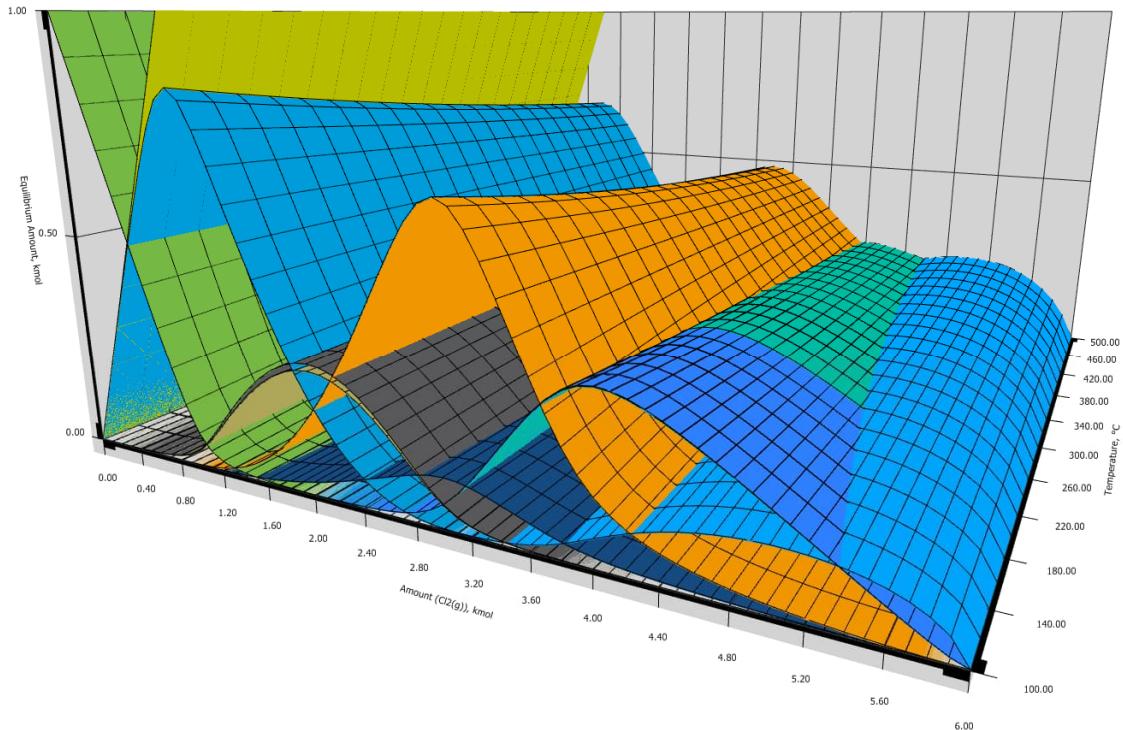


13. Equilibrium Module - Description of Menus and Options



SUMMARY

HSC Equilibrium module enables user 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 method¹. 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 ***.gem9**, 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

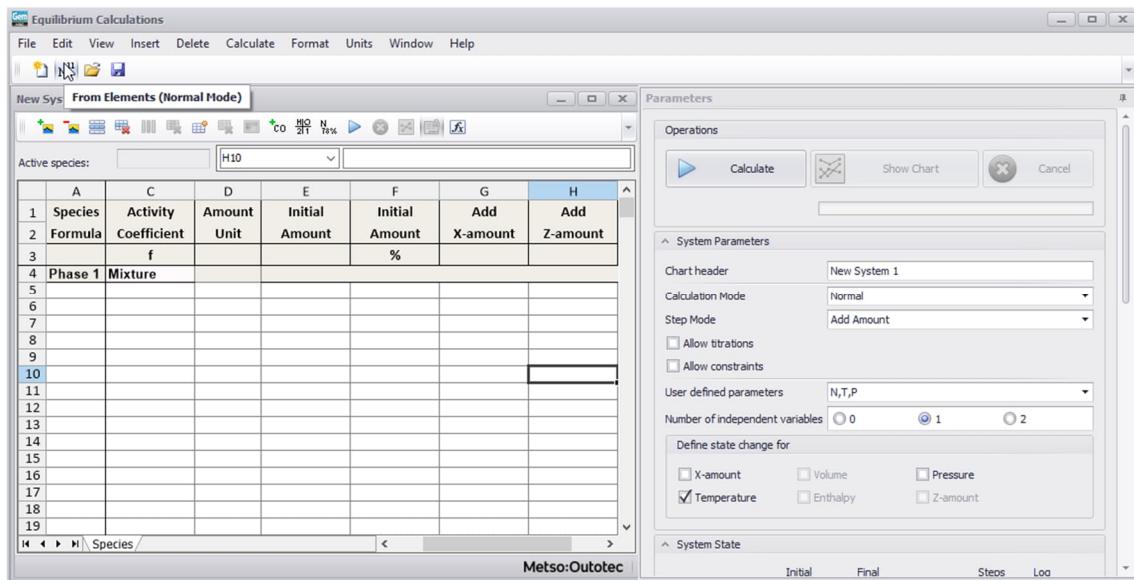


Fig. 1. Starting screen.

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

1. Press **From Elements**. Then specify the elements which are present in users 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 **Empty file** if user is already certain of the possible substances and phases of the system.
3. Press **Open** if user already has an input file which can be used as a starting file. Edit the input table and save it using a different name.

If user has an old file format (*.GEM or *.IGI) user can import it from the **File** menu by selecting **Import** and working with it. User can update thermodynamic data of the file to HSC database values by **Update species data** from **Edit** menu, see **Fig. 2.**

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

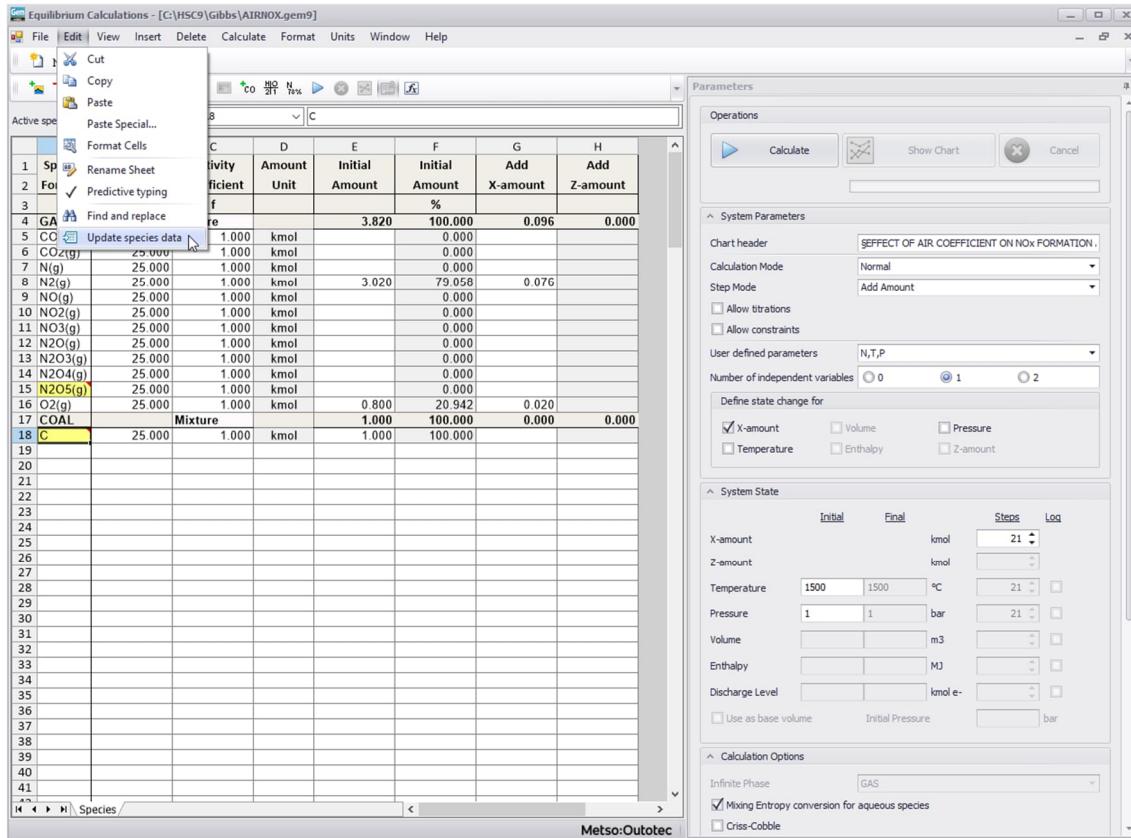


Fig. 2. Update species data of the old file.

13.2. Starting by Defining the Elements

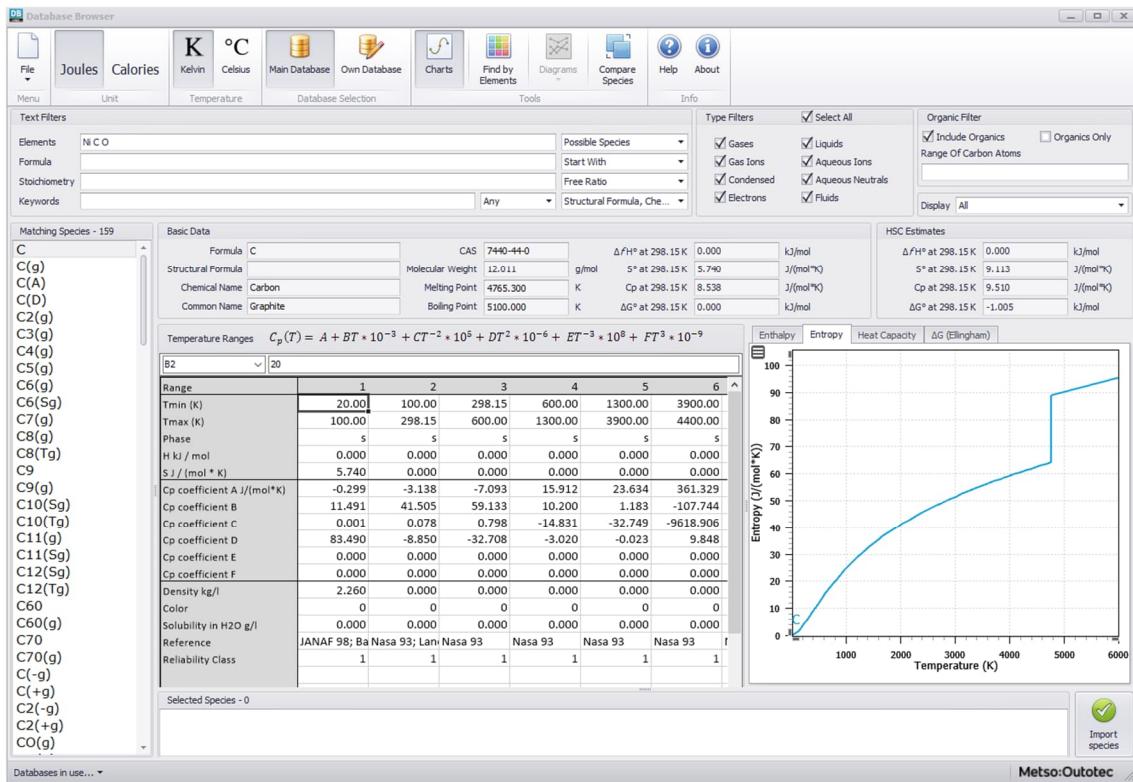


Fig. 3. Specifying the elements of the chemical system.

Choose element from periodic chart or type them to first text filter. If user wants to choose only some of the species in the list in calculations, then select them (with ctrl button) and right-click and **Import to Selected Species**, see **Fig. 4**.

By decreasing the number of species, user can increase the calculation speed and make the solution easier. Especially if user has selected C and/or H among the other elements, a very large number of species will be included in the calculation and user is advised to decrease the number of species. User 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 user 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.

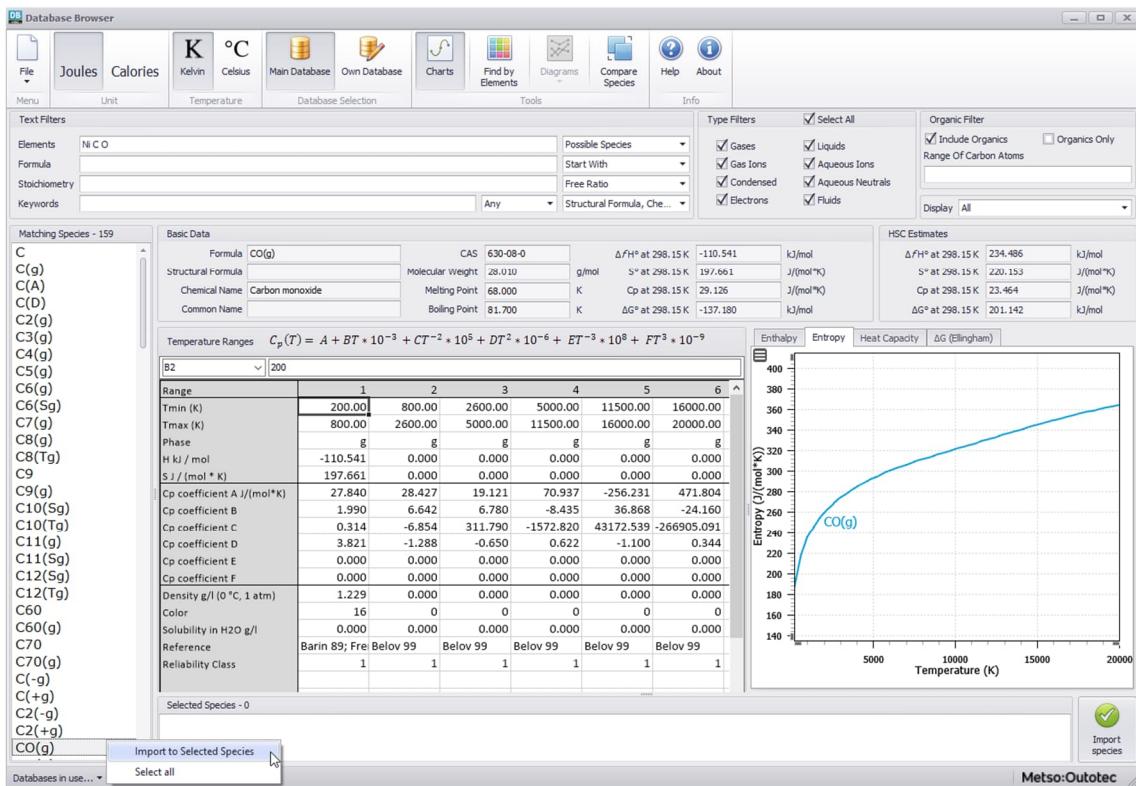


Fig. 4. Choosing desired species to calculation.

Press **Import Species** and user can also set the sorting order for the species. User 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 user has chosen sorting order of species, press **OK** and user will return to the Equilibrium Editor window, see **Fig. 5**.

13.3. Giving Input Data for Equilibrium Calculations

The screenshot shows the HSC software interface. At the top, there is a 'Sort Species' dialog box with the following options:

- Add N₂(g) for calculation stability
- Phases
- Gas, Aqua, Pure
- No sorting
- Gas, Aqua, Liquids

Below the dialog is the main software window titled 'C:\Program Files (x86)\HSC10\Gibbs\NICO.gem9'. The window has a toolbar at the top with various icons. The 'Active species:' dropdown is set to 'C13' and the 'Mixture' tab is selected.

The main area is a table titled 'Species' with columns labeled A through H. The table rows represent different species and their properties. Row 13 is highlighted, showing 'Phase #2' and 'Mixture' selected in column C. A context menu is open over this cell, listing 'Mixture', 'Pure', and 'Aqua'.

