

## 17. Eh - pH - DIAGRAMS (Pourbaix-diagrams)

Eh-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 with dotted lines. Traditionally these diagrams have been taken from different handbooks<sup>12</sup>. However, in most handbooks these diagrams are available only for a limited number of temperatures, concentrations and element combinations.

The Eh-pH module of 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 Eh-pH-module is based on STABCAL - Stability Calculations for Aqueous Systems - developed by H.H. Haung, at Montana Tech., USA<sup>9,10</sup>.

### 17.1 Introduction

Eh-pH-diagrams are also known as **Pourbaix Diagrams** according to author of the famous Pourbaix diagram handbook<sup>12</sup>. The most simple type of these diagrams is based on a chemical system consisting of one element and 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 Eh-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 (Eh > 0). These conditions may exist near the anode in the electrochemical cell, but can also be generated with some oxidizing agents (Cu + H<sub>2</sub>O<sub>2</sub> = CuO + H<sub>2</sub>O). In reducing conditions, when potential is low (Eh < 0), the system is able to supply electrons to the species, for example, with a cathode electrode or with some reducing agents.

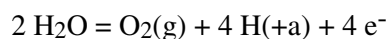
The **pH** of the system describes its ability to supply protons (H(+a)) to the species. In acid conditions (pH < 7) the concentration of the protons is high and in caustic conditions (pH > 7) the concentration of protons is low.

Usually a large amount of different species exist simultaneously in the aqueous mixtures in fixed Eh-pH-conditions. The Pourbaix diagrams simplify this situation a lot by showing only the predominant species which content is highest in each stability areas. The **lines** in the diagrams represent the Eh-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.

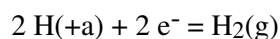
The lines in the diagrams can also be represented with chemical reaction equations. These reactions may be divided into three groups according to reaction types:

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

The chemical **stability area of the water** is shown in the Eh-pH-diagrams with dotted lines. The upper stability limit of water is based on the potential when the 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 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 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 the other sources. This will distort the results if the missing species are stable in 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 SO<sub>4</sub>(-2a) 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 the experimental laboratory results.

The HSC user must be very careful when drawing conclusions from Eh-pH-diagrams due to these limitations and assumptions. However, these diagrams may offer extremely valuable information when combining the results with the experimental work and with a

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good knowledge of aqueous chemistry. There is no universal kinetic or thermochemical theory available, which could entirely substitute traditional experimental laboratory work with pure theoretical calculation models.

More information on Eh-pH-diagrams, calculation methods and applications can be found from different handbooks, for example, from the Pourbaix Atlas<sup>12</sup>.

