

13. EQUILIBRIUM MODULE

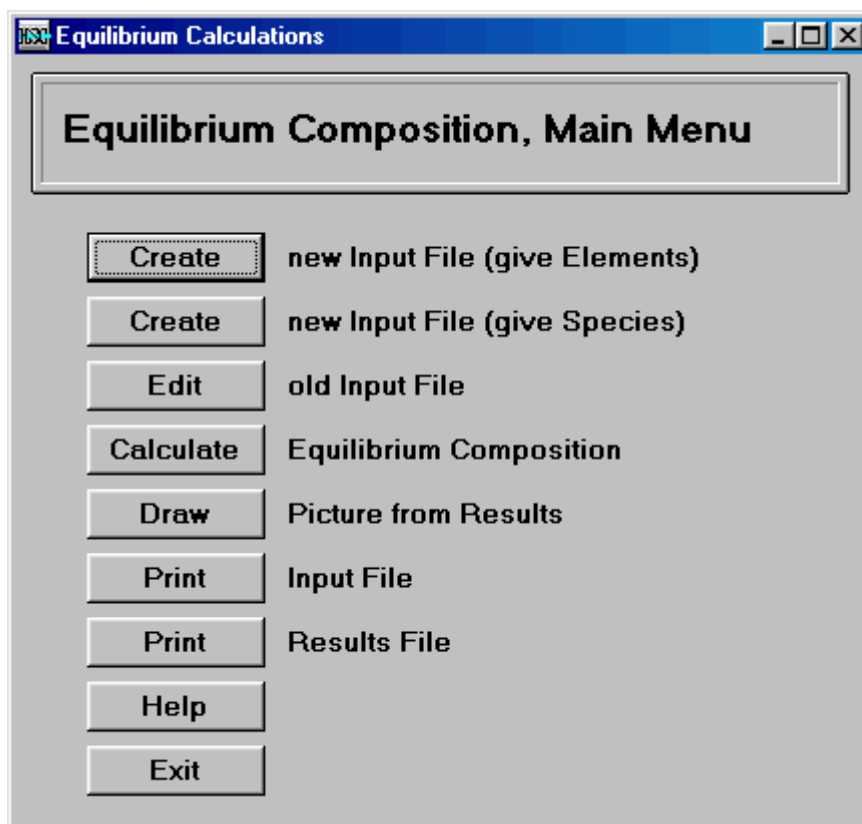


Fig. 1. Equilibrium Module Menu.

This module enables you to calculate multi-component equilibrium compositions in heterogeneous systems easily. The user simply needs to specify the reaction system, with its phases and species, and gives the amounts of the raw materials. The program calculates the amounts of products at equilibrium in isothermal and isobaric conditions.

The user must specify the substances and potentially stable phases to be taken into account in the calculations as well as the amounts and temperatures of raw materials. Note that if a stable substance or phase is missing in the system definition, the results will be incorrect. The specification can easily be made in the HSC program interface, and the input data file must be saved before the final calculations are made.

The equilibrium composition is calculated using the GIBBS or SOLGASMIX solvers, which use the Gibbs energy minimization method. The results are saved in *.OGI or *.OSG text files respectively. The post-processing PIC-program reads the result files and draws pictures of the equilibrium configurations if several equilibria have been calculated. The user can toggle between the equilibrium and graphics programs by pressing the buttons shown in Figs. 1, 4, 6 and 7.

The Equilibrium module reads and writes the following file formats:

1. ***.GEM-File Format**

This file format contains all the data and formatting settings of each definition sheet as well as the phase names, etc. The equilibrium module always saves this

file regardless of which file format is selected for saving the actual input file for equilibrium calculations. If you want to use formatting settings, please use the **Open Normal** selection from **File** menu, see Fig. 4.

2. ***.IGI-file Format**

This file format contains the data for calculations for the GIBBS-solver only and it can read these files.

3. ***.ISG-file Format**

This file format contains the data for calculations with the Solgasmix-solver only and it can read these files.

4. ***.DA2-file Format**

This file format contains the data for calculations for the ChemSAGE 2.0 only. The equilibrium module also reads *.DA2-files, but not if solution model parameters have been added to the file manually. *Note that this equilibrium solver is not included in HSC 5.0.*

5. ***.DAT-file Format**

This file format contains the data for calculations for ChemSAGE 3.0 and 4.0 only. The equilibrium module also reads *.DAT-files, but not if solution model parameters have been added to the file manually. *Note that this equilibrium program is not included in HSC 5.0.*

The equilibrium solvers GIBBS, Solgasmix and ChemSAGE deliver their results in ASCII text-files. The PIC-module reads these files and generates graphics and tables as described in Chapter 13.7.

There are three ways of creating an input file (*.IGI, *.ISG):

1. Press the **top button** in the menu, see Fig. 1. Then specify the elements which are present in your system, see Fig. 2. The HSC-program will search for all the available species in the database and divide them, as default, into gas, condensed and aqueous phases. The user can then edit this preliminary input table.
2. Press the **second button** of the menu if you already know for sure the possible substances and the phases of the system, see Fig. 1.
3. Press **Edit Old Input File** if you already have an input file which can be used as a starting file. Edit the input table and save it using a different name, see Fig. 1.

If you only want to calculate the equilibrium compositions with the existing *.IGI-files press **Calculate**, see Fig. 1. If you want to draw pictures from the existing *.OGI files made by the GIBBS-solver press **Draw**, see Fig. 1. Using **Print** you can get a paper copy of the *.IGI and *.OGI files.

13.1 Starting from defining the Elements

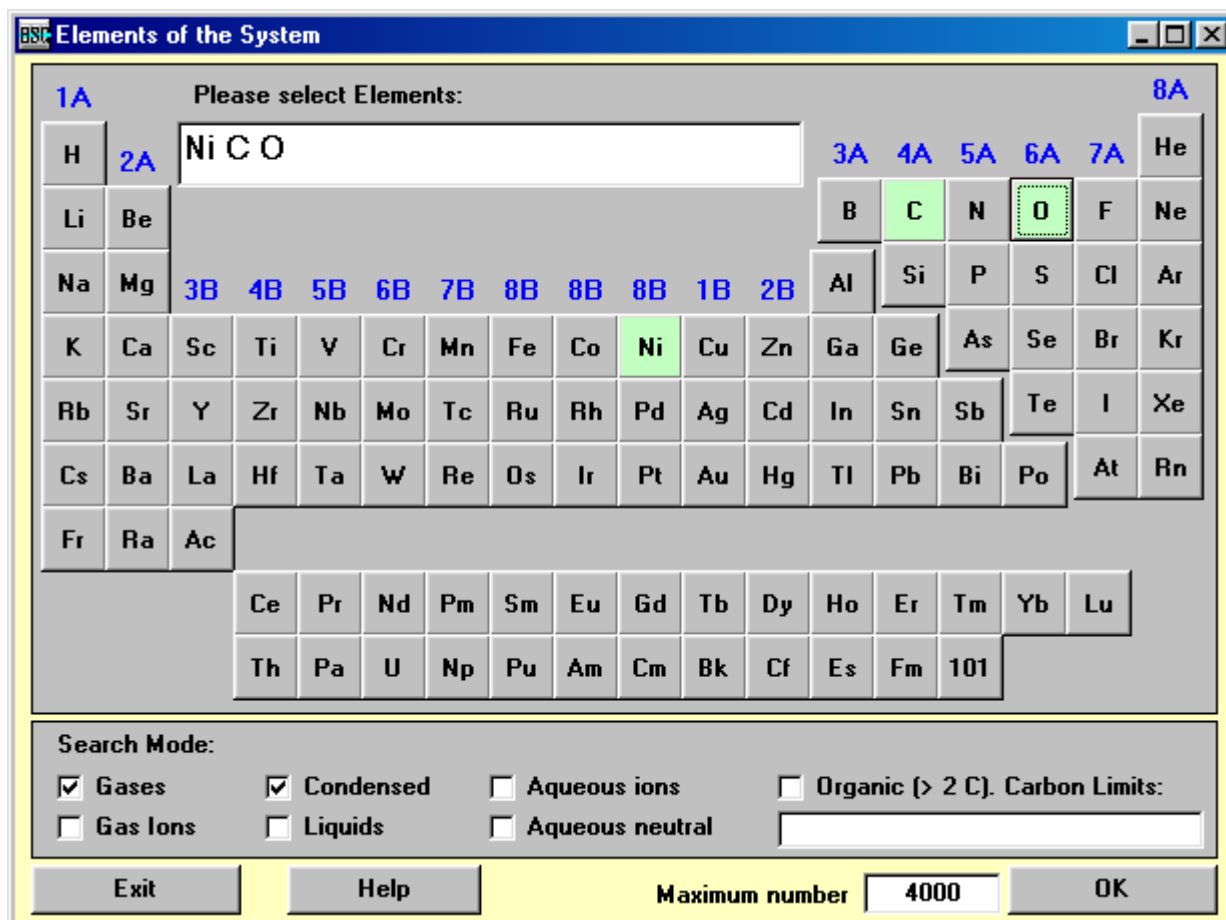


Fig. 2. Specifying the elements of the system.

If you do not know the substances of the system you may also start by specifying its elements, i.e. a selection of the system components. The elements selected will be displayed in the Elements Window, see Fig. 2. After pressing **Elements** in the Equilibrium Menu, see Fig. 1, you can continue with the following steps:

1. Select one or more **elements**: Press buttons or type the elements directly into the box. Try for example Ni, C, O, as given in Fig. 2. Do not select too many elements, to avoid a large number of species. In practice 1 - 5 elements is OK
2. Select the form of species from **Search Mode** in which you are interested. You may specify up to 9 **carbon limits** for the organic species, for example 4, 6, 7.
3. Press **OK** and you will see the species found, see Fig. 3. The HSC-program will search for all species which contain one or more of the elements given, first from the Own database and, if not found there, from the Main database.

By decreasing the number of species you may increase the calculation speed and make the solution easier. Therefore select only those species, which you are sure to be unstable in your system and press **Delete Selected**. Be careful, because if you delete the stable ones the calculated equilibrium results will be incorrect. If you are not sure of some substance then do not delete it.

If you want to use only some of the species in the calculations then select only these and press **Delete Unselected**, which will remove the unnecessary species.

Especially if you have selected C and/or H among the other elements you will get a very large number of species for the calculation and you are advised to decrease the number of species. See Chapter 13.4 for selection criteria for phases and species.

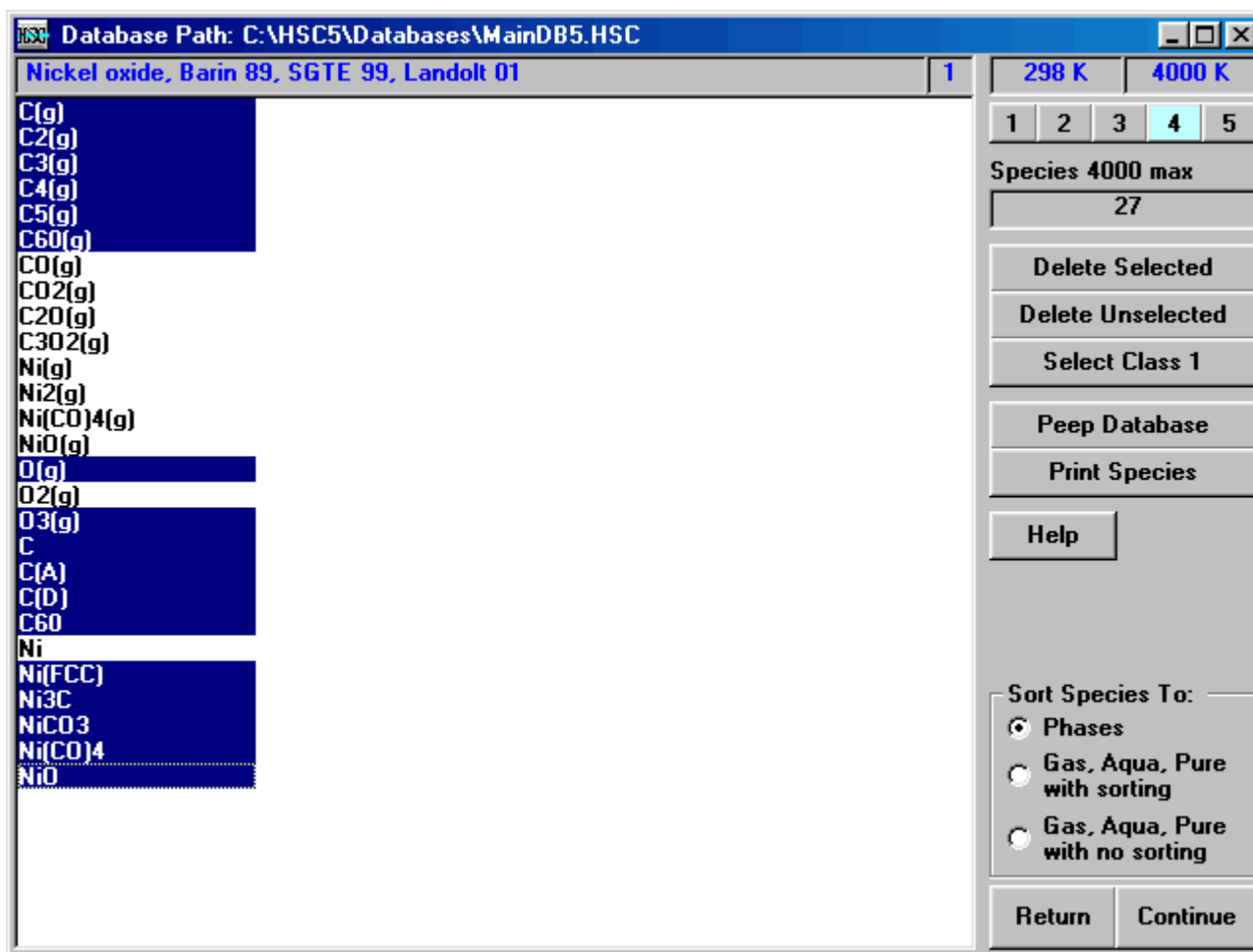


Fig. 3. Deleting undesired species.

