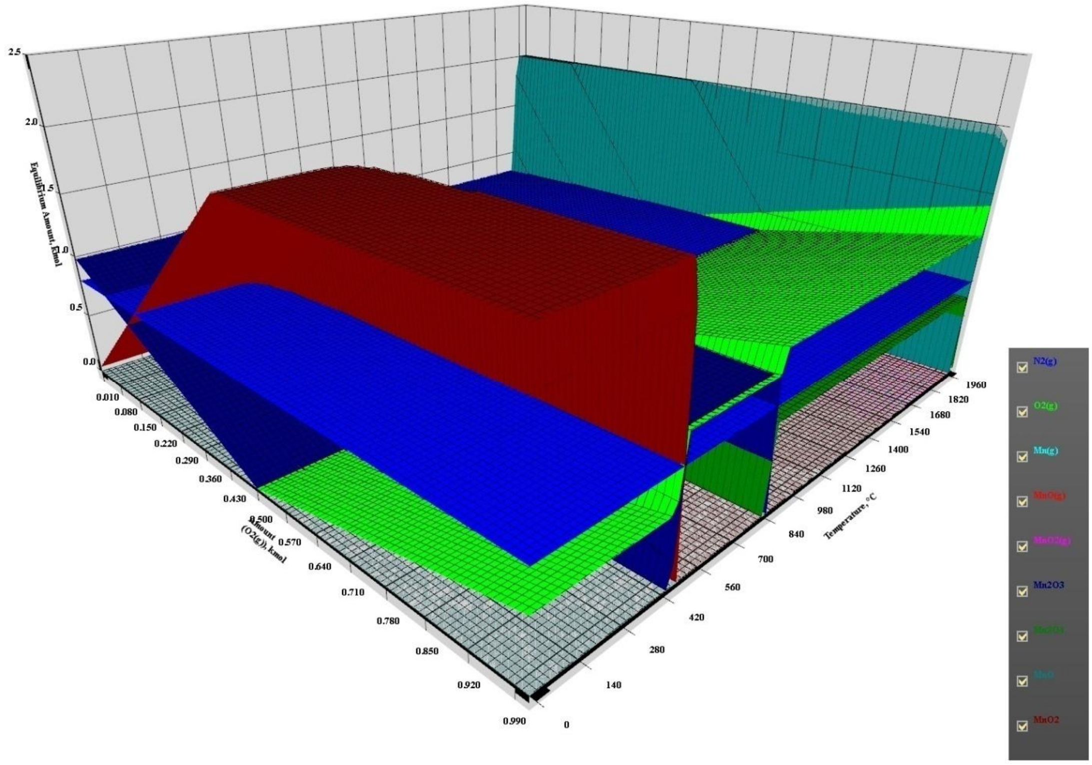
13. Equilibrium Module - Description of Menus and Options



SUMMARY

HSC Equilibrium module enables you to calculate multi-component equilibrium compositions in heterogeneous systems easily. The user simply needs to specify the chemical reaction system, with its phases and species, and give the amounts of 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. Please 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.

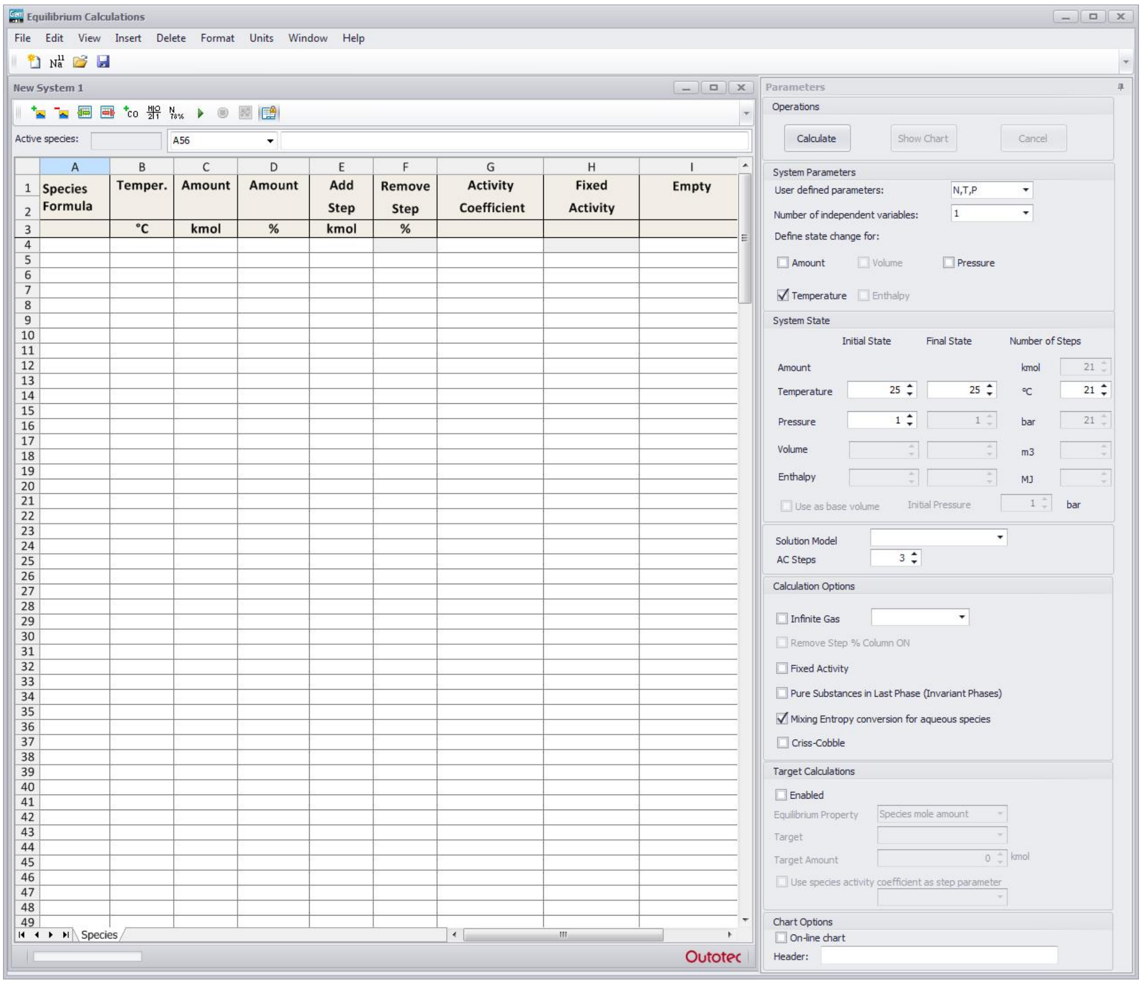
The equilibrium composition is calculated using the GIBBS solver, which uses the Gibbs energy minimization method[1]. The program reads the result files and draws pictures and tables of the equilibrium configurations if several equilibria have been calculated. The user can toggle between the equilibrium and graphics programs by pressing the buttons.

This version of the Equilibrium module also includes support for electrochemical calculations (previously known as Cell module). In Cell Equilibrium calculations, user also needs to specify the electrode phases, types of phases (gas/liquid/solid/metal), capacitances and discharge equation for the charging/discharging reaction.

The main format Equilibrium module is ***.gem8**, which contains all the data and formatting settings of each definition sheet as well as the phase names. The program can also read **imported** files from the previous HSC versions:

***.GEM** file format contains all the data and formatting settings of each definition sheet as well as the phase names, etc. while the ***.IGI** file format contains the data for calculations only. ***.ICE** file format contains the data for single-point calculations of Cell Equilibrium.

13.1. Starting the HSC Equilibrium Module



Active species: A56

A	B	C	D	E	F	G	H	I
Species Formula	Temper.	Amount	Amount	Add Step	Remove Step	Activity Coefficient	Fixed Activity	Empty
	°C	kmol	%	kmol	%			

System Parameters
User defined parameters: N,T,P
Number of independent variables: 1
Define state change for:
☐ Amount ☐ Volume ☐ Pressure
☑ Temperature ☐ Enthalpy

System State

	Initial State	Final State		Number of Steps
Amount			kmol	21
Temperature	25	25	°C	21
Pressure	1	1	bar	21
Volume			m3	
Enthalpy			MJ	

☐ Use as base volume Initial Pressure 1 bar

Solution Model
AC Steps 3

Calculation Options
☐ Infinite Gas
☐ Remove Step % Column ON
☐ Fixed Activity
☐ Pure Substances in Last Phase (Invariant Phases)
☑ Mixing Entropy conversion for aqueous species
☐ Criss-Cobble

Target Calculations
☐ Enabled
Equilibrium Property: Species mole amount
Target
Target Amount: 0 kmol
☐ Use species activity coefficient as step parameter

Chart Options
☐ On-line chart
Header:

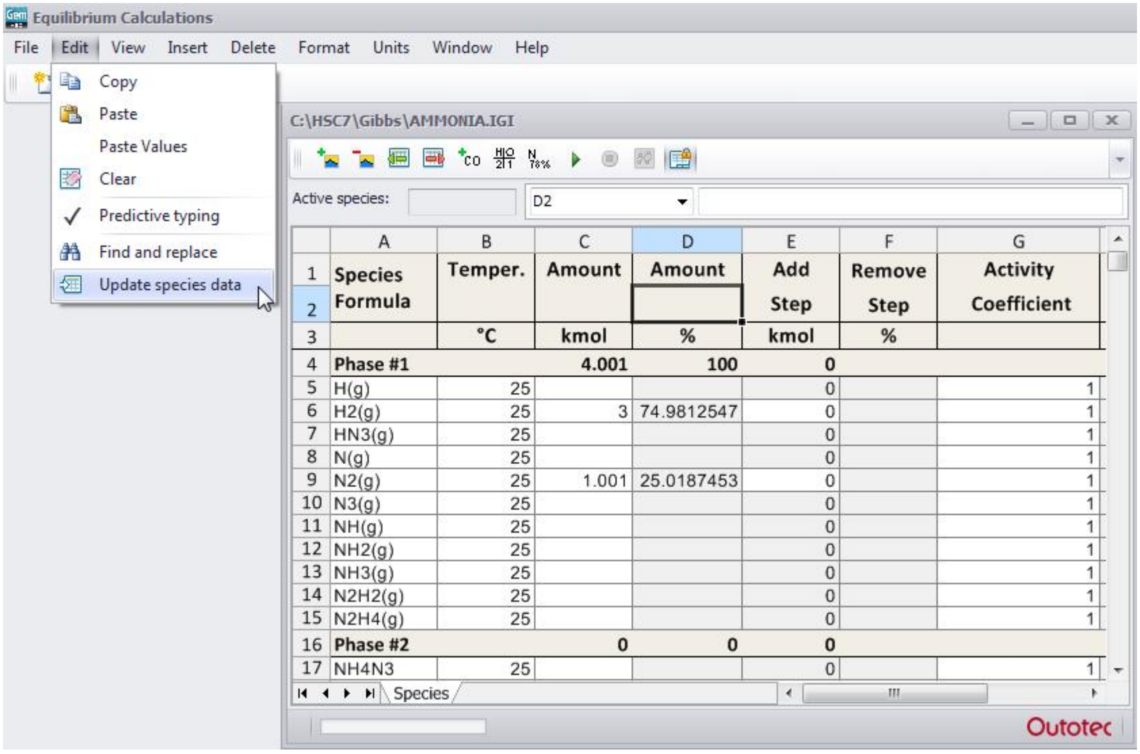
Fig. 1. Starting screen.

There are three ways of creating an input file, see **Fig. 1**.

1. Press **Empty File From Elements**. Then specify the elements which are present in your system, see **Fig. 3**. 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 **Create Empty file** if you are already certain of the possible substances and phases of the system.
3. Press **Open** 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.

If you have an old file format (*.GEM or *.IGI) you can import it from the **File** menu by selecting **Import** and working with it. You can update thermodynamic data of the old igi file to HSC8 database values by **update species data** from **Edit** menu, see **Fig. 2**.

If you only want to calculate the equilibrium compositions and draw a picture with the existing files, press **Calculate** and then press **Show Chart**.

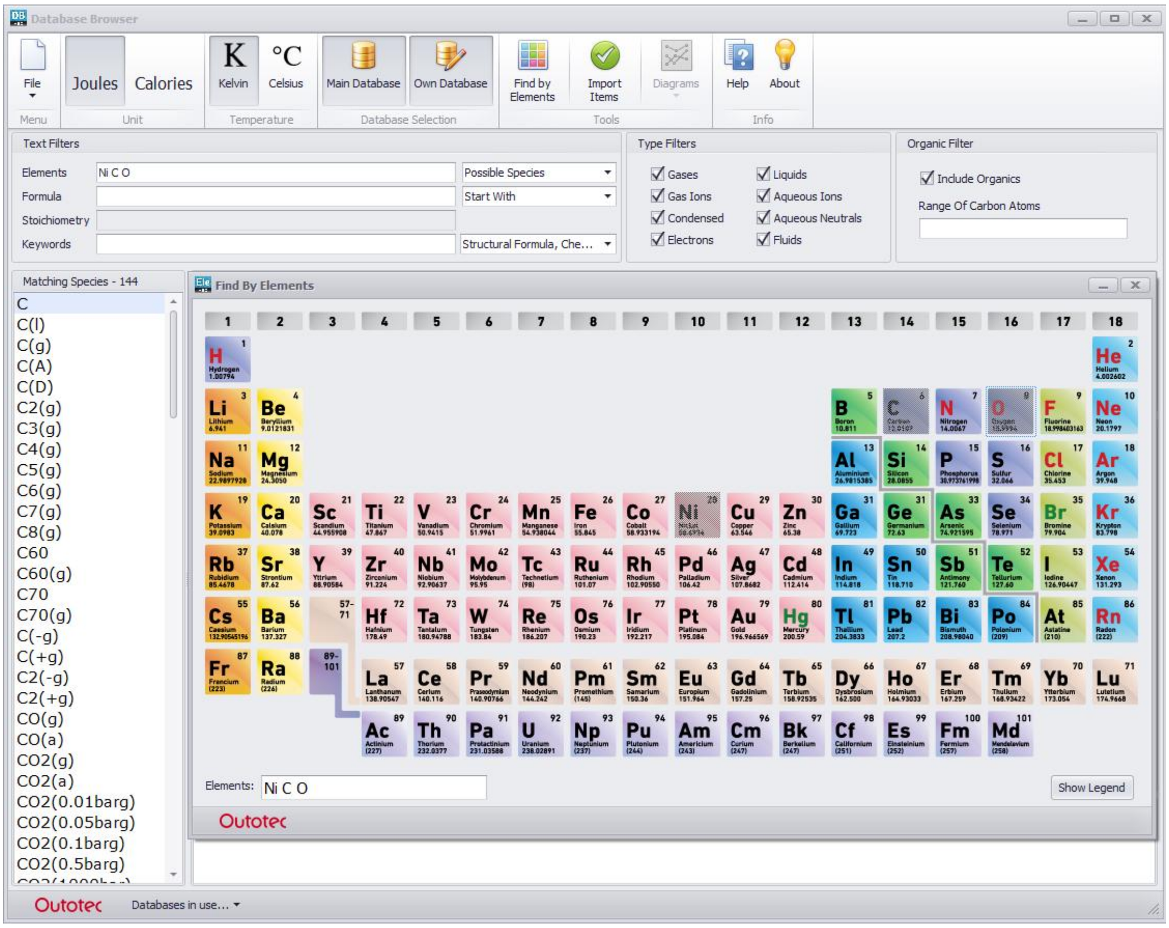


D2

	A	B	C	D	E	F	G
1 2	**Species Formula**	**Temper.**	**Amount**	**Amount**	**Add Step**	**Remove Step**	**Activity Coefficient**
3		**°C**	**kmol**	**%**	**kmol**	**%**	
4	**Phase #1**		**4.001**	**100**	**0**		
5	H(g)	25			0		1
6	H2(g)	25	3	74.9812547	0		1
7	HN3(g)	25			0		1
8	N(g)	25			0		1
9	N2(g)	25	1.001	25.0187453	0		1
10	N3(g)	25			0		1
11	NH(g)	25			0		1
12	NH2(g)	25			0		1
13	NH3(g)	25			0		1
14	N2H2(g)	25			0		1
15	N2H4(g)	25			0		1
16	**Phase #2**		**0**	**0**	**0**		
17	NH4N3	25			0		1

Fig. 2. Update species data of an old igi file.

13.2. Starting by Defining the Elements



Text Filters

Elements: Ni C O — Possible Species
Formula: — Start With
Stoichiometry:
Keywords: — Structural Formula, Che...

Type Filters

☑ Gases ☑ Liquids
☑ Gas Ions ☑ Aqueous Ions
☑ Condensed ☑ Aqueous Neutrals
☑ Electrons ☑ Fluids

Organic Filter

☑ Include Organics
Range Of Carbon Atoms

Matching Species - 144

C
C(l)
C(g)
C(A)
C(D)
C2(g)
C3(g)
C4(g)
C5(g)
C6(g)
C7(g)
C8(g)
C60
C60(g)
C70
C70(g)
C(-g)
C(+g)
C2(-g)
C2(+g)
CO(g)
CO(a)
CO2(g)
CO2(a)
CO2(0.01barg)
CO2(0.05barg)
CO2(0.1barg)
CO2(0.5barg)

Elements: Ni C O

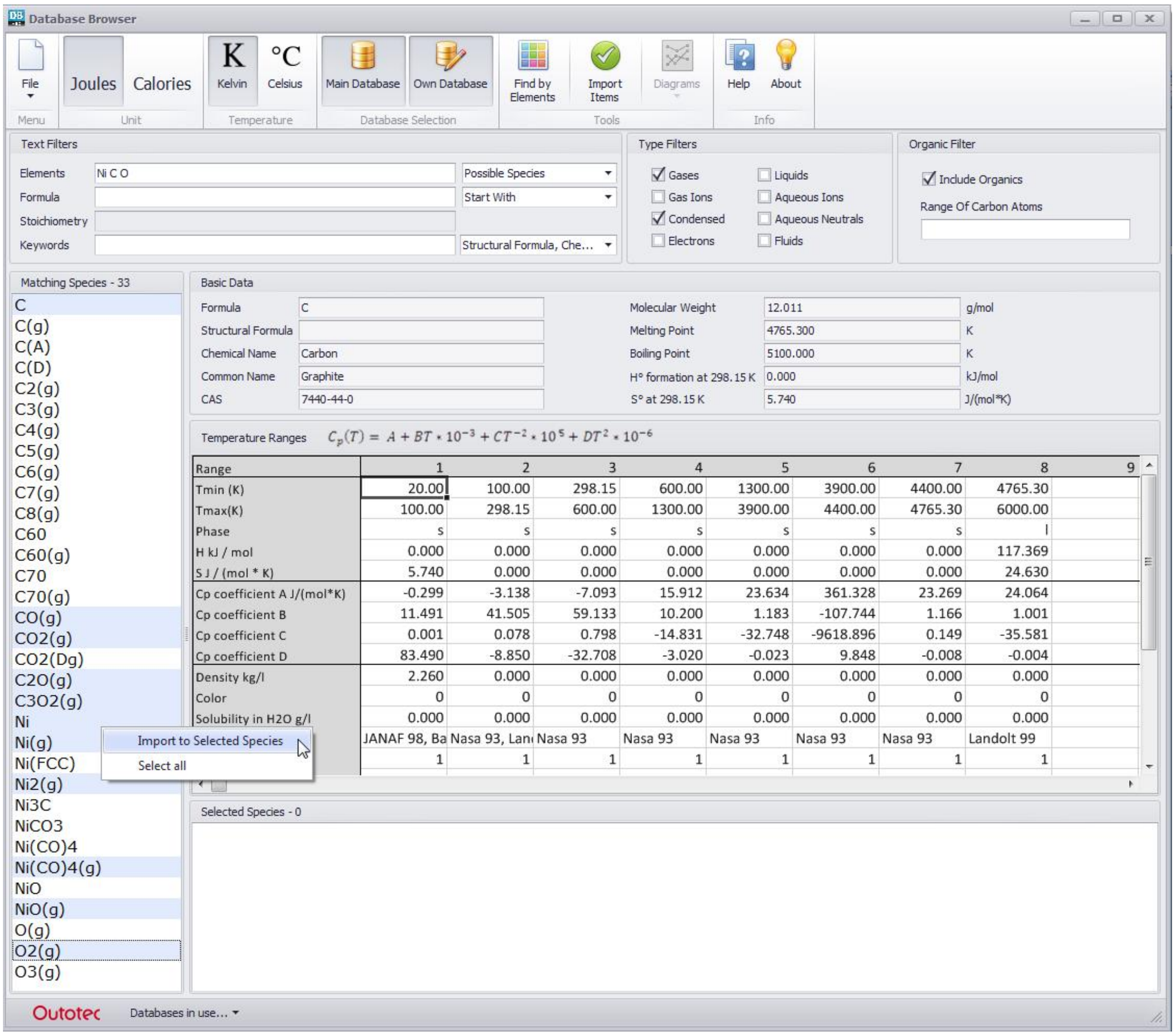
Fig. 3. Specifying the elements of the chemical system.

If you want to use only some of the species in the calculations, then select them and press **Import to Selected Species**. By decreasing the number of species, you can increase the calculation speed and make the solution easier. Especially if you have selected C and/or H among the other elements, a very large number of species will be included in the calculation and you are advised to decrease the number of species. You can of course try with all the species, but usually it is wise to select only such species to the system which may be stable.

However, if the stable species are not chosen, the calculated equilibrium results will be incorrect.

If there is an odd species in the list then you can click the relevant formula in the list which will reveal the whole data set of the species in the database, 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**.



Elements: Ni C O — Possible Species
Formula: — Start With
Stoichiometry:
Keywords: — Structural Formula, Che...

