

## 17. E - pH (Pourbaix) Diagrams Module

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E - pH diagrams show the thermodynamic stability areas of different species in an **aqueous solution**. Stability areas are presented as a function of pH and electrochemical potential scales. Usually the upper and lower stability limits of water are also shown in the diagrams by dotted lines. Traditionally, these diagrams have been taken from different handbooks<sup>1</sup>. However, in most handbooks, these diagrams are available only for a limited number of temperatures, concentrations, and element combinations.

The Eh - pH module (Eph module is used hereafter) in HSC Chemistry allows the construction of diagrams in a highly flexible and fast way, because the user can draw the diagrams exactly at the selected temperature and concentration.

The Eph module is based on STABCAL - Stability Calculations for Aqueous Systems - developed by H.H. Haung, at Montana Tech., USA<sup>2,3</sup>.

## 17.1. Introduction

E - pH diagrams are also known as Pourbaix Diagrams, after the author of the famous Pourbaix diagram handbook<sup>1</sup>. The simplest type of these diagrams is based on a chemical system consisting of one element and a water solution, for example, the Mn-H<sub>2</sub>O system. The system can contain several types of species, such as dissolved ions, condensed oxides, hydroxides, oxides, etc. The E - pH diagram shows the stability areas of these species in the redox potential-pH coordinates.

Usually the redox potential axis is based on the Standard Hydrogen Electrode (SHE) scale designated Eh, but other scales can also be used. The redox potential of the system represents its ability to change electrons. The system tends to remove electrons from the species when the potential is high ( $E > 0$ ). These conditions may exist near the anode in an electrochemical cell, but can also be generated with some oxidizing agents ( $\text{Cu} + \text{H}_2\text{O}_2 = \text{CuO} + \text{H}_2\text{O}$ ). In reducing conditions, when the potential is low ( $E < 0$ ), the system is able to supply electrons to the species, for example, with a cathode electrode or with some reducing agents.

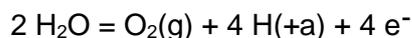
The pH of the system describes its ability to supply protons ( $\text{H}^{(+a)}$ ) to the species. In acid conditions ( $\text{pH} < 7$ ), the concentration of protons is high and in caustic conditions ( $\text{pH} > 7$ ) the concentration of protons is low.

Usually, a large amount of different species exist simultaneously in the aqueous mixtures in fixed E - pH conditions. Pourbaix diagrams simplify this situation a lot by showing only the predominant species whose content is highest in each stability area. The lines in the diagrams represent the E - pH conditions where the content of the adjacent species is the same in the equilibrium state. However, these species always exist in small amounts on both sides of these lines and may have an effect on practical applications.

The lines in the diagrams can also be represented with chemical reaction equations. These reactions may be divided into three groups according to the reaction types:

1. **Horizontal lines.** These lines represent reactions that are involved with electrons, but are independent of pH. Neither  $\text{H}^{(+a)}$  ions nor  $\text{OH}^{(-a)}$  ions participate in these reactions.
2. **Diagonal lines** with either a positive or negative slope. These lines represent reactions that are involved with both electrons and  $\text{H}^{(+a)}$ - and  $\text{OH}^{(-a)}$  ions.
3. **Vertical lines.** These lines represent reactions that are involved either with  $\text{H}^{(+a)}$ - or  $\text{OH}^{(-a)}$  ions, but are independent of E. In other words, electrons do not participate in these reactions.

The chemical **stability area of the water** is shown in the E-pH diagrams by dotted lines. The upper stability limit of water is based on the potential when oxygen generation starts on the anode. It is specified by the reaction:



The lower stability limit is based on hydrogen formation on the cathode. It is specified by the reaction:



