

The *EpH* module

- Use *EpH* to calculate and plot isothermal EpH (Pourbaix) diagrams.
- **Note:** *EpH* accesses compound databases, i.e. treats the aqueous phase as an ideal solution.

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The *EpH* module



1° Click on *EpH* in the main *FactSage* window.

Preparing a calculation

The following five slides show how a simple **metal-water Pourbaix diagram** is generated.

The **type of system** is selected, the desired **element(s)** is (are) entered, the **axes ranges** are defined, the **type of output** is selected.

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**.

The other frames are activated when the **data search** is completed.

The screenshot shows the 'Eph' software window with the following configuration:

- Elements:** Radio buttons for '1-Metal', '2-Metal', and '3-Metal' are present. The '1-Metal' option is selected. Below are input fields for 'Metals' (containing 'Cu') and 'Non-metals' (containing 'O' and 'H'). A 'Next >>' button is circled in red.
- Parameters:** Includes 'Pressure' (Isobar checkbox, P(atm) field), 'Constants' (Temperature T(K) set to 298.15, Z dropdown), and 'Y-axis' (log10(Y) with max: 1.8, min: -1.2, step: 0.1). The 'X-axis' is log10(X) with max: 16, min: -2, step: 1.
- Metal Mole Fractions:** Sections for '2-Metal Diagram' and '3-Metal Diagram' are visible.
- Species:** Checkboxes for 'gas', 'liquids', 'aqueous', and 'solids'. 'aqueous' and 'solids' are checked. A 'List' button is present.
- Labels and Display:** Radio buttons for 'chemical', 'number', and 'none'. 'chemical' is selected. 'full screen' checkbox is checked. 'View Figure' and 'Figure' radio buttons are also present.
- Calculate:** Radio buttons for 'diagram', 'invariant point', and 'detailed point'. 'diagram' is selected. A 'Calculate >>' button is present.

At the bottom, the status bar shows 'FactSage 5.2' and 'Compound: ELEM EXAM FACT SGPS SGLL'.

When you **click** the **Next >>** button the pure substances databases are automatically searched to find all the compounds (and henrian solutes) involving the indicated elements. Any time you make changes in the **Elements** frame all other frames are deactivated and 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 *E_{pH}* 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 on [slides 6.0 to 6.2](#). Note that the calculation of the isobar for a large system can be time consuming.

Parameters

Pressure
Isobar: P(atm): [no gas]

Constants
Temperature: 298.15 K
log₁₀(Z): -1

Y-axis
Y: Eh(volts)
max: 2.2
min: -1.8
step: 0.1

X-axis
X: pH
max: 16
min: -2
step: 1

Labels and Display
 chemical
 number size: 12
 none
 full screen
 View Figure
 Figure

Constants: Here, $T = 298.15$ 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: Here, the limits are: **-1.8** to **2.2** for the **potential** and **-2** to **16** for the **pH**.

The axes are always Eh(volts) and pH. 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 size (8 – 20) and type of labels on the calculated diagrams. **View Figure** produces a crude *E_{pH}* diagram that can not be edited. However it is a very efficient module that only requires a small amount of computer memory. **Figure** creates an *E_{pH}* diagram that can be **edited**, **manipulated** and **stored** in a variety of ways. However, **Figure** requires a lot of computer memory and may overwhelm the resources of the PC.

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, $m = 1 \times 10^{-6}$. To **examine** the species or to **add** or **remove** a particular species or **change** its activity, molality or partial pressure, **click** the "List" button.

Species

gas 0

liquids 0

aqueous 11 m: 1e-6

solids 5

List

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

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

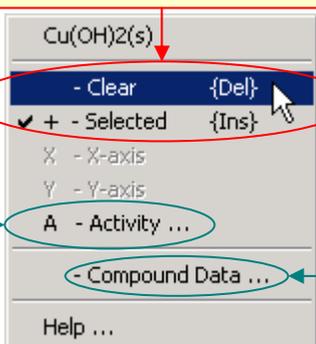
File Edit Help

+ 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: $\text{Cu}(\text{OH})_2$ in order to compare the calculated diagram with one published in the «Atlas of Electrochemical Equilibria in Aqueous Solution» (M. Pourbaix, Pergamon 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**.



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.

+	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				H2O(a)	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		298 - 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.

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

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

The screenshot shows the FactSage 5.2 EpH software interface. The 'Species' section is highlighted with a green oval, showing 11 aqueous species and 4 solid species selected. The 'Compound' selection at the bottom shows 'FACT' selected. A red box highlights the 'FACT' button, and a red arrow points from a text box below to it.

State	Count	Mass (mol)
gas	0	
liquids	0	
aqueous	11	1e-6
solids	4	

Here, only the **FACT compound** database is included. See [slides 9.0 to 9.2](#) for **inclusion** or **exclusion** of a **database**.

Executing the calculation and generating a diagram

In the following three slides is shown how the **Pourbaix diagram** for the **Cu-O-H system** is generated.

