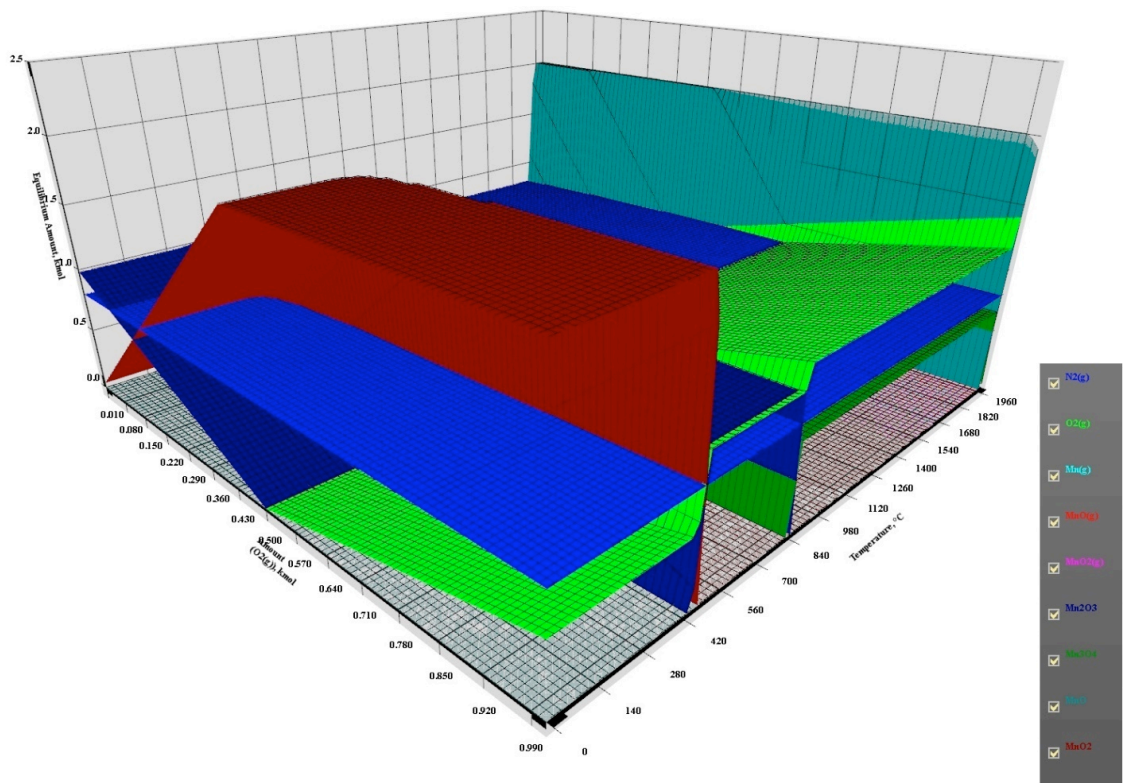


14. Equilibrium – Step by Step Examples



14.1. Creating 2D Diagrams

1. Start the Equilibrium Module. The starting screen is shown in **Fig. 1**.
2. Open, Import or Create a file.
If you want to open an existing file (*.gem8) you should press **Open** or select **Open** in the **File** menu. You can also work with files in *.IGI and *.GEM formats by selecting **Import** in the **File** menu. It is also possible to create a new file by selecting **Create Empty File** or **Empty File From Elements**.
 - a) Select Empty File From Elements, see **Fig. 1**.
 - b) Select H, Ca, C and O from the elements.
 - c) Select the form of species in which you are interested from the Search mode, in this example select Gases, Gas ions and Aqueous ions, see **Fig. 2**.
 - d) Press Next and you will see the species found, see **Fig. 3**.
 - e) Select species (using Ctrl and the left mouse button) as in **Fig. 3** and press Delete Unselected.
 - f) Select Gas, Aqua, Pure in the Sort menu see **Fig. 3** (Choose yes when Pure substances at last phase is requested).
 - g) Press Finish.
3. Edit system parameters as in **Fig. 4**.
4. Edit file or change options on the **Parameters** panel if necessary, see **Fig. 5**.
 - a) Select T, P, N in the **User Defined Parameters** menu.
 - b) Select 1 in **Number of independent variables** (2D diagram).
 - c) Check **Temperature**.
 - d) Specify the temperature range (from 25 to 225 °C), and give the **Number of Steps** required (default value is 21), see **Fig. 5**.

The screenshot shows the 'Equilibrium Calculations - [New System 1]' window. The main table has the following columns: A (Species Formula), B (Temper.), C (Amount), D (Amount), E (Add Step), F (Remove Step), G (Activity Coefficient), H (Fixed Activity), and I (Empty). The table is currently empty except for the headers. The right-hand panel contains several sections for configuring the calculation:

- Operations:** Buttons for 'Calculate', 'Show Chart', and 'Cancel'.
- System Parameters:**
 - User defined parameters:
 - Number of independent variables:
 - 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
- Solution Model:**
 - AC Steps:
- 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:
 - Target:
 - Target Amount: kmol
 - ☐ Use species activity coefficient as step parameter
- Chart Options:**
 - ☐ On-line chart
 - Header:

Fig. 1. Starting screen.

The screenshot shows the Outotec Database Browser interface. The 'Text Filters' section has 'Elements' set to 'H O C Ca'. The 'Matching Species' list on the left includes various carbon species, with 'C(g)' selected. The 'Basic Data' section for 'C(g)' shows its properties: Formula C(g), Structural Formula, Chemical Name Carbon, Common Name, CAN 7440-44-0, Molecular Weight 12.011 g/mol, Melting Point 3820.000 K, Boiling Point 5100.000 K, H° formation at 298.15 K 716.679 kJ/mol, and S° at 298.15 K 158.099 J/(mol·K). The 'Temperature Ranges' table shows data for three ranges (1, 2, 3) for various properties like T_{min}, T_{max}, Phase, H, S, Cp coefficients, Density, Color, Solubility, Reference, and Reliability Class.

Fig. 2. Specifying the elements of the system H - O - C - Ca.

The screenshot shows the Outotec Database Browser interface with the 'Matching Species' list expanded. A context menu is open over the list, showing options 'Import to Selected Species' and 'Select all'. The 'Basic Data' section for 'Ca(OH)2' is visible, showing its properties: Formula Ca(OH)2, Structural Formula CaH2O2, Chemical Name Calcium hydroxide, Common Name, CAN 1305-62-0, Molecular Weight 74.095 g/mol, Melting Point 0.000 K, Boiling Point 0.000 K, H° formation at 298.15 K -985.899 kJ/mol, and S° at 298.15 K 83.400 J/(mol·K). The 'Temperature Ranges' table shows data for two ranges (1, 2) for various properties. The 'Selected Species' list at the bottom includes: CO2(g), H2O, Ca(+2a), HCO2(-a), OH(-a), H2O(g), CO3(-2a), CaOH(+a), HCO3(-g), CaCO3, O2(g), C2O4(-2a), H(+a), HO2(-a), and Ca(OH)2.

Fig. 3. Selecting system species from the list.

SpeciesSort

☒ Add N2(g) for calculation stability

☐ Add e-(g)

Sort species to:

☐ Phases

☒ Gas, Aqua, Pure

☐ No sorting

☐ Gas, Aqua, Liquids

OK

C:\HSC8\Gibbs\H-C-O-Ca System.gem8

Protect Sheet

G14 1

	A	B	C	D	E	F	G
1	Species	Temper.	Amount	Amount	Add	Remove	Activity
2	Formula				Step	Step	Coefficient
3		°C	kmol	%	kmol	%	
4	GAS		1.00101	100	0.15		
5	CO2(g)	25	0.001	0.0998991	0.15		1
6	H2O(g)	25		0			1
7	O2(g)	25	0.00001	9.9899E-04			1
8	N2(g)	25	1	99.8991019			1
9	AQUA		58.5	100	0		
10	H2O	25	55.5	94.8717949			1
11	CO3(-2a)	25		0			1
12	C2O4(-2a)	25		0			1
13	Ca(+2a)	25	1	1.70940171			1
14	CaOH(+a)	25		0			1
15	H(+a)	25		0			1
16	HCO2(-a)	25		0			1
17	HCO3(-a)	25		0			1
18	HO2(-a)	25		0			1
19	OH(-a)	25	2	3.41880342			1
20	PURE		0	0			
21	CaCO3	25					1
22	Ca(OH)2	25					1
23							

Species

Outotec

Fig. 4. Created species input file.

The screenshot shows the 'Parameters' dialog box in HSC 8, divided into two main sections: 'Parameters' on the left and 'Calculation Options' on the right.

Parameters Section:

- Operations:** Contains buttons for 'Calculate', 'Show Chart', and 'Cancel'.
- System Parameters:**
 - User defined parameters:
 - Number of independent variables:
 - Define state change for:
 - ☐ Amount
 - ☐ Volume
 - ☐ Pressure
 - ☒ Temperature
 - ☐ Enthalpy
- System State:** A table for defining initial and final states.

	Initial State	Final State	Number of Steps
Amount			kmol <input type="text" value="21"/>
Temperature	<input type="text" value="25"/>	<input type="text" value="225"/>	°C <input type="text" value="21"/>
Pressure	<input type="text" value="1"/>	<input type="text" value="1"/>	bar <input type="text" value="21"/>
Volume	<input type="text"/>	<input type="text"/>	m3 <input type="text"/>
Enthalpy	<input type="text"/>	<input type="text"/>	MJ <input type="text"/>

 - ☐ Use as base volume
 - Initial Pressure: bar
- Solution Model:**
- AC Steps:

Calculation Options Section:

- ☐ Infinite Gas:
- ☐ Delete % phase
- ☐ Fixed Activity
- ☒ Pure Substances in Last Phase (Invariant Phases)
- ☒ Mixing Entropy conversion for aqueous species
- ☒ Criss-Cobble

Target Calculations Section:

- ☐ Enabled
- Equilibrium Property:
- Target:
- Target Amount: kmol
- ☐ Use species activity coefficient as step parameter

Chart Options Section:

- ☐ On-line chart
- Header:

Fig. 5. Specifying calculation parameters.

5. Press **Calculate** (and OK on the warnings page) and Equilibrium will be calculated for the defined parameters.
6. Press **Show Chart** on the Parameters panel or select **Show Chart** in the **View** menu and the **Axis** menu will be shown, see **Fig. 6**.
7. Select one of the types for each axis – Temperature for X-Axis, Equilibrium Amount for Y-Axis.
8. Select kmol unit for the Y-Axis.
9. Press **Finish**, then the diagram will be drawn, see **Fig. 7**.
10. You can format the appearance of the table or save the results. For more details, please see Chapter 13.

New chart wizard

Chart

Select data for axes

X - Axis (Horizontal Axis)

- ☒ Temperature
- ☐ Equilibrium Amount
- ☐ Equilibrium Composition
- ☐ Activity
- ☐ Volume
- ☐ pH
- ☐ 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
- ☐ pH
- ☐ Reaction Enthalpy
- ☐ Partial Pressure
- ☐ Step
- ☐ Partial Pressures + Total

Units for Temperature

- ☒ °C
- ☐ K

Units for Amount

- ☒ kmol
- ☐ kg
- ☐ kg, Nm3

Number of species in diagram: 16

Finish Cancel

Fig. 6. Select data for axes.

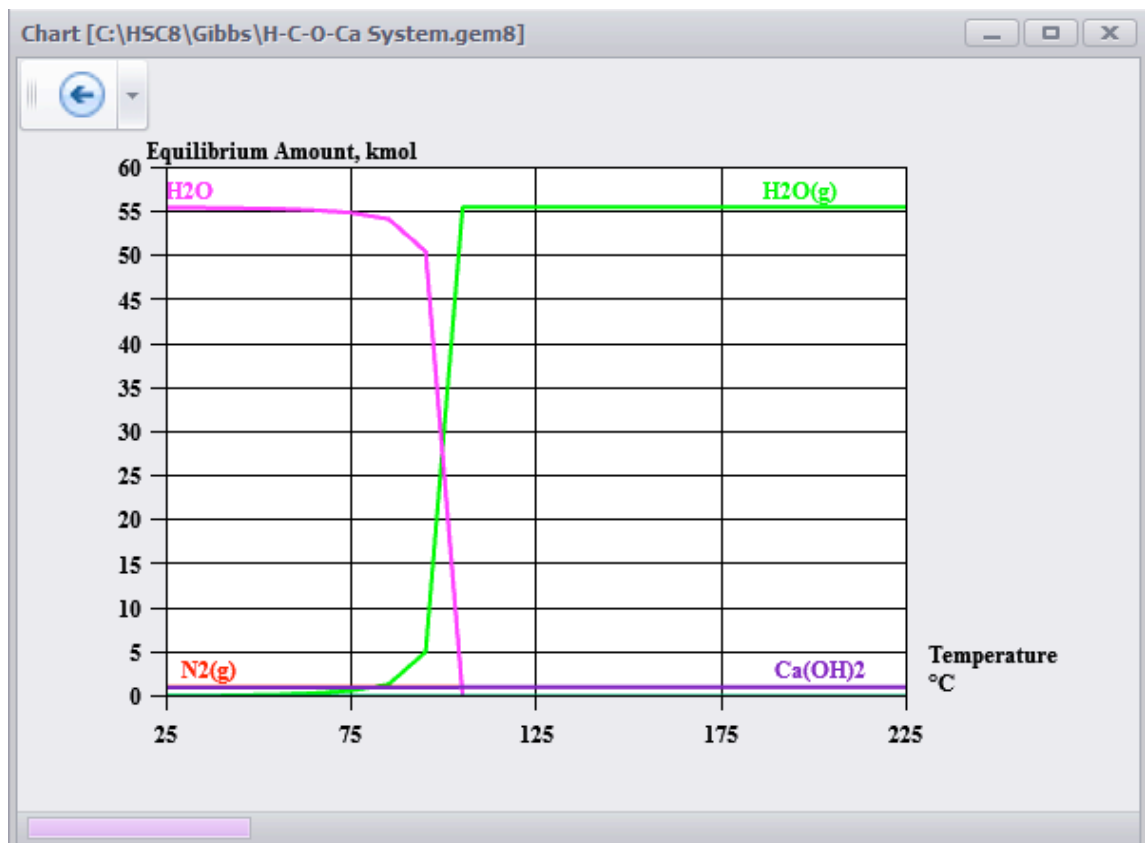


Fig. 7. 2D diagram.

14.2. Creating 3D Diagrams

Repeat steps 1 – 10 from “Working with 2D diagrams”, except:

3. Add step 0.15 to $\text{CO}_2(\text{g})$.
4. a) Select 2 in the **Number of independent variables** (3D diagram).
4. b) Check **Temperature** and **Amount**.
4. c) Set the number of steps to 21 in **Amount**.
7. Select one of the types for each axis – Amount for X-Axis with Select Species, see **Fig. 9**, Equilibrium Amount (kmol) for Y-Axis, Temperature for Z-Axis ($^{\circ}\text{C}$).

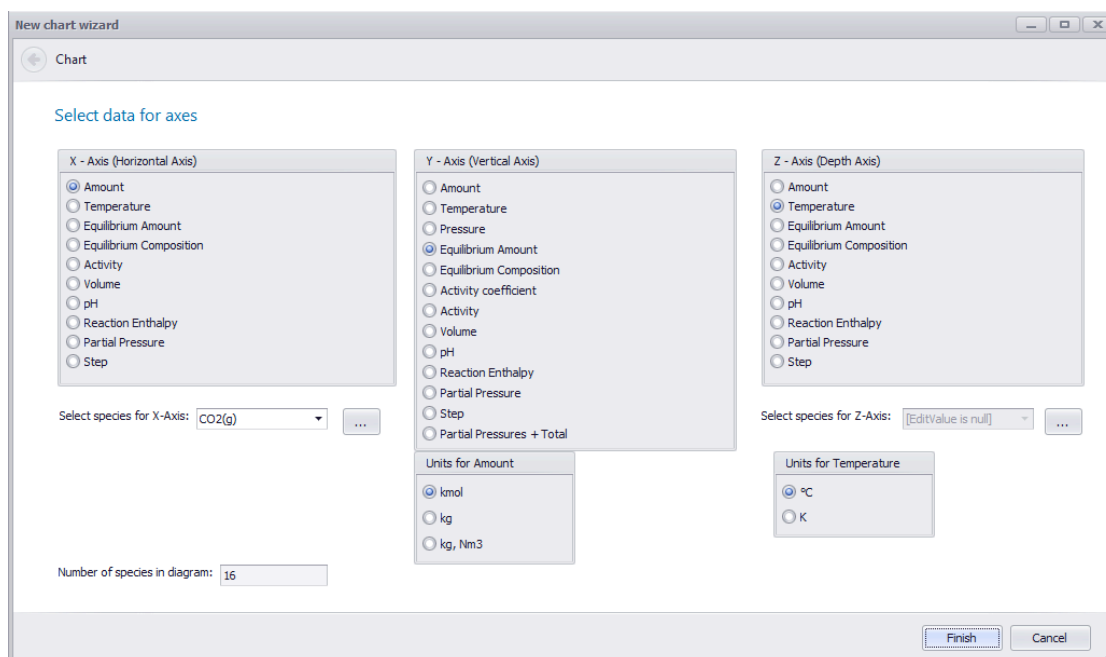


Fig. 8. Select data for axes.

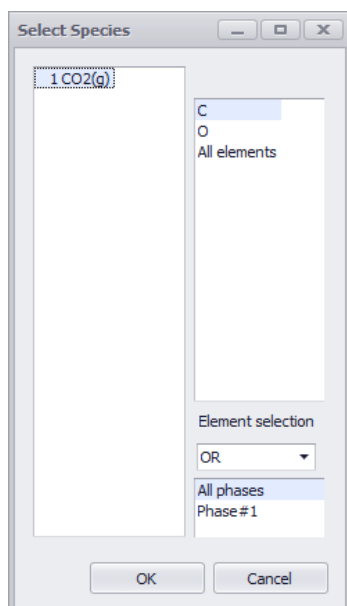


Fig. 9. Select Species.

When you press **Finish**, the 3D diagram will be drawn, see **Fig. 10**.

