1.0207	35	Cu3(AsO4)2(s)	31	As2O3(s)	25	H3AsO4(aq)	15	Cu[2+]
0.3394	2.0837	34	Cu3As(s)	28	Cu2O(s)	26	Cu(s)	15	Cu[2+]
0.4035	3.1670	35	Cu3(AsO4)2(s)	29	Cu(OH)2(s)	28	Cu2O(s)	15	Cu[2+]
0.3661	2.5354	35	Cu3(AsO4)2(s)	34	Cu3As(s)	28	Cu2O(s)	15	Cu[2+]
0.3880	2.0269	35	Cu3(AsO4)2(s)	34	Cu3As(s)	31	As2O3(s)	15	Cu[2+]
-0.2215	11.5659	28	Cu2O(s)	26	Cu(s)	23	HAsO4[2-]	20	AsO4[3-]
-0.2490	11.5659	34	Cu3As(s)	26	Cu(s)	23	HAsO4[2-]	20	AsO4[3-]

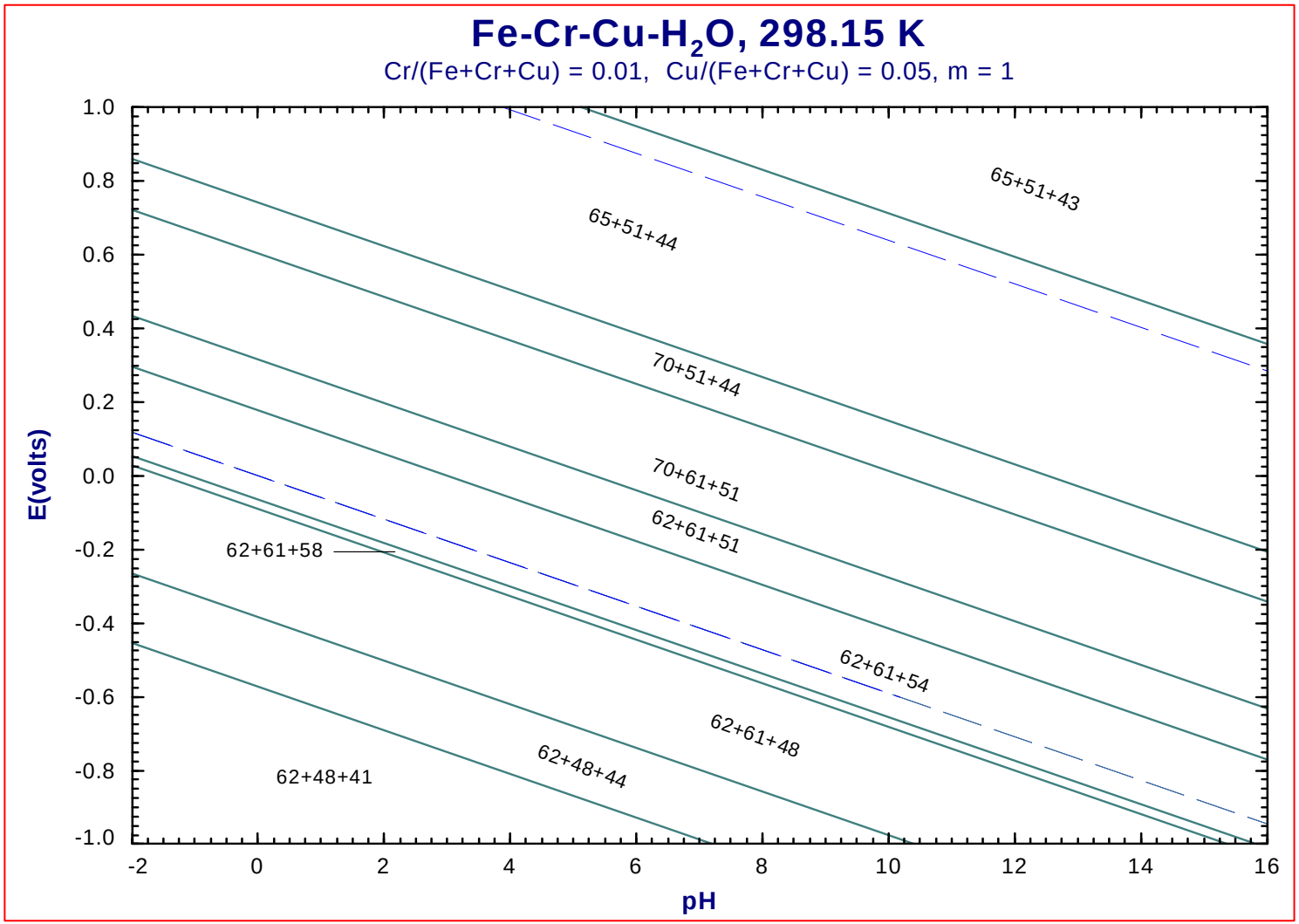
Note the **4 coexisting species** at **each invariant point** which is consistent with the **Gibbs Phase Rule**.

