Outokumpu HSC Chemistry® for Windows

Chemical Reaction and Equilibrium Software
with Extensive Thermochemical Database

ABSTRACT

HSC Chemistry is designed for various kinds of **chemical reactions and equilibria calculations.** The current version contains fourteen calculation modules displayed as fourteen options in the HSC main menu:

1.	Reaction Equations	**8.**	H, S, C and G Diagrams
2.	Heat and Material Balances	**9.**	Phase Stability Diagrams
3.	Heat Loss Calculations	**10.**	Mineralogy Iterations
4.	Equilibrium Compositions	**11.**	Composition Conversions
5.	Electrochemical Equilibria	**12.**	Elements
6.	Formula Weights	**13.**	Water (Steam Tables)
7.	Eh - pH – Diagrams	**14.**	Units

The name of the program is based on the feature that all fourteen calculation options automatically utilize the same extensive **thermochemical database** which contains enthalpy

(**H**), entropy (**S**) and heat capacity (**C**) data for more than 17000 chemical compounds. This database is equivalent to more than seventeen thick data books.

The objective of HSC is to make conventional thermodynamic calculations fast and easy to carry out using personal computers. Therefore HSC has a wide range of application possibilities in scientific education, industry and research. Thermochemical calculations are useful, for example, when **developing new chemical processes and improving old ones**. HSC Chemistry is also a useful tool for universities and schools in chemical practicals and studies.

Traditionally, thermodynamic calculations based on experimental or assessed data have utilized stability functions in various thermodynamic data books and papers in scientific journals. The difficult searching stage and complicated calculations, as well as inconsistencies arising from different selections of standard and reference states, have made this calculation procedure quite time-consuming.

HSC Chemistry offers powerful calculation methods for studying the effects of different variables on the chemical system at equilibrium. For example, if the user gives the raw materials, amounts and other conditions of almost any chemical process, the program will give the amounts of the product as a result. HSC also makes heat and material balance calculations of different processes much more easily than any manual method. The Eh-pH-diagrams option of HSC also offers a very fast way of studying the dissolution and corrosion behavior of different materials.

Of course, HSC does not solve all chemical problems, because it does not take into account the kinetics (rates) of the chemical reactions and non-ideality of solutions. However, in many cases it is a very inexpensive and useful tool which helps to find the optimum reaction conditions and yields for experimental investigations without expensive trial-and-error chemistry.

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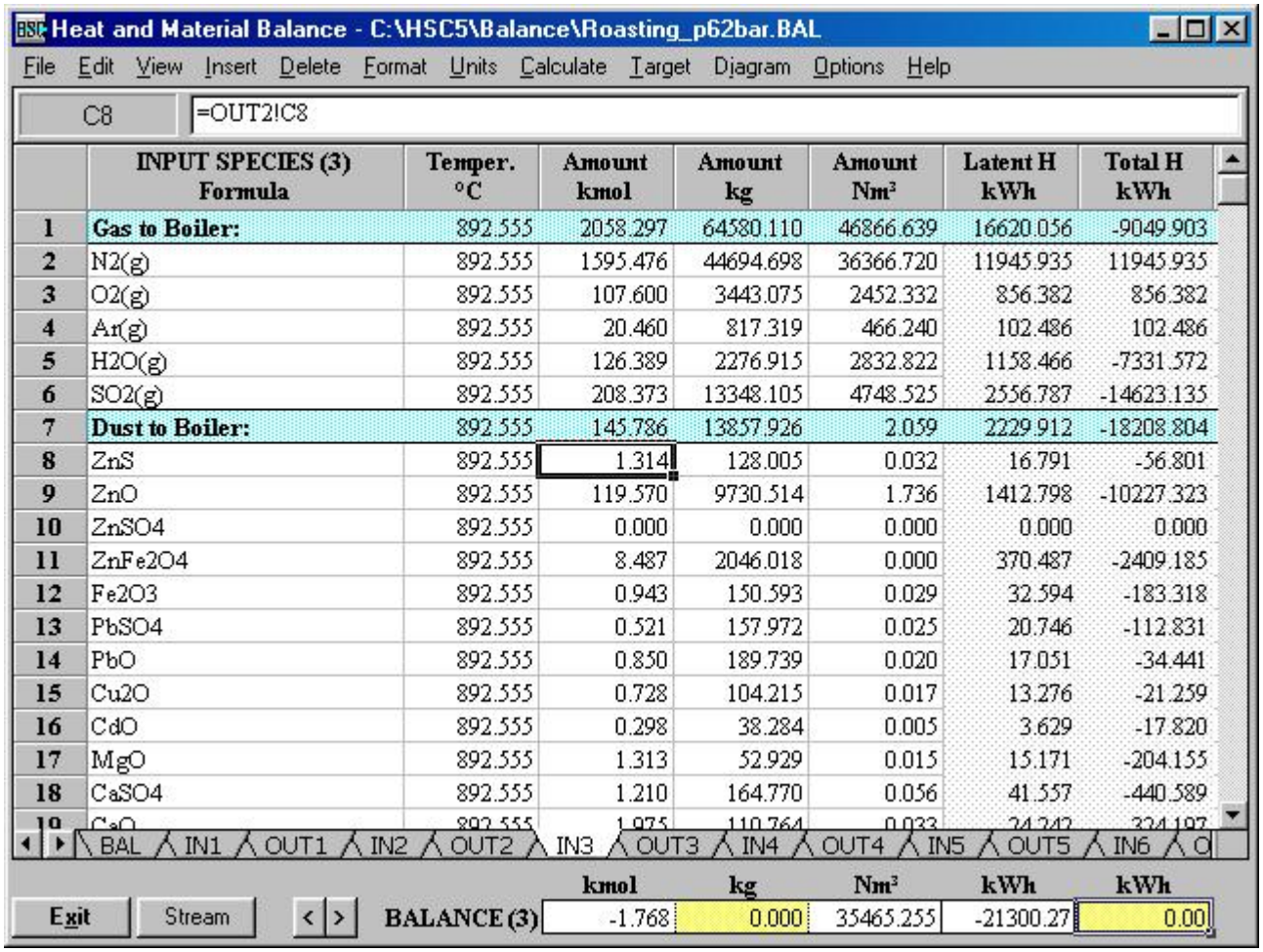
6. WHAT'S NEW IN HSC CHEMISTRY 5.0

The new HSC version 5 contains several new calculation routines, new properties and a larger database with updated data. The familiar HSC style user interface and file formats have been maintained in order to minimize the training requirements for current HSC users. The new features can be summarized as follows:

6.1 Updated Heat and Mass Balance Module

- HSC version 4 calculated only one balance area at a time. With the new HSC 5 up to 127 balances may be calculated simultaneously.
- Balance areas may be connected with each other using cell references or built-in element amount functions.
- Temperatures may be used as variables.
- Target routine is also available in Diagram option.
- New stream elemental composition calculator.
- Graphical objects may be added to sheets.
- Link to the new Steam enthalpy calculator (0.01 - 1000 bar).
- Link to the new Heat Loss routine.
- Many small improvements such as iteration routine fixes.