	A	B	C	D	E	F	G	H
1	Species	Feed	Activity	Amount	Initial	Initial	Add	Add
2	Formula	Temperature	Coefficient	Unit	Amount	Amount	X-amount	Z-amount
3		°C	f			%		
4	Phase #1		Mixture		4.000	100.000	0.000	0.000
5	CO(g)	25.000	1.000	kmol	4.000	100.000		
6	CO ₂ (g)	25.000	1.000	kmol		0.000		
7	C ₂ O(g)	25.000	1.000	kmol		0.000		
8	C ₃ O ₂ (g)	25.000	1.000	kmol		0.000		
9	Ni(g)	25.000	1.000	kmol		0.000		
10	Ni(CO) ₄ (g)	25.000	1.000	kmol		0.000		
11	NiO(g)	25.000	1.000	kmol		0.000		
12	O ₂ (g)	25.000	1.000	kmol		0.000		
13	Phase #2		Mixture		1.000	100.000	0.000	0.000
14	Ni	25.000	Mixture	kmol	1.000	100.000		
15			Pure					
			Aqua					

Fig. 5. Specification of the species and phases for the reaction system. User can change solution model from Species sheet phase row (Column C).

The calculation data is specified using the Parameters panel, **Fig. 6**. User gives 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**. User can move around the table using the mouse, or Tab and Arrow keys. The other points user should consider are:

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

User can type the names of the species directly into the Species column, without a preliminary search in the Elements window. If user has made the search on the basis of the elements, user will already have the species in the Species column.

User 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 Row** 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 Row** from the pop-up menu.

User 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.

Use the (l)-suffix for a species only if user wants to use the data of liquid phases at temperatures below their melting point. For example, type **SiO₂(l)** if SiO₂ is present in a liquid oxide phase at temperatures below the melting point of pure SiO₂. User may also use (s)-suffix if user wants 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 user will find the species that user needs. User can use search, or type a formula or chemical name in the search string, and the program will find the species.

User can also type a species formula in a new row in the Equilibrium Editor window, and the program will suggest species if predictive typing is selected in the Edit menu.

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 user inserts a new phase row in the sheet and:

1. Requests a name for the new phase, which user 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 Nm³ units.

When the insert procedure is ready, user 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 user cannot type formulas in the amount column of the phase row, because the SUM formulas are located there. User 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 user starts 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 user has an aqueous phase with aqueous ions, user must also have water in the phase!

If user expects 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 in one phase and select the Solution model **Pure Substance** option on the Parameters panel, see **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 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

User 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 user provides some input amount for a species user should also give its temperature. The input temperature does not affect the equilibrium composition. User can select the temperature unit by selecting °C or K from the Units menu. Equilibrium temperatures must be specified in the **Parameters panel**, see **Fig. 6**.

5. Amount of the Species

In this column user gives 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. User may divide these amounts between the species as user likes. If the correct heat balance is required, user must divide the amounts of elements exactly into the same phases and in a similar manner as in the real physical world.

User can choose between mol, kmol or kg/Nm³ units by selecting mol, kmol or kg/Nm³ from the Units menu. Note that kilograms refer to condensed substances and standard cubic meters (Nm³) to gaseous substances.

6. Amount Step for Raw Materials

If user wishes to calculate several successive equilibria, user has 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 give the number of steps. Some 21 - 51 steps are usually enough to give smooth curves to the equilibrium diagram.

User can give step values for several species simultaneously. For example, if user wants to add air to the system, give a step value for both O₂(g) and N₂(g). Please remember to specify the number of steps if a diagram is to be drawn from the results.

User can also add secondary amount step to plot 3D graphs with different amount additions as axis.

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:

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

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:

$$f = \frac{a}{x} \quad (2)$$

In an ideal solution, they are therefore defined as $a = x$ and $f = 1$. As default in Gem module, 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 C. User can choose activity coefficient (f) or natural logarithm of activity coefficient ($\ln f$) to column C from **Units** menu. This **Units** menu (f or $\ln f$) will change units to all phases.

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

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

where:

T	= Temperature in K
X_24	= Mole fraction ($X_{\text{--}}$) 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 13.4.5, 13.10 and Chapter 36.

13.4. Panel Parameters

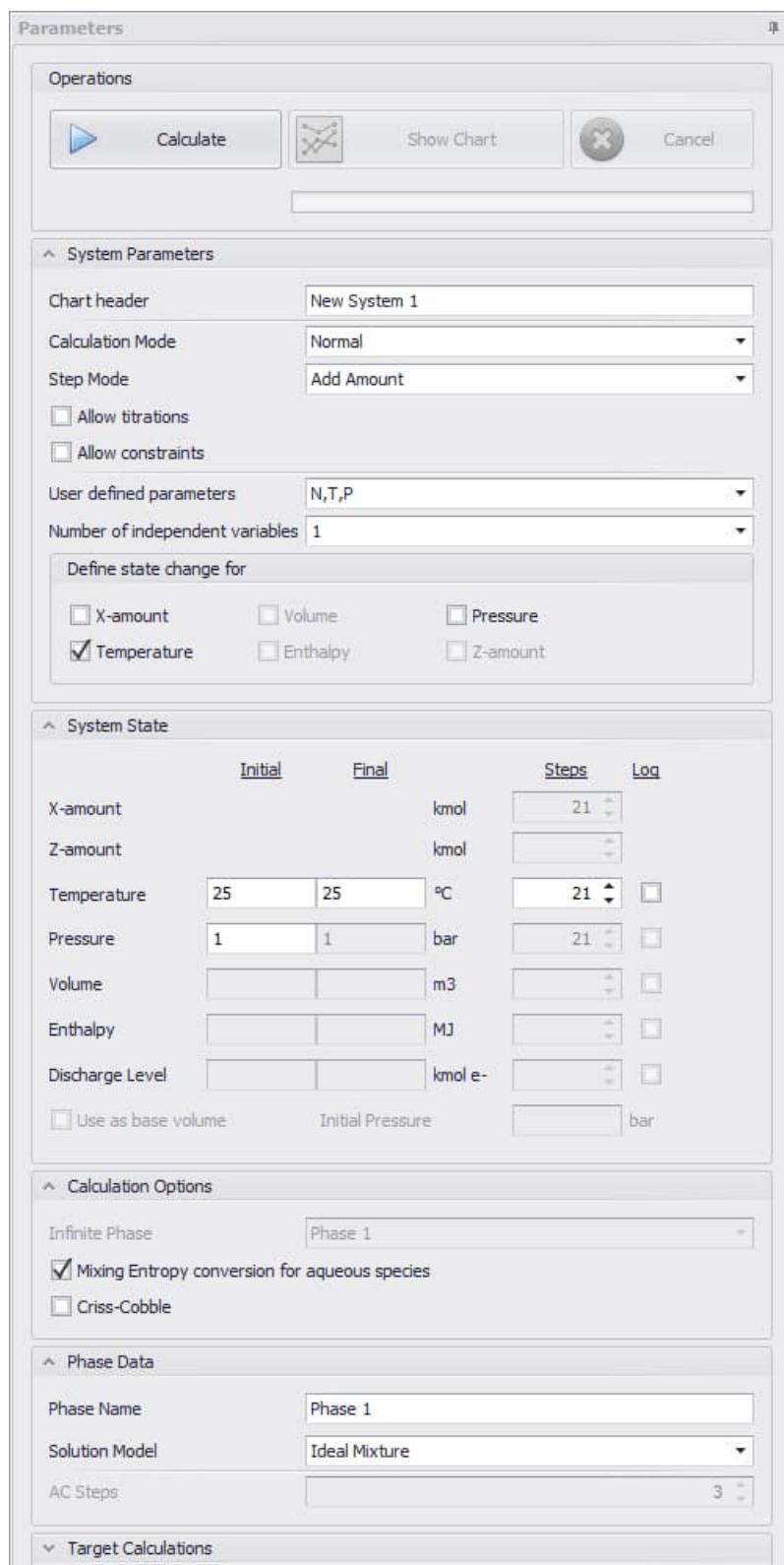


Fig. 6. Specifying calculation parameters.

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** – User can cancel users last operation.

13.4.2. System Parameters

User 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**.

Default Calculation mode is Normal and Step mode is Add Amount. For advanced calculation modes see section 13.4.7.

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

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

Volume of the system is calculated as sum of volumes of all gaseous phases. User can select one of the options in the **user defined** parameters menu. There are temperature, pressure, and amount in every case, for example, if user selects the **N, H, P** system, it means that the temperature will be constant in this system.

Specify a one calculation, 2D or 3D diagram by selecting 0, 1 or 2 in the **number of independent variables**, respectively.

Specify, which parameters are changed.

13.4.3. System State

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

If user has defined increments (steps) for raw material species or a specified range for selected parameters then user 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. It is now also possible to add steps using log mode for each parameter. This is especially useful when stepping from low to high pressures.

If user has given an amount step for a raw material species, the calculations should be made using an increasing species amount.

If user checks 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 user specified earlier.

13.4.4. Calculation Options

Mixing Entropy conversion

HSC converts the entropy values of aqueous components from the molality scale to the mole fraction scale if the **Mixing Entropy conversion for aqueous species** option is selected. Therefore, the entropy values in the results1 sheet are not the same as those in the HSC database. Identical results will be achieved if the Raoultian activity coefficients of the aqueous species are changed to $55.509/x(H_2O)$, which converts the Raoultian activity scale to the aqueous activity scale.

Criss-Cobble

HSC will utilize Criss-Cobble extrapolation for the heat capacity of aqueous species at elevated temperatures ($> 25^\circ\text{C}$) if the **Criss-Cobble** option is selected.

13.4.5. Phase Data - solution models for phases

User first choose the phase where user wants to use a solution model in the system sheet. Then user choose the solution model from the parameters panel and give the number of iterations used in the calculations (AC steps). If system consist of Ideal Mixture and Pure Substance phases only AC step option is disabled.

Ideal Mixture

Default setting for phase is ideal mixture. Gas phase is a typical assumed to behave as ideal mixture.

Pure Substance (“Invariant phases”)

All species in the phase can be set to be pure substances with the **Pure Substance** option, see **Fig. 5** and **Fig. 6**.

Aqua

Aqua modul can be used in aqueous phase. This model uses Pitzer model to calculate mean activity coefficients of the aqueous species (H_2O and species ionic and neutral species with “ a ”). User can find the theory of the Aqua solution model in Chapter 36.

Other solution models

There are two solution models available: Ga - As Mixture, Al - Zn Mixture. User can activate those from Windows menu Add-Ins.

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

It is also possible to enter an activity coefficient formula in **column C** of the input sheet, see section 13.3 (numbered list 7. Activity coefficients).

13.4.6. Target Calculations

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, user wants to find the temperature where $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ has an amount of 0.25 kmoles. Enable Target Calculations and set the parameters as in **Fig. 7**.

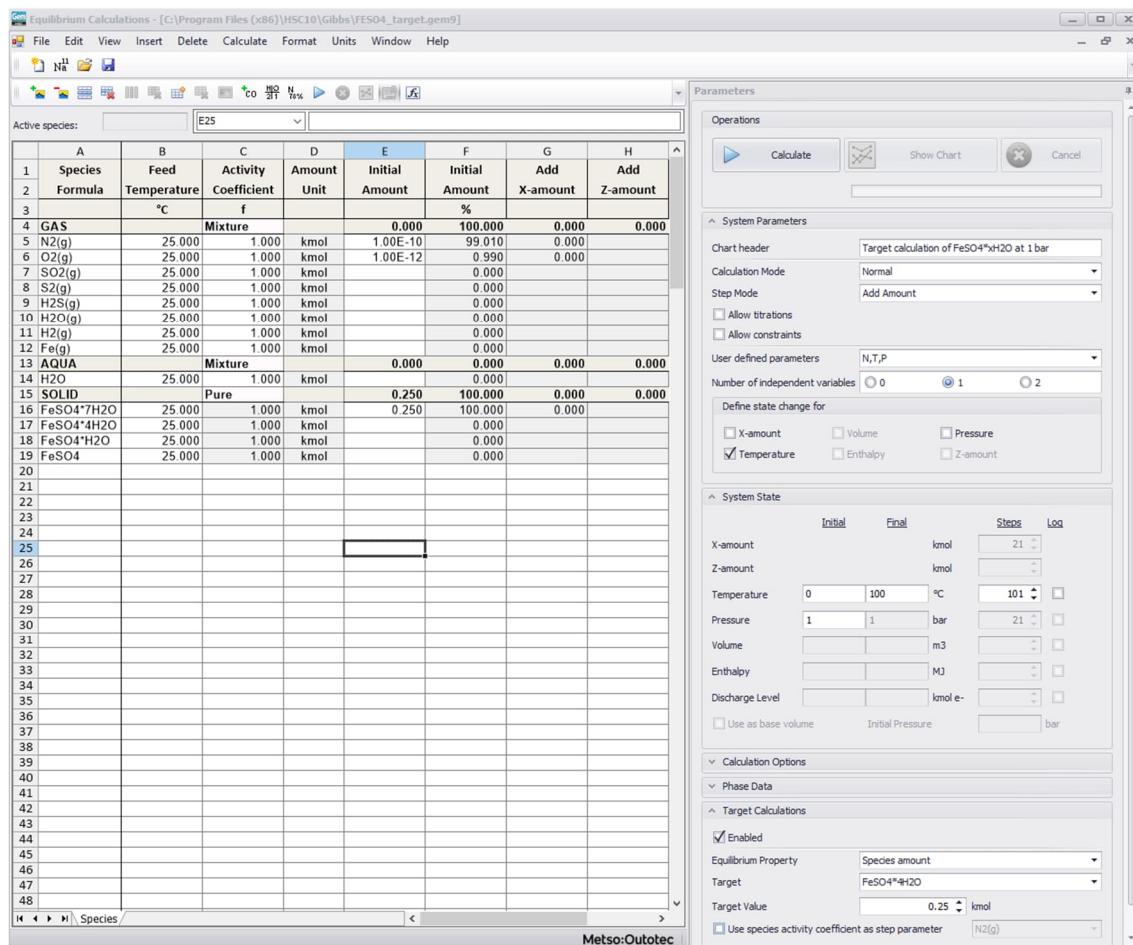


Fig. 7. Parameters for Target Calculation mode.

When user presses the Calculate button, the program will make the calculation and show the results as in **Fig. 8**.

C:\Program Files (x86)\HSC10\Gibbs\FESO4_target.gem9					
Active species:		A1			
	A	B	C	D	E
1		Units			
2	Sought-for function	FeSO4*4H2O	Equilibrium Amount		
3	Sought-for value	kmol	0.25		
4					
5	Results found		1		
6	Achieved value	kmol	0.25		
7	Variable step parameters				
8	Temperature	°C	43		
9	Constant parameters				
10	Pressure	bar	1		
11	Amount				
12	N2(g)	kmol	1E-10		
13	O2(g)	kmol	1E-12		
14	FeSO4*7H2O	kmol	0.25		
15	Calculated results				
16	Volume	m3	2.90542E-09		
17	Reaction Enthalpy	MJ	8.787749943		
18		Equilibrium Amount	Equilibrium Composition	Activity coefficient	Activity
19		kmol	mol fraction		mol fraction
20	GAS	1.10533E-10	1.10533E-10	1.10533E-10	
21	N2(g)	1E-10	0.904709841	1	0.904709841
22	O2(g)	9.99989E-13	0.009047003	1	0.009047003
23	SO2(g)	1.55554E-84	1.40731E-74	1	1.40731E-74
24	S2(g)	3.32571E-266	3.0088E-256	1	3.0088E-256
25	H2S(g)	3.79818E-164	3.43625E-154	1	3.43625E-154
26	H2O(g)	9.53269E-12	0.086243156	1	0.086243156
27	H2(g)	2.33431E-48	2.11187E-38	1	2.11187E-38
28	Fe(g)	1.55554E-84	1.40731E-74	1	1.40731E-74
29	AQUA	0.75	0.75	0.75	
30	H2O	0.75	1	1	1
31	SOLID	0.25	0.25	0.25	
32	FeSO4*7H2O	0	0	1	0
33	FeSO4*4H2O	0.25	1	1	1
34	FeSO4*H2O	0	0	1	0
35	FeSO4	0	0	1	0

Fig. 8. Results for Target Calculation mode

13.4.7. Advanced Calculation Options

Default calculation mode is **Normal** but user can specify other more advanced calculation modes which are listed here. It is also possible to use different step modes than **Add Amount**.