The diagram is compared with the appropriate diagram from the **Pourbaix Atlas**.

Furthermore explanations are given on the **non-graphical types of output** which can be generated with **EpH** calculations.

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

- **Diagram:**

Here the diagram is calculated and plotted. It may then be stored as a *.fig file or other graphics format.

- **Invariant Point:**

This gives the precise position of the triple points as shown in [slide 5.1](#) where three domains meet.

Please note the **custom (*) selection** of **solid** species.

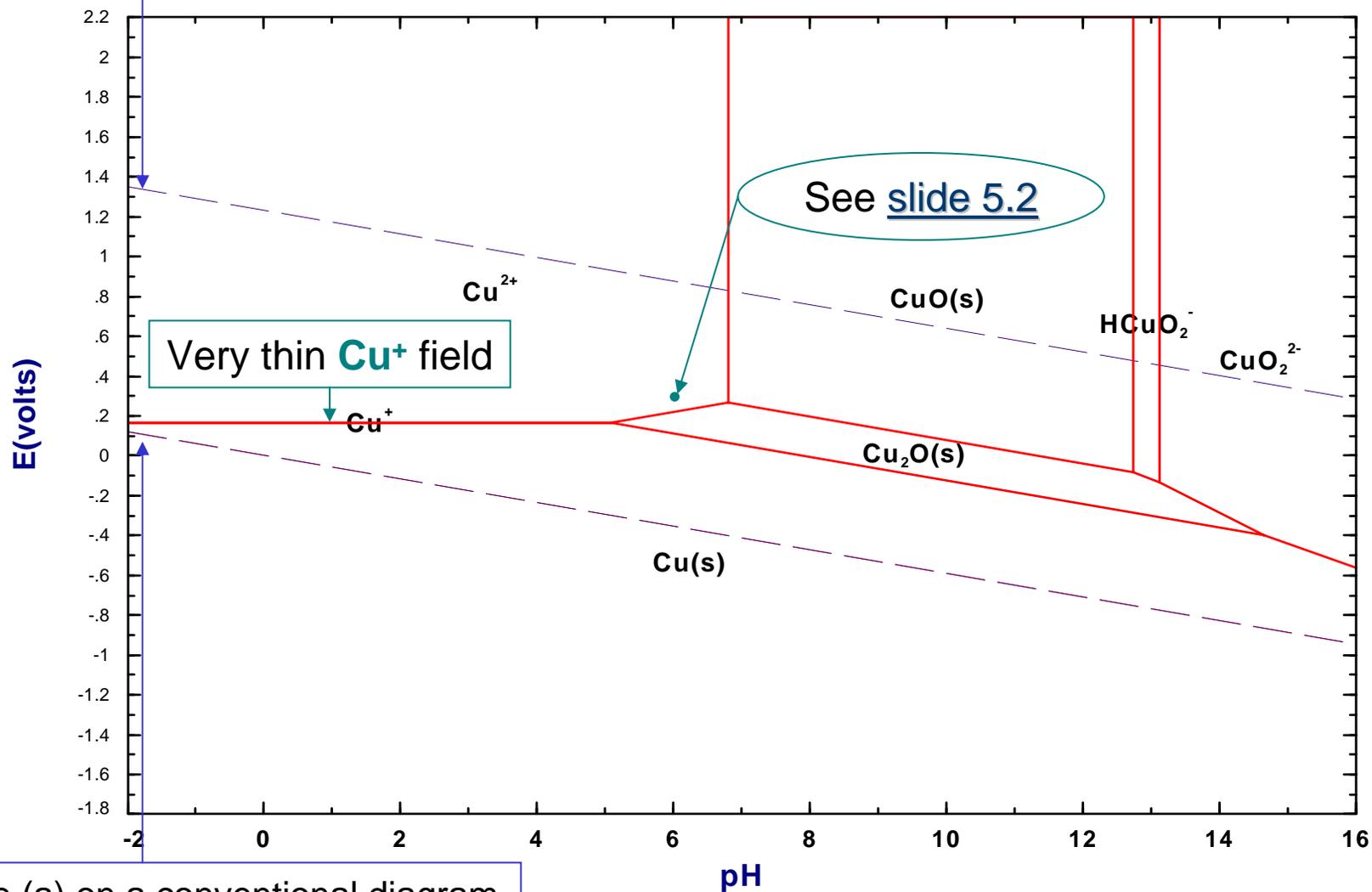
- **Detailed Point:**

This enables you to display the equilibrium activity or partial pressure of all species at a specified coordinate on the diagram. In the output shown in [Slide 5.3](#), the specified coordinate falls in the field of Cu^{2+} . That is 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 1×10^{-6} for the other aqueous species. The further the field of a species is from the specified coordinate the lower its activity.

Cu-H₂O Eh-pH diagram: Graphical Output

O₂ (1 atm) line (b) on a conventional diagram

Cu-H₂O, 298.15 K
 $m = 1 \times 10^{-6}$



H₂ (1 atm) line (a) on a conventional diagram

Published Pourbaix diagram for **Cu-H₂O**

Lines for $m = 1 \times 10^{-6}$ are highlighted in red.