If there are some odd species in the list then you can double click that formula in the list or press the Peep Database button and see the whole data set of the species in the database. If you want to remove it press **Remove** in the Database Window. This will remove the species from the list but not from the database.

When making first time calculations it may be a good idea to take a paper copy of the species selected by pressing **Print**. Then you can also easily add or delete species in the following window, see Fig. 4.

The species have been divided into rough reliability classes in the database; you may select the species available in the most reliable class 1 by pressing **Select Class 1**.

You may also set the sorting order for the species using the option buttons above the Continue button. The sorting order will determine the order of species in the Equilibrium Editor, see Fig. 4.

When you have finished deleting the species, press **Continue** and you will return to the Equilibrium Editor window, see Fig. 4.

13.2 Giving Input Data for Equilibrium Calculations

The screenshot shows the 'Equilibrium Calculations' window in HSC Chemistry 7.0. The window title is 'Equilibrium Calculations C:\Hsc5\Gibbs\Nico.igi'. The menu bar includes File, Edit, View, Insert, Delete, Format, Units, Calculate, and Help. The main area contains a table with columns: SPECIES Formula, Temper. C, Amount kmol, Amount %, Step kmol, Step %, and Activity Coeff. The table is divided into two sections: GASES and ELEMENTS. The GASES section includes CO(g), CO2(g), C2O(g), C3O2(g), Ni(g), Ni(CO)4(g), NiO(g), and O2(g). The ELEMENTS section includes Ni. The Amount kmol and Amount % columns are populated with values for the first few rows. The bottom of the window has a toolbar with buttons: Exit, Ins Phase, Del Phase, Ins Row, Del Row, Open, Save, and Gibbs. The file path 'C:\Hsc5\Gibbs\Nico.igi' is displayed next to the Open button.

	SPECIES Formula	Temper. C	Amount kmol	Amount %	Step kmol	Step %	Activity Coeff.
1	GASES		4.000	100.000			
2	CO(g)	25.000	4.000	100.000			1.000
3	CO2(g)	25.000					1.000
4	C2O(g)	25.000					1.000
5	C3O2(g)	25.000					1.000
6	Ni(g)	25.000					1.000
7	Ni(CO)4(g)	25.000					1.000
8	NiO(g)	25.000					1.000
9	O2(g)	25.000					1.000
10	ELEMENTS		1.000	100.000			
11	Ni	25.000	1.000	100.000			1.000
12							
13							
14							
15							
16							
17							

Fig. 4. Specification of the species and phases for the reaction system.

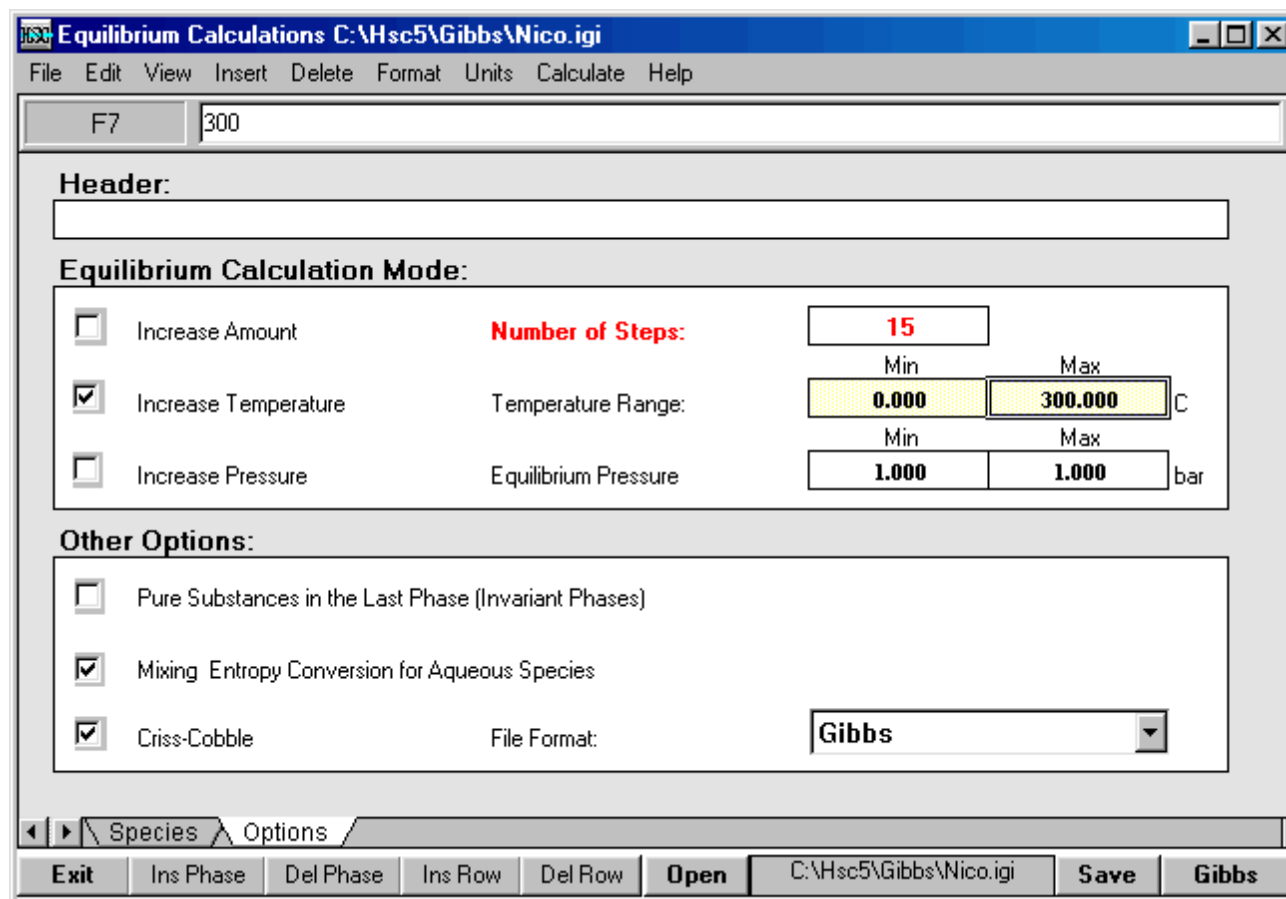


Fig. 5. Specification of the calculation mode.

The Equilibrium Editor consists of two sheets for determining the conditions of the equilibrium calculations. In **Species** and **Options** sheets, Figs. 4 and 5, you give all the data required to create an input file for the equilibrium solvers and for calculating the equilibrium compositions. Equilibrium calculations are made in three steps:

1. The user gives the necessary input data using the Species and Options sheets in the Equilibrium Editor Window, Fig. 4, and saves this data as a text file.
2. The equilibrium compositions will be calculated using the equilibrium solvers, which read the input-files and save the results in corresponding output-files.
3. The results in the output-file can be further processed to graphical form by pressing **Draw** in Fig. 1 or 6 if several successive equilibria have been calculated.

The most demanding step is the selection of the species and phases, ie. the definition of the chemical system. This is done in the Species sheet of the Equilibrium Editor, Fig. 4. You can move around the table using the mouse, or Tab and Arrow keys. The other things which you should consider are:

1. Species (substances, elements, ions...)

You may write the names of the species directly into the Species column, without a preliminary search in the Elements window. If you have made the search on the basis of the elements you already have the species in the Species column.

You can check the names and the data of the species by pressing the right mouse button and selecting **Peep Database** from the popup menu. If you press the Insert button you can collect species for the equilibrium calculations sheet. Pressing **Remove** will remove an active species from the equilibrium calculations.

You can insert an empty row in the table by selecting **Row** from the **Insert** menu or pressing the right mouse button and selecting **Ins Row** from the popup menu.

Rows can be deleted by selecting **Row** from the **Insert** menu or by pressing the right mouse button and then electing **Del Row** from the popup menu.

You can change the order of the substances by inserting an empty row and using the copy - paste method to insert substance in the new row. The drag and drop method can also be used. *However, it is extremely important to move the whole row, because there is a lot of auxiliary data in the hidden columns on the right side of the sheet.*

Please keep the **Copy Mode** selection **on** in the **Edit** menu when rearranging species. This will force the program to select the whole row. When formatting the columns and cells, turn **off** the **Copy Mode** selection in the **Edit** menu.

Use the (l)-suffix for a species only if you want to use the data of liquid phases at temperatures below its melting point. For example, type **SiO2(l)** if SiO₂ is present in a liquid oxide phase at temperatures below the melting point of pure SiO₂. See Chapter 28.2.

2. Phases

The species selected in the previous step must be divided into physically meaningful phases as determined by the phase rows. This finally defines the chemical reaction system for the equilibrium calculation routines. Definition of the phases is necessary because the behavior of a substance in a mixture phase is different from that in pure form. For example, if we have one mole of pure magnesium at 1000 °C, its vapor pressure is 0.45 bar. However, the magnesium vapor pressure is much smaller if the same amount has been dissolved into another metal.

The phase rows must be inserted in the sheet using **Phase** selection in **Insert** menu or using the same selection in the popup menu of the right mouse button. The Equilibrium module makes the following modifications to the sheet *automatically* when you insert a new phase row in the sheet and:

1. Asks a name for the new phase, which you can change later, if necessary.
2. Inserts a new empty row above the selected cell of the sheet with a light blue pattern.
3. Assumes that all rows under the new row will belong to the new phase down to the next phase row.
4. Inserts new Excel type SUM formulae in the new phase row. These formulae calculate the total species amount in the phase using kmol, kg or Nm³ units.

When the insert procedure is ready, you may edit the phase row in the following way:

1. The phase name can be edited directly in the cell.
2. The phase temperature can also be changed directly in the cell and it will change the temperatures of all the species within the phase.
3. Note that you can not type formulae to the amount column of the phase row, because the SUM formulae are located there.
You can change the amount of species in a phase using kmol, kg or Nm³ units, simply by typing the new amount to the corresponding cell. The program will automatically update the total amount and the composition of the phase.

The first phase to be defined is always the gas phase, and all gaseous species must exist under the gas phase row. Species of the same phase must be given consecutively one after another in the table. As default, HSC Chemistry automatically relocates all the gaseous species, condensed oxides, metals, aqueous species, etc. into their own phases if you start from the “give Elements” option, see Fig. 1. The final allocation, however, must be done by the user.

If there is no aqueous phase, all aqueous species must be deleted. Note that if you have an aqueous phase with aqueous ions, you must also have water in the phase !

If you expect pure substances (invariant phases) to exist in the equilibrium configuration, insert them as their own phases by giving them their own phase rows or insert all these species under the last phase row and select the **Pure Substances in the Last Phase** option, see Fig. 5. Formation of pure substances is possible especially in the solid state at low temperatures. For example, carbon C, iron sulfide FeS₂, calcium carbonate CaCO₃, etc. might form their own pure phases.

One of the most common mistakes is to insert a large amount of relatively “inert” substance to the mixture phase. For example, large amounts of solid carbon at 1500 °C do not dissolve into molten iron. However, if these both species are inserted into the same phase then the equilibrium program assumes that iron and carbon form an ideal mixture at 1500 °C. This will, for example, cause much too low vapor pressure for the iron. Therefore carbon should nearly always be inserted into its own phase at low temperatures.

3. Input Temperatures of the Species

Input temperatures for the raw material species are essential only in the equilibrium **heat balance** calculations, i.e. if you provide some input amount for a species you should also give its temperature. The input temperature does not affect the equilibrium composition. You may select the temperature unit by selecting **C** from the Units menu, see Fig. 4.

4. Amount of the Species

In this column you give the input amounts of the raw material species. The most important thing for the equilibrium composition is to give the **correct amounts of elements** to the system. You may divide these amounts between the species as you like. If the **correct heat balance** is required, you must divide the amounts of elements exactly into the same phases and in a similar manner as in the real physical world.