Calculation modes

1. Infinite Phase (Open Atmosphere)

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.

2. 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, Reactor, and Adiabatic calculation modes.

3. Cell mode

The Cell Equilibrium calculation mode allows calculating equilibrium composition of an electrochemical cell using the same calculation method as GIBBS-solver. See more in section 13.9.

Step modes

By checking **Allow titrations** user can give species concentrations in g/l or mol/l. It is also possible to give known density of solution (default value is 1 kg/l). If concentration column is filled, then user gives initial and step amounts in liters for those species and amount of H₂O in that solution is automatically calculated. At same input sheet user can also give species amounts in normal way using mol, kmol, kg or Nm³ units if concentration cells are not filled and only amount cells are used, see example file **Allow_Titration.gem9** in Gibbs folder.

1. Final Amount (and Add Amount)

With **Final Amount** step mode user specifies final amount that is added instead of amount that is added in each step that is done in **Add Amount**, which is default step mode.

2. Remove % (Add Amount or Final Amount)

The idea of this step 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 Remove % mode is calculation procedure where part of the gas phase is removed from the chemical system after each calculation step. You can choose between Remove % (Add amount) and Remove % (Final amount).

3. Reactor

The idea of this Reactor (Standard or Sheets View) step mode is to allow user freedom to add or remove species (or phases) in each step. It is also possible to change temperature and pressure in each step. User can for example increase temperature and decrease temperature in one calculation round (heating and cooling). It is also possible to give inconstant add amounts of species. With **Show AC in each reactor step** option user can specify activity coefficient for each step or specify activity coefficients just once and those values are used in each step.

Please note that this mode **cannot be** used together with the Fixed activity mode, because Fixed activity mode need to know type of phases (pure phases). Nor can this calculation mode be used together with the Target Calculations.

Typical example of Reactor mode is calculation procedure where part of the gas phase is removed from the chemical system after each calculation step. You can choose between Reactor (Standard) and Reactor (Sheets View).

13.4.8. Examples of the Remove %, Infinite phase and Fixed Activity modes

The system consists of H_2O , $\text{N}_2(\text{g})$, $\text{O}_2(\text{g})$, $\text{CO}_2(\text{g})$, and $\text{CO}_2(\text{a})$. Initially, only H_2O , $\text{N}_2(\text{g})$, $\text{O}_2(\text{g})$ and $\text{CO}_2(\text{g})$ are present in the system; gases are added to the system in each step, see **Fig. 9 - Fig. 15** (for detailed information of these systems, see Chapter 14).

By calculating this system in the step mode Remote % (Add Amount), (**Remove Amount %** is here 100 of gas phase - Cell H4 - after each step and re-filling the gas phase with option), we get the results in **Fig. 10**.

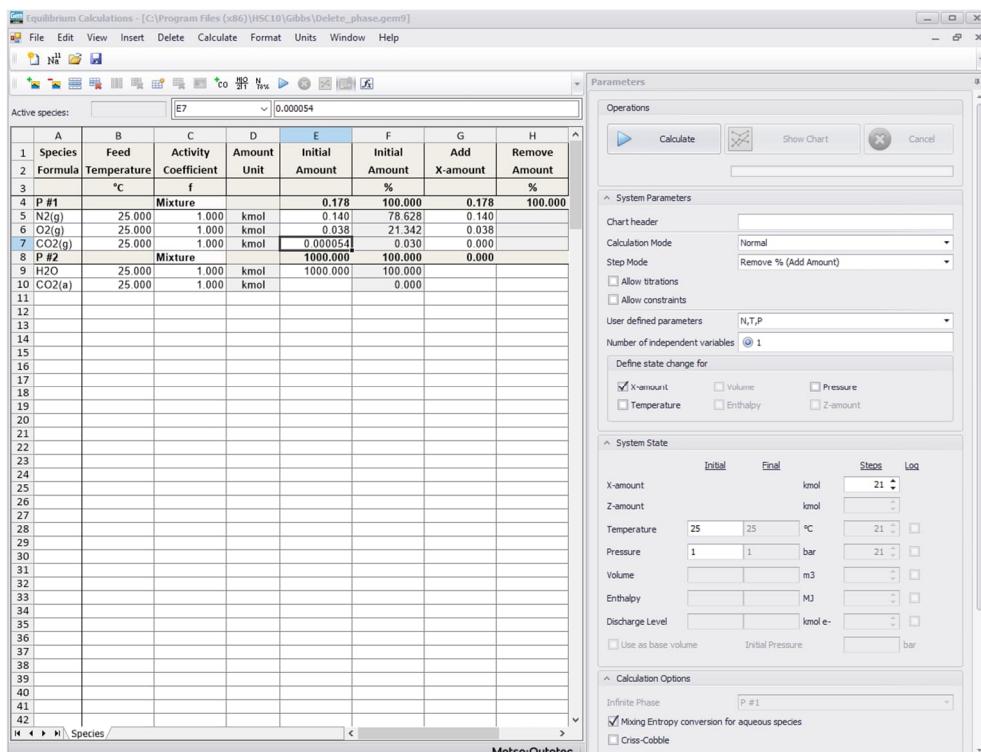


Fig. 9. Parameters for Remove % mode.

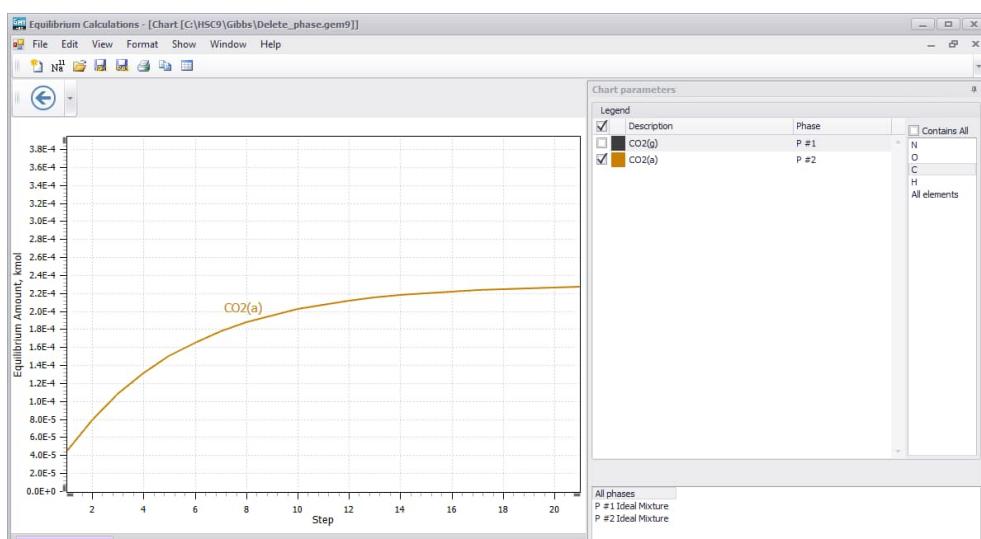


Fig. 10. Diagram for Remove % mode.

By calculating this system in the Infinite Phase mode (calculation option **P #1**) with temperature as the step parameter, we get **Fig. 11**. This chart corresponds to the expected values of CO₂ dissolution from **Fig. 10**.

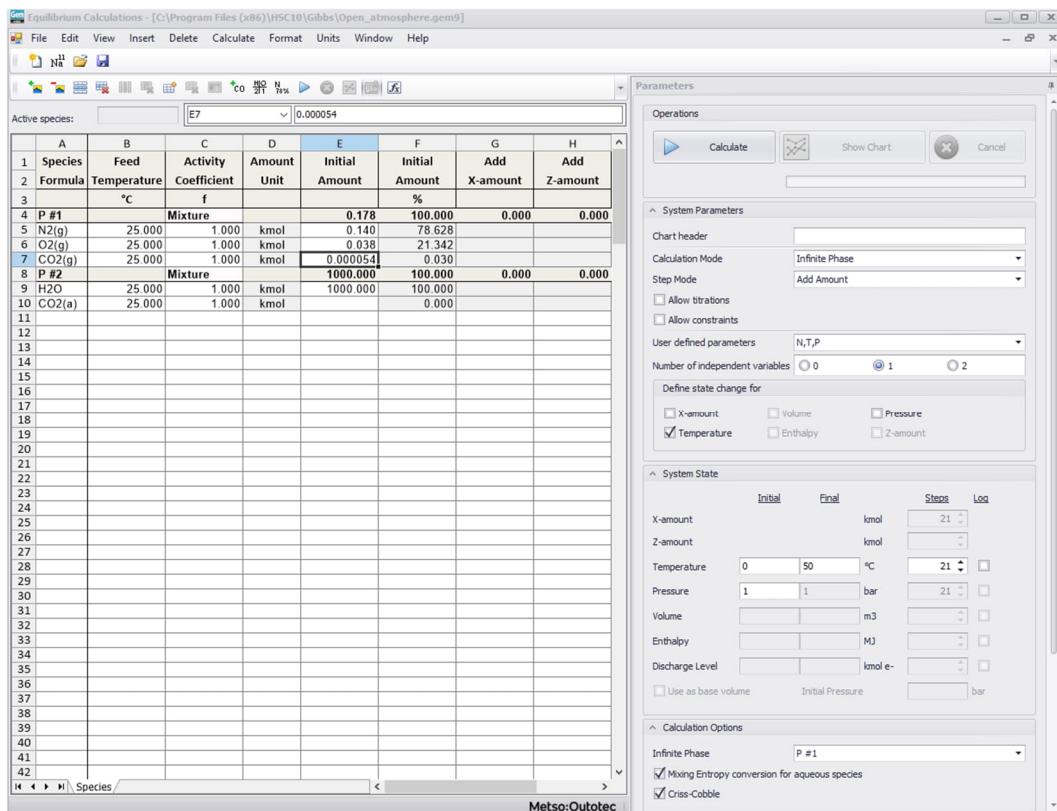


Fig. 11. Parameters for Infinite Phase mode.

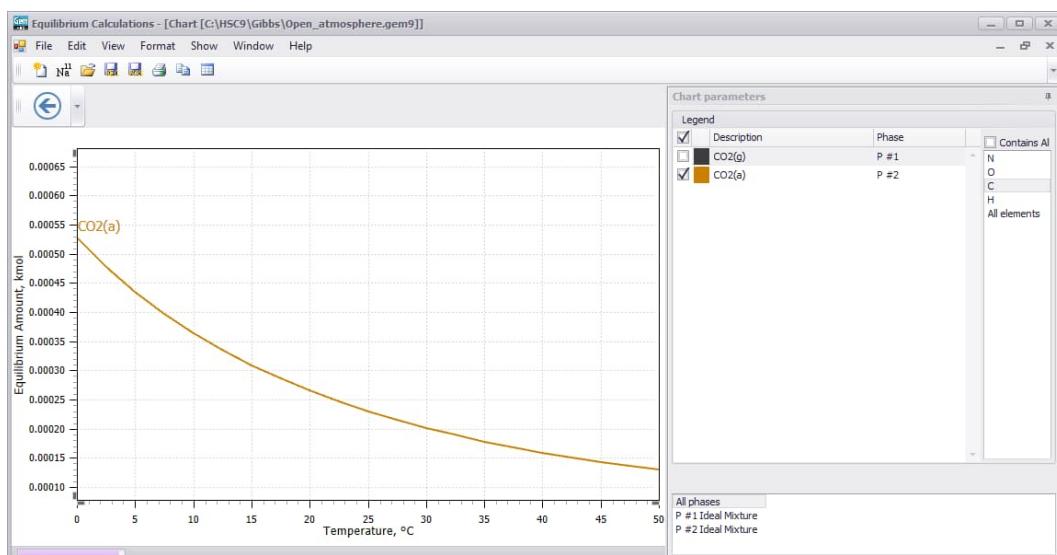


Fig. 12. Diagram for Infinite Phase mode.

User can also calculate this system in the Fixed Activity mode with a coefficient of 0.0003 for CO₂(g), see **Fig. 13**.

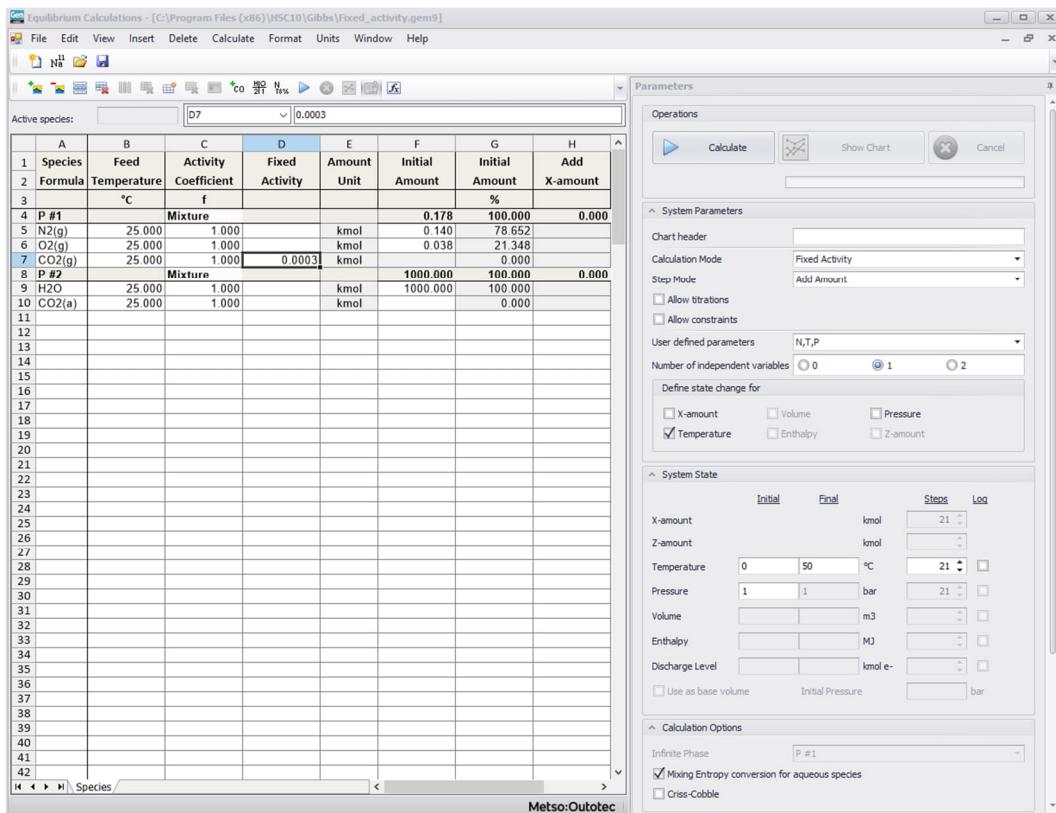


Fig. 13. Parameters for Fixed Activity mode.