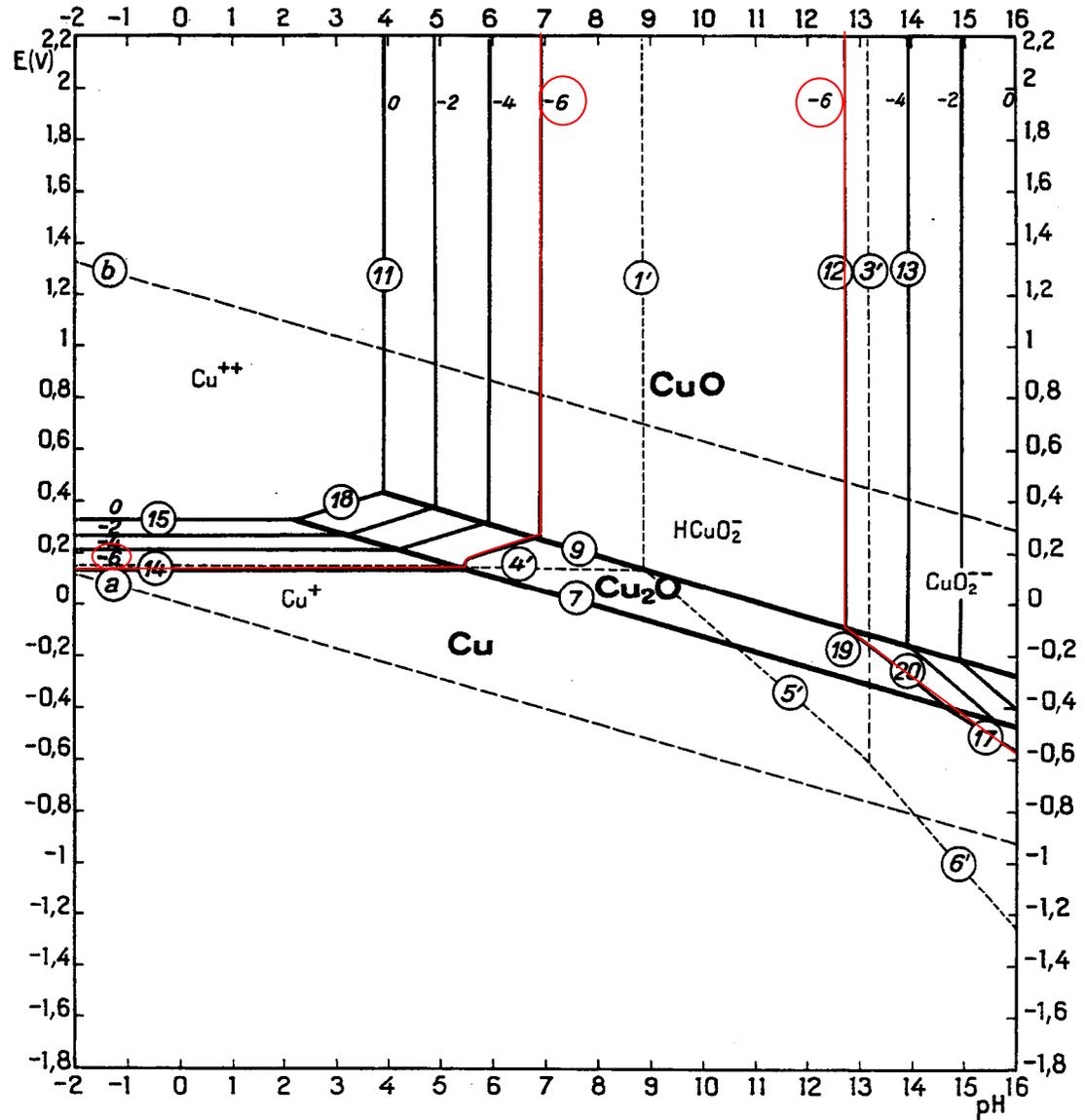


FIG. 1. Potential-pH equilibrium diagram for the system copper-water, at 25°C. [Considering the solid substances Cu, Cu₂O and CuO. Cu(OH)₂ is not considered.]

Output options to obtain numerical results

The following three slides show the type of numerical/tabular result that is also possible with EpH.

Tables of invariant points and of a point calculation are shown for the system Cu-O-H.

Cu-H₂O Eh-pH diagram: Computation of invariant points

Select **invariant point** in the **Calculate** frame to **calculate invariant points**.