## 17.2 Chemical System Specifications

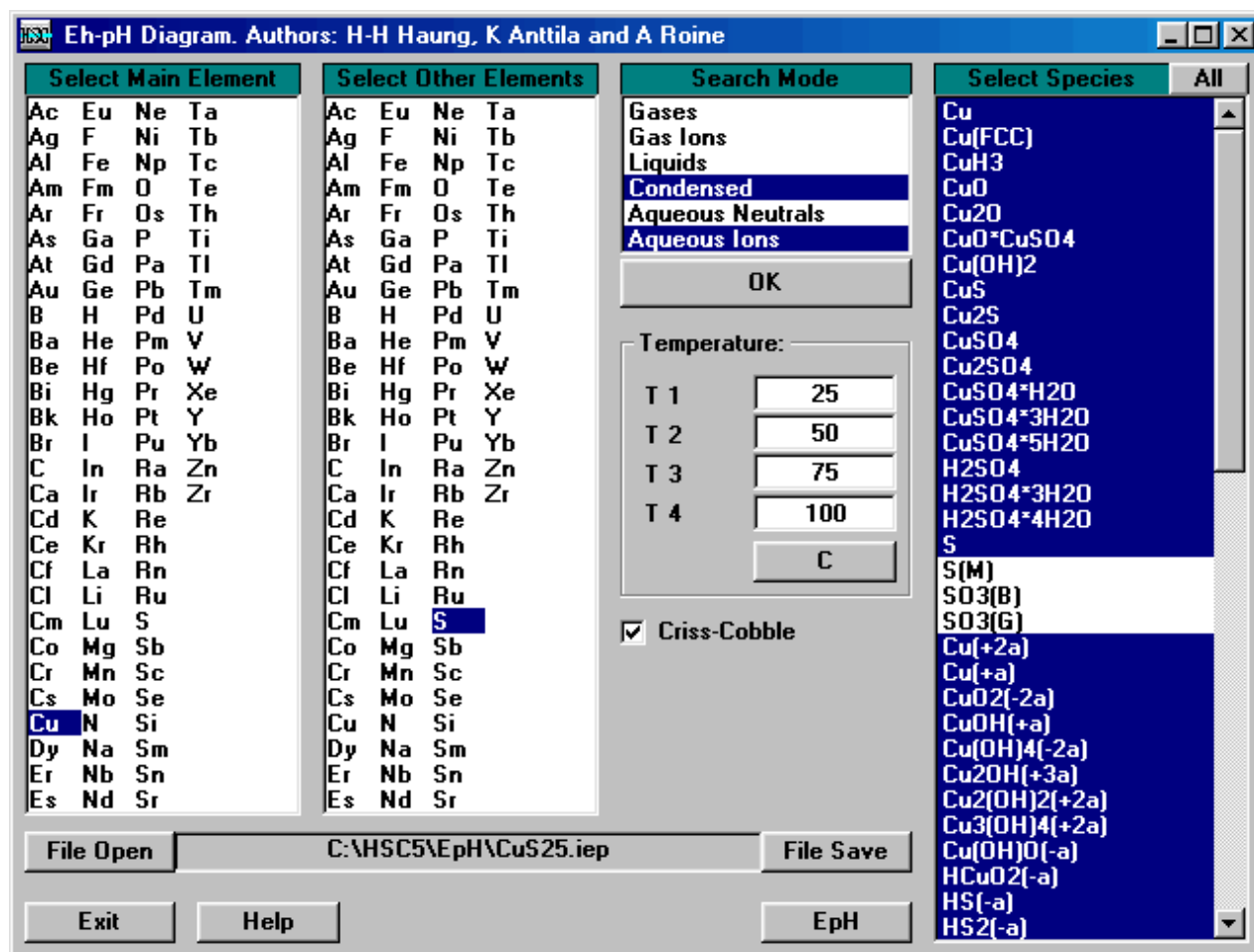


Fig. 1. Selecting elements and species for the Eh - pH - diagram.

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. Assume that system contains Cu, S and H<sub>2</sub>O. The following steps should be specified in order to create the diagram:

1. **Select Main Element:** Select one element from the list. This element 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. The **Cu** has been selected in this example, but **S** may be selected to main element by pressing S button in Fig. 3.
2. **Select Other Elements:** Select other elements to the system. Up to 7 elements can be selected but it is recommended to use less, because large amount of elements and species increase 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.

3. **Search Mode:** This selection specifies the type of species, which will be collected from the database. It is recommended to use 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.
4. **OK:** Press OK to start the search from the database.
5. **Select Species:** Usually you can select all species to the diagram by pressing **All**. In some cases, however, it is useful to remove unnecessary species from the system. This will decrease calculation time and simplify diagrams. **Note:** A) By pressing simultaneously **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 of the species. Load CUS25.IEP file to see the selected species of this example.

The selection of the species is the most critical step of the EpH calculation specifications. **Due to the kinetic reasons the formation especially of large molecules may be take quite a long time in aqueous solutions. For example, the formation of large polysulfide, sulfate, etc. molecules (S4O6(-2a), HS2O6(-a), HS7O3(-a), ...) may take quite a while. If these are included into the chemical system then they may easily consume all the sulfur and the formation of simple sulfides (AgS, Cu2S, ...) decreases due to lack of sulfur. Therefore in some cases the large molecules should be rejected from the chemical system.**

The data of some species may also be unreliable, especially if the reliability class of the species is not 1 in the database. Such species may be rejected from the chemical system. Note also that species with (ia) suffix are not recommended to use, see Chapter 28.4 for details.

1. **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, Figs. 1 and 2.
2. **Criss-Cobble:** This option enables HSC to extrapolate the heat capacity function of the aqueous species if this data is not given in the database<sup>11</sup>, see Chapter 28.4.
3. **EpH:** Press EpH to start the File Save dialog and Calculation of the diagram. You can also press **File Save** in order to save the data for later use without running the calculation procedure.
4. **Diagram:** Pressing the EpH button will show the Diagram specification form, see Chapter 17.3 and Fig 2. By pressing **Diagram** in Fig. 2 you will see the default diagram.

## 17.3 Eh - pH - Diagram Menu

	Species	DeltaG / T1 kcal/mol	DeltaC kcal/
1	Cu	0.000	
2	Cu(FCC)	0.004	
3	CuH3	67.731	
4	CuO	-30.663	-
5	Cu2O	-35.345	-
6	CuO*CuSO4	-189.353	-1
7	Cu(OH)2	-85.808	-
8	CuS	-12.780	-
9	Cu2S	-20.666	-
10	CuSO4	-158.242	-1
11	Cu2SO4	-156.429	-1
12	CuSO4*H2O	-219.417	-2
13	CuSO4*3H2O	-334.581	-3
14	CuSO4*5H2O	-449.263	-4
15	H2SO4	-164.885	-1
16	H2SO4*3H2O	-345.100	-3
17	H2SO4*4H2O	-402.912	-3
18	S	0.000	
19	Cu(+2a)	15.668	
20	Cu(+a)	11.947	
21	CuO2(-2a)	-41.219	
22	CuOH(+a)	-30.209	

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Temperature C  
 25.000     75.000  
 50.000     100.000

Dielectric Constant    78.382  
DeltaG of H2O    -56.678  
Ion Strength    0.000  
Correction Factor:    1.000  
Max Eh    2.000  
Min Eh    -2.000  
Max pH    14.000  
Min pH    0.000

Ele- ment	Molality m mol/kg H2O	Pressure p bar
Cu	1.000E+00	1.000E+00
S	1.000E+00	1.000E+00

Show Predominance Areas of Ions

Exit    File Open    C:\HSC5\EpH\CuS25.iep    Combine    Diagram

Fig. 2. Default values for the Eh - pH - diagram.

The EpH-diagram menu shows a summary of the chemical system specifications as well as selected default values for the diagram. The fastest way to go forward is to accept all the default values and press **Diagram** for simple EpH diagrams or **Combine** for combined diagrams. 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 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 \*.IEP files by pressing **File Open**. *Normally the system*

specifications are automatically transferred from the system specification sheet to the diagram menu, Fig. 2.

The diagram specifications can be modified in the diagram menu. The selections can be saved for later use with **File Save IEP** selection from the menu. The IEP-files may also be edited by any text editor like Windows Notepad. Please be careful as any mistake may cause unpredictable results. The calculation results may be saved to \*.EPH file with **File Save EpH** selection and loaded back with **File Open EPH** selection which causes the diagram to be automatically recalculated.