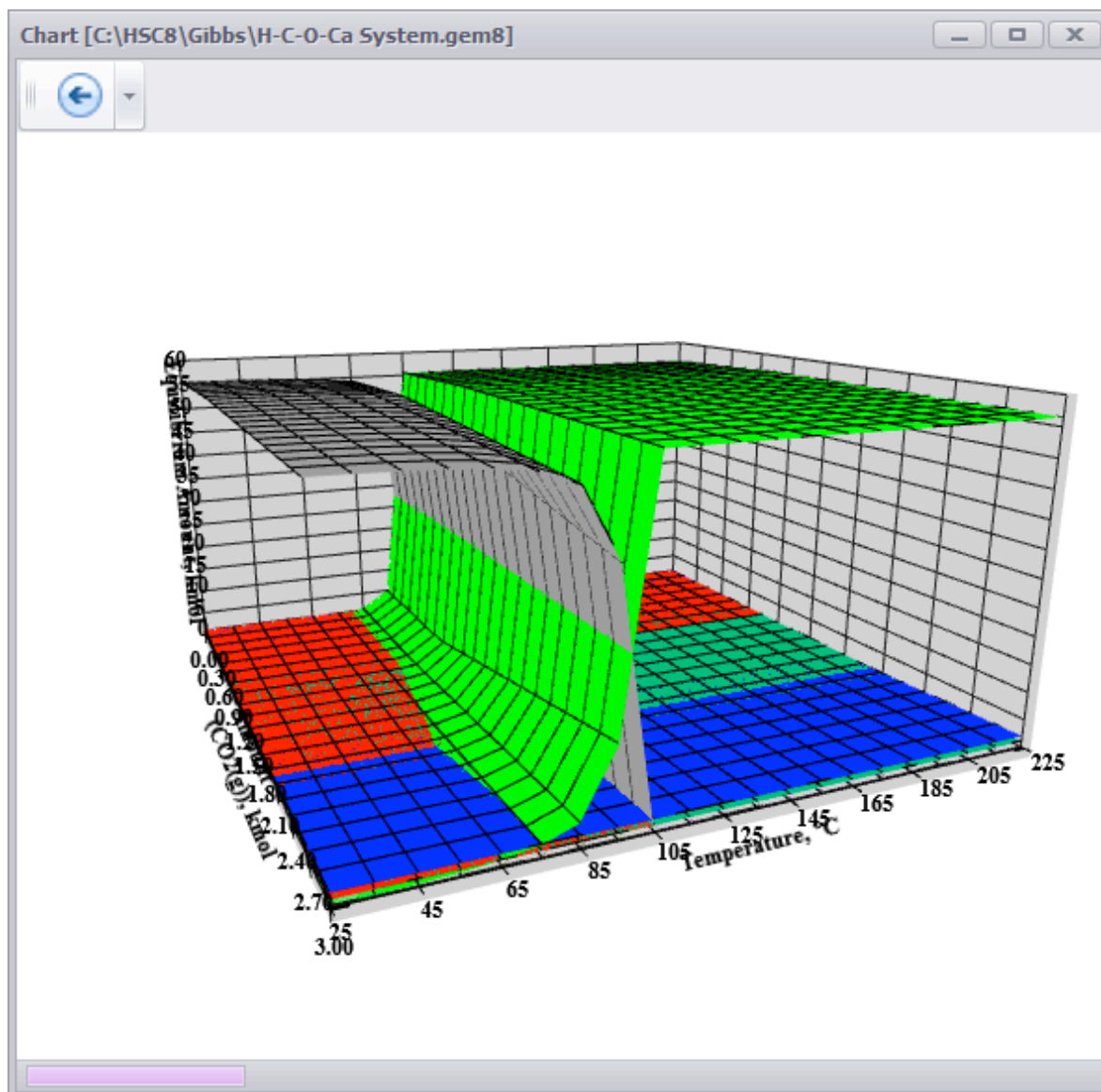


Fig. 10. 3D diagram.

14.3. Drawing on the Diagram Using the Toolbar

You can add different objects or write some labels on the diagram, which can be very helpful in some cases.

1. Create diagram.
2. Select **Toolbar** in the **Show** menu in the Diagram window.
3. Select one of the shapes (line, arrow, rectangle or circle) or label, see **Fig. 11**.
4. Draw the shape using the mouse cursor.
5. You can format the shape by selecting an inner color or border color, line width, line type. You can make the figure transparent, move it back or to the front, see **Fig. 11**.
6. If you do not like it, you can delete any shapes.



Fig. 11. Toolbar.

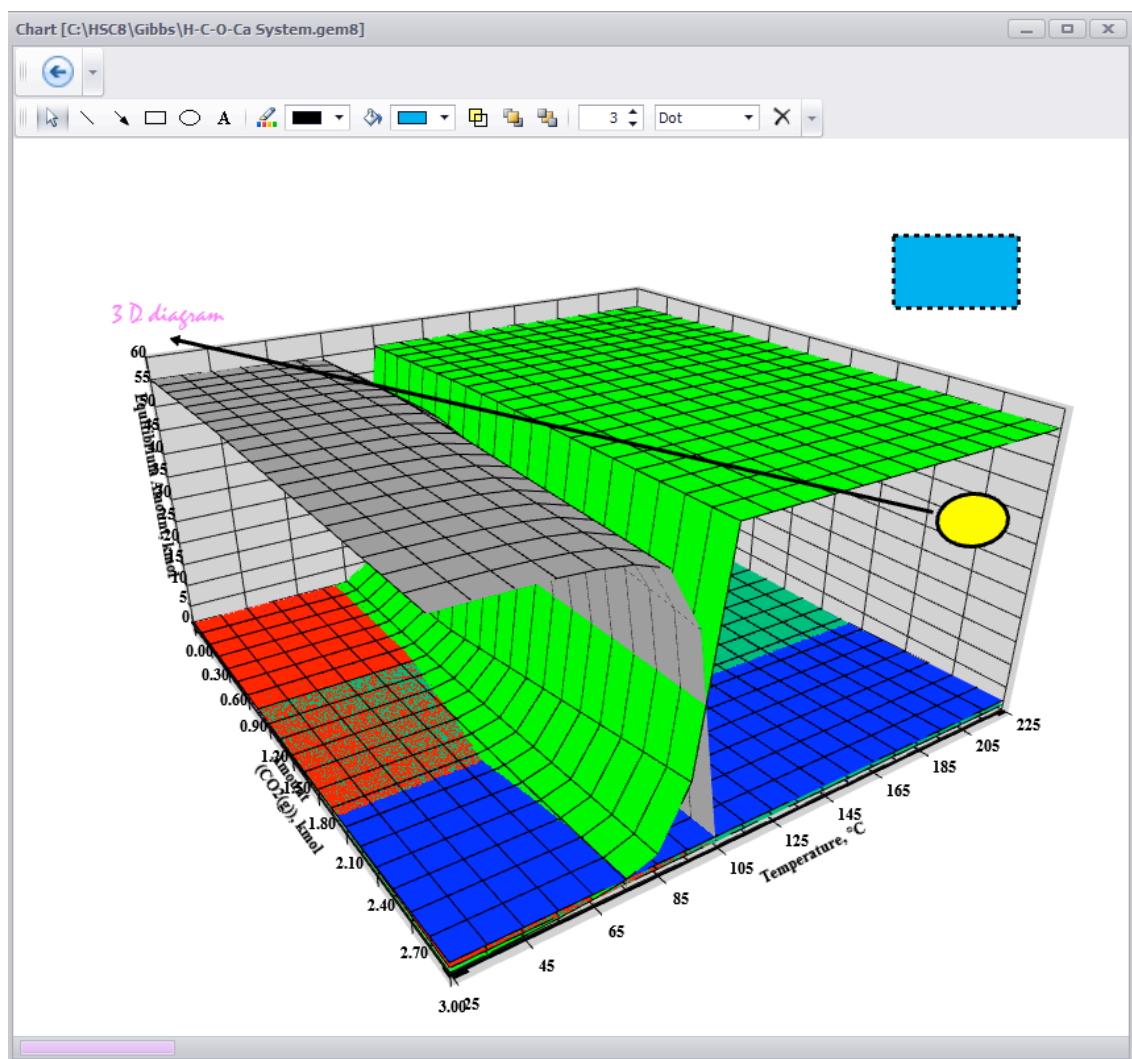
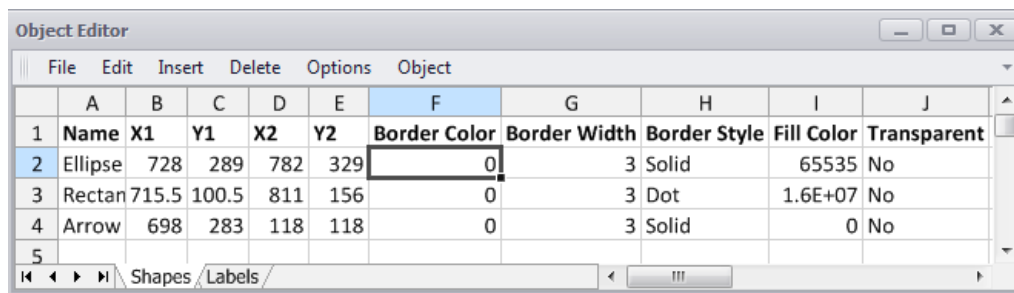


Fig. 12. 3D diagram with shapes.

14.4. Drawing on the Diagram Using Object Editor

There is one more way to modify diagrams by specifying the coordinates, sizes and colors of an object in Object Editor.

1. Create diagram.
2. Select **Object Editor** in the **Show** menu in the Diagram window.
3. In the **Insert** menu, select one of the shapes (line, arrow, rectangle, circle) on the **Shapes** sheet or label on the **Labels** sheet, see **Fig. 13**.
4. Specify all shape parameters (coordinates, border color, border width, etc.), see **Fig. 13**.
5. You can change these parameters later.
6. If you do not like it, you can delete any shape in the **Delete** menu or via the button on the toolbar.



The screenshot shows the 'Object Editor' window with a menu bar (File, Edit, Insert, Delete, Options, Object) and a table of object parameters. The table has columns A through J. Row 2 is selected, showing an 'Ellipse' with coordinates (728, 289, 782, 329), a border color of 0, a border width of 3, a solid border style, a fill color of 65535, and a transparent flag set to 'No'.

	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. 13. Object Editor of the objects in **Fig. 12**.

14.5. Transitory Evaporation and Open Atmosphere 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, and gases are added to the system in each step (see Fig. 14).

Transitory Evaporation (Remove Step %)

1. Create file as in Fig. 14.
2. Select the **T, P, N** system and **1** in the **Number of independent variables**.
3. Check **Amount** in the **Define state change for** menu.
4. Check **Remove Step % Column ON**
5. Specify GAS phase **Remove step %** (100 in cell F4), see Fig. 14.
6. Press **Calculate** and **Show Chart** when program has calculated the equilibrium.
7. Select **Step** as **X-Axis**.
8. Press **Finish**.
9. Select only **CO2(a)** in the legend in the Diagram window and check **AutoScale** option, see Fig. 15.

Open Atmosphere,(Infinite Gas)

1. Create file as in Fig. 16.
2. Select **T, P, N** system and **1** in **Number of independent variables**.
3. Check **Temperature** in the **Define state change for** menu.
4. Check **Infinite Gas** mode, see Fig. 16.
5. Select **Gas phase (P #1)**.
6. Press **Calculate** and **Show Chart** and the program will calculate the system.
7. Select **Temperature** as the parameter for **X-Axis**.
8. Press **Finish**.
9. Select only **CO2(a)** in the legend in the Diagram window and check the **AutoScale** option, see Fig. 17.

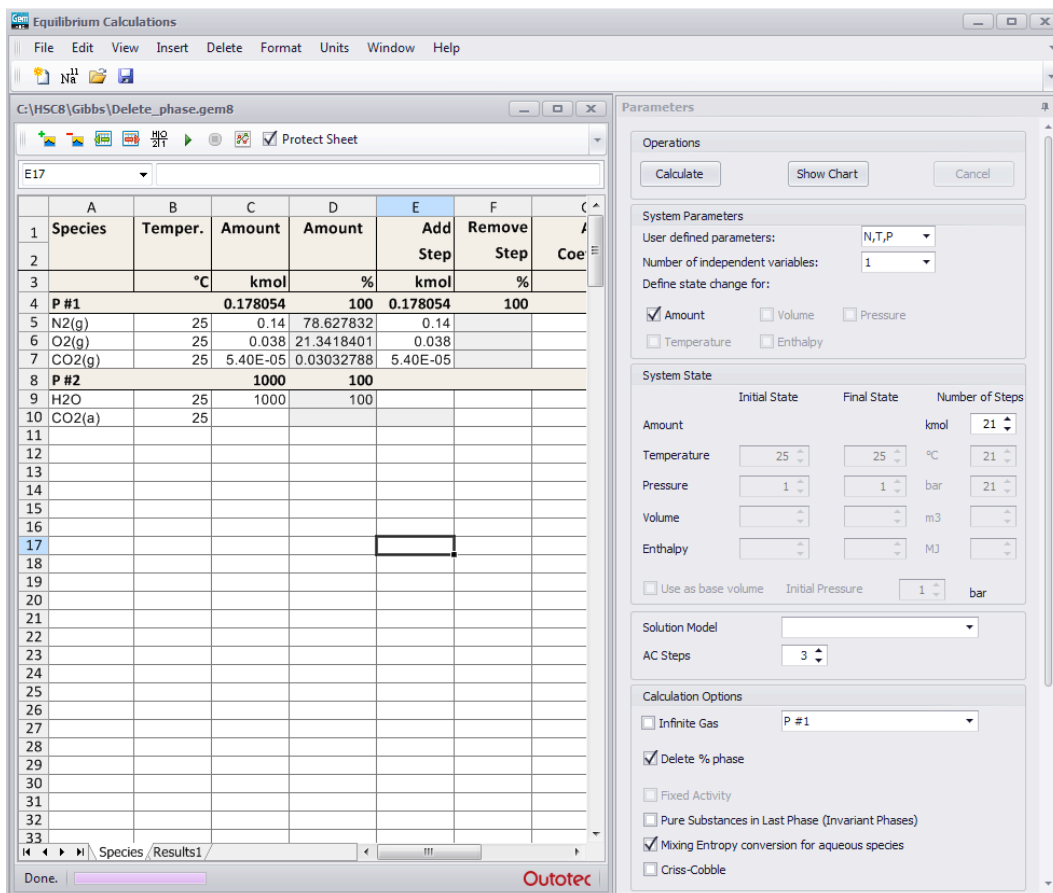


Fig. 14. Parameters for Transitory Evaporation mode.

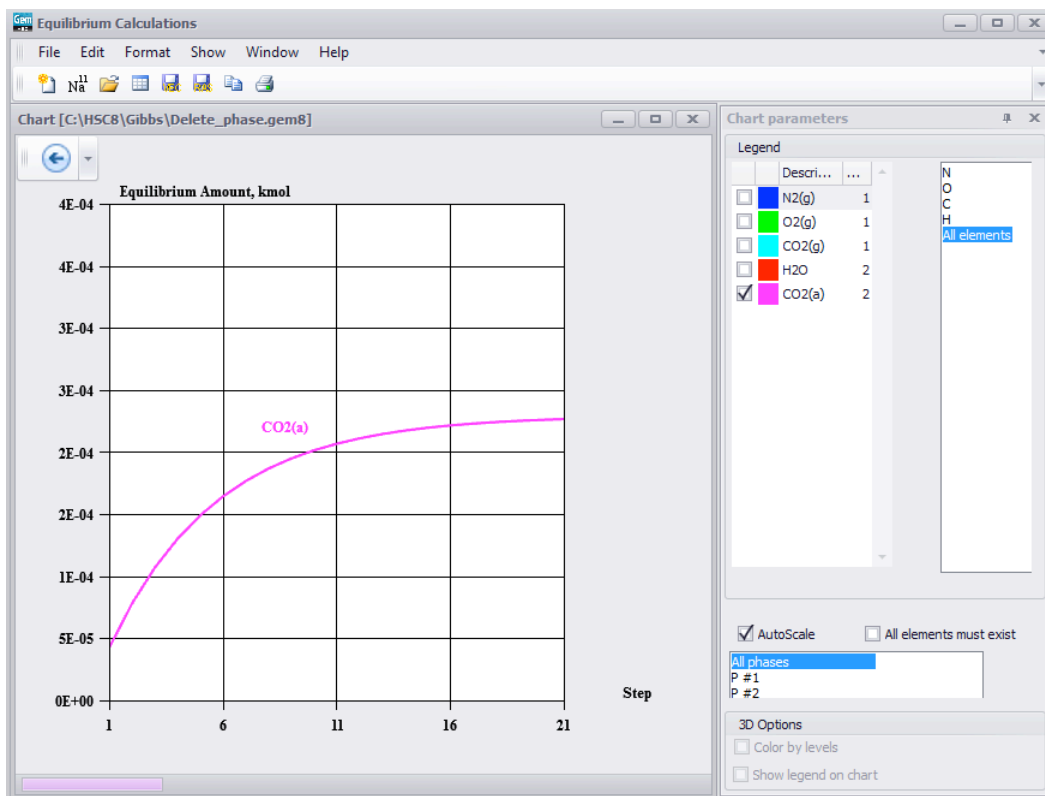


Fig. 15. Diagram for Transitory Evaporation mode.

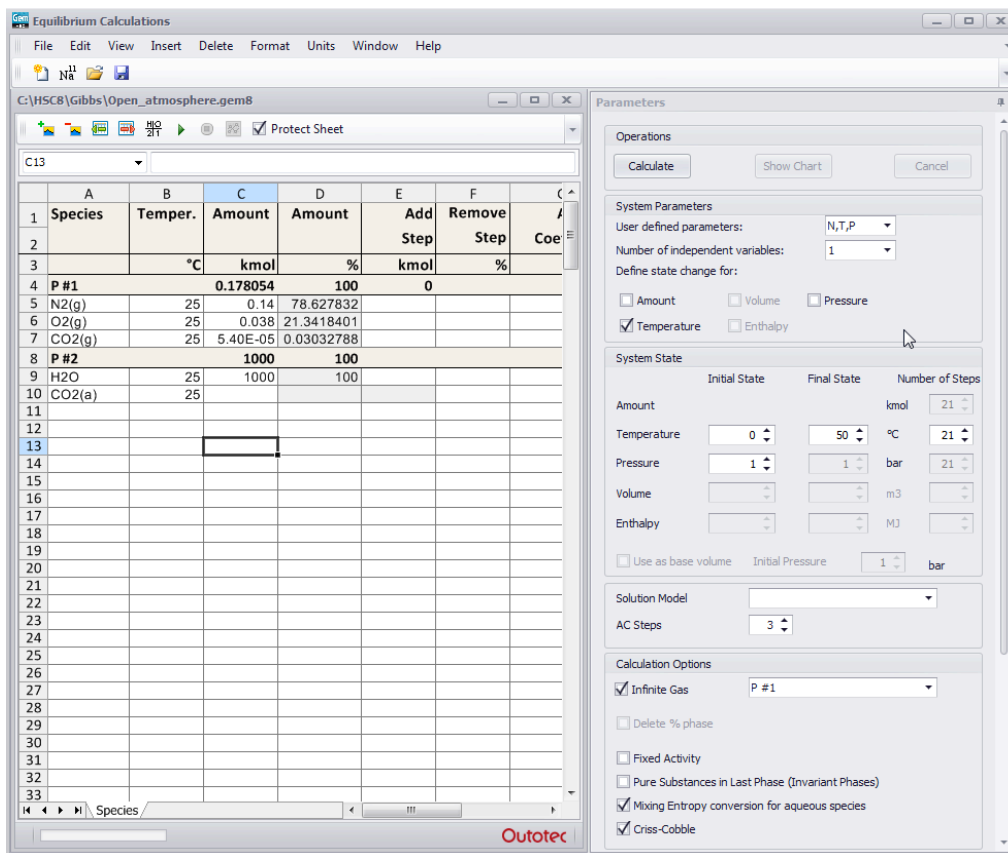


Fig. 16. Parameters for Open Atmosphere mode.