☑ Gases ☐ Liquids
☐ Gas Ions ☐ Aqueous Ions
☑ Condensed ☐ Aqueous Neutrals
☐ Electrons ☐ Fluids

☑ Include Organics
Range Of Carbon Atoms:

Matching Species - 33

- C
- C(g)
- C(A)
- C(D)
- C2(g)
- C3(g)
- C4(g)
- C5(g)
- C6(g)
- C7(g)
- C8(g)
- C60
- C60(g)
- C70
- C70(g)
- CO(g)
- CO2(g)
- CO2(Dg)
- C2O(g)
- C3O2(g)
- Ni
- Ni(g)
- Ni(FCC)
- Ni2(g)
- Ni3C
- NiCO3
- Ni(CO)4
- Ni(CO)4(g)
- NiO
- NiO(g)
- O(g)
- O2(g)
- O3(g)

Basic Data

Formula: C
Structural Formula:
Chemical Name: Carbon
Common Name: Graphite
CAS: 7440-44-0
Molecular Weight: 12.011 g/mol
Melting Point: 4765.300 K
Boiling Point: 5100.000 K
H° formation at 298.15 K: 0.000 kJ/mol
S° at 298.15 K: 5.740 J/(mol*K)

Temperature Ranges $C_p(T) = A + BT \cdot 10^{-3} + CT^{-2} \cdot 10^{5} + DT^{2} \cdot 10^{-6}$

Range	1	2	3	4	5	6	7	8	9
Tmin (K)	20.00	100.00	298.15	600.00	1300.00	3900.00	4400.00	4765.30	
Tmax(K)	100.00	298.15	600.00	1300.00	3900.00	4400.00	4765.30	6000.00	
Phase	s	s	s	s	s	s	s	l	
H kJ / mol	0.000	0.000	0.000	0.000	0.000	0.000	0.000	117.369	
S J / (mol * K)	5.740	0.000	0.000	0.000	0.000	0.000	0.000	24.630	
Cp coefficient A J/(mol*K)	-0.299	-3.138	-7.093	15.912	23.634	361.328	23.269	24.064	
Cp coefficient B	11.491	41.505	59.133	10.200	1.183	-107.744	1.166	1.001	
Cp coefficient C	0.001	0.078	0.798	-14.831	-32.748	-9618.896	0.149	-35.581	
Cp coefficient D	83.490	-8.850	-32.708	-3.020	-0.023	9.848	-0.008	-0.004	
Density kg/l	2.260	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
Color	0	0	0	0	0	0	0	0	
Solubility in H2O g/l	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
	JANAF 98, Ba	Nasa 93, Lan	Nasa 93	Nasa 93	Nasa 93	Nasa 93	Nasa 93	Landolt 99	
	1	1	1	1	1	1	1	1	

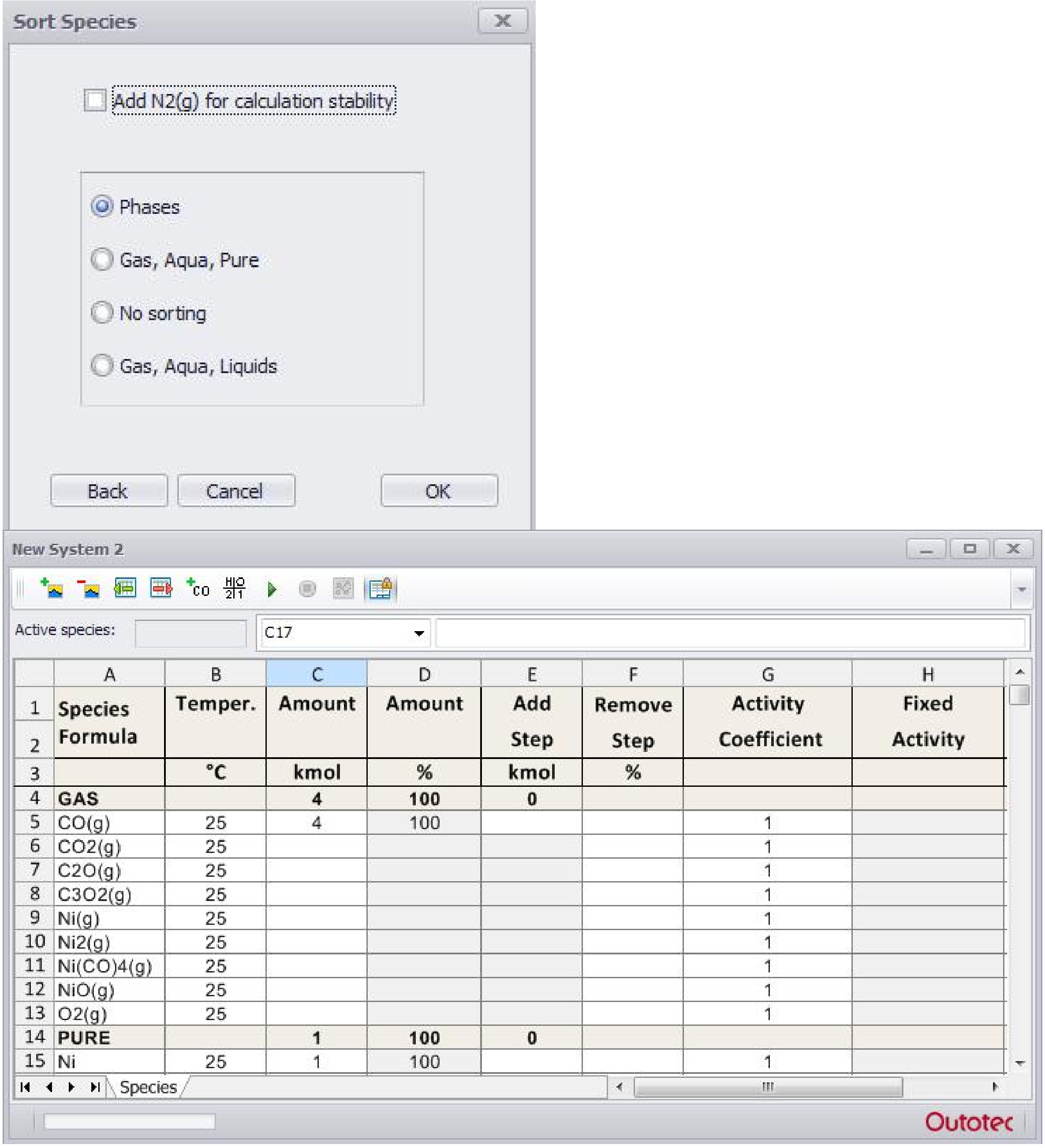
Selected Species - 0

Fig. 4. Deleting undesired species.

Press **Import Items** and you can also set the sorting order for the species. You can select one of the following sorting methods: **Phases** (species will be sorted by classes), **Gas, Aqua, Pure** (this sorting method is used for low temperatures), **No sorting** (all species will be in one phase) and **Gas, Aqua, Liquids** (melt will be added to individual class). The sorting order will determine the order of species in the Equilibrium Editor, see **Fig. 5**.

When you have chosed sorting order of species, press **Ok** and you will return to the Equilibrium Editor window, see **Fig. 5**.

13.3. Giving Input Data for Equilibrium Calculations



☐ Add N2(g) for calculation stability

● Phases
○ Gas, Aqua, Pure
○ No sorting
○ Gas, Aqua, Liquids

C17

	A	B	C	D	E	F	G	H
1–2	Species Formula	Temper.	Amount	Amount	Add Step	Remove Step	Activity Coefficient	Fixed Activity
3		°C	kmol	%	kmol	%		
4	**GAS**		**4**	**100**	**0**			
5	CO(g)	25	4	100			1	
6	CO2(g)	25					1	
7	C2O(g)	25					1	
8	C3O2(g)	25					1	
9	Ni(g)	25					1	
10	Ni2(g)	25					1	
11	Ni(CO)4(g)	25					1	
12	NiO(g)	25					1	
13	O2(g)	25					1	
14	**PURE**		**1**	**100**	**0**			
15	Ni	25	1	100			1	

Fig. 5. Specification of the species and phases for the reaction system.

The Equilibrium Editor consists of two sheets for determining the conditions of the equilibrium calculations. In Gibbs version 8 the Options sheet is hided and calculation data is specified using the Parameters panel, **Fig. 6**. You give all the data required to create an input file for the equilibrium solvers and for calculating the equilibrium compositions in the **Species and Parameters panel** sheets, see **Fig. 5** and **Fig. 6**.

The most demanding step is the selection of the species and phases, i.e. the definition of the chemical system. This is done in the Species sheet of the Equilibrium Editor, **Fig. 5**. You can move around the table using the mouse, or Tab and Arrow keys. The other points you should consider are:

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

You can type 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 will already have the species in the Species column.

You can insert an empty row in the table by selecting **Row** from the **Insert** menu or by pressing the right mouse button and selecting **Insert Cells** from the pop-up menu.

Rows can be deleted by selecting **Row** from the **Delete** menu or by pressing the right mouse button and then selecting **Delete Cells** from the pop-up menu.

You can change the order of the substances by inserting an empty row and using the copy - paste method to insert a substance in a new row. The drag and drop method can also be used. ***However, it is extremely important to move the whole row, because there are 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 their melting point. For example, type **SiO_2(l)** if SiO_2 is present in a liquid oxide phase at temperatures below the melting point of pure SiO_2. You may also use (s)-suffix if you want to force Gibbs to use solid data at any temperature.

The species can be inserted by selection **Species** in the **Insert** menu. Then the Browse Database window will appear where you will find the species that you need. You can use search, or type a formula or chemical name in the search string, and the program will find the species.

You can also type a species formula in a new row in the Equilibrium Editor window, and the program will suggest species.

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. The 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 the **Phase** selection in the **Insert** menu or using the same selection in the pop-up 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. Requests 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 beige 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 Nm^3 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 will change the temperatures of all the species within the phase. Note that phase and species temperatures have effect only on the reaction enthalpy balances. Equilibrium temperatures must be specified in the Parameters panel, see **Fig. 6**.
3. Note also that you cannot type formulae in the amount column of the phase row, because the SUM formulae are located there. You can change the unit used from the Units menu.

The first phase to be defined is always the gas phase, and all gaseous species must be 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 on the Parameters panel, see **Fig. 5** and **Fig. 6**. Formation of pure substances is possible, especially in the solid state at low temperatures. For example, carbon **C**, iron sulfide FeS_2, calcium carbonate $CaCO_3$, etc. might form their own pure phases.

One of the most common mistakes is to insert a large amount of relatively “inert” substances into the mixture phase. For example, large amounts of solid carbon at 1500 °C do not dissolve into molten iron. However, if both of these 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 far too low a vapor pressure for the iron. Therefore, carbon should nearly always be inserted into its own phase at low temperatures.

3. Format

You can format row height, column width, and cells in table of the Equilibrium Editor by selecting the Format menu.

4. 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 can select the temperature unit by selecting °C or K from the Units menu. Equilibrium temperatures must be specified in the **Paremeters panel**, see **Fig. 6**.

5. Amount of the Species

In this column you give the input amounts of the raw material species. The most important point for the equilibrium composition is to put the correct amounts of elements in 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 can choose between kmol or kg/Nm^3 units by selecting kmol or kg/Nm^3 from the Units menu. Note that kilograms refer to condensed substances and standard cubic meters (Nm^3) to gaseous substances.

6. Amount Step for Raw Materials

If you wish to calculate several successive equilibria, you have to give an incremental step for one or more raw material species. Then the programs will 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 also give the number of steps. Some 21 - 51 steps are usually enough to give smooth curves to the equilibrium diagram.
You can give step values for several species simultaneously. For example, if you want to add air to the system, give a step value for both O_2(g) and N_2(g). Please remember to specify the number of steps if a diagram is to be drawn from the results.

7. Activity Coefficients

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

$$a = \frac{p(over\ solution)}{p(pure)} \tag{1}$$

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

$$f = \frac{a}{x} \tag{2}$$

In an ideal solution, they are therefore defined as a = x and f = 1. As default in GIBBS, the activity coefficient of a species in the mixture phase is always 1.

Activity coefficients can be entered as a function of mole fraction of species in the input sheet column G. If a constant number is used it is given as an activity coefficient (f) to column G, however if an equation is used it should be given as a natural logarithm of activity coefficient (lnf) to column G.

Only simple binary or ternary expressions can be utilized directly by the GIBBS solver within HSC, such as:

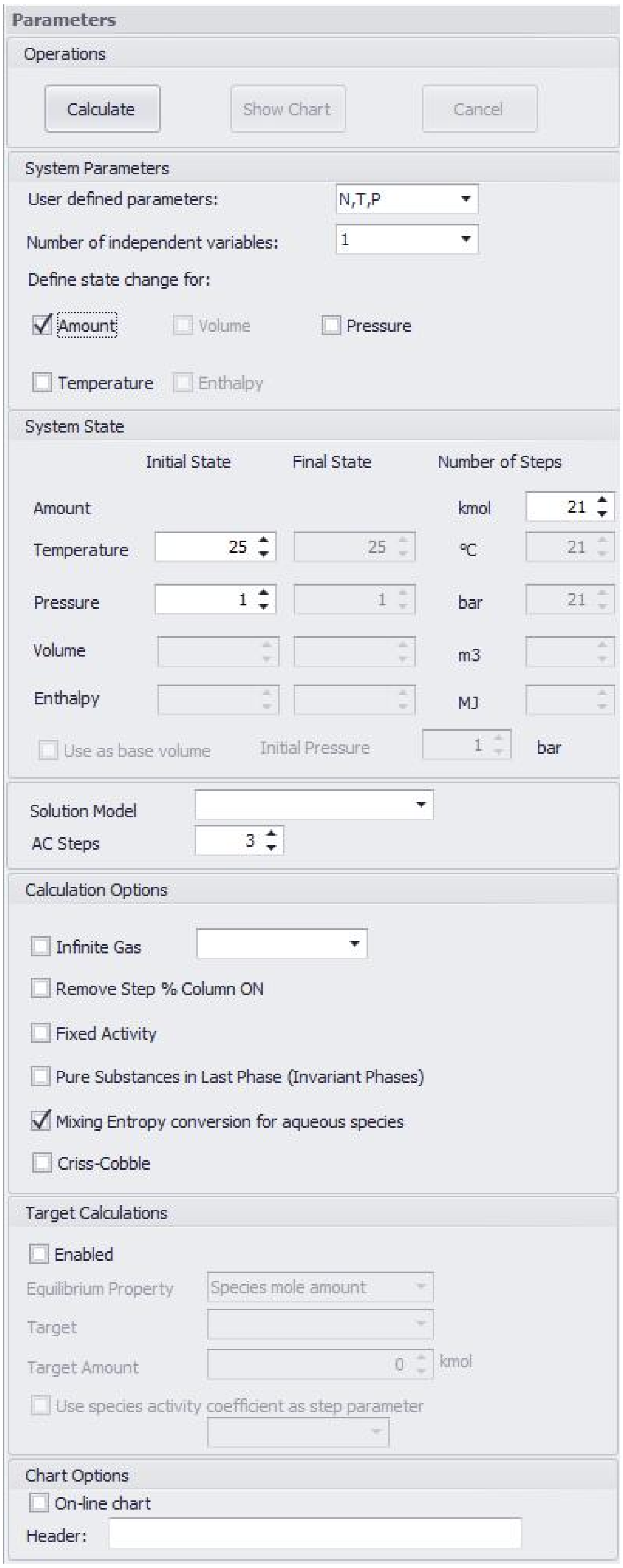
Ln(f) = 8495/T - 2.653
Ln(f) = 0.69 + 56.8·X24 + 5.45·X25

Ln(f) = -3926/T
Ln(f) = -1.21·X7^2 - 2.44·X8^2

where:
T = Temperature in K
X24 = Mole fraction of the species with row number 24 in the sheet.
f = Activity coefficient.

Instead of manually entering the activity coefficient, it is also possible to use pre-defined activity models. For example, to calculate the activity coefficients with the Pitzer model using the Aqua module, please select “Aqua” in the solution model drop-down list when aqueous phase is selected, see **Fig. 6**. For more information, see sections 13.4.4, 13.10 and Chapter 36.

13.4. Panel Parameters



Parameters

Operations

System Parameters

User defined parameters: N,T,P

Number of independent variables: 1

Define state change for:

☑ Amount ☐ Volume ☐ Pressure

☐ Temperature ☐ Enthalpy

System State

	Initial State	Final State		Number of Steps
Amount			kmol	21
Temperature	25	25	℃	21
Pressure	1	1	bar	21
Volume			m3	
Enthalpy			MJ	

☐ Use as base volume   Initial Pressure 1 bar

Solution Model

AC Steps 3

Calculation Options

☐ Infinite Gas

☐ Remove Step % Column ON

☐ Fixed Activity

☐ Pure Substances in Last Phase (Invariant Phases)

☑ Mixing Entropy conversion for aqueous species

☐ Criss-Cobble

Target Calculations

☐ Enabled

Equilibrium Property: Species mole amount

Target

Target Amount 0 kmol

☐ Use species activity coefficient as step parameter

Chart Options

☐ On-line chart

Header:

Fig. 6. Specifying calculation parameters.

13.4.1. Operations

There are three buttons in this section. **Calculate** – Equilibrium will be calculated using the user defined parameters. **Show Chart** – Diagram will be drawn. **Cancel** – You can cancel your last operation.

13.4.2. System Parameters

In this section you can specify parameters and define which of them will be changed.

T – Temperature, **P** – Pressure, **N** – Amount, **V** – Volume, **H** – Enthalpy.

You can select one of the options in the **user defined** parameters menu. There are temperature, pressure, and amount in every case, for example, if you select the **N, H, P** system, it means that the temperature will be constant in this system.

Specify a 2D or 3D diagram by selecting 1 or 2 in the **number of independent variables**, respectively.

13.4.3. System State

In this section you can specify values or a range of values for the parameters that you selected above.

If you have defined increments (steps) for raw material species or a specified range for selected parameters then you should also give the **Number of Steps** required, see **Fig. 6**. Usually 21 - 51 steps give quite smooth curves in the equilibrium diagram. A large number will only add more points to the diagram and involve 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 check the **Use as base volume** option and enter a value for **Initial Pressure**, the program will calculate the initial volume and add to it the value for the volume (or range of values) that you specified earlier.

13.4.4. Solution model

User can find the theory of the solution models and instructions of how to make your own solution models in section 13.10 for solid and liquid solutions and Chapter 36 for aqueous solutions.

First choose the phase where you want to use a solution model in the system sheet. Then choose the solution model from the parameters panel and give the number of iterations used in the calculations (AC steps). There are three solution models available: Ga - As Mixture, Al - Zn Mixture, and Aqua. If the solution model is left blank then this phase is treated as an ideal solution.

It is also possible to enter an activity coefficient formula in **column G** of the input sheet. Manually written equations should be entered as a natural logarithm of the activity coefficient, see section 13.3. (numbered list 7. Activity coefficients)

13.4.5. Advanced Calculation Options

Open Atmosphere Mode (Infinite phase)

The idea of this calculation mode is to balance the system with the external environment as a single Gibbs Energy Minimization (GEM) problem.

The system state is termed stationary if the system state does not change in steps.

It is not always possible to find the stationary state for a given system and environment, because it is possible that some species will accumulate infinitely in the system. For example, if water steam from the environment is condensed in the system's aqueous phase, it is possible that the steam will condense infinitely. In such cases the algorithm will determine these species and consider their molar amount to be infinite, and the stationary state will be found for the rest of the species.

Note: The selection of the species present in the "open" phase should be made with caution and only significant species should be added to the open phase. For example, if zinc vapor is added to the open gas phase at room temperature, it is possible that solid zinc will fully evaporate, which would appear as an incorrect result in the practical sense. Of course, zinc evaporation occurs in normal calculations, but is insignificant, because it would require something like 10^{30} steps of Transitory Evaporation to evaporate the zinc.

This mode **can be** used with some of the other modes. Because the step parameter is not defined by this mode, it is possible to use T, P, or raw material amounts as a step parameter in the normal mode; and T, V, P or raw material amounts in the Constant Volume mode. This mode can be used with the Target Calculations mode. This mode **cannot be** used together with the Adiabatic mode.

Transitory Evaporation Mode (Remove Step % Column ON)

The idea of this calculation mode is to balance the system with the external environment step by step.

Unlike the normal calculation mode, when initial parameters for each step are defined by the user, in this mode initial parameters are based on the results of the previous step. Some part of the "open" phase is deleted, initial species are added, and the next step is calculated.

This calculation mode **can be** used with some of the other modes. In normal mode, **T and P are fixed** across all calculation steps. In the Constant Volume mode, **V is fixed** (either defined by the user or calculated based on the initial gas phase amount), and T or P is adjusted automatically. So user must choose **amount** as step parameter.

Please note that this mode **cannot be** used together with the Target Calculation mode, because it is impossible to determine intermediate (i.e. between adjacent steps) initial parameters. Nor can this calculation mode be used together with the Adiabatic mode.

Typical example of Transitory Evaporation mode is calculation procedure where part of the gas phase is removed from the chemical system after each calculation step.

Fixed Activity mode

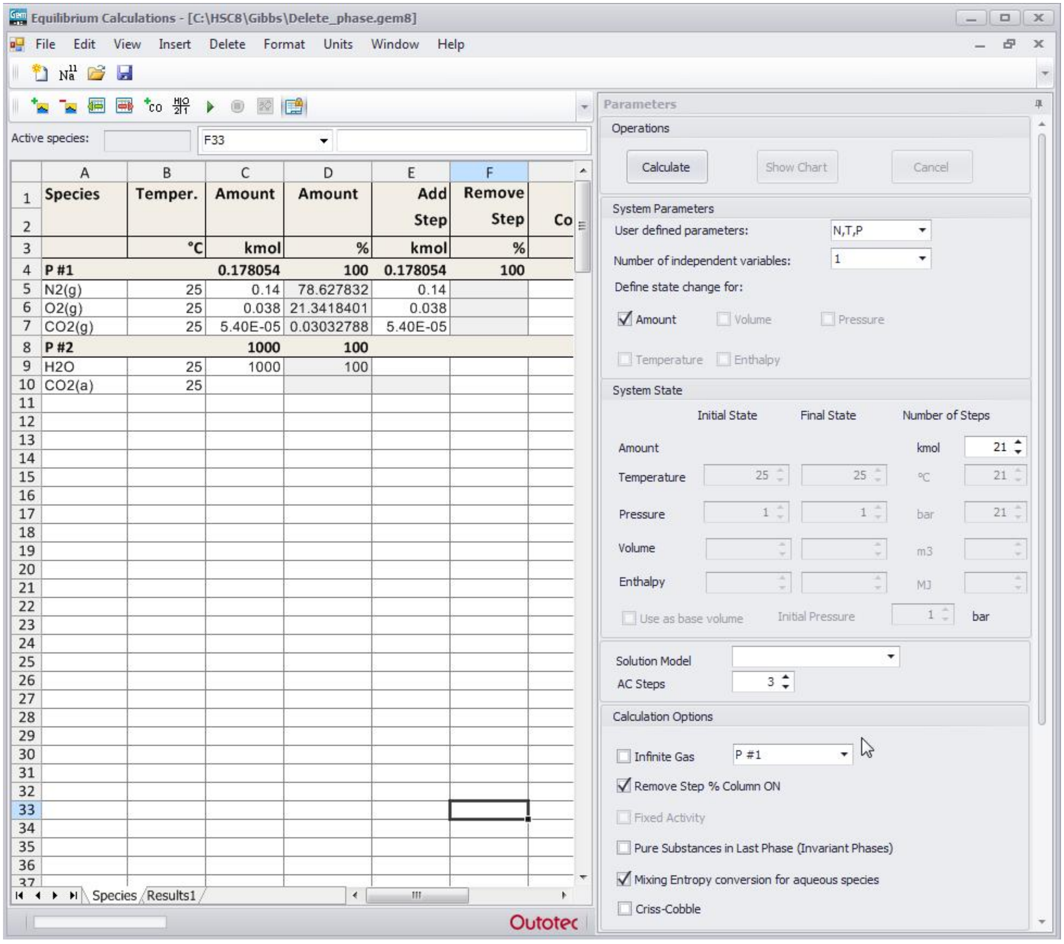
This section deals with the Fixed Activity Calculation mode. The main idea of this mode is to fix the activity of some species (corresponding to the molar fraction of that species) and adjust the initial amount of the species so that this activity constraint is satisfied at equilibrium.

This mode **supports** the Constant Volume and Target Calculations modes. This mode **does not support** the Transitory Evaporation, Open Atmosphere, and Adiabatic calculation modes.

Examples of the Transitory Evaporation, Open Atmosphere and Fixed Activity modes

The system consists of H_2O, N_2 (g), O_2 (g), CO_2 (g), and CO_2 (a). Initially, only H_2O, N_2 (g), O_2 (g) and CO_2 (g) are present in the system; gases are added to the system in each step, see **Fig. 7- Fig. 13** (for detailed information of these systems, see Chapter 14).

By calculating this system in the Transitory Evaporation mode (Calculation option **Remove Step % Column ON** checked and **Remove step %** is here 100 of gas phase - Cell F4 - after each step and re-filling the gas phase with option), we get the results in **Fig. 8**.