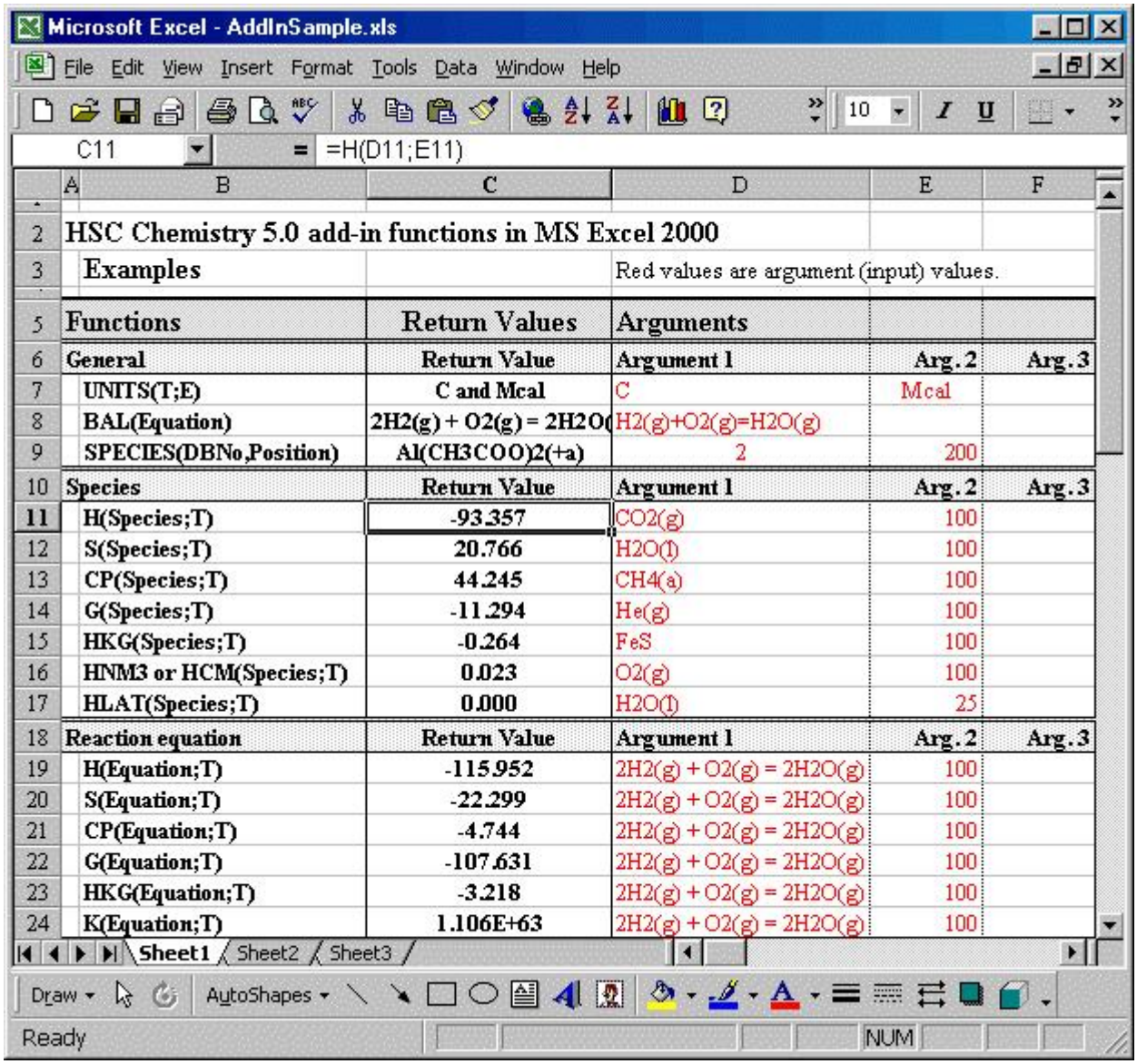
	INPUT SPECIES (3) Formula	Temper. °C	Amount kmol	Amount kg	Amount Nm³	Latent H kWh	Total H kWh
1	Gas to Boiler:	892.555	2058.297	64580.110	46866.639	16620.056	-9049.903
2	N2(g)	892.555	1595.476	44694.698	36366.720	11945.935	11945.935
3	O2(g)	892.555	107.600	3443.075	2452.332	856.382	856.382
4	Ar(g)	892.555	20.460	817.319	466.240	102.486	102.486
5	H2O(g)	892.555	126.389	2276.915	2832.822	1158.466	-7331.572
6	SO2(g)	892.555	208.373	13348.105	4748.525	2556.787	-14623.135
7	Dust to Boiler:	892.555	145.786	13857.926	2.059	2229.912	-18208.804
8	ZnS	892.555	1.314	128.005	0.032	16.791	-56.801
9	ZnO	892.555	119.570	9730.514	1.736	1412.798	-10227.323
10	ZnSO4	892.555	0.000	0.000	0.000	0.000	0.000
11	ZnFe2O4	892.555	8.487	2046.018	0.000	370.487	-2409.185
12	Fe2O3	892.555	0.943	150.593	0.029	32.594	-183.318
13	PbSO4	892.555	0.521	157.972	0.025	20.746	-112.831
14	PbO	892.555	0.850	189.739	0.020	17.051	-34.441
15	Cu2O	892.555	0.728	104.215	0.017	13.276	-21.259
16	CdO	892.555	0.298	38.284	0.005	3.629	-17.820
17	MgO	892.555	1.313	52.929	0.015	15.171	-204.155
18	CaSO4	892.555	1.210	164.770	0.056	41.557	-440.589
19	CaO	892.555	1.975	110.764	0.033	24.242	324.197
			kmol	kg	Nm³	kWh	kWh
	BALANCE (3)		-1.768	0.000	35465.255	-21300.27	0.00

6.2 New HSC AddIn Functions for Excel 2000

HSC Excel AddIn makes native HSC functions and databases available directly within a normal Excel spreadsheet. Highly specialized applications may be created with these new Excel AddIn functions.

These functions work like normal Excel functions such as the **SUM** function. For example, **H(FeO 500)** function returns the enthalpy of FeO at 500 Kelvin. An other example is **WTP(Na Na2SO4)** function which returns the weight percent of sodium in sodium sulphate.