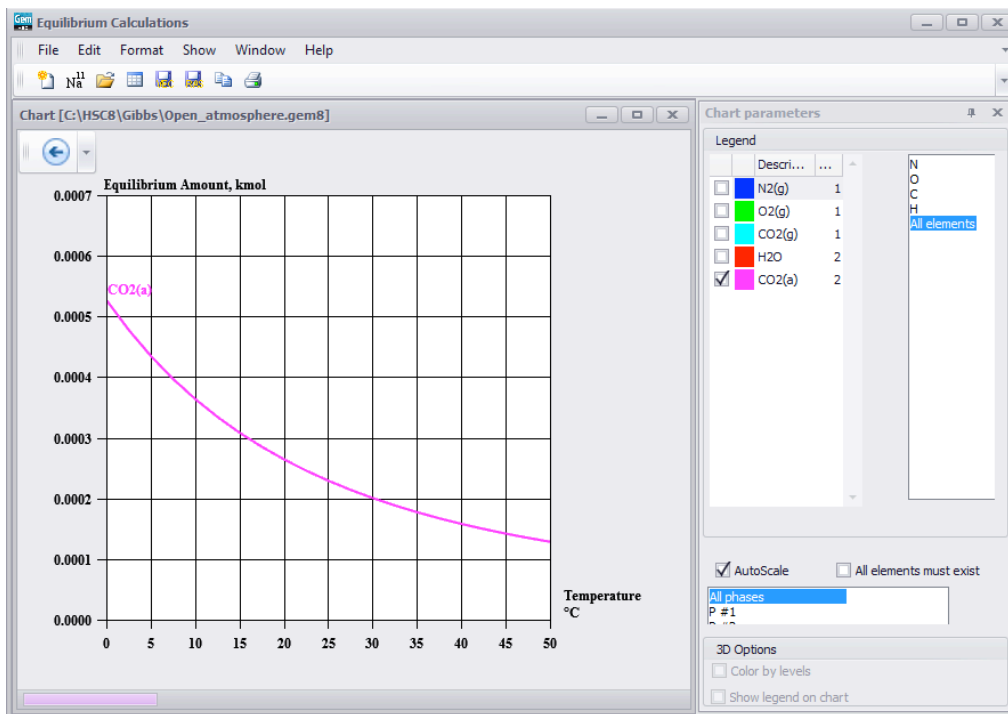


Fig. 17. Diagram for Open Atmosphere mode.

14.6. Fixed Activity Mode

You can also calculate the system from the previous example in the Fixed Activity mode with a coefficient of 0.0003 (equal to mole fraction or vapor pressure of CO₂(g) since an ideal gas is assumed) for CO₂(g), see Fig. 18.

1. Create new file as in Fig. 18.
2. Check Fixed Activity on the Parameters panel.
3. Enter 0.0003 in the Fixed Activity column (H7) in the table for CO₂(g).
4. Press Calculate.
5. Press Show Chart and the program will calculate the system.
6. Select **Temperature** as the parameter for **X-Axis**.
7. Press **Finish**.
8. Select only **CO2(a)** in the legend in the Diagram window and check **AutoScale** option, see Fig. 19.
9. Press **Back** in the Diagram window.
10. Select **Activity** as the parameter for the **Y-Axis**.
11. Select only **CO2(g)** in legend on Diagram window and check the **AutoScale** option, see Fig. 20.

The screenshot displays the HSC8 Equilibrium Calculations software interface. The main window shows a spreadsheet with columns for Species, Temper., Amount, Add Step, Remove Step, and Coe. The Parameters panel on the right is configured for Fixed Activity mode.

Parameters Panel Configuration:

- Operations:** Calculate, Show Chart, Cancel
- 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
- Solution Model:**
 - AC Steps: 3
- Calculation Options:**
 - ☐ Infinite Gas
 - ☐ Delete % phase
 - ☒ Fixed Activity
 - ☐ Pure Substances in Last Phase (Invariant Phases)
 - ☒ Mixing Entropy conversion for aqueous species
 - ☐ Criss-Cobble

Fig. 18. Parameters for Fixed Activity mode.

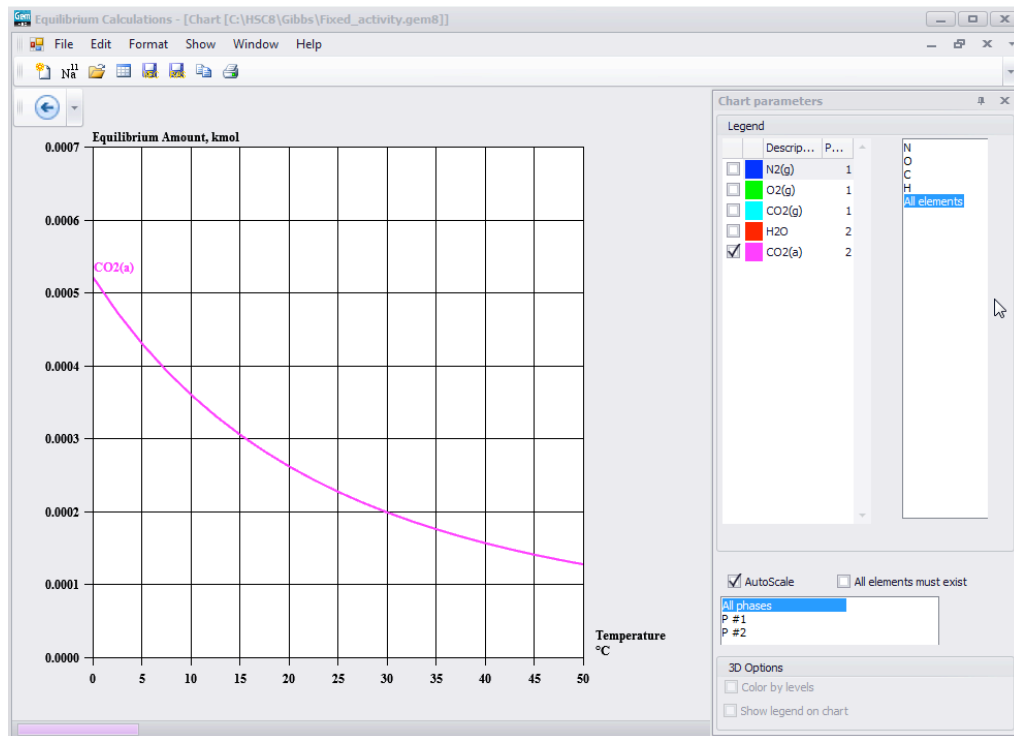


Fig. 19. Diagram with Fixed Activity.

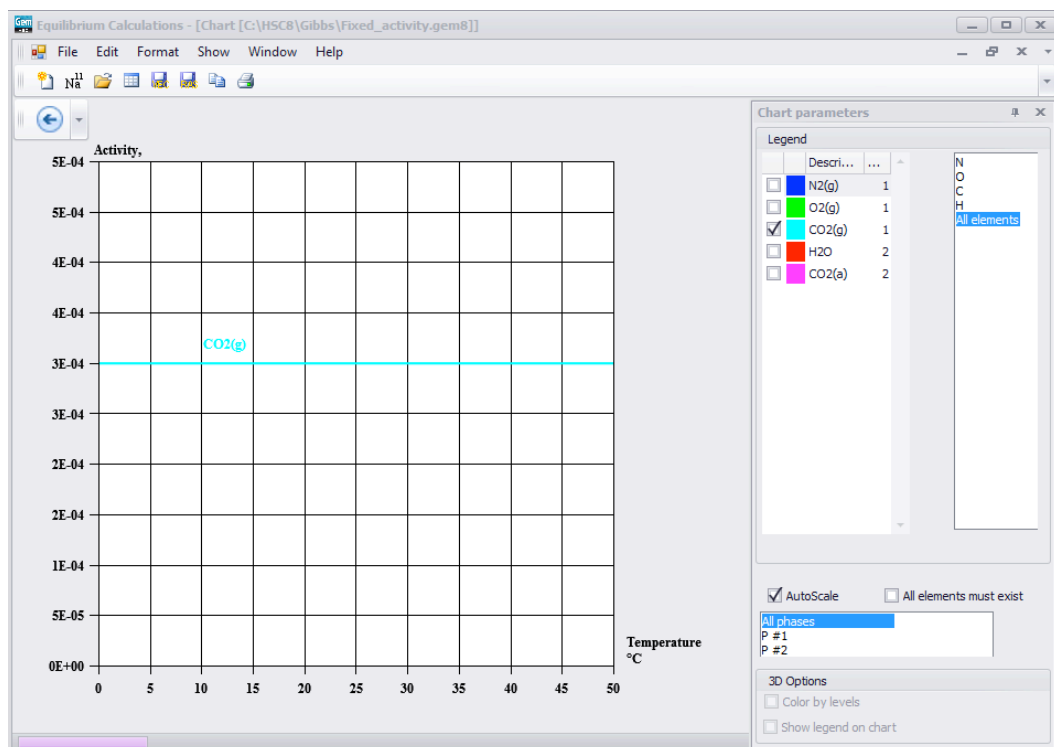


Fig. 20. Fixed activity of $\text{CO}_2(\text{g})$.

You will then see a diagram as in the Open Atmosphere mode, see **Fig. 19**, and you can check that Activity for $\text{CO}_2(\text{g})$ is constant as specified in the Fixed Activity coefficient, see **Fig. 20**.

14.7. Target Calculation

If you want to find out the equilibrium condition where the amount of H₂O is 1 mole, enable Target Calculations and set the parameters as in **Fig. 21** (you can open the FESO4_target.gem8 file).

The screenshot shows the HSC8 Equilibrium Calculations software interface. The main window displays a spreadsheet with columns for Species Formula, Temper., Amount, Add Step, and Remove Step. The spreadsheet is divided into two phases: Phase #1 and Phase #2. Phase #1 includes N2(g), O2(g), SO2(g), S2(g), H2S(g), H2O(g), and Fe(g). Phase #2 includes FeSO4*7H2O, FeSO4*4H2O, FeSO4*H2O, Fe2(SO4)3, FeSO4, FeO*OH, FeO, Fe2O3, Fe3O4, and H2O. The Parameters panel on the right is configured for Target Calculation. The System Parameters section shows User defined parameters set to N,T,P, Number of independent variables set to 1, and Define state change for set to Temperature. The System State section shows Initial State and Final State values for Amount, Temperature, Pressure, Volume, and Enthalpy. The Calculation Options section shows various checkboxes for Infinite Gas, Delete % phase, Fixed Activity, Pure Substances in Last Phase, Mixing Entropy conversion, and Criss-Cobble. The Target Calculations section shows Target Calculations set to Enabled, Equilibrium Property set to Species mole amount, Target set to H2O, and Target Amount set to 1 kmol. The Chart Options section shows On-line chart set to Header: sDecomposition of FeSO4*7H2O at 1 ba.

Species Formula	Temper.	Amount	Add Step	Remove Step
Phase #1	°C	kmol	%	kmol
N2(g)	25	4.462E-03	99.990001	0
O2(g)	25	4.462E-07	0.009999	0
SO2(g)	25			0
S2(g)	25			0
H2S(g)	25			0
H2O(g)	25			0
H2(g)	25			0
Fe(g)	25			0
Phase #2	°C	kmol	%	kmol
FeSO4*7H2O	25	0.359698	100	0
FeSO4*4H2O	25			0
FeSO4*H2O	25			0
Fe2(SO4)3	25			0
FeSO4	25			0
FeO*OH	25			0
FeO	25			0
Fe2O3	25			0
Fe3O4	25			0
H2O	25			0

Fig. 21. Parameters for Target Calculation.

1. Open the FESO4_target.gem8 file
2. Check **Enabled** in the **Target Calculation** menu on the **Parameters** panel.
3. Select **Species mole amount** in **Equilibrium Property**.
4. Select **H2O** in **Target**.
5. Specify 1 in **Target Amount**.
6. Press **Calculate** and view the results, see **Fig. 22**.

C:\HSC8\Gibbs\FES04_target.gem8

<

Fig. 22. Results of the Target Calculation.

14.8. HSC Equilibrium Module Examples

The screenshot displays the HSC Equilibrium Calculations software interface. The left pane shows a spreadsheet for specifying chemical species and phases. The right pane shows the Parameters dialog box for setting calculation options.

Species Formula Table:

Species Formula	Temper.	Amount	Amount	Add Step	Remove Step	Activity Coefficient	Fixed Activity
	°C	kmol	%	kmol	%		
Phase #1		0.002	100	2.385			
N2(g)	25	0.001	50	1.885		1	
O2(g)	25	0.001	50	0.5		1	
SO2(g)	25			0		1	
Phase #2		0.001	100	0.125			
*2FeO*SiO2(l)	25			0		1	
SiO2(l)	25	0.001	100	0.125		1	
Cu2O(l)	25			0		1	
Phase #3		3	100	0			
Cu2S	25	1	33.333333	0		1	
FeS	25	2	66.666667	0		1	
Phase #4		0	0	0			
Cu	25			0		1	

Parameters Dialog Box:

- Operations:** Calculate, Show Chart, Cancel
- 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 13
Temperature	1300	1300	°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
 - ☐ Delete % phase
 - ☐ Fixed Activity
 - ☐ Pure Substances in Last Phase (Invariant Phases)
 - ☒ Mixing Entropy conversion for aqueous species
 - ☒ Criss-Cobble

Fig. 23. Specification of the chemical system. i.e. specification of phases, species, and raw materials (left side) and specification of the calculation type: Increase Amount, Temperature, or Pressure (right side).

Case 1: Hydration of Magnesia Chrome Bricks (ANKROM01.gem8)

Magnesia chrome bricks are widely used as a lining material in pyrometallurgical applications because of their stability in process conditions. However, at room temperatures they easily react with moisture and crumble due to hydration reactions. HSC software can be used to estimate the lowest temperature that must be exceeded to prevent such reactions and to specify these reactions.

Magnesia chrome bricks contain magnesium, chromium, iron, and oxygen. All species which contain these elements and hydrogen can easily be collected in the Equilibrium module from the database. The following ideas were used to specify the system (see **Fig. 25**):

- Metallic substances were removed, as they are not needed in these conditions.
- Gas species (16) were inserted into the gas phase.
- Other species (25) were assumed to exist as pure substances (invariant phases), because of the low temperatures where molten mixtures do not exist.
- MgO , Cr_2O_3 and Fe_2O_3 raw materials were added according to their amount in the brick: MgO 60, Cr_2O_3 18 and Fe_2O_3 14 kg.
- Water gas was added to the gas phase. The amount was set slightly higher than needed to hydrate all the species in the brick.
- A small amount of nitrogen was added to the gas phase.

The results of the calculations are shown in **Fig. 24**. This diagram shows that hydration of the bricks is possible if the temperature of the lining is lower than 270 °C. Hydration damage is caused only due to the formation of magnesium hydroxide; the chromium and iron do not take part in hydration reactions. Magnesium oxide (periclase) forms the matrix of the brick, therefore hydration of magnesium oxide crumbles the whole construction.

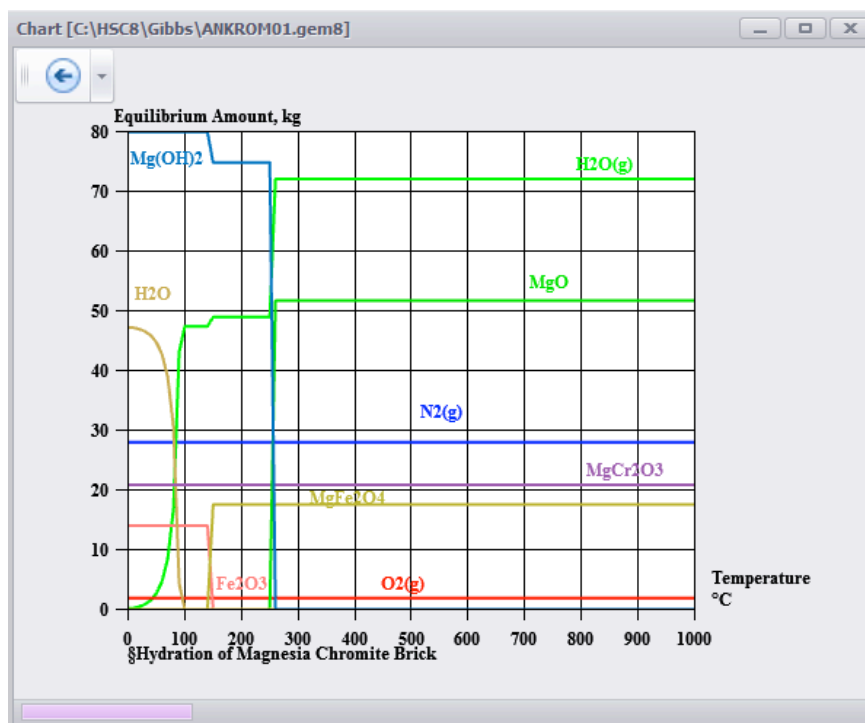


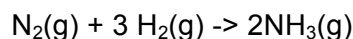
Fig. 24. Calculation results for hydration of magnesia chrome brick.

The screenshot displays the HSC 8 Equilibrium Calculations software interface. The main window is a spreadsheet titled 'Species Formula' with columns for Species, Formula, Temper. (°C), Amount (kmol), Add Step (kmol), Remove Step (kmol), and Activity Coefficient. The spreadsheet is divided into two main sections: Phase #1 and Phase #2. Phase #1 includes species like N2(g), H2O(g), H2(g), O2(g), Cr(g), CrO(g), CrO2(g), CrO3(g), Fe(g), FeO(g), Fe(OH)2(g), Mg(g), MgH(g), MgO(g), MgOH(g), and Mg(OH)2(g). Phase #2 includes species like Cr2FeO4, Cr2MgO4, CrO2, CrO3, Cr2O3, Cr5O12, Cr8O21, Cr(OH)2, Cr(OH)3, Fe0.945O, Fe0.947O, FeO, FeO1.056, Fe2O3, Fe3O4, Fe(OH)2, Fe(OH)3, Fe2O3*H2O, H2O, MgCr2O3, MgFe2O4, MgO, MgO2, and Mg(OH)2. The 'Parameters' panel on the right allows for setting system parameters such as User defined parameters (N,T,P), Number of independent variables (1), Define state change for (Temperature, Enthalpy), System State (Initial State, Final State, Number of Steps), Amount (kmol), Temperature (°C), Pressure (bar), Volume (m3), Enthalpy (MJ), Solution Model, AC Steps, Calculation Options (Infinite Gas, Delete % phase, Fixed Activity, Pure Substances in Last Phase, Mixing Entropy conversion for aqueous species, Criss-Cobble), Target Calculations (Enabled, Equilibrium Property, Target, Target Amount), and Chart Options.

Fig. 25. Specification of phases and species in the Magnesia Chrome brick example.

Case 2: Ammonia Synthesis (by Panu Talonen; AMMONIA.gem8)

Ammonia was expensive to produce before the invention of the current process, which uses high pressure and iron catalyst. The synthesis is usually made at a temperature of 370 – 540 °C. The effect of pressure on ammonia formation can easily be evaluated with the HSC Equilibrium module. The formation reaction can be written as follows:



The number of gas moles decreases in this reaction and therefore high pressure may be assumed to favor the synthesis. The equilibrium calculation can be carried out as described in Chapter 13. The chemical system specification and other calculation parameters are shown in **Fig. 27**. The calculations are carried out by increasing the pressure from 0.001 to 1000 bar at a constant temperature of 480 °C.

The calculated results are shown in **Fig. 26**. It is easy to see that at normal pressure of 1 bar it is impossible to produce high amounts of ammonia. It also seems that synthesis should be made at the highest possible pressure. However, modern ammonia plants operate at about 150 bar pressure for economic reasons. The ammonia is condensed from the gas mixture and the unreacted hydrogen and nitrogen are recycled back to the reactor.