	A	B	C	D	E	F
1-2	Species	Temper.	Amount	Amount	Add Step	Remove Step
3		°C	kmol	%	kmol	%
4	**P #1**		**0.178054**	**100**	**0.178054**	**100**
5	N2(g)	25	0.14	78.627832	0.14	
6	O2(g)	25	0.038	21.3418401	0.038	
7	CO2(g)	25	5.40E-05	0.03032788	5.40E-05	
8	**P #2**		**1000**	**100**		
9	H2O	25	1000	100		
10	CO2(a)	25				

System Parameters
User defined parameters: N,T,P
Number of independent variables: 1
Define state change for:
☑ Amount ☐ Volume ☐ Pressure
☐ Temperature ☐ Enthalpy

System State

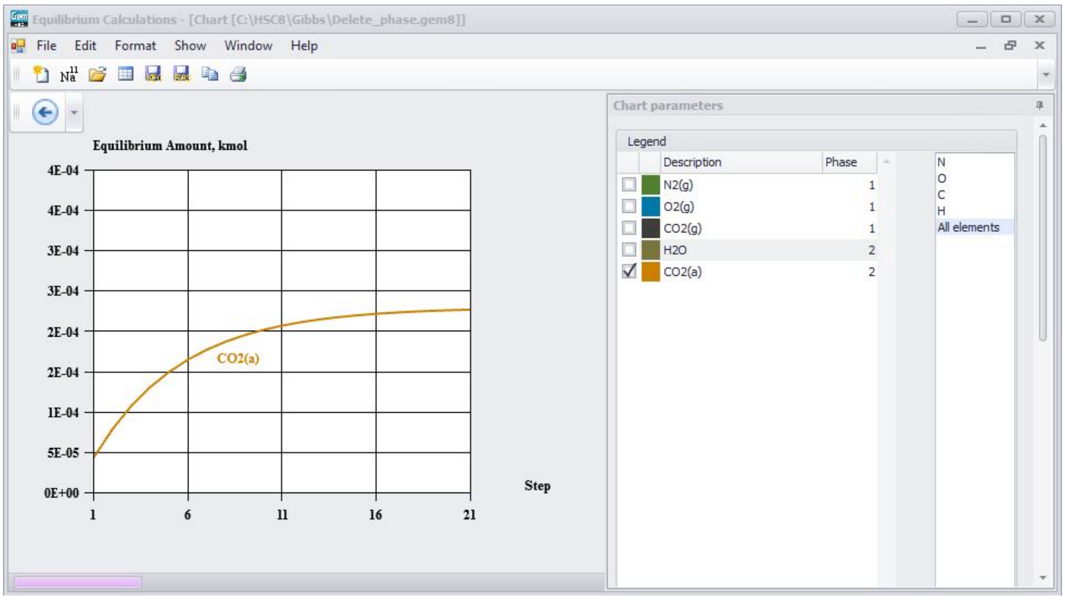
	Initial State	Final State		Number of Steps
Amount			kmol	21
Temperature	25	25	°C	21
Pressure	1	1	bar	21
Volume			m3	
Enthalpy			MJ	

☐ Use as base volume Initial Pressure 1 bar

Solution Model
AC Steps 3

Calculation Options
☐ Infinite Gas P #1
☑ Remove Step % Column ON
☐ Fixed Activity
☐ Pure Substances in Last Phase (Invariant Phases)
☑ Mixing Entropy conversion for aqueous species
☐ Criss-Cobble

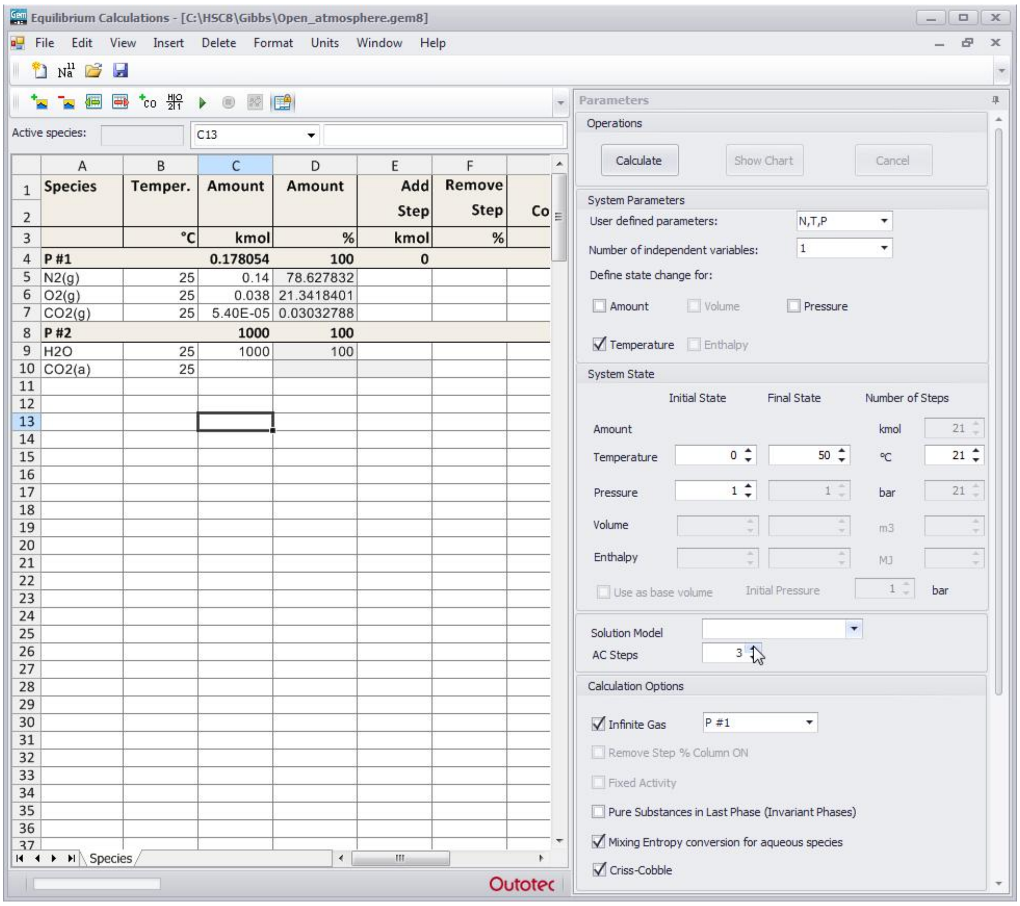
Fig. 7. Parameters for Transitory Evaporation mode.



	Description	Phase
☐ 🟩	N2(g)	1
☐ 🟦	O2(g)	1
☐ ■	CO2(g)	1
☐ 🟫	H2O	2
☑ 🟧	CO2(a)	2

Fig. 8. Diagram for Transitory Evaporation mode

By calculating this system in the Open Atmosphere mode (Calcuation options **Infinite Gas** and **P #1**) with temperature as the step parameter, we get **Fig. 9Fig. 9**. This chart corresponds to the expected values of CO2 dissolution from **Fig. 8**.



	A	B	C	D	E	F	
1	Species	Temper.	Amount	Amount	Add	Remove	
2					Step	Step	Co
3		°C	kmol	%	kmol	%	
4	**P #1**		**0.178054**	**100**	**0**		
5	N2(g)	25	0.14	78.627832			
6	O2(g)	25	0.038	21.3418401			
7	CO2(g)	25	5.40E-05	0.03032788			
8	**P #2**		**1000**	**100**			
9	H2O	25	1000	100			
10	CO2(a)	25					

System Parameters
User defined parameters: N,T,P
Number of independent variables: 1
Define state change for:
☐ Amount ☐ Volume ☐ Pressure
☑ Temperature ☐ Enthalpy

System State

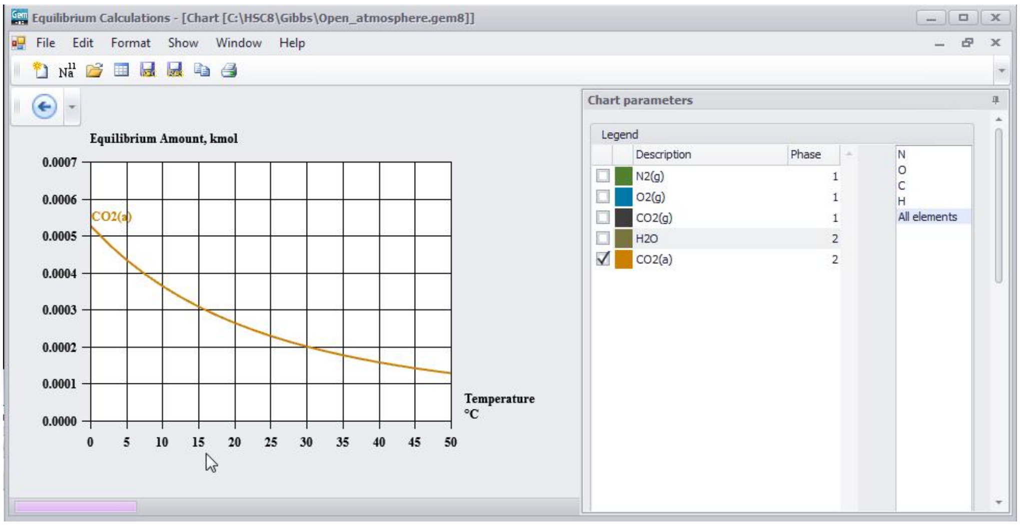
	Initial State	Final State		Number of Steps
Amount			kmol	21
Temperature	0	50	°C	21
Pressure	1	1	bar	21
Volume			m3	
Enthalpy			MJ	

☐ Use as base volume   Initial Pressure 1 bar

Solution Model
AC Steps 3

Calculation Options
☑ Infinite Gas   P #1
☐ Remove Step % Column ON
☐ Fixed Activity
☐ Pure Substances in Last Phase (Invariant Phases)
☑ Mixing Entropy conversion for aqueous species
☑ Criss-Cobble

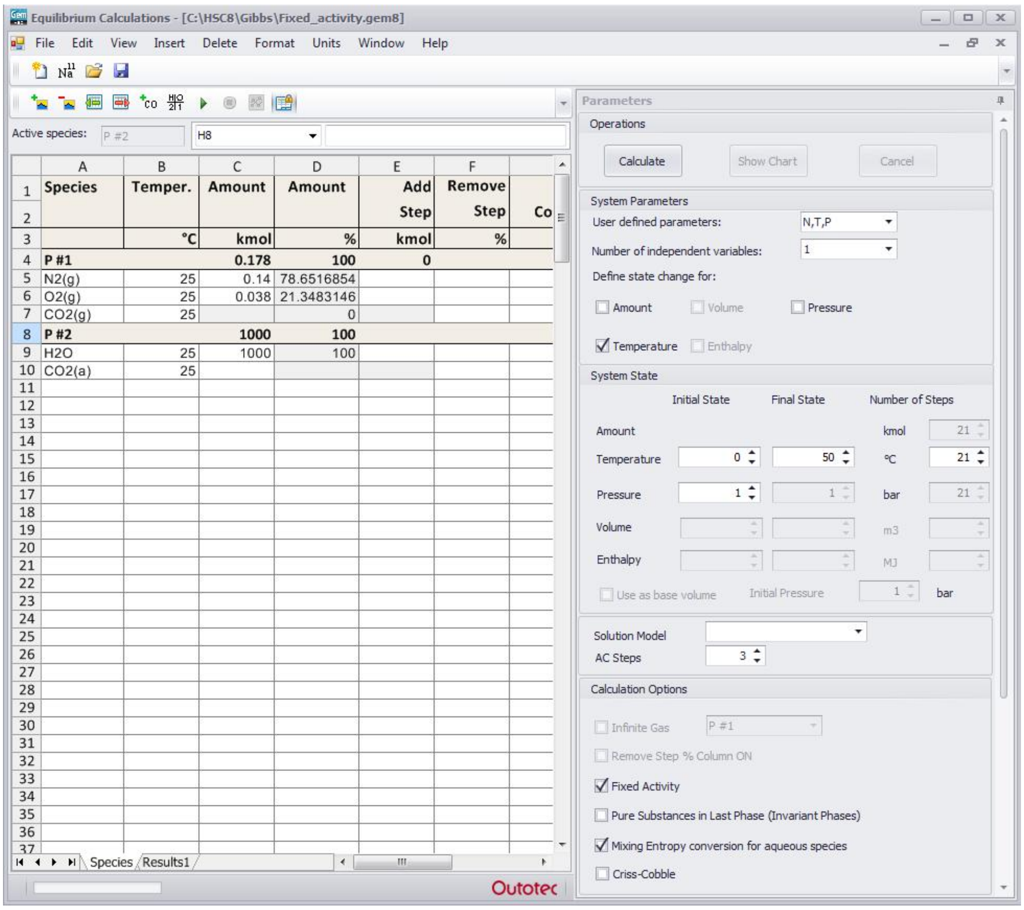
Fig. 9. Parameters for Open Atmosphere mode.



	Description	Phase
☐ 🟩	N2(g)	1
☐ 🟦	O2(g)	1
☐ ■	CO2(g)	1
☐ 🟫	H2O	2
☑ 🟧	CO2(a)	2

Fig. 10. Diagram for Open Atmosphere mode.

You can also calculate this system in the Fixed Activity mode with a coefficient of 0.0003 for CO_2 (g), see **Fig. 11**.



Active species: P #2 H8

	A	B	C	D	E	F	
1 2	Species	Temper.	Amount	Amount	Add Step	Remove Step	Co
3		°C	kmol	%	kmol	%	
4	**P #1**		**0.178**	**100**	**0**		
5	N2(g)	25	0.14	78.6516854			
6	O2(g)	25	0.038	21.3483146			
7	CO2(g)	25		0			
8	**P #2**		**1000**	**100**			
9	H2O	25	1000	100			
10	CO2(a)	25					

System Parameters
User defined parameters: N,T,P
Number of independent variables: 1
Define state change for:
☐ Amount ☐ Volume ☐ Pressure
☑ Temperature ☐ Enthalpy

System State

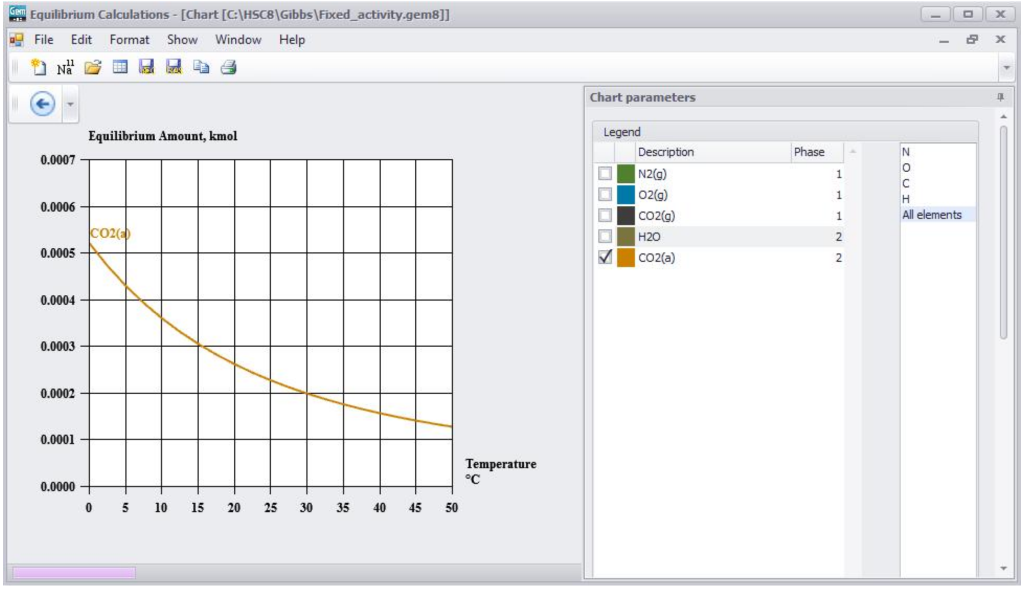
	Initial State	Final State		Number of Steps
Amount			kmol	21
Temperature	0	50	°C	21
Pressure	1	1	bar	21
Volume			m3	
Enthalpy			MJ	

☐ Use as base volume Initial Pressure 1 bar

Solution Model
AC Steps 3

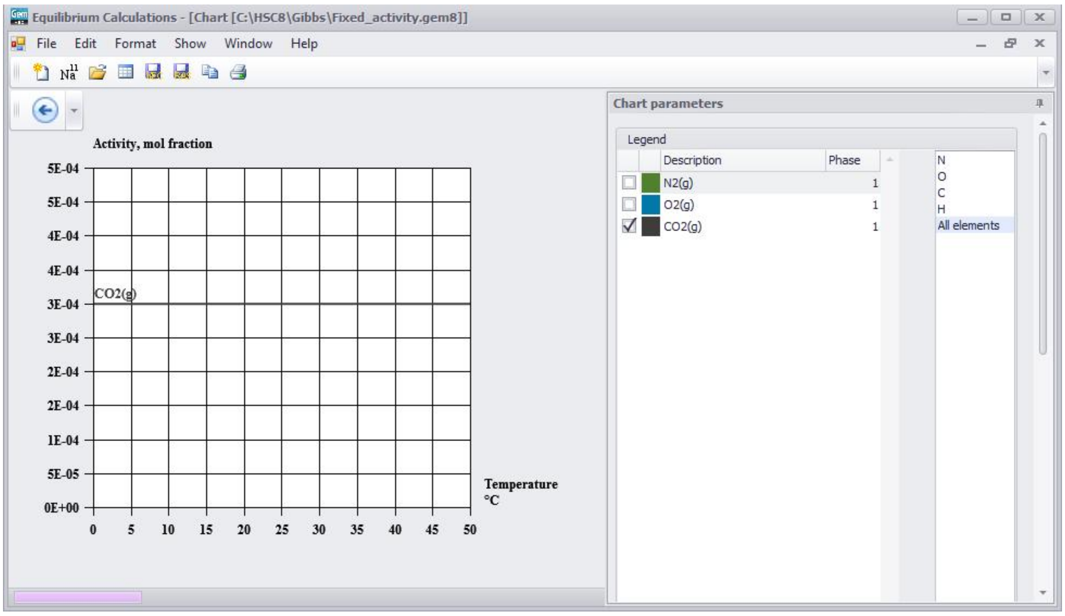
Calculation Options
☐ Infinite Gas P #1
☐ Remove Step % Column ON
☑ Fixed Activity
☐ Pure Substances in Last Phase (Invariant Phases)
☑ Mixing Entropy conversion for aqueous species
☐ Criss-Cobble

Fig. 11. Parameters for Fixed Activity mode.



		Description	Phase
☐	🟩	N2(g)	1
☐	🟦	O2(g)	1
☐	■	CO2(g)	1
☐	🟫	H2O	2
☑	🟧	CO2(a)	2

Fig. 12. Diagram with Fixed Activity.



		Description	Phase
☐	🟩	N2(g)	1
☐	🟦	O2(g)	1
☑	■	CO2(g)	1

Fig. 13. Activity of CO_2(g).

This results in a diagram as in the Open Atmosphere mode, see **Fig. 12**, and you can check that the Activity for CO_2(g) is constant as specified in the Fixed Activity coefficient, see **Fig. 13**.

Pure Substances (“Invariant phases”)

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. 6**.

Criss-Cobble

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.

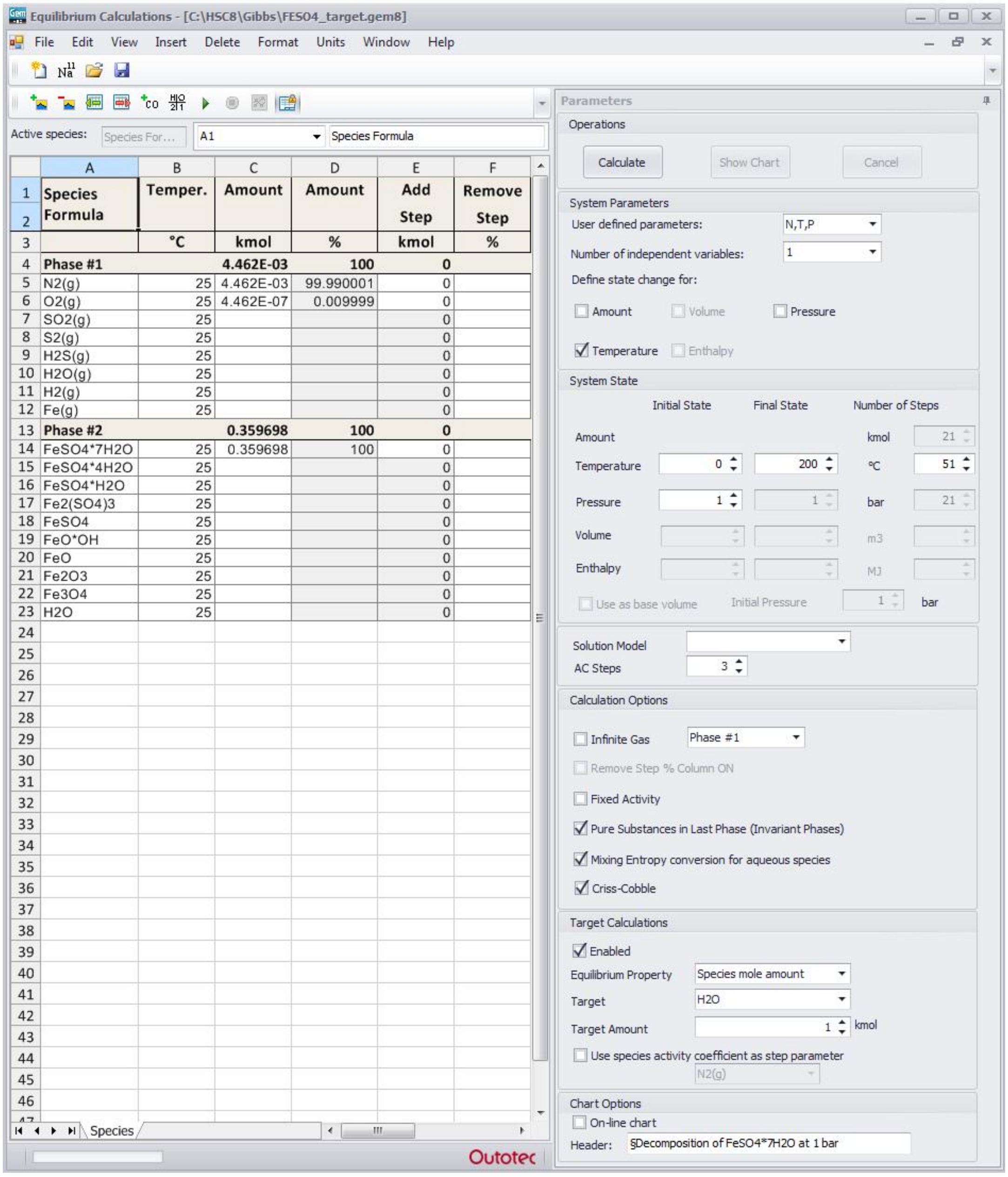
NB! If the Criss-Cobble option is not selected for the GIBBS program, then the activity coefficients of aqueous species may be set to 55.509/X(H2O), which will convert the Raoultian activity scale to the aqueous activity scale. This trick will also give the activities of the results on an aqueous scale, where the concentration units are expressed as moles per liter of H_2O (mol/l).

13.4.6. Target Calculation

The idea of the Target Calculations mode is to add a specific constraint to the general Gibbs Energy Minimization problem and to use a GEM routine to find the point (with specific pressure, temperature, raw material amounts) at which this constraint is fulfilled.