## 2. Species and $\Delta G$ -data workbook

The selected species and calculated  $\Delta G$ -data based on the enthalpy, entropy and heat capacity values of the HSC database is shown on the **Species sheet** of the diagram workbook, Fig. 2. The species are arranged according to elements and species type. The user can modify the  $\Delta G$ -data as well as add or remove species in this sheet. The Species sheet makes it possible to use data and species which cannot be found in the HSC database, for example:

- A. The published Pourbaix diagrams are often based on  **$\Delta G$ -data** which is given in the original papers. This  $\Delta G$ -data can be used in the Species sheet to replace the default values based on the HSC database if necessary. 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:** Give  $\Delta G$ -data for the selected temperatures, usually these values are only available at 25 °C.

- B. Sometimes all 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 inserting empty row with **Insert Row** selection and typing formula and  $\Delta G$ -values to this row.

The new species can be inserted into any location, but it is recommended to add the same type of species sequentially, because it makes the list easier to read and update. Note: A) Do not insert any new elements, new elements must be added in the EpH-element selection window, Fig. 1. B) **Do not create empty rows.**

- C. 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. Such species can be removed by **Delete Row** selection.

The **Labels** and **Lines** sheets are in the programs internal use and it is not necessary to make any modifications to these sheets. The **Labels** sheet contains format data for the

labels such as; text, area number, coordinates, font name and properties, and labels visibility and orientation. The **Lines** sheet contains format data of the equilibrium lines of the diagram: Species names, line area numbers, line endpoint coordinates, and line properties.

### 3. Temperature

The 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 in columns 2 – 5 are calculated at the given temperatures. The  $\Delta G$ -values at column 2 are calculated using the first temperature, column 2 using the second temperature, etc.

### 4. Other parameters

The default values for **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>15</sup> and water vapor pressure<sup>16</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.

### 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 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 maximum value given in the **Pressure** column as the chemical system total pressure. It is not possible to select a smaller pressure value than 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

The “**Show Predominance Areas of Ions**” selection causes the EpH-module to calculate

two diagrams for the same system. The first one is a normal Eh-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 Eh-pH-diagrams (see Chapter 17.4).

## 8. Diagram and Combine Buttons

**Diagram** starts the calculations and automatically shows the normal Pourbaix-diagram. **Combine** will show still one more menu for combined diagram specifications, see Chapter 17.5 for more details.

## 9. Other options

The active worksheet may be printed using **File Print** selection. You can make changes to the setting using normal **Page Setup**, **Print Setup**, and **Preview** dialogs in the **File** menu. The **File Print All** selection prints all three sheets.

The **Edit Copy** selection provides normal copy and paste operations, the **Edit Copy All** selection copies all three sheets to the clipboard. The worksheet layout may be changed by 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 back 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 **Diagram**. Continue from Chapter 17.4.

# 17.4 Normal Eh-pH-Diagrams

The calculated Eh-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 Eh-scales. The dotted cyan lines show the upper and lower stability areas of water, see Chapter 17.1. The stability areas of ions are shown with blue dotted lines if the “**Show Predominance Areas of Ions**” option has been selected, see Fig. 2.