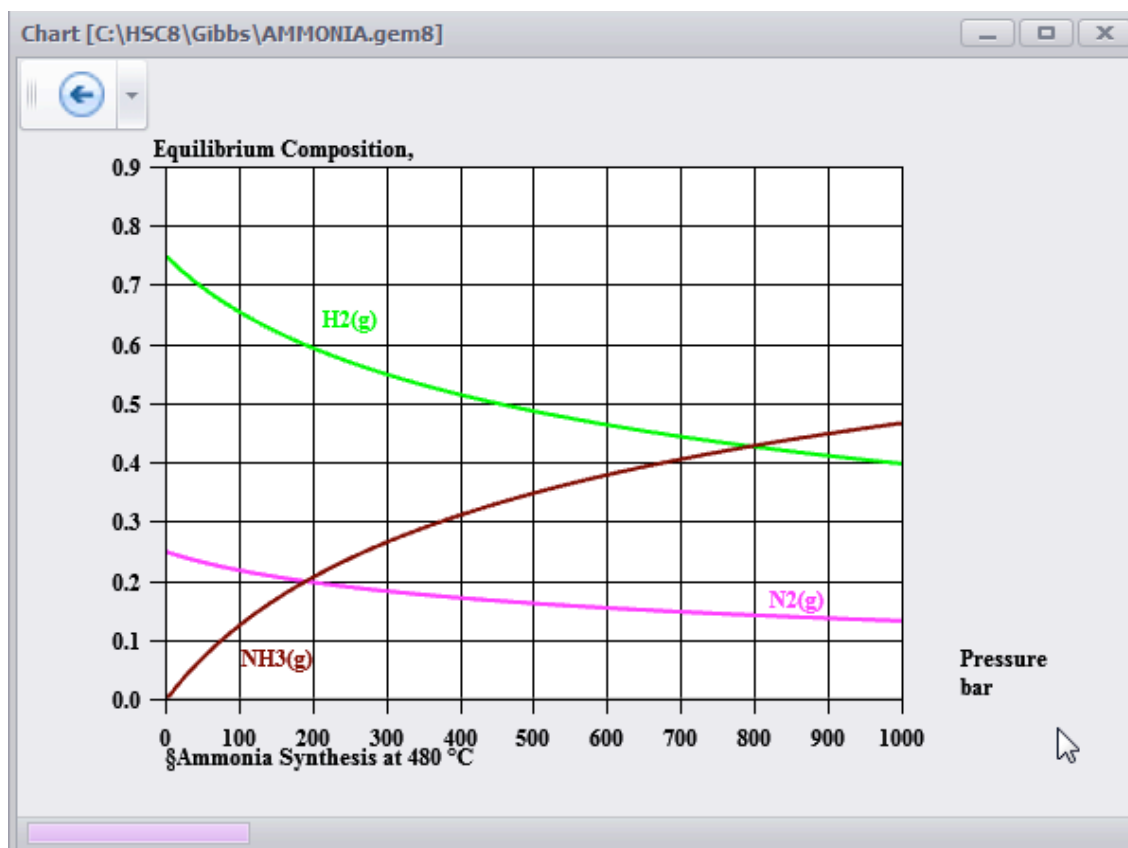


Fig. 26. Calculation results for the ammonia synthesis example.

The screenshot displays the 'Equilibrium Calculations' window with a spreadsheet for species and phases, and a 'Parameters' panel on the right.

Species and Phases Table:

Species	Formula	Temper. °C	Amount kmol	Amount %	Add Step kmol	Remove Step %	Activity Coefficient
Phase #1							
H(g)		25	4.001	100	0		1
H ₂ (g)		25		3	74.9812547	0	1
NH ₃ (g)		25			0		1
N(g)		25			0		1
N ₂ (g)		25	1.001	25.0187453	0		1
N ₃ (g)		25			0		1
NH(g)		25			0		1
NH ₂ (g)		25			0		1
NH ₃ (g)		25			0		1
N ₂ H ₂ (g)		25			0		1
N ₂ H ₄ (g)		25			0		1
Phase #2							
NH ₄ N ₃		25	0	0	0		1

Parameters Panel:

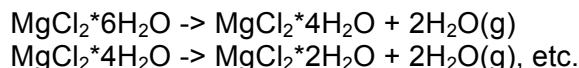
- Operations:** Calculate, Show Chart, Cancel
- System Parameters:**
 - User defined parameters: N,T,P
 - Number of independent variables: 1
 - Define state change for:
 - ☐ Amount
 - ☐ Volume
 - ☒ Pressure
 - ☐ Temperature
 - ☐ Enthalpy
- System State:**

	Initial State	Final State	Number of Steps
Amount			21
Temperature	480	480	21
Pressure	0.001	1000.00	51
Volume			
Enthalpy			
- Solution Model:**
 - AC Steps: 3
- Calculation Options:**
 - ☐ Infinite Gas
 - ☐ Delete % phase
 - ☐ Fixed Activity
 - ☐ Pure Substances in Last Phase (Invariant Phases)
 - ☒ Mixing Entropy conversion for aqueous species
 - ☒ Criss-Cobble

Fig. 27. Specification of phases and species in the ammonia synthesis example.

Case 3: Decomposition of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (MGCL2.gem8)

All compounds will decompose if the temperature is high enough. Especially substances with crystalline water will decompose at quite low temperatures. The decomposition temperatures can be found in many different handbooks, but they may also be calculated with the HSC Equilibrium module if the basic data is available on the HSC database. Magnesium chloride forms a $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ compound, which decomposes according to the reactions:



The decomposition temperature as well as the decomposition vapor pressure may be calculated using the chemical system specification shown in **Fig. 28**. The user must specify all possible condensed phases as well as a gas phase. **Please note:** A) A small amount of nitrogen will stabilize the gas phase, B) small amounts of $\text{Cl}_2(\text{g})$ and $\text{O}_2(\text{g})$ shift the material balance out from the stoichiometric one and C) $\text{Mg}(\text{g})$ allows magnesium to enter the gas phase also.

The results of the calculations are shown in **Fig. 29** and **Fig. 30**. The decomposition seems to start at 100 °C, see **Fig. 29**. The vapor composition is drawn in **Fig. 30** by selecting the Equilibrium Composition option. This diagram shows that the vapor pressure of water is 0.67 bar at 175 °C and 1 bar total pressure. To calculate vapor pressure at higher temperatures, the total pressure must be increased, for example, to 10 bar.

The screenshot displays the 'Equilibrium Calculations' window. The main table lists species and their amounts for two phases. The right-hand 'Parameters' panel shows system parameters and calculation options.

Species Formula	Temper.	Amount	Amount	Add Step	Remove Step	Activity Coefficient
	°C	kmol	%	kmol	%	
Phase #1		0.10002	100	0		
N2(g)	25	0.1	99.980004	0		1
Cl2(g)	25	0.00001	0.009998	0		1
HCl(g)	25			0		1
H2O(g)	25			0		1
O2(g)	25	0.00001	0.009998	0		1
H2(g)	25			0		1
Mg(g)	25			0		1
Phase #2		1	100	0		
MgCl2*6H2O	25	1	100	0		1
MgCl2*4H2O	25			0		1
MgCl2*2H2O	25			0		1
MgCl2*H2O	25			0		1
MgCl2	25			0		1
Mg(OH)Cl	25			0		1
MgO	25			0		1
H2O	25			0		1

Parameters Panel:

- Operations:** Calculate, Show Chart, Cancel
- 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			21
Temperature	0 °C	400 °C	81
Pressure	1 bar	1 bar	21
Volume			m3
Enthalpy			MJ
- Solution Model:**
 - AC Steps: 3
- Calculation Options:**
 - ☐ Infinite Gas
 - ☐ Delete % phase
 - ☐ Fixed Activity
 - ☒ Pure Substances in Last Phase (Invariant Phases)
 - ☒ Mixing Entropy conversion for aqueous species
 - ☒ Criss-Cobble

Fig. 28. Specification of phases and species in the $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ example.

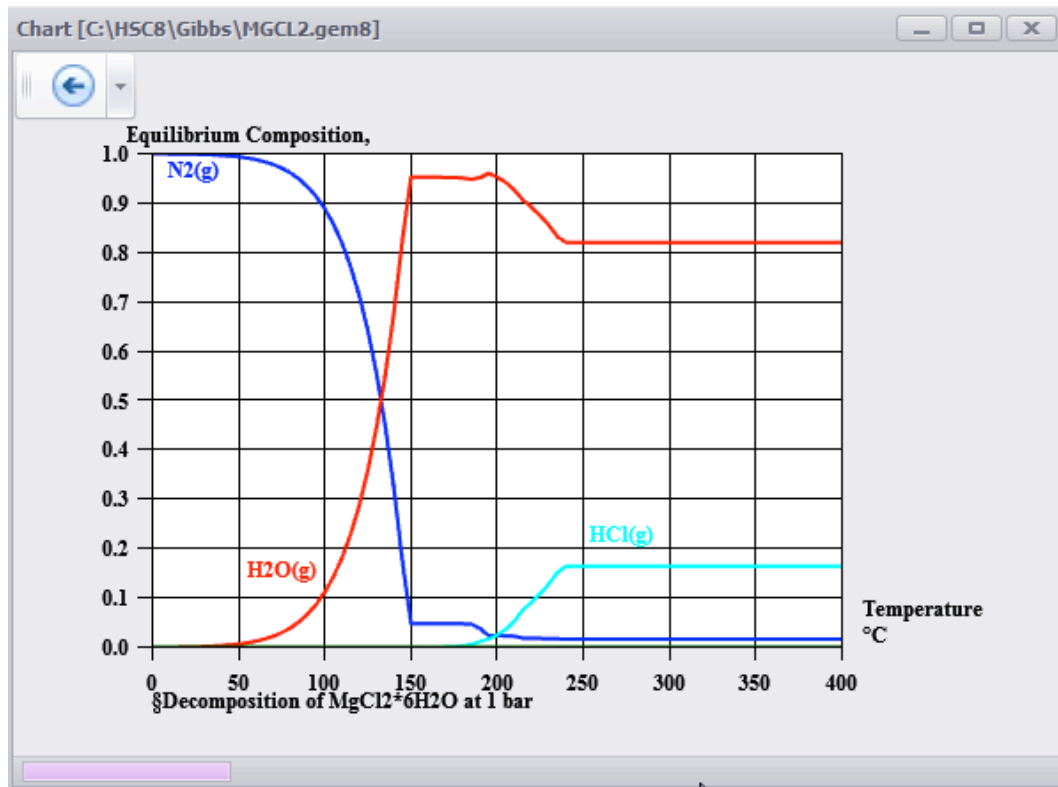


Fig. 29. Vapour composition at a total pressure of 1 bar.

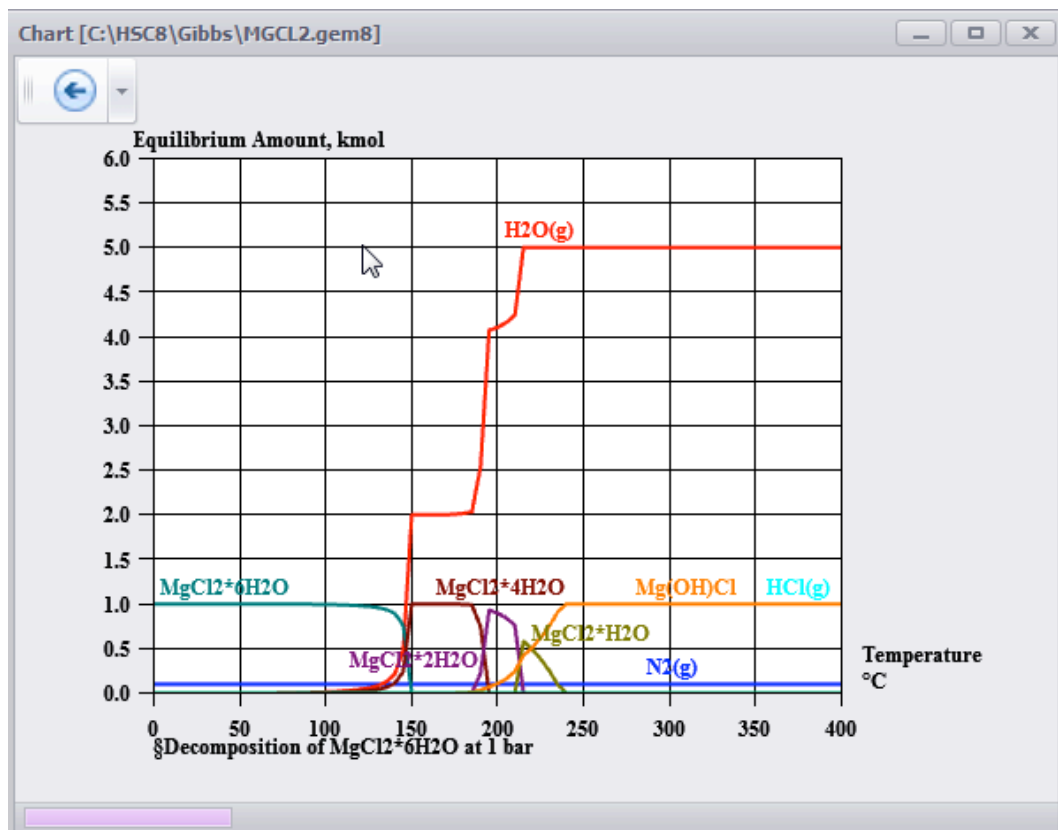


Fig. 30. Equilibrium calculation results for the $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ decomposition example.

Case 4: Decomposition of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (by Ben Karlemo; FESO4.gem8)

The thermal decomposition of a chemical compound will sometimes give valuable information of its behavior in a real chemical process. This evaluation may be carried out with the HSC Equilibrium module and with a thermo-gravimetric analyzer. These evaluations have been made in this example for $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. The chemical system specifications for the HSC equilibrium module are shown in **Fig. 31**. **Please note** (see Chapter 13 (13.4.): A) A small amount of nitrogen stabilizes the gas phase, B) a small amount $1\text{E-}5$ kmol of $\text{O}_2(\text{g})$ shifts the material balance away from the stoichiometric one, C) $\text{Fe}(\text{g})$ allows iron to enter the gas phase also. The results are shown in **Fig. 32**.

The hydrates gradually decompose at 50 to 200 °C and sulfates at 400 to 650 °C. Hematite will reduce to magnetite at 1250 °C. These results may be used to explain the experimental thermo-gravimetric results shown in **Fig. 33**. The TG curve shows the actual weight change and the DSC curve shows the enthalpy change compared to the reference test.

The screenshot displays the HSC Equilibrium Calculations window. The main area is a table for defining the system. The table has columns for Species, Formula, Amount, Add Step, and Remove Step. The table is divided into two phases: Phase #1 and Phase #2. Phase #1 includes $\text{N}_2(\text{g})$, $\text{O}_2(\text{g})$, $\text{SO}_2(\text{g})$, $\text{S}_2(\text{g})$, $\text{H}_2\text{S}(\text{g})$, $\text{H}_2\text{O}(\text{g})$, $\text{H}_2(\text{g})$, and $\text{Fe}(\text{g})$. Phase #2 includes $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot \text{H}_2\text{O}$, $\text{Fe}_2(\text{SO}_4)_3$, FeSO_4 , $\text{FeO} \cdot \text{OH}$, FeO , Fe_2O_3 , Fe_3O_4 , and H_2O . The right-hand side of the window shows the Parameters panel, which includes System Parameters, System State, Solution Model, and Calculation Options. The System State panel shows Initial State and Final State values for Amount, Temperature, Pressure, Volume, and Enthalpy. The Calculation Options panel includes checkboxes for Infinite Gas, Delete % phase, Fixed Activity, Pure Substances in Last Phase (Invariant Phases), Mixing Entropy conversion for aqueous species, and Criss-Cobble.

Species	Formula	Amount	Add Step	Remove Step	
Phase #1		4.462E-03	100	0	
1	$\text{N}_2(\text{g})$	25	4.462E-03	99.990001	0
2	$\text{O}_2(\text{g})$	25	4.462E-07	0.009999	0
3	$\text{SO}_2(\text{g})$	25		0	0
4	$\text{S}_2(\text{g})$	25		0	0
5	$\text{H}_2\text{S}(\text{g})$	25		0	0
6	$\text{H}_2\text{O}(\text{g})$	25		0	0
7	$\text{H}_2(\text{g})$	25		0	0
8	$\text{Fe}(\text{g})$	25		0	0
9	Phase #2	0.359698	100	0	
10	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	25	0.359698	100	0
11	$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$	25		0	0
12	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$	25		0	0
13	$\text{Fe}_2(\text{SO}_4)_3$	25		0	0
14	FeSO_4	25		0	0
15	$\text{FeO} \cdot \text{OH}$	25		0	0
16	FeO	25		0	0
17	Fe_2O_3	25		0	0
18	Fe_3O_4	25		0	0
19	H_2O	25		0	0

Fig. 31. The specification of phases and species for the equilibrium calculations.

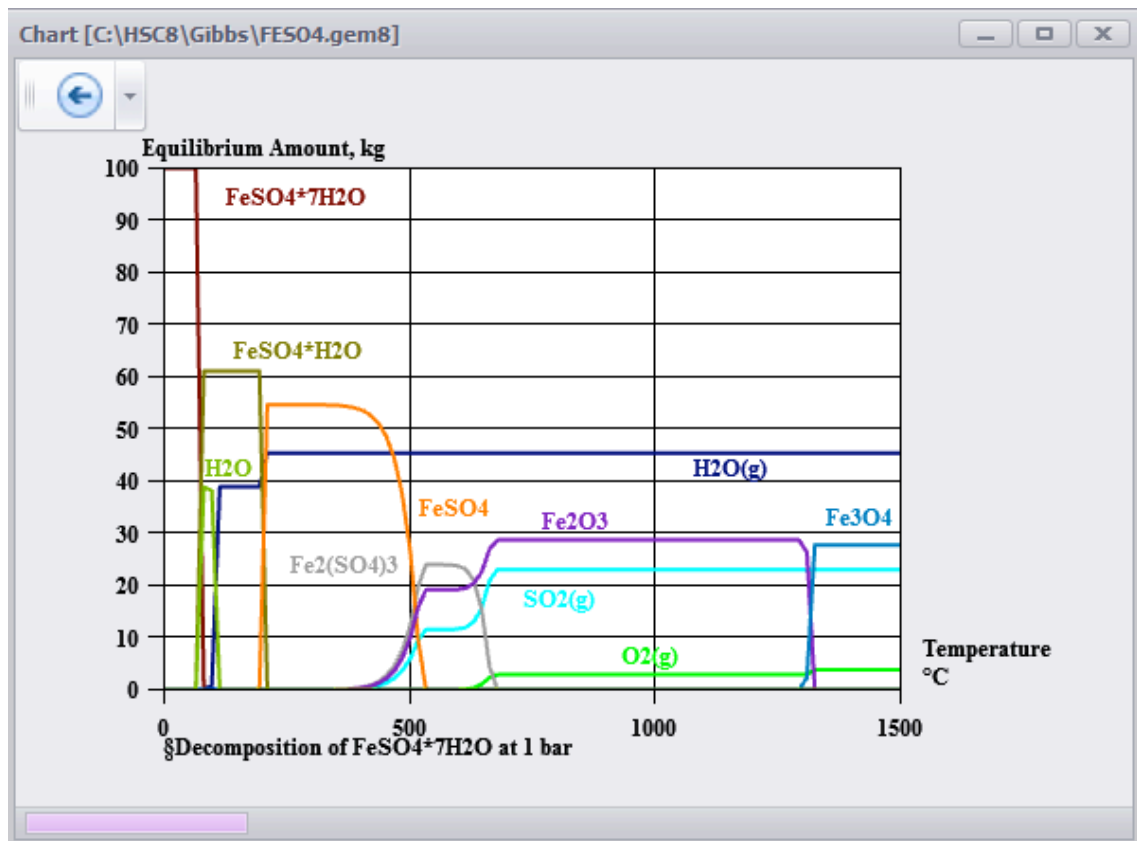


Fig. 32. The result of the calculated decomposition of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.

The theoretical and experimental weight change curves are compared in **Fig. 34**, which is calculated in MS Excel. Both curves are in quite good correlation with each other. The decomposition occurs at slightly higher temperatures in the experimental results than in the calculated ones, but this may be explained by some kinetic effects. The final weight of the sample was nearly the same in the experimental and theoretical results at high temperatures. The decomposition reactions may also be verified by comparing the analyzed and the calculated gas composition with each other.