Unlike the Constant Volume and Adiabatic calculation modes, the search can be performed over any valid system parameter (raw material amounts, temperature, pressure, volume, reaction enthalpy) and the user has to set the search interval explicitly. The result is a list of system states within the interval that satisfy the constraint.

For example, you want to find the point where H_2O has an amount of 1 mole. Enable Target Calculations and set the parameters as in **Fig. 14**.



Active species: Species For… A1 Species Formula

	A	B	C	D	E	F
1	**Species**	**Temper.**	**Amount**	**Amount**	**Add**	**Remove**
2	**Formula**				**Step**	**Step**
3		**°C**	**kmol**	**%**	**kmol**	**%**
4	**Phase #1**		**4.462E-03**	**100**	**0**	
5	N2(g)	25	4.462E-03	99.990001	0	
6	O2(g)	25	4.462E-07	0.009999	0	
7	SO2(g)	25			0	
8	S2(g)	25			0	
9	H2S(g)	25			0	
10	H2O(g)	25			0	
11	H2(g)	25			0	
12	Fe(g)	25			0	
13	**Phase #2**		**0.359698**	**100**	**0**	
14	FeSO4*7H2O	25	0.359698	100	0	
15	FeSO4*4H2O	25			0	
16	FeSO4*H2O	25			0	
17	Fe2(SO4)3	25			0	
18	FeSO4	25			0	
19	FeO*OH	25			0	
20	FeO	25			0	
21	Fe2O3	25			0	
22	Fe3O4	25			0	
23	H2O	25			0	

System Parameters

User defined parameters: N,T,P
Number of independent variables: 1
Define state change for:
☐ Amount ☐ Volume ☐ Pressure
☑ Temperature ☐ Enthalpy

System State

	Initial State	Final State		Number of Steps
Amount			kmol	21
Temperature	0	200	°C	51
Pressure	1	1	bar	21
Volume			m3	
Enthalpy			MJ	

☐ Use as base volume Initial Pressure 1 bar

Solution Model
AC Steps 3

Calculation Options

☐ Infinite Gas Phase #1
☐ Remove Step % Column ON
☐ Fixed Activity
☑ Pure Substances in Last Phase (Invariant Phases)
☑ Mixing Entropy conversion for aqueous species
☑ Criss-Cobble

Target Calculations

☑ Enabled
Equilibrium Property Species mole amount
Target H2O
Target Amount 1 kmol
☐ Use species activity coefficient as step parameter
N2(g)

Chart Options

☐ On-line chart
Header: §Decomposition of FeSO4*7H2O at 1 bar

Fig. 14. Parameters for Target Calculation mode.

When you press the Calculate button, the program will make the calculation and show the results as in **Fig. 15**.

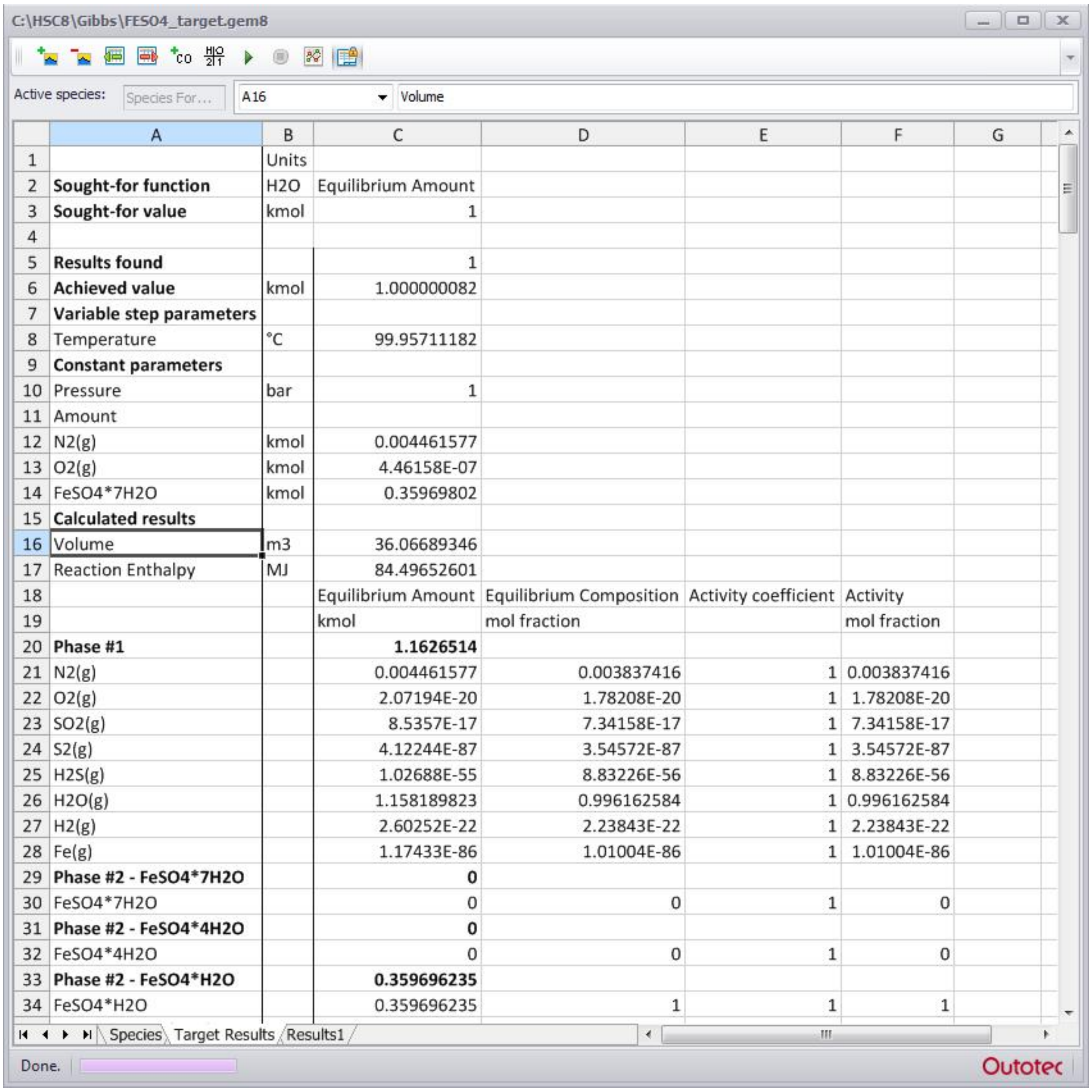
13.4.7. Chart Options

Online Chart

If you check this option, the points on the chart will be drawn at the same time as they are calculated.

Header

You may add any kind of heading for the input file, see **Fig. 6**. The maximum number of characters allowed in the heading is 80. The program automatically adds the heading to the diagrams, see **Fig. 16**.


C:\HSC8\Gibbs\FESO4_target.gem8

Active species: Species For... | A16 | Volume

	A	B	C	D	E	F	G
1		Units					
2	**Sought-for function**	H2O	Equilibrium Amount				
3	**Sought-for value**	kmol	1				
4							
5	**Results found**		1				
6	**Achieved value**	kmol	1.000000082				
7	**Variable step parameters**						
8	Temperature	°C	99.95711182				
9	**Constant parameters**						
10	Pressure	bar	1				
11	Amount						
12	N2(g)	kmol	0.004461577				
13	O2(g)	kmol	4.46158E-07				
14	FeSO4*7H2O	kmol	0.35969802				
15	**Calculated results**						
16	Volume	m3	36.06689346				
17	Reaction Enthalpy	MJ	84.49652601				
18			Equilibrium Amount	Equilibrium Composition	Activity coefficient	Activity	
19			kmol	mol fraction		mol fraction	
20	**Phase #1**		**1.1626514**				
21	N2(g)		0.004461577	0.003837416	1	0.003837416	
22	O2(g)		2.07194E-20	1.78208E-20	1	1.78208E-20	
23	SO2(g)		8.5357E-17	7.34158E-17	1	7.34158E-17	
24	S2(g)		4.12244E-87	3.54572E-87	1	3.54572E-87	
25	H2S(g)		1.02688E-55	8.83226E-56	1	8.83226E-56	
26	H2O(g)		1.158189823	0.996162584	1	0.996162584	
27	H2(g)		2.60252E-22	2.23843E-22	1	2.23843E-22	
28	Fe(g)		1.17433E-86	1.01004E-86	1	1.01004E-86	
29	**Phase #2 - FeSO4*7H2O**		**0**				
30	FeSO4*7H2O		0	0	1	0	
31	**Phase #2 - FeSO4*4H2O**		**0**				
32	FeSO4*4H2O		0	0	1	0	
33	**Phase #2 - FeSO4*H2O**		**0.359696235**				
34	FeSO4*H2O		0.359696235	1	1	1	

Fig. 15. Results for Target Calculation mode

13.5. Diagrams

The diagrams can be drawn, for example, as a function of a specified reactant amount or equilibrium temperature. You can draw a diagram by pressing **Show Chart** on the **Parameters Panel** or select **Show Chart** in the **View** menu.

You can select species for the axes by clicking the desired button "..." and selecting the 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. You can select a group of species by selecting different phases or/and elements and then selecting the item from this group.

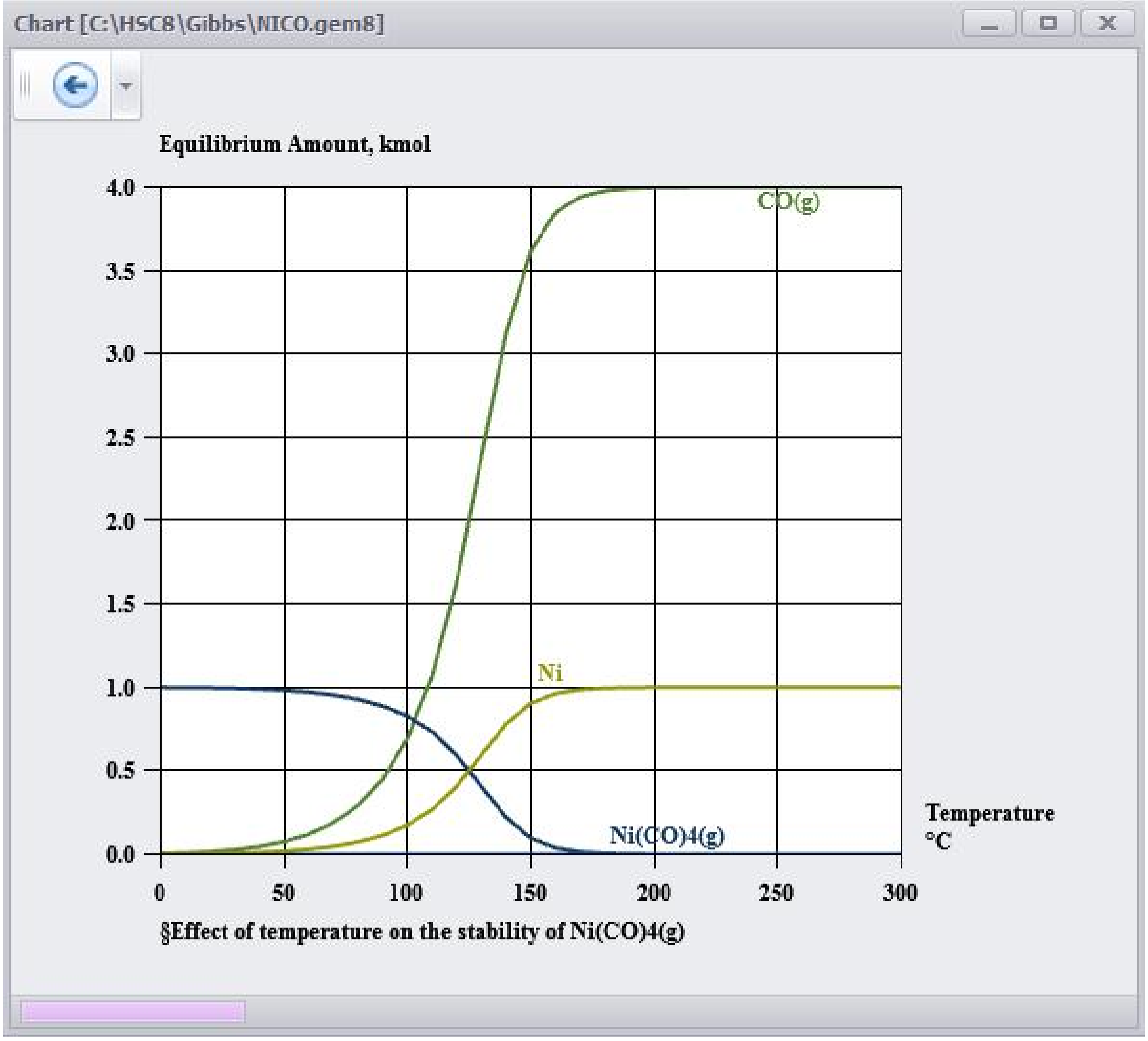
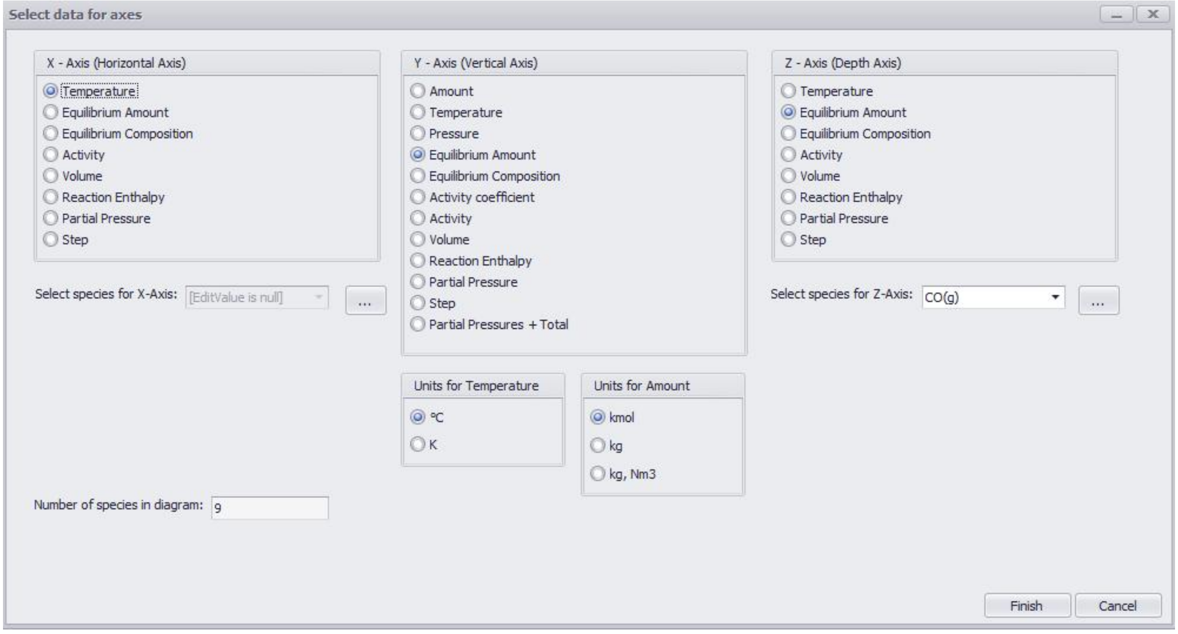


Fig. 16. 2D diagram.



X - Axis (Horizontal Axis)
- ● Temperature
- ○ Equilibrium Amount
- ○ Equilibrium Composition
- ○ Activity
- ○ Volume
- ○ Reaction Enthalpy
- ○ Partial Pressure
- ○ Step

Select species for X-Axis: [EditValue is null]

Y - Axis (Vertical Axis)
- ○ Amount
- ○ Temperature
- ○ Pressure
- ● Equilibrium Amount
- ○ Equilibrium Composition
- ○ Activity coefficient
- ○ Activity
- ○ Volume
- ○ Reaction Enthalpy
- ○ Partial Pressure
- ○ Step
- ○ Partial Pressures + Total

Z - Axis (Depth Axis)
- ○ Temperature
- ● Equilibrium Amount
- ○ Equilibrium Composition
- ○ Activity
- ○ Volume
- ○ Reaction Enthalpy
- ○ Partial Pressure
- ○ Step

Select species for Z-Axis: CO(g)

Units for Temperature
- ● °C
- ○ K

Units for Amount
- ● kmol
- ○ kg
- ○ kg, Nm3

Number of species in diagram: 9

Fig. 17. Select data for axes.

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

If you are working with an aqueous system, you will be given a **pH** option for the x-axis. This option will draw the results as a function of pH.

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 for the diagram.

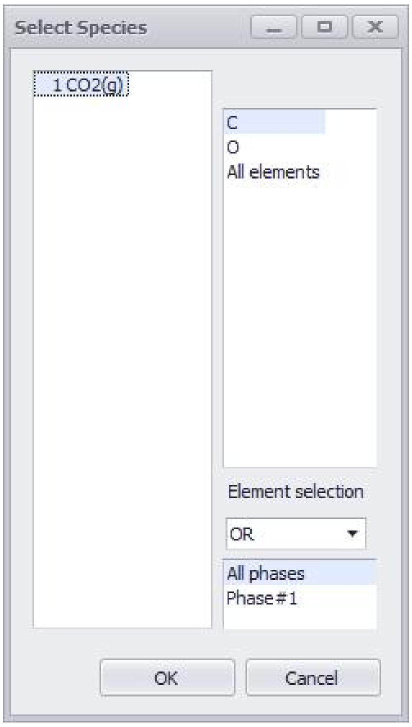


Fig. 18. Select Species.

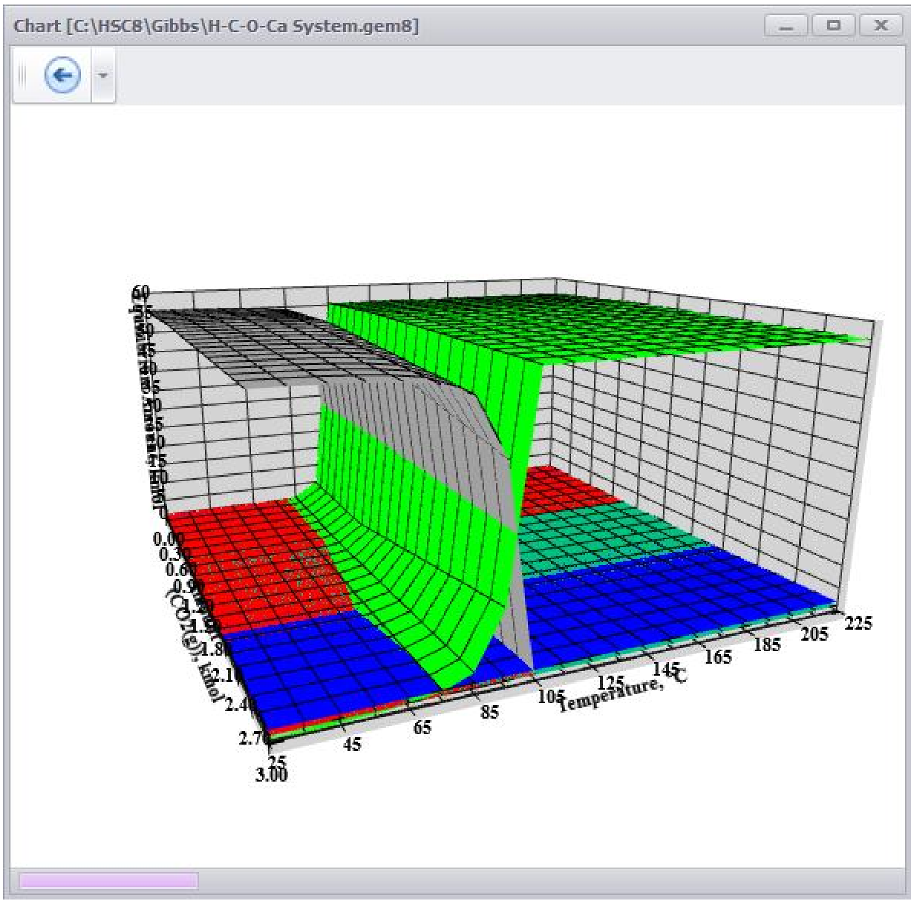


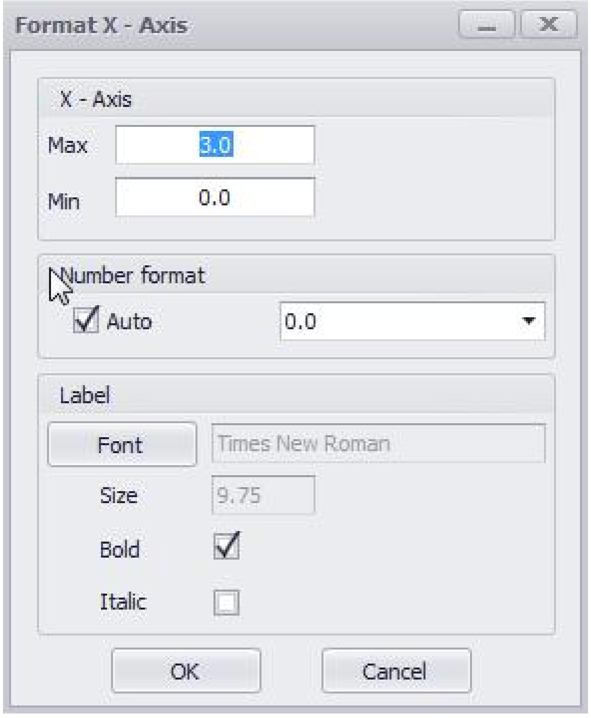
Fig. 19. 3D diagram.

When you press **Finish** in the Axis menu, **Fig. 16**, the program reads the equilibrium results and draws the diagram using the default scale, font, line width, etc. selections, see **Fig. 16** and **Fig. 19**. 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. 16** and **Fig. 19**, by using several formatting options:

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-axes, see **Fig. 20**. In some cases it is also advantageous to change the y-axis to logarithmic scale in order to display 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.

1. When the scales are OK, you can relocate any **label** (species, x- and y-axis heading, etc.) with the 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.
2. The **line width** of curves, species label font, etc. may be changed by double clicking the species labels or selecting the label with the 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. 21**. Note that line styles other than solid are available only for line widths smaller than 0.3 mm.
3. The walls in a 3D diagram may be changed by selecting **Format Walls** from the Format menu. You can change gridlines, color, axis, etc, see **Fig. 22**.

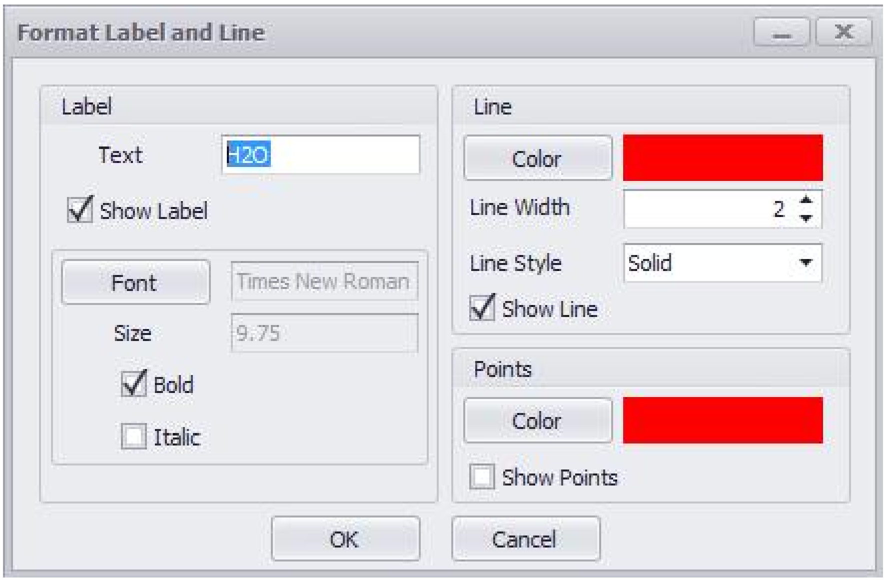

Format X - Axis

X - Axis
Max 3.0
Min 0.0

Number format
☑ Auto 0.0

Label
Font Times New Roman
Size 9.75
Bold ☑
Italic ☐

Fig. 20. Changing scales, scale number format and font settings.