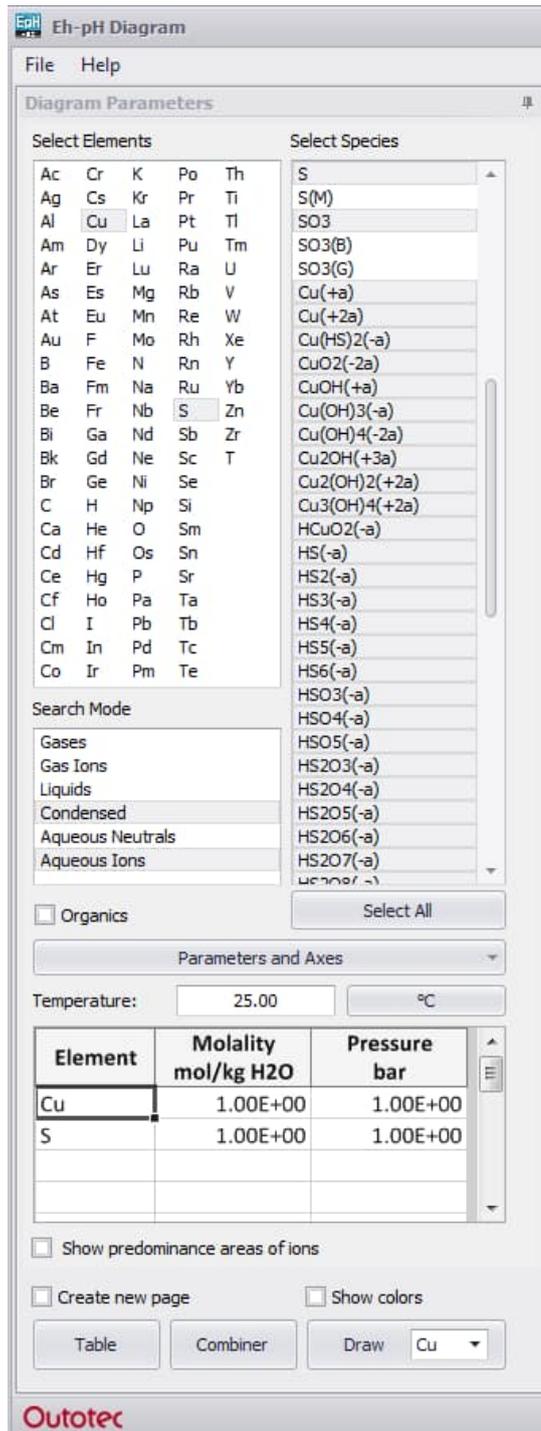
The construction of the diagrams with the HSC Chemistry EpH module is quite a simple task. However, several aspects must be taken into account when specifying the chemical system and analyzing the calculation results, for example:

1. **A basic knowledge** of chemistry, aqueous systems and electrochemistry or hydrometallurgy is always needed in order to draw the correct conclusions.
2. The EpH module carries out the calculations using **pure stoichiometric substances**. In practice, minerals may contain impurity elements and the composition may deviate slightly from the stoichiometric one.
3. There are always some **errors** in the basic thermochemical data of the species. This may have a significant effect on the results, especially if the chemical driving force of the reaction is small. Usually small differences between Pourbaix diagrams from different sources can be explained by the slightly different basic data used.
4. Sometimes data for all existing **species is not available** from the HSC database or from other sources. This will distort the results if the missing species are stable in the given conditions. The missing unstable species will have no effect on the results.
5. The EpH module does not take into account **the non-ideal behavior of aqueous solutions**. However, in many cases these ideal diagrams give a quite good idea of the possible reactions in aqueous solutions, especially if the driving force of the reactions is high.
6. Thermochemical calculations do not take into account the **speed of the reactions** (kinetics). For example, the formation of the  $\text{SO}_4^{2-}$  ion may be a slow reaction. In these cases, metastable diagrams created by removing such species from the system may give more consistent results with experimental laboratory results.

Due to these limitations and assumptions, the HSC user must be very careful when drawing conclusions from E - pH diagrams. However, these diagrams can offer extremely valuable information when combining the results with experimental work and with a good knowledge of aqueous chemistry. There is no universal kinetic or thermochemical theory available that could entirely substitute traditional experimental laboratory work with pure theoretical calculation models.

More information on E - pH diagrams, calculation methods, and applications can be found in different handbooks, for example, from the Pourbaix Atlas<sup>1</sup>.

## 17.2. Chemical System Specifications



**Fig. 1.** Selecting elements and species for the E - pH diagram.

The EpH Diagram selection in the HSC main menu will show the EpH form, **Fig. 1**. The user must specify the chemical system which will be used to calculate the diagram in this form. Let us assume that the system contains Cu, S, and H<sub>2</sub>O. The following steps should be specified in order to create the diagram:

- Select Elements:** Select one or more elements from the list. The element chosen first will be used as the “main” element in the first diagram, i.e. all species, which are shown in the diagram, will contain this element. The user can easily change the main element selection later on in the diagram form, see **Fig. 3**. **Cu** has been selected in this example, but **S** may be selected as the main element by pressing **S** in **Fig. 3**. Up to 7 elements can be selected but it is recommended to use fewer, because a large amount of elements and species increases calculation time and could cause some other problems. **S** has been selected in this example. **Note:** It is not necessary to select **H** and **O**, because these are always automatically included.
- Search Mode:** This selection specifies the type of species which will be collected from the database. It is recommended to use the default selections. **Note:** *Condensed* = solid substances, *Aqueous Neutrals* = dissolved species without charge, *Aqueous Ions* = dissolved ions, *Gases* = gaseous species without charge, *Gas Ions* = gaseous ions, and *Liquids* = liquid species. Check Organics, if you want to include organic species to your system (carbon need to be one of the selected elements).
- Select Species:** Usually you can select all species for the diagram by pressing **All**. However, in many cases, **it is useful to remove unnecessary species from the system**. This will decrease calculation time and simplify the diagrams. Note: A) By pressing simultaneously the **Ctrl key** and clicking with the mouse it is easy to make any kind of selection. B) By double clicking the species it is possible to see more information on the species. Load CUS25.eph8 file to see the selected species of this example.