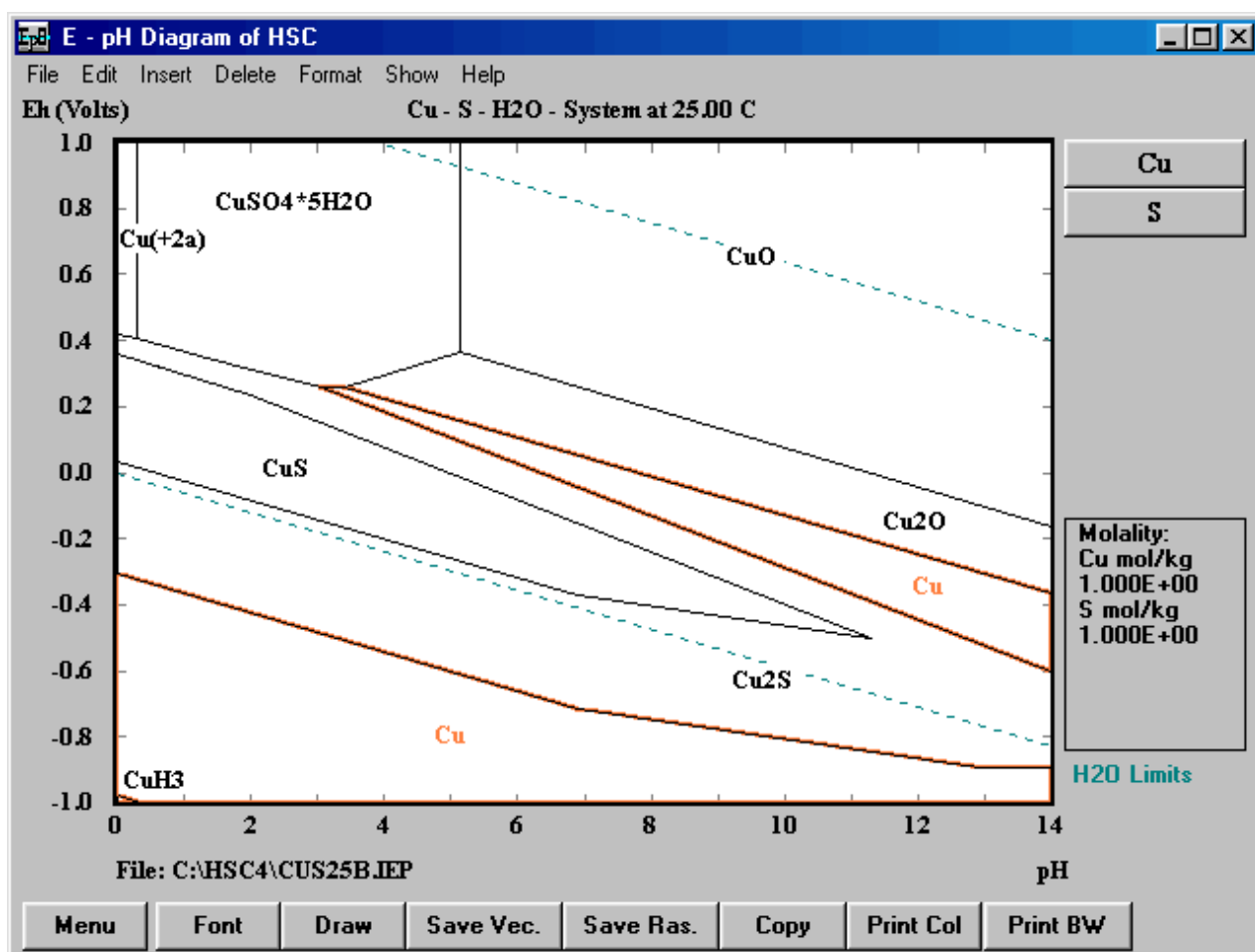
### 1. Main Elements

*The Eh-pH-diagrams show only those species, which 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 pressing **Element buttons** on the upper right side of the diagram form, 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.

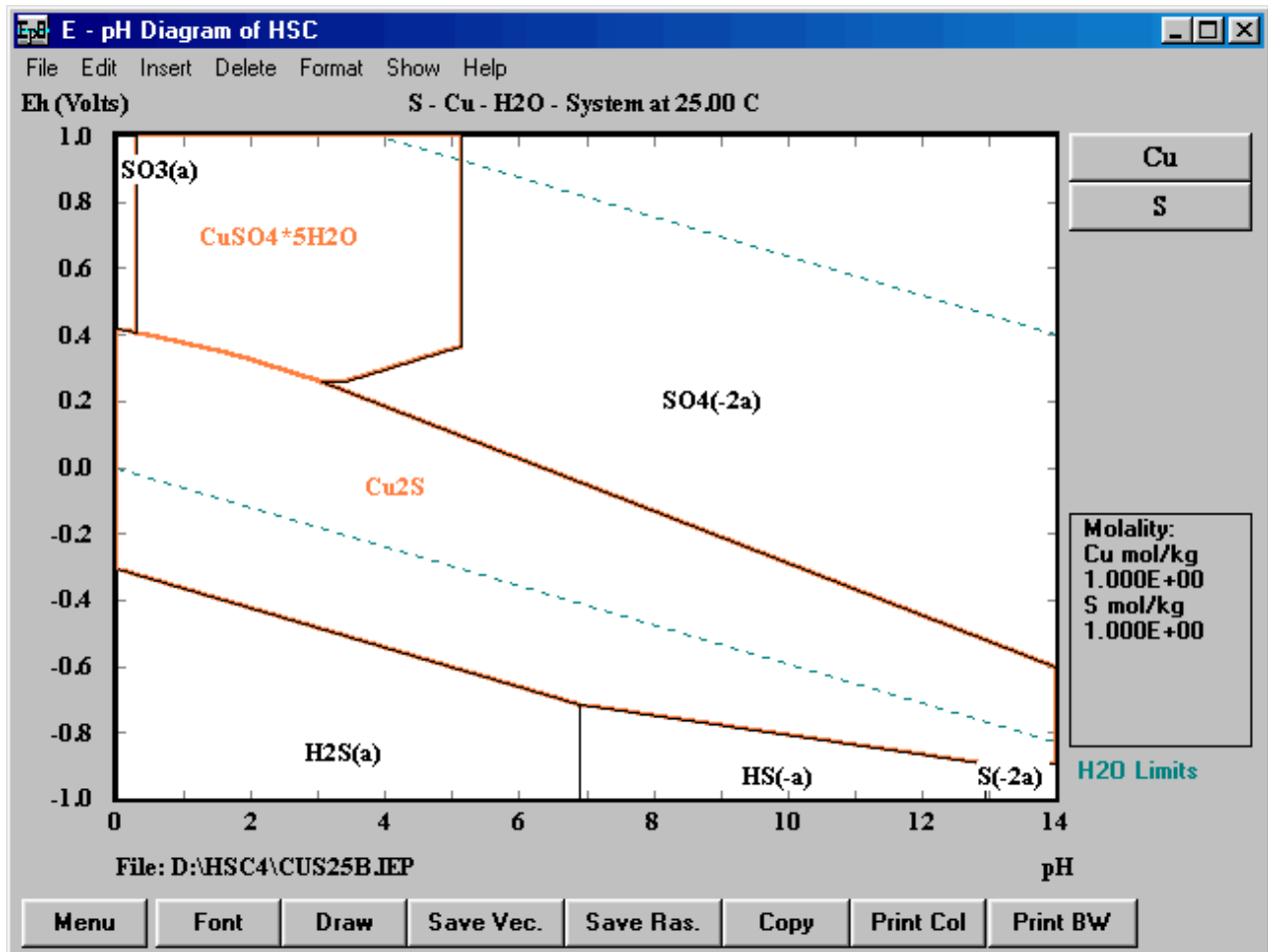
### 2. Labels and Lines

The EpH-module locates the area labels automatically on the widest point of the stability areas. You can easily **relocate** the labels by dragging 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 by starting to type. You can start the **Label Format** dialog by double clicking the label or by the **Format Label** selection. This dialog makes it possible to change text and lines properties, such as font, type, size, line width, color, etc.