Text: H2O
☑ Show Label
Font: Times New Roman
Size: 9.75
☑ Bold
☐ Italic

Line
Color: 🟥
Line Width: 2
Line Style: Solid
☑ Show Line

Points
Color: 🟥
☐ Show Points

Fig. 21. Changing label and line specifications.

Y - Axis
Gridlines: ● On ○ Off
Line style: Solid

X - Axis
Gridlines: ● On ○ Off
Line style: Solid

Fig. 22. Changing wall specifications.

1. When you are satisfied with the diagram you can print it by pressing **Print**.
2. 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 **Show Table**.
3. You can copy the diagram to the Clipboard by pressing **Copy**, and paste the diagram into 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.
4. With **Save as vector** and **Save as raster** you can save the diagram in a file.

13.5.1. Toolbar

Drawing additional objects or writing some labels on a diagram can be very helpful in some cases. You can select one of the shapes (line, arrow, rectangle or circle) or label, see **Fig. 23**. If you want some other shape or label you can use the toolbar options. You can format the shape by selecting the inner color or border color, line width, line type. You can make the figure transparent, move to the back or to the front, see **Fig. 23**.
You can delete any shape using × on the toolbar.

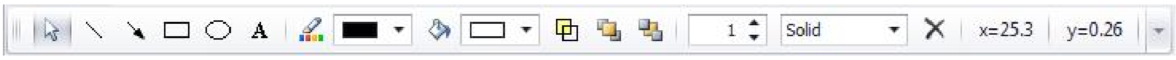


Fig. 23. Toolbar.

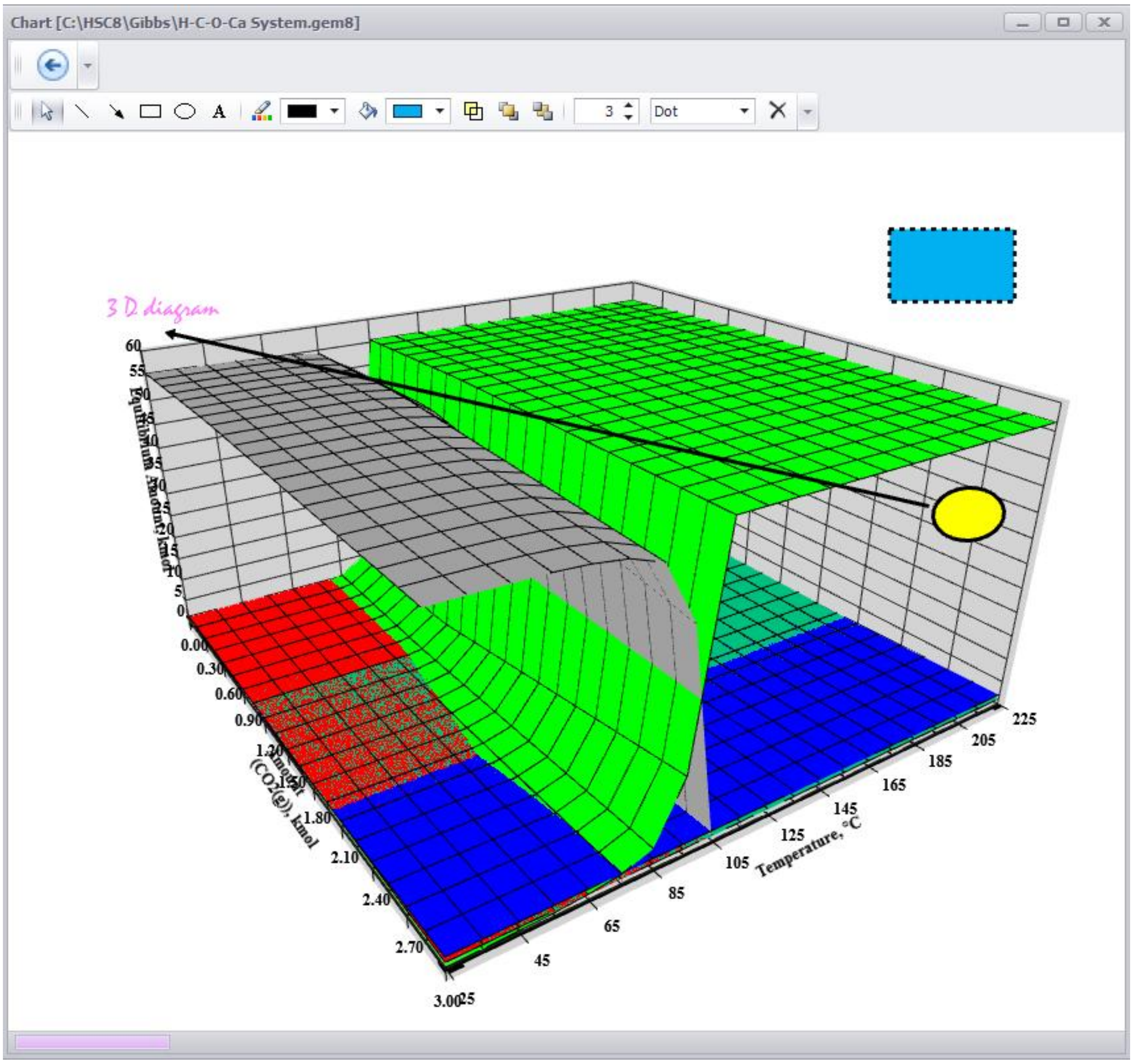
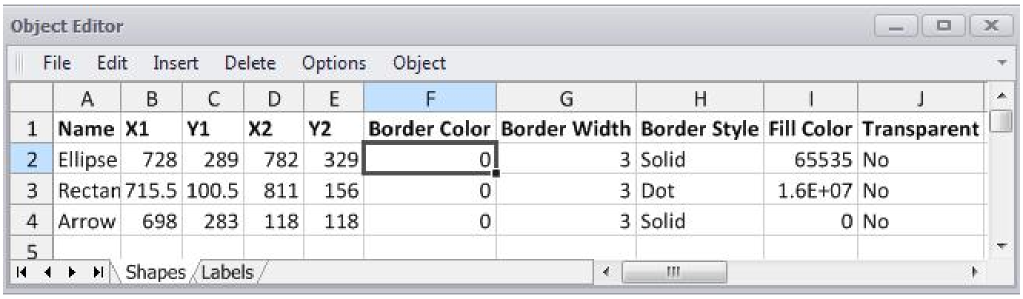


Fig. 24. 3D diagram with shapes.

The X and Y labels on the toolbar show the cursor's location. These are only for 2D diagrams.

13.5.2. Object Editor



	A	B	C	D	E	F	G	H	I	J
1	Name	X1	Y1	X2	Y2	Border Color	Border Width	Border Style	Fill Color	Transparent
2	Ellipse	728	289	782	329	0	3	Solid	65535	No
3	Rectan	715.5	100.5	811	156	0	3	Dot	1.6E+07	No
4	Arrow	698	283	118	118	0	3	Solid	0	No
5										

Fig. 25. Object Editor of the objects in **Fig. 24**.

There is one more way to modify diagrams by specifying the coordinates, sizes and colors of objects in Object Editor. You can **Insert, Delete** or **Edit** the shape. In order to edit you should change the parameters of the shape. There are two sheets in Object Editor: **Shapes** and **Labels**.

13.5.3. Chart Parameters

The Diagram window appears with the Chart Parameters panel instead of the Parameters panel. You can use filter options to change the diagram's appearance.

Filter

The main idea of this option is to filter the list of species on the diagram. You can change this list by selecting different phases and elements. You can select one, several, or all at once (by selecting "**All phases**" or "**All elements**"). The option "**All must exist**" means that if you select several elements, the filter should find only the species that include all of the selected elements.

	Description	Phase
☑	CO2(g)	1
☑	H2O(g)	1
☑	O2(g)	1
☑	N2(g)	1
☑	CO3(-2a)	2
☑	C2O4(-2a)	2
☑	Ca(+2a)	2
☑	CaOH(+a)	2
☑	H(+a)	2
☑	HCO2(-a)	2
☑	HCO3(-a)	2
☑	H2O	2
☑	HO2(-a)	2
☑	OH(-a)	2
☑	CaCO3	3
☑	Ca(OH)2	4

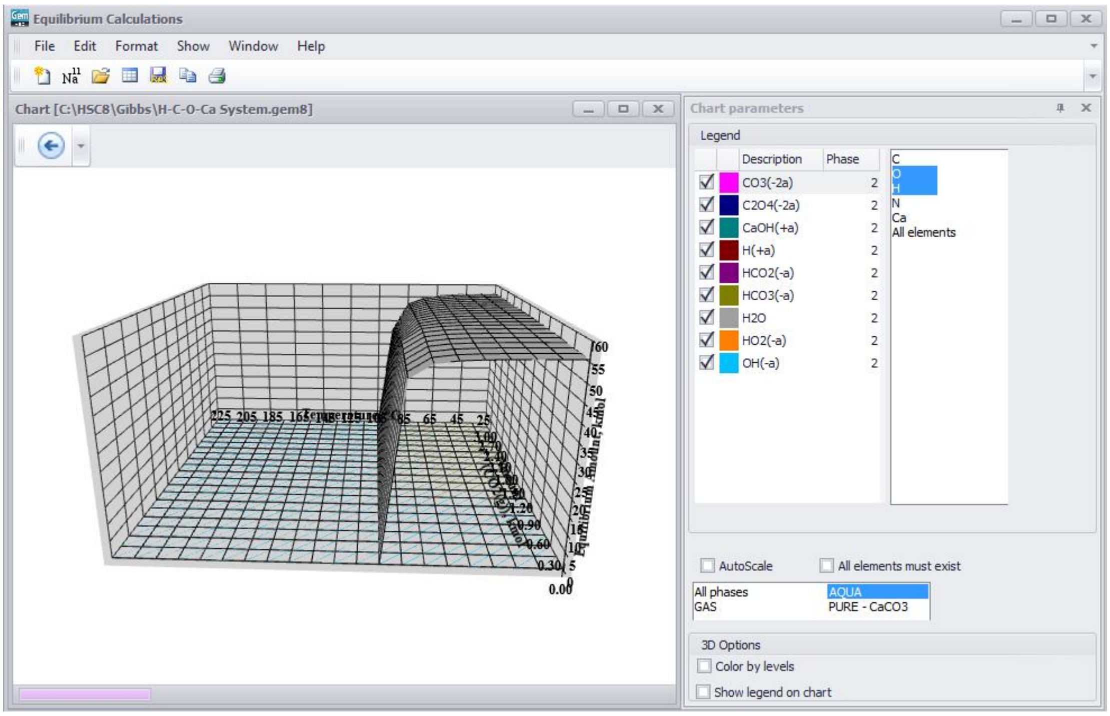
C
O
H
N
Ca
All elements

☐ AutoScale ☐ All elements must exist

All phases
GAS
AQUA
PURE - CaCO3
PURE - Ca(OH)2

3D Options
☐ Color by levels
☐ Show legend on chart

Fig. 26. Chart parameters.



	Description	Phase
☑	CO3(-2a)	2
☑	C2O4(-2a)	2
☑	CaOH(+a)	2
☑	H(+a)	2
☑	HCO2(-a)	2
☑	HCO3(-a)	2
☑	H2O	2
☑	HO2(-a)	2
☑	OH(-a)	2

C
O
H
N
Ca
All elements

☐ AutoScale ☐ All elements must exist

All phases
GAS
AQUA
PURE - CaCO3

3D Options
☐ Color by levels
☐ Show legend on chart

Fig. 27. Filtering species in a diagram.

Auto Scale

This option helps you to use an appropriate scale when the maximum value of the diagram's lines is very small. When you check this option, the scale changes automatically and you can work with lines with small values.

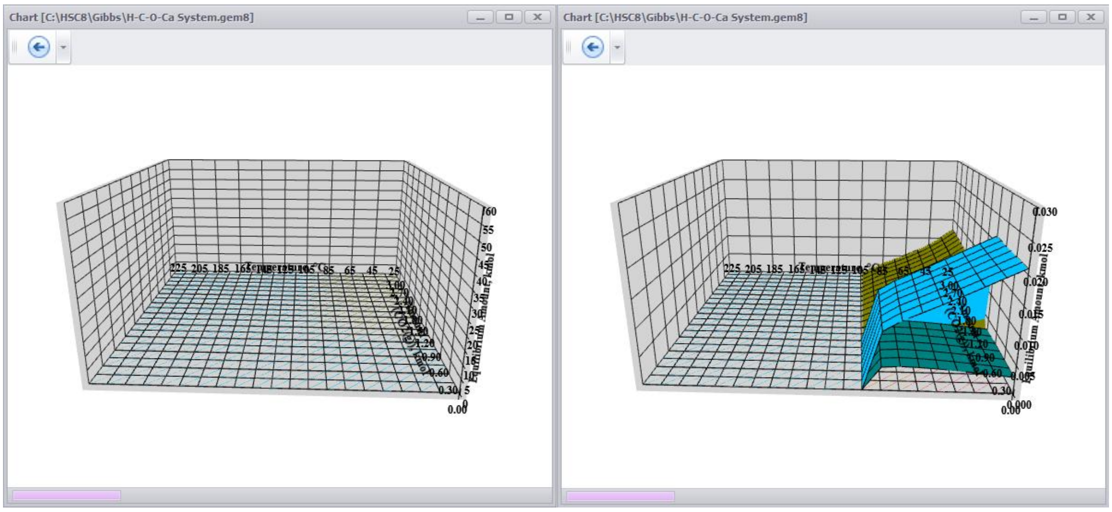
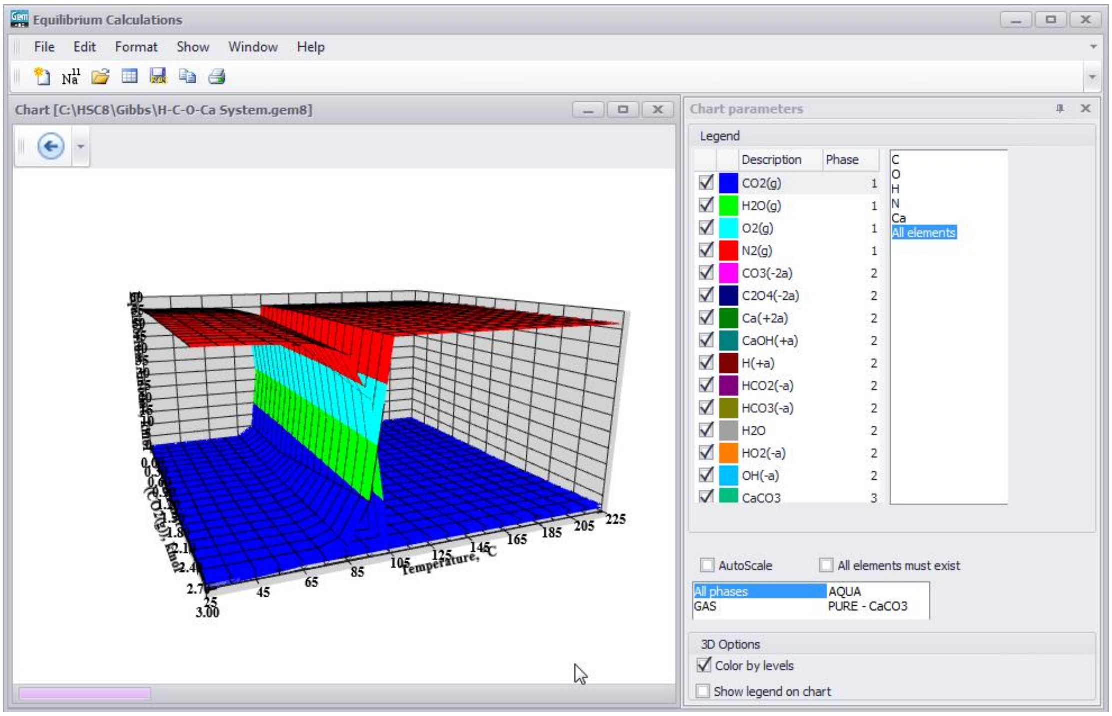


Fig. 28. Auto scale option: uncheck and check (see speciation in **Fig. 27** with H2O not chosen).

Color by Levels

This option allows you to colorize different levels of height charts in different colors. You can use this option only in a 3D diagram, see **Fig. 29**.



		Description	Phase
☑	🟦	CO2(g)	1
☑	🟩	H2O(g)	1
☑	🟦	O2(g)	1
☑	🟥	N2(g)	1
☑	🟪	CO3(-2a)	2
☑	🟦	C2O4(-2a)	2
☑	🟩	Ca(+2a)	2
☑	🟩	CaOH(+a)	2
☑	🟥	H(+a)	2
☑	🟪	HCO2(-a)	2
☑	🟨	HCO3(-a)	2
☑	⬜	H2O	2
☑	🟧	HO2(-a)	2
☑	🟦	OH(-a)	2
☑	🟩	CaCO3	3

C
O
H
N
Ca
All elements

☐ AutoScale ☐ All elements must exist

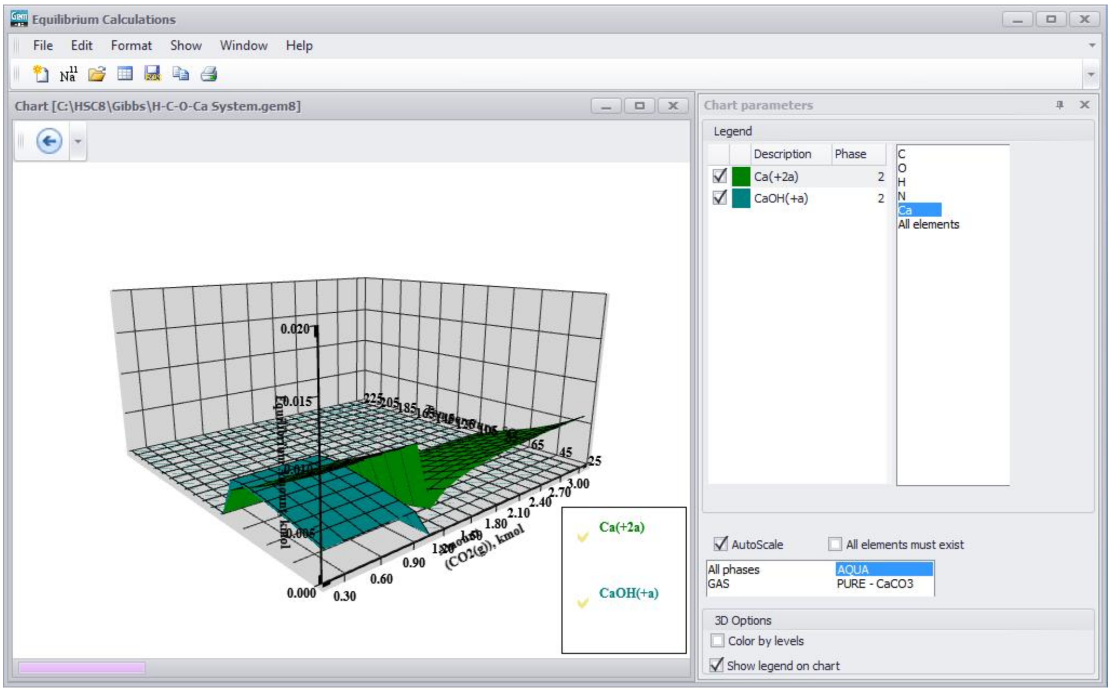
All phases
AQUA
GAS
PURE - CaCO3

3D Options
☑ Color by levels
☐ Show legend on chart

Fig. 29. Option Color by levels on diagram, see **Fig. 19** for comparison.

Show Legend on Chart

This option allows you to add one more panel on a 3D diagram legend panel, see **Fig. 30**. This panel duplicates the legend on the Chart Parameters panel, so you can check and uncheck species. The filter also changes it.



Legend

	Description	Phase
☑ 🟩	Ca(+2a)	2
☑ 🟩	CaOH(+a)	2

C
O
H
N
Ca
All elements

☑ AutoScale
☐ All elements must exist

All phases
GAS
AQUA
PURE - CaCO3

3D Options
☐ Color by levels
☑ Show legend on chart

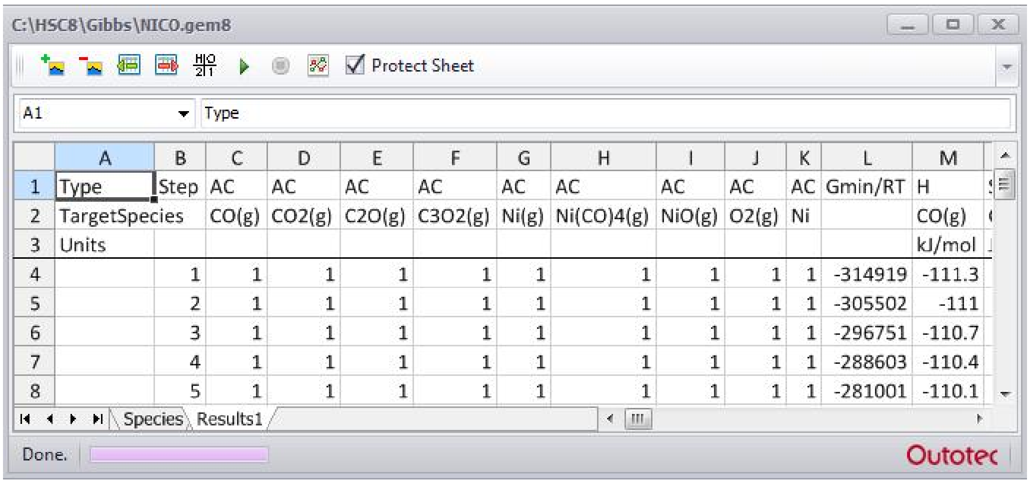
Fig. 30. 3D diagram with legend.