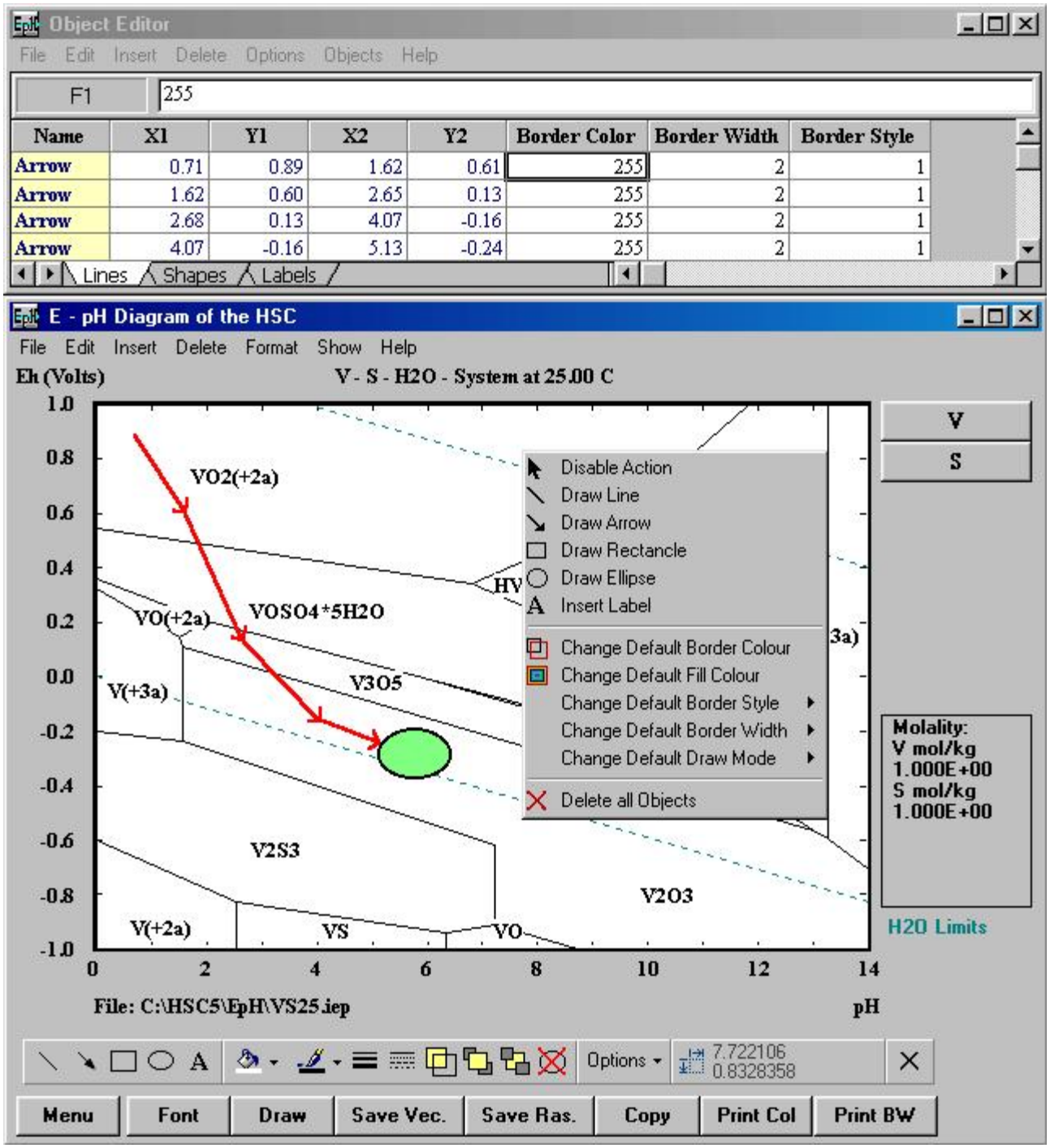
Up to 45 different HSC functions are available in Excel which automatically reads the HSC database.



6.3 New Drawing Toolbar

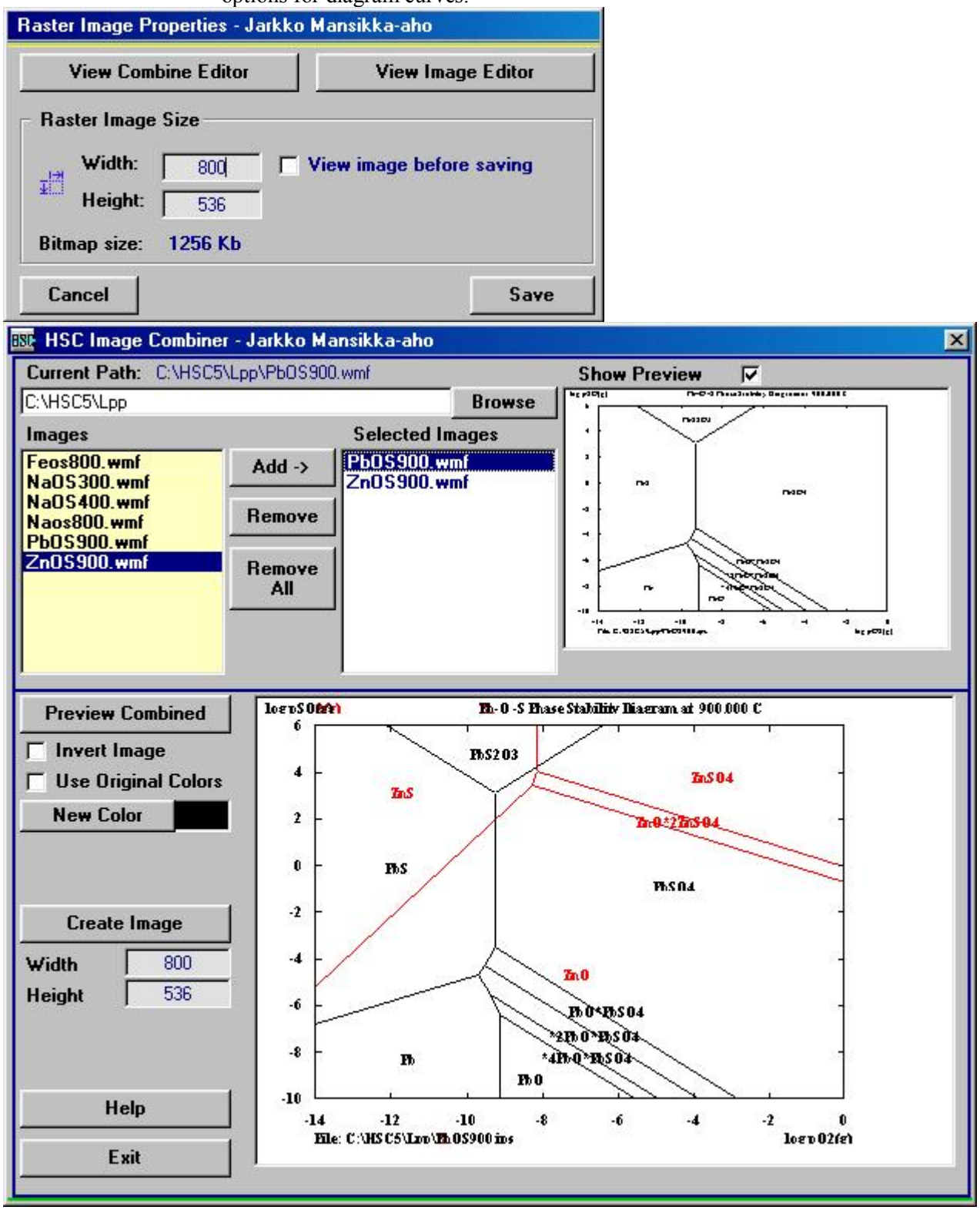
The new Drawing Toolbar may be used to draw basic graphical objects (lines, arrows, rectangles, ellipses) in HSC diagrams. These shapes may be used, for example, to illustrate experimental conditions. Versatile formatting options may be used to edit lines or add fill colour, line widths and styles.

Drawing Objects may be created and edited with the mouse or using the Object Editor, which enables very exact editing with numerical values. Drawing Objects may be fixed so that they can be used in all diagrams or they may be saved for later use in files.