You may choose between kmol or kg/Nm³ units by selecting **mol** or **kg** from the **Units** menu. Note that kilograms refer to condensed substances and standard cubic meters (Nm³) to gaseous substances, see Fig. 4.

5. Amount Step for Raw Materials

If you wish to calculate several successive equilibria you give an incremental step for one or more raw material species. Then the programs automatically calculate several equilibria by increasing the amount of this species by the given step. Please remember to select the **Increase Amount** option, see Fig. 5, and give also the number of steps. The maximum number of steps which can be drawn is 251 for the GIBBS solver and 50 for Solgasmix solver. Some 21 - 51 steps are usually enough to give smooth curves to the equilibrium diagram.

You may give step values for several species simultaneously. For example, if you want to add air to the system give a step value for both O₂(g) and N₂(g). Please do not forget to specify the number of steps, if a diagram is to be drawn from the results.

6. Activity Coefficients (in Gibbs-solver)

The simple definition of Raoultian activity is the ratio between vapor pressure of the substance over the solution and vapor pressure of the pure substance at the same temperature.

$$a = \frac{p(\text{over solution})}{p(\text{pure})} \quad [1]$$

Activity coefficient describes the deviation of a real solution from an ideal mixture. Activity coefficient **f** is defined as the ratio between activity **a** and mole fraction **x** of the species in the mixture.

$$f = \frac{a}{x} \quad [2]$$

In an ideal solution they are therefore defined as $a = x$ and $f = 1$. As a default in GIBBS and SOLGASMIX, the activity coefficient of a species in the mixture phases is always 1. However, if non-ideal activity coefficients are available they may be introduced in the right column. Only simple binary or ternary expressions can be utilized directly by the GIBBS solver within HSC, such as:

$$\begin{aligned} \ln(f) &= 8495/T - 2.653 \\ \ln(f) &= 0.69 + 56.8 \cdot X_{24} + 5.45 \cdot X_{25} \\ \ln(f) &= -3926/T \\ \ln(f) &= -1.21 \cdot X_7^2 - 2.44 \cdot X_8^2 \end{aligned}$$

where:

$$\begin{aligned} T &= \text{Temperature in K} \\ X_{24} &= \text{Mole fraction of the species with a row number 24 in the sheet.} \\ f &= \text{Activity coefficient.} \end{aligned}$$

Formulae are written using the same syntax as in Excel, the defined names T and P are available for temperature and pressure. Mole fractions are given as cell references to

column X. Please note that the returning values of the formulae are insignificant, because the mole fraction values in column X are zero, see Figs. 16 - 17.

7. Heading

You may add any kind of heading for the input file, see Fig. 5. The maximum number of characters allowed in the heading is 80. The PIC post-processing program automatically adds the heading to the diagrams, see Figs. 11 and 17.

8. Equilibrium Temperature

Equilibrium will be calculated at this temperature, and each equilibrium is isothermal and thus has a constant temperature throughout the system, see Fig. 5. You may also give the temperature range if you wish to calculate several sequential equilibria. Please remember to also select the **Increase Temperature** option and give the **Number of Steps**, see Fig. 5. Several equilibria are needed in order to create graphics from the results.

Temperatures in the Species Sheet, Fig. 4, have no effect on the equilibrium compositions. They are only needed if the reaction enthalpy is necessary to calculate correctly, see Chapter 13.7.1, Fig. 10 and Y-Axis selections.

9. Equilibrium Pressure

Equilibrium calculations are always made in constant pressure or in isobaric conditions. Normally a total pressure of 1 bar is used, and it is also given as default in HSC. In autoclave or vacuum furnace applications you may need to change the pressure. You can also increase pressure incrementally by giving a **Pressure Range**, please remember to also define the **Increase Pressure** option for this selection, see Fig. 5

The total pressure P° has effect on gas phase activity values a_i in formula 3. The fugacity F_i of gas species i may be calculated from this value with formula 4.

$$a_i = P^\circ * x_i \quad [3]$$

$$F_i = a_i * 1 \text{ bar} \quad [4]$$

10. Number of Steps

If you have defined increments (steps) for raw material species or specified a temperature or a pressure range then you should also give the **Number of Steps** required, see Fig. 5. The maximum number of steps in Gibbs solver is 251 and for Solgasmix the maximum available is 51. Usually 21 - 51 steps give quite smooth curves in the equilibrium diagram. A large number will only give more points to the picture and a longer calculation time.

If you have given an amount step for a raw material species, the calculations should be made using an increasing species amount. If you have given a temperature or pressure range, then the calculations should be made by increasing the temperature or pressure. No simultaneous increments in composition, temperature and pressure are allowed. Please do not forget to select the correct increase option, see Fig. 5

11. Criss-Cobble and Mixing Entropy of Aqueous Species

HSC will utilize **Criss-Cobble extrapolation** for the heat capacity of aqueous species at elevated temperatures (> 25 C) if the **Criss-Cobble** option is selected, Fig. 5 Refer to the details in Chapter 28.4. Note that:

- A) It is necessary to select the Mixing Entropy option for the GIBBS and SOLGASMIX routines. In this case, the activities of the results will be presented on the Raoultian scale which is based on mole fractions, see Chapter 13.3.
- B) It is not recommended to select the Mixing Entropy option for the ChemSAGE or for the SOLGASMIX if the conventional activity coefficients of aqueous species are to be given in the FACTOR subprogram.

If the Criss-Cobble and Mixing Entropy options are not selected for the GIBBS or SOLGASMIX programs, then the activity coefficients of aqueous species may be set to 55.509/X(H₂O), which will convert the Raoultian activity scale to the aqueous activity scale. This trick will also give the activities of the results on an aqueous scale, where the concentrations units are expressed as moles per liter of H₂O (mol/l).

12. GIBBS, SOLGASMIX and ChemSAGE File Format

With this option you can select the input file formats accepted by the GIBBS, SOLGASMIX³ or ChemSAGE⁴ Gibbs energy minimization routines, Fig. 5

If you save the file in GIBBS format you can carry out the calculations in HSC Chemistry with the GIBBS-solver by pressing **Gibbs**. If you have selected SOLGASMIX format you can carry out the calculations with a modified SOLGASMIX-solver by pressing **SGM**, see Fig. 5 ChemSAGE is a separate software product, which is not included in the HSC Chemistry package.

Note: the activity coefficients and formulae specifications, see Fig. 4 are valid only in the GIBBS-solver. Non-ideal mixtures for SOLGASMIX and ChemSAGE must be defined separately.

13. Pure Substances (“Invariant phases”)

The SOLGASMIX and ChemSAGE solvers require information on the number of pure substances defined in the system. The internal name for pure substances in the programs is the invariant phase, referring to the fixed or invariant composition of a pure substance. All species in the last substance group can be set to be pure substances with the **Pure Substances in the Last Phase** option, see Fig. 5

14. File Save and File Open

You must first save the input data for the calculations, see Figs. 4 and 5. When this is done you may activate the equilibrium program and carry out the calculations. With **File/Open** you can read an old input file for editing. Note that from **File** menu you can easily select file types for **Open** and **Save**. Note also that the *.IGI, *.ISG and *.DAT file types do not save edited phase names and formatting settings. The Equilibrium module always saves automatically a *.GEM file which can be used to return these settings.

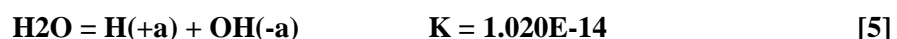
15. Exit

If you want to return to the previous menu press **Exit**. Remember, however, to save your input data first !

13.3 Aqueous Equilibria

Equilibrium calculations of aqueous solutions can be made in a similar manner as presented previously for non-electrolyte solutions. However, some points need special attention (see also Chapter 28.4 for information of aqueous species):

1. Always remember to add water to the aqueous phase. For example, 55.509 mol (= 1 kg) is a good selection if the amount of ions is some 0.01 - 5 moles.
2. Add some charged species (electrons) to the system, for example, by 0.001 mol OH(-a) and the same amount of H(+a). Be sure to maintain the electronic neutrality of the system if you will carry out the calculations with the Gibbs solver.
3. If you are calculating, for example, the dissolution of 1 mole of CaCO₃ into water and you have stoichiometric raw material amounts, please also add a small amount of O₂(g) to the gas phase, for example, 1E-5 moles. If you have stoichiometric NaCl in the system please add a minor amount of Cl₂(g) to the gas phase (1E-5 mol). These tricks help the GIBBS and SOLGASMIX solvers to find the equilibrium composition in cases of fully stoichiometric overall compositions.
4. HSC converts the entropy values of aqueous components from the *molality scale* to *mole fraction* scale if the **Mixing Entropy** option is selected, Fig. 33. Therefore, the entropy values in the input files are not the same as in the HSC database. Identical results will be achieved if the Raoultian activity coefficients of the aqueous species are changed to 55.509/X(H₂O) which converts the Raoultian activity scale to the aqueous activity scale.
5. For some aqueous species only G values are available at 25 °C. These can be saved in the database as H values if S = 0. Note, however, that these can only be used in the calculations at 25 °C.
6. You may check the equilibrium results by doing simple element balance checks or comparing the equilibrium constants. For example, you can calculate the equilibrium constant for reaction 18 using the Reaction Equations option at 25 C, see Fig. 12:



You may also calculate the same equilibrium constant from the equilibrium results of the GIBBS program using equation 10 in Chapter 8. *Introduction*. You can read the necessary molal concentrations, for example, from the equilibrium results \HSC3\CaCO₃.OGI file, see Table 1. This calculation should give nearly the same results as the Reaction Equation option.

$$K = \frac{[\text{H}(+a)] * [\text{OH}(-a)]}{[\text{H}_2\text{O}]} = \frac{4.735\text{E-}13 * 2.159\text{E-}2}{55.468/55.509} = 1.023\text{E-}14 \quad [6]$$

PHASE 1:	mol	mol	COEFFICI	ACTIVITY	ACTIVITY
N2(g)	1.0000E+00	1.0000E+000	9.683E-01	1.00E+00	9.683E-01
H2O(g)	0.0000E+00	3.2678E-002	3.164E-02	1.00E+00	3.164E-02
O2(g)	1.0000E-05	1.0000E-005	9.683E-06	1.00E+00	9.683E-06
CO2(g)	1.0000E-03	1.5986E-013	1.548E-13	1.00E+00	1.548E-13

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Total :	1.0010E+00	1.0327E+000	1.000E+00		
PHASE 2 :					
	MOLE FRACT				
H2O	5.5500E+01	<u>5.5468E+001</u>	9.994E-01	1.00E+00	9.994E-01
CO3(-2a)	0.0000E+00	4.7507E-007	8.560E-09	1.00E+00	8.560E-09
C2O4(-2a)	0.0000E+00	8.0560E-061	0.000E+00	1.00E+00	0.000E+00
Ca(+2a)	1.0000E+00	1.0797E-002	1.945E-04	1.00E+00	1.945E-04
CaOH(+a)	0.0000E+00	1.4656E-010	2.641E-12	1.00E+00	2.641E-12
H(+a)	0.0000E+00	<u>4.7348E-013</u>	8.531E-15	1.00E+00	8.531E-15
HCO2(-a)	0.0000E+00	8.1514E-048	0.000E+00	1.00E+00	0.000E+00
HCO3(-a)	0.0000E+00	4.9071E-009	8.842E-11	1.00E+00	8.842E-11
HO2(-a)	0.0000E+00	1.1549E-020	2.081E-22	1.00E+00	2.081E-22
OH(-a)	2.0000E+00	<u>2.1593E-002</u>	3.890E-04	1.00E+00	3.890E-04
Total :	5.8500E+01	5.5501E+001	1.000E+00		

Table 1. A part of the equilibrium result file \HSC5\GIBBS\CaCO3.OGI.

13.4 General Considerations

Although equilibrium calculations are easy to carry out with HSC Chemistry, previous experience and knowledge of the fundamental principles of thermodynamics is also needed. Otherwise, the probability of making serious errors in basic assumptions is high.

There are several aspects, which should be taken into account, because these may have considerable effects on the results and can also save a great deal of work. For example:

1. Before any calculations are made, the system components (elements in HSC Chemistry) and substances must be carefully defined in order to build up all the species and substances as well as mixture phases which may be stable in the system. Phase diagrams and solubility data as well as other experimental observations are often useful when evaluating possible stable substances and phases.
2. Defining all the phases for the calculation, which may stabilize in the system, is as important as the selection of system components. You may also select a large number of potential phases just to be sure of the equilibrium configuration, but it increases the calculation time and may also cause problems in finding the equilibrium.
3. The definition of mixtures is necessary because the behavior of a substance (species) in a mixture phase is different from that in the pure form. The microstructure or activity data available often determines the selection of species for each mixture. Many alternatives are available even for a single system, depending on the solution model used for correlating the thermochemical data.

Note: the same species may exist in several phases simultaneously; their chemical characters in such a case are essentially controlled by the mixture and not by the individual species.