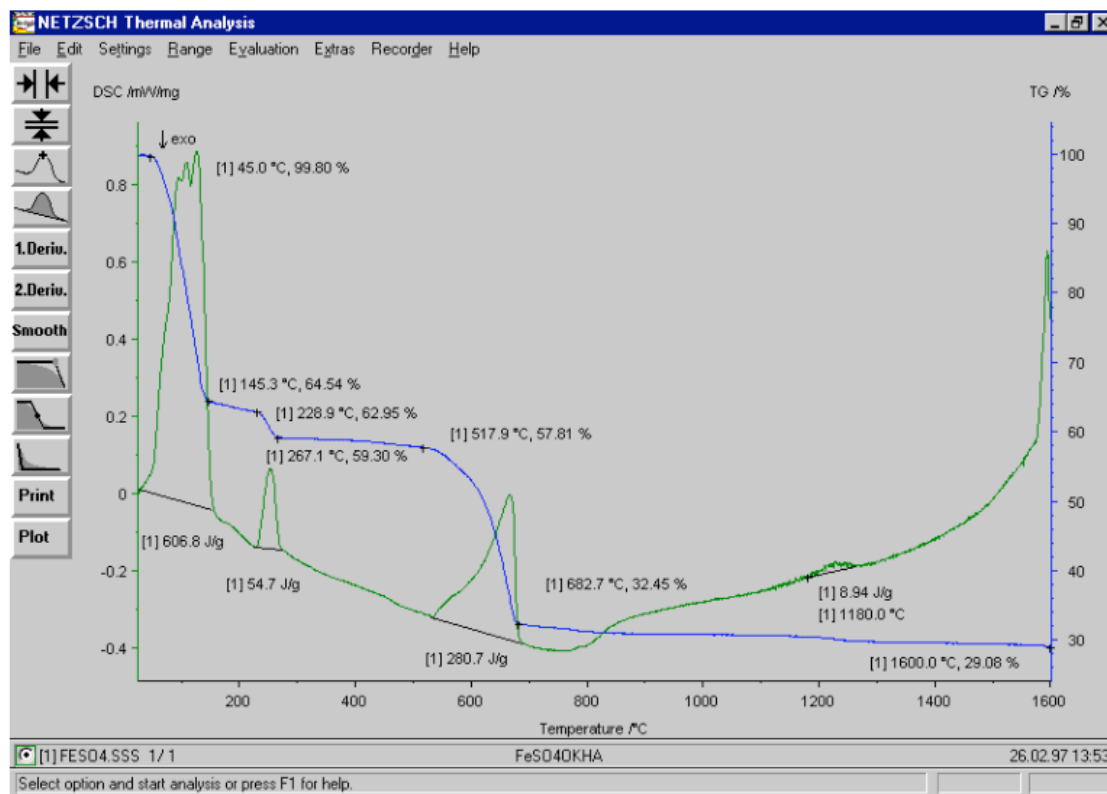


Fig. 33. Results of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ run on a NETZSCH TG-DSC analyzer under nitrogen atmosphere showing TG and DSC curves. Heating rate was $5^\circ\text{C}/\text{min}$.

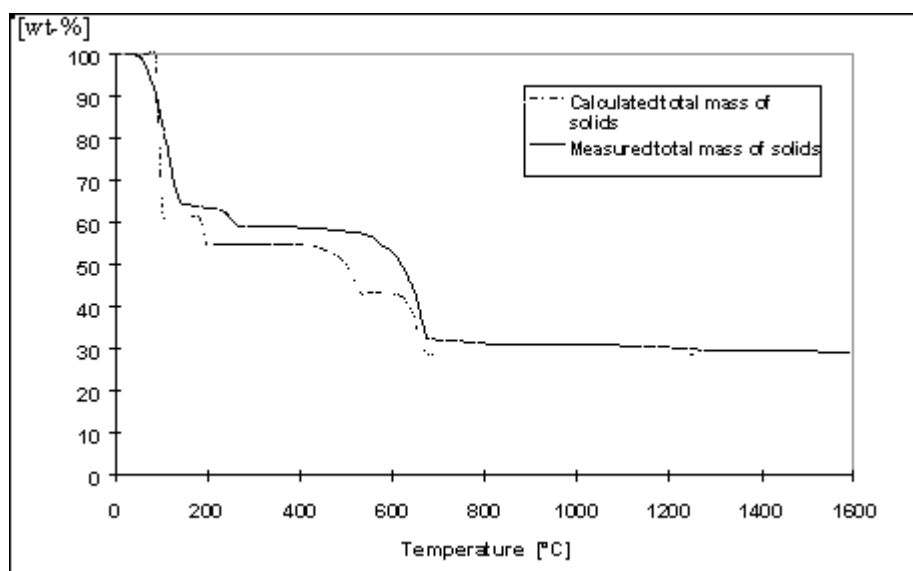


Fig. 34. The comparison of the measured and calculated mass change of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.

Case 5: Alkali Circulation in a Blast Furnace (by Riku Sarkkinen; ALKAL1.gem8)

Alkali metals tend to enrich in an iron blast furnace. The alkali content in raw materials (pellets, sinter and coke) is not so high, but they evaporate at the bottom of the furnace (~1500 °C) and do not exit with the products (slag, iron) easily. Nor do they exit with the process gas, which goes upward, because the temperature is quite low at the top of the furnace (~100 °C). This problem may be evaluated with the HSC Equilibrium module.

The chemical system specification is shown in **Fig. 36**. The raw material amounts are based on the following assumptions: Coke ash analysis (main components): SiO₂ 53, CaO 3, MgO 2, and Al₂O₃ 27 wt %. Process gas is formed by air reaction with coke, and the main components in the gas phase are CO(g), CO₂(g) and N₂(g). The alkali elements are K and Na. The calculations are carried out as described in Chapter 13 by increasing the temperature from 500 to 2000 °C. Iron has not been taken into account because the alkali circulation occurs above the liquid iron zone. Equilibrium calculations were made as described in Chapter 13.

The calculation results are shown in **Fig. 35**. At high temperatures almost all the sodium and most of the potassium seems to be in elemental form in the gas phase. These gas species flow with the main process gases upward where the cold charge materials decrease the temperature and alkalis react with the slag components. The reaction products are mainly sodium and potassium carbonates, sodium silicates, and potassium alumina silicates. These solid compounds flow downward with the blast furnace charge materials to the high temperature zone at the bottom of the furnace, where the alkali components vaporize again, which leads to the alkali circulation.

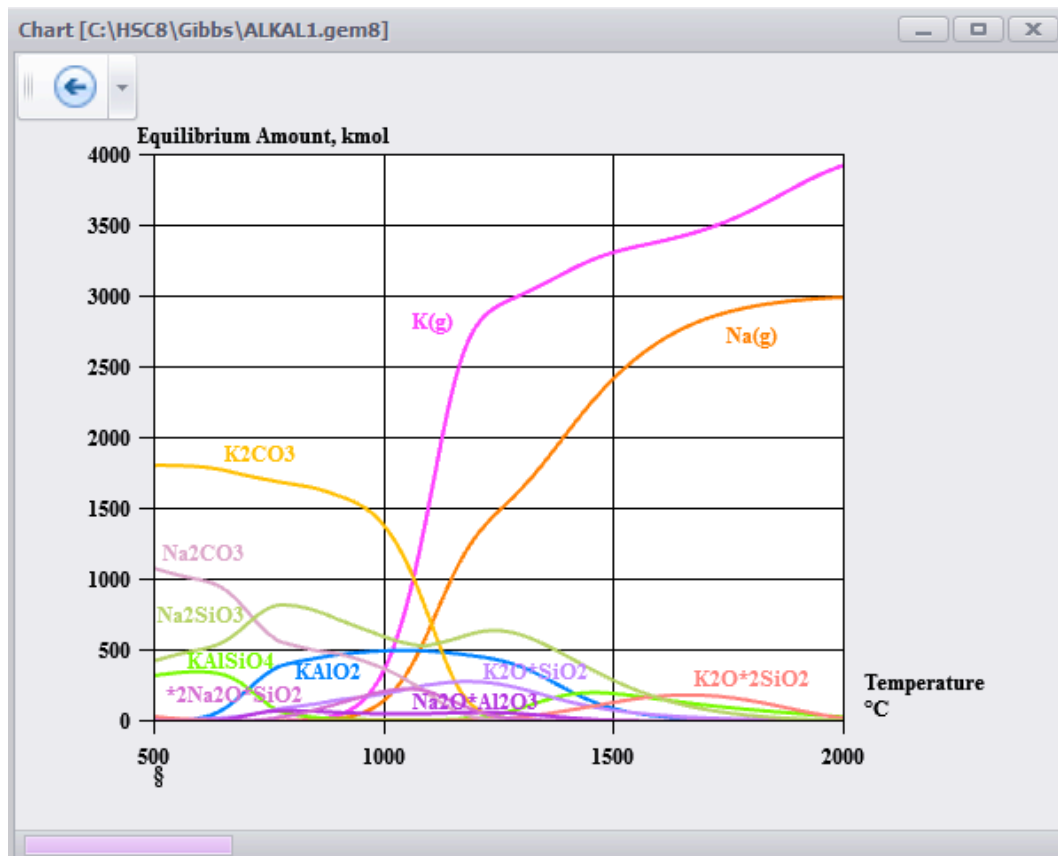


Fig. 35. Equilibrium results of alkalis and slag components as a function of temperature.

The screenshot displays the HSC 8 Equilibrium Calculations software interface. The main window is a spreadsheet titled 'Equilibrium Calculations' with the following columns: Species Formula, Temper. (*C), Amount (kmol), Amount (%), Add Step (kmol), Remove Step (%), and Activity Coefficient. The spreadsheet is divided into two phases: Phase #1 and Phase #2. Phase #1 lists various chemical species with their initial amounts and percentages. Phase #2 lists additional species. The 'Parameters' panel on the right includes sections for Operations (Calculate, Show Chart, Cancel), System Parameters (User defined parameters: N,T,P; Number of independent variables: 1), System State (Initial State, Final State, Number of Steps), Solution Model, and Calculation Options (Infinite Gas, Delete % phase, Fixed Activity, Pure Substances in Last Phase, Mixing Entropy conversion, Criss-Cobble).

Species Formula	Temper. (*C)	Amount (kmol)	Amount (%)	Add Step (kmol)	Remove Step (%)	Activity Coefficient
Phase #1						
AlO(g)	25	197000	100	0		1
CO(g)	25			0		1
CO2(g)	25			0		1
Ca(g)	25			0		1
K(g)	25	4000	2.03045685	0		1
K2(g)	25			0		1
K2CO3(g)	25			0		1
KNa(g)	25			0		1
KO(g)	25			0		1
Mg(g)	25			0		1
MgO(g)	25			0		1
N2(g)	25	150000	76.142132	0		1
Na(g)	25	3000	1.52284264	0		1
Na2(g)	25			0		1
NaO(g)	25			0		1
O(g)	25			0		1
O2(g)	25	40000	20.3045685	0		1
SiO(g)	25			0		1
Phase #2						
AlO	25	1417	100	0		1
Al2O3	25	300	21.1714891	0		1
Al2O3*SiO2(D)	25			0		1
*2CaO*Al2O3*SiO2	25			0		1
*3CaO*Al2O3*3SiO2	25			0		1
CaO	25	60	4.23429781	0		1
Ca2SiO4(A)	25			0		1
KAlO2	25			0		1
KAlSiO4	25			0		1
K2CO3	25			0		1

Fig. 36. Specification of phases and species in the Blast Furnace example.

Case 6: Ga-As System (by Petri Kobylin; Ga-As_example.gem8)

The theory of the solution models is given in Chapter 13 (section 13.10). The following step-by-step example explains how to use such models.

This example shows how a solution model can be used and results are then compared to an ideal solution at 1000 K. The solution model parameters used in this example are not assessed properly, so the calculated phase boundaries differ from those found in the Ga-As phase diagrams in the literature.

Step 1. Insert the phases and species:

LIQUID phase

Ga(l)

As(l)

SOLID phase

GaAs

Step 2. Give the input amounts and add a step, see **Fig. 37** and **Fig. 38**.

Step 3. Give 101 as the number of amount steps 1000 K (726.85 °C) as the temperature and 1 bar as the pressure. Units can be changed from the **Units menu**.

Step 4. Activate the solution model. First, choose the phase from the input sheet where you want to use a solution model (here LIQUID is chosen), then select a Ga-As mixture from the solution model list and give the number of iteration rounds (120 rounds here) to calculate the activity coefficients (AC steps). If the solution model is left blank, an ideal solution is calculated, see **Fig. 38**.

User can also open the file C:\HSC8\Gibbs\Ga-As_example.gem8 if he/she does not want to do steps 1-4.

Step 5. Press calculate and Show Chart. Then choose the Amount (X-axis) and Equilibrium amount (Y-axis) and Finish. **Fig. 39** shows the solution model results and **Fig. 40** the results for the ideal solution. It takes some time to calculate the results using the solution model since many iteration rounds are used. **Fig. 41** and **Fig. 42** show the results of using only 10 iteration rounds, which is not quite enough since the lines bend on the Arsenic-rich side of **Fig. 41** and the values of activity coefficients in the two phase region in **Fig. 42** are not constant.

The screenshot shows the HSC8 software interface for the Ga-As system. The main window displays a table of species and their properties. The 'Active species' are Ga(l) and As(l). The 'LIQUID' phase is selected, and the 'Ga - As Mixture' solution model is active. The 'Parameters' panel on the right shows the 'System Parameters' section with 'User defined parameters' set to 'N,T,P'. The 'Number of independent variables' is 1. The 'Define state change for' section has 'Amount' checked. The 'System State' section shows 'Initial State' and 'Final State' for Amount, Temperature, Pressure, Volume, and Enthalpy. The 'Solution Model' is 'Ga - As Mixture' and 'AC Steps' is 120.

Species	Formula	Temper.	Amount	Amount	Add Step	Remove Step	Activity Coefficient
		K	kmol	%	kmol	%	
LIQUID			1.002	100	0		Ga - As Mixture
5	Ga(l)	298.15	1.001	99.9001996	-0.01		1
6	As(l)	298.15	0.001	0.0998004	0.01		1
SOLID			0	0			
8	GaAs	298.15					1

Fig. 37. Ga-As system parameters LIQUID phase solution model active.

The screenshot shows the HSC8 software interface for the Ga-As system. The main window displays a table of species and their properties. The 'Active species' are Ga(l) and As(l). The 'LIQUID' phase is selected, and the 'Ga - As Mixture' solution model is inactive. The 'Parameters' panel on the right shows the 'System Parameters' section with 'User defined parameters' set to 'N,T,P'. The 'Number of independent variables' is 1. The 'Define state change for' section has 'Amount' checked. The 'System State' section shows 'Initial State' and 'Final State' for Amount, Temperature, Pressure, Volume, and Enthalpy. The 'Solution Model' is 'Ga - As Mixture' and 'AC Steps' is 120.

Species	Formula	Temper.	Amount	Amount	Add Step	Remove Step	Activity Coefficient
		K	kmol	%	kmol	%	
LIQUID			1.002	100	0		Ga - As Mixture
5	Ga(l)	298.15	1.001	99.9001996	-0.01		1
6	As(l)	298.15	0.001	0.0998004	0.01		1
SOLID			0	0			
8	GaAs	298.15					1

Fig. 38. Ga-As system parameters LIQUID phase solution model inactive (ideal solution).

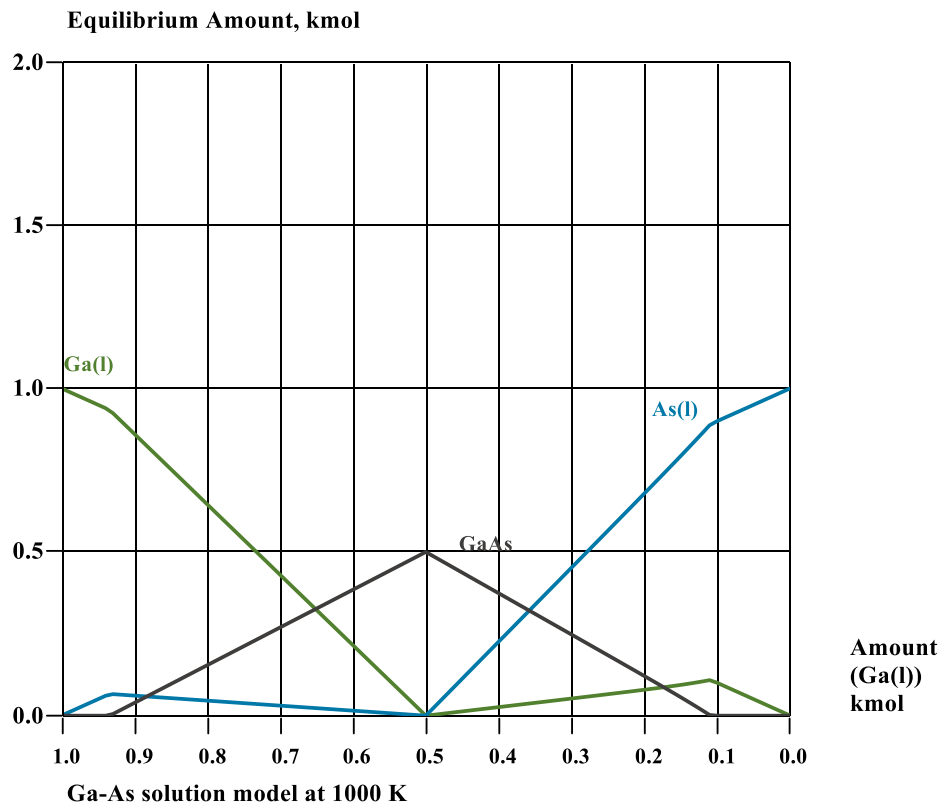


Fig. 39. Results of Ga-As system with solution model at 1000 K, 120 iterations.

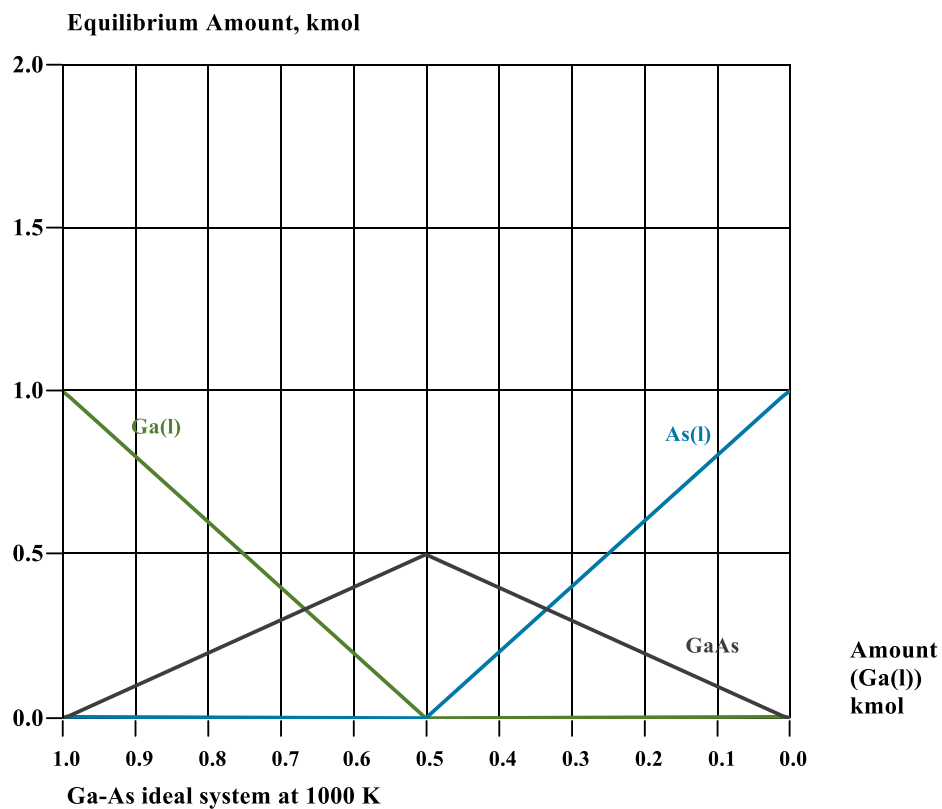


Fig. 40. Results of ideal Ga-As system at 1000 K.