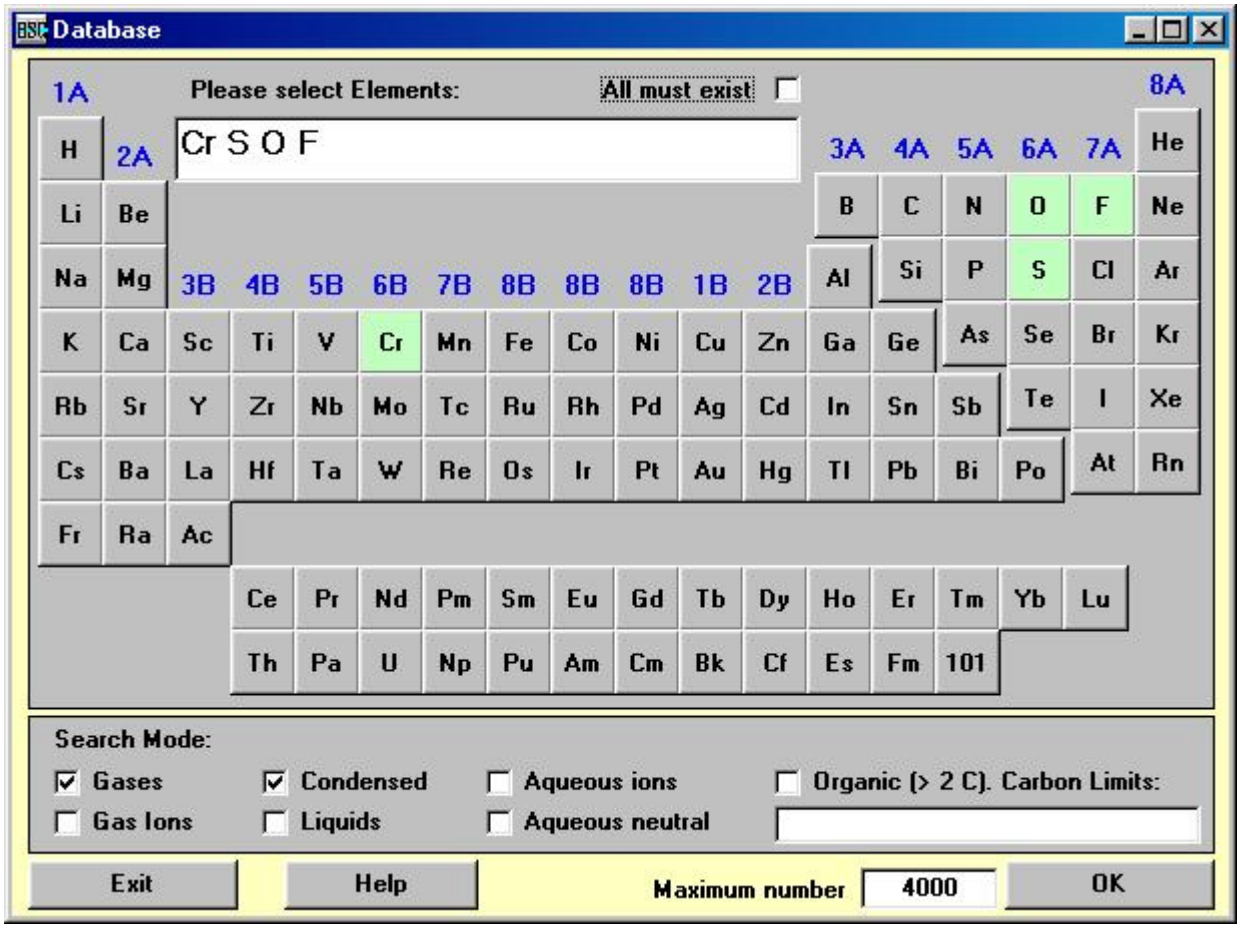
6.4 New Diagram Options

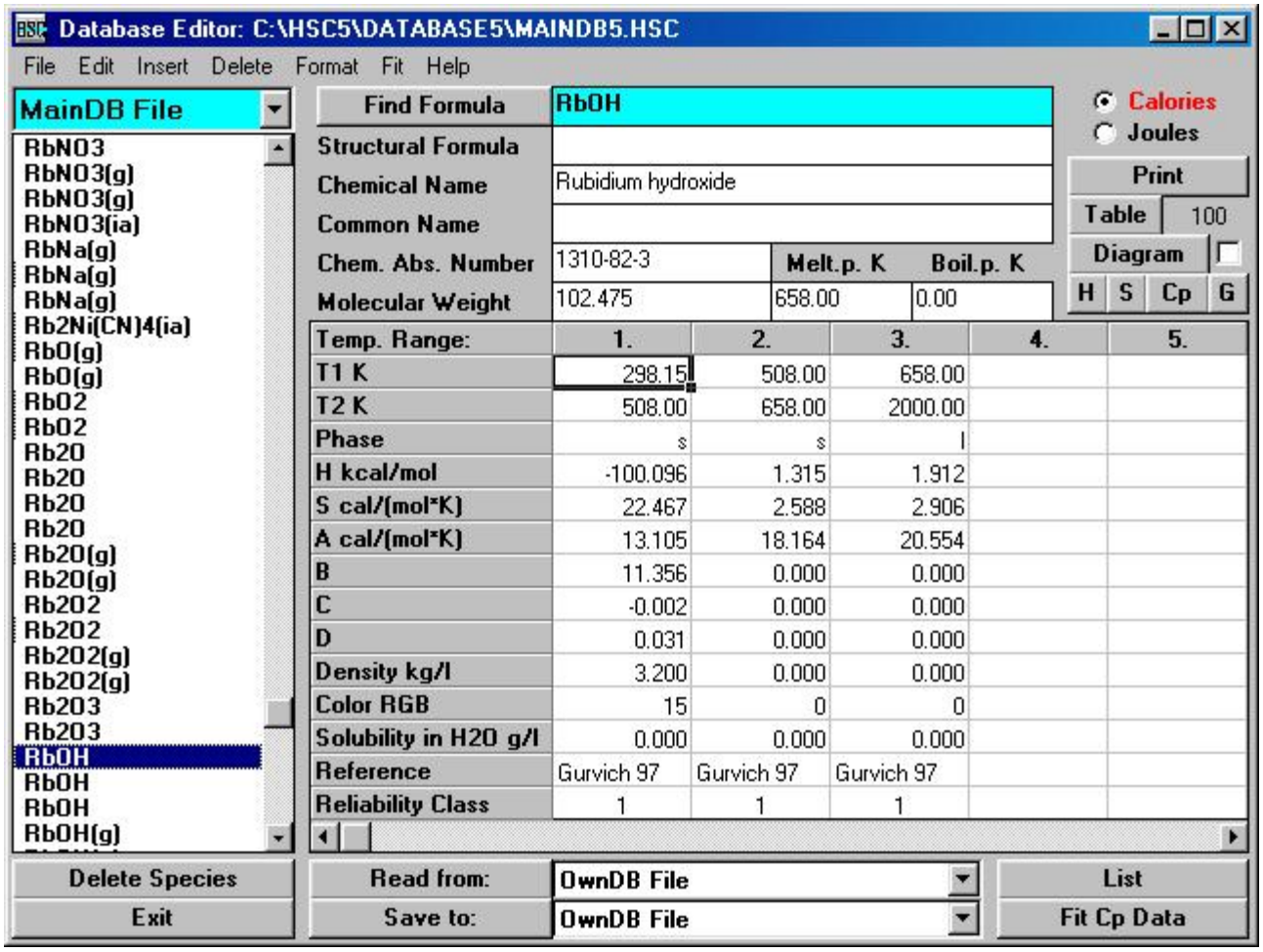
- HSC 4 was able to save diagrams using only one WMF format. Now more than 30 file formats are available, such as PG, BMP, etc.
- Diagrams may also be edited using the new HSC Image Editor.
- Several diagrams may be combined with the new HSC Image Combiner if the same X- and Y-scales have been used.
- There is a new Diagram Grid format option as well as some new formatting options for diagram curves.