4. If you expect a substance to exist in the pure form or precipitate from a mixture as a pure substance, define such a species in the system also as a pure (*invariant*) phase. This is often a valid approximation although pure substances often contain some impurities in real processes. All species in the last phase can be set to be pure substances using the **Pure Substances in the Last Phase** option, see Fig. 5
5. The raw materials must be given in their actual state (s, l, g, a) and temperature if the correct enthalpy and entropy values for equilibrium heat balance calculations are required. These do not affect the equilibrium compositions.
6. Gibbs energy minimization routines do not always find the equilibrium configuration. You may check the results by a known equilibrium coefficient or mass balance tests. SOLGASMIX provides a note on error in such cases. It is evident that results are in error if you get random scatter in the curves of the diagram, see Figs. 11, 17 and 19. You can then try to change species and their amounts as described in Chapter 13.2 (2. Phases, 4. Amount of Species).
7. Sometimes when calculating equilibria in completely **condensed systems** it is also necessary to add small amounts of an inert gas as the gas phase, for example, Ar(g) or N₂(g). This makes calculations easier for the equilibrium programs.
8. It may also be necessary to avoid **stoichiometric raw material atom ratios** by inserting an additional substance, which does not interfere with the existing equilibrium. For example, if you have given 1 mol Na and 1 mol Cl as the raw

materials and you have NaCl as the pure substance, all raw materials may fit into NaCl due its high stability. The routines meet difficulties in calculations, because the amounts of all the other phases and species, except the stoichiometric one, go to zero. You can avoid this situation by giving an additional 1E-5 mol Cl₂(g) to the gas phase, see Fig. 46.

9. Quite often the most simple examples are the most difficult ones for the Gibbs energy minimization routines due to matrix operations. However, the new GIBBS 4.0 version usually finds the solution for the simple systems too, such as the two phase H₂O(g) - H₂O -system between 0 - 200 °C.
10. Sometimes a substance is very stable thermodynamically, but its amount in experiments remains quite low, obviously due to kinetic reasons. You may try to eliminate such a substance in the calculations in order to **simulate the kinetic (rate) phenomena**, which have been proven experimentally.
11. It is also important to note that different basic thermochemical data may cause differences to the calculation results. For example, use of HSC MainDB4.HSC or MainDB5.HSC database files may lead to different results.

The definition of phases and their species is the crucial step in the equilibrium calculations and it must be done carefully by the user. The program is able to remove unstable phases and substances, but it can not invent those stable phases or species which have not been specified by the user. The definition of phases is often a problem, especially if working with an unknown system.

Usually it is wise, as a first approximation, to insert all gas, liquid and aqueous species in their own mixture phases, as well as such substances which do not dissolve into them, for example, carbon, metals, sulfides, oxides, etc. in their own invariant phases (one species per phase), according to basic chemistry. If working with a known system it is, of course, clear to select the same phase combinations and structural units for the system as found experimentally. These kinds of simplifications make the calculations much easier and faster.

The user should give some amount for all the components (elements) which exist in the system for Gibbs solver. However, Solgasmix solver is also able to reduce the number of components (elements) automatically if a component is absent in the raw materials.

It is also important to understand that due to simplifications (ideal solutions, pure phases, etc.) the calculations do not always give the same amounts of species and substances as found experimentally. However, the trends and tendencies of the calculations are usually correct. In many cases, when developing chemical processes, a very precise description of the system is not necessary and the problems are often much simpler than, for example, calculation of phase diagrams.

For example, the user might only want to know at which temperature Na₂SO₄ can be reduced by coal to Na₂S, or how much oxygen is needed to sulfatize zinc sulfide, etc.:

The Na₂SO₄.IGI example in the \HSC5\GIBBS directory shows the effect of temperature on Na₂SO₄ reduction with coal; the same example can be seen also in the HSC color brochure, page 3. The calculated compositions are not exactly the same as found experimentally, but from these results we can easily see that at least 900 C will be needed to reduce the Na₂SO₄ to Na₂S, which has also been verified experimentally.

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The real Na-S-O-C-system is quite complicated. In order to describe this system precisely from 0 to 1000 C, solution models for each mixture phase would be needed to describe the activities of the species. Kinetic models would also be necessary at least for low temperatures. To find the correct parameters from the literature for all these models might take several months. However, with HSC Chemistry the user can get preliminary results in just minutes. This information is often enough to design laboratory and industrial scale experiments.

13.5 Limitations

The present version of the GIBBS program has no limitations as to numbers of substances and phases because it uses dynamic arrays. However in practice, 3 - 250 species and 1 - 5 phases are suitable numbers to carry out the calculations within a reasonable time.

Although the maximum number of rows in the spreadsheet editor used in Fig. 4 is 16384, the practical maximum number of species is much smaller. The maximum number of equilibrium points, which can be drawn on the Equilibrium diagram, is 251. However, a much smaller number of equilibrium points usually give smooth curves to the diagram.

The modified SOLGASMIX provided in the HSC package has the following limitations:

- | | |
|--|-----|
| - maximum number of components | 20 |
| - maximum number of mixtures | 31 |
| - maximum number of pure substances (“invariant phases”) | 30 |
| - maximum number of species in the mixture phases | 150 |
| - maximum number of Cp ranges in input files | 7 |
| - SGM neglect phase transitions < 298.15 K | |

The most important limitation of the old GIBBS 2.0 was that, in some cases, only one pure substance was allowed. Otherwise the program provided unpredictable results. If pure substances (invariant phases) do not, however, contain the same elements, several of them are usually accepted. You can avoid this limitation by putting a minor amount of dissolving species into such a pure substance and defining it as a solution phase. In any case, the new GIBBS 5.0 is much more reliable in these situations.

At least a tiny amount for all elements defined in the system must be given as input if you use the GIBBS routine. For example, if you have any Fe-containing species in the system, you must also give some Fe to the raw materials.

SOLGASMIX can handle systems with several pure substances usually without difficulty. It also can calculate equilibria in systems smaller than originally defined in HSC. The SOLGASMIX routine can therefore treat systems with less components than defined in its input file and thus a certain system component may be absent in the raw materials.

The SOLGASMIX provided with the HSC package is a modified version of the original code from the University of Umeå, Sweden. The modification allows the use of grams as input and in this case the result is given both in molar fractions and moles as well as in weight percentages and grams. The input file has therefore additional rows for each system components (elements). The locations and contents of these rows can be found in the input file listing in Chapter 14. *Equilibrium samples*.

If you have an aqueous phase with ionic species you should also be sure to maintain electric neutrality in the system, because the GIBBS solver treats electrons in the same way as elements. SOLGASMIX can usually handle a small deviation from the electron neutrality.

13.6 Calculation Routines

13.6.1 GIBBS Equilibrium Solver

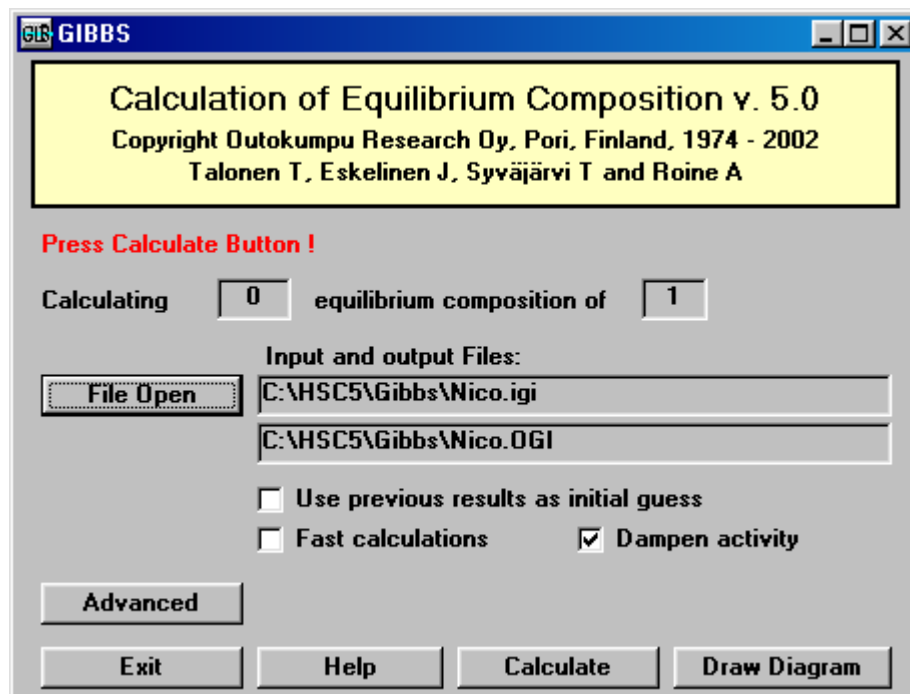


Fig. 6. GIBBS equilibrium solver.

Equilibrium calculations in the GIBBS routine are made using the Gibbs energy minimization method. The GIBBS program finds the most stable phase combination and seeks the phase compositions where the Gibbs energy of the system reaches its minimum at a fixed mass balance (a constraint minimization problem), constant pressure and temperature. This method has been described in detail elsewhere⁵.

Operation Instructions:

1. Select *.IGI file for calculations by pressing **File Open**, if the file is not already selected.
2. **Use previous results as the initial guess** option will slightly speed up calculations, but it is recommended to disable this option, because sometimes GIBBS does not give valid results with this option. The default setting is **off**.
3. **Fast calculations** option will speed up the calculations - the default value is **on**.
4. Press **Calculate** and wait for the All Calculated message.
5. Press **Draw Diagram** if you want the results in graphical form.
6. Press **Exit** to return to HSC.

Advanced options belong to properties not supported yet, these may be available in the next HSC version as tested and supported form.

13.6.2 SOLGASMIX Equilibrium Solver

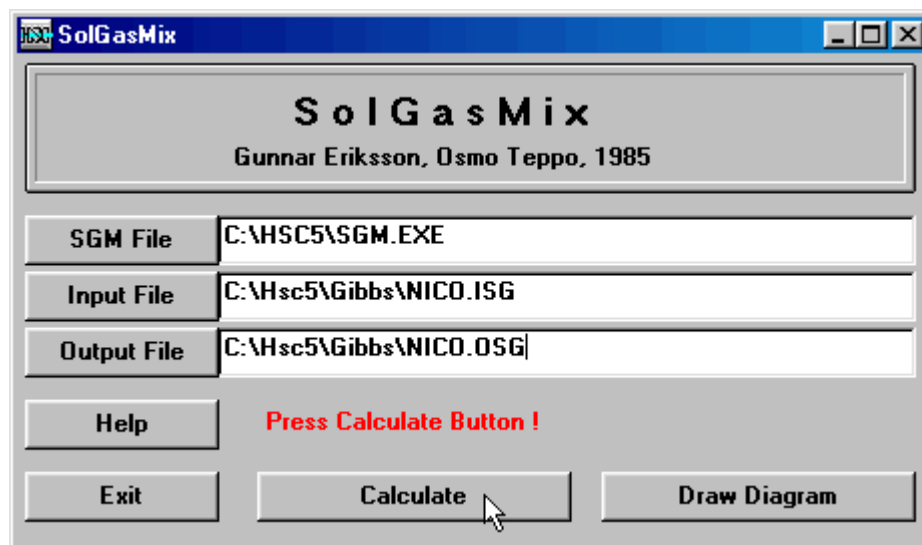


Fig. 7. Message box of the SOLGASMIX program.

The SOLGASMIX equilibrium routine has been integrated in the HSC Chemistry package in a different way to the GIBBS routine, because it is not a Windows-based program. No own icon is provided, but the program has been connected with the HSC interface through a direct data link using files.

The SOLGASMIX routine uses a similar Gibbs energy minimization calculation method as the GIBBS program. All its mixture phases can be defined as non-ideal mixtures in the FACTOR subroutine, but this option is not supported by HSC interface. For further reference, the original input guide and the thesis of Gunnar Eriksson should be consulted⁶.

The original SOLGASMIX code has been modified to accept grams instead of moles as input amounts. The equilibrium composition in the gram mode is given both as a conventional table with moles and mole fractions and also as grams and weight percentages. The alterations in the input files due to this modification can be found in Chapter 14. *Equilibrium samples*.

SOLGASMIX can also be activated in the HSC directory as an independent, stand-alone equilibrium solver. In this case, its input file name created in HSC must be defined as INPUT. The equilibrium calculations results will be stored with the file name RESULT. Equilibria calculated as a function of temperature, pressure or other process variables can be later post-processed to graphics using the PIC-module by HSC Chemistry.

You may run SOLGASMIX by pressing **SGM** when **SGM format** has been selected, see Fig. 5, or by selecting **Solgasmix** in the Calculate menu. Wait for the calculations until **Draw Diagram** is activated, see Fig. 7. After calculations you can draw a diagram from the results by pressing **Draw Diagram** or return to Equilibrium Window by pressing **Exit**.