**The selection of species is the most critical step in the EpH calculation specifications.** For kinetic reasons the formation especially of large molecules may take quite a long time in aqueous solutions. For example, the formation of large polysulfide, sulfate, etc. molecules (S<sub>4</sub>O<sub>6</sub>(-2a), HS<sub>2</sub>O<sub>6</sub>(-a), HS<sub>7</sub>O<sub>3</sub>(-a), ...) may take quite a while. If these are included in the chemical system then they may easily consume all the sulfur and the formation of simple sulfides (AgS, Cu<sub>2</sub>S, ...) will decrease due to the lack of sulfur. Therefore in some cases large molecules should be rejected from the chemical system.

The data on some species may also be unreliable, especially if the reliability class of the species in the database is not 1. Such species may be rejected from the chemical system. Note also that it is not recommended to use species with the (ia) suffix, see Chapter 28 (section 28.4.) for details.
- Temperature:** The user must specify at least one temperature for the diagram. Up to four temperatures may be specified in order to draw combined diagrams, which show the effect of temperature. The temperatures 25, 50, 75, and 100 °C have been selected in this example, **Fig. 1** and **Fig. 2**.
- Draw:** Pressing the Table button will show the Diagram specification form, see section 17.3. and **Fig. 2**. By pressing **Draw** in **Fig. 2** you will see the default diagram.

## 17.3. E - pH Diagram Menu

	A	B	C	D	E	F	G
1	<b>Cu - S - System at 25.00 °C</b>						
2	Elements	Molality	Pressure		Temperature	25.000 °C	
3	Cu	1.00E+00	1.00E+00		Show Colors:	FALSE	
4	S	1.00E+00	1.00E+00		Dielectric Coef	78.382	
5					DeltaG of H2	-56.678	
6					Davies Meth	FALSE	
7					Ion Strength:	0.000	
8					Connection F	1.000	
9					Criss Cobble:	FALSE	
10					Max Eh	-2.000	
11					Max Eh:	2.000	
12					Min pH:	0.000	
13	Potential Scale:	1.000			Max pH:	14.000	
14	Search modes:	Condensed;Aqueous Ions			Show Predon	FALSE	
15							
16	Species	DeltaG kcal/mol	Area no	X1 pH	Y1 V	X2 pH	Y2 V
17	Cu	0.000					
18	Cu(FCC)	0.003					
19	CuO	-30.974					
20	CuO(T)	-30.563					
21	Cu2O	-35.335					
22	Cu(OH)2	-89.079					

Fig. 2. Default values for the E - pH diagram (Table button).

The EpH diagram menu shows a summary of the chemical system specifications as well as the selected default values for the diagram. The fastest way to go forward is to accept all the default values and press **Draw** for simple E - pH diagram. Usually at the beginning, there is no need for modifications to the default values. However, it is important to understand the meaning of these settings because they may have a strong effect on the diagram. The details of the diagram menu options are explained in the following paragraphs.

### 1. File Open

The EpH module can also be used as an independent application; in these cases the data for the diagram may be read from \*.eph8 files by pressing File Open. *Normally the system specifications are automatically transferred from the system specification sheet to the diagram menu, Fig. 2.*

The calculation results may be saved in a \*.eph8 file by selecting Save from the file menu and loaded back by selecting Open from the file menu, which causes the diagram to be automatically recalculated.

### 2. Table sheet

The selected species and calculated  $\Delta G$ -data based on the enthalpy, entropy, and heat capacity values of the HSC database is shown in the Table sheet, Fig. 2. The species are arranged according to elements and species type.

The published Pourbaix diagrams are often based on  $\Delta G$ -data which is given in the original papers. Note that these  $\Delta G$ -values can also be calculated from the standard potential values using Equation (1):

$$\Delta G = -n \cdot F \cdot E \quad (1)$$

where  $n$  is the charge transferred in the cell reaction,  $F$  is the Faraday constant (23045 cal/(V·mol)), and  $E$  is the standard electrode potential in volts. Note:  $\Delta G$ -data is temperature dependent; usually these values are only available at 25 °C in the literature.