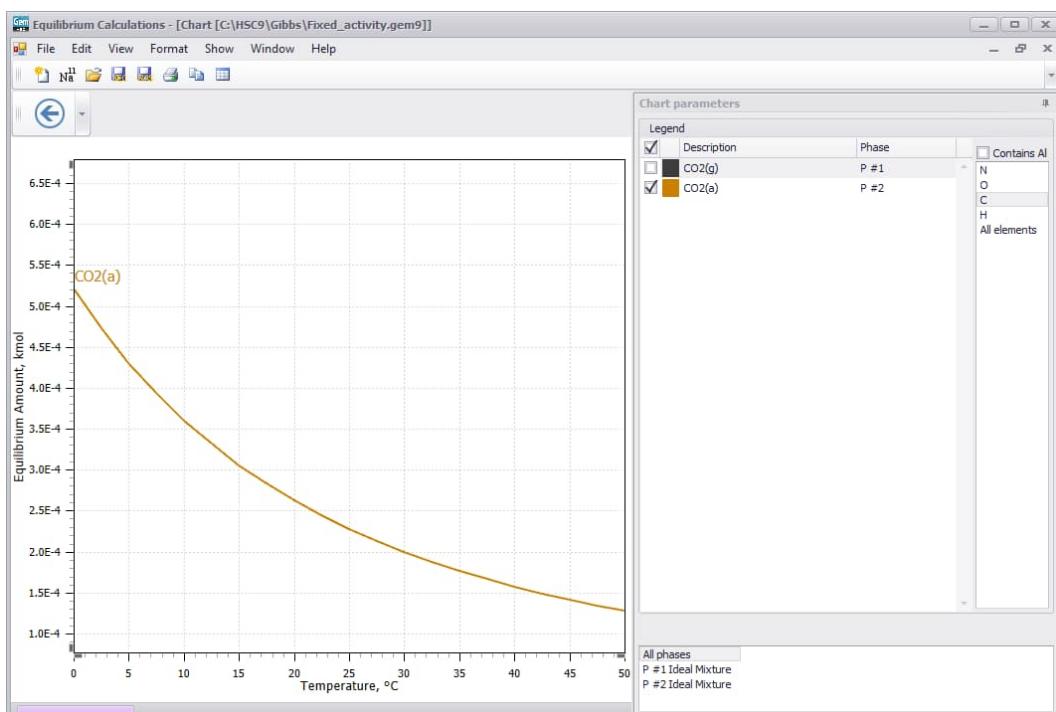


Fig. 14. Diagram with Fixed Activity.

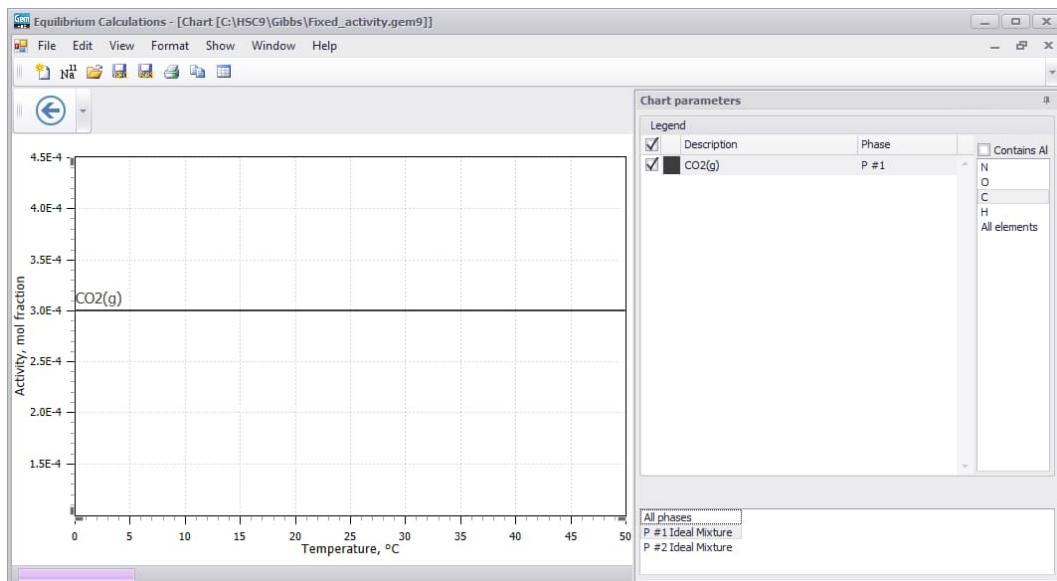


Fig. 15. Activity of CO₂(g).

This results in a diagram as in the Infinite Phase mode, see **Fig. 14**, and user can check that the Activity for CO₂(g) is constant as specified in the Fixed Activity coefficient, see **Fig. 15**.

13.5. Diagrams

The diagrams can be drawn, for example, as a function of a specified reactant amount or equilibrium temperature. User can draw a diagram by pressing **Show Chart** on the **Parameters Panel** or select **Chart** in the **View** menu. Gem module now uses same chart routine as other HSC modules.

User 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. User can select a group of species by selecting different phases or/and elements and then selecting the item from this group.

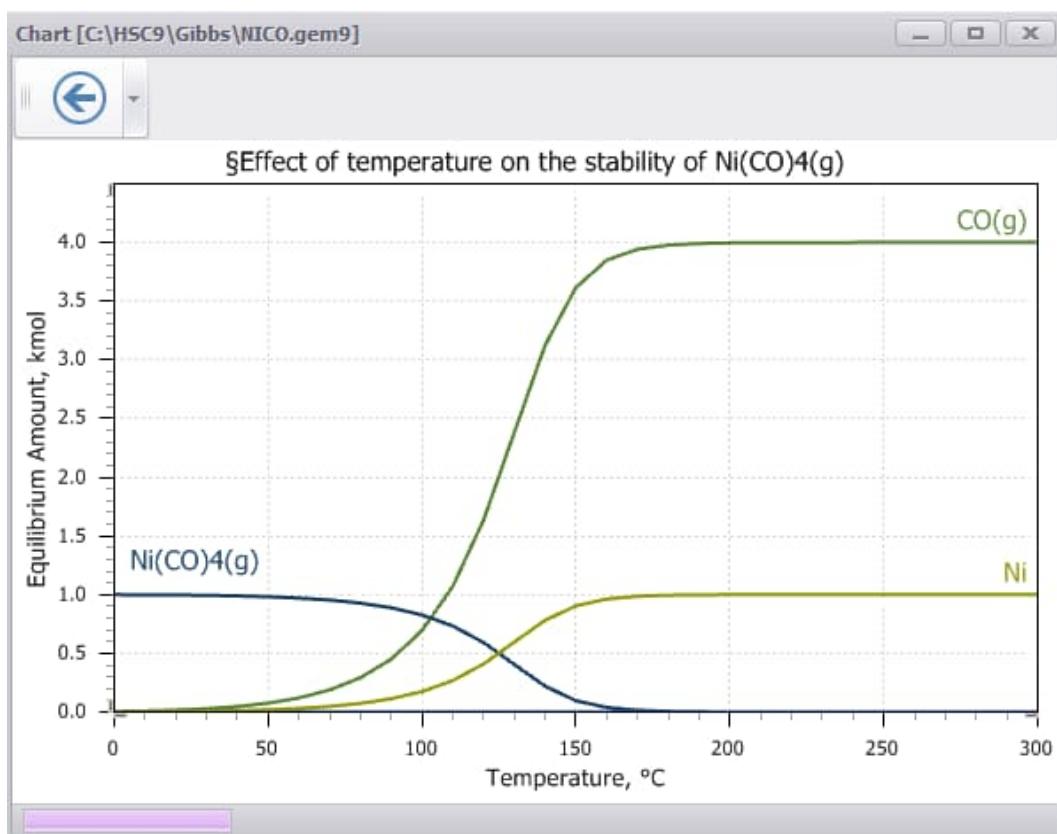


Fig. 16. 2D diagram.

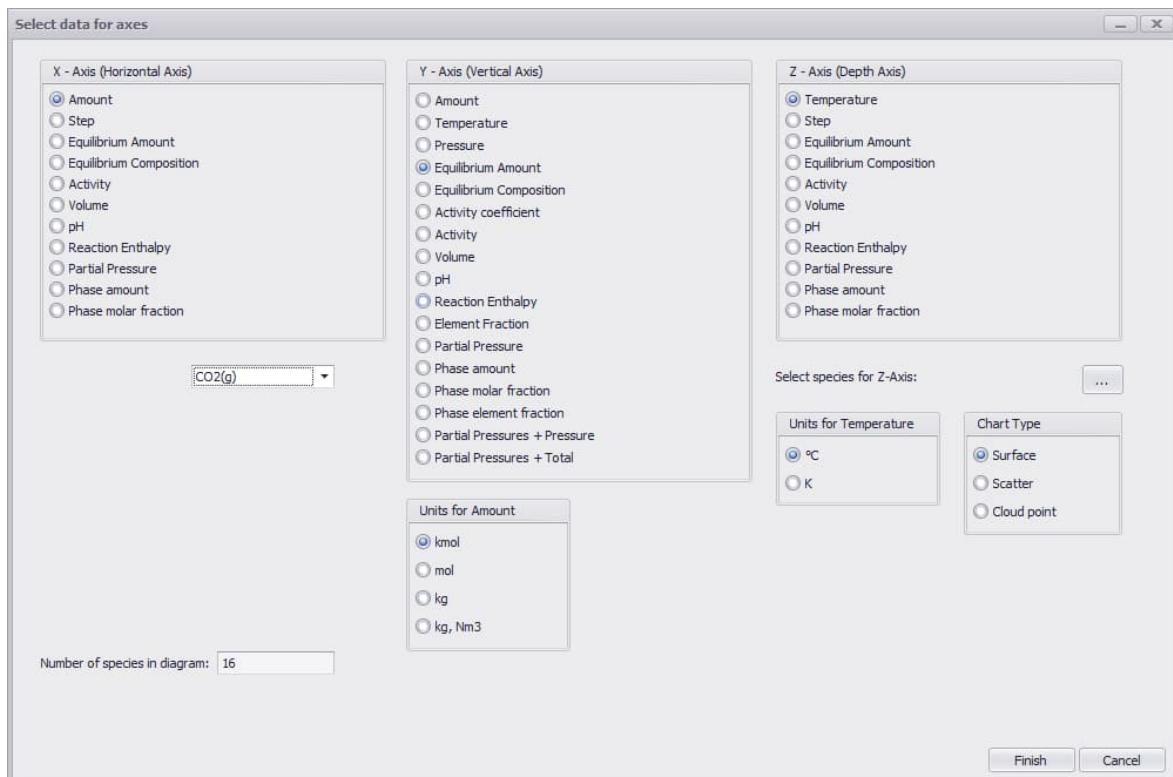


Fig. 17. Select data for axes.

In this menu user can select the data type for the diagram. Usually user can accept the default selections by pressing **Finish**, but the output may be modified. For example, user 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 user is working with an aqueous system, user 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.

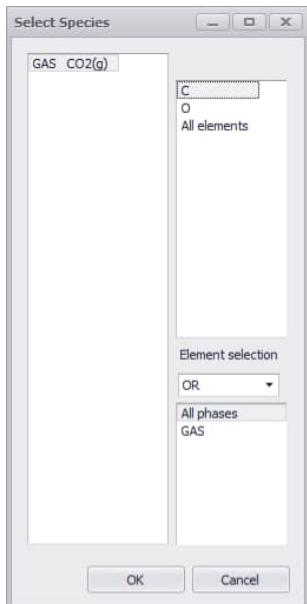


Fig. 18. Select Species.

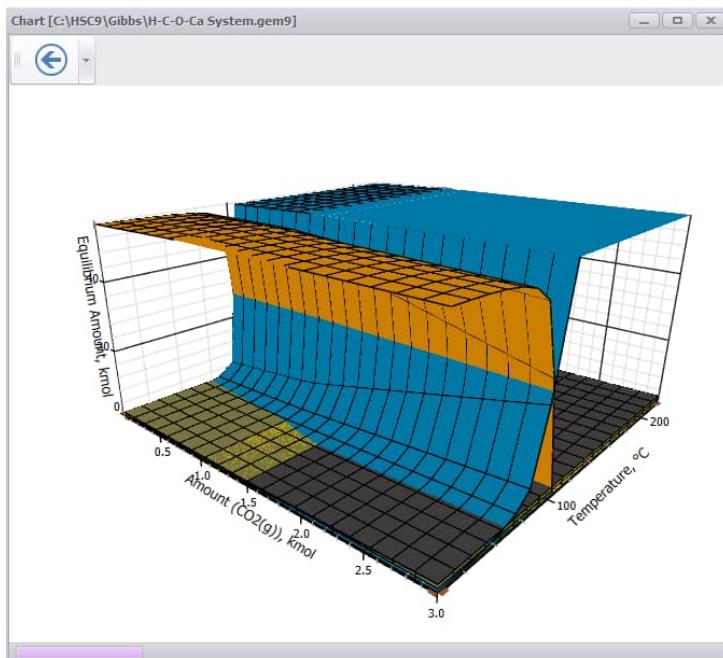


Fig. 19. 3D diagram.

When user presses **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.

User 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 to display large variations in amounts or concentrations. From the same window user 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, user 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. User 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 3D Diagram** sheet. User can change label, surface, wire frameline, etc. see **Fig. 22**.

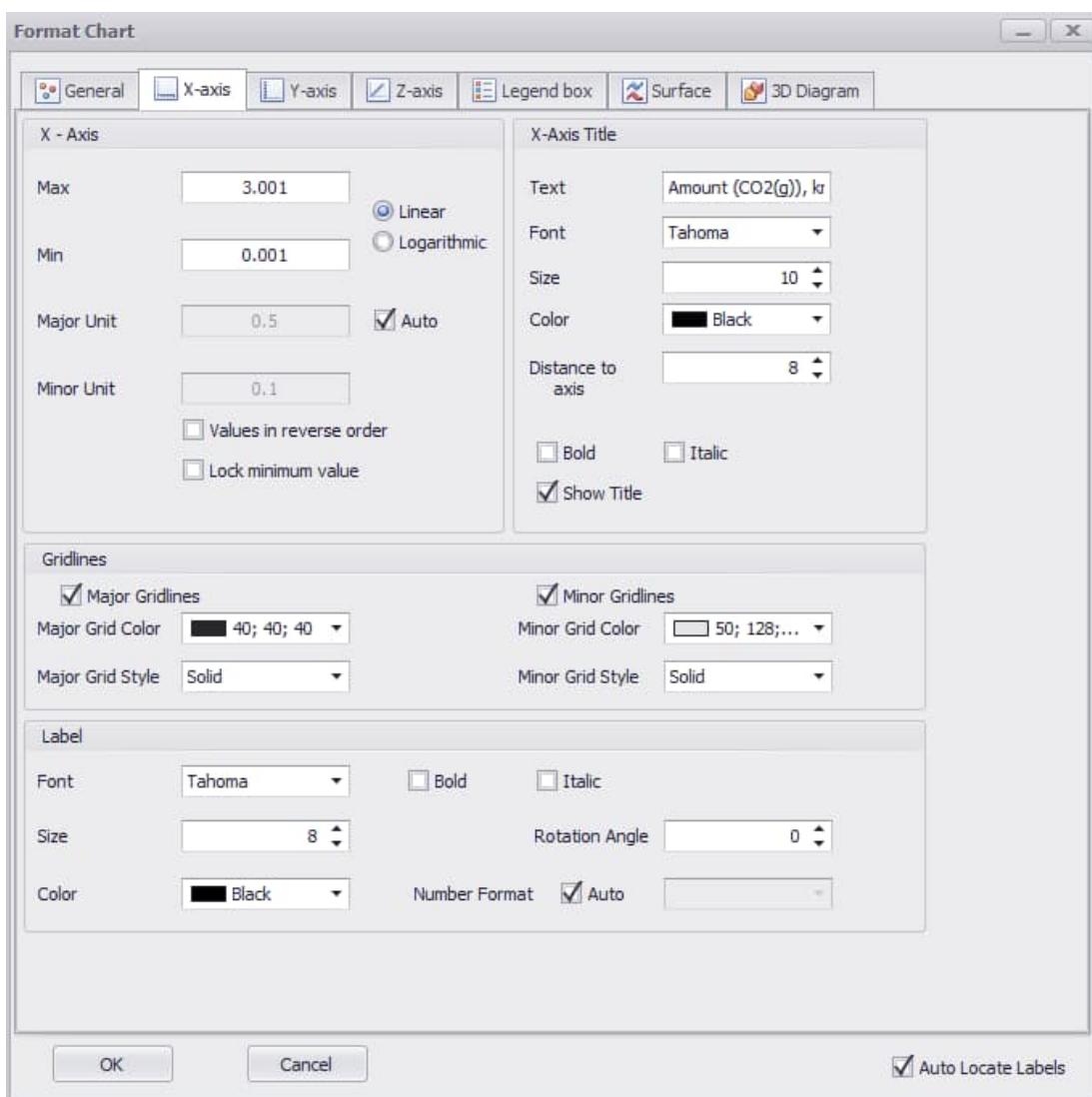


Fig. 20. Changing scales, scale number format and font settings.