13.6. Equilibrium Diagram Tables

You can display the equilibrium results in tabular format by pressing **Show Table** in the Diagram window. The Table window has several Excel-type features in a similar way to the other spreadsheets in HSC. The most important features are:

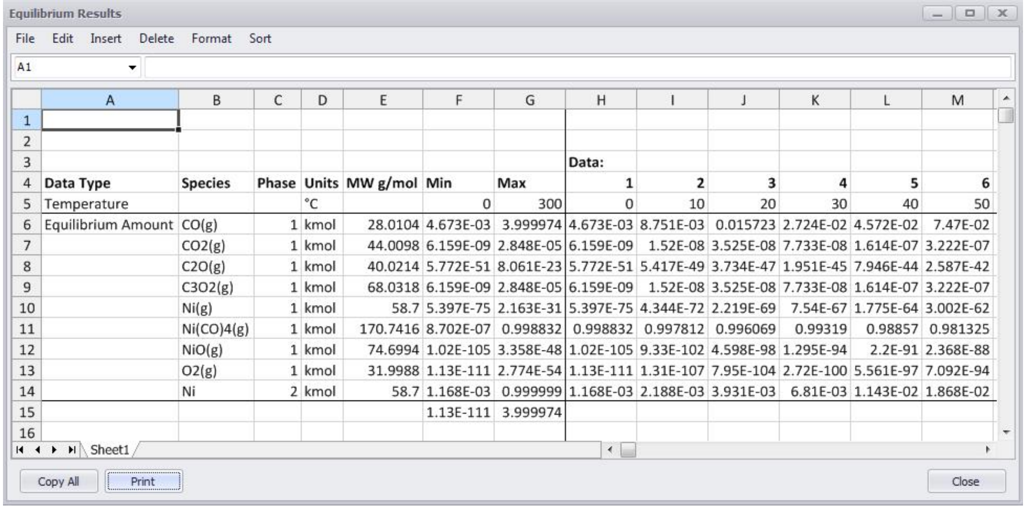
1. **Copy All** puts the whole table on the Clipboard, and pastes this table, for example, into MS Excel. You can also copy and paste smaller cell ranges using the **Copy** and **Paste** selections in the **Edit** menu, see **Fig. 32**.
2. You can also save the table using different formats, such as ASCII text and Excel by selecting **Save** from the **File** menu.
3. The **Species** sheet contains the data of the diagram; the figures in this sheet can be edited if you are not satisfied with the results.

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. 32**. Setup and Preview options are also available for printing.



	A	B	C	D	E	F	G	H	I	J	K	L	M
1	Type	Step	AC	AC	AC	AC	AC	AC	AC	AC	AC	Gmin/RT	H
2	TargetSpecies		CO(g)	CO2(g)	C2O(g)	C3O2(g)	Ni(g)	Ni(CO)4(g)	NiO(g)	O2(g)	Ni		CO(g)
3	Units												kJ/mol
4		1	1	1	1	1	1	1	1	1	1	-314919	-111.3
5		2	1	1	1	1	1	1	1	1	1	-305502	-111
6		3	1	1	1	1	1	1	1	1	1	-296751	-110.7
7		4	1	1	1	1	1	1	1	1	1	-288603	-110.4
8		5	1	1	1	1	1	1	1	1	1	-281001	-110.1

Fig. 31. Results sheet, calculated automatically.



	A	B	C	D	E	F	G	H	I	J	K	L	M
1													
2													
3								Data:					
4	Data Type	Species	Phase	Units	MW g/mol	Min	Max	1	2	3	4	5	6
5	Temperature			°C		0	300	0	10	20	30	40	50
6	Equilibrium Amount	CO(g)	1	kmol	28.0104	4.673E-03	3.999974	4.673E-03	8.751E-03	0.015723	2.724E-02	4.572E-02	7.47E-02
7		CO2(g)	1	kmol	44.0098	6.159E-09	2.848E-05	6.159E-09	1.52E-08	3.525E-08	7.733E-08	1.614E-07	3.222E-07
8		C2O(g)	1	kmol	40.0214	5.772E-51	8.061E-23	5.772E-51	5.417E-49	3.734E-47	1.951E-45	7.946E-44	2.587E-42
9		C3O2(g)	1	kmol	68.0318	6.159E-09	2.848E-05	6.159E-09	1.52E-08	3.525E-08	7.733E-08	1.614E-07	3.222E-07
10		Ni(g)	1	kmol	58.7	5.397E-75	2.163E-31	5.397E-75	4.344E-72	2.219E-69	7.54E-67	1.775E-64	3.002E-62
11		Ni(CO)4(g)	1	kmol	170.7416	8.702E-07	0.998832	0.998832	0.997812	0.996069	0.99319	0.98857	0.981325
12		NiO(g)	1	kmol	74.6994	1.02E-105	3.358E-48	1.02E-105	9.33E-102	4.598E-98	1.295E-94	2.2E-91	2.368E-88
13		O2(g)	1	kmol	31.9988	1.13E-111	2.774E-54	1.13E-111	1.31E-107	7.95E-104	2.72E-100	5.561E-97	7.092E-94
14		Ni	2	kmol	58.7	1.168E-03	0.999999	1.168E-03	2.188E-03	3.931E-03	6.81E-03	1.143E-02	1.868E-02
15						1.13E-111	3.999974						
16													

Fig. 32. Equilibrium Diagram Table.

13.7. Restriction of C_p Extrapolation

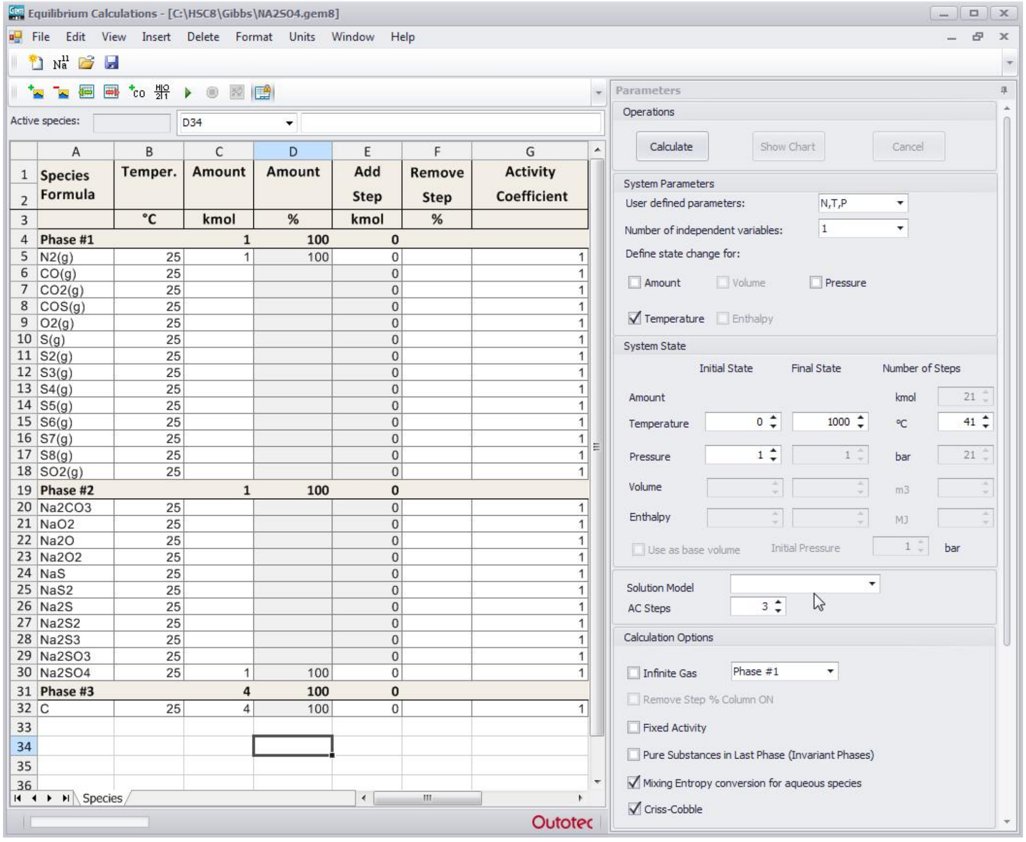
This feature allows the user to remove the selected species from the calculation if the system temperature falls outside the temperature range of C_p data for that species. The Cp data is always given for limited temperature ranges in HSC database. HSC automatically extrapolates Cp data outside these ranges. Usually this works just fine, however, in some cases Cp extrapolation may lead to errors. Automatic removal of species will solve this problem.

The basic approach is as follows: if there are any temperature points at which some of the species will be outside its defined temperature range, the user is shown the Warnings window that allows marking of the species to be removed outside its temperature range.

Note: the old IGI file format does not contain an upper temperature limit for species. When importing IGI files, the program sets the upper limit to 20000 K.

Plain Calculations

The simplest approach is the normal calculations mode (N, T, P). The Warnings window uses the temperature range defined in the System State section of the Parameters panel. For example, consider the system in NA2SO4.gem8. If the user presses Calculate, the Warnings window will be shown, see **Fig. 34**.



Active species: D34

	A	B	C	D	E	F	G
1-2	Species Formula	Temper.	Amount	Amount	Add Step	Remove Step	Activity Coefficient
3		°C	kmol	%	kmol	%	
4	**Phase #1**		**1**	**100**	**0**		
5	N2(g)	25	1	100	0		1
6	CO(g)	25			0		1
7	CO2(g)	25			0		1
8	COS(g)	25			0		1
9	O2(g)	25			0		1
10	S(g)	25			0		1
11	S2(g)	25			0		1
12	S3(g)	25			0		1
13	S4(g)	25			0		1
14	S5(g)	25			0		1
15	S6(g)	25			0		1
16	S7(g)	25			0		1
17	S8(g)	25			0		1
18	SO2(g)	25			0		1
19	**Phase #2**		**1**	**100**	**0**		
20	Na2CO3	25			0		1
21	NaO2	25			0		1
22	Na2O	25			0		1
23	Na2O2	25			0		1
24	NaS	25			0		1
25	NaS2	25			0		1
26	Na2S	25			0		1
27	Na2S2	25			0		1
28	Na2S3	25			0		1
29	Na2SO3	25			0		1
30	Na2SO4	25	1	100	0		1
31	**Phase #3**		**4**	**100**	**0**		
32	C	25	4	100	0		1
33							
34							
35							
36							

System Parameters
User defined parameters: N,T,P
Number of independent variables: 1
Define state change for:
☐ Amount ☐ Volume ☐ Pressure
☑ Temperature ☐ Enthalpy

System State

	Initial State	Final State		Number of Steps
Amount			kmol	21
Temperature	0	1000	°C	41
Pressure	1	1	bar	21
Volume			m3	
Enthalpy			MJ	

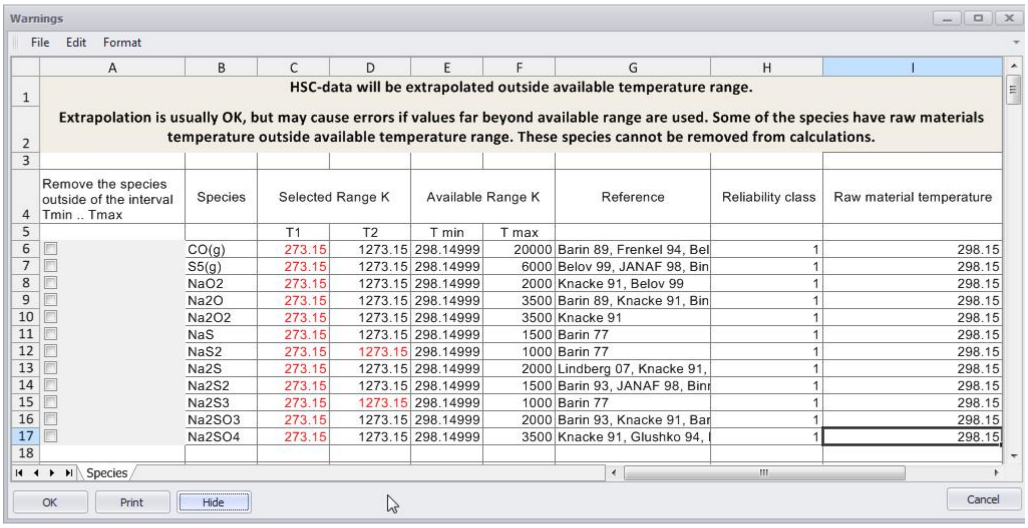
☐ Use as base volume Initial Pressure 1 bar

Solution Model
AC Steps 3

Calculation Options
☐ Infinite Gas Phase #1
☐ Remove Step % Column ON
☐ Fixed Activity
☐ Pure Substances in Last Phase (Invariant Phases)
☑ Mixing Entropy conversion for aqueous species
☑ Criss-Cobble

Fig. 33. NA2SO4.gem8 test case.

The Warnings windows show all the species that do not have Cp data at least for some points in the system temperature range. This window allows the user to check the species that should be deleted outside the defined range. If at some temperature point the selection requires the deletion of all species containing some element, a message is shown to the user and the calculation is prevented.

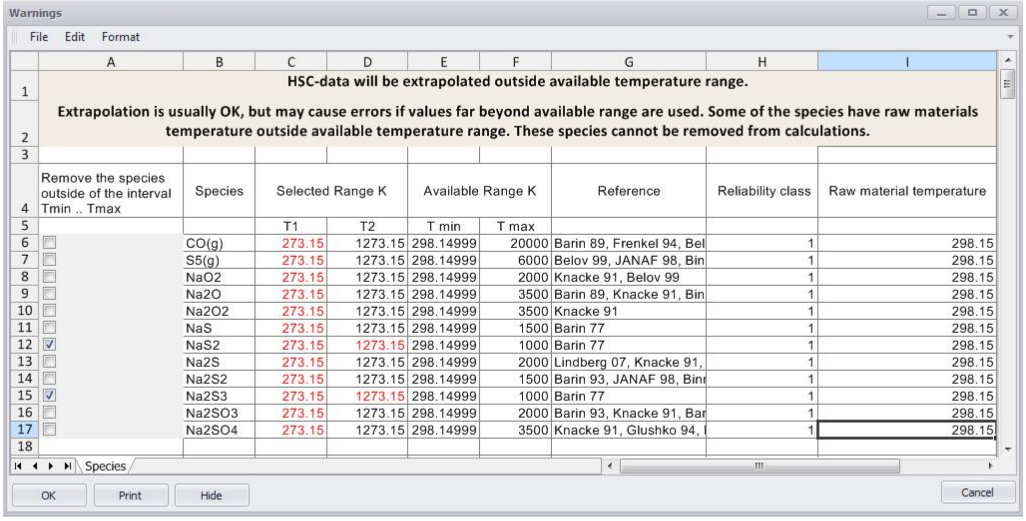


HSC-data will be extrapolated outside available temperature range.

Extrapolation is usually OK, but may cause errors if values far beyond available range are used. Some of the species have raw materials temperature outside available temperature range. These species cannot be removed from calculations.

Remove the species outside of the interval Tmin .. Tmax	Species	Selected Range K		Available Range K		Reference	Reliability class	Raw material temperature
		T1	T2	T min	T max			
☐	CO(g)	273.15	1273.15	298.14999	20000	Barin 89, Frenkel 94, Bel	1	298.15
☐	S5(g)	273.15	1273.15	298.14999	6000	Belov 99, JANAF 98, Bin	1	298.15
☐	NaO2	273.15	1273.15	298.14999	2000	Knacke 91, Belov 99	1	298.15
☐	Na2O	273.15	1273.15	298.14999	3500	Barin 89, Knacke 91, Bin	1	298.15
☐	Na2O2	273.15	1273.15	298.14999	3500	Knacke 91	1	298.15
☐	NaS	273.15	1273.15	298.14999	1500	Barin 77	1	298.15
☐	NaS2	273.15	1273.15	298.14999	1000	Barin 77	1	298.15
☐	Na2S	273.15	1273.15	298.14999	2000	Lindberg 07, Knacke 91,	1	298.15
☐	Na2S2	273.15	1273.15	298.14999	1500	Barin 93, JANAF 98, Bin	1	298.15
☐	Na2S3	273.15	1273.15	298.14999	1000	Barin 77	1	298.15
☐	Na2SO3	273.15	1273.15	298.14999	2000	Barin 93, Knacke 91, Bar	1	298.15
☐	Na2SO4	273.15	1273.15	298.14999	3500	Knacke 91, Glushko 94,	1	298.15

Fig. 34. Warnings window for NA2SO4.gem8 example.



HSC-data will be extrapolated outside available temperature range.

Extrapolation is usually OK, but may cause errors if values far beyond available range are used. Some of the species have raw materials temperature outside available temperature range. These species cannot be removed from calculations.

Remove the species outside of the interval Tmin .. Tmax	Species	Selected Range K		Available Range K		Reference	Reliability class	Raw material temperature
		T1	T2	T min	T max			
☐	CO(g)	273.15	1273.15	298.14999	20000	Barin 89, Frenkel 94, Bel	1	298.15
☐	S5(g)	273.15	1273.15	298.14999	6000	Belov 99, JANAF 98, Bin	1	298.15
☐	NaO2	273.15	1273.15	298.14999	2000	Knacke 91, Belov 99	1	298.15
☐	Na2O	273.15	1273.15	298.14999	3500	Barin 89, Knacke 91, Bin	1	298.15
☐	Na2O2	273.15	1273.15	298.14999	3500	Knacke 91	1	298.15
☐	NaS	273.15	1273.15	298.14999	1500	Barin 77	1	298.15
☑	NaS2	273.15	1273.15	298.14999	1000	Barin 77	1	298.15
☐	Na2S	273.15	1273.15	298.14999	2000	Lindberg 07, Knacke 91,	1	298.15
☐	Na2S2	273.15	1273.15	298.14999	1500	Barin 93, JANAF 98, Bin	1	298.15
☑	Na2S3	273.15	1273.15	298.14999	1000	Barin 77	1	298.15
☐	Na2SO3	273.15	1273.15	298.14999	2000	Barin 93, Knacke 91, Bar	1	298.15
☐	Na2SO4	273.15	1273.15	298.14999	3500	Knacke 91, Glushko 94,	1	298.15

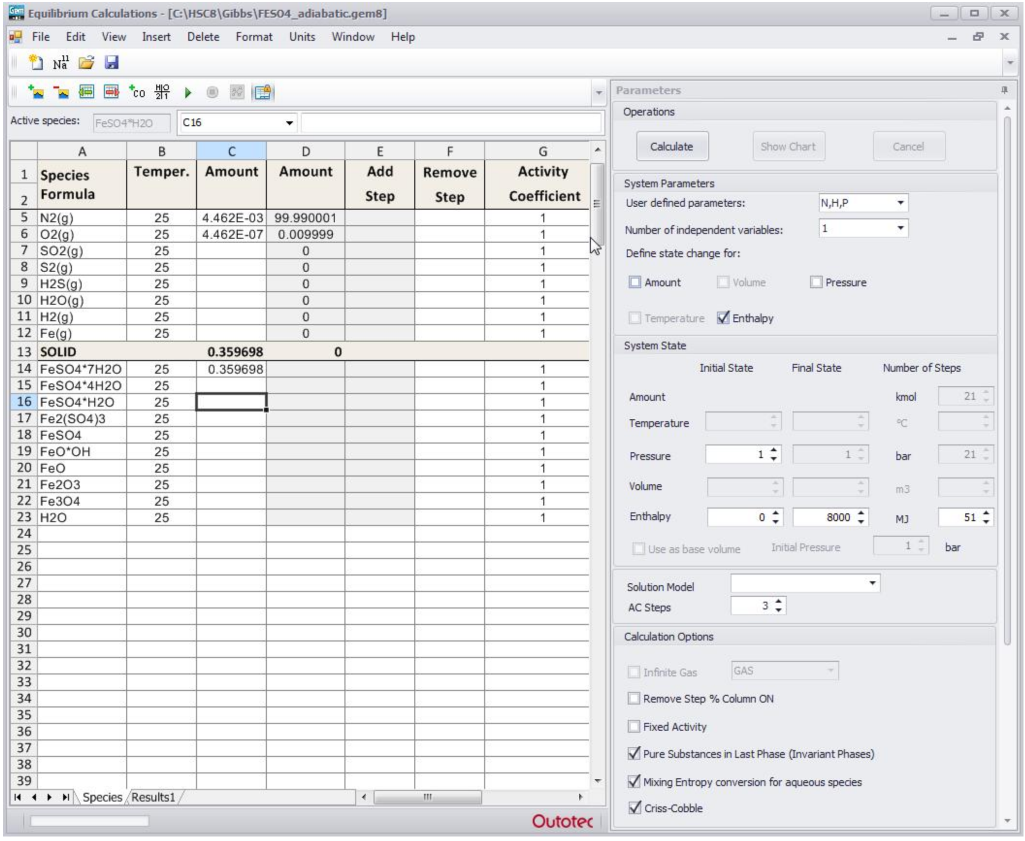
Fig. 35. Warnings window for NA2SO4.gem8 with species selected for removal.

After the user presses OK, the calculation will begin. The species marked for removal will be removed outside the available temperature range.

Calculations That Search for Temperature (Adiabatic System)

While in the normal calculation mode (N, T, P) the user defines the temperature range for the system, there are calculation modes where the temperature range is defined by the program. In the Constant Volume (N, P, V) and Adiabatic (N, H, P) modes, the temperature is found by binary search in the range 0 – 20000 K. This means that more species are subject to extrapolation. The new warnings window handles this by setting the selected range to 0 – 20000 K. If the user selects a species to be removed, it will be removed at the search points outside the species temperature range.

In the Adiabatic and Constant Volume modes with base volume calculation, the temperature of the raw material should be taken into account. If the temperature of the raw material lies outside the temperature range for that species, a warning is shown. The removal of the species in this case is prohibited because it would lead to an illogical result (the user calculates initial system enthalpy based on data that they consider incorrect).



Active species: FeSO4*H2O
C16

	A	B	C	D	E	F	G
1–2	Species Formula	Temper.	Amount	Amount	Add Step	Remove Step	Activity Coefficient
5	N2(g)	25	4.462E-03	99.990001			1
6	O2(g)	25	4.462E-07	0.009999			1
7	SO2(g)	25		0			1
8	S2(g)	25		0			1
9	H2S(g)	25		0			1
10	H2O(g)	25		0			1
11	H2(g)	25		0			1
12	Fe(g)	25		0			1
13	**SOLID**		**0.359698**	**0**			
14	FeSO4*7H2O	25	0.359698				1
15	FeSO4*4H2O	25					1
16	FeSO4*H2O	25					1
17	Fe2(SO4)3	25					1
18	FeSO4	25					1
19	FeO*OH	25					1
20	FeO	25					1
21	Fe2O3	25					1
22	Fe3O4	25					1
23	H2O	25					1

System Parameters
User defined parameters: N,H,P
Number of independent variables: 1
Define state change for:
☐ Amount ☐ Volume ☐ Pressure
☐ Temperature ☑ Enthalpy

System State

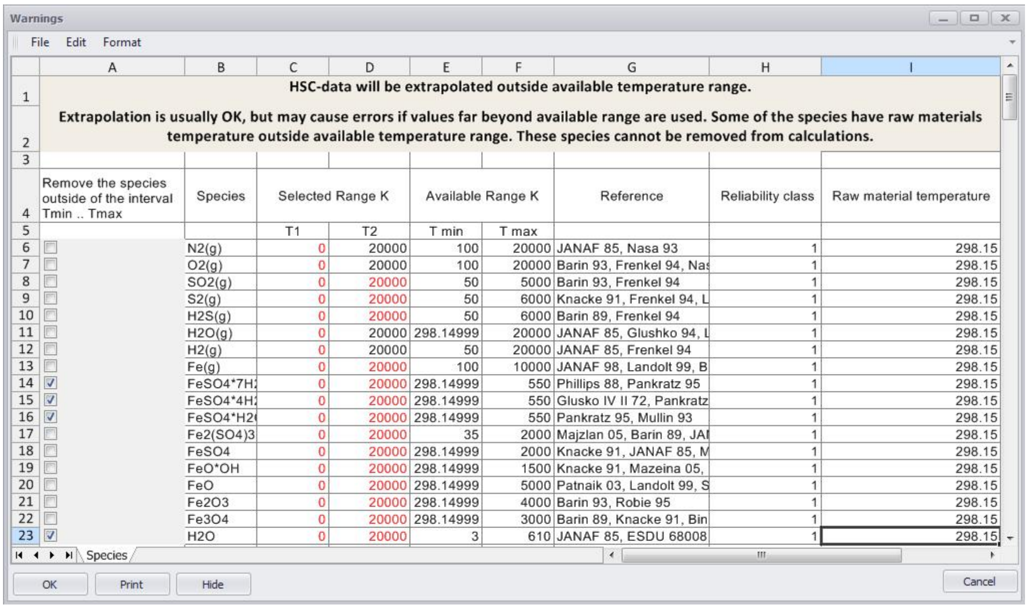
	Initial State	Final State		Number of Steps
Amount			kmol	21
Temperature			°C	
Pressure	1	1	bar	21
Volume			m3	
Enthalpy	0	8000	MJ	51

☐ Use as base volume Initial Pressure 1 bar

Solution Model
AC Steps 3

Calculation Options
☐ Infinite Gas GAS
☐ Remove Step % Column ON
☐ Fixed Activity
☑ Pure Substances in Last Phase (Invariant Phases)
☑ Mixing Entropy conversion for aqueous species
☑ Criss-Cobble

Fig. 36. FESO4_adiabatic.gem8 example for adiabatic calculation.