13.7 Drawing Equilibrium Diagrams

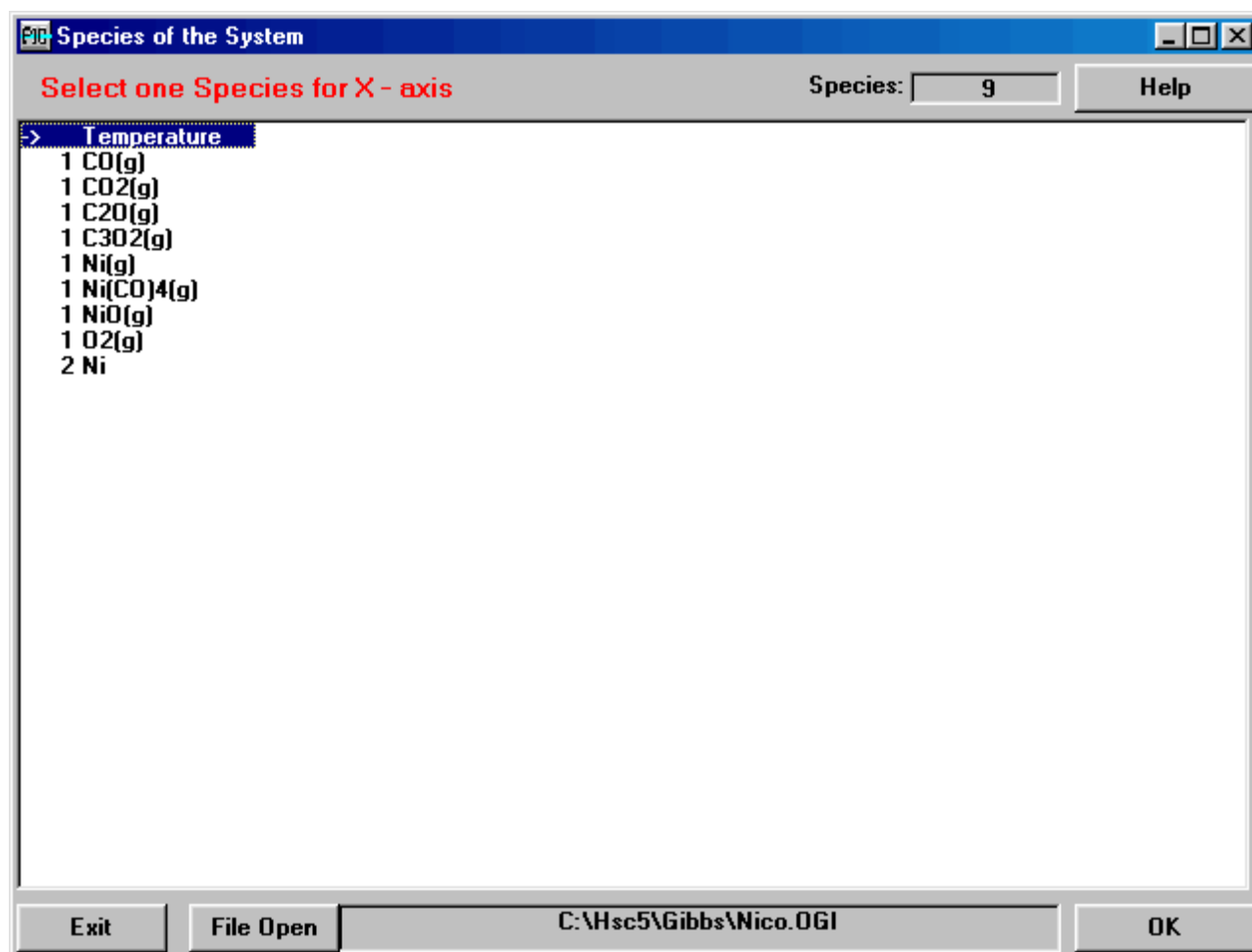


Fig. 8. Selecting the x-axis for an Equilibrium Diagram.

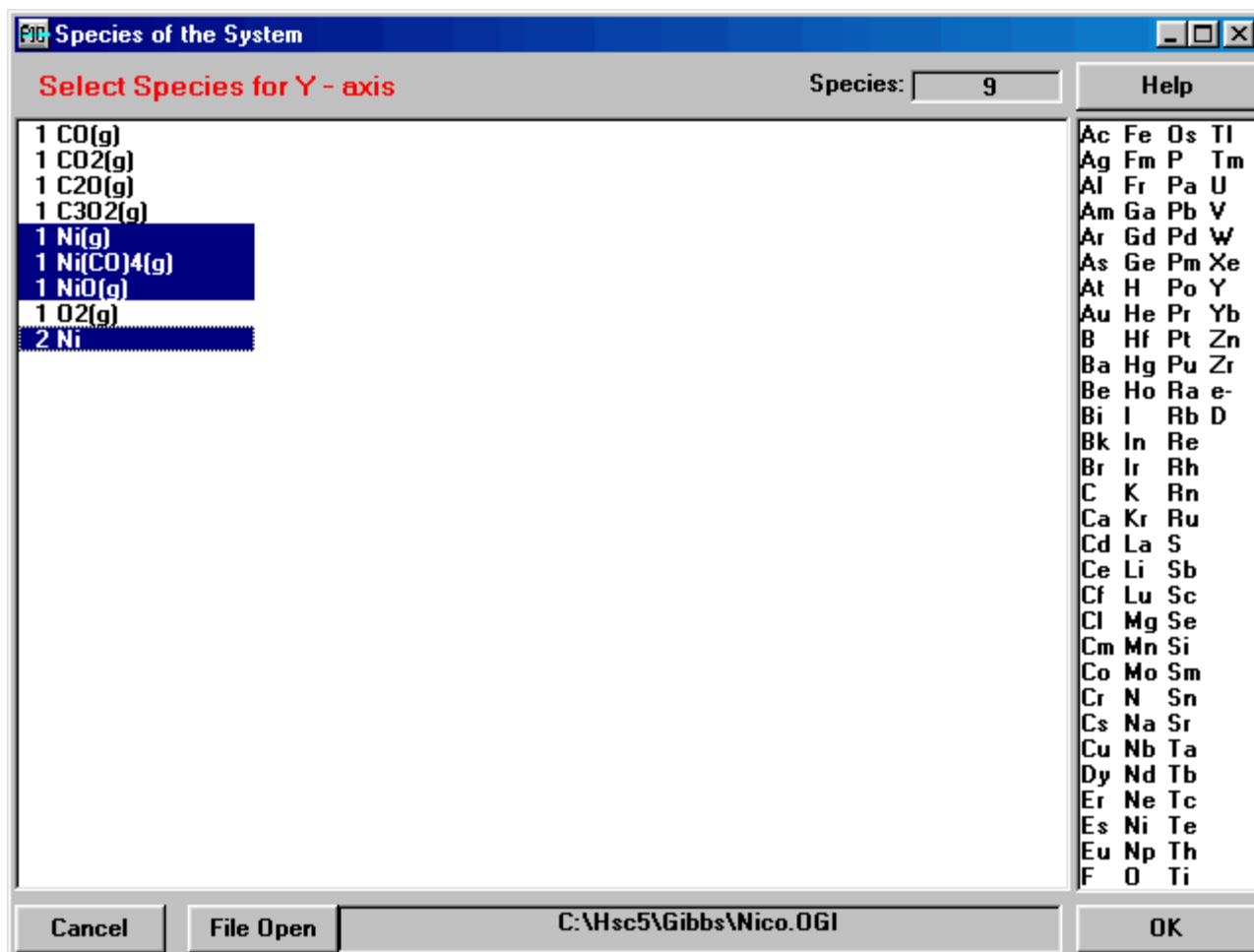


Fig. 9. Selecting the x-axis for an Equilibrium Diagram.

The PIC post-processor draws diagrams on the basis of the output files of the GIBBS program (*.OGI-files), as well as from the SOLGASMIX (*.OSG) and ChemSAGE (*.RES) result files. These diagrams can be drawn, for example, as a function of a specified reactant amount or equilibrium temperature. Start the PIC program by pressing **Draw** in Fig. 6 or 7 and follow these instructions:

1. Select the *.OGI file for diagram by pressing **File Open** if not yet selected, see Fig. 8. This file contains the results of the equilibrium program.
2. Select the species or temperature for the **x-axis** by clicking the desired item in the list box using the mouse. The program shows the recommended selection with an arrow, which is the variable used in the calculations, see Fig. 8.
3. Press **OK**.
4. Select the species for the **y-axis** by keeping **Ctrl Key** down and clicking with the mouse. Sometimes it is convenient to select only those species, which contain the same element, for example Ni, for one diagram. This can easily be done using the element list, see Fig. 9. In standard cases you can get more illustrative diagrams by drawing all gaseous species on one diagram and all other species on another.

The number of selected species is not limited. All species included in the calculation can be selected to the diagram.
5. Press **OK**.
6. Note: You can return to HSC by pressing **Cancel** or **Exit**.

13.7.1 Selecting Data Type for the X- and Y-axis

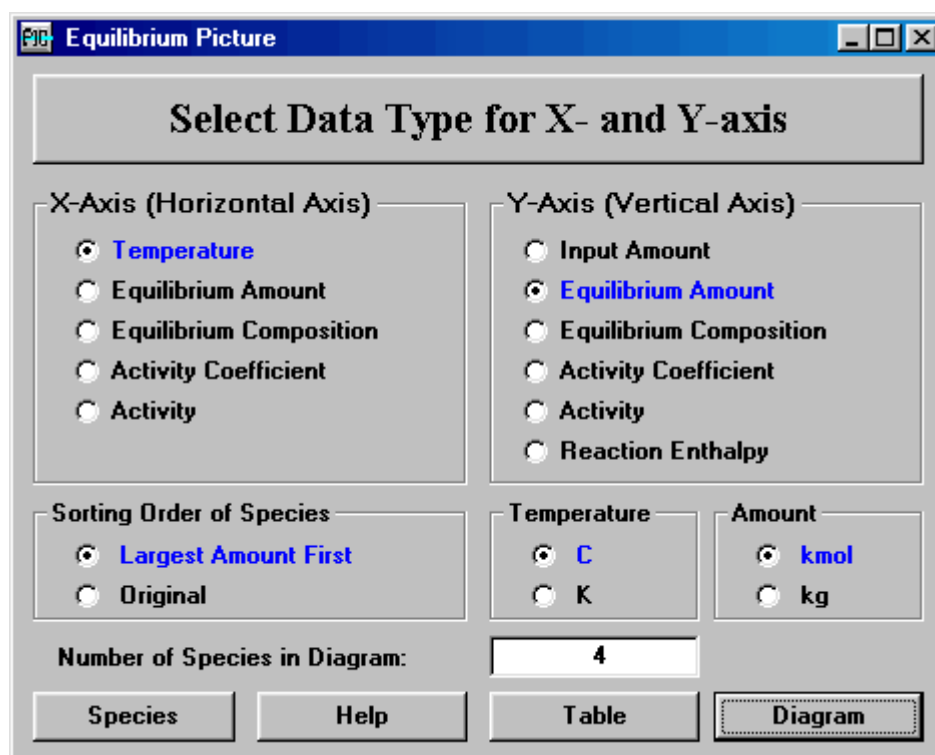


Fig. 10. Selecting data type for the x- and y-axis.

In this menu you can select the data type for the diagram. Usually you may accept the default selections by pressing **Diagram**, but the output may be modified. For example, you can draw the composition of a gas phase by clicking **Equilibrium Compositions** option for the y-axis instead of **Equilibrium Amount**. All the species in one phase must be selected if composition of this phase will be drawn to the diagram.

If you are working with an aqueous system you will get a pH option for the X - Axis. This option will draw the results as a function of pH.

By pressing **Species** you will return to the previous window, see Fig. 9.

If you only want the results in tabular format, press **Table**.

You can also sort the species in descending order, or leave them in the original order using **Sorting Order of Species** option. This selection will determine the order of species in the results table.

Temperature and amount units may be selected using the **Temperature** and **Amount** options.

The number of species is not limited, and all the species included in the equilibrium calculations can be selected to the diagram.