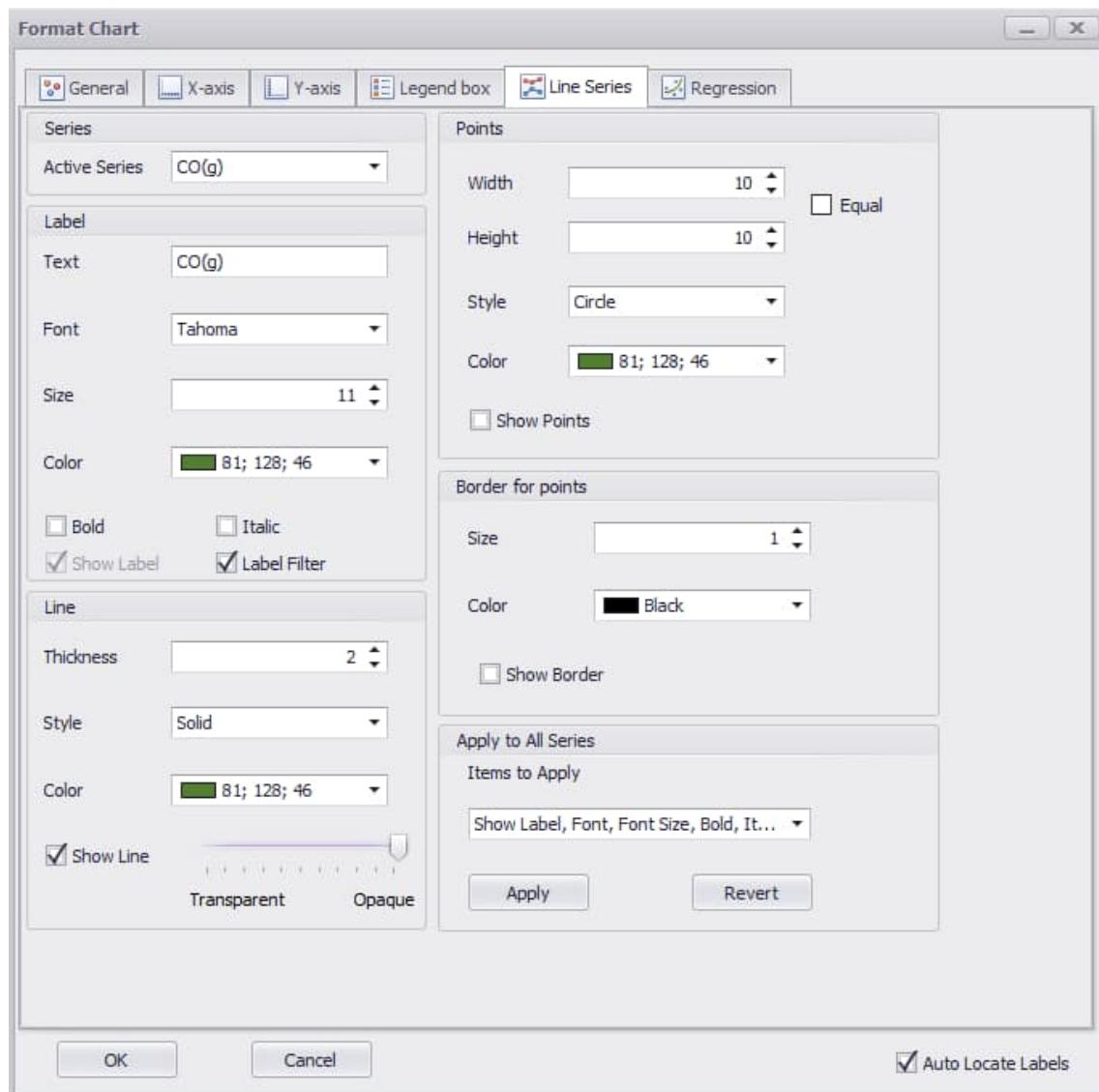


Fig. 21. Changing label and line specifications.

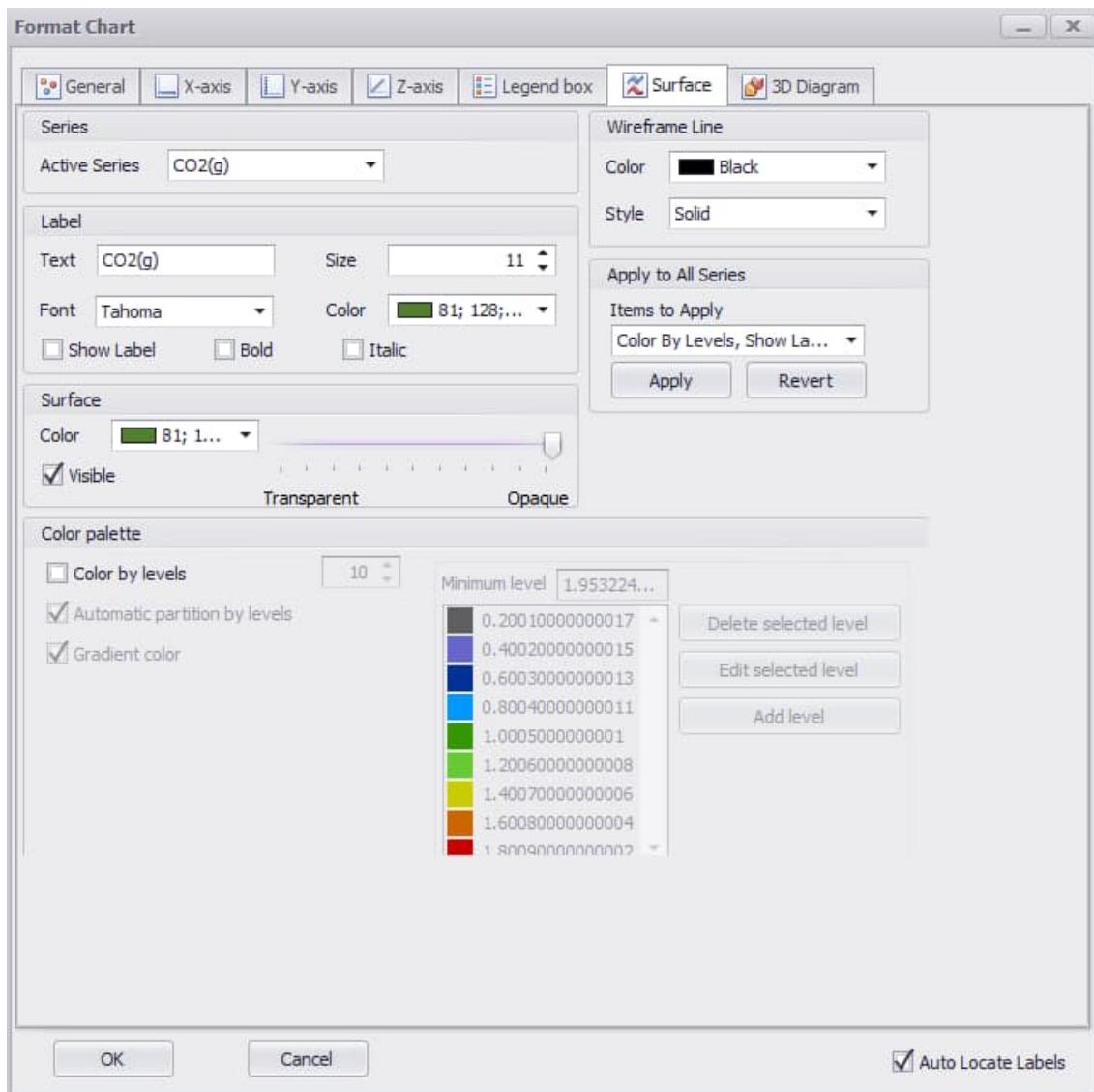


Fig. 22. Changing 3D surface specifications.

1. When user is satisfied with the diagram user can print it by pressing **Print** in top left corner **Chart Menu**.
2. If user wants to see the diagram in a tabular format or use the data of the diagram in other programs, such as MS Excel, press **Show menu Table** or select **Table Values** in top left corner **Chart Menu**.
3. User can copy the diagram to the Clipboard by pressing **Copy as Vector** or **Copy as Raster** and paste the diagram into other Windows programs. The **Copy** command uses the Windows Metafile format, which enables user to resize the diagram in other Windows applications in full resolution.
4. With **Clone** user can clone the diagram in a separate file which is outside Gem module.

13.5.1. User Formulas

This feature can be activated by clicking formula icon or View...User Formulas. User Formulas can be used for custom variable visualization, see **Fig. 23**.

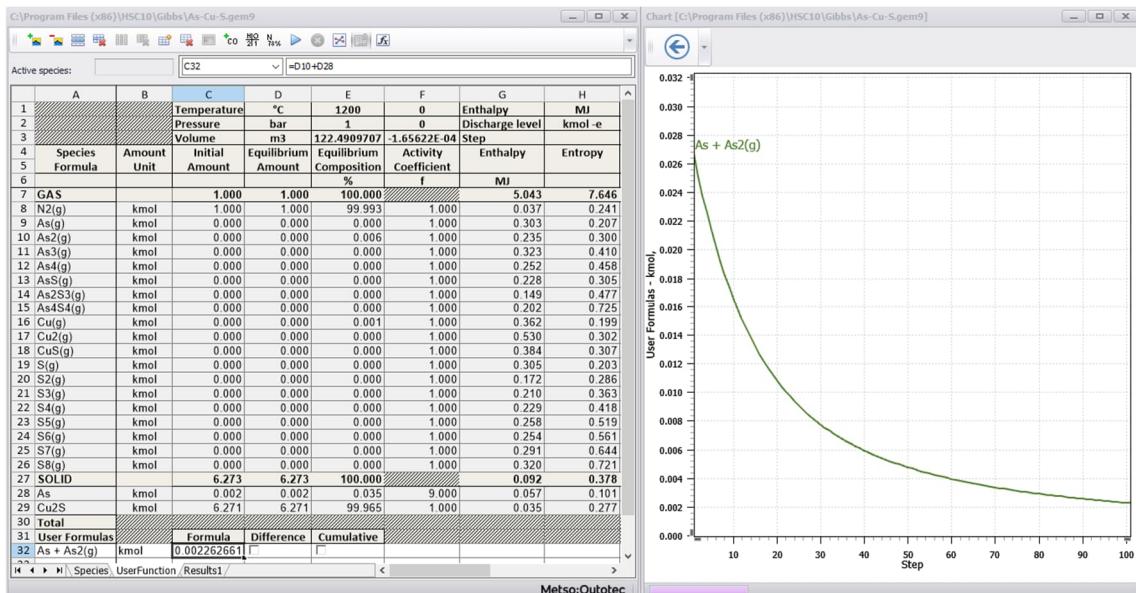


Fig. 23. User Formulas  for custom variable visualization.

13.5.2. Toolbar

Drawing additional objects or writing some labels on a diagram can be very helpful in some cases. User can select one of the shapes (line, arrow, rectangle or circle) or label, see **Fig. 24**. If user wants some other shape or label user can use the toolbar options. User can format the shape by selecting the inner color or border color, line width, line type. User can make the figure transparent, move to the back or to the front, see **Fig. 24**.

User can delete any shape using  on the toolbar.



Fig. 24. Toolbar.

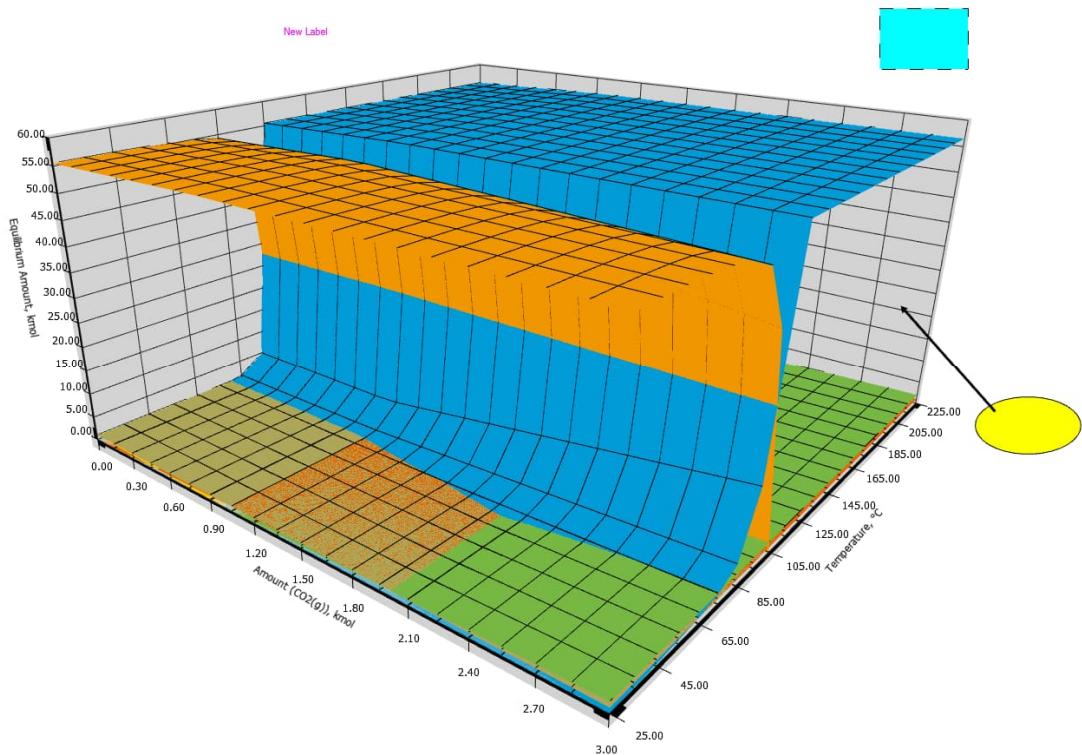


Fig. 25. 3D diagram with shapes.