Sometimes all the necessary species are not available in the HSC database. These missing species can be added to the chemical system specification if the user has the  $\Delta G$ -values or chemical potential data for these species. The new species may be added by using Own Database, see Chapter 28 (section 28.6).

In some cases it is necessary to remove certain species from the system, e.g. if some kinetic barriers are found to slow down the reaction rate in the experiments.

Table sheet is for the program's internal use and user should not make any modifications to this sheet.

### 3. Temperature

Pourbaix diagrams are drawn at a constant temperature. The user must select one temperature for the diagram from the list of temperatures, **Fig. 2**. The actual temperature values can only be changed from the system specification form, **Fig. 1**. No temperature selection is needed here for the Combined diagrams.

The default  $\Delta G$ -values in the Species sheet are calculated at the given temperatures.

### 4. Other parameters

The default values for the Dielectric Constant and  $\Delta G$  of H<sub>2</sub>O are automatically calculated on the basis of the selected temperature and pressure. The calculation of Dielectric Constant is based on experimental values<sup>4</sup> and water vapor pressure<sup>5</sup>, which are valid from 0 to 373 °C, and from 1 to 5000 bar. Outside this range the Dielectric Constant will be extrapolated.

The Ion Strength and Correction Factor constants are automatically calculated by the program and usually they do not need to be modified by the user.

Criss-Cobble option enables HSC to extrapolate the heat capacity function of the aqueous species if this data is not given in the database<sup>6</sup>, see Chapter 28 (28.4.)

## 5. Potential and pH scale ranges

The user may change the default range (Max Eh and Min Eh) for the potential scale as well as the range of the pH scale (Max pH and Min pH). The scale settings can also be changed by clicking the x- or y-axis on the diagram form. The minimum difference between Min and Max values is 0.2 and there is no upper limit for the difference.

## 6. Molality and Pressure

The diagrams are calculated using constant molalities (concentrations) for all the elements. The default values may be changed in the table in the bottom right corner of the diagram menu, see **Fig. 2**. Molality values are given in mol/kg H<sub>2</sub>O units.

The total pressure of the system is also given in the Molality table. The EpH module uses the maximum value given in the Pressure column as the chemical system total pressure. It is not possible to select a smaller pressure value than the water vapor pressure at the selected temperature. In other words, the total pressure must always be bigger than the water vapor pressure at the selected temperature. The default value for the pressure is 1 bar.

## 7. Show Predominance Areas of Ions

Selecting Show Predominance Areas of Ions causes the EpH module to calculate two diagrams for the same system. The first one is a normal E - pH diagram with all species, and the second one is the predominance diagram with only aqueous species. Both diagrams are drawn into the same figure; the first diagram in black and the second one in blue. This option is recommended for use only with normal E - pH diagrams (see section 17.4.).

## 8. Draw and Combiner Buttons

Draw starts the calculations and automatically shows the normal Pourbaix diagram. Combiner will show one more menu for combined diagram specifications; see section 17.5. for further details.

## 9. Other options

The Chart may be printed clicking Print. Data table can be printed by clicking Table and selecting Print from the file menu.

Edit Copy provides normal copy and paste operations, Edit Copy All copies all three sheets to the clipboard. The worksheet layout may be changed using the Format menu, which contains dialogs for column width, row height, font, alignment, and number formats.

Press Exit or select File Exit when you want to return to the system specifications form, **Fig. 1**. The Help menu opens the HSC Help dialog.

## 10. Example of Normal Pourbaix Diagrams (Cu-S-H<sub>2</sub>O system)

Accept all the default values and press Draw.

## 17.4. Normal E - pH Diagrams

The calculated E - pH diagrams are shown in **Fig. 3**. In the Diagram window it is possible, for example, to modify the layout and format of the diagram. The solid black lines show the stability areas of the most stable species on the pH and E scales. The dotted black lines show the upper and lower stability areas of water, see section 17.1. The stability areas of ions are shown by a blue dotted line if the “**Show Predominance Areas of Ions**” option has been selected, see **Fig. 2**.