E(volts)	pH		Species A		Species B		Species C		Species D
0.6589	-1.0427	31	As2O3(s)	25	H3AsO4(aq)	18	AsO[+]	15	Cu[2+]
0.4486	-1.0427	34	Cu3As(s)	31	As2O3(s)	18	AsO[+]	15	Cu[2+]
0.5368	1.0207	35	Cu3(AsO4)2(s)	31	As2O3(s)	25	H3AsO4(aq)	15	Cu[2+]
0.3394	2.0837	34	Cu3As(s)	28	Cu2O(s)	26	Cu(s)	15	Cu[2+]
0.4035	3.1670	35	Cu3(AsO4)2(s)	29	Cu(OH)2(s)	28	Cu2O(s)	15	Cu[2+]
0.3661	2.5354	35	Cu3(AsO4)2(s)	34	Cu3As(s)	28	Cu2O(s)	15	Cu[2+]
0.3880	2.0269	35	Cu3(AsO4)2(s)	34	Cu3As(s)	31	As2O3(s)	15	Cu[2+]
-0.2215	11.5659	28	Cu2O(s)	26	Cu(s)	23	HAsO4[2-]	20	AsO4[3-]
-0.2490	11.5659	34	Cu3As(s)	26	Cu(s)	23	HAsO4[2-]	20	AsO4[3-]
-0.0934	11.5659	29	Cu(OH)2(s)	28	Cu2O(s)	23	HAsO4[2-]	20	AsO4[3-]
-0.1530	10.4070	34	Cu3As(s)	28	Cu2O(s)	26	Cu(s)	23	HAsO4[2-]
0.1329	7.7413	35	Cu3(AsO4)2(s)	29	Cu(OH)2(s)	28	Cu2O(s)	23	HAsO4[2-]
0.1142	6.7938	35	Cu3(AsO4)2(s)	34	Cu3As(s)	28	Cu2O(s)	23	HAsO4[2-]