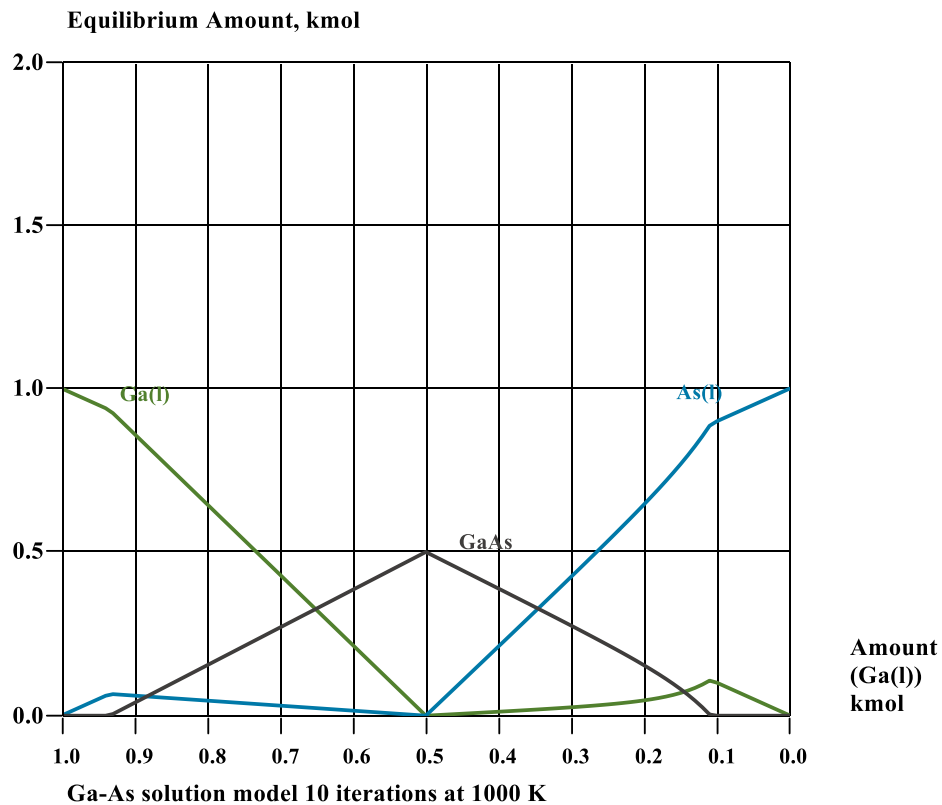


Fig. 41. Results of Ga-As system with solution model at 1000 K, 10 iterations.

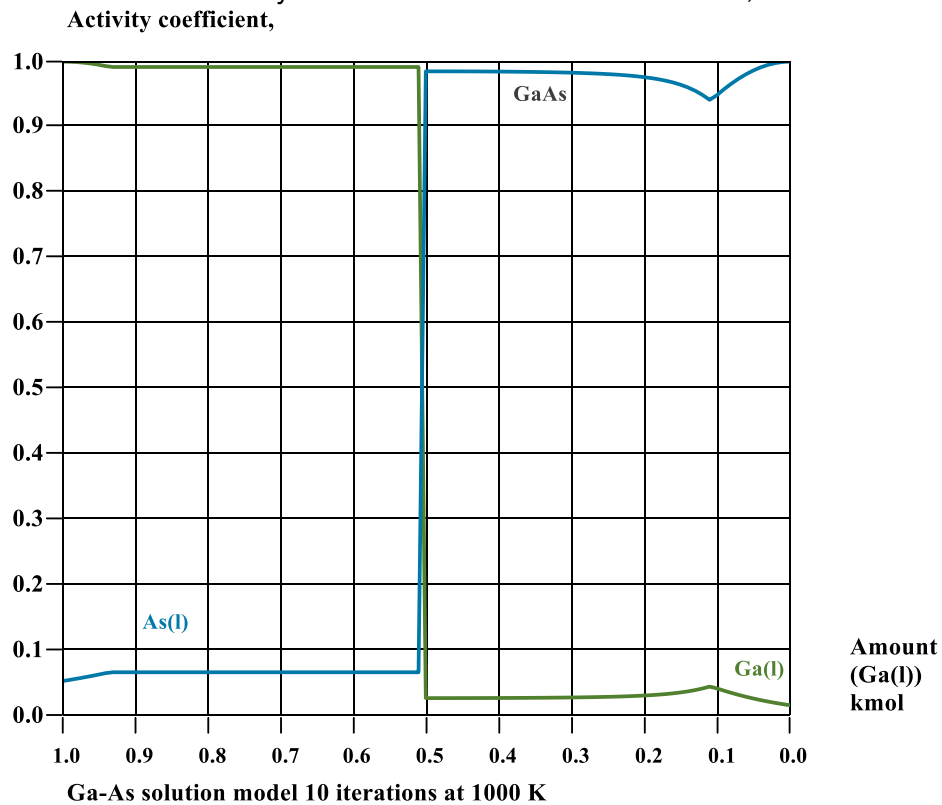


Fig. 42. Activity coefficient of Ga-As system with solution model at 1000 K, 10 iterations.

Case 7: As-Cu-S Transitory Evaporation Example (by Petri Kobylin; As-Cu-S.gem8)

In this example, the results of a transitory evaporation calculation are compared to a normal equilibrium calculation.

Step 1. Insert the phases and species, see **Fig. 37**.

Step 2. Give the input amounts, put 9 as the activity of As and add a step, see **Fig. 43**.

Step 3. Give 101 as the number of amount steps, 1200 °C (1473.15 K) as the temperature, and 1 bar as the pressure. The units can be changed from the **Units menu**.

Step 4. Choose the Gas and Activate Remove Step % Column in the Calculation options. Add 20 % to the GAS phase (cell F4), see **Fig. 43**.

User can also open the file C:\HSC8\Gibbs\ As-Cu-S.gem8 if he/she does not want to do steps 1-4.

Step 5. Press Calculate, Click OK to note that As is extrapolated and press Show Chart. Then choose Amount Added (Raw materials) as the X-axis and Equilibrium amount as the Y-axis and press Finish. Filter the results to show only As compounds, see **Fig. 44**. The results look different when Remove Step is not used (i.e. can be unchecked from the Calculation options, see **Fig. 45** and **Fig. 46**.

The screenshot displays the HSC8 software interface for the As-Cu-S system. The main window shows a table with columns A through G, representing different species and their properties. The table is divided into two sections: GAS and SOLID. The GAS section includes species like N2(g), As(g), As2(g), As3(g), As4(g), AsS(g), As2S3(g), As4S4(g), Cu(g), Cu2(g), CuS(g), S(g), S2(g), S3(g), S4(g), S5(g), S6(g), S7(g), and S8(g). The SOLID section includes As and Cu2S. The table columns are: Species, Formula, Temper. (°C), Amount (kmol), Amount (%), Add Step (kmol), Remove Step (%), and Activity Coefficient. The table shows values for each species, with the GAS section having a total amount of 0.001 kmol and 100%, and the SOLID section having a total amount of 6.2977 kmol and 100%.

On the right side, the Parameters panel is visible, showing the following settings:

- Operations:** Calculate, Show Chart, Cancel
- 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: Amount (1200), Temperature (1200), Pressure (1), Volume, Enthalpy
 - Final State: Amount (1200), Temperature (1200), Pressure (1), Volume, Enthalpy
 - Number of Steps: 101
- 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

Fig. 43. As-Cu-S system with parameters, gas removal of 20 %.

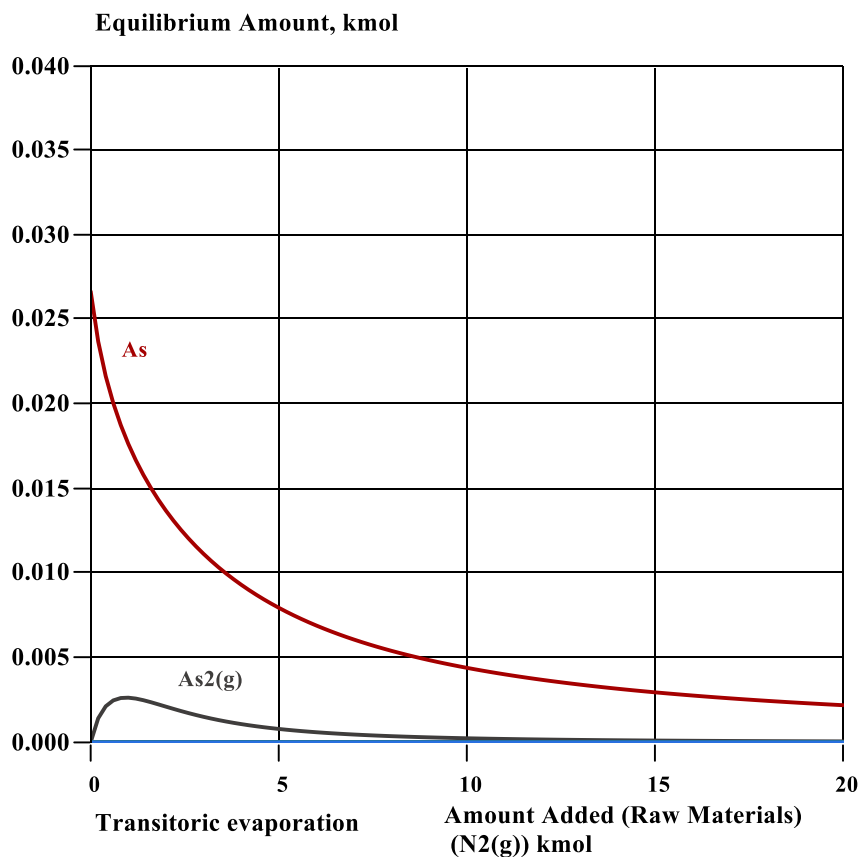


Fig. 44. Results of As-Cu-S system with 20 % removal of the gas phase at 1200 °C.

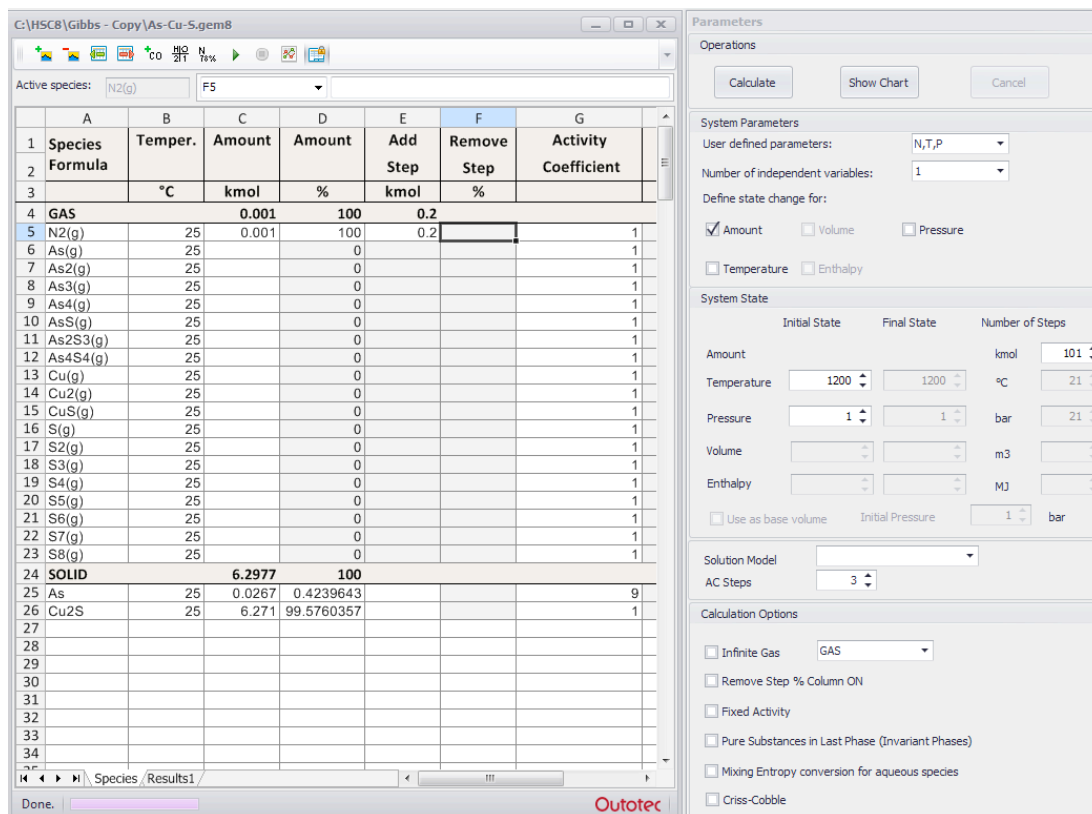


Fig. 45. As-Cu-S system with parameters, no gas removal.

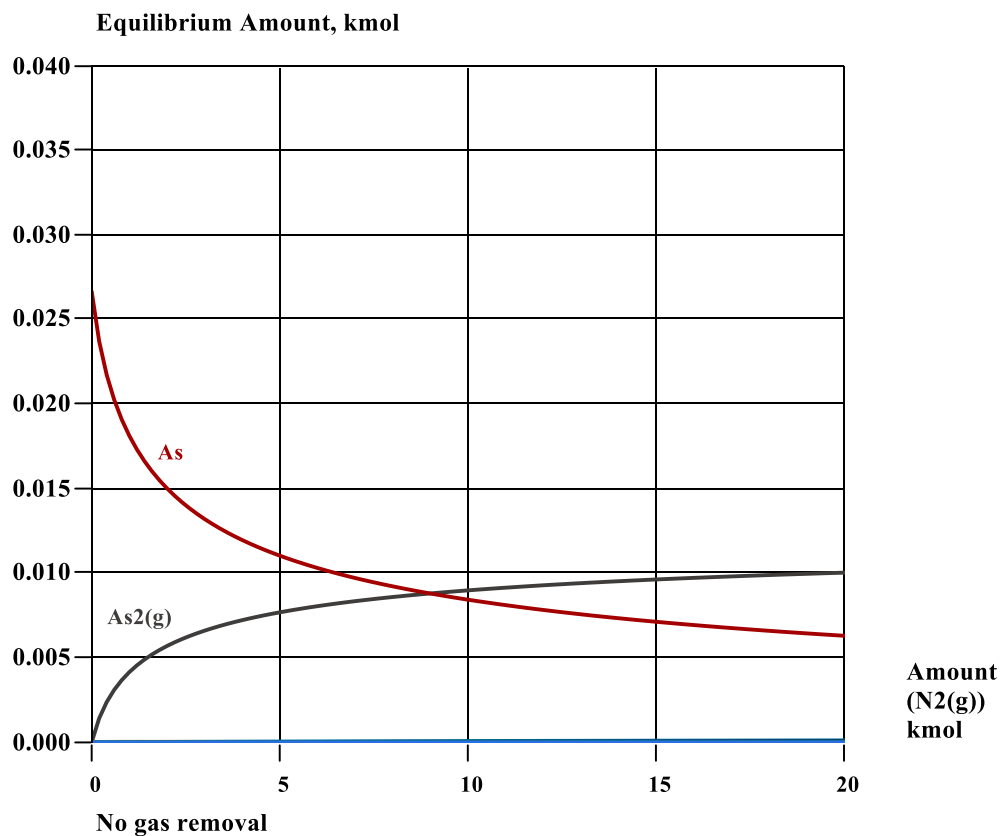


Fig. 46. Results of As-Cu-S system without gas removal at 1200 °C.

Seawater

The HSC Chemistry 8.0 Equilibrium module can be used for many types of applications. This sample case demonstrates water solution calculations using the activity coefficients that have been calculated with the HSC Aqua module.

In this example, the Equilibrium module will be used to estimate the effect of the global temperature on the equilibrium pressure of the carbon dioxide above the seawater.

Carbon Dioxide Cause or Effect?

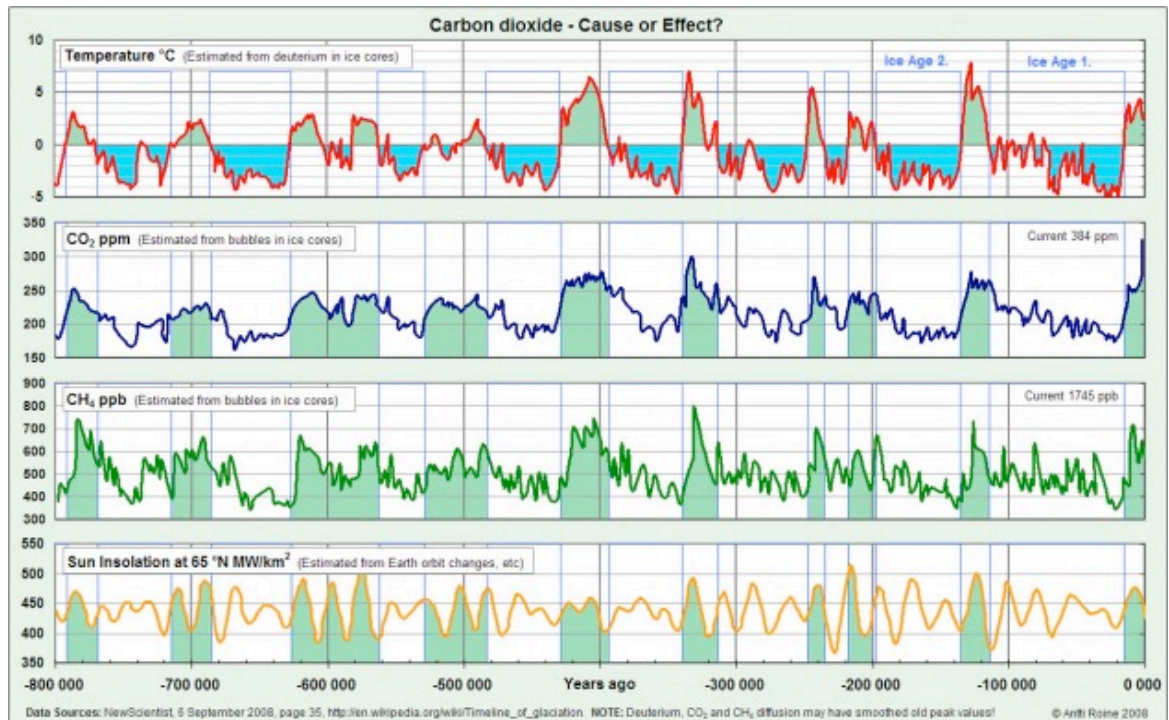


Fig. 47. Our climate has never been stable. Carbon dioxide may increase temperature or vice versa. Both are valid conclusions based on currently available experimental data.

Mainstream science and the media believe that the main reason for climate change is the man-made carbon dioxide content increase in the atmosphere (AGW). The truth may, however, be the other way round. Ice cream consumption increases in warm weather in the summertime, but that does not mean ice cream is the cause of or reason for the warm weather.