6.5 Larger Database with new Options

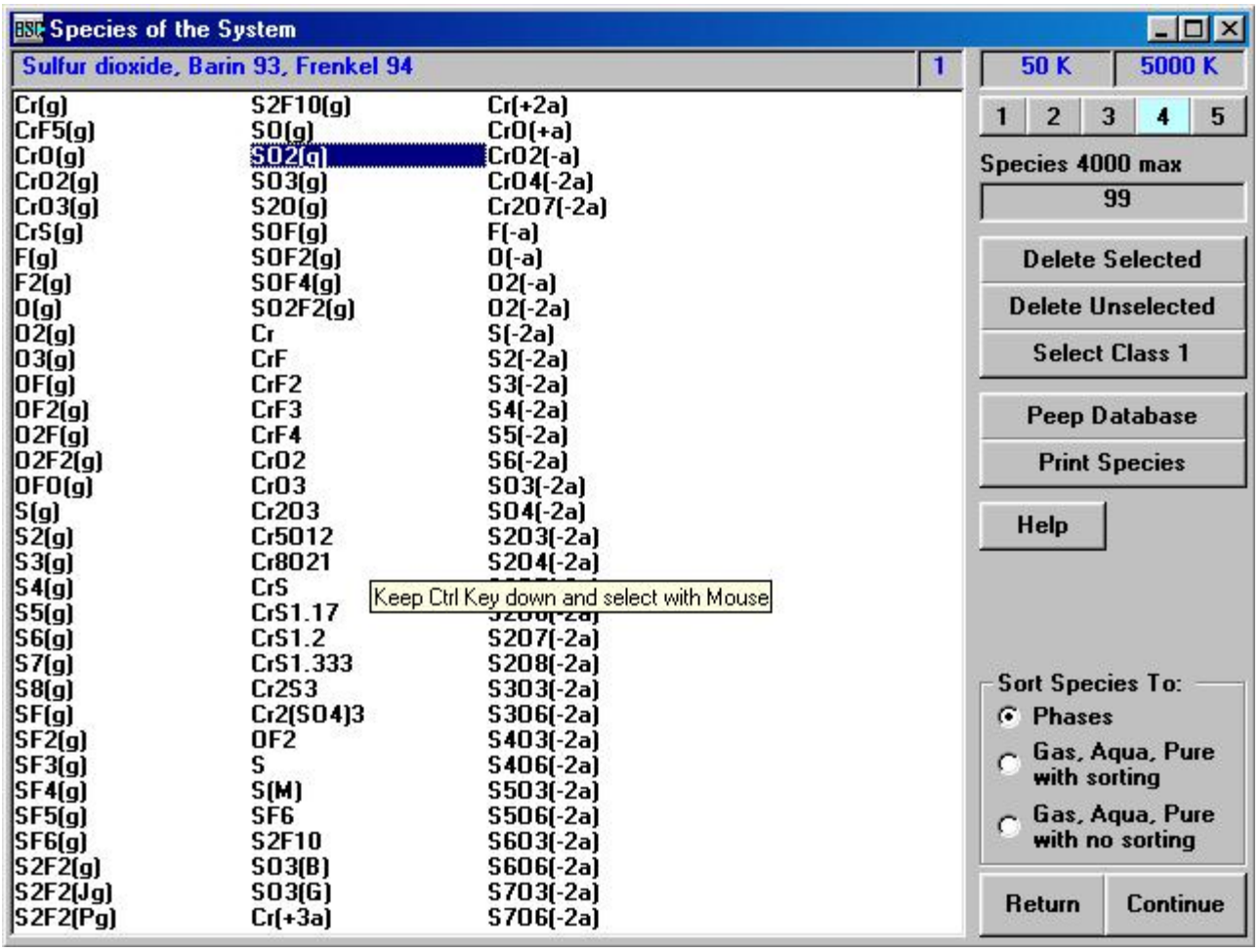
- The number of species in the database has been increased from 15000 to more than 17000. The quality of the database has been improved and the temperature ranges of the available data have also been expanded more than 5000 changes have been made.
- New water data at pressures from 0.01 - 1000 bar are now available.
- Limitation of 2000 species has been removed from the Search routine.
- New Search mode has been added (All elements must exist).
- New fast Table and Diagram routines have been added to Database Editor.
- Several other small improvements have also been made.

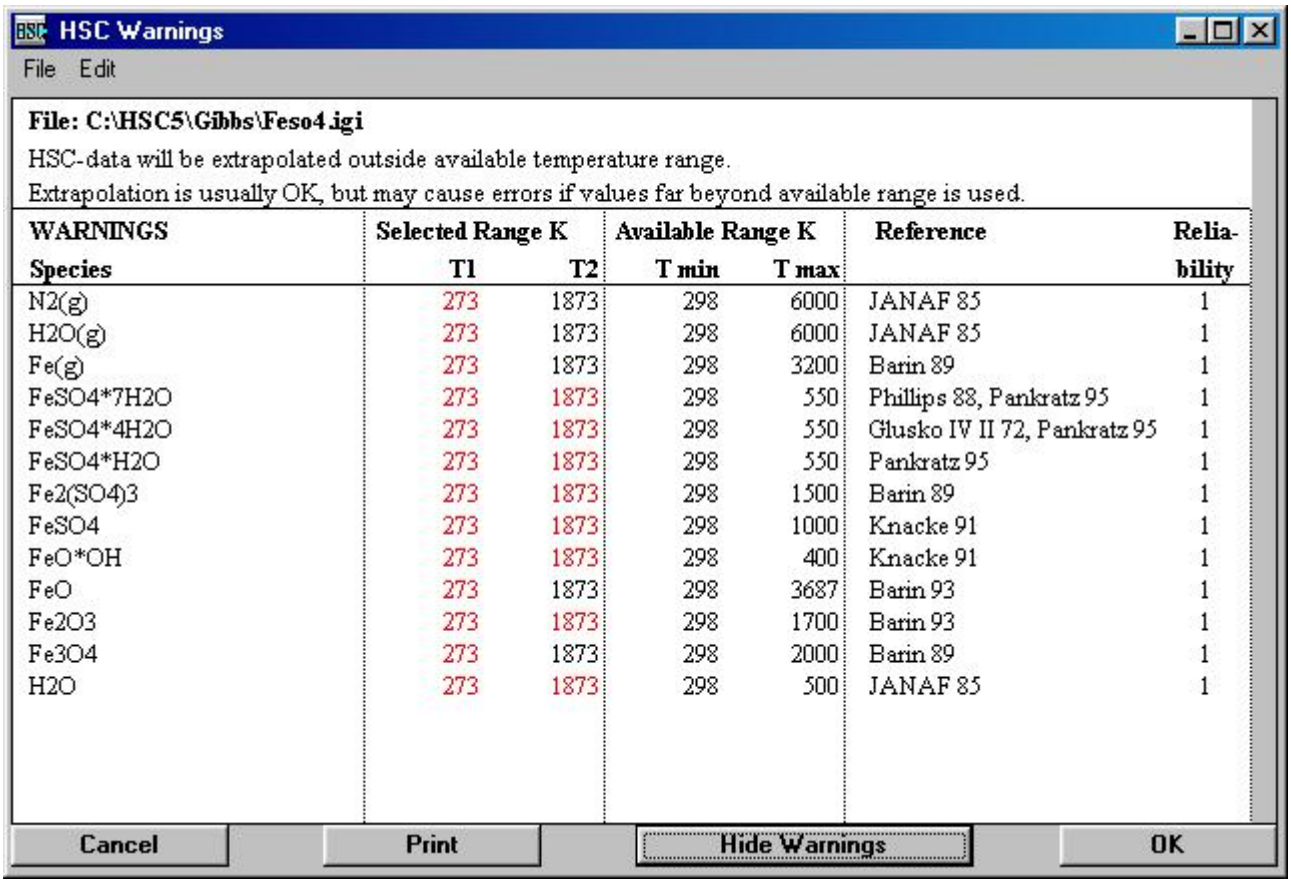




6.6 Improved Equilibrium Module

- Calculation reliability has been improved in many of the test cases.
- New database search options without the limit of 2000 species.
- New Species Name display added to the database search routine.
- New Warnings routine for temperature range extrapolation.
- Small fixes e.g. species name length increased from 20 to 24 characters.