You can insert new labels using the **Insert Label** selection. You can delete these labels using the **Delete Label** selection. Note that you cannot delete the default labels, but you can hide these labels by removing all text from the label.



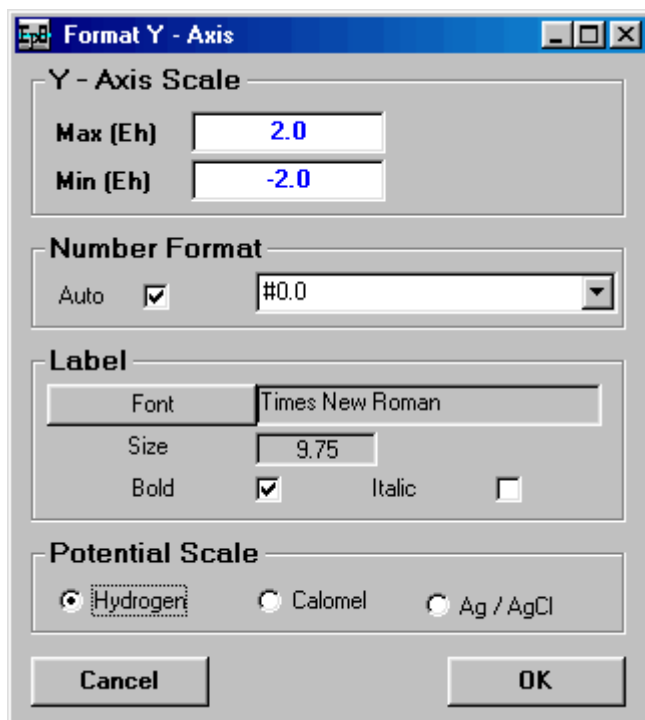
**Fig. 3.** Eh-pH-diagram of Cu-S-H<sub>2</sub>O-system at 25 °C using Cu as the main element. The molalities of Cu and S are 1 mol/kg H<sub>2</sub>O.



**Fig. 4.** Eh-pH-diagram of 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.

The **Format H<sub>2</sub>O Stability Lines** selection opens the format dialog, which makes it possible to modify the water stability lines formats and properties. This dialog can not 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 double clicking the axis numbers, see Fig. 3, or by the **Format Scale** selection, see Fig. 5. A special feature of the Eh-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, which is used in the calculations. The difference between the Min and Max values must be at least 0.2 units.

#### 4. Printing

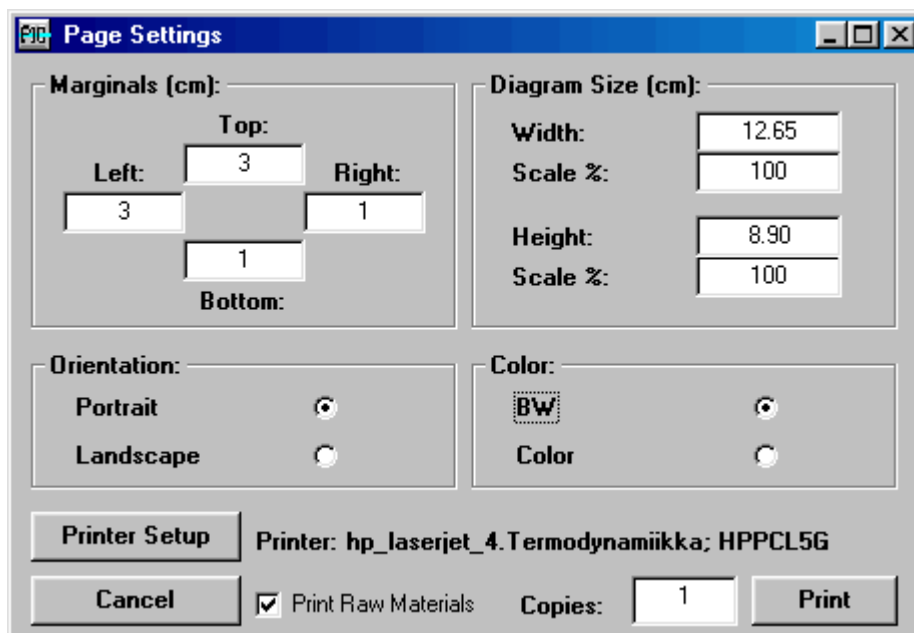


Fig. 6. EpH-Diagram Print Dialog.

You may open the Print dialog by pressing **Print BW** or **Print Col** or by selecting **File Print Special**, see Fig. 3. This dialog allows the user to select margins and size of the diagram as well as the orientation, see Fig. 6. If you have a color printer you can select the **Color** option. **Print** will print a hard copy of the diagram.

#### 5. Other Options

The default diagram font dialog can be opened by pressing **Font** or with the **Format Default Font** selection from the menu. This dialog allows the user to set the default font, which is saved into HSC.INI file.

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

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

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

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

The Cu-S- and S-Cu-H<sub>2</sub>O-diagrams are shown in Figs. 3 and 4. These diagrams may give 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 ( $E_h > 0$ ) and sulfides in cathode conditions ( $E_h < 0$ ). However, it will dissolve as Cu(+2a) in acid conditions at anode ( $E_h > 0$ ) and precipitate on a cathode ( $E_h < 0$ ) in metallic form.

## 17.5 Specifications for Combined Diagrams

The normal Eh-pH-diagrams show the effect of pH and potential on the stability areas of different species. The **Combine** option, see Fig. 2, enables you to see the effect of other variables on the same diagram. Basically, these combined diagrams are made by superimposing up to four normal diagrams together. These separate diagrams can be calculated using the **main element**, **temperature**, **molality** (concentration) or **pressure** as a variable. The traditional Pourbaix-diagrams<sup>12</sup> usually show the effect of molality on the same diagram. These combined diagrams make it easy to compare the effect of the main process variables on the chemical system behavior.