13.7.2 Result Graphics (Equilibrium Diagram)

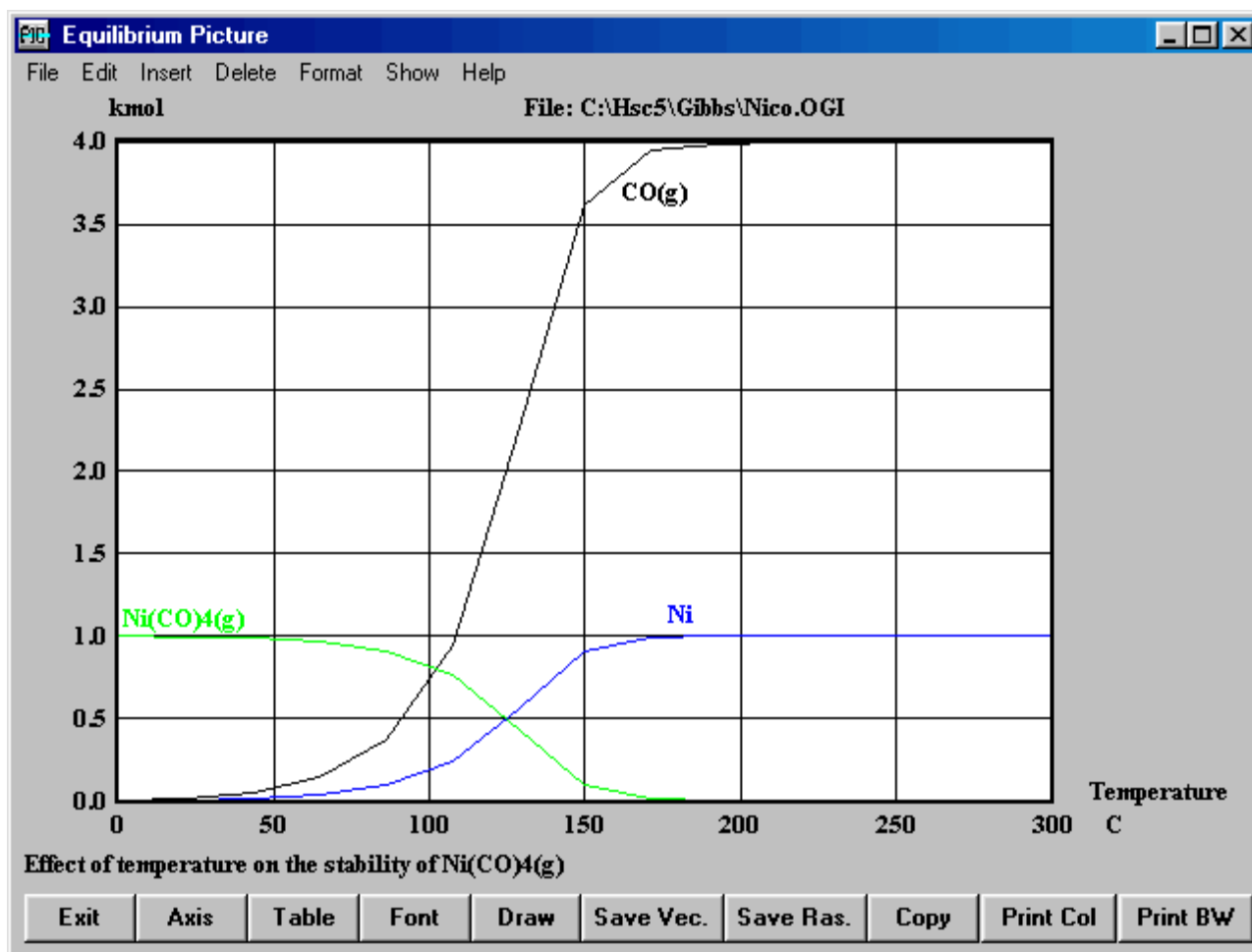


Fig. 11. Equilibrium Diagram.

When you press **Diagram** in the Axis menu, Fig. 10, then the PIC post-processor module reads the equilibrium results from the file and draws the diagram using default scale, font, line width, etc. selections, see Fig. 11. Note that the program inserts the species labels automatically above the maximum point of the curve using the same color for the curve and label. If the line is not within the selected x- and y-range or it is on the border then the program will not draw the line or the label.

You can edit the diagram, Fig. 11, by using several formatting options:

1. Double click the x- or y-scale numbers or select **X-Axis** or **Y-Axis** from the **Format** menu to change, for example, the minimum and maximum values of the X- and Y-axis, see Fig. 12. In some cases it is also advantageous to change the y-axis to logarithmic scale in order to display the large variations in amounts or concentrations.
From the same window you can change the number format of x- and y-axis numbers as well as their font size, color, etc.
2. When the scales are OK, you can relocate any **label** (species, x- and y-axis heading, etc.) by mouse using the drag and drop method. First select the label, keep

the left mouse button down and drag the label to a new location, release the mouse button and the label will drop.

- The **line width** of curves, species label font, etc. may be changed by double clicking the species labels or selecting the label with mouse and selecting **Format Label** from the menu. You cannot do this by double clicking the line. The label and curve editing window is shown in Fig. 13. Note that other line styles than solid are available only for line widths smaller than 0.3 mm.

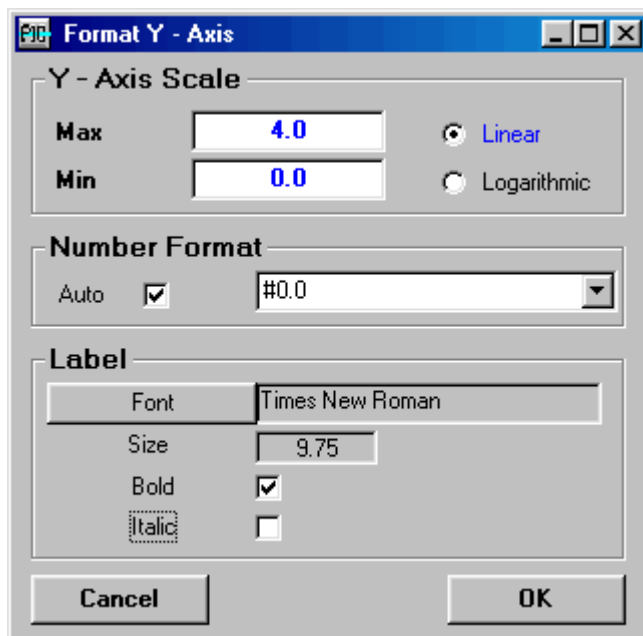


Fig. 12. Changing scales, scale number format and font settings.

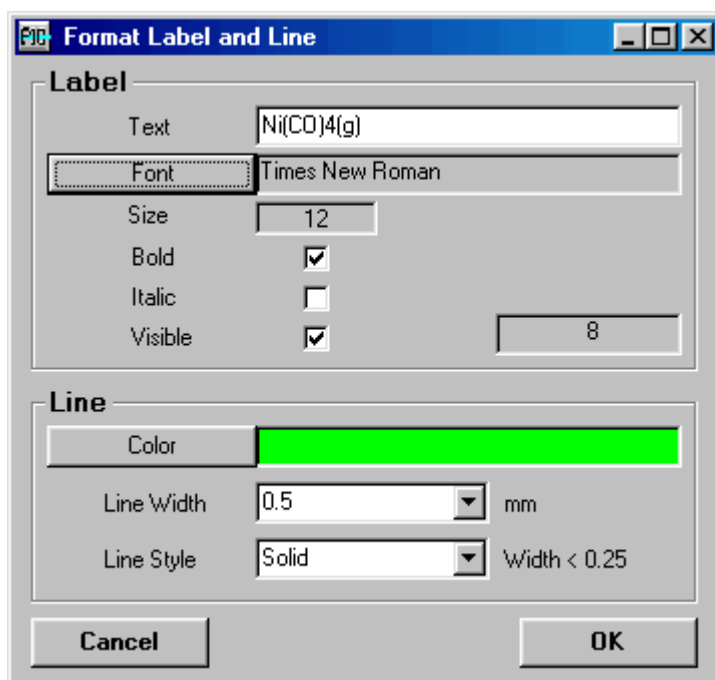


Fig. 13. Changing label and line specifications.

4. You can edit any label and heading on the screen by simply clicking the text in the label by mouse and starting to edit. For example you can change the label “Ni” to a non-abbreviated form “Nickel”.
5. You can create new labels by selecting **Label** from the **Insert** menu. These new labels can be deleted using the Label selection in the Delete menu. Default labels cannot be deleted, and the only possibility is to remove all text from them.
6. The first time you use HSC Chemistry it may be necessary to change the default fonts by selecting the **Default Font** from the **Format** menu, because the available fonts vary from one computer to another. Usually Times New Roman, bold, size 11 font is a good selection. The selection will be automatically saved in the HSC.INI-file in your Windows directory.
7. When you are satisfied with the diagram you can print it by pressing **Print B&W**. If you have a color printer press **Print Col**. The print dialog gives several useful options for a hard copy, see Fig. 14.

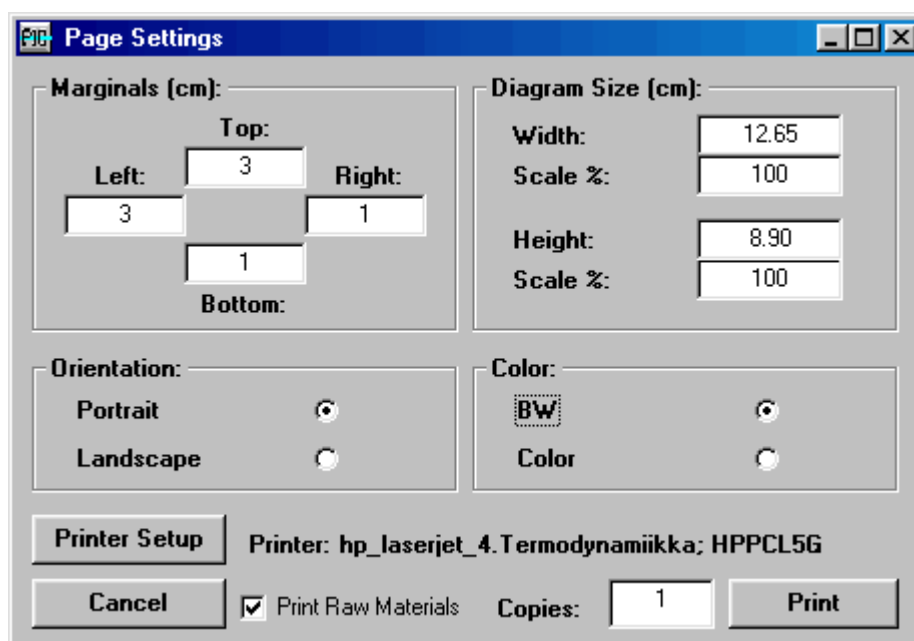


Fig. 14. HSC print dialog for graphics.

8. If you want to see the diagram in a tabular format or use the data of the diagram in other programs, such as MS Excel, press **Table**.
9. You can copy the diagram to the Clipboard by pressing **Copy**, and paste the diagram to other Windows programs. The **Copy** command uses the Windows Metafile format, which enables you to resize the diagram in other Windows applications in full resolution.
10. With **Save** you can save the diagram into a file using the Windows Metafile format.
11. Press **Axis** to return to the previous Axis menu, Fig 10.
12. Press **Exit** to return the Species window, Fig. 8, or to exit the PIC program.

13.7.3 Equilibrium Diagram Table

The screenshot shows a window titled "Equilibrium Results" with a menu bar (File, Edit, View, Insert, Delete, Format, Help) and a toolbar (Axis, Print, Copy All, Diagram). The main area is a table with columns A through H. Row 2 shows the file path "C:\Hsc5\Gibbs\Nico.OGI". Row 3 is a header for "Data:" with sub-headers "Phase", "Units", "MW g/mol", "Min", and "Max". Row 4 shows "0", "C", "0.000", "0.000", and "4.000". Row 5 is a header for "Temperature" with values "0", "C", "0.000", "0.000", "300.000", "0.00E-01", and "2.14". Rows 6-14 list species like CO(g), Ni, Ni(CO)4(g), CO2(g), C3O2(g), C2O(g), Ni(g), NiO(g), and O2(g) with their respective phase, units, molecular weight, and equilibrium values.

	A	B	C	D	E	F	G	H
1								
2	C:\Hsc5\Gibbs\Nico.OGI						Data:	
3		Phase	Units	MW g/mol	Min	Max		
4					0.000	4.000	1	2
5	Temperature	0	C	0.000	0.000	300.000	0.00E-01	2.14
6	CO(g)	1	kmol	28.010	0.005	4.000	4.66E-03	1.70
7	Ni	2	kmol	58.700	0.001	1.000	1.17E-03	4.25
8	Ni(CO)4(g)	1	kmol	170.742	0.000	0.999	9.99E-01	9.96
9	CO2(g)	1	kmol	44.010	0.000	0.000	6.24E-09	4.02
10	C3O2(g)	1	kmol	68.032	0.000	0.000	6.24E-09	4.02
11	C2O(g)	1	kmol	40.021	0.000	0.000	1.00E-36	1.00
12	Ni(g)	1	kmol	58.700	0.000	0.000	1.00E-36	1.00
13	NiO(g)	1	kmol	74.699	0.000	0.000	1.00E-36	1.00
14	O2(g)	1	kmol	31.999	0.000	0.000	1.00E-36	1.00
15								

Fig. 15. Equilibrium Diagram Table.

You can display the equilibrium results in a tabular format by pressing **Table** the Axis menu, Fig. 10, or in the Diagram window, Fig. 11. The Table window has several Excel type features in a similar way to the other spreadsheets in HSC. The most important features are:

1. With **Copy All** you can get the whole table into the Clipboard, and paste this table, for example, to MS Excel. You can also copy and paste smaller cell ranges using the **Copy** and **Paste** selections in the **Edit** menu, see Fig. 15.
2. You can also save the table using different formats, such as ASCII text and Excel by selecting **Save** from the **File** menu.
3. The Table window has two sheets. The **Species** sheet contains the data of the diagram; the figures in this sheet can be edited, if you are not satisfied with the results. The **Format** sheet contains the format specifications of the diagram. It is not recommended to edit the Format sheet.