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

13.5.3. Object Editor

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	0	Solid	65535	No
3	Rectan	715.5	100.5	811	156	0	0	Dot	1.6E+07	No
4	Arrow	698	283	118	118	0	0	Solid	0	No
5										

Shapes Labels

Fig. 26. Object Editor of the objects in **Fig. 25**.

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

13.5.4. Chart Parameters

The Diagram window appears with the Chart Parameters panel instead of the Parameters panel. User 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. User can change this list by selecting different phases and elements. User can select one, several, or all at once (by selecting "All phases" or "All elements"). The option "**Contains All**" means that if user selects several elements, the filter should find only the species that include all of the selected elements.

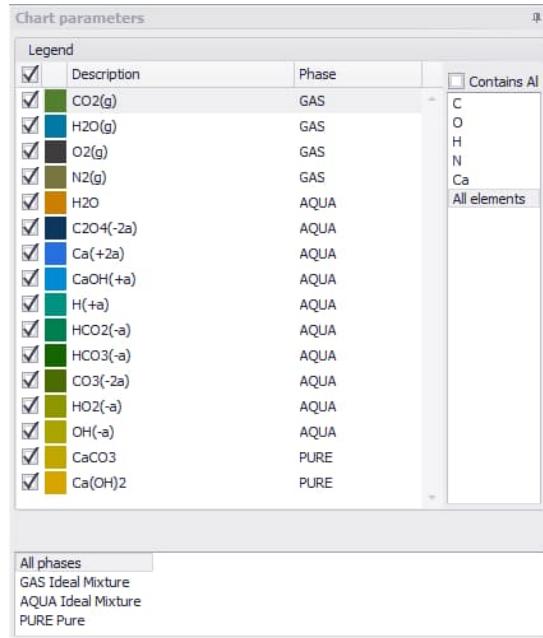


Fig. 27. Chart parameters.

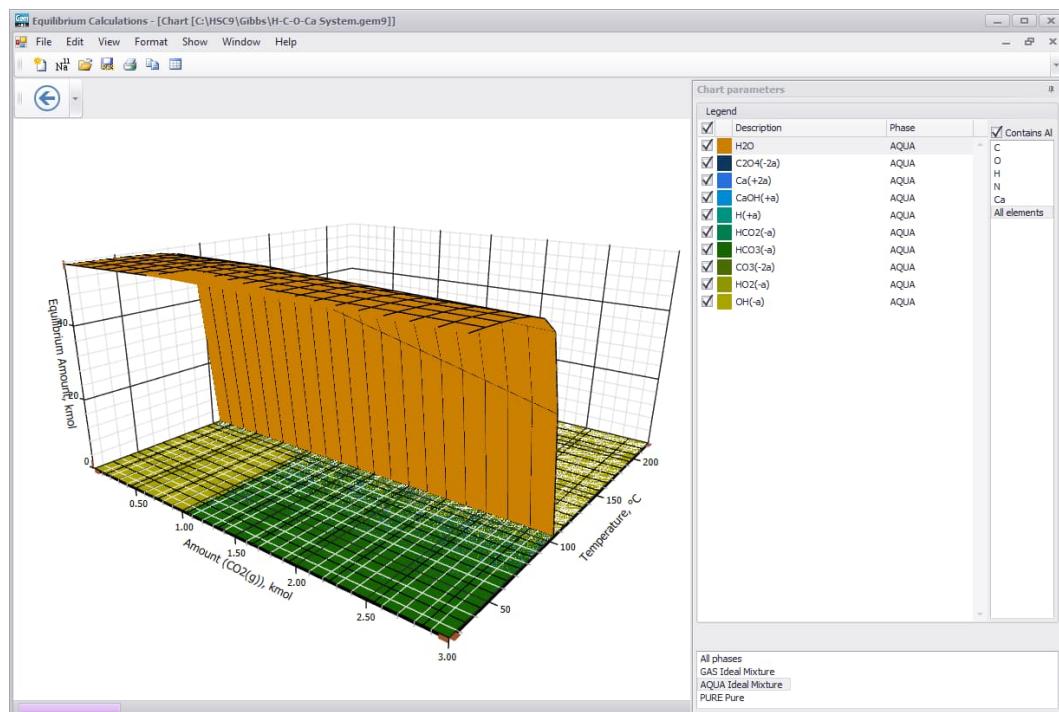


Fig. 28. Filtering species in a diagram (AQUA phase chosen here).

Auto Scale

This option helps user to use an appropriate scale when the maximum value of the diagram's lines is very small. When user unchecks some of the main species, the scale changes automatically and user can work with lines with smaller values.

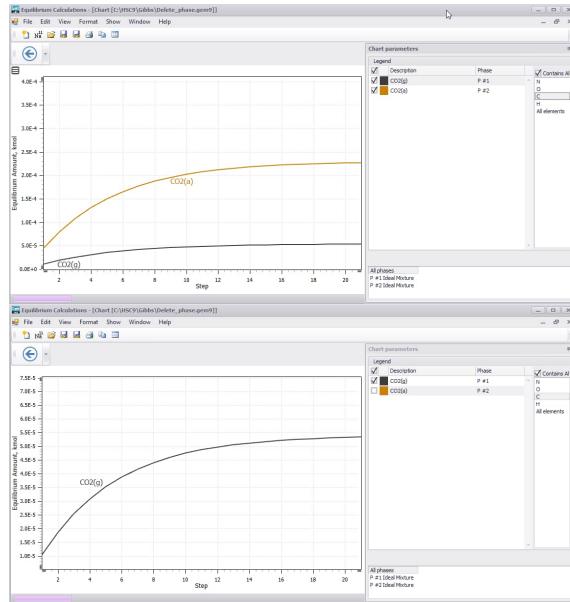


Fig. 29. Chart uses automatic scaling when species are filtered (here CO₂(a) is unchecked).

Color by Levels

This option allows user to colorize different levels of height charts in different colors. User can use this option only in a 3D diagram, see **Fig. 30**.

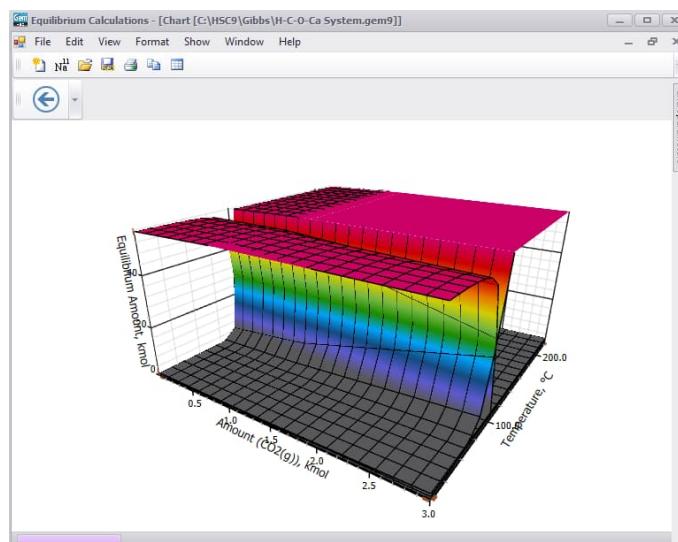


Fig. 30. Option Color by levels on diagram, see **Fig. 19** for comparison.

Show Legend on Chart

This option allows user to add one more panel on a 3D diagram legend panel, see **Fig. 31**. This panel duplicates the legend on the Chart Parameters panel, so user can check and uncheck species. The filter also changes it.

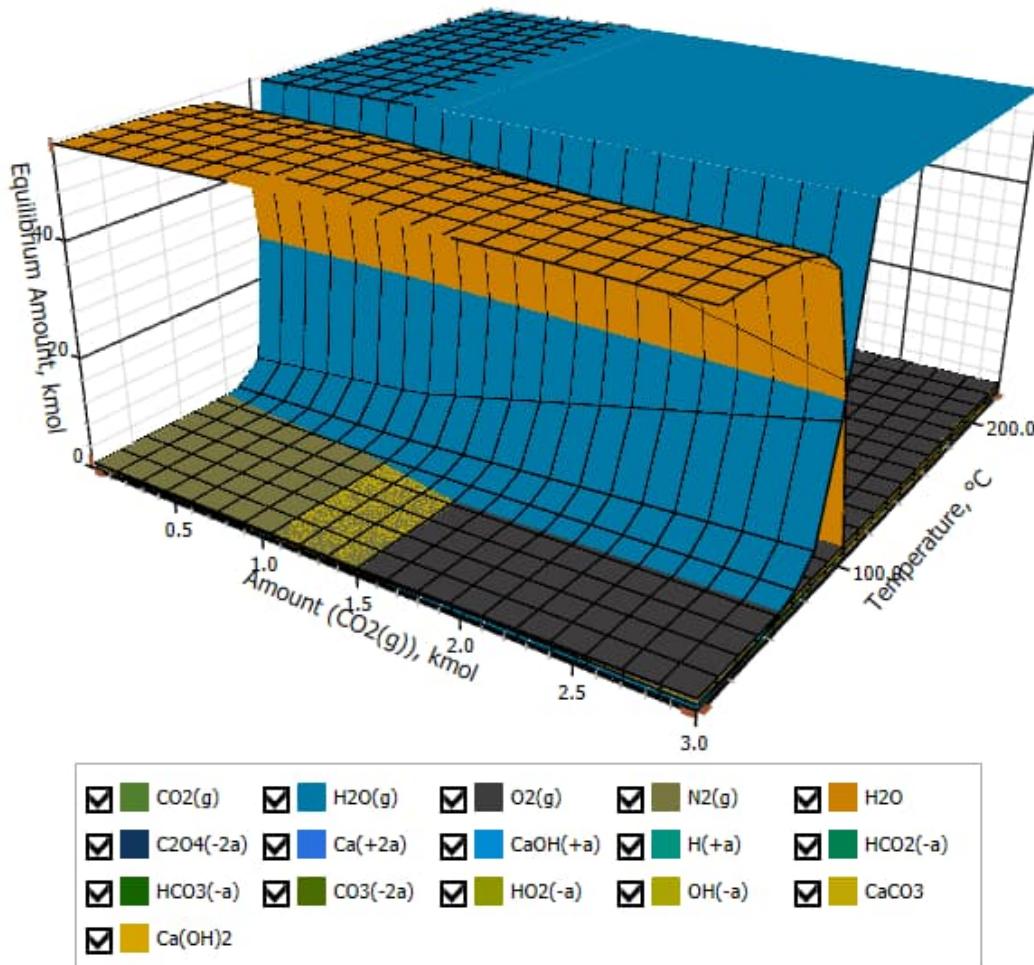


Fig. 31. 3D diagram with legend.

13.6. Equilibrium Diagram Tables

User can display the equilibrium results in tabular format by selecting **Table Values** (results in columns) in top left corner of the **Chart Menu**. Other table option is to select **Table** (results in rows) in the Show menu 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. User can also copy and paste smaller cell ranges using the **Copy** and **Paste** selections in the **Edit** menu, see **Fig. 33**.
2. User 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 user is 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. 33**. Setup and Preview options are also available for printing.

The screenshot shows the 'Species' results sheet in the HSC software. The table has columns labeled A through M. Row 1 defines the headers: Type, Step, AC, AC, AC, AC, AC, AC, AC, AC, AC, Gmin/RT, and H. Rows 2 and 3 provide target species and units information. Rows 4 through 8 contain numerical data for each species across the temperature range from 1.000 to 5.000. The software interface includes a toolbar at the top and a status bar at the bottom.

Fig. 32. Results sheet calculated automatically.

The screenshot shows the 'Equilibrium Results' dialog box. It displays a table with columns for Data Type, Species, Phase, Units, MW g/mol, Min, Max, and temperature values (1, 2, 3, 4, 5, 6). The 'Max' column shows values like 300, 0, 300, etc. The dialog box has a menu bar with File, Edit, Insert, Delete, Format, and Sort options. Buttons at the bottom include Copy All, Print, and Close.

Fig. 33. Equilibrium Diagram Table (Show...Table).

13.7. Restriction of Cp 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 C_p data is always given for limited temperature ranges in HSC database. HSC automatically extrapolates C_p data outside these ranges. Usually this works just fine, however, in some cases C_p 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.gem9. If the user presses Calculate, the Warnings window will be shown, see **Fig. 35**.

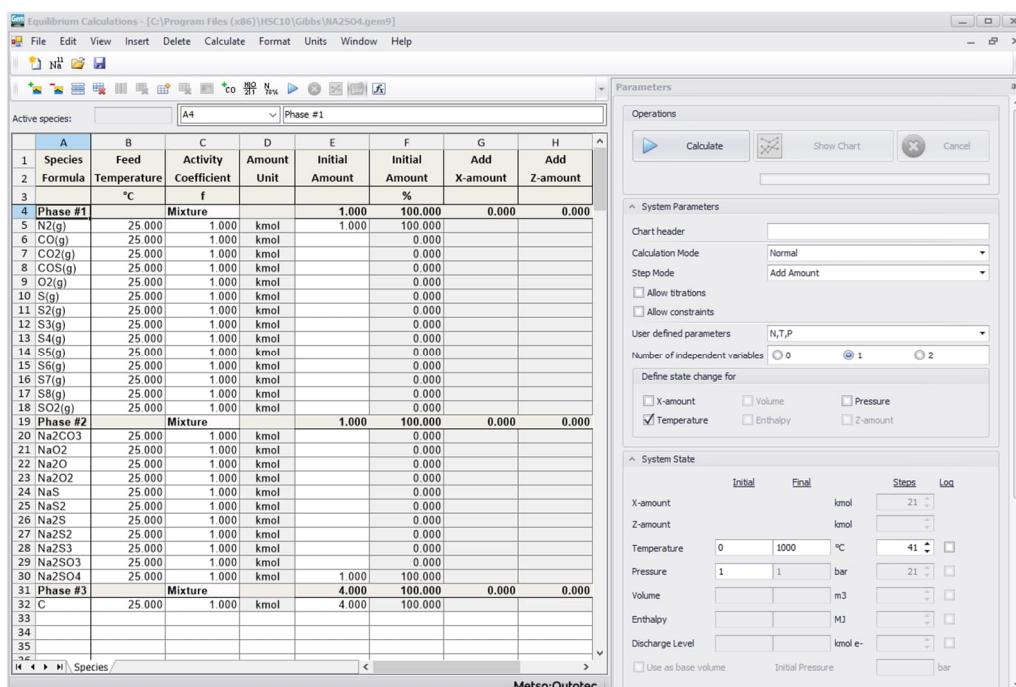


Fig. 34. NA2SO4.gem9 test case.

The Warnings windows show all the species that do not have C_p 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.

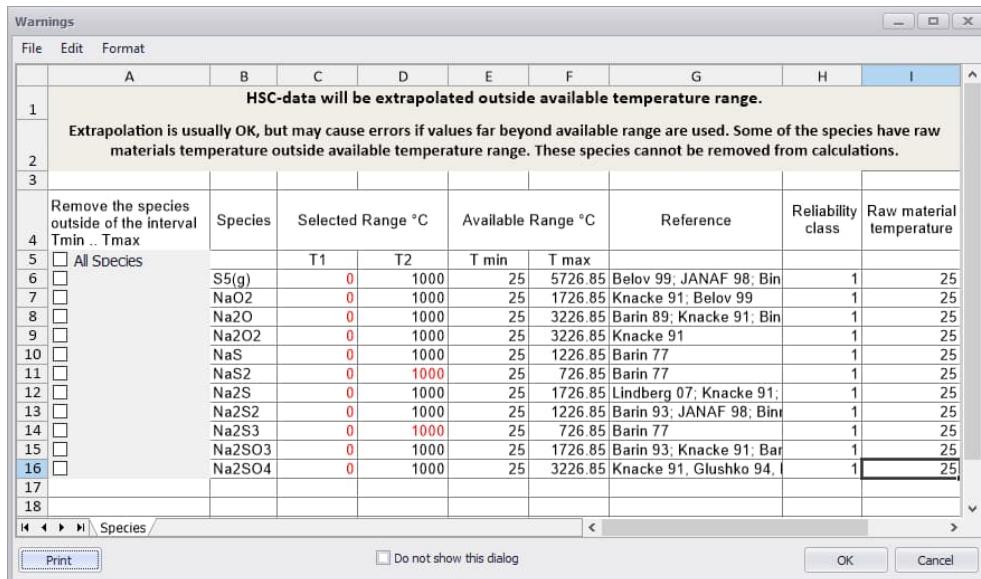


Fig. 35. Warnings window for NA2SO4.gem9 example. Warnings can be disabled or enabled from “Do not show this dialog” check box.