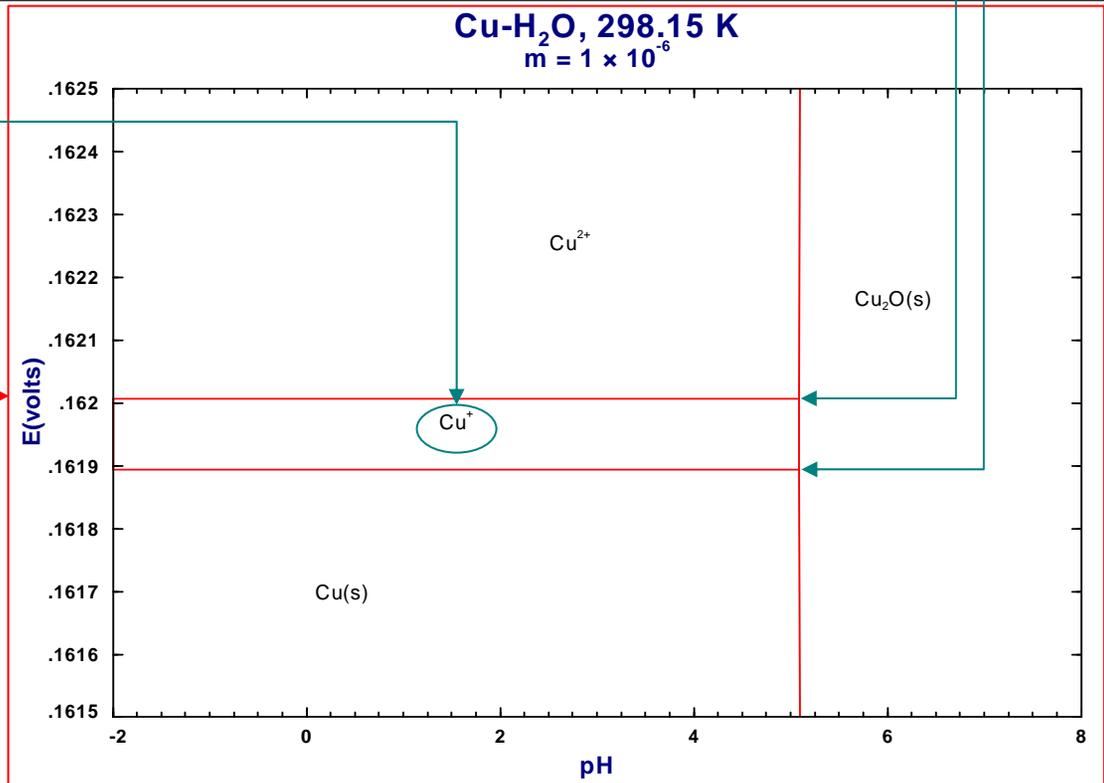
F Invariant Points - E(volts), pH, T(K) = 298.15

File Edit

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

A very thin **Cu⁺** field indeed!

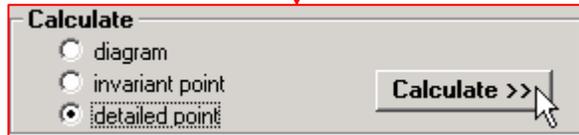
Enlargement of the previous diagram



Cu-H₂O Eh-pH diagram: Detailed Point Calculation

The point calculation gives activities and ideal concentrations for all metal-element containing species at the specified coordinate.

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.

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

File Edit Help

+	Code	T	Species	Data	A/P/M	Cp range
Cu gases:						
	1		Cu(g)	FACT	1.0000E+00	298 - 6000
	2		Cu ₂ (g)	FACT	1.0000E+00	298 - 6000
	3		CuO(g)	FACT	1.0000E+00	298 - 6000
Cu liquids:						
	4		Cu(l)	FACT	1.0000E+00	298 - 4000
	5		Cu ₂ O(l)	FACT	1.0000E+00	298 - 2000
Cu aqueous species:						
+	6		Cu(+)	FACT	1.0000E-06	298 - 573
+	7		Cu(2+)	FACT	1.0000E-06	298 - 573
+	8		CuO ₂ (2-)	FACT	1.0000E-06	298 - ****
+	9		HCuO ₂ (-)	FACT	1.0000E-06	298 - ****
Cu solids:						
+	10		Cu(s)	FACT	1.0000E+00	298 - 2001
+	11		CuO(s)	FACT	1.0000E+00	298 - 2000
+	12		Cu ₂ O(s)	FACT	1.0000E+00	298 - 2000
	13		Cu(OH) ₂ (s)	FACT	1.0000E+00	298 - 1500

Point Calculation

E(volts): 0.3

pH: 6

Calculate

The specified coordinate is in the **domain of Cu²⁺** set at **10⁻⁶** (the **green dot** on [slide 4.2](#)).

Cu-H₂O Eh-pH diagram: Detailed Point Calculation – Output

F List - Cu-H2O, T = 298.15K

File Edit Help

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

Domain: Cu(2+)

Point Calculation
 E(volts): 0.3
 pH: 6
 Calculate

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	298 - 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

Cu²⁺ 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.

A metal-water-gas system: Ti-O-H-F

The following two slides show the input and calculated diagram for a metal-water-gas system.

The results are for the Ti-O-H-F system.

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 as metal with **O**, **H** and **F** as non-metallic elements.

2° Press **Next** to search the compound databases.

4° You must enter **2** constants.