HSC Warnings

File Edit

File: C:\HSC5\Gibbs\Feso4.igi

HSC-data will be extrapolated outside available temperature range.

Extrapolation is usually OK, but may cause errors if values far beyond available range is used.

WARNINGS	Selected Range K		Available Range K		Reference	Relia-
Species	T1	T2	T min	T max		bility
N2(g)	273	1873	298	6000	JANAF 85	1
H2O(g)	273	1873	298	6000	JANAF 85	1
Fe(g)	273	1873	298	3200	Barin 89	1
FeSO4*7H2O	273	1873	298	550	Phillips 88, Pankratz 95	1
FeSO4*4H2O	273	1873	298	550	Glusko IV II 72, Pankratz 95	1
FeSO4*H2O	273	1873	298	550	Pankratz 95	1
Fe2(SO4)3	273	1873	298	1500	Barin 89	1
FeSO4	273	1873	298	1000	Knacke 91	1
FeO*OH	273	1873	298	400	Knacke 91	1
FeO	273	1873	298	3687	Barin 93	1
Fe2O3	273	1873	298	1700	Barin 93	1
Fe3O4	273	1873	298	2000	Barin 89	1
H2O	273	1873	298	500	JANAF 85	1

Cancel Print Hide Warnings OK

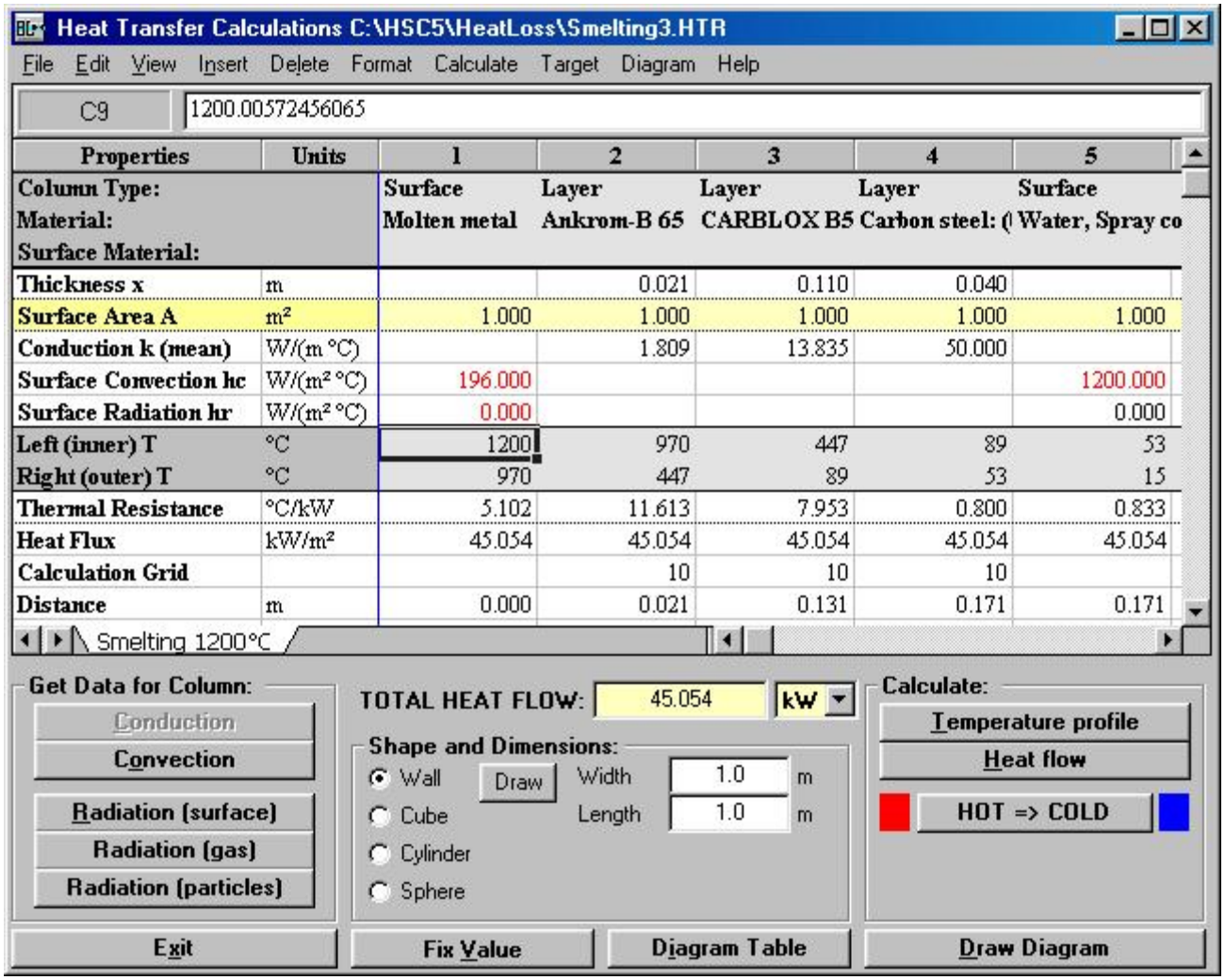
6.7 New Heat Loss Module

The new Heat Loss module may be used, for example, to estimate heat loss values needed in the Balance module. The user must first specify the wall layers, layer materials and thickness of these layers. Two basic types of calculations may be carried out:

1 **Temperature profile** with fixed heat loss and one temperature point.
2 **Heat Loss** with two fixed temperature points will return the heat loss but also the temperature profile.

The calculation routine handles conduction, convection and radiation properties as functions of temperature, but fixed values may also be used by selecting the value and pressing the Fix Value button. These fixed values are shown in red on the calculation sheet.

Temperature profile as well as some other user specified values may also be presented in graphical form. The Target Dialog may be used to find, for example, minimum layer thickness. The calculation specifications may be saved to files for later use.