Several times within the past million years the seawater temperature has begun to rise BEFORE a similar growth in atmospheric carbon dioxide and methane concentrations. Recent analysis show that CO₂ lags behind the warming and cooling of climate by 200 - 800 years; this may be the time which is needed to reach steady state within the oceans and atmosphere.

The latest evidence shows that the Earth's climate is constantly changing, as continuous change seems to be the normal state of nature, see **Fig. 47**. These changes have created and destroyed huge empires during the history of mankind. In fact, we should be talking about the temperature change of the oceans, because they control the climate - and there is 260 times more seawater than air on our planet, **Fig. 48**.



Fig. 48. There is some 260 times more seawater on the Earth than air. The amount of seawater is roughly 1.35×10^{21} kg. The amount of air is 5.15×10^{18} kg, which equals $3.99 \times 10^{18} \text{ Nm}^3$. The heat capacity of the oceans is 1000 times more than the heat capacity of the atmosphere.

Carbon Balance of the Earth

Carbon Balance (rough estimates)	Carbon	CO₂	CO₂
© Antti Roine 2010	Gt / year	Gt / year	ppm
EMISSIONS TOTAL	233.6		
Manmade (anthropogenic), coal, oil, gas, biofuels,...	5.5	20	2.6
Oceans in warm areas, near equator	106.0		
Respiration (vegetation, animals, natural fires,...)	60.0		
Soil respiration (rotting, decay, decomposition)	60.0		
Land use (deforestation, fires)	2.0		
Vulcanos	0.1		
ABSORPTION TOTAL	230.4		
Oceans in cold areas (absorption, photosynthesis, ...)	108.5		
Biosphere (photosynthesis, GPP, land areas, ...)	121.3		
Forest regrowth, wooden durable goods, paper, ...	0.5		
Weathering (carbonate-silicate cycle)	0.1		
CARBON BALANCE (accumulation to air = 1.5 ppm/year)	3.2	12	1.5
Ocean balance (Ocean = carbon sink)	-2.5		
Land balance (Land = carbon source)	5.7		

Carbon Storages (rough estimates)	Carbon	CO₂	CO₂
© Antti Roine 2010	Gt	Gt	ppm
Atmosphere	780	2 858	365
Vegetation (terrestrial, forest, ...)	610		
Soils, organic material, ...	1 580		
Ocean surface (< 100 m)	1 020		
Ocean deep (> 100 m)	38 140		
Ocean (marine organic material)	3		
Oceans dissolved organic carbon	700		
Oceans reactive sediments (calcite, ...)	150		
Polar ice	540		
Coal fields	4 000		
Oil sands	1 000		
Oil	500		
Natural gas	500		
Sedimentary rocks (limestone)	70 000 000		
TOTAL CARBON:	70 049 523		

Fig. 49. Carbon balance and storage.

In practice, limestone is the "final destination" of carbon. Organic carbon returns back to the atmosphere due to respiration and fires. Bacteria and fungi decompose and oxidize organic material back into methane and CO₂. In this respect, plants are only temporal carbon sinks.

Manmade emissions are quite small compared to the natural carbon cycles. Oceans are the main carbon sink; they have harvested huge amounts of carbon into limestone over millions of years. In fact, biofuels also increase emissions, but it is still better to burn organic waste materials and utilize their energy content rather than letting them form methane in landfills or dumps.

The carbon dioxide emissions of oceans increase along with the surface temperature of the oceans. This is a fact which has been verified experimentally and can also be verified by chemical equilibrium calculations. Hot areas of oceans emit and cold areas absorb carbon dioxide.

There are three key questions in the climate change discussion:

- 1) The carbon dioxide content has increased rapidly many times in history and every time this increase has reversed and become a decrease, see **Fig. 47**. If the carbon dioxide really is the main cause of the climate temperature increase then why has this effect not auto catalytically increased the temperature and evaporated oceans? Which effect has stopped the temperature increase in spite of the high carbon dioxide content?
- 2) Why has the temperature usually started to increase first and then after a few hundred years the carbon dioxide content has started to rise? The same delay seems to exist also when the temperature starts to decrease. In a normal industrial process, the cause always happens first and just before the effect and response. Why is this not true for the climate?
- 3) Why has the Climatic Research Unit (CRU) heavily underestimated the effect of cities on global temperature data? Why has it even modified the raw data in order to obtain the temperature rise, and why has the original data been deleted?

We can try to find an answer to these questions using chemical equilibrium calculations.

Chemical Equilibrium Calculations

One important question in the climate change discussion is the effect that carbon dioxide has on the temperature. A lot of different models with a huge number of fitting and tuning parameters have been created to estimate the effect of CO₂ on the global temperature. These parameters have been needed to make the models agree with the global temperature data made by the CRU.

However, far fewer calculations have been made to estimate the effect of temperature on the equilibrium pressure of the CO₂ over seawater. This effect may be estimated using the HSC Equilibrium module, **Fig. 50**. This module does not use any tuning parameters; all the results are based on the basic thermochemical properties of the chemical species. These calculations are based on the chemical equilibria of theoretical aqueous solution models.

The screenshot displays the HSC Equilibrium Calculations software interface. The main window shows a table of species formulas and their properties. The table is organized into columns: Species Formula, Temper. (°C), Amount (kmol), Amount (%), Add Step (kmol), Remove Step (%), and Activity Coefficient. The table is divided into three phases: Phase #1, Phase #2, and Phase #3. The parameters panel on the right shows various settings for the calculation, including System Parameters, System State, Solution Model, Calculation Options, Target Calculations, and Chart Options.

Species Formula	Temper. °C	Amount kmol	Amount %	Add Step kmol	Remove Step %	Activity Coefficient
Phase #1		0.1780169	100	0.00001		
N2(g)	15	0.1403181	78.8228952	0		1
O2(g)	15	0.0376446	21.1466214	0		1
CO2(g)	15	5.391E-05	0.03028156	0.00001		1
CH4(g)	15	2.695E-07	1.5141E-04	0		1
H2(g)	15	8.984E-08	5.0469E-05	0		1
H2O(g)	25					1
CO(g)	25			0		1
Cl2(g)	25			0		1
HCl(g)	25			0		1
H2S(g)	25			0		1
SO2(g)	25			0		1
Phase #2		73.821252	100	0		
H2O	15	72.313286	97.9572737	0		1.002
CO2(a)	15	2.272E-05	3.0783E-05	0		1.195
CO3(-2a)	25			0		0.123
Ca(+2a)	15	0.0134999	0.01828725	0		0.19
CaCl(+a)	25			0		0.524
CaHCO3(+a)	25			0		0.524
CaOH(+a)	25			0		0.524
Cl(-a)	15	0.7370934	0.99848396	0		0.692
ClO(-a)	25			0		0.524
ClO2(-a)	25			0		0.524
H(+a)	15	1.3E-08	1.761E-08	0		0.672
OH(-a)	15	3.493E-06	4.7312E-06	0		0.572
HCO3(-a)	15	0.0027	0.00365745	0		0.595
HS(-a)	25			0		0.689
HSO3(-a)	25			0		0.769
HSO4(-a)	25			0		0.706
K(+a)	15	0.0134999	0.01828725	0		0.603
KSO4(-a)	25			0		0.524
Mg(+2a)	15	0.0715494	0.09692243	0		0.259
MgCl(+a)	25			0		0.524
Mg(HCO3)(+a)	25			0		0.524
MgOH(+a)	25			0		0.905
Na(+a)	15	0.6317978	0.85584811	0		0.65
NaCO3(-a)	25			0		0.524
NaSO4(-a)	25			0		0.524
O2(-a)	25			0		0.524
S2(-2a)	25			0		0.075
SO3(-2a)	25			0		0.112
SO4(-2a)	15	0.0377997	0.05120431	0		0.128
Phase #3		29.974763	100	0		
NaCl	25			0		1
NaOH	15	1.5E-03	0.00500458	0		1
CaCO3	15	29.973263	99.9949954	0		1
MgCO3	25			0		1
CaSO4*2H2O	25			0		1

Fig. 50. Air - seawater - limestone chemical system specification in the HSC Equilibrium module. All the amounts have been divided by 1E+18 just to make the figures more readable. NB! This does not have any effect on the results.

	Temperature	Amount		Activity coefficients						
	°C	kmol	mol-%	°C	°C	°C	°C	°C	°C	°C
Sea Water	25	73.821	100.000	0	10	15	20	25	30	40
H ₂ O	25	72.313	97.957	1.002	1.002	1.002	1.002	1.002	1.002	1.002
CO ₂ (a)	25	0.000	0.000	1.230	1.207	1.195	1.184	1.174	1.164	1.148
CO ₃ (-2a)	25	0.000	0.000	0.125	0.124	0.123	0.122	0.121	0.120	0.118
Ca(+2a)	25	0.013	0.018	0.195	0.192	0.190	0.187	0.185	0.182	0.176
CaCl(+a)	25	0.000	0.000	0.532	0.527	0.524	0.521	0.518	0.515	0.508
CaHCO ₃ (+a)	25	0.000	0.000	0.532	0.527	0.524	0.521	0.518	0.515	0.508
CaOH(+a)	25	0.000	0.000	0.532	0.527	0.524	0.521	0.518	0.515	0.508
Cl(-a)	25	0.737	0.998	0.686	0.691	0.692	0.693	0.693	0.693	0.691
ClO(-a)	25	0.000	0.000	0.532	0.527	0.524	0.521	0.518	0.515	0.508
ClO ₂ (-a)	25	0.000	0.000	0.532	0.527	0.524	0.521	0.518	0.515	0.508
H(+a)	25	0.000	0.000	0.697	0.679	0.672	0.666	0.659	0.653	0.641
OH(-a)	25	0.000	0.000	0.554	0.567	0.572	0.575	0.578	0.579	0.578
HCO ₃ (-a)	25	0.003	0.004	0.602	0.597	0.595	0.592	0.589	0.586	0.580
HS(-a)	25	0.000	0.000	0.691	0.690	0.689	0.688	0.687	0.686	0.682
HSO ₃ (-a)	25	0.000	0.000	0.817	0.785	0.769	0.754	0.739	0.725	0.698
HSO ₄ (-a)	25	0.000	0.000	0.716	0.710	0.706	0.703	0.699	0.696	0.688
K(+a)	25	0.013	0.018	0.596	0.602	0.603	0.605	0.605	0.606	0.605
KSO ₄ (-a)	25	0.000	0.000	0.532	0.527	0.524	0.521	0.518	0.515	0.508
Mg(+2a)	25	0.072	0.098	0.278	0.265	0.259	0.253	0.248	0.242	0.232
MgCl(+a)	25	0.000	0.000	0.532	0.527	0.524	0.521	0.518	0.515	0.508
Mg(HCO ₃)(+a)	25	0.000	0.000	0.532	0.527	0.524	0.521	0.518	0.515	0.508
MgOH(+a)	25	0.000	0.000	0.919	0.910	0.905	0.900	0.895	0.889	0.878
Na(+a)	25	0.632	0.856	0.643	0.648	0.650	0.651	0.651	0.651	0.649
NaCO ₃ (-a)	25	0.000	0.000	0.532	0.527	0.524	0.521	0.518	0.515	0.508
NaSO ₄ (-a)	25	0.000	0.000	0.532	0.527	0.524	0.521	0.518	0.515	0.508
O ₂ (-a)	25	0.000	0.000	0.532	0.527	0.524	0.521	0.518	0.515	0.508
S ₂ (-2a)	25	0.000	0.000	0.080	0.077	0.075	0.074	0.072	0.070	0.067
SO ₃ (-2a)	25	0.000	0.000	0.131	0.118	0.112	0.106	0.100	0.095	0.085
SO ₄ (-2a)	25	0.038	0.051	0.135	0.130	0.128	0.127	0.126	0.125	0.123

Fig. 51. Effect of temperature on the activity coefficients in seawater.

We can put all the oceans, atmosphere, and lot of calcite into a single chemical reaction unit and run equilibrium calculations. This chemical system specification is shown in **Fig. 50**. The amounts and compositions of gas and water phases correspond to the average amounts and composition of the atmosphere and seawater. Calcite has been assumed to consist mainly of CaCO₃.

The equilibrium calculations can be carried out for different temperatures and CO₂ amounts in the air. The Equilibrium module calculation routine uses the Gibbs Energy Minimization method, which determines the phase amount, and the composition combination where the Gibbs free energy of the chemical system reaches its minimum. This method automatically takes into account all the possible chemical reactions that may occur in this system.

The enthalpy, entropy, and heat capacity data for the pure chemical compounds shown in **Fig. 50** are based on the extensive HSC 8 thermochemical database. The non-ideal behavior of the water solution is calculated using the HSC Aqua module, **Fig. 51**, which uses an extensive aqueous solution database. The amounts and compositions of the air and seawater are based on average values available in public encyclopedias and Internet sources.

Results

The current average CO₂ content of the atmosphere is some 383 ppm. The average temperature at sea level is 15 °C. The equilibrium pressure of CO₂ above the seawater in these conditions is only 157 ppm. This is the thermochemical explanation of why the oceans are the most important carbon sinks, see **Fig. 49** and **Fig. 52**.

The chemical potential and activity of carbon dioxide is lower in cold seawater than in air, and this is the chemical explanation of why carbon enters the sea in cold areas. If the chemical potential of carbon dioxide were higher in seawater, then seawater would release much more carbon dioxide into the air in hot areas, however, luckily this is not the case.

On the other hand, at high surface temperatures, like 25 - 35 °C, the oceans may release carbon dioxide because the equilibrium pressure increases rapidly along with the temperature, see **Fig. 52** and **Fig. 53**. The sun may easily warm up a thin surface layer of the sea and this is enough to increase CO₂ emissions. At medium surface temperatures, this layer may behave as a barrier which prevents CO₂ dissolution in seawater.

Fig. 52 and **Fig. 53** also show why the CO₂ content in the atmosphere within the last 800 000 years has never been lower than 160 ppm, **Fig. 47**.

The carbon dioxide pressure and chemical potential difference decrease along with an increase in temperature. This simply means that the driving force for carbon dioxide absorption and accumulation in the sea is decreasing radically, **Fig. 52**. This always happens if the temperature of the oceans increases for any reason. Seawater emits CO₂ when the surface temperature of seawater is high, because carbon dioxide pressure is higher in seawater than in the atmosphere.

The sea can easily absorb large amounts of carbon dioxide. **Fig. 53** shows what happens if we change the amount of CO₂ in the atmosphere. The result is that if we remove carbon dioxide from the atmosphere, then the sea will release CO₂ until the CO₂ content reaches 140 ppm. On the other hand, if we double the CO₂ amount in the atmosphere, then sea will absorb CO₂ until the CO₂ level in atmosphere reaches 180 ppm. Of course, in the long term, the conditions of the whole chemical system will change, but this calculation illustrates the direction of the chemical reactions.

In fact, the total CO₂ absorption potential of seawater is very high because the equilibrium partial pressure of CO₂ decreases along with pressure, see **Fig. 54**, i.e. carbon dioxide dissolution into seawater increases along with pressure. This promotes formation of limestone, because seawater is generally supersaturated in calcite, CaCO₃. The shells of marine organisms made of calcite can form limestone sediments, because calcite does not dissolve into seawater. Limestone is the most important destination for carbon, see **Fig. 49**.

However, at very high pressure calcite also starts to dissolve into seawater; usually this happens about 4500 meters below sea level. This depth is called the carbonate compensation depth (CCD) or lysocline. Below this depth limestone sediments may dissolve.

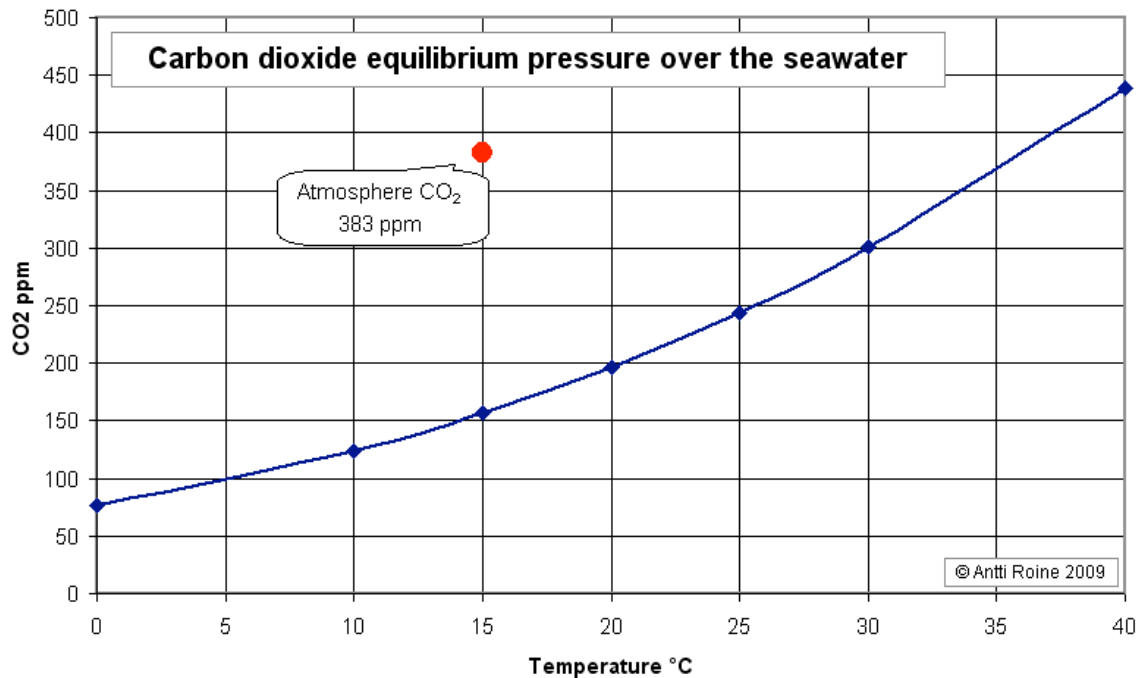


Fig. 52. The effect of temperature on the carbon dioxide equilibrium pressure over seawater at steady state with homogenous phases. The average temperature is assumed to be 15 °C and the CO₂ content in the atmosphere 383 ppm. The difference between the equilibrium curve and 383 ppm level creates the driving force of CO₂ absorption.

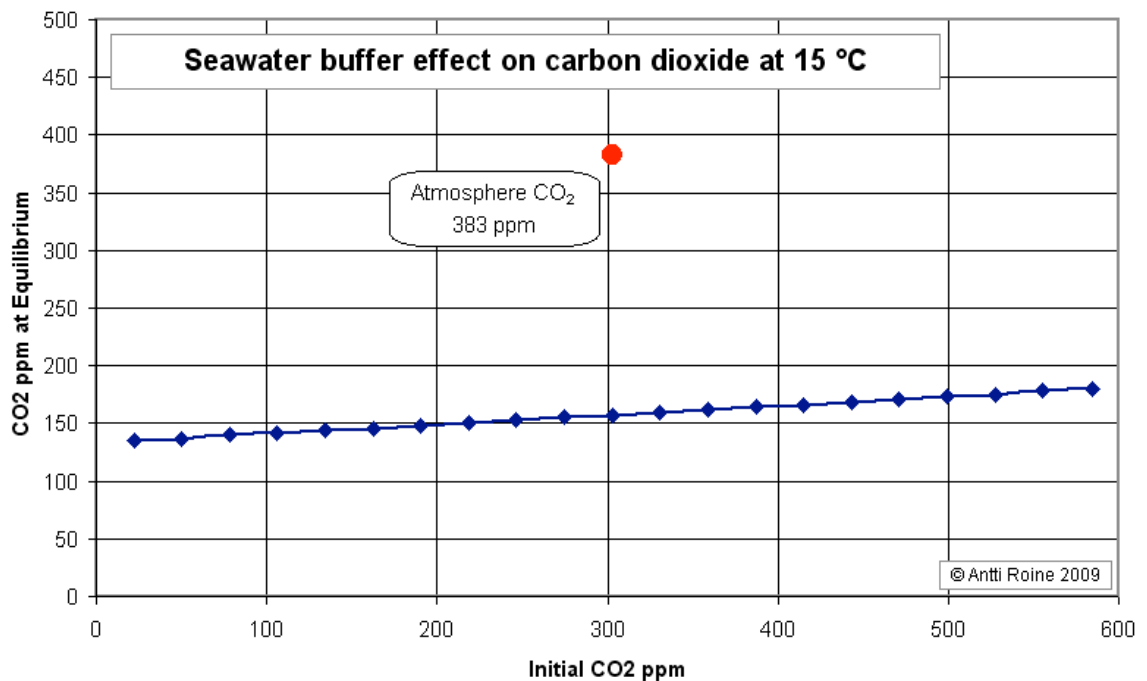


Fig. 53. Seawater may effectively buffer temporal CO₂ variations in the atmosphere. The calculations have been carried out by changing the amount of CO₂ in the atmosphere.