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

5° Select what you want to calculate and press **Calculate**.

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

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

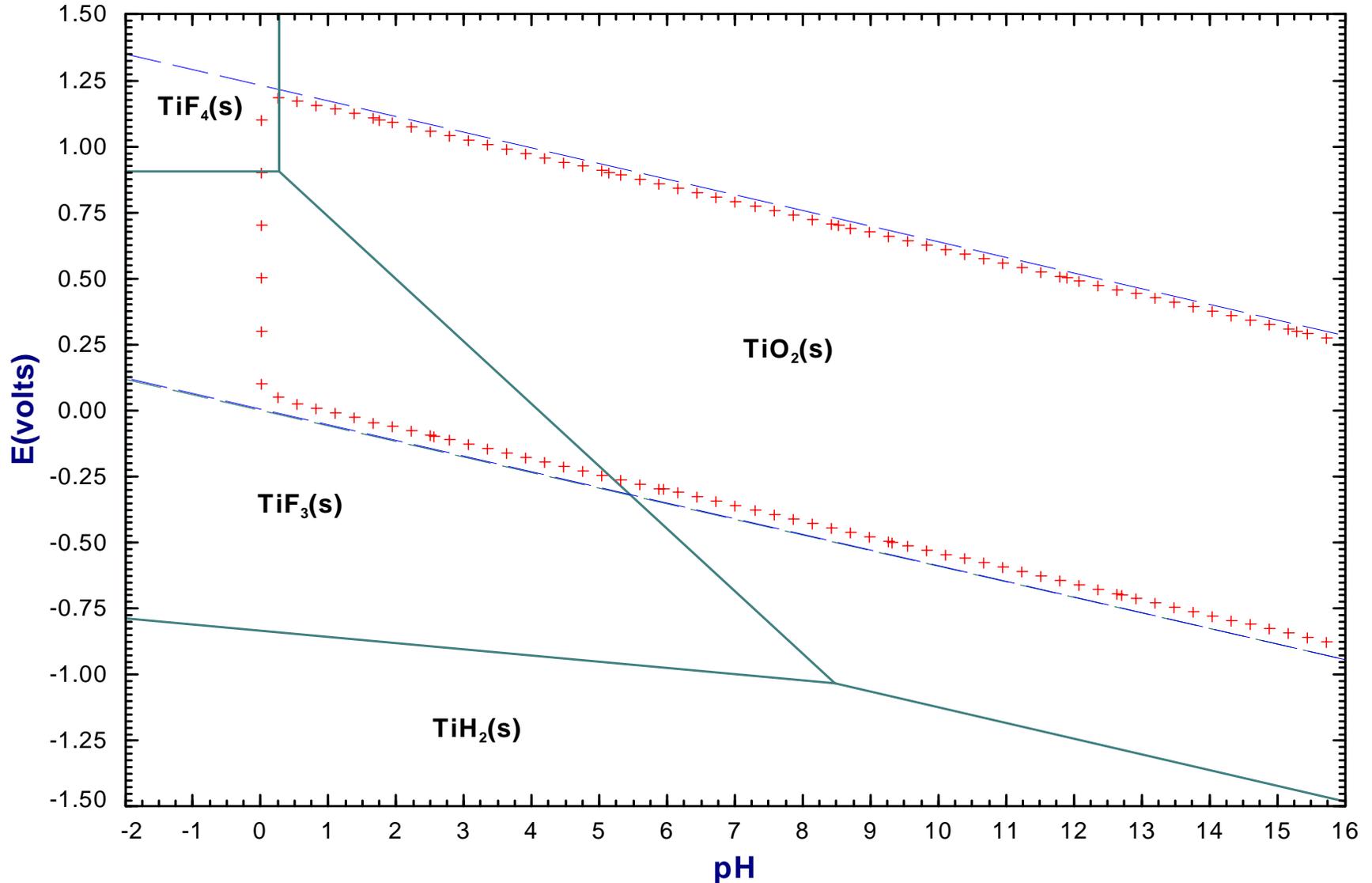
Note: to activate the Pressure frame, select gaseous species in the Species frame.

The screenshot shows the FactSage 5.2 EpH software interface. The 'Elements' section is highlighted with a red box, showing '1-Metal' selected, 'Ti' in the 'Metals' field, and 'O', 'H', 'F' in the 'Non-metals' field. The 'Parameters' section is also highlighted with a red box, showing 'Isobar' checked, 'P(atm): 0.05', 'Temperature' set to '298.15', and 'log10[Z]' set to '-1'. The 'Y-axis' is 'Eh(volts)' and the 'X-axis' is 'pH'. The 'Species' section has 'gas', 'liquids', and 'aqueous' checked, with 'solids' also checked but marked with an asterisk. The 'Calculate' section has 'diagram' selected. A 'Next >>' button is circled in the 'Elements' section, and a 'Calculate >>' button is circled in the 'Calculate' section. Red arrows point from the text boxes to these buttons and the 'solids' checkbox.