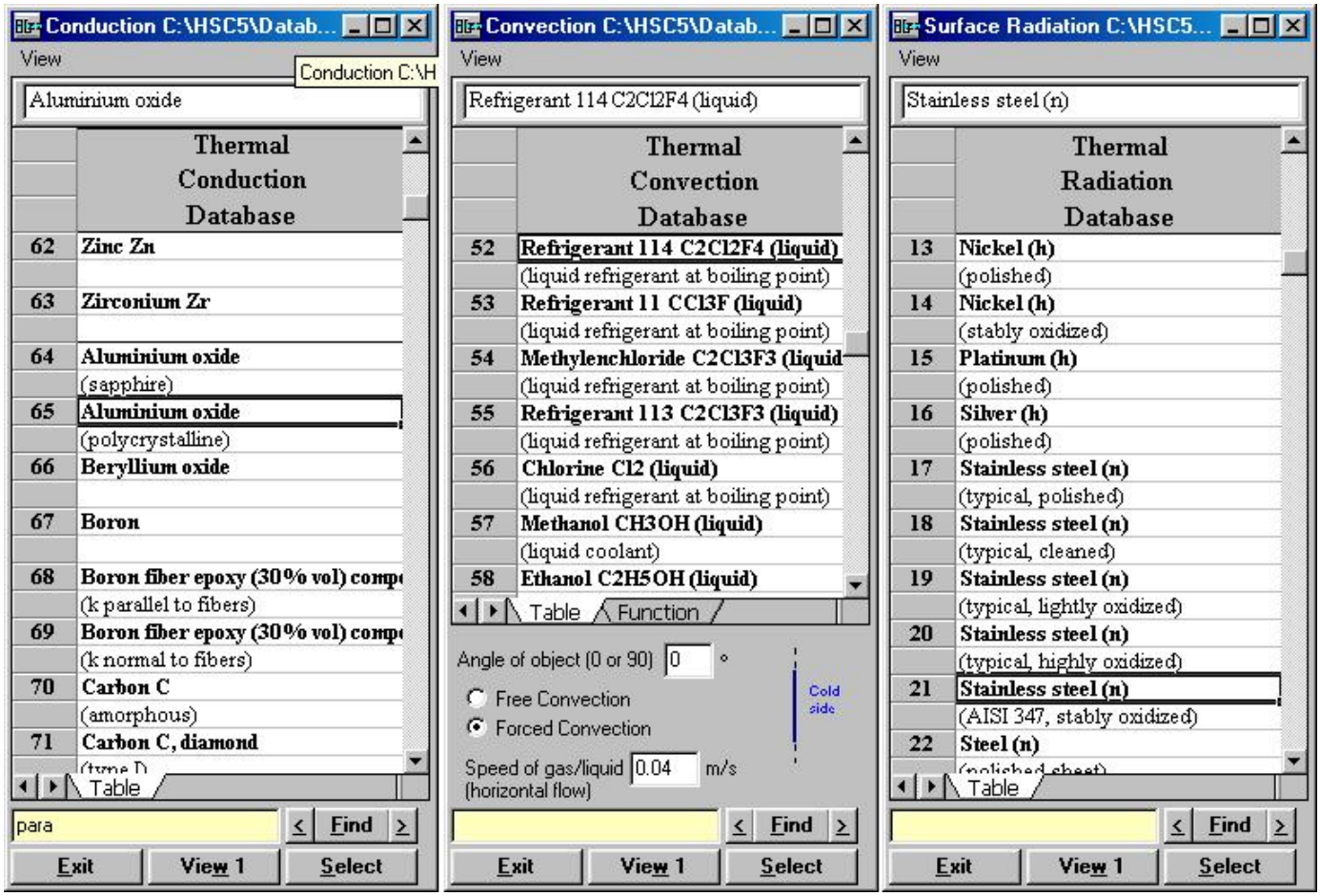


Properties	Units	1	2	3	4	5
Column Type:		Surface	Layer	Layer	Layer	Surface
Material:		Molten metal	Ankrom-B 65	CARBLOX B5	Carbon steel: (	Water, Spray co
Surface Material:						
Thickness x	m		0.021	0.110	0.040	
Surface Area A	m²	1.000	1.000	1.000	1.000	1.000
Conduction k (mean)	W/(m °C)		1.809	13.835	50.000	
Surface Convection hc	W/(m² °C)	196.000				1200.000
Surface Radiation hr	W/(m² °C)	0.000				0.000
Left (inner) T	°C	1200	970	447	89	53
Right (outer) T	°C	970	447	89	53	15
Thermal Resistance	°C/kW	5.102	11.613	7.953	0.800	0.833
Heat Flux	kW/m²	45.054	45.054	45.054	45.054	45.054
Calculation Grid			10	10	10	
Distance	m	0.000	0.021	0.131	0.171	0.171

The Heat Loss module is integrated with three databases and two calculators:

- Conduction database with 718 substances
- Convection database with 111 substances and 4 functions
- Radiation database with 61 surface materials
- Gas Radiation Calculator with H2O, CO2, CO, NO, SO2 and CH4 data
- Particle Radiation Calculator.

The user may edit or add new data to these databases.



Gas Mixture Radiation Calculator - Tapio Ahokainen

User Input

Species	vol-%
H2O(g)	5.00
CO2(g)	23.00
CO(g)	3.20
NO(g)	0.10
SO2(g)	12.00
CH4(g)	0.01

Results

Nyy-Low	Nyy-Upp	F-Low	F-Upp	DF	SumDF
1	417	1.0000	0.9970	0.0030	0.0030
459	757	0.9961	0.9844	0.0117	0.0146
957	963	0.9710	0.9705	0.0005	0.0151
1057	1063	0.9624	0.9619	0.0006	0.0157
1099	1203	0.9585	0.9478	0.0107	0.0264
1290	1432	0.9378	0.9198	0.0180	0.0444

Gas / Wall

Gas Properties

Temperature [°C]: 1200

Pressure [bar]: 1

Optical Depth [m]: 0.45

Surface Properties

Temperature [°C]: 970

Emissivity 0.85

Gas Emissivity at Gas Temperature 0.1655

Gas Absorptivity at Surface Temperature 0.2044

Heat Flux [kW/m²] 15.27

Calculate

Exit | Select at fixed T | Select iterative

Particle Suspension Radiation Calculator

User Input:

Property	Unit	Value
Gas Amount	Nm³/h	24100
Particle Amount	t/h	69
Particle Density	g/ml	4.3
Particle Diameter	mm	0.050
Particle Emissivity		1.000
Cube Width & Height	m	0.002
Cube Thickness	m	0.100
Tube diameter	m	4.200

Results:

Property	Unit	Value
Gas	m³/h	129976
Particles	m³/h	16.0
Gas + Particles	m³/h	129992
Particles	g/m³	531
Particles	ml/m³	123.4
Particles	vol-%	0.0123
Particle Radius	mm	0.02500
P. Cross-sectional Area	mm²	0.00196
Particle Volume	mm³	0.00007
Particle Weight	g	2.81E-07
Particles/m³		1.89E+09
Cube Volume	m³	4E-007
Particles in Cube		754
Particle Distances	mm	0.81
Gas Speed	m³/sec	36.11
Gas Speed in Tube	m/sec	2.61