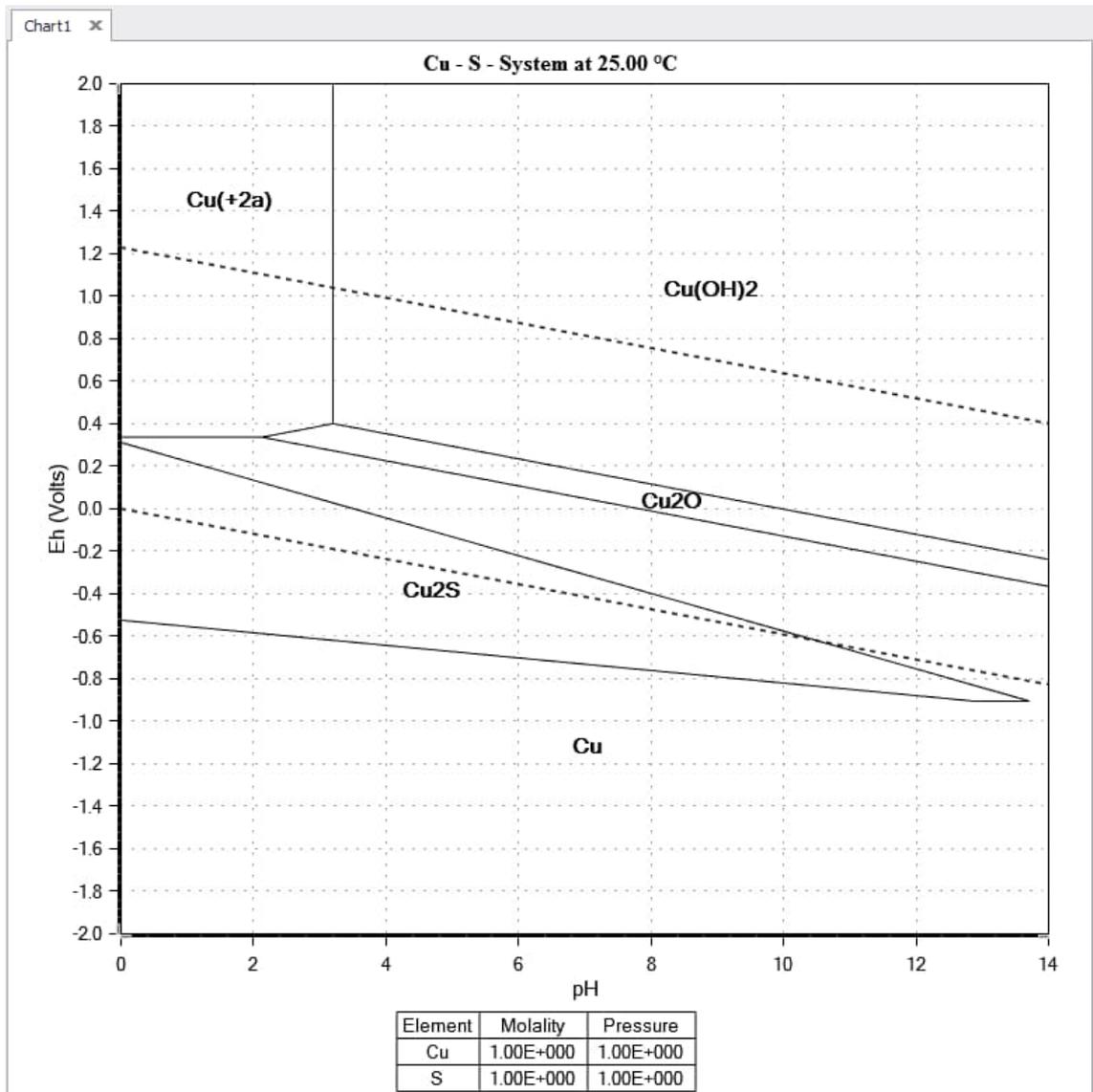
### 1. Main Elements

*The E - pH diagrams show only the species that contain the selected main element.* The default main element (Cu) must be selected in the system specification form, **Fig. 1**. However, the active main element can easily be changed in the diagram form by selecting Element inside **Draw** button, see **Fig. 3** for the Cu-S-H<sub>2</sub>O diagram and **Fig. 4** for the S-Cu-H<sub>2</sub>O diagram. Usually it is useful to check all the diagrams with different main elements to get a better idea of the equilibria.