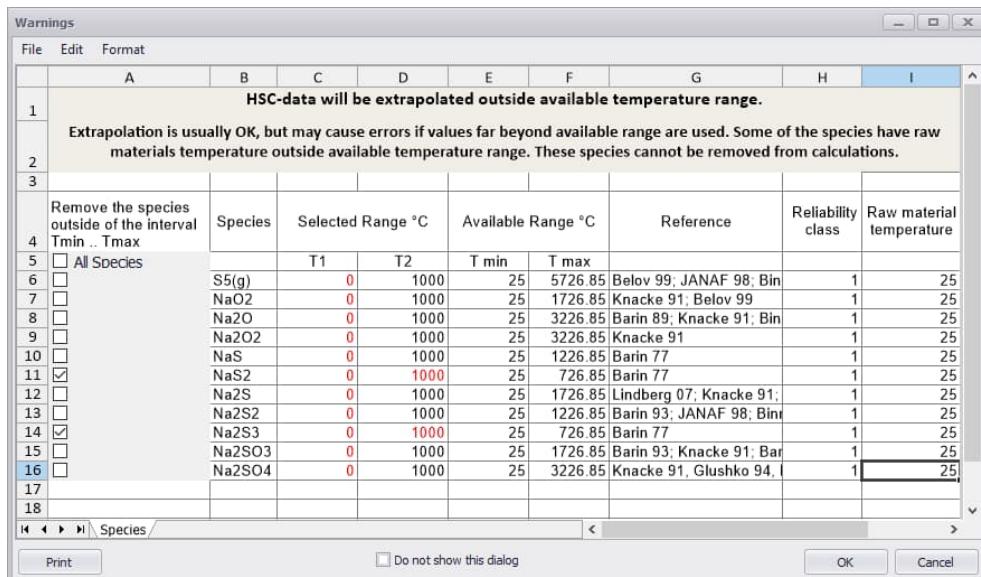


Fig. 36. Warnings window for NA2SO4.gem9 with species selected for removal.

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 considered. 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).

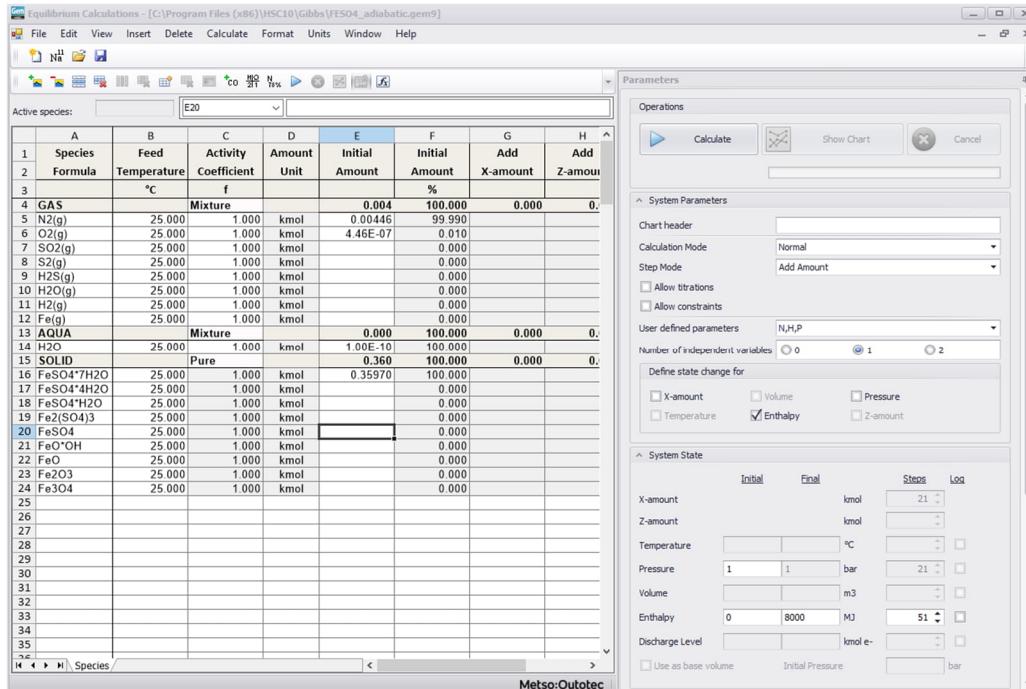


Fig. 37. FESO4_adiabatic.gem9 example for adiabatic calculation.

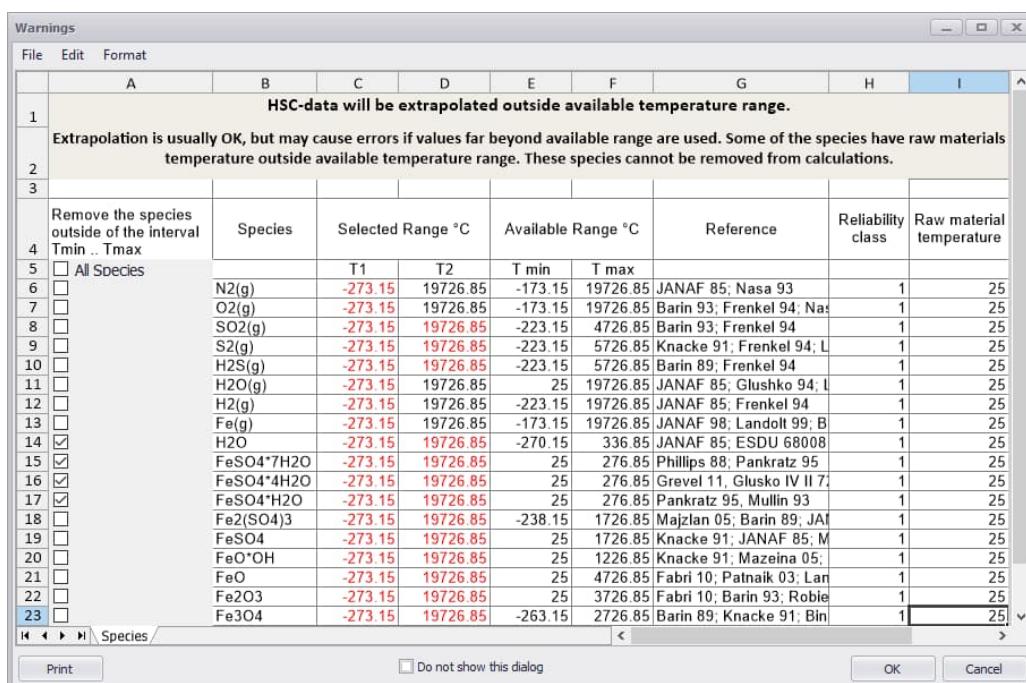


Fig. 38. Warnings for adiabatic calculation.

An example of adiabatic calculation with and without the removal of some species is presented in **Fig. 37- Fig. 40**. 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. 38**.

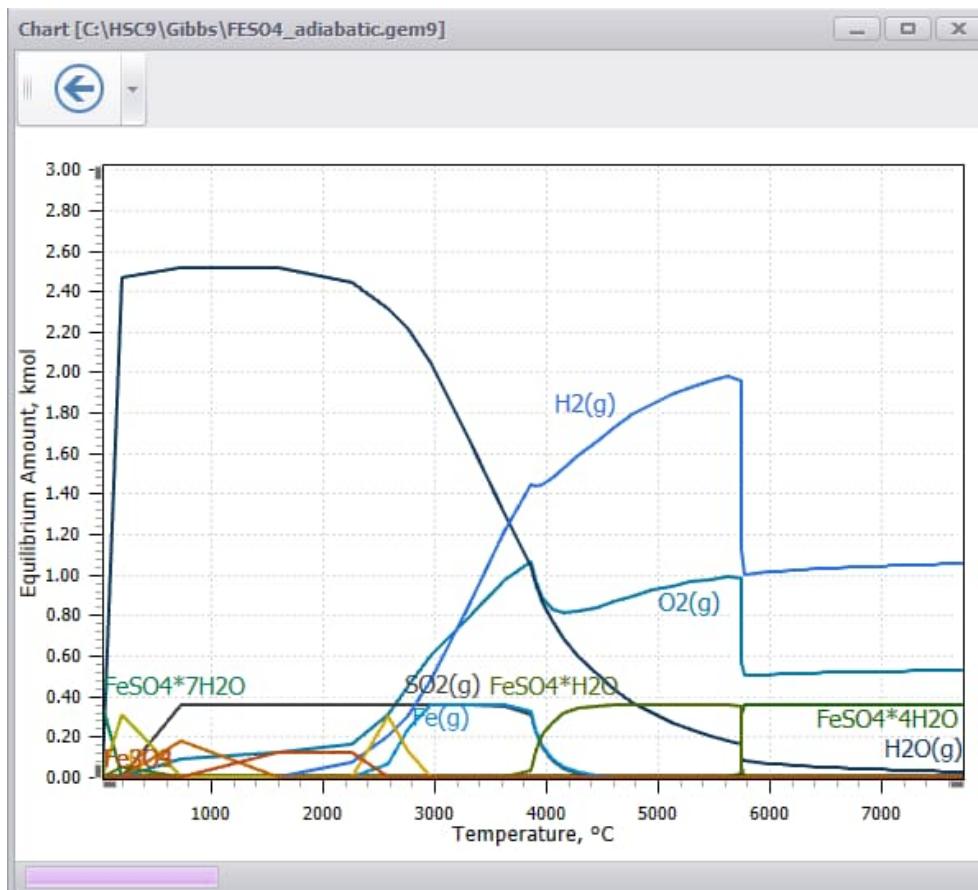


Fig. 39. Adiabatic calculation – without species removal, hydrates are formed at high temperatures.

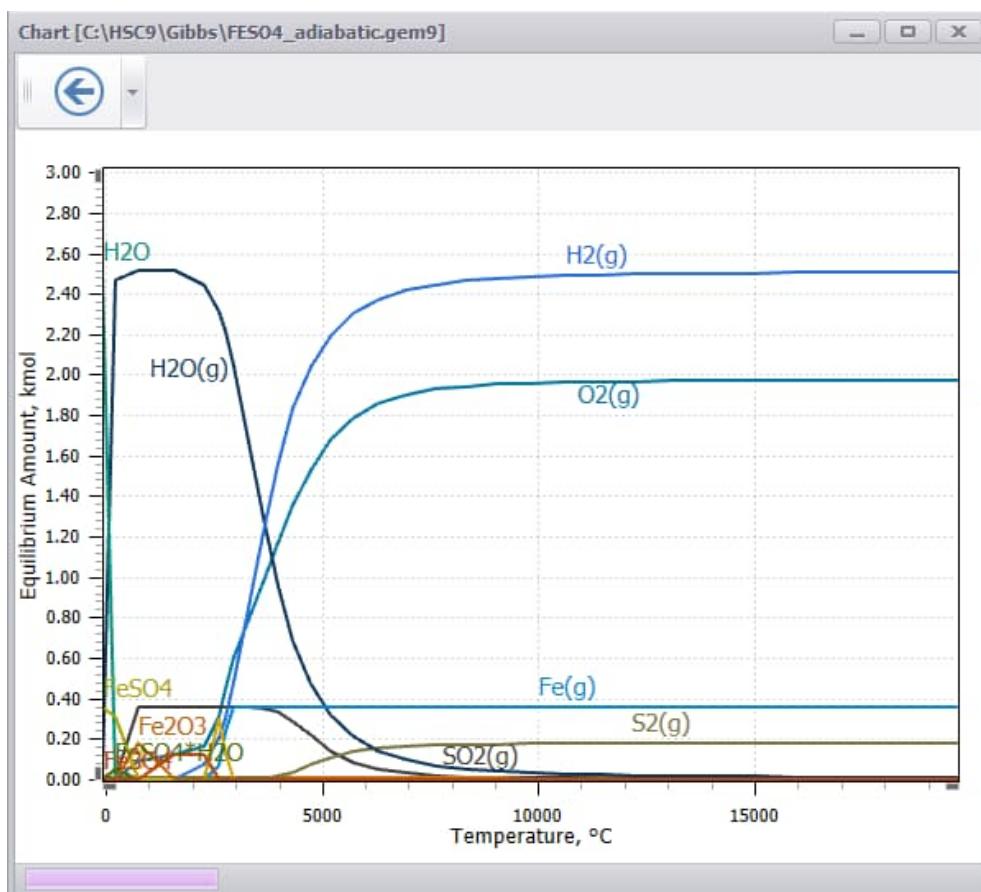


Fig. 40. Adiabatic calculation – species “H₂O”, “FeSO₄*7H₂O”, “FeSO₄*4H₂O”, “FeSO₄*H₂O” removed at high temperatures.

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 considered 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 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. User may also select many 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 behaviour 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 user expects 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 phase can be set as pure substances using the Solution model **Pure Substance** 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. User can check the results by a known equilibrium coefficient or mass balance tests. It is evident that results are erroneous if user obtains a random scatter in the curves of the diagram. User 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 N₂(g). This makes calculations easier for the equilibrium programs.
8. It may also be necessary to avoid **stoichiometric raw material atom ratios** by inserting an additional substance which does not interfere with the existing equilibrium. For example, if user has given 1 mol Na and 1 mol Cl as the raw materials and user has 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. User can avoid this situation by giving an additional 1E-5 mol Cl₂(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 H₂O(g) - H₂O-system between 0 - 200 °C.

10. Sometimes a substance is very stable thermodynamically, but its amount in experiments remains quite low, obviously for kinetic reasons. User can try to eliminate such a substance in the calculations 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** or **MainDB9** database 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 can 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 $\text{Na}_2\text{SO}_4.\text{gem9}$ example in the $\backslash\text{HSC10}\backslash\text{GIBBS}$ 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 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. 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 must provide its type (gas/liquid/solid/metal), whether it is an electrode phase (anode or cathode), phase electric capacitance (in Farads)
2. The user must 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.

C:\Program Files (x86)\HSC10\Cell\LEADBATT.gem9 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. 41**). 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).