Gas Properties

Temperature [°C]: 1200

Gas emissivity at gas temp: 0.1655

Gas absorptivity at surface temp: 0.2044

Surface Properties

Temperature [°C]: 970

Emissivity 0.85

Particle cloud Emissivity 0.3095

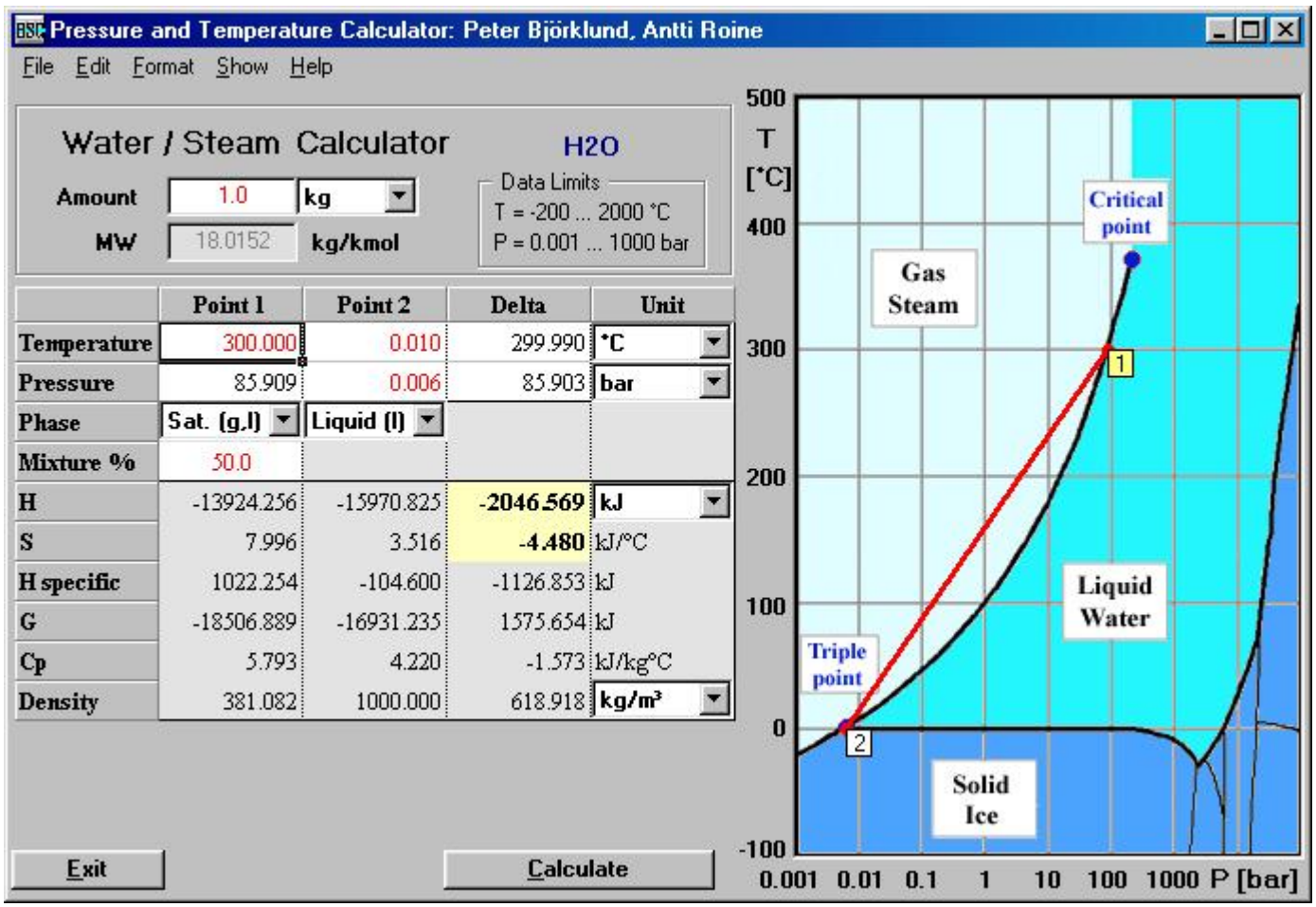
Heat Flux [kW/m²] 48.29

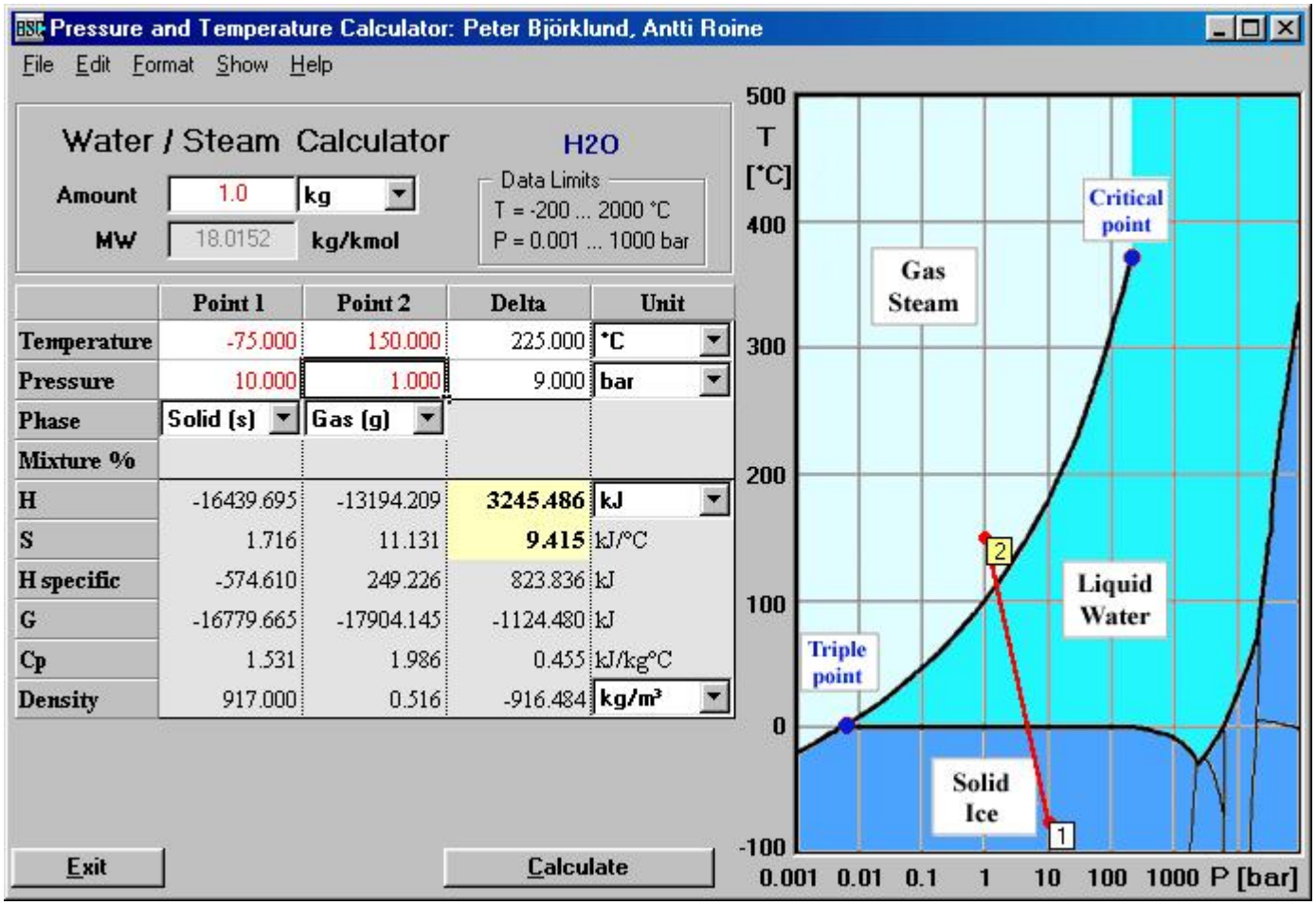
Calculate

Exit | Diagram | Select at fixed T | Select iterative

6.8 New Steam Calculator Module