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

Ti-F-H₂O, 298.15 K

$\log_{10}m(\text{F}^-) = -1, m = 1, '+' = 0.05 \text{ atm } P_{\text{total}} \text{ isobar}$



Two metals and water: Cu-As-O-H

The following four slides show how the input is prepared for a **two-metal water** system.

Note the additional selection of the **Me₁/Me₂ ratio** that is required in order to find proper results according to the intermetallic compounds and the double oxides and their respective Me₁/Me₂ ratios.

As an example the system **Cu-As-O-H** is chosen.

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 as metals 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 screenshot shows the EpH software interface with the following settings:

- Elements:** 2-Metal selected. Metals: Cu, As. Non-metals: O, H. A "Next >>" button is highlighted.
- Metal Mole Fractions:** 2-Metal Diagram selected. Formula: $R = \text{As}/(\text{Cu} + \text{As})$. Range: (1) 0.0000 < R < 0.2500.
- Parameters:** Temperature: 298.15 K. Y-axis: Eh(volts). X-axis: pH.
- Calculate:** diagram selected.

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, $\text{Cu}_3(\text{AsO}_4)_2$ has a R value of 0.40 and Cu_3As has $R = 0.25$

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

6° Select **diagram** and press **Calculate**.

- (1) $0.0000 < R < 0.2500$
- (2) $0.2500 < R < 0.4000$
- (3) $0.4000 < R < 1.0000$

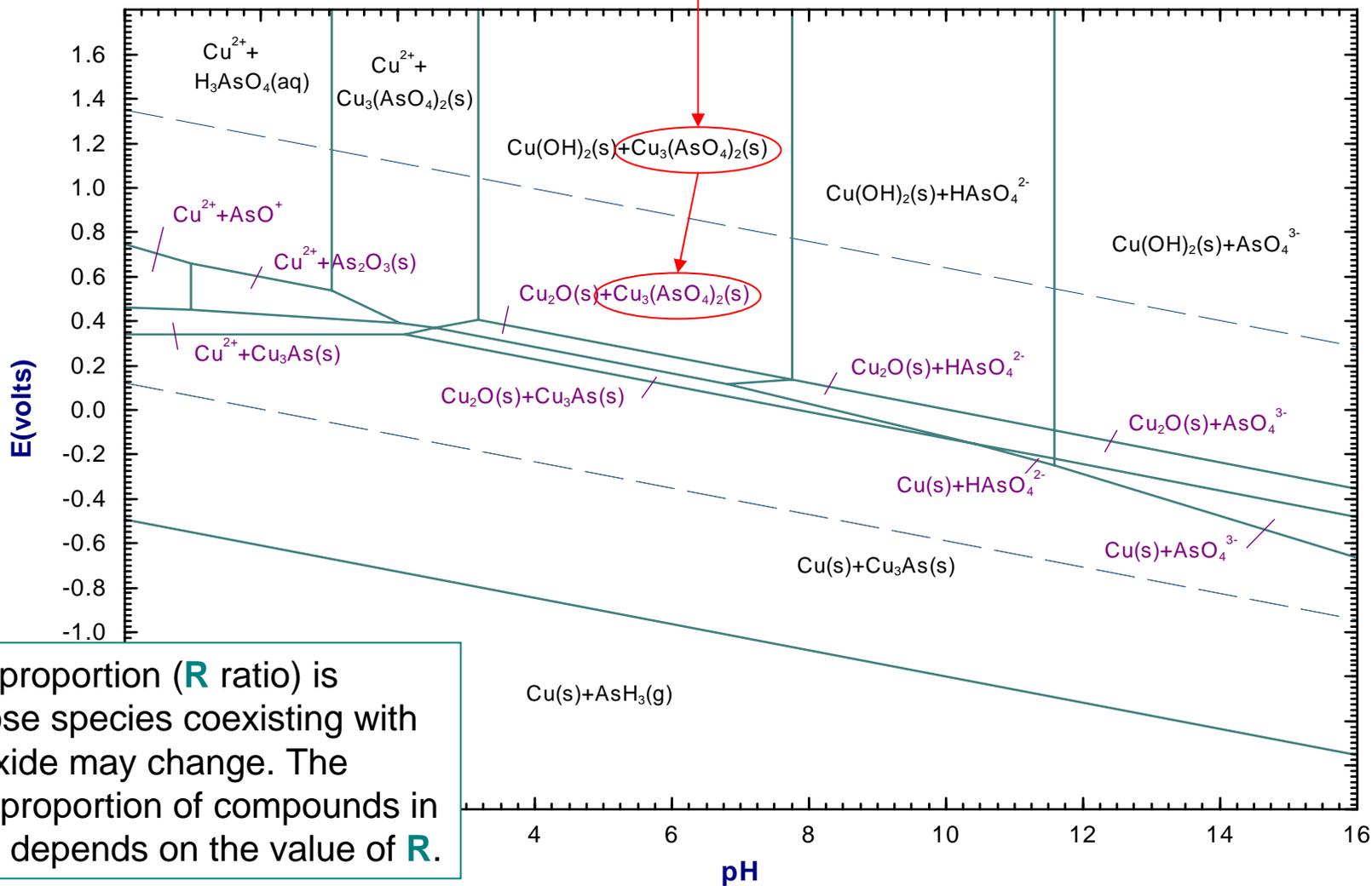
Note that the **all liquid (non-aqueous) base metal species are suppressed.**