The Fe-Cr-Cu-water Eh-pH diagram: input



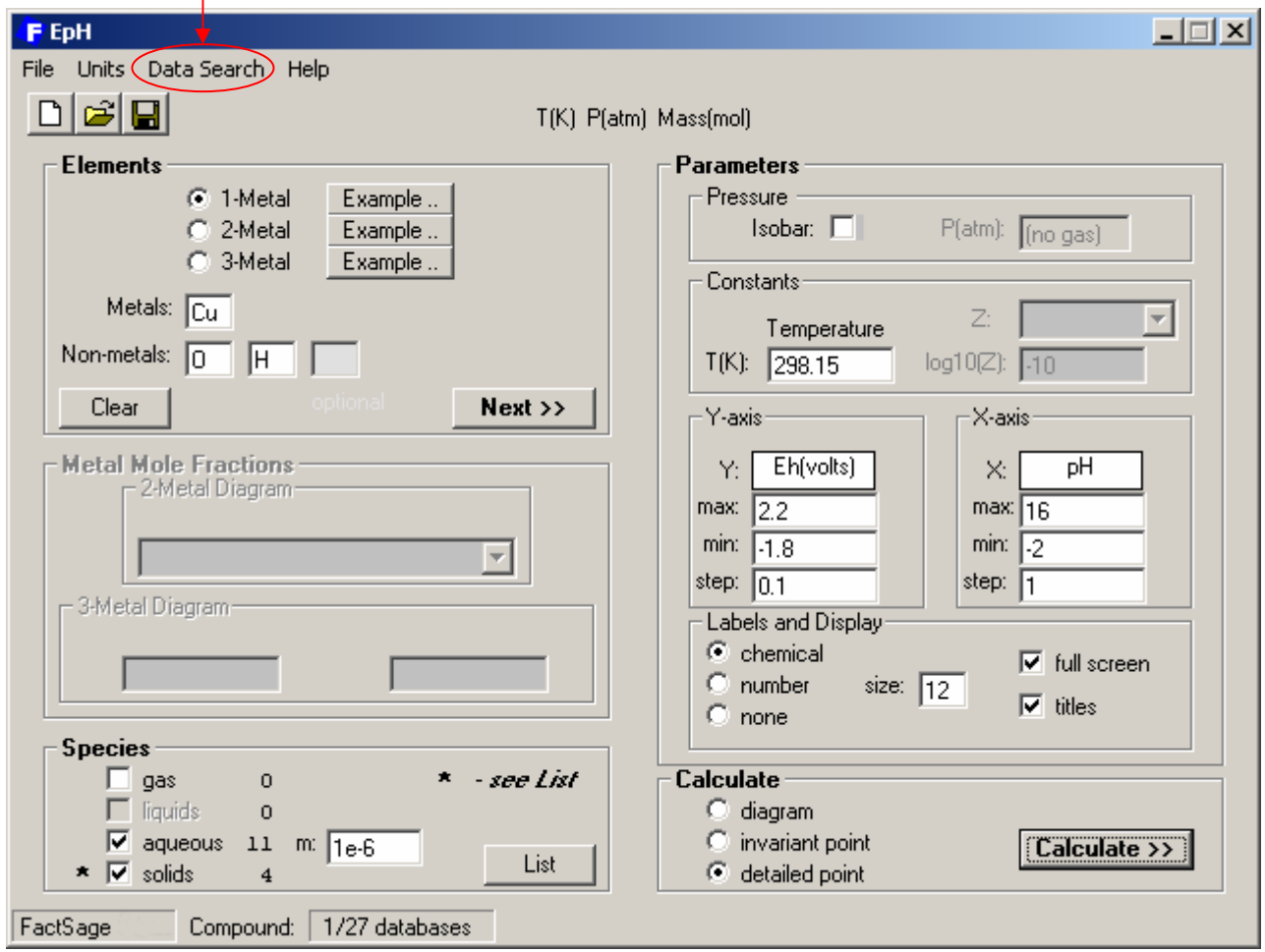
The Fe-Cr-Cu-water Eh-pH diagram: graphical output and list



		Fe, Cr, Cu solids:
41		Cr(s)
42		CrO2(s)
43		CrO3(s)
44		Cr2O3(s)
45	T	Cr3O4(s)
46		Cr5O12(s)
47		Cr8O21(s)
48		Fe(s)
49		Fe(s2)
50		FeO(s)
51		Fe2O3(s)
52		Fe2O3(s2)
53	T	Fe2O3(s3)
54		Fe3O4(s)
55	T	Fe3O4(s2)
56		Fe3O4(s3)
57	T	Fe3O4(s4)
58		Fe(OH)2(s)
59		Fe(OH)3(s)
60		Fe2O3(H2O)(s)
61		FeCr2O4(s)
62		Cu(s)
63		CuO(s)
64		Cu2O(s)
65		Cu(OH)2(s)
66		CuFeO2(s)
67		(CuO)(Fe2O3)(s)
68	T	(CuO)(Fe2O3)(s2)
69	T	(CuO)(Fe2O3)(s3)
70		(Cu2O)(Fe2O3)(s)
71	T	(Cu2O)(Fe2O3)(s2)