HSC-data will be extrapolated outside available temperature range.

Extrapolation is usually OK, but may cause errors if values far beyond available range are used. Some of the species have raw materials temperature outside available temperature range. These species cannot be removed from calculations.

	Remove the species outside of the interval Tmin .. Tmax	Species	Selected Range K		Available Range K		Reference	Reliability class	Raw material temperature
5			T1	T2	T min	T max			
6	☐	N2(g)	0	20000	100	20000	JANAF 85, Nasa 93	1	298.15
7	☐	O2(g)	0	20000	100	20000	Barin 93, Frenkel 94, Nas	1	298.15
8	☐	SO2(g)	0	20000	50	5000	Barin 93, Frenkel 94	1	298.15
9	☐	S2(g)	0	20000	50	6000	Knacke 91, Frenkel 94, L	1	298.15
10	☐	H2S(g)	0	20000	50	6000	Barin 89, Frenkel 94	1	298.15
11	☐	H2O(g)	0	20000	298.14999	20000	JANAF 85, Glushko 94, L	1	298.15
12	☐	H2(g)	0	20000	50	20000	JANAF 85, Frenkel 94	1	298.15
13	☐	Fe(g)	0	20000	100	10000	JANAF 98, Landolt 99, B	1	298.15
14	☑	FeSO4*7H	0	20000	298.14999	550	Phillips 88, Pankratz 95	1	298.15
15	☑	FeSO4*4H	0	20000	298.14999	550	Glusko IV II 72, Pankratz	1	298.15
16	☑	FeSO4*H2	0	20000	298.14999	550	Pankratz 95, Mullin 93	1	298.15
17	☐	Fe2(SO4)3	0	20000	35	2000	Majzlan 05, Barin 89, JA	1	298.15
18	☐	FeSO4	0	20000	298.14999	2000	Knacke 91, JANAF 85, M	1	298.15
19	☐	FeO*OH	0	20000	298.14999	1500	Knacke 91, Mazeina 05,	1	298.15
20	☐	FeO	0	20000	298.14999	5000	Patnaik 03, Landolt 99, S	1	298.15
21	☐	Fe2O3	0	20000	298.14999	4000	Barin 93, Robie 95	1	298.15
22	☐	Fe3O4	0	20000	298.14999	3000	Barin 89, Knacke 91, Bin	1	298.15
23	☑	H2O	0	20000	3	610	JANAF 85, ESDU 68008	1	298.15

Fig. 37. Warnings for adiabatic calculation.

An example of adiabatic calculation with and without the removal of some species is presented in **Fig. 36- Fig. 39**. Without species removal, hydrates begin to form at temperatures exceeding 4000 °C. The user can prevent this by removing hydrates at high temperatures, see **Fig. 37**.

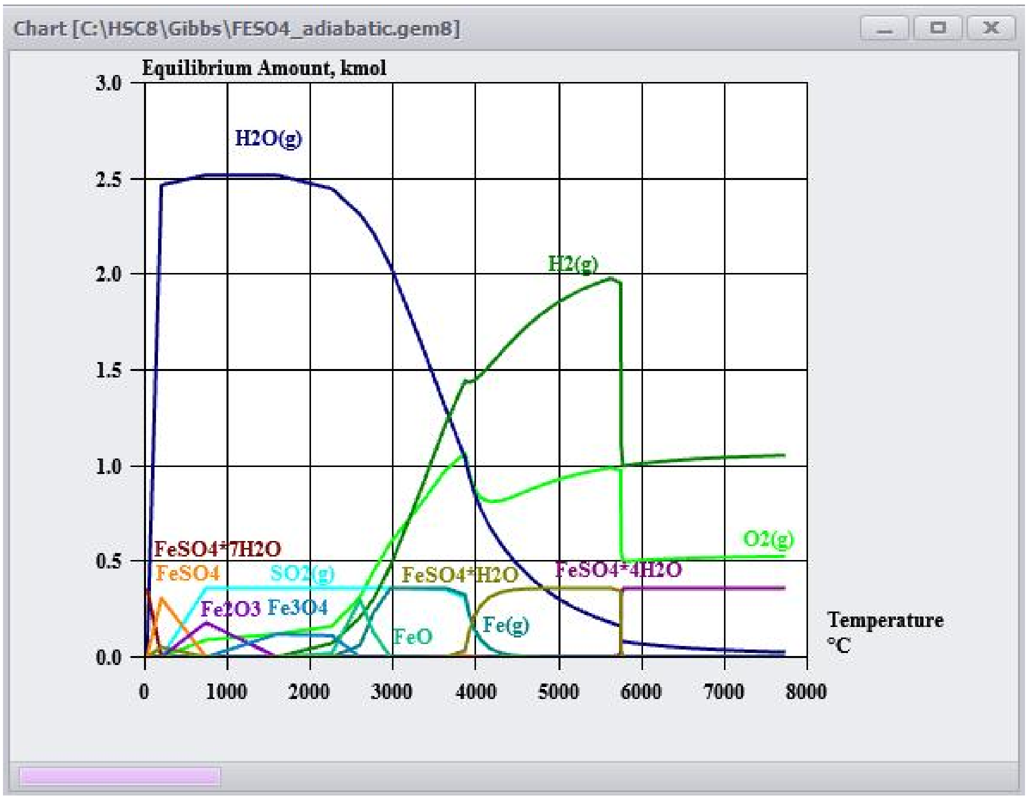


Fig. 38. Adiabatic calculation – without species removal, hydrates are formed at high temperatures.

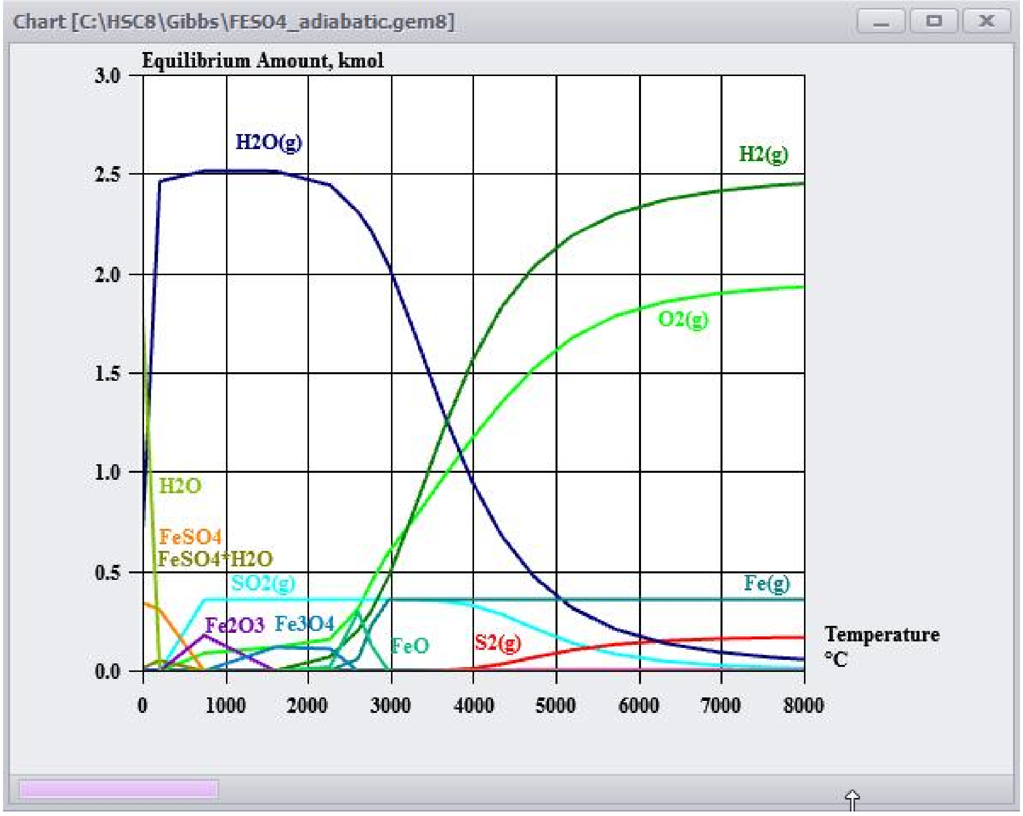


Fig. 39. Adiabatic calculation – species “H2O”, “FeSO4*7H2O”, “FeSO4*4H2O”, “FeSO4*H2O” removed at high temperatures.

13.8. 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 that 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 equally 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 this may 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.

   NB! The same species may exist in several phases simultaneously; their chemical characteristics 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, please define such a species in the system as a pure (*invariant)* phase also. This is a valid approximation although pure substances often contain some impurities in real processes. All species in the last phase can be set as pure substances using the **Pure Substances in the Last Phase** option, see **Fig. 6**.
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 can check the results by a known equilibrium coefficient or mass balance tests. It is evident that results are erroneous if you obtain a random scatter in the curves of the diagram. You can then try to change species and their amounts as described in section 13.3. (2. Phases, 5. 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 N_2(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 present 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 Cl_2(g) to the gas phase.

9. Quite often the simplest examples are the most difficult ones for the Gibbs energy minimization routines due to matrix operations. For example, the two-phase $H_2O(g)$ - H_2O -system between 0 - 200 °C.
10. Sometimes a substance is very stable thermodynamically, but its amount in experiments remains quite low, obviously for kinetic reasons. You can 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 in the calculation results. For example, use of HSC **MainDB7.hsc8** or **MainDB8.hsc8** database files may lead to different results.

The definition of phases and their species is the crucial step in the equilibrium calculations and this must be done carefully by the user. The program is able to remove unstable phases and substances, but it cannot invent 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 into their own mixture phases, as well as such substances which do not dissolve into them, for example, carbon, metals, sulfides, oxides, etc. into their own invariant phases (one species per phase), according to basic chemistry. If working with a known system, it is, of course, clear that the same phase combinations and structural units are selected for the system as those found experimentally. These kinds of simplifications make the calculations easier.

The user should give some amount for all the components (elements) that exist in the system for the Gibbs solver.

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 those 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, the calculation of phase diagrams. For example, the user might only want to know at which temperature Na_2SO_4 can be reduced by coal to Na_2S, or how much oxygen is needed to sulfatize zinc sulfide, etc.

The Na2SO4.gem8 example in the \HSC8\GIBBS directory shows the effect of temperature on Na_2SO_4 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 those found experimentally, but from these results it can be seen easily that at least 900 °C will be needed to reduce the Na_2SO_4 to Na_2S, which has also been verified experimentally.

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 obtain preliminary results in a matter of minutes. This information is often enough to design laboratory- and industrial-scale experiments.

13.9. Cell Equilibrium calculations

The Cell Equilibrium calculation mode allows calculating equilibrium composition of an electrochemical cell using the same calculation method as GIBBS-solver.

The basic definition of an electrochemical system is the same as of a normal system, with the following additions[2,3]:

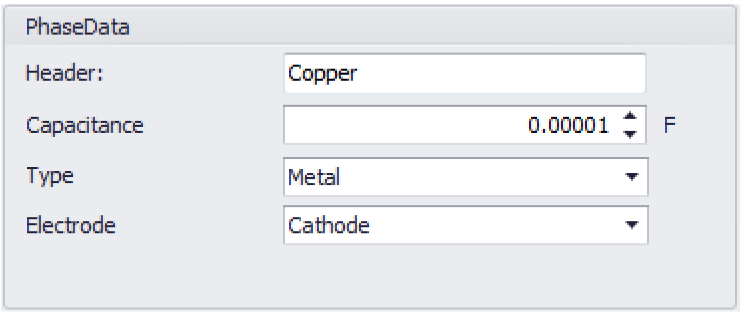
1. For each phase the user has to provide its type (gas/liquid/solid/metal), whether it is an electrode phase (anode or cathode), phase electric capacitance (in Farads)
2. The user has to provide discharge equation coefficients and total discharge level for the system.

Note: in the HSC Cell 7 the capacitance parameter was set as an inverse value of the actual electric capacitance, with the unit being inverse Farads (F^{-1}). In the new Cell calculations the capacitance is set as actual capacitance, with unit being Farads (F). This conversion is handled automatically when importing an *.ICE file.

To create a new Cell calculation file, the same approach as for normal files is used, but the menu items with “Cell mode” should be used, like “File -> New -> Empty File (Cell Mode)”.

Open file menu is the same for both Cell and normal calculations. **LEADBATT.gem8** have been used here as an example.

The phase and species input in the Cell mode is the same as in normal mode. Once the phase (or any of the species in it) has been selected,the information in the Phase Data section on the right is updated (see **Fig. 40**). Here the user can set the capacitance (value of 0.00001 is typically used for metals), phase type and electrode type (if the phase is electrode phase).



Header: Copper
Capacitance 0.00001 F
Type Metal
Electrode Cathode

Fig. 40. Phase data information in Cell mode (LEADBATT.gem8).

For a complete cell with two or more electrodes, the total charge and the amount of atoms present in the system are not sufficient conditions of equilibrium. The additional constraint used in the CELL routine is the so-called DISCHARGE EQUATION. This equation describes how much charge can be transferred from the cathode to the anode due to the redox reactions taking place in the cell before the equilibrium state is reached from the initial equilibrium state.

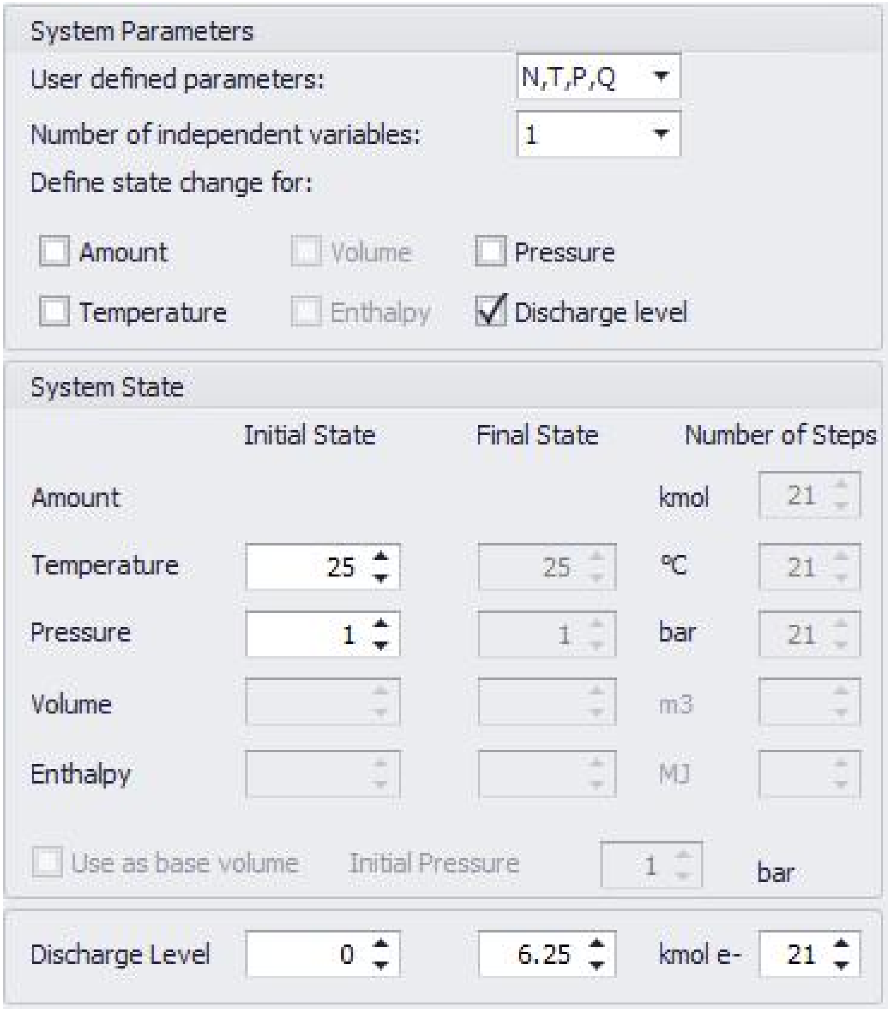
To define discharge equation, one should do the following:

1. Define oxidation numbers for species that participate in the discharge reaction at either anode or cathode. If, for example, oxygen gas $O_2(g)$ is decomposed on the cathode, its oxidation number is 2 * (-2) = -4. The oxidation number of electron species is always 1.

2. Set the discharge amount (i.e. the amount of electricity that is transferred from anode to cathode in equilibrium). By changing the discharge amount you can calculate potentials and compositions at different discharge levels of the cell. The discharge amount is set in the System state parameter section similar to other parameters like temperature or pressure (see **Fig. 41**) and can be used as an X-axis value on charts. The unit for discharge amount is kmol of electron (kmol e-).

After the electrochemical system has been defined the calculation process and creating charts is similar to the normal calculations. Aside from general parameters that can be shown on the chart, Cell calculations support Discharge level and Cell voltage as axis values (see **Fig. 42** and **Fig. 43**).

Note! Discharge level can also be negative value for certain cells. However if user gives negative discharge level for this example LEADBATT.gem8 cell, incorrect very high voltage is calculated $9.2 \cdot 10^8$ V by the model.



System Parameters

User defined parameters: N,T,P,Q

Number of independent variables: 1

Define state change for:

☐ Amount ☐ Volume ☐ Pressure

☐ Temperature ☐ Enthalpy ☑ Discharge level

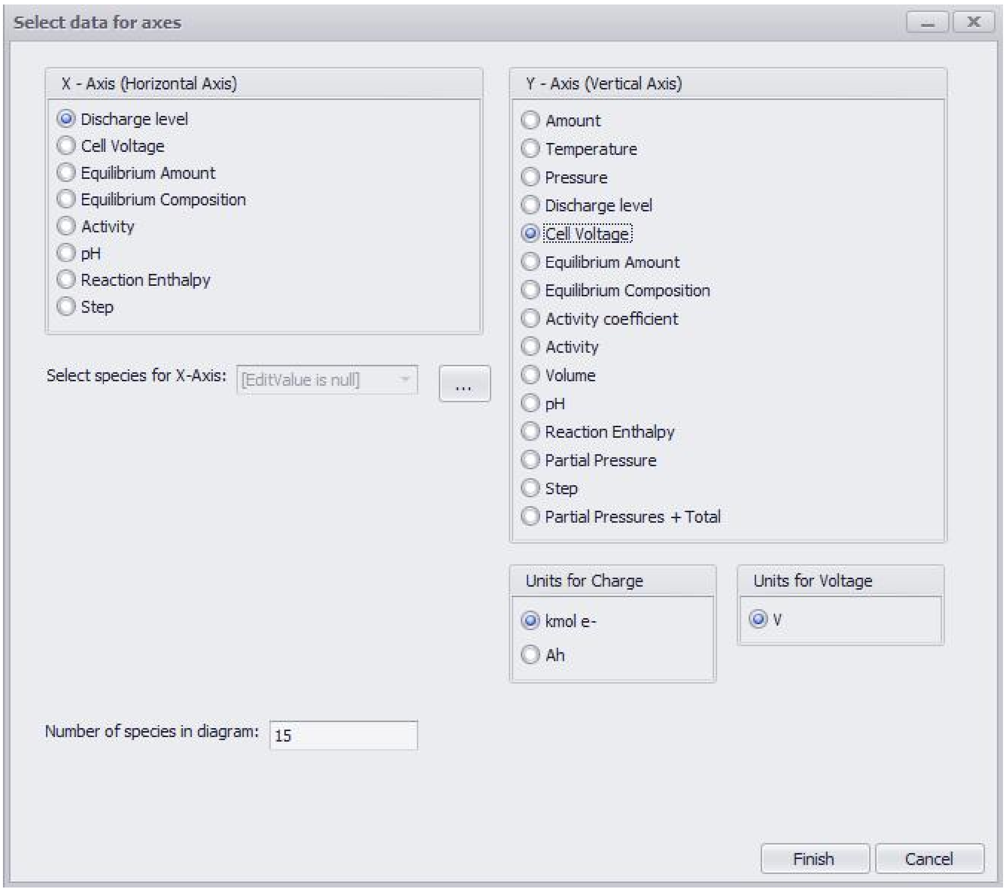
System State

	Initial State	Final State		Number of Steps
Amount			kmol	21
Temperature	25	25	℃	21
Pressure	1	1	bar	21
Volume			m3	
Enthalpy			MJ	

☐ Use as base volume Initial Pressure 1 bar

	Initial State	Final State		Number of Steps
Discharge Level	0	6.25	kmol e-	21

Fig. 41. System parameters in Cell mode (LEADBATT.gem8).


Select data for axes

X - Axis (Horizontal Axis)
- ● Discharge level
- ○ Cell Voltage
- ○ Equilibrium Amount
- ○ Equilibrium Composition
- ○ Activity
- ○ pH
- ○ Reaction Enthalpy
- ○ Step

Select species for X-Axis: [EditValue is null] ...

Y - Axis (Vertical Axis)
- ○ Amount
- ○ Temperature
- ○ Pressure
- ○ Discharge level
- ● Cell Voltage
- ○ Equilibrium Amount
- ○ Equilibrium Composition
- ○ Activity coefficient
- ○ Activity
- ○ Volume
- ○ pH
- ○ Reaction Enthalpy
- ○ Partial Pressure
- ○ Step
- ○ Partial Pressures + Total

Units for Charge
- ● kmol e-
- ○ Ah

Units for Voltage
- ● V

Number of species in diagram: 15

Fig. 42. Chart parameters in Cell mode (LEADBATT.gem8).