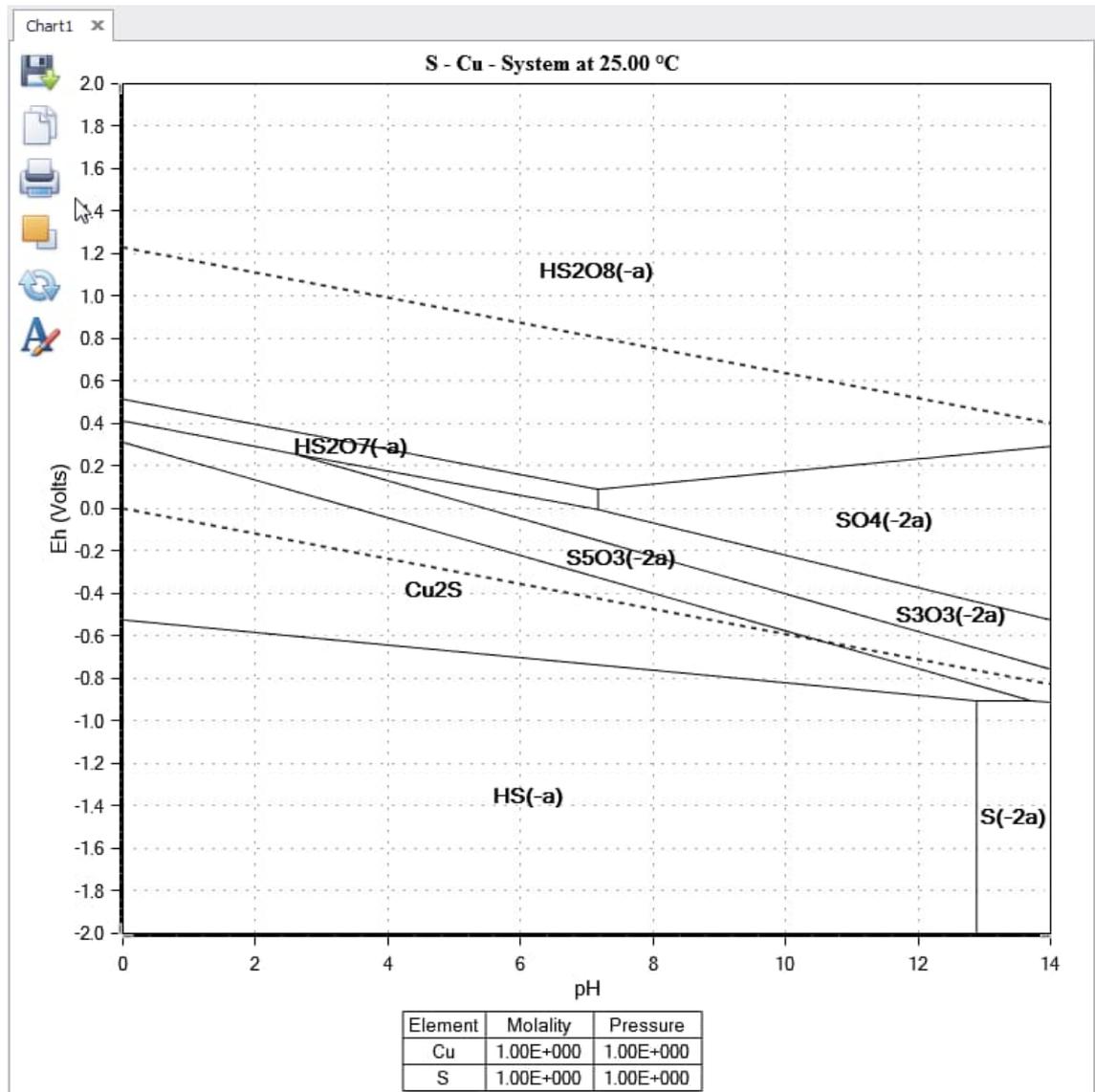
### 2. Labels and Lines

The EpH module locates the area labels automatically on the widest point of the stability areas. You can easily **relocate** the labels by dragging them with the mouse cursor if necessary. The text of the labels and headings can be **modified** by inserting the cursor into the correct location within the text row and then starting to type. You can start the **Label Format** dialog by double clicking the label. This dialog makes it possible to change text and lines properties, such as font, type, size, line width, color, etc.

Note that you cannot delete the default labels, but you can hide these labels by removing all the text from the label.



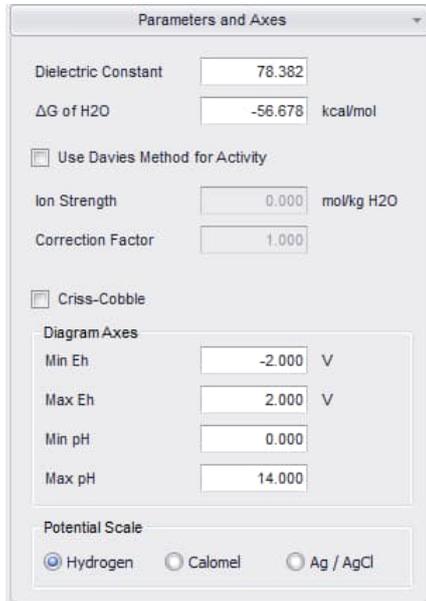
**Fig. 3.** E - pH diagram of Cu-S-H<sub>2</sub>O system at 25 °C using Cu as the main element. The molalities of Cu and S are 1 mol/kg H<sub>2</sub>O.



**Fig. 4.** E - pH diagram of the S-Cu-H<sub>2</sub>O system at 25 °C using S as the main element. The molalities of Cu and S are 1 mol/kg H<sub>2</sub>O.