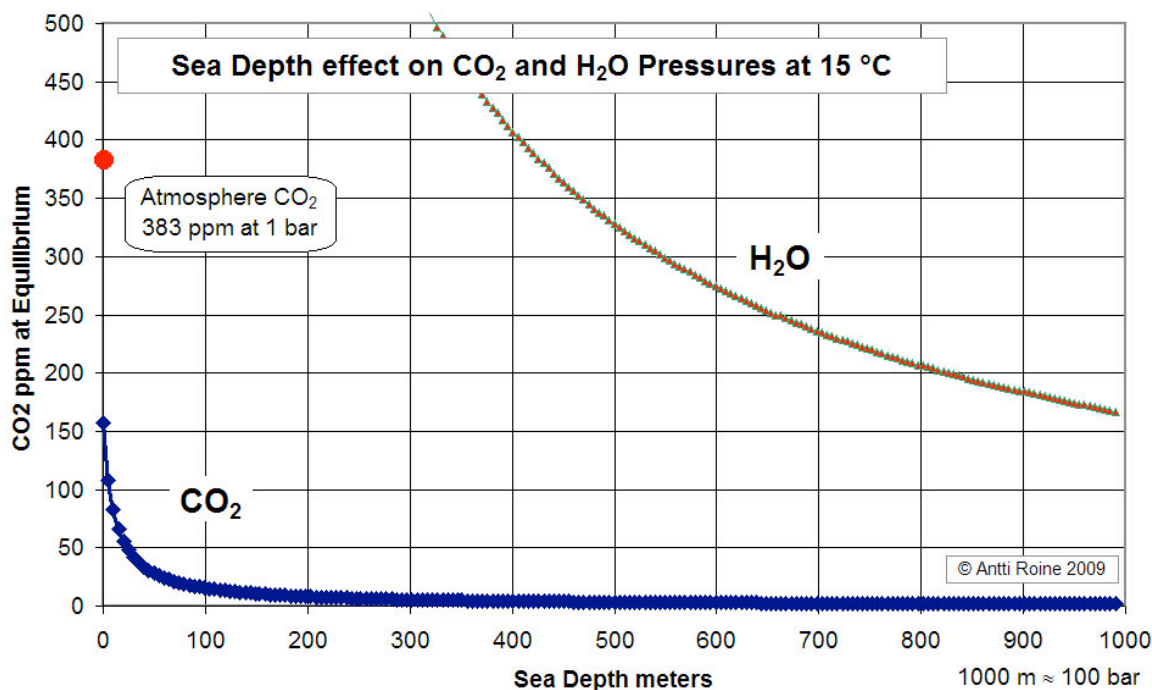


Fig. 54. Effect of sea depth on the partial pressures of carbon dioxide and water vapor. The CO₂ absorption potential of seawater increases rapidly when the total pressure increases. CO₂ dissolution into seawater increases along with pressure. However, at very high pressure calcite also starts to dissolve into seawater and this prevents the precipitation of limestone. Usually this happens when the depth is more than 4500 m.

Most of the carbon in seawater is in deep areas, see **Fig. 49**. Theoretical chemical calculation results in **Fig. 54** are in good agreement with this experimental fact.

All these results are based on theoretical aqueous solution data. These thermochemical models could also be used inside climate models to calculate the dependence between the climate temperature and carbon dioxide content of the atmosphere. Then of course some calibration parameters should be used to fix these results more exactly with the experimental data.

Discussion

Carbon dioxide dissolution into seawater increases when temperature decreases and pressure increases. See for example: http://www.geochem-model.org/publications/41-MC_98_131.pdf

These results are in good agreement with the current calculations.

The heat capacity of the oceans is 1000 times larger than the heat capacity of the atmosphere. Therefore we should monitor the temperature changes of the oceans because the oceans determine the climate of the Earth.

The density of cold seawater is always less than that of warm seawater. This is why warm seawater will rise to the surface and cold sinks to the bottom. This also means that all the geothermal heat will rise to the surface from the seafloor, because warm seawater is always lighter than cold seawater. In lakes, the situation is of course different because the density of pure water is highest at a temperature of 4 °C.

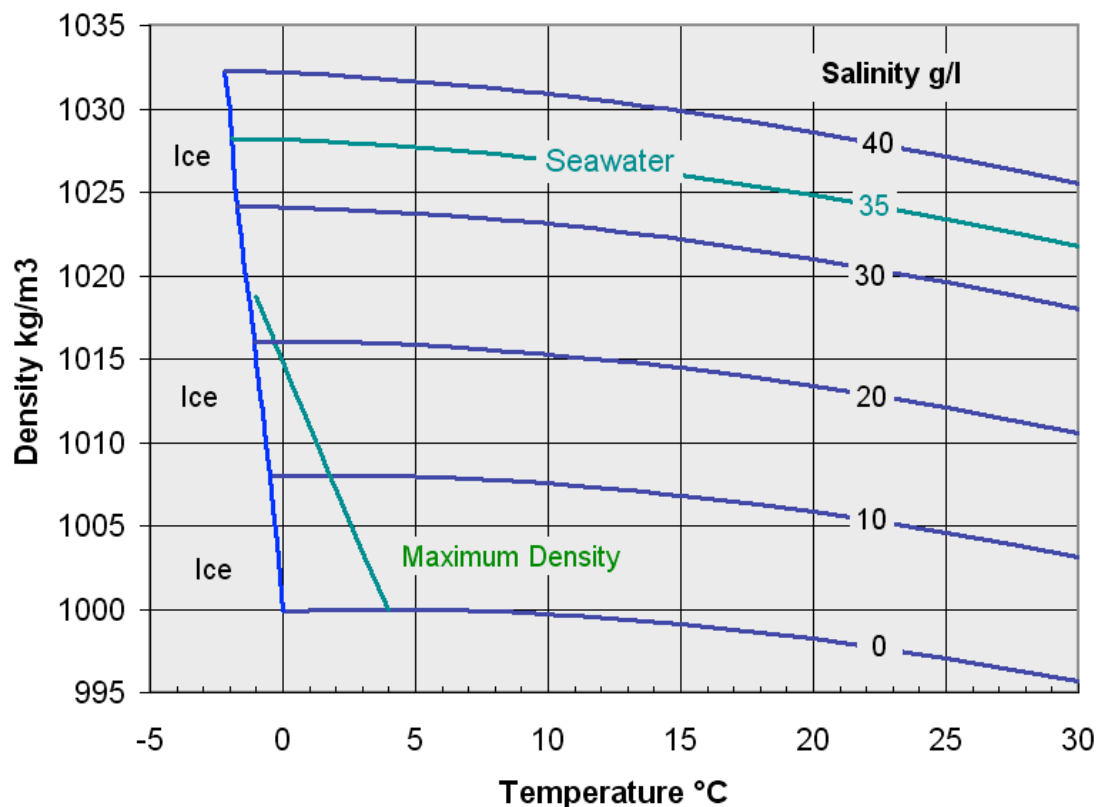


Fig. 55. Effect of temperature on seawater density.

The primary reasons for global temperature changes are changes in solar activity and variations in the Earth's orbit, rotation and axis. See for example:

http://www.gao.spb.ru/english/astrometr/abduss_nkj_2009.pdf

<http://myweb.wvu.edu/dbunny/research/global/geoev.pdf>

http://myweb.wvu.edu/dbunny/research/global/easterbrook_climate-cycle-evidence.pdf

Summary

These very preliminary and brief chemical equilibrium calculations show that carbon dioxide may not be the only reason for the increase in the temperature of the Earth's climate. In fact, it seems that a temperature increase may be the cause and the carbon dioxide content increase in the atmosphere the natural effect of the climate change processes. It is most likely that carbon dioxide contributes to global warming, but it is hardly the primary reason for global warming.

These preliminary and simple equilibrium calculations prove that we should invest much more effort on atmosphere and ocean chemistry research. We have to improve the basic data of the equilibrium calculations and take into account also kinetics, temperature, pressure and concentration gradients, as well as validating the calculation models experimentally.

We also have to remember that we must find sustainable, low cost, new energy sources and solve the extensive environmental and emission problems, because energy costs and recycling are the key issues if we want to improve worldwide welfare. This is a fact, whether climate change is due to human activity or not.

The basic ideas of this paper may be summarized in the following conclusions:

- 1) The oceans are and always have been the most important and pre-eminent carbon sinks, **Fig. 49**.
- 2) The effect of humans is much less than 5% of the natural carbon cycle.
- 3) Huge amounts of CO₂ are released from the sea when the sun heats up the thin surface layer of seawater, **Fig. 52**. There are delays in this process due to diffusion and convection.
- 4) In cold areas the oceans absorb huge amounts of CO₂, see **Fig. 52**. There are delays in this process due to diffusion and convection.
- 5) Deep oceans contain gigantic amounts of carbon, because carbon dissolution into seawater increases along with pressure, **Fig. 54**.

Comparison to Experimental Data

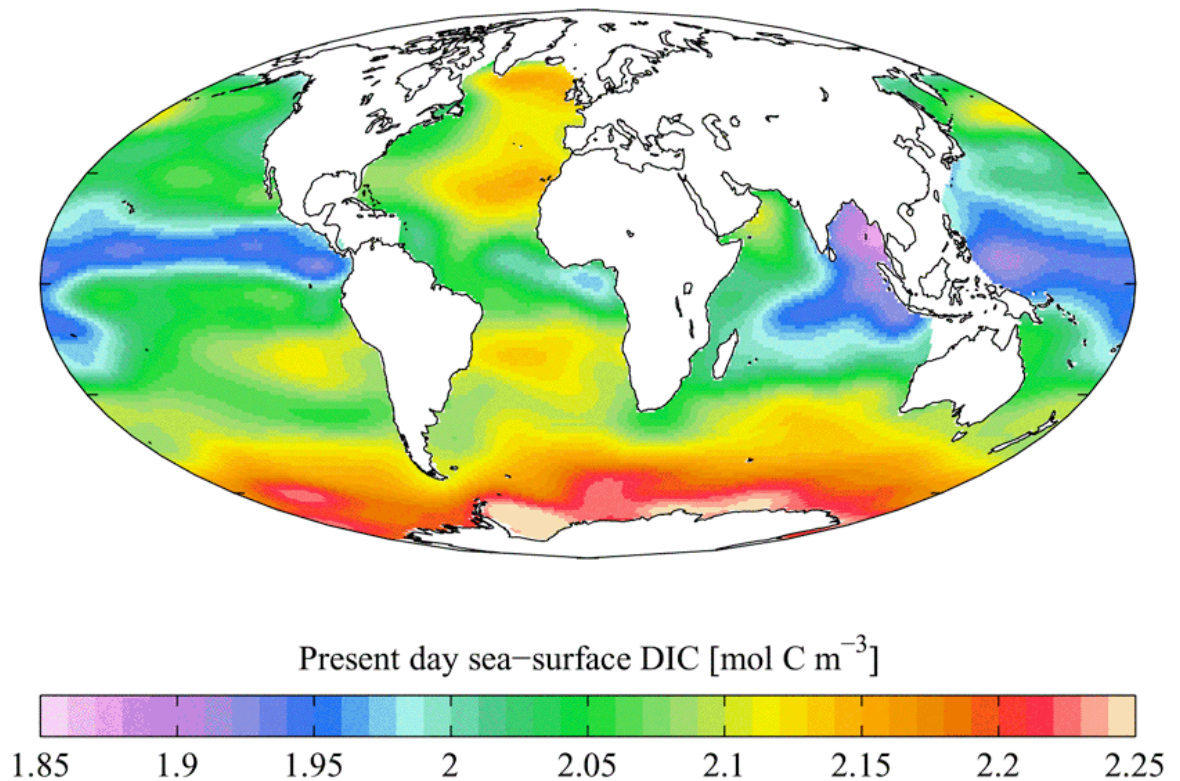


Fig. 56. Annual mean sea surface dissolved inorganic carbon. The cold red areas absorb much more carbon than the blue hot ones, i.e. the Arctic seas are CO_2 absorbers. This experimental result is in good agreement with the current calculated results given in **Fig. 52**.

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Mean Annual Air-Sea Flux for 2000 [Rev Jun 09] (NCEP II Wind, 3,040K, $\Gamma=.26$)

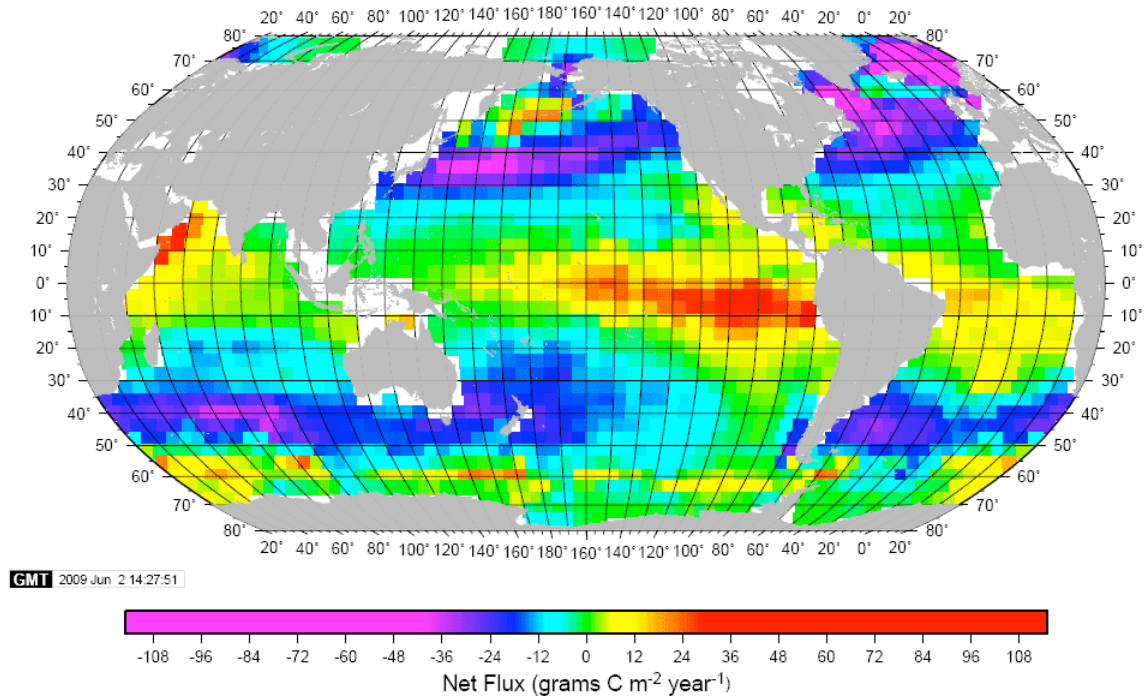


Fig. 57. Annual CO₂ Flux Estimated from Air-Sea Difference in CO₂ Partial Pressure. The red areas may emit and the blue ones absorb CO₂.

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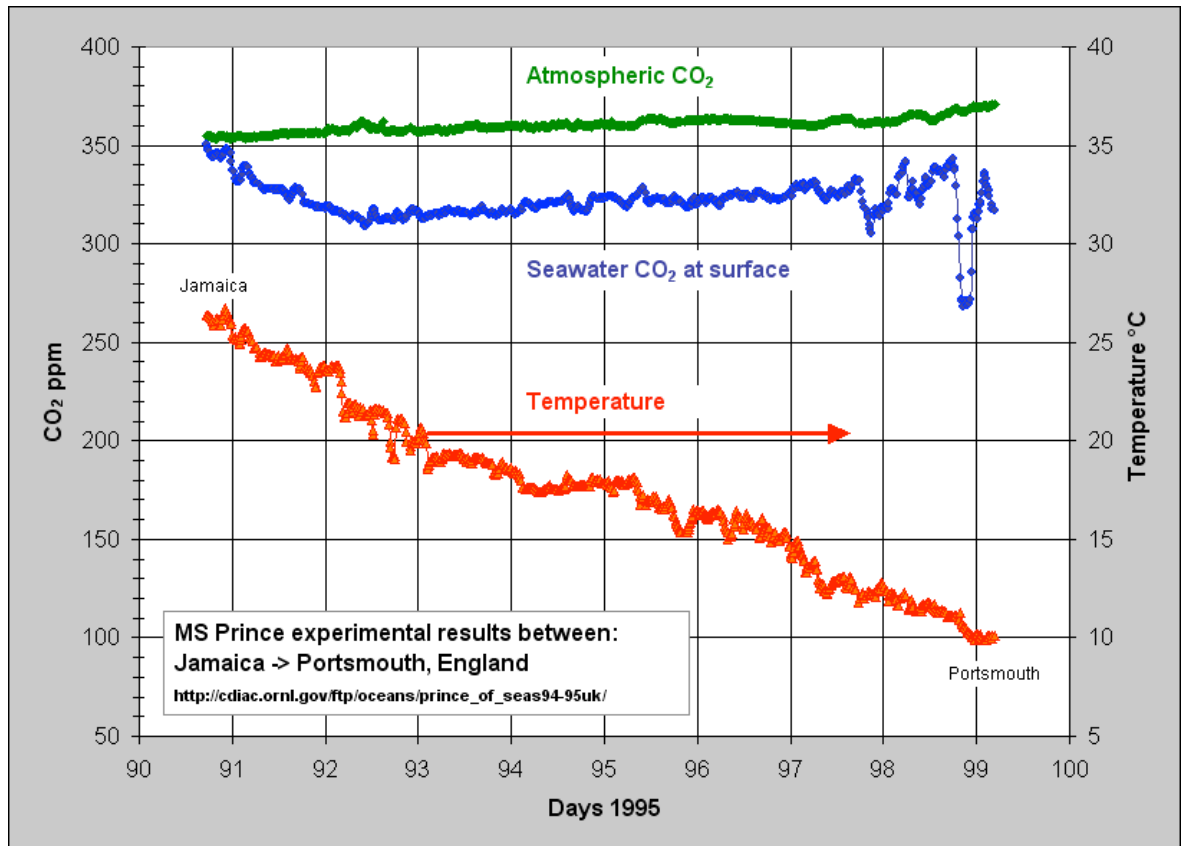


Fig. 58. Partial pressure of CO_2 may be very high at the sea surface at higher temperatures such as 26°C . In these conditions seawater cannot absorb CO_2 at all. The average CO_2 partial pressure in homogenous seawater is some 150 - 200 ppm, **Fig. 52**, but at the sea surface it may be much higher due to the slowness of diffusion and convection.

In fact, the total CO_2 absorption potential of seawater is very high because the equilibrium partial pressure of CO_2 at deeper levels is very low, see **Fig. 54**.

<http://joannenova.com.au/global-warming/ice-core-graph/>