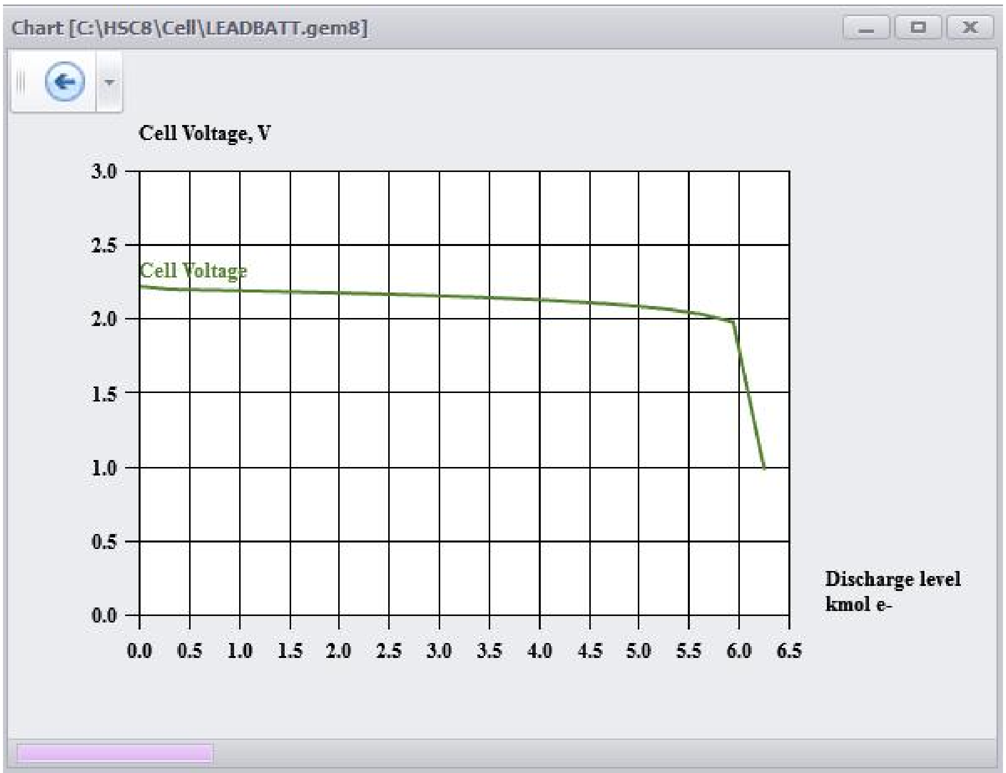


Fig. 43. Chart window in Cell mode.

13.10. Add-In Development

SUMMARY

The HSC Equilibrium module allows the calculation of multi-component equilibrium compositions in non-ideal conditions. The non-ideality of the system is achieved by using species activity coefficients that differ from 1.

NB! solution model parameters taken from the literature are dependent on thermodynamic data used in the assessment of those parameters and those may differ from the data in HSC8 database. That is why it is suggested to use original thermodynamic H, S and Cp data inserted in users Own database when new solution models are created and used.

The activity coefficients can be calculated in three ways: 1) by entering the formula into the Equilibrium spreadsheet, 2) by using a built-in model (e.g. Aqua) and 3) by using third-party DLL add-ins that calculate activity coefficients.

In this document the development of DLL add-ins is discussed.

13.10.1. Structure and Overview of DLL Add-Ins

From the technical point of view, activity coefficient DLLs are Microsoft .NET class libraries that implement the specific programming interface, IActivityCoefficientModel. These class libraries are loaded on program startup and the activity models found can be used in the calculations.

Here are the interfaces that are used by add-ins (VB.NET source code).

```
<AddInBase()>
Public Interface IActivityCoefficientModel

    ReadOnly Property Name As String

    Sub Init(ByVal species As ISpecies())

    Function CalculateActivityCoefficients(ByVal amounts As Double(),
            ByVal data As ICalculationData) As Double()

End Interface

Public Interface ICalculationData

    ReadOnly Property Temperature As Double

    ReadOnly Property Pressure As Double

End Interface

Public Interface ISpecies

    ReadOnly Property Formula As String

    Function GetBaseFormula() As String

End Interface
```

The main interface is the IActivityCoefficientModel. Add-ins should implement this interface. The equilibrium program searches for the implementations of this interface on startup.

13.10.2. Calculation interface of activity coefficient model

An activity coefficient model is a routine that gives a list of species in the phase, their amounts, temperature and pressure, and calculates the activity coefficients of the species.

Input parameters:

Species names - passed into the `Init` method (as an array of `ISpecies` objects, each object has a Formula property)

Amounts (mol) - double-array passed into the `CalculateActivityCoefficients` method (order of species is the same as in the array passed into the `Init` method).

Temperature (K) - passed into the `CalculateActivityCoefficients` method as part of the `ICalculationData` object.

Pressure (bar) - passed into the `CalculateActivityCoefficients` method as part of the `ICalculationData` object.

Output parameters:

Activity coefficients - double-array returned from the `CalculateActivityCoefficients` method. The array should have the same size as the amounts array. Values are dimensionless, 1 means ideal activity.

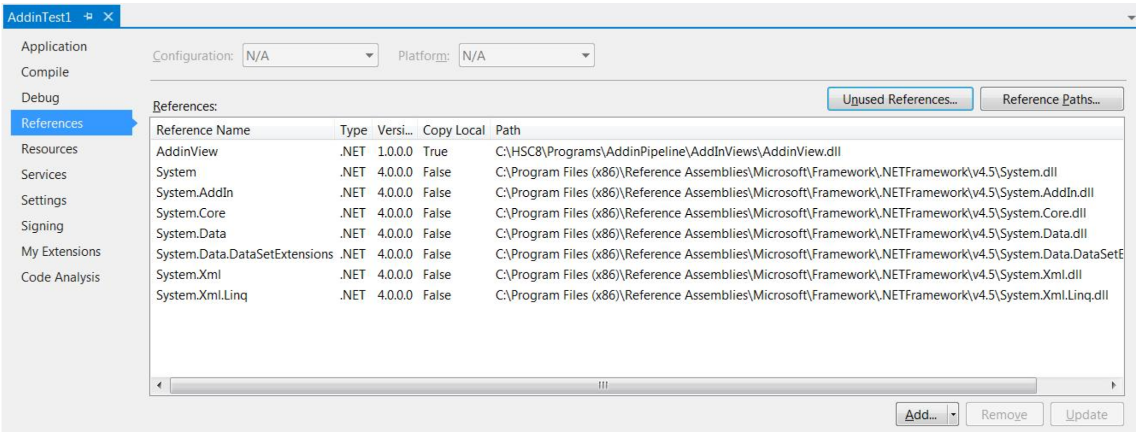
13.10.3. Creating a new Add-In

To create a new add-in, first you need to create a new Visual Studio 2012/2013 project with the type Class Library, using .NET Framework 4.5. In this manual we use VB.NET, but the same operations can be done using C#.

Add the following references to the project:

System.AddIn (from .NET Framework)

AddinView (from HSC 8, the default path is C:\HSC8\Programs\AddinPipeline\AddInViews\AddinView.dll)



Configuration: N/A
Platform: N/A

References:

Reference Name	Type	Versi...	Copy Local	Path
AddinView	.NET	1.0.0.0	True	C:\HSC8\Programs\AddinPipeline\AddInViews\AddinView.dll
System	.NET	4.0.0.0	False	C:\Program Files (x86)\Reference Assemblies\Microsoft\Framework\.NETFramework\v4.5\System.dll
System.AddIn	.NET	4.0.0.0	False	C:\Program Files (x86)\Reference Assemblies\Microsoft\Framework\.NETFramework\v4.5\System.AddIn.dll
System.Core	.NET	4.0.0.0	False	C:\Program Files (x86)\Reference Assemblies\Microsoft\Framework\.NETFramework\v4.5\System.Core.dll
System.Data	.NET	4.0.0.0	False	C:\Program Files (x86)\Reference Assemblies\Microsoft\Framework\.NETFramework\v4.5\System.Data.dll
System.Data.DataSetExtensions	.NET	4.0.0.0	False	C:\Program Files (x86)\Reference Assemblies\Microsoft\Framework\.NETFramework\v4.5\System.Data.DataSetE
System.Xml	.NET	4.0.0.0	False	C:\Program Files (x86)\Reference Assemblies\Microsoft\Framework\.NETFramework\v4.5\System.Xml.dll
System.Xml.Linq	.NET	4.0.0.0	False	C:\Program Files (x86)\Reference Assemblies\Microsoft\Framework\.NETFramework\v4.5\System.Xml.Linq.dll

Fig. 44. Project references.

Next, you need to implement the add-in interface, by creating a class that implements the interface Outotec.HSC.AddinPipeline.AddinViews.IActivityCoefficientModel.

In order for the class to be recognized as a loadable add-in, it needs to have an AddIn attribute.

This leads to the following minimal implementation:

```
Imports System.AddIn
Imports Outotec.HSC.AddinPipeline.AddinViews

<AddIn("AddinTest", Version:="1.0.0.0")>
Public Class AddinTest
    Implements IActivityCoefficientModel

    Public ReadOnly Property Name As String _
        Implements IActivityCoefficientModel.Name
        Get
            Throw New NotImplementedException()
        End Get
    End Property

    Public Sub Init(ByVal species As ISpecies()) _
        Implements IActivityCoefficientModel.Init
        Throw New NotImplementedException()
    End Sub

    Public Function CalculateActivityCoefficients(amounts As Double(),
```

```
                                                  data As ICalculationData) As
Double() _
        Implements IActivityCoefficientModel.CalculateActivityCoefficients
        Throw New NotImplementedException()
    End Function

End Class
```

Below is a detailed description of the implementation.

The AddIn attribute has to include the add-in name and version.

```
<AddIn("AddinTest", Version:="1.0.0.0")>
```

The name property should return the string that will be shown as the model name in the HSC Gibbs interface.

```
Public ReadOnly Property Name As String _
    Implements IActivityCoefficientModel.Name
    Get
        Return "Addin Test"
    End Get
End Property
```

The Init method is called by HSC Gibbs before the calculation of the phase, and an array of ISpecies objects is passed into it. It is expected that the method keeps the species names from this array somewhere.

```
Private _species As IEnumerable(Of ISpecies)

Public Sub Init(ByVal species As ISpecies()) _
    Implements IActivityCoefficientModel.Init
    _species = species
End Sub
```

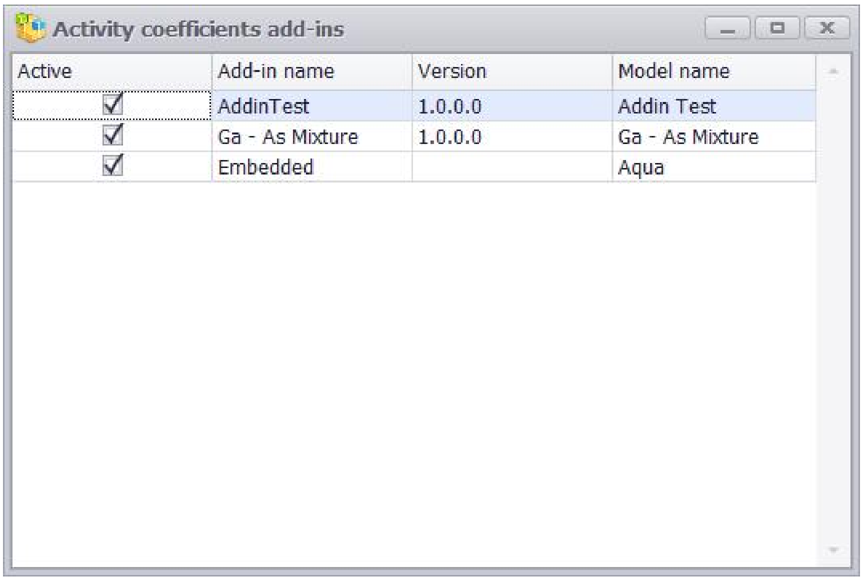
The CalculateActivityCoefficients method is called by HSC Gibbs during the phase calculations. The parameters passed are the amounts of species in mol (species order and number correspond to the species passed into the Init method) and the ICalculationData object that provides the temperature in Kelvins and pressure in bars. The method should return a double-array with the same size as the species and amounts of arrays.

```
Public Function CalculateActivityCoefficients(amounts As Double(),
                                              data As ICalculationData) As Double() _
    Implements IActivityCoefficientModel.CalculateActivityCoefficients
    Dim result() As Double
    ReDim result(_species.Count - 1)
    For i As Integer = 0 To _species.Count - 1
        result(i) = 1.0
    Next
    Return result
End Function
```

The values returned by the CalculateActivityCoefficients method are treated by HSC Gibbs as species activity coefficients, with 1 meaning an ideal system. During the Gibbs energy calculations, the natural logarithm of the activity coefficient is used. So, if your activity coefficient model provides the logarithm of the activity coefficient, you need to exponentiate it in the CalculateActivityCoefficients method, so that the correct logarithm is achieved in the Gibbs energy calculations.

After you have compiled the class library, you need to place the DLL into a separate folder in the Programs/AddinPipeline/Addins directory of the HSC 8 installation. The folder should have the same name as the addin DLL. For example, the addin DLL called AddinTest1.dll should be placed in the folder C:\HSC8\Programs\AddinPipeline\Addins\AddinTest1

Once the library has been placed in the corresponding folder, you can start HSC Gibbs. The new model should be available in the solution model drop-down list. You can also check the available models in the Window - Add-Ins menu (**Fig. 45**).



Active	Add-in name	Version	Model name
☑	AddinTest	1.0.0.0	Addin Test
☑	Ga - As Mixture	1.0.0.0	Ga - As Mixture
☑	Embedded		Aqua

Fig. 45. Available add-ins in HSC Gibbs module.

13.11. References

1. White W.B., Johnson S.M. and Dantzig G.B.: Chemical Equilibrium in Complex Mixtures. Journal of Chemical Physics **28**(1958), pp. 751-755.
2. Lampinen M.J., Vuorisalo J.: Thermodynamic Analysis of Chemical and Electrochemical Systems with a Computer Program; Basic Theory with Illustrations. Acta Polytechn. Scand., Series No. 202, Helsinki 1992.
3. Lampinen M.J., Vuorisalo J.: Mathematical analysis of phase rule for systems with electrostatic energy. J. Chem. Phys. **95**(1991)11, pp. 8401-9.

APPENDIX A. Redlich-Kister solution model

In this appendix, the Redlich-Kister solution model equation for a binary system has the form of Equation (1).

$$^{Ex}G = x_i x_j \Sigma k_n \cdot (x_i - x_j)^n, \qquad (1)$$

where k_n can be any temperature- and pressure-dependent term.

This can be written for each component of the binary system as

$$^{Ex}G_i = RT\ln f_i = x_j^2[k_0 + \Sigma k_n \cdot (x_i - x_j)^{n-1}[(2n+1)x_i - x_j]] \qquad (2)$$

$$^{Ex}G_j = RT\ln f_j = x_i^2[k_0 + \Sigma k_n \cdot (x_i - x_j)^{n-1}[x_i - (2n+1)x_j]], \qquad (3)$$

where R is the gas constant 8.31431 $Jmol^{-1}K^{-1}$

APPENDIX B. Ga - As solution model

HSC 8 includes a model for a Ga - As liquid binary phase. The Redlich-Kister parameters used in this example are:

LIQUID phase
$k_0 = -25503.6 - 4.3109 \cdot T$
$k_1 = 5174.7$

where the temperature unit is Kelvin.

```
Imports System.AddIn
Imports Outotec.HSC.AddinPipeline.AddinViews

<AddIn("Ga - As Mixture", Version:="1.0.0.0")>
Public Class GaAsMixtureAddin
    Implements IActivityCoefficientModel

    Private _species As IEnumerable(Of ISpecies)

    Private _GAindex As Integer = -1
    Private _ASindex As Integer = -1
    Private _phaseCorrect As Boolean = False

    Public ReadOnly Property Name As String Implements IActivityCoefficientModel.Name
        Get
            Return "Ga - As Mixture"
        End Get
    End Property

    Public Sub Init(ByVal species As ISpecies()) Implements
IActivityCoefficientModel.Init
        _species = species
        _phaseCorrect = False
        _GAindex = -1
        _ASindex = -1

        For i As Integer = 0 To _species.Count - 1
            Dim formula = _species(i).Formula
            If formula = "Ga(l)" Then
                _GAindex = i
            End If

            If formula = "As(l)" Then
                _ASindex = i
            End If
            If _GAindex >= 0 And _ASindex >= 0 Then
                _phaseCorrect = True
                Exit For
            End If
        Next
        If _species.Count <> 2 Then
            _phaseCorrect = False
        End If
        If Not _phaseCorrect Then
            Throw New Exception("Cannot apply model to this phase")
        End If
    End Sub
```

```
    Public Function CalculateActivityCoefficients(amounts As Double(), data As
ICalculationData) As Double() Implements
IActivityCoefficientModel.CalculateActivityCoefficients
        Dim result() As Double
        ReDim result(_species.Count - 1)
        If amounts(0) + amounts(1) <= 0 Then
            Return {1.0, 1.0}
        End If
        Dim fractions() As Double = {amounts(0) / (amounts(0) + amounts(1)),
amounts(1) / (amounts(0) + amounts(1))}
        For i As Integer = 0 To _species.Count - 1
            result(i) = 1.0
            If _phaseCorrect Then
                If i = _GAindex Then
                    result(i) = Math.Pow(Math.E, ((fractions(_ASindex)) ^ 2) * (-
25503.6 - 4.3109 * data.Temperature + 5174.7 * (3 - 4 * fractions(_ASindex))) /
(8.31431 * data.Temperature))
                ElseIf i = _ASindex Then
                    result(i) = Math.Pow(Math.E, ((1 - fractions(_ASindex)) ^ 2) * (-
25503.6 - 4.3109 * data.Temperature + 5174.7 * (1 - 4 * fractions(_ASindex))) /
(8.31431 * data.Temperature))
                End If
            End If
        Next
        Return result
    End Function

End Class
```

APPENDIX C. Al - Zn solution model

HSC 8 includes a model for an Al - Zn binary system (liquid, solid FCC, and solid HCP phases). The Redlich-Kister parameters used in this example are:

LIQUID phase
$k_0 = 10483.5 - 4.74442 \cdot T$
$k_1 = -210.4 + 0.85139 \cdot T$

FCC phase
$k_0 = 11014.8 - 3.71812 \cdot T$
$k_1 = 1546.9 + 1.60179 \cdot T$
$k_2 = -308.7$

HCP phase
$k_0 = 17047.8 - 10.37525 \cdot T$

where the temperature unit is Kelvin.

```
Imports System.AddIn
Imports Outotec.HSC.AddinPipeline.AddinViews

<AddIn("Al - Zn Mixture", Version:="1.0.0.0")>
Public Class AlZnMixtureAddin
    Implements IActivityCoefficientModel

    Private _species As IEnumerable(Of ISpecies)
    Private _phaseMode As PhaseMode
    Private _indexAl As Integer = -1
    Private _indexZn As Integer = -1
    Private _phaseCorrect As Boolean = False

    Public Function CalculateActivityCoefficients(amounts() As Double, data As
ICalculationData) As Double() Implements
IActivityCoefficientModel.CalculateActivityCoefficients
        If Not _phaseCorrect Then
            Return Nothing
        End If
        Dim result() As Double
        ReDim result(_species.Count - 1)
        If amounts(0) + amounts(1) <= 0 Then
            Return {1.0, 1.0}
        End If
        Dim fractions() As Double = {amounts(0) / (amounts(0) + amounts(1)),
amounts(1) / (amounts(0) + amounts(1))}
        If _phaseMode = PhaseMode.Liquid Then
            For i As Integer = 0 To _species.Count - 1
                result(i) = 1.0
                Dim T = data.Temperature
                Dim x7 = fractions(_indexZn)
                Dim x6 = fractions(_indexAl)
                If i = _indexAl Then
                    result(i) = Math.Pow(Math.E, (x7 ^ 2) * (10483.5 - 4.74442 * T +
(-210.4 + 0.85139 * T) * (3 * x6 - x7)) / (8.31431 * T))
                ElseIf i = _indexZn Then
                    result(i) = Math.Pow(Math.E, (x6 ^ 2) * (10483.5 - 4.74442 * T +
(-210.4 + 0.85139 * T) * (x6 - 3 * x7)) / (8.31431 * T))
                End If
            Next
```

```
        ElseIf _phaseMode = PhaseMode.SolidFCC Then
            For i As Integer = 0 To _species.Count - 1
                result(i) = 1.0
                Dim T = data.Temperature
                Dim x10 = fractions(_indexZn)
                Dim x9 = fractions(_indexAl)
                If i = _indexAl Then
                    result(i) = Math.Pow(Math.E, (x10 ^ 2) * (11014.8 - 3.71812 * T +
(1546.9 + 1.60179 * T) * (3 * x9 - x10) - 308.7 * (x9 – x10) * (5 * x9 - x10)) /
(8.31431 * T))
                ElseIf i = _indexZn Then
                    result(i) = Math.Pow(Math.E, (x9 ^ 2) * (11014.8 - 3.71812 * T +
(1546.9 + 1.60179 * T) * (x9 - 3 * x10) - 308.7 * (x9 – x10) * (x9 - 5 * x10)) /
(8.31431 * T))
                End If
            Next
        ElseIf _phaseMode = PhaseMode.SolidHCP Then
            For i As Integer = 0 To _species.Count - 1
                result(i) = 1.0
                Dim T = data.Temperature
                Dim x13 = fractions(_indexZn)
                Dim x12 = fractions(_indexAl)
                If i = _indexAl Then
                    result(i) = Math.Pow(Math.E, (x13 ^ 2) * (17047.8 - 10.37525 * T)
/ (8.31431 * T))
                ElseIf i = _indexZn Then
                    result(i) = Math.Pow(Math.E, (x12 ^ 2) * (17047.8 - 10.37525 * T)
/ (8.31431 * T))
                End If
            Next
        End If
        Return result
    End Function

    Public Sub Init(species() As ISpecies) Implements IActivityCoefficientModel.Init
        _indexZn = -1
        _indexAl = -1
        _phaseCorrect = False
        _species = species
        Dim hasSolidsFCC = False
        Dim hasSolidsHCP = False
        Dim hasLiquids = False
        For i As Integer = 0 To _species.Count - 1
            Dim formula = species(i).Formula
            If formula = "Al(l)" Then
                hasLiquids = True
                _phaseMode = PhaseMode.Liquid
                _indexAl = i
            ElseIf formula = "Zn(l)" Then
                hasLiquids = True
                _phaseMode = PhaseMode.Liquid
                _indexZn = i
            ElseIf formula = "Al" OrElse formula = "Al(FCC)" OrElse formula = "Al(s)"
Then
                hasSolidsFCC = True
                _phaseMode = PhaseMode.SolidFCC
                _indexAl = i
            ElseIf formula = "Zn" OrElse formula = "Zn(FCC)" OrElse formula = "Zn(s)"
Then
                hasSolidsFCC = True
                _phaseMode = PhaseMode.SolidFCC
                _indexZn = i
```

```
            ElseIf formula = "Al(HCP)" Then
                hasSolidsHCP = True
                _phaseMode = PhaseMode.SolidHCP
                _indexAl = i
            ElseIf formula = "Zn(HCP)" Then
                hasSolidsHCP = True
                _phaseMode = PhaseMode.SolidHCP
                _indexZn = i
            Else
                Throw New ArgumentException("Cannot apply this model to this phase:
invalid species " & species(i).Formula)
            End If
        Next
        If (hasLiquids And hasSolidsFCC) Or (hasLiquids And hasSolidsHCP) Or
(hasSolidsFCC And hasSolidsHCP) Then
            Throw New ArgumentException("Cannot apply this model to this phase:
mixing solids and liquids (or different solid types) in one phase")
        End If
        If Not hasLiquids And Not hasSolidsFCC And Not hasSolidsHCP Then
            Throw New ArgumentException("Cannot apply this model to this phase:
missing required species")
        End If
        If _indexZn < 0 OrElse _indexAl < 0 OrElse _species.Count <> 2 Then
            Throw New ArgumentException("Cannot apply this model to this phase: two
species excepted (Al and Zn)")
        End If
        _phaseCorrect = True
    End Sub

    Public ReadOnly Property Name As String Implements IActivityCoefficientModel.Name
        Get
            Return "Al - Zn Mixture"
        End Get
    End Property

    Private Enum PhaseMode
        Liquid
        SolidFCC
        SolidHCP
    End Enum
End Class
```