There are several formatting options in the Format menu, which can be used to create representative tables for printing. The table can be printed using the **Print** selection in the **File** menu, Fig. 15. There are also available options Setup and Preview for printing.

The **Axis** button will open the Axis menu, Fig. 10, and **Diagram** will draw the diagram, Fig. 11.

13.8 Non-ideal mixture: GaAs Example with Activity formulae

	SPECIES Formula	Temper. C	Amount kmol	Amount %	Step kmol	Step %	Activity Coeff.
1	PHASE 1:		1.001	100.000			
2	As(l)	25.000	0.000	0.010	0.025		-2.964
3	Ga(l)	25.000	1.001	99.990	-0.025		0.000
4	PHASE 2:						
5	GaAs	25.000					1.000
6							
7							
8							
9							
10							
11							
12							
13							
14							
15							
16							
17							
18							
19							
20							

Fig. 16. Input data of an activity formula example.

$$\text{LOGf}(1) = ((1-X1)^2) * (-25503.6 - 4.3109 * T + 5174.7 * (1 - 4 * X1)) / (8.31431 * T)$$

$$\text{LOGf}(2) = (X1)^2 * (-25503.6 - 4.3109 * T + 5174.7 * (3 - 4 * X1)) / (8.31431 * T)$$

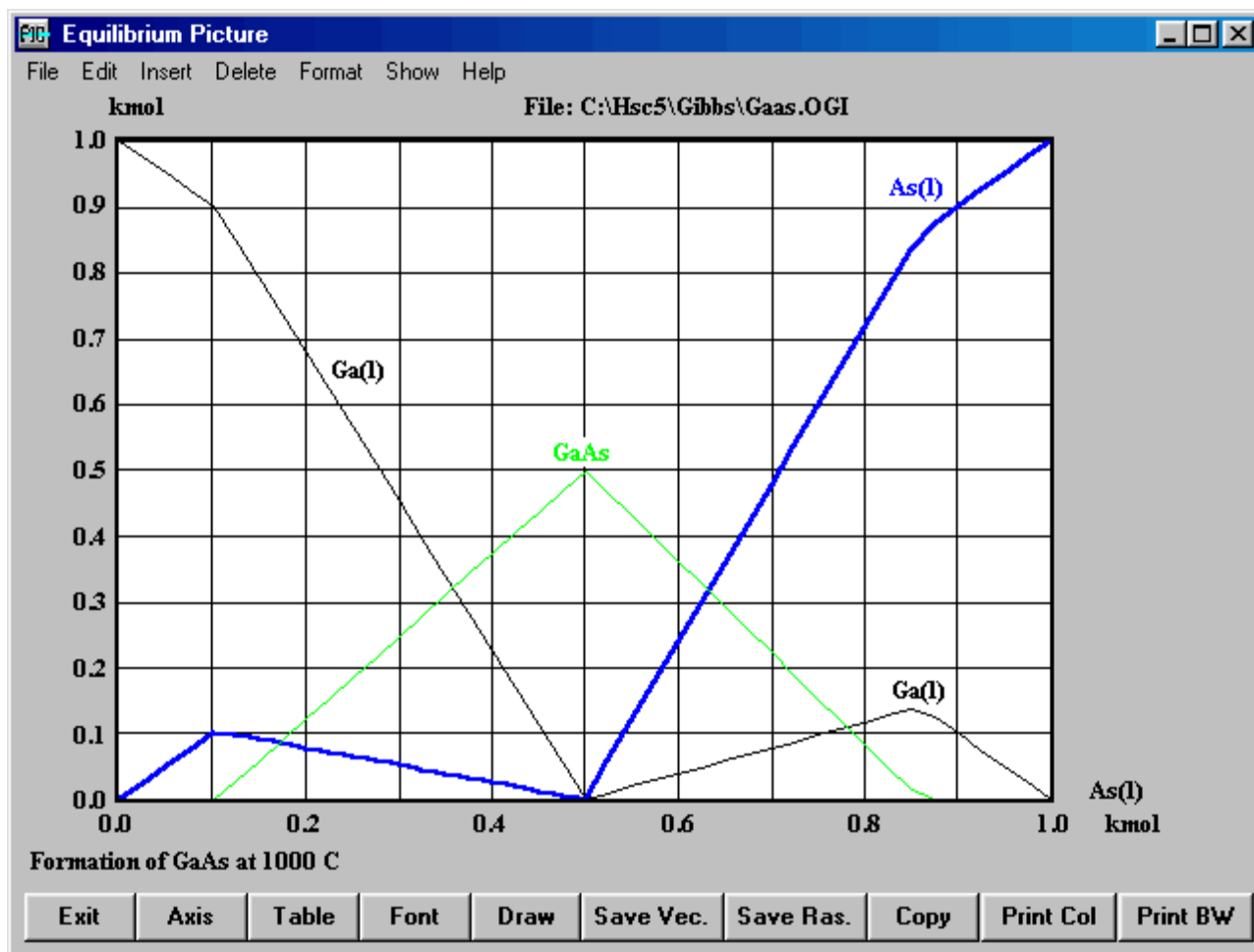


Fig. 17. Results as a function of arsenic amount. Different colors have been used for species, but these do not show up well in this B&W copy.

13.9 CaCO₃ Example (Aqueous solution exists)

	SPECIES Formula	Temper. C	Amount kmol	Amount %	Step kmol	Step %	Activity Coeff.
1	PHASE 1:		1.001	100.000	0.100		
2	N2(g)	25.000	1.000	99.899			1.000
3	H2O(g)	25.000					1.000
4	O2(g)	25.000	1.00E-05	0.001			1.000
5	CO2(g)	25.000	0.001	0.100	0.100		1.000
6	PHASE 2:		58.500	100.000			
7	H2O	25.000	55.500	94.872			1.000
8	CO3(-2a)	25.000					1.000
9	C2O4(-2a)	25.000					1.000
10	Ca(+2a)	25.000	1.000	1.709			1.000
11	CaOH(+a)	25.000					1.000
12	H(+a)	25.000					1.000
13	HCO2(-a)	25.000					1.000
14	HCO3(-a)	25.000					1.000
15	HO2(-a)	25.000					1.000
16	OH(-a)	25.000	2.000	3.419			1.000
17	PHASE 3:						
18	CaCO3	25.000					1.000
19	PHASE 4:						

Fig. 18. Input data of example CaCO₃.IGI.

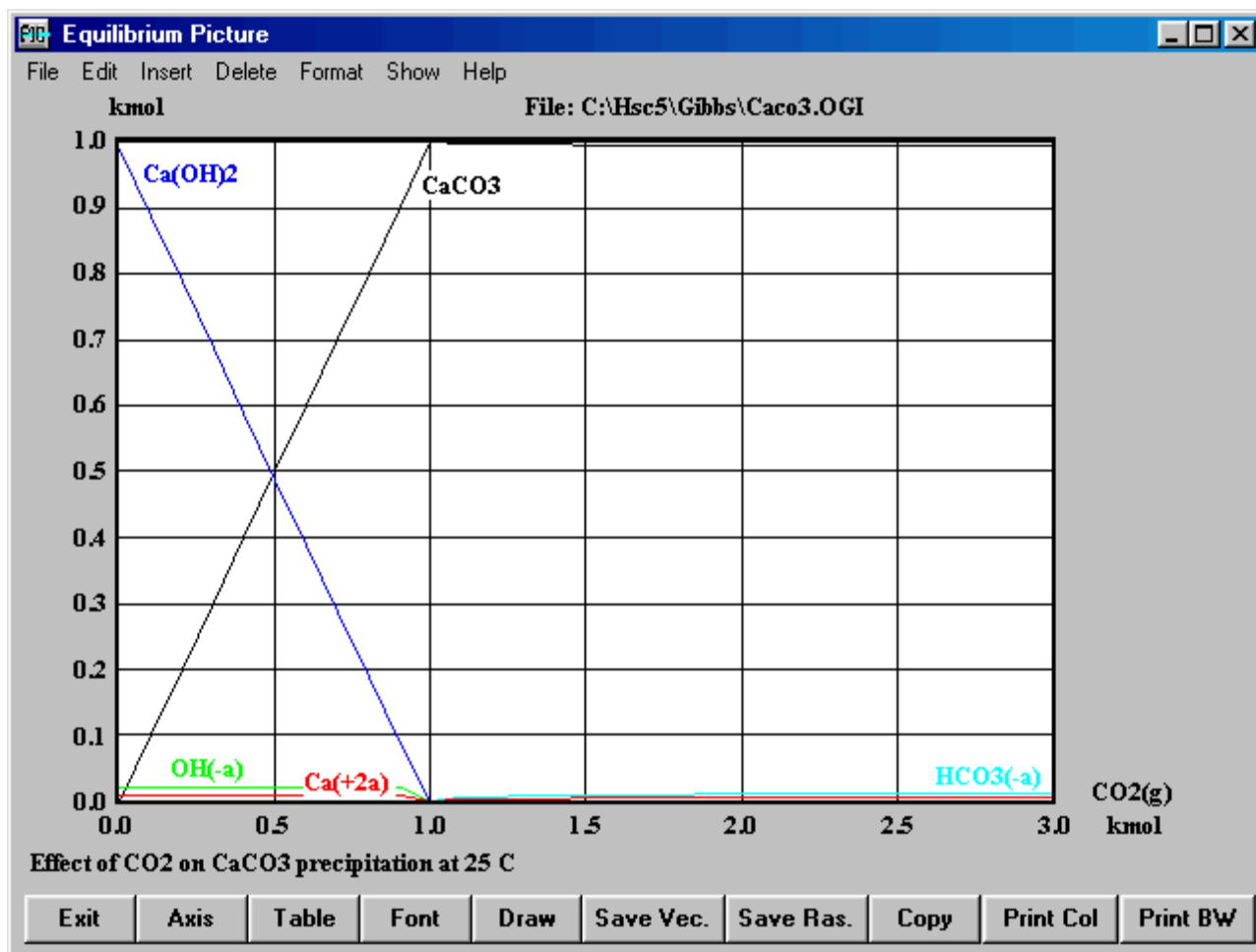


Fig. 19. Results as a function of added CO₂(g). Different colors have been used for the species, but these do not show up well in this B&W copy.

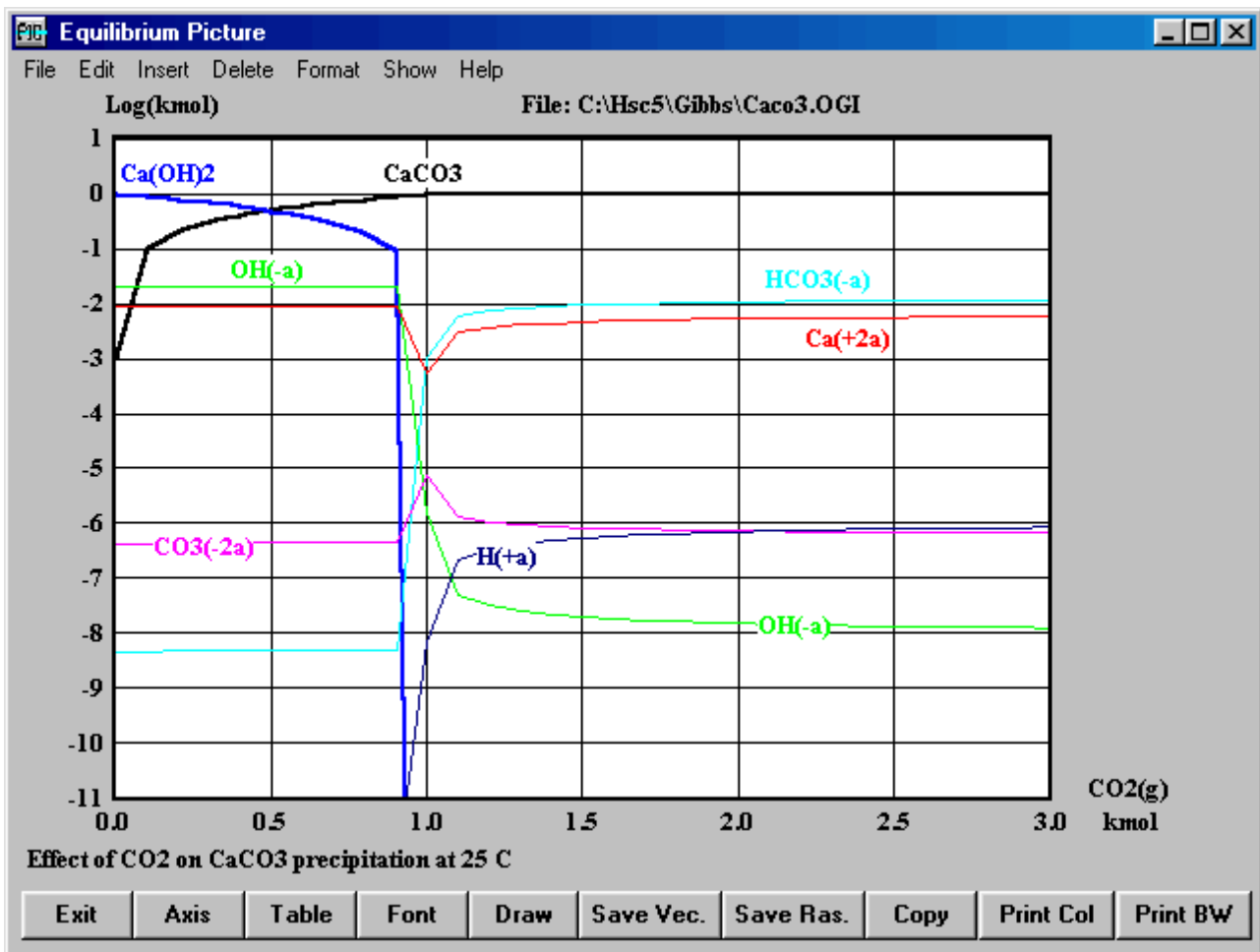


Fig. 20. Results on logarithmic scale, the default example is shown in Fig. 19.