The Combine option only draws combined diagrams for the same chemical system. Other limitations are the same as for the normal Eh-pH diagrams. Note that the user may select different variables to be used simultaneously in the same combined diagram. However, *it is strongly recommended to use only one variable*, such as molality or temperature, because multivariable combined diagrams will be difficult to read. The combined diagram may become extremely complicated if more than two different main elements are selected in one diagram.

### 1. Chemical System Specifications

The chemical system specifications for the combined diagrams are made exactly in the same manner as for normal diagrams, see Chapter 17.2. The Fe-S-H<sub>2</sub>O-system is used here as an example when the combined diagrams approach and properties are described. The selections are shown in Fig. 7. The available temperatures must be specified in the system specifications form, Fig 1.

### 2. Eh-pH-Diagram Menu

The modification of the chemical system as well as other settings are made in **Diagram Menu** in the same way as for the normal diagrams described in Chapter 17.3. In this example no changes were made into the default selections. The only action was to press **Combine**, see Fig. 2.

### 3. Combine Menu

The variable, which is used to draw the combined diagrams, is selected in the **Combine Menu**, see Fig. 8. The user may select up to four data sets to be used in the calculations with the **Select** option. Each data set specifies settings for one normal diagram, which will be included in the combined diagram.

The basic idea is that all values must originally be the same in each data set. **Reset Values**

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will restore the original values. The user may then give different values for one variable in each data set. The molality of iron has been selected for the variable in Fig. 8 by giving the value 1.00E+00 for Data Set 1, 1.00E-03 for Data Set 2 and 1.00E-06 for Data Set 3. The **Select** option and **Line Text** are usually automatically selected whenever a data set is modified.

A combined diagram can be drawn by pressing **Diagram** when the variable values for the data sets have been given.

Different variables can be used simultaneously in each data set. However, it is recommended to use only one variable because multivariable diagrams are difficult to read. Note also that only the Hydrogen electrode potential is available if more than one temperature is used for the combined Eh-pH-diagram.

Eh-pH Diagram. Authors: H-H Haug, K Anttila and A Roine

Select Main Element	Select Other Elements	Search Mode	Select Species
Ac Eu Ne Ta	Ac Eu Ne Ta	Gases	Fe
Ag F Ni Tb	Ag F Ni Tb	Gas Ions	Fe0.9450
Al <b>Fe</b> Np Tc	Al Fe Np Tc	Liquids	Fe0.9470
Am Fm O Te	Am Fm O Te	Condensed	Fe0
Ar Fr Os Th	Ar Fr Os Th	Aqueous Neutrals	Fe01.056
As Ga P Ti	As Ga P Ti	Aqueous Ions	Fe01.5(W)
At Gd Pa Tl	At Gd Pa Tl	OK	Fe2O3
Au Ge Pb Tm	Au Ge Pb Tm	Temperature:	Fe2O3(H)
B H Pd U	B H Pd U	T 1 25	Fe3O4
Ba He Pm V	Ba He Pm V	T 2 50	Fe3O4(H)
Be Hf Po W	Be Hf Po W	T 3 75	Fe(OH)2
Bi Hg Pr Xe	Bi Hg Pr Xe	T 4	Fe(OH)3
Bk Ho Pt Y	Bk Ho Pt Y	C	Fe2O3*H2O
Br I Pu Yb	Br I Pu Yb	<input checked="" type="checkbox"/> Criss-Cobble	FeO*OH
C In Ra Zn	C In Ra Zn		Fe0.8775
Ca Ir Rb Zr	Ca Ir Rb Zr		FeS
Cd K Re	Cd K Re		FeS2
Ce Kr Rh	Ce Kr Rh		FeS2(M)
Cf La Rn	Cf La Rn		Fe2S3
Cl Li Ru	Cl Li Ru		Fe7S8
Cm Lu <b>S</b>	Cm Lu <b>S</b>		FeS04
Co Mg Sb	Co Mg Sb		Fe2(SO4)3
Cr Mn Sc	Cr Mn Sc		FeSO4*H2O
Cs Mo Se	Cs Mo Se		FeSO4*4H2O
Cu N Si	Cu N Si		FeSO4*7H2O
Dy Na Sm	Dy Na Sm		H2SO4
Er Nb Sn	Er Nb Sn		H2SO4*3H2O
Es Nd Sr	Es Nd Sr		H2SO4*4H2O

File Open C:\HSC5\EpH\CuS25.iep File Save

Exit Help EpH

S  
S(M)  
SO3(B)  
SO3(G)  
Fe(+3a)

Fig. 7. Specification of an Fe-S-H<sub>2</sub>O-system for an Eh-pH-diagram.

Combined EpH-diagrams of HSC Chemistry

File Edit Format Help

**DATA SET 1:** Select

Main Element:

Temperature (C):

Element	Molality m mol/kg H <sub>2</sub> O	Pressure p bar
Fe	1.00E+00	1.00E+00
S	1.00E+00	1.00E+00

**DATA SET 2:** Select

Main Element:

Temperature (C):

Element	Molality m mol/kg H <sub>2</sub> O	Pressure p bar
Fe	1.00E+00	1.00E+00
S	1.00E+00	1.00E+00

**DATA SET 3:** Select

Main Element:

Temperature (C):

Element	Molality m mol/kg H <sub>2</sub> O	Pressure p bar
Fe	1.00E-06	1.00E+00
S	1.00E+00	1.00E+00

**DATA SET 4:** Select

Main Element:

Temperature (C):

Element	Molality m mol/kg H <sub>2</sub> O	Pressure p bar
Fe	1.00E+00	1.00E+00
S	1.00E+00	1.00E+00

**LINE TEXT:**

Main Element  
 Temperature  
 Molality  
 Pressure  
 Data Set Number  
 None

Source:

Fig. 8. Specification of a combined diagram layout for an Fe-S-H<sub>2</sub>O system.