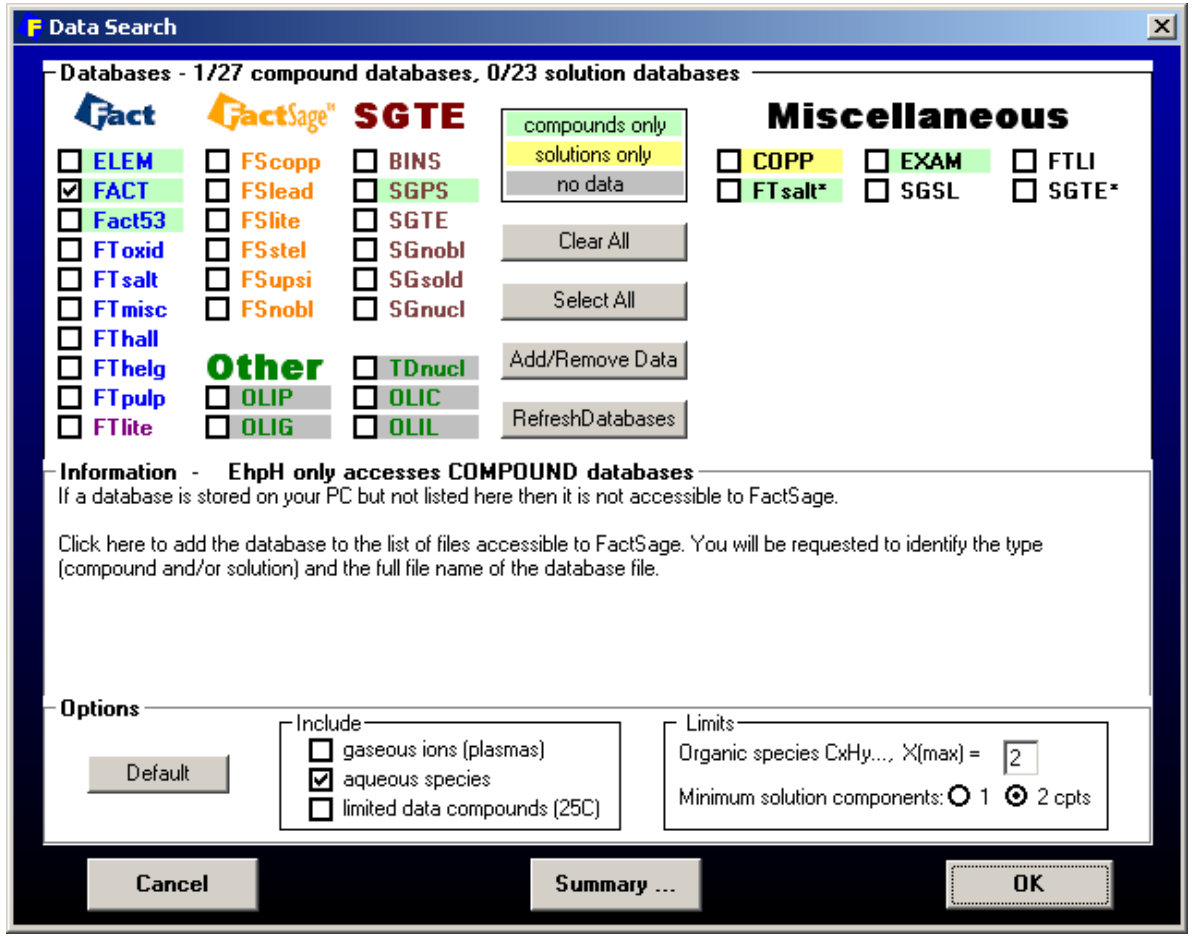
Loading another Compound database

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



Specifying the Cu-water Eh-pH diagram: Databases window

EpH can only access the compound databases – these databases include **dilute Henrian solute data**.



Concentrated aqueous solutions (for example: ***FACT***, **OLI Solutions**) are not accessible to ***EpH***.