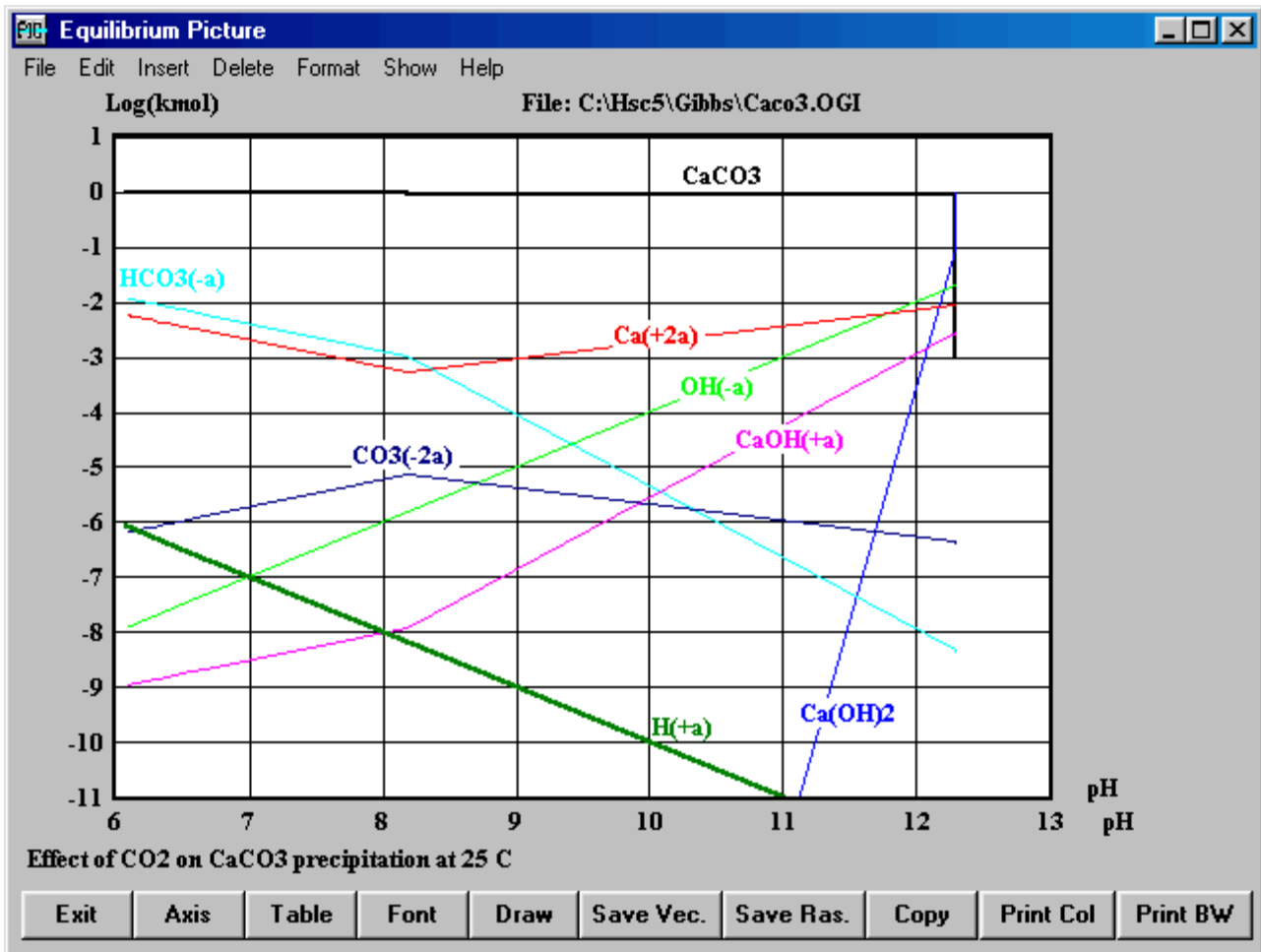


Fig. 21. Results as a function of pH, the default example is shown in Fig. 19.

13.10 Vapor Pressures

HSC Equilibrium module may be used to calculate vapor pressures for substances. "VaporPressurePbS.igi" sample case is available in your \HSC5\Gibbs- folder, see Fig. 22. It is made for **PbS vapor pressure** calculation. This case has been created with the same procedure as described in Chapter 13.1. Note that:

1. Nearly all Pb- and S-containing species have been selected to the chemical system.
2. Some nitrogen has been added to stabilize the gas phase.
3. Some extra sulfur has been added to make the case easier to solve for Gibbs.exe. Usually this trick is not needed but it may be used just to be safe.
4. Calculations are made from 0 to 2000 C°.
5. Selection of 100 bar total pressure makes possible calculation of vapor pressure up to 100 bar. Total pressure 1 bar would give vapor pressures up to 1 bar.
6. The equilibrium module calculates the equilibrium composition of the phases. In this case, the equilibrium composition of the gas phase.
7. All gas species have been selected to the diagram in the species dialog, see Fig. 9. Do not select PbS !
8. "Equilibrium Composition" has been selected to Y-axis in the Axis dialog, see Fig. 10.
9. The calculation results are shown in Fig. 23. The default Y-scale of the diagram is 0 - 100 mol-%, but it has been changed to 0 - 2 mol-%.
10. PbS(g) composition at 1330 C° is 1 mol-%. PbS(g) partial pressure is then 0.01, this means that PbS(g) vapor pressure is $0.01 * 100 \text{ bar} = 1 \text{ bar}$, see Fig. 23.
11. The total pressure of PbS is the sum of all the partial pressures of the gas species formed of PbS, ie. sum of: PbS(g), Pb(g), S2(g), Pb2S2(g), Pb2(g), etc.

HSC 5.0 can not calculate the total vapor pressures automatically. However, this may be carried out, for example, in MS Excel. Press the Table button in the diagram menu (see Fig. 23) to see the diagram data in tabular form and use the Copy - Paste procedure to transfer this data to MS Excel. You may also save this table in Excel format. In Excel you may calculate the sum of all the partial pressures, see the VaporPressurePbS.XLS example in your \HSC5\Gibbs-folder.

HSC database reference Knacke 91 gives 1314 C° for PbS boiling point and Janaf 98 gives 1320 - 1344 C° depending on the measurement or calculation method. These values are in reasonable agreement with the calculated PbS boiling point of 1327 C° in VaporPressurePbS.XLS.

The gas phase above PbS contains mainly PbS(g). However, in many cases the gas above pure substances may be composed of many different species. In these cases it is important to note that the total vapor pressure is the sum of the partial pressures of all the different gas species formed of the evaporating substance (not N2(g)).

Equilibrium Calculations C:\HSC5\Gibbs\VaporPressurePbS.igi

File Edit View Insert Delete Format Units Calculate Help

C17 1

	SPECIES Formula	Temper. C	Amount kmol	Amount %	Step kmol	Step %	Activity Coeff.
1	PHASE 1:		0.100	100.000			
2	N2(g)	25.000	0.100	100.000			1.000
3	Pb(g)	25.000					1.000
4	Pb2(g)	25.000					1.000
5	PbS(g)	25.000					1.000
6	PbS2(g)	25.000					1.000
7	Pb2S2(g)	25.000					1.000
8	S(g)	25.000	1.00E-20	0.000			1.000
9	S2(g)	25.000					1.000
10	S3(g)	25.000					1.000
11	S4(g)	25.000					1.000
12	S5(g)	25.000					1.000
13	S6(g)	25.000					1.000
14	S7(g)	25.000					1.000
15	S8(g)	25.000					1.000
16	PURE SUBSTANCES:		1.000	100.000			
17	PbS	25.000	1.000	100.000			1.000
18							
19							
20							

Species / Options

Exit Ins Phase Del Phase Ins Row Del Row Open HSC5\Gibbs\VaporPressurePbS Save Gibbs

Fig. 22. Chemical system specification for PbS vapor pressure calculations.

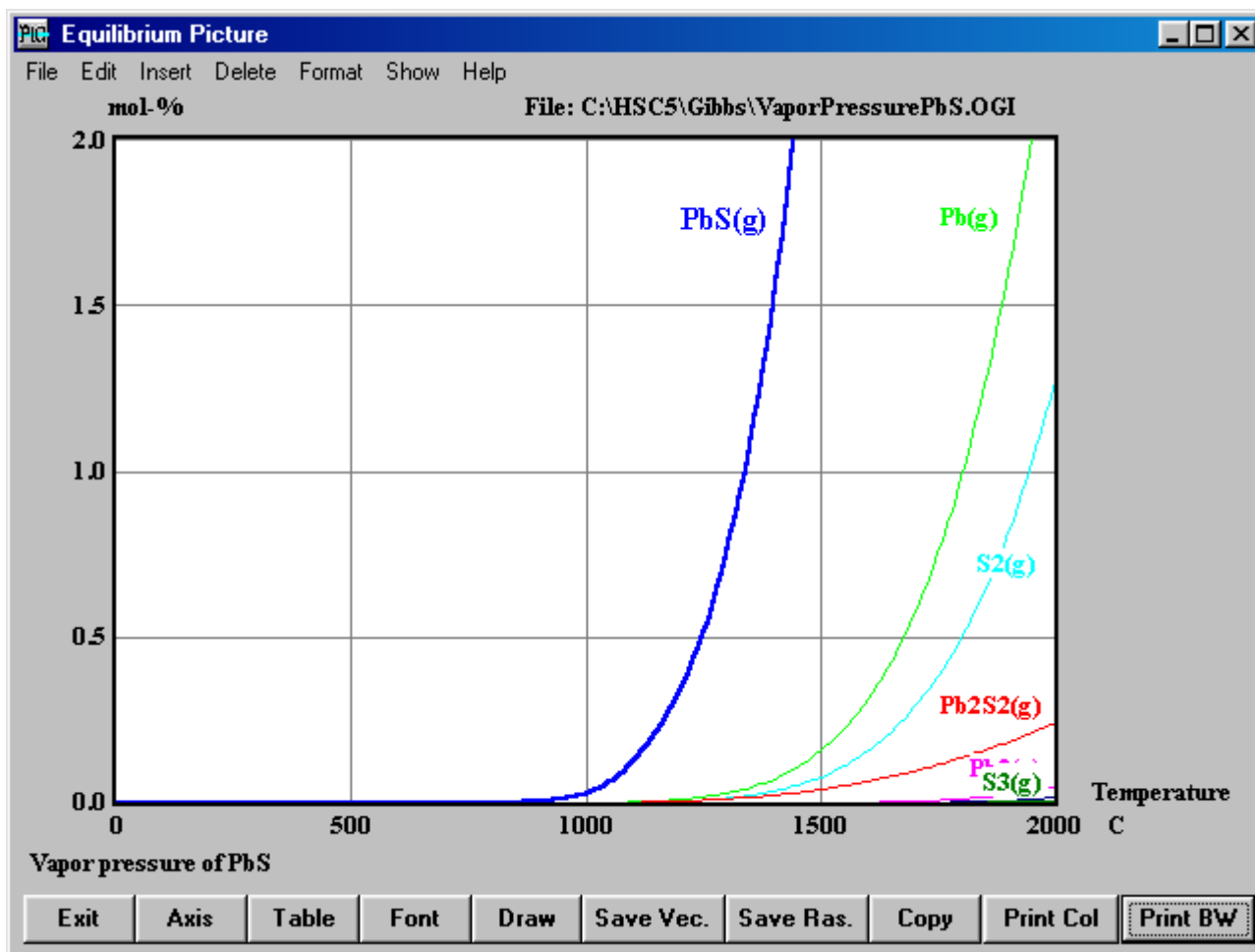


Fig. 23. Results of PbS vapor pressure calculations.