The **Line Text** options specify which variable values are used as line labels. Usually the combined diagrams are so complicated that labels on the lines are needed to distinguish the lines of different data sets from each other. The line labels are automatically located in the middle point of the lines. The Line Text option is automatically selected on the basis of the last changed variable. However, the user can change this selection just before starting the final calculations with **Diagram**.

The following **Line Text** options may be used:

- **Main Element**
- **Temperature:** (all numbers rounded to integers)
- **Molality and Pressure:** Only the last three characters of the numbers are used. For example, "1.00E-03" is shortened to "-03".
- **Data Set Number**
- **None:** Line labels are not used.

The **Source** option refers to the element which is used for the **Molality** and **Pressure** line labels. It is automatically selected according to the last edited variable. However the user can change this before pressing **Diagram**. The line label format dialog can be opened by pressing **Line Text Font**, see Fig. 8.

The **Edit Copy** and **Paste** selections may be used to edit the Molality and Pressure values. **Table** shows all the calculation results, which are used to draw the final diagram, see Chapter 17.7.

**Diagram** calculates all the selected data sets and shows the combined diagram, see Chapter 17.6. **Exit** returns the control to the Diagram Menu form, Fig. 1.

#### **4. Brief Instructions to create a Combined Eh-pH-diagram**

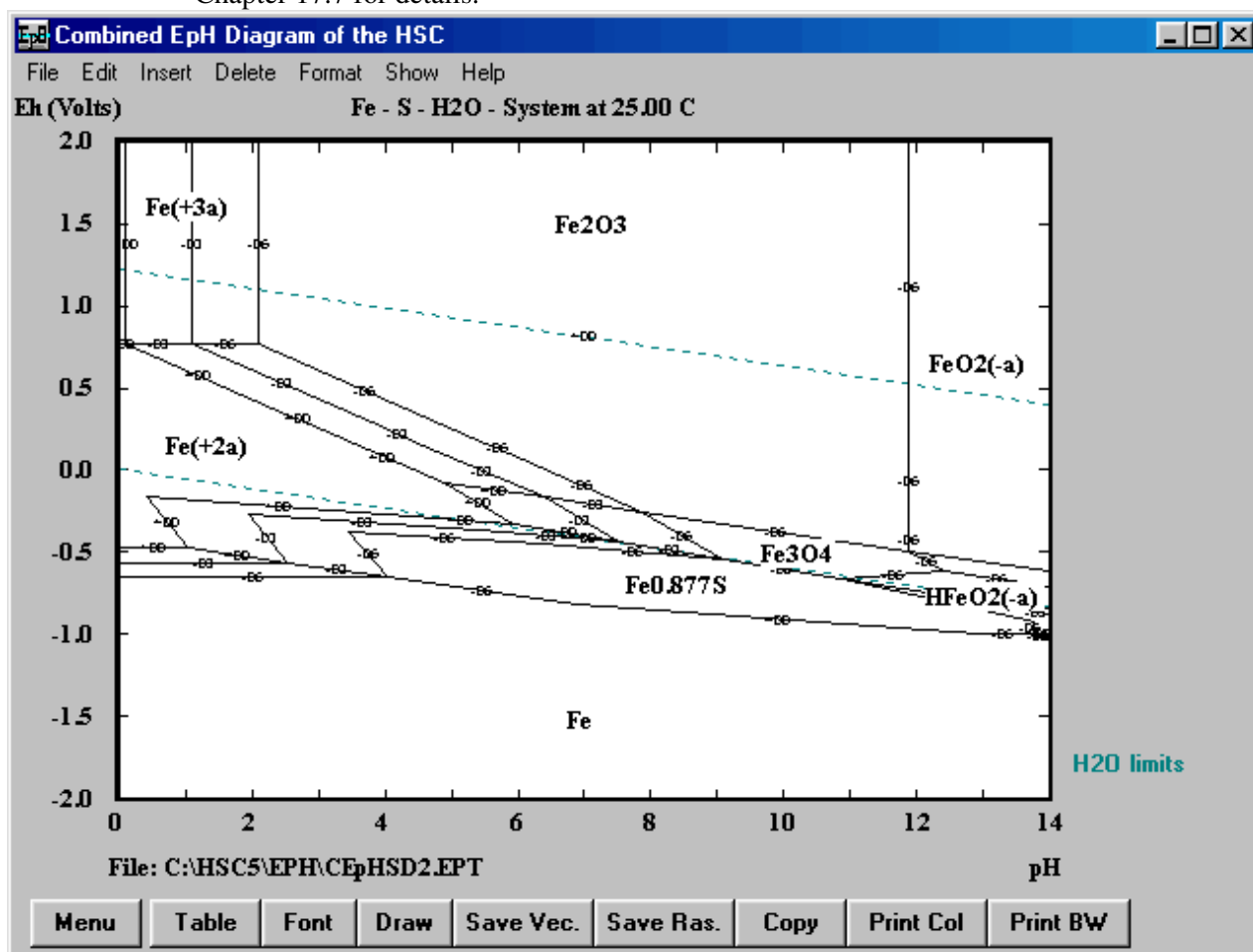
1. Specify chemical system and press **EpH**, see Fig. 7.
2. Accept default settings and press **Combine**, see Fig. 2.
3. Give values for one variable, for example, molality 1.00E+00 for Data Set 1, 1.00E-03 for Data Set 2 and 1.00E-06 for Data Set 3. Press **Diagram** to calculate the combined diagram, see Fig. 8 and Fig. 9.