	A	B	C	D	E	F	G	H	I
1	Species	Feed	Activity	Discharge	Amount	Initial	Initial	Add	Add
2	Formula	Temperature	Coefficient	Coefficient	Unit	Amount	Amount	X-amount	Z-amount
3		°C	f				%		
4	GAS		Mixture			10.000	100.000	0.000	0.000
5	N2(g)	25.000	1.000		kmol	10.000	100.000		
6	Copper		Mixture			1.000	100.000	0.000	0.000
7	Cu	25.000	1.000	0.000	kmol	1.000	100.000		
8	e-(Cu)	25.000	1.000	-1.000	kmol	0.000	0.000		
9	Lead		Mixture			20.000	100.000	0.000	0.000
10	Pb	25.000	1.000	-2.000	kmol	20.000	100.000		
11	e-(Pb)	25.000	1.000	-1.000	kmol		0.000		
12	Electrolyte		Mixture			74.250	100.000	0.000	0.000
13	H2O	25.000	1.000		kmol	55.500	74.747		
14	H(+a)	25.000	1.000		kmol	12.500	16.835		
15	OH(-a)	25.000	1.000		kmol	0.000	0.000		
16	Pb(+2a)	25.000	1.000		kmol	0.000	0.000		
17	SO4(-2a)	25.000	1.000		kmol	6.250	8.418		
18	Lead-oxide		Mixture			20.000	100.000	0.000	0.000
19	PbO2	25.000	1.000		kmol	20.000	100.000		
20	e-(Pb)	25.000	1.000		kmol		0.000		
21	Copper		Mixture			1.000	100.000	0.000	0.000
22	Cu	25.000	1.000		kmol	1.000	100.000		
23	e-(Cu)	25.000	1.000		kmol		0.000		
24	Solid		Mixture			0.000	0.000	0.000	0.000
25	PbSO4	25.000	1.000		kmol	0.000	0.000		

Fig. 41. Phase data information in Cell mode (LEADBATT.gem9).

For a complete cell with two or more electrodes, the total charge and the number 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 user can calculate potentials and compositions at different discharge levels of the cell. The discharge amount is set in the System state parameter section like other parameters like temperature or pressure (see **Fig. 42**) 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 like 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. 43** and **Fig. 44**).

Note! Discharge level can also be negative value for certain cells. However, if user gives negative discharge level for this example LEADBATT.gem9 cell, incorrect very high voltage is calculated $9.2 \cdot 10^8$ V by the model.

System Parameters

Chart header	<input type="text"/>	
Calculation Mode	Cell Mode	
Step Mode	Add Amount	
<input type="checkbox"/> Allow titrations		
<input type="checkbox"/> Allow constraints		
User defined parameters	N,T,P,Q	
Number of independent variables	1	
Define state change for:		
<input type="checkbox"/> X-amount	<input type="checkbox"/> Volume	<input type="checkbox"/> Pressure
<input type="checkbox"/> Temperature	<input type="checkbox"/> Enthalpy	<input type="checkbox"/> Z-amount
<input checked="" type="checkbox"/> Discharge level		

System State

	Initial	Final	Steps	Log
X-amount		kmol	21	<input type="checkbox"/>
Z-amount		kmol		<input type="checkbox"/>
Temperature	25	25 °C	21	<input type="checkbox"/>
Pressure	1	1 bar	21	<input type="checkbox"/>
Volume		m ³		<input type="checkbox"/>
Enthalpy		MJ		<input type="checkbox"/>
Discharge Level	0	6.25 kmol e-	21	<input type="checkbox"/>
<input type="checkbox"/> Use as base volume	Initial Pressure			
			bar	

Fig. 42. System parameters in Cell mode (LEADBATT.gem9).

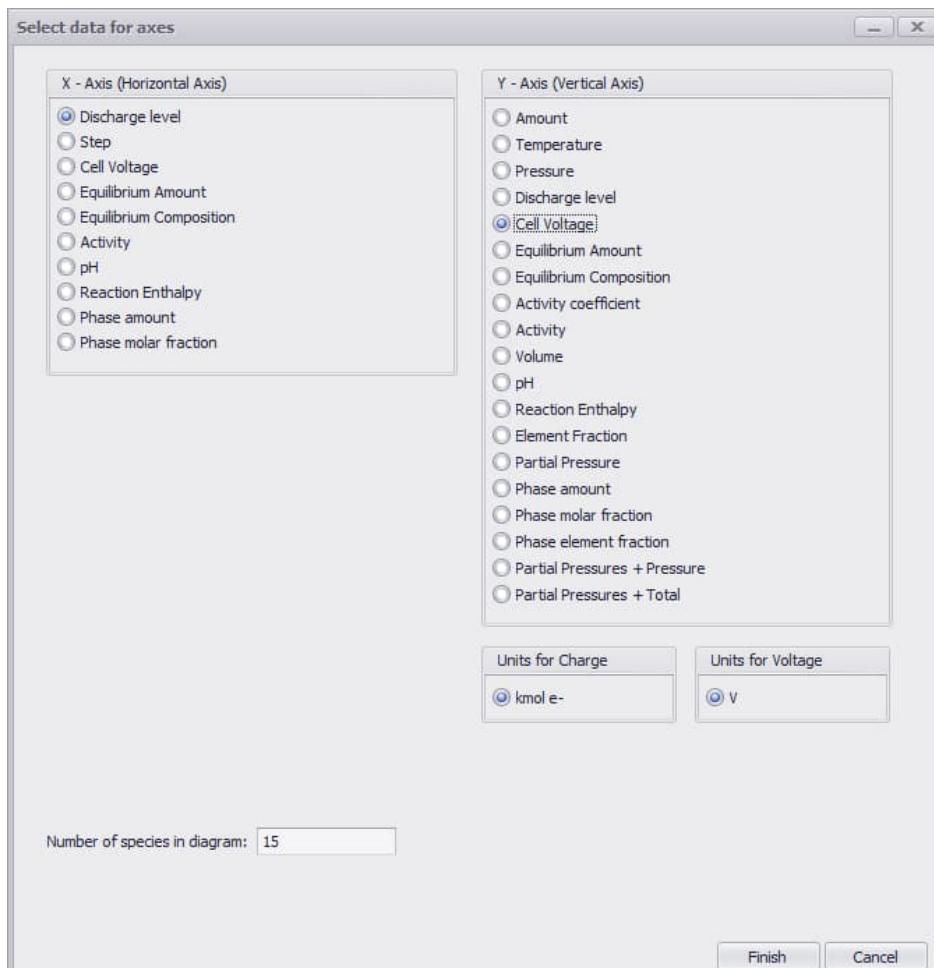


Fig. 43. Chart parameters in Cell mode (LEADBATT.gem9).

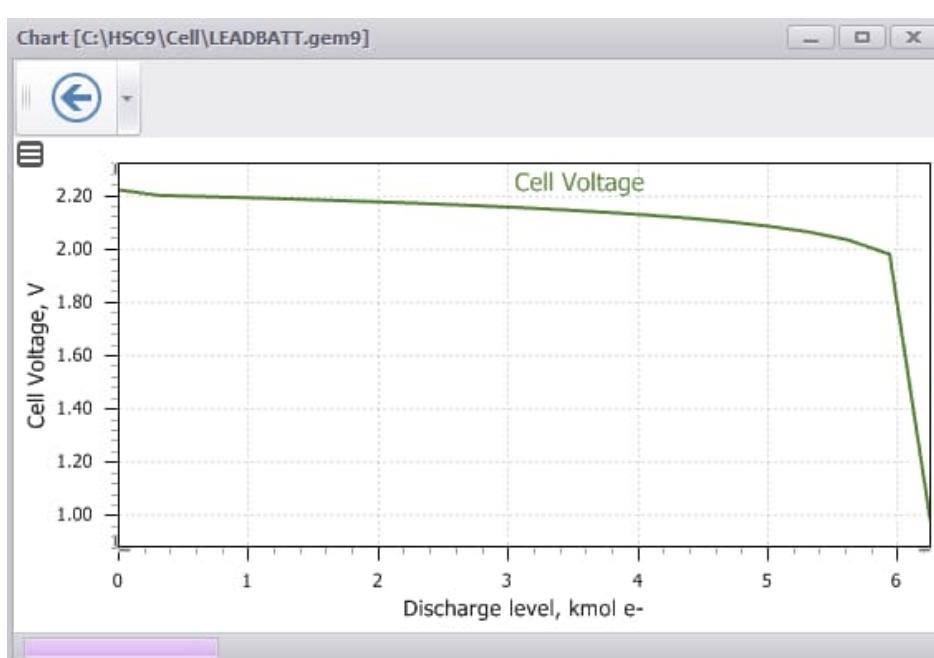


Fig. 44. Chart window in Cell mode.

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 HSC 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, `IActivityCoefficientModel2`. 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 IActivityCoefficientModel2
    Sub Initialize(species As String())
        Function CalculateActivityCoefficients(ByVal amounts As Double(),
                                                temperature As Double, pressure As Double) As
            Double()
    End Interface
End In
```

The main interface is the `IActivityCoefficientModel2`. 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 strings)

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.

Pressure (bar) - passed into the `CalculateActivityCoefficients` method.

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 user needs 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, the default path is

C:\Program Files (x86)\HSC10\Programs\AddinPipeline\AddInViews\AddinView.dll)

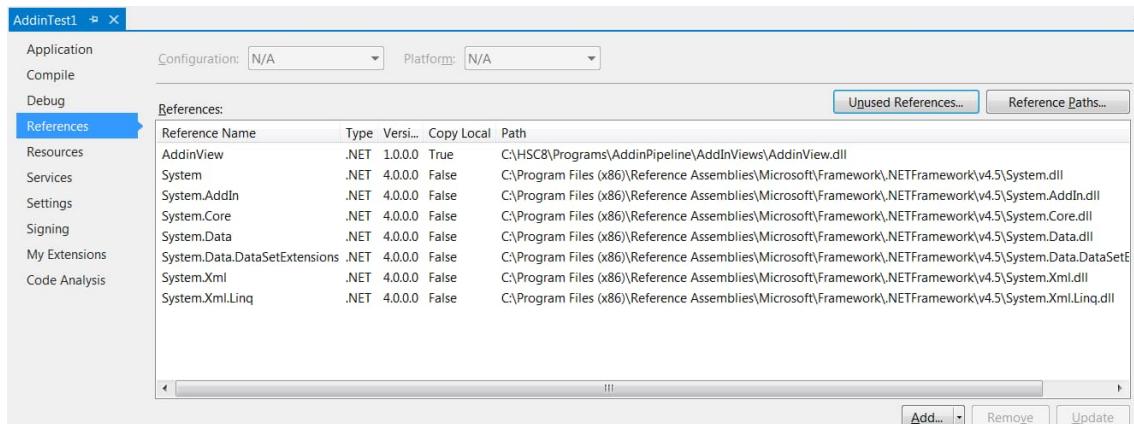


Fig. 45. Project references.

Next, user needs to implement the add-in interface, by creating a class that implements the interface Outotec.HSC.AddinPipeline.AddinViews.IActivityCoefficientModel2.

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 IActivityCoefficientModel2

    Public Sub Init(ByVal species As String) _
        Implements IActivityCoefficientModel2.Init
        Throw New NotImplementedException()
    End Sub

    Public Function CalculateActivityCoefficients(amounts As Double(), _
        temperature As Double, pressure As Double) As Double() _
        Implements IActivityCoefficientModel2.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 Init method is called by HSC Gibbs before the calculation of the phase, and an array of strings with species formulas is passed into it. It is expected that the method keeps the species names from this array somewhere.

```
Private _species As IEnumerable(Of String)  
Public Sub Init(ByVal species As String())  
    Implements IActivityCoefficientModel2.Init  
    _species = species  
End Sub
```

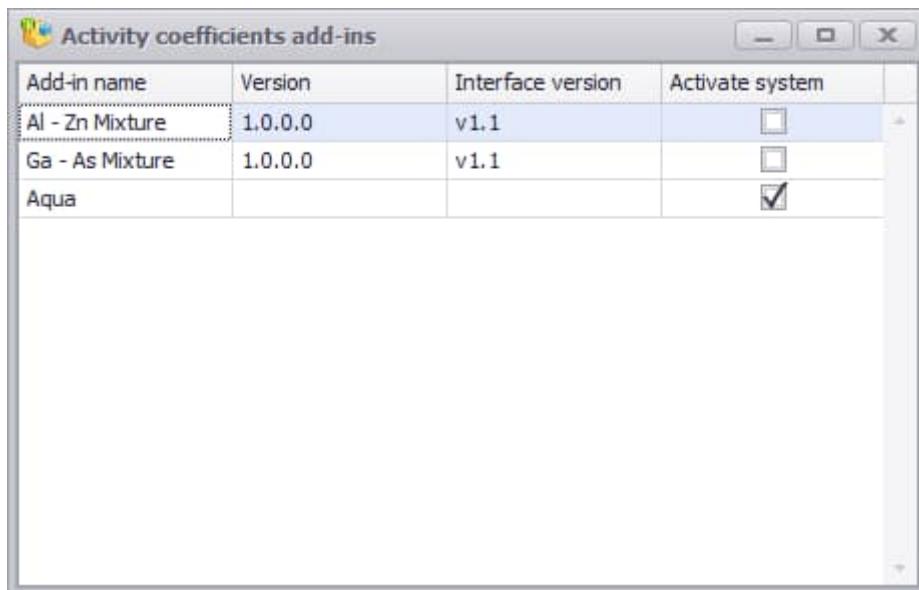
The CalculateActivityCoefficients method is called by HSC Gibbs during the phase calculations. The parameters passed are the amounts of species in mol (species order and number correspond to the species passed into the Init method), temperature in Kelvins and pressure in bars. The method should return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

```
Public Function CalculateActivityCoefficients(amounts As Double(),  
                                              temperature As Double, pressure As Double) As Double()  
    Implements IActivityCoefficientModel2.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 users activity coefficient model provides the logarithm of the activity coefficient, user needs to exponentiate it in the CalculateActivityCoefficients method, so that the correct logarithm is achieved in the Gibbs energy calculations.

After user has compiled the class library, user needs to place the DLL into a separate folder in the Programs\AddinPipeline\Addins directory of the HSC 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:\Program Files (x86)\HSC10\Programs\AddinPipeline\Addins\AddinTest1

Once the library has been placed in the corresponding folder, user can start HSC Gibbs. The new model should be available in the solution model drop-down list. User can also check the available models in the Window - Add-Ins menu (**Fig. 46**).



Add-in name	Version	Interface version	Activate system
Al - Zn Mixture	1.0.0.0	v1.1	<input type="checkbox"/>
Ga - As Mixture	1.0.0.0	v1.1	<input type="checkbox"/>
Aqua			<input checked="" type="checkbox"/>

Fig. 46. 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).

$${}^{\text{Ex}}G = x_i x_j \sum k_n \cdot (x_i - x_j)^n, \quad (1)$$

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

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

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

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

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

APPENDIX B. Ga - As solution model

HSC 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 _GAIIndex As Integer = -1
    Private _ASIIndex 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
        _GAIIndex = -1
        _ASIIndex = -1

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

            If formula = "As(I)" Then
                _ASIIndex = i
            End If
            If _GAIIndex >= 0 And _ASIIndex >= 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
End Class
```

```
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 = _GAIIndex 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 = _ASIIndex 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 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
        End If
    End Function

```

```

        End If
        Next
    ElseIf _phaseMode = PhaseMode.Sol i dFCC 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(_indexAI)
            If i = _indexAI 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.Sol i dHCP 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(_indexAI)
            If i = _indexAI 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
    _indexAI = -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(I)" Then
            hasLiquids = True
            _phaseMode = PhaseMode.Liquid
            _indexAI = i
        ElseIf formula = "Zn(I)" 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
            _indexAI = i
        End If
    Next
End Sub

```

```

        If self.formula = "Zn" OrElse formula = "Zn(FCC)" OrElse formula =
        "Zn(s)" Then
            hasSolidFCC = True
            _phaseMode = PhaseMode.SolidFCC
            _indexZn = i
        ElseIf formula = "Al (HCP)" Then
            hasSolidHCP = True
            _phaseMode = PhaseMode.SolidHCP
            _indexAl = i
        ElseIf formula = "Zn(HCP)" Then
            hasSolidHCP = 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 (hasLiquidAnd hasSolidFCC) Or (hasLiquidAnd hasSolidHCP) Or
(hasSolidFCC And hasSolidHCP) 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 hasLiquid And Not hasSolidFCC And Not hasSolidHCP 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

```