The screenshot shows the 'F EpH' software window. The 'Elements' section has '2-Metal' selected. The 'Metals' list contains 'Cu' and 'As'. The 'Metal Mole Fractions' section is circled in red, showing the formula $R = \text{As}/(\text{Cu} + \text{As})$ and a dropdown menu with three options: (1) $0.0000 < R < 0.2500$, (2) $0.2500 < R < 0.4000$, and (3) $0.4000 < R < 1.0000$. The 'Species' section has 'liquids' checked, while 'gas', 'aqueous', and 'solids' are unchecked. The 'Calculate' section at the bottom right has 'diagram' selected, and a 'Calculate >>' button is present.

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

The mixed oxide $\text{Cu}_3(\text{AsO}_4)_2(\text{s})$ is shown – this species could not appear on the one-metal Cu or As Pourbaix diagrams.

Cu-As- H_2O , 298.15 K
 $0 < \text{As}/(\text{Cu}+\text{As}) < 0.25, m = 1$



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

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

File Edit

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-)

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-)

Three metals and water: Fe-Cr-Cu-O-H

The following two slides show a **three-metal water** system.

Note the use of **numerical labels** and a **legend** in the resulting Pourbaix diagram.

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

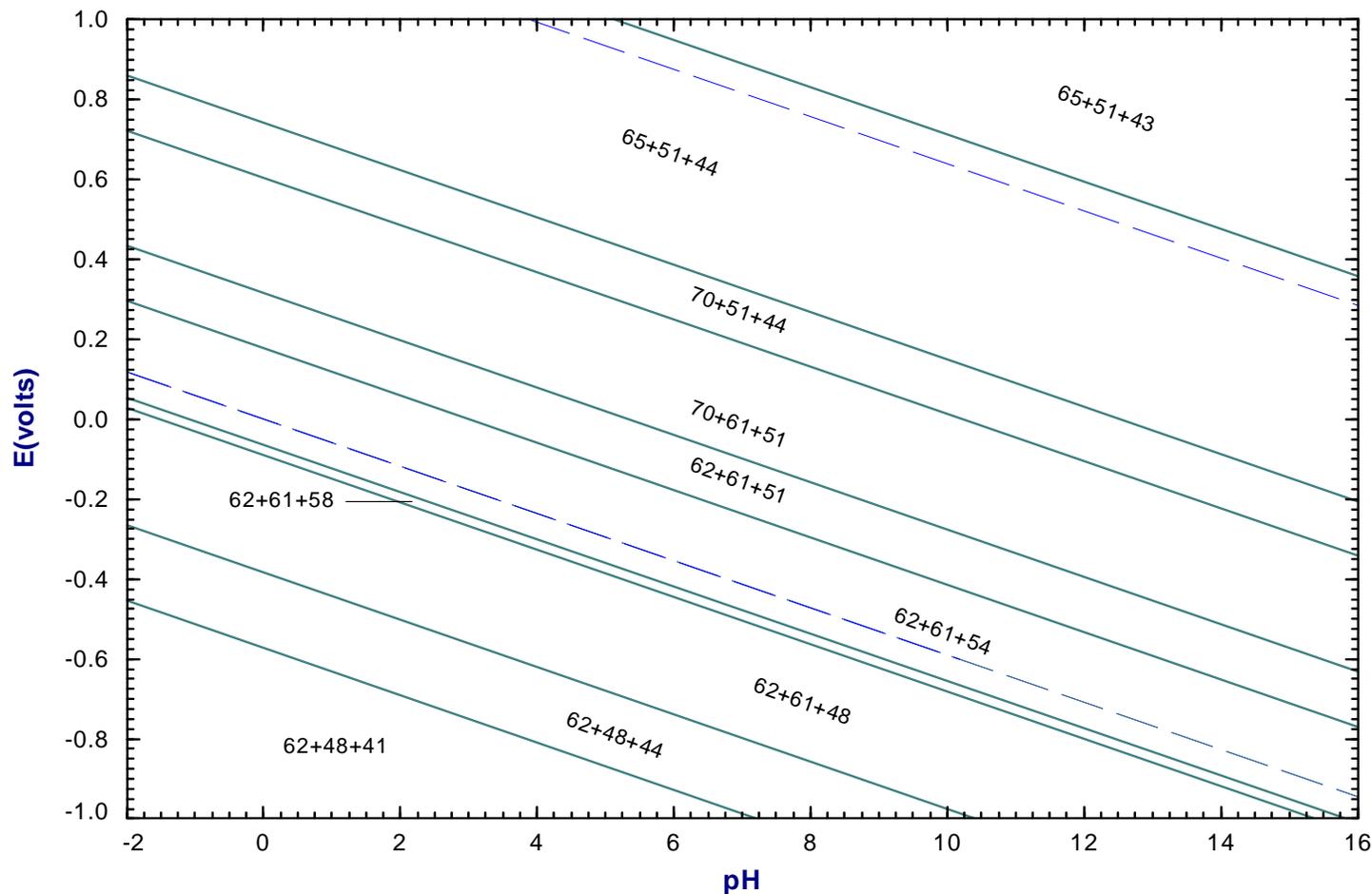
The screenshot shows the 'E pH' software window with the following settings:

- File Units Data Search Help**
- T(K) P(atm) Mass(mol)**
- Elements:** 1-Metal, 2-Metal, 3-Metal (selected). Metals: Fe, Cr, Cu. Non-metals: O, H. Buttons: Clear, optional, Next >>
- Metal Mole Fractions:** 2-Metal Diagram, 3-Metal Diagram. R1=Cr/(Fe+Cr+Cu), R2=Cu/(Fe+Cr+Cu). R1: 0.01, R2: 0.05. Button: List
- Species:** gas (0), liquids (0), aqueous (0), solids (32, checked). Button: List
- Parameters:** Pressure: Isobar (checkbox), P(atm): (no gas). Constants: Temperature: 298.15, Z: (dropdown), log10(Z): -1. Y-axis: Y: Eh(volts), max: 1, min: -1, step: 0.1. X-axis: X: pH, max: 16, min: -2, step: 1. Labels and Display: chemical (radio), number (radio, selected), none (radio), size: 12, full screen (checkbox, checked), View Figure (radio), Figure (radio, selected).
- Calculate:** diagram (radio, selected), invariant point (radio), detailed point (radio). Button: Calculate >>
- FactSage 5.2** Compound: ELEM EXAM FACT SGPS SGSL

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

Fe-Cr-Cu-H₂O, 298.15 K

Cr/(Fe+Cr+Cu) = 0.01, Cu/(Fe+Cr+Cu) = 0.05, m = 1



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 database

In the following two slides is shown how **another database** of the **Compound type** can be loaded in order to perform calculations with the ***EpH*** module.

Note that the appropriate database would have to contain data for aqueous species according to the **dilute solution approach**. Non-ideal aqueous solution using for example the **Pitzer model** or the **OLI model** are **not permitted** in the ***EpH*** module.

Loading another **Compound** database

The screenshot shows the FactSage 5.2 EpH software interface. The 'Data Search' menu is highlighted in red, and the 'Databases...' option is selected. The 'Compound' section at the bottom shows 'FAC' selected, indicating the 'FACT' database is loaded. Other sections include 'Elements', 'Parameters', 'Metal Mole Fractions', and 'Species'.

Data Search

- ✓ Limit organic species CxHy..., X(max) = 4 ...
- Databases ...

EpH

File Units **Data Search** Help

T(K) P(atm) Mass(mol)

Elements

- 1-Metal Example ..
- 2-Metal Example ..
- 3-Metal Example ..

Metals: Cu

Non-metals: O H optional

Clear Next >>

Metal Mole Fractions

2-Metal Diagram

3-Metal Diagram

Species

<input type="checkbox"/> gas	0	* - see List
<input type="checkbox"/> liquids	0	
<input checked="" type="checkbox"/> aqueous	11	m: 1e-6
* <input checked="" type="checkbox"/> solids	4	List

Parameters

Pressure

Isobar: P(atm): [no gas]

Constants

Temperature T(K): 298.15 Z: [dropdown]

log10(Z): -1

Y-axis

Y: Eh(volts)

max: 2.2 min: -1.8 step: 0.1

X-axis

X: pH

max: 16 min: -2 step: 1

Labels and Display

- chemical
- number size: 12
- none

full screen

View Figure

Figure

Calculate

- diagram
- invariant point
- detailed point

Calculate >>

FactSage 5.2 Compound: ELEM EXAM **FAC** SGPS SGSL

Click here (or, from the menu bar, select **Data Search > Databases...**) 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

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

F Databases

File

Compound Databases (1/5)

+	Database	Name
	ELEMBASE.CDB	ELEM
	EXAMPLEBASE.CDB	EXAM
+	FS50BASE.CDB	FACT
	SGPSBASE.CDB	SGPS
	SGSLBASE.CDB	SGSL

View FACT compound data

Solution Databases

solution databases not active in module
EhpH

View solution data

Click on "+" column to include/exclude database in the data search.
Click on the "Name" column for "Information" on that database.

Information

Location: C:\FACT-51\FACTDATA\FS50BASE.CDB
Type: FactSage 5.00 compound database (Mar. 2001)

To Add a Database to the List

If a database does not appear in the list click on the menu bar (top left corner) "File > Add a database to the list ...".

To remove a database from the list click on its "Name" column and then click on the menu bar "File > Remove database from the list". Note, this does not delete the database.

Cancel OK

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