## **17.6 Combined Eh-pH-Diagrams**

The calculation basis and appearance of the combined diagrams is the same as for the normal Eh-pH-diagrams discussed in previous chapters. The combined diagrams are reduced to normal diagrams if only one data set is selected, see Fig. 8. However, there are some differences which will be discussed in this chapter. The combined diagram of the Fe-S-H<sub>2</sub>O example is shown in Fig. 9.

The main element selection of the combined diagrams is made in the four Data Sets options, Fig. 8. The selected main element can be seen from the heading of the diagram. The first element in the heading "Fe-S-H<sub>2</sub>O-system at 25 °C" is always the main element. **Table** shows all the calculation results, which are used to draw the final diagram, see

Chapter 17.7 for details.



**Fig. 9.** Combined Eh-pH-diagram for an Fe-S-H<sub>2</sub>O-system at 25 °C. The Fe molality values 1, 10<sup>-3</sup>, and 10<sup>-6</sup> have been used as parameter.

Results for Composite EpH diagram											
	Lines	Area No	X1 pH	Y1 V	X2 pH	Y2 V	Width	Style	Color	Data-set	SI
1	Fe - S - H2O - System at		0.00000	-2.00000	14.00000	2.00000	1	0	0		
2	C:\HSC5\EPH\FES25.IEP						0	0	0		
3	pH						0	0	0		
4	Eh (Volts)						0	0	0		
5	X-heading 2						0	0	0		
6	X-axis Grid						0	0	0		
7	Y-axis Grid						0	0	0		
8							0	0	0		
9	O2 Formation		0.00000	1.22880	14.00000	0.40061	0	2	8421376	1	-0.
10	H2 Formation		0.00000	0.00000	14.00000	-0.82819	0	2	8421376	1	-0.
11	Fe	1	1.04340	-0.47426	2.54340	-0.56299	0	0	0	1	-0.
12	Fe	1	0.00000	-0.47426	1.04340	-0.47426	0	0	0	1	0.
13	Fe	1	6.89225	-0.82026	12.94450	-0.99927	0	0	0	1	-0.
14	Fe	1	13.66000	-0.99927	14.00000	-0.99927	0	0	0	1	0.
15	Fe	1	0.00000	-2.00000	0.00000	-0.47426	0	0	0	1	0.
16	Fe	1	14.00000	-0.99927	14.00000	-2.00000	0	0	0	1	0.
17	Fe	1	0.00000	-2.00000	14.00000	-2.00000	0	0	0	1	0.
18	Fe	1	2.54340	-0.56299	4.04340	-0.65173	0	0	0	2	-0.
19	Fe	1	0.00000	-0.56299	2.54340	-0.56299	0	0	0	2	0.
20	Fe	1	0.00000	-2.00000	0.00000	-0.56299	0	0	0	2	0.
21	Fe	1	14.00000	-0.99927	14.00000	-2.00000	0	0	0	2	0.
22	Fe	1	4.04340	-0.65173	6.89225	-0.82026	0	0	0	3	-0.
23	Fe	1	0.00000	-0.65173	4.04340	-0.65173	0	0	0	3	0.
24	Fe	1	13.66000	0.00027	14.00000	1.02044	0	0	0	2	0.

**Fig. 10.** Calculation results used to draw the final diagram. This form can be opened by pressing **Table** on Diagram form, see Fig. 9.

## 17.7 Calculation Results of Combined Diagrams

The EpH module automatically carries out all the calculations needed to draw the diagram. The result workbook may be seen by pressing **Table** in the Diagram form, see Fig. 9. Normally you do not need to worry about these sheets at all. You may utilize this information, for example, to see the exact numerical coordinates of the lines or to identify some very small and complex stability areas, etc. The modification of this worksheet has no effect on the diagram.

The result workbook contains six sheets. The first four sheets (**DS1, DS2, DS3, DS4**) are for the line coordinates based on data sets 1 to 4. These sheets contain the species names, area numbers, line coordinates and line properties.

The **Label** sheet contains the label names and label coordinates as well as the area numbers, which connect the label to the final lines specified in the **Lines** sheet. This sheet gives the calculated coordinates of the lines in the final diagram. These two sheets also show all the format properties used to draw the labels and lines on the diagram. The area number is calculated using the formula

$$DS = \sum_{n=1}^4 2^{(n-1)}, \quad [2]$$

where n is the data set number.

For example,  $6 = 2^{(2-1)} + 2^{(3-1)}$  means that label is combined from data in sets 2 and 3.

You can print the active sheet (or all sheets) by pressing **Print**. **Exit** closes the result workbook and returns you to the previous form.

## 17.8 Eh - 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>12</sup>.

In hydrometallurgy, the Eh-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 the Pourbaix diagrams quite commonly to study the weathering process and chemical sedimentation. The weathering process is used to predict what will happen to a mineral, which is exposed to acid oxidizing conditions at high temperature and pressure. Pourbaix diagrams can also be used to estimate the conditions, which were needed to form certain sediments and other minerals<sup>17</sup> in the geological past.

**Antti Roine, Kai Anttila**

**August 10, 2006**

**09006-ORC-J**

Some application examples of EpH module and Pourbaix diagrams are given in Chapter 18, as well as an example of the EpH file format.