Selecting **Format H<sub>2</sub>O Stability Lines** opens the format dialog, which makes it possible to modify the water stability lines formats and properties. NB! This dialog cannot be opened by double clicking the water stability lines.

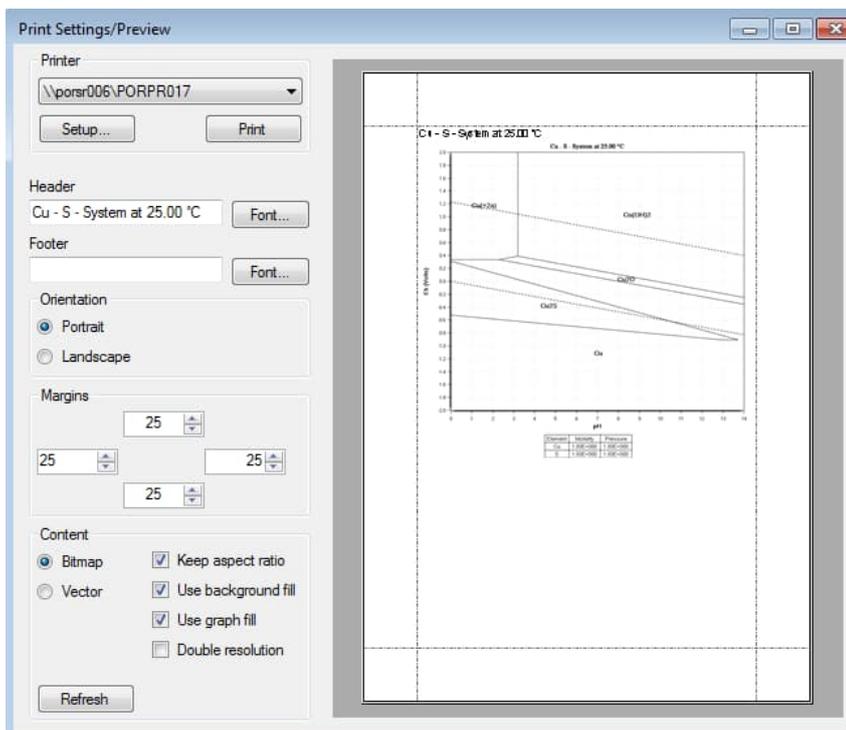
### 3. Scales



**Fig. 5.** Menu for formatting y-axis; note the different potential scale options.

The scale format dialog can be opened by clicking the **Parameters and Axis**, see **Fig. 5**. A special feature of the E - pH diagram scale dialog is the scale unit option. You can select between the Hydrogen, Saturated Calomel, and Ag / AgCl scales. The default scale is Hydrogen (Eh), which is used in the calculations. The difference between the Min and Max values must be at least 0.2 units.

### 4. Printing



**Fig. 6.** E - pH Diagram Print Dialog.

You can open the Print dialog by clicking **Print**, see **Fig. 3**. This dialog allows the user to select margins and size of the diagram as well as the orientation, see **Fig. 6**.

## **5. Other Options**

The default diagram font dialog can be opened by pressing **Font** or by selecting **Format Default Font** from the menu.

Selecting **Copy** as well as **Edit Copy** will copy the diagram into the Windows Clipboard, which makes it possible to paste the diagram into other Windows applications in Windows Metafile format. Selecting **Edit Copy All** will also copy the molality and pressure values into the diagram. **Edit Copy Special** will copy scaled diagrams.

Selecting **Save** or **File Save** will save the E - pH diagram in Windows Metafile format (\*.WMF). These diagrams cannot be read back to HSC.

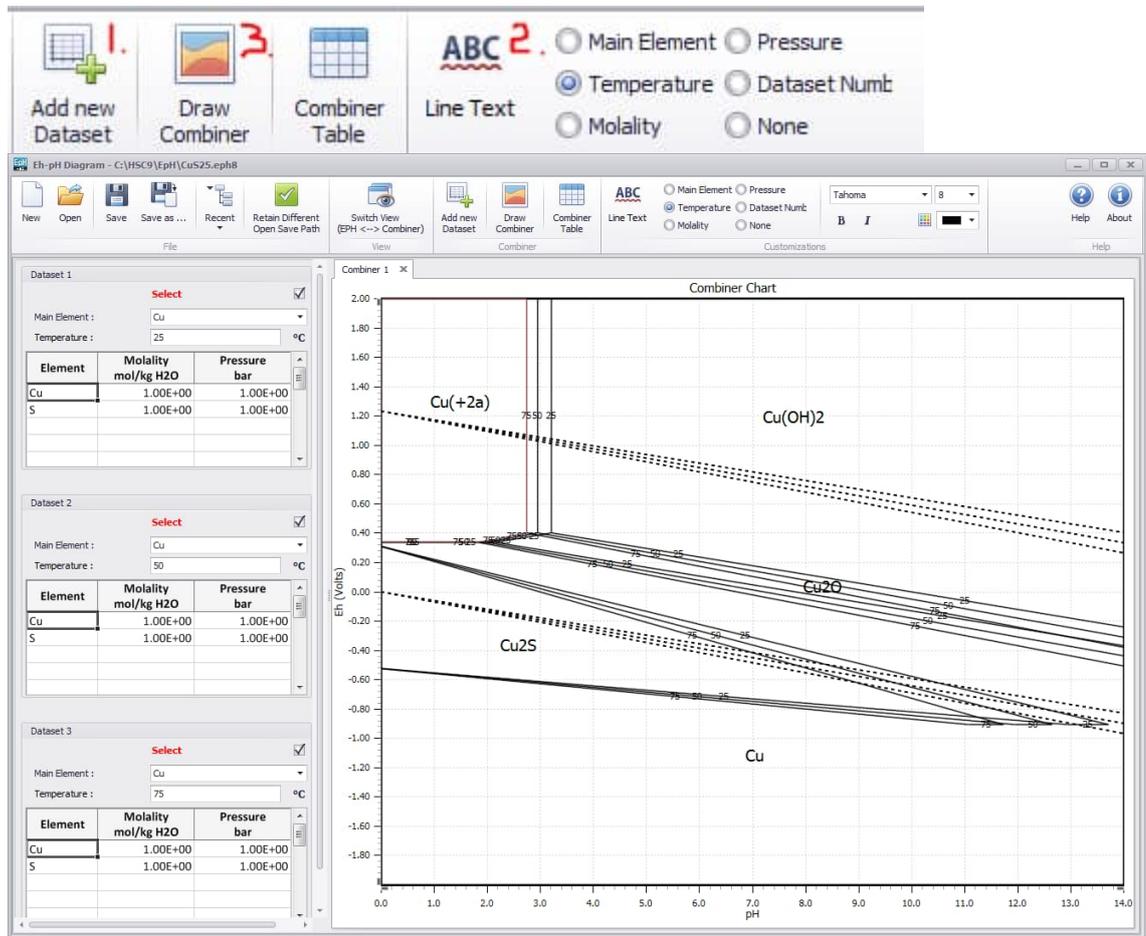
Selecting **Menu** or **File Exit** will reactivate the Diagram Menu form, see **Fig. 3**. Selecting **Help** will open the HSC Help dialog.

## **6. Example: Cu-S-H<sub>2</sub>O System**

The Cu-S and S-Cu diagrams are shown in **Fig. 3** and **Fig. 4**. These diagrams provide a lot of valuable information. For example, the dissolution behavior of copper can easily be estimated from **Fig. 3**. It is easy to see that in neutral and caustic solutions metallic copper is stable near zero potential values. It will form oxides in anode conditions ( $E > 0$ ) and sulfides in cathode conditions ( $E < 0$ ). However, it will dissolve as Cu(+2a) in acid conditions at the anode ( $E > 0$ ) and precipitate on the cathode ( $E < 0$ ) in metallic form.

## 17.5. Combined E - pH Diagrams

Combiner will show one more menu for combined diagram specifications see **Fig. 7**. First you select your system see section 17.4. Then you click combiner button. Then 1. add new Dataset and give values to each dataset (here 25, 50 and 75 °C), 2. select variable (here Temperature) and 3. Draw Combiner.



**Fig. 7.** EpH combiner showing Cu-S diagram at 25, 50 and 75 °C.

## 17.6. E - pH Diagrams in Practice

The HSC EpH module enables fast and easy creation of Pourbaix diagrams for the required chemical system in user-specified conditions. These diagrams contain the basic information of the aqueous system in a compact and illustrative form. These diagrams have found many applications in corrosion engineering, geochemistry, and hydrometallurgy since the publication of the famous Pourbaix Atlas handbook<sup>1</sup>.

In hydrometallurgy, E - pH diagrams may be used, for example, to specify the conditions for selective leaching or precipitation. In corrosion engineering, they may be used to analyze the dissolution and passivation behavior of different metals in aqueous environments. These diagrams may also be used to illustrate the chemical behavior of different ions in aqueous solutions.

Geochemists use Pourbaix diagrams quite frequently to study the weathering process and chemical sedimentation. The weathering process is used to predict what will happen to a mineral exposed to acid oxidizing conditions at high temperature and pressure. Pourbaix diagrams can also be used to estimate the conditions needed to form certain sediments and other minerals<sup>7</sup> in the geological past.

Some application examples of the EpH module and Pourbaix diagrams are given in Chapter 18.

## 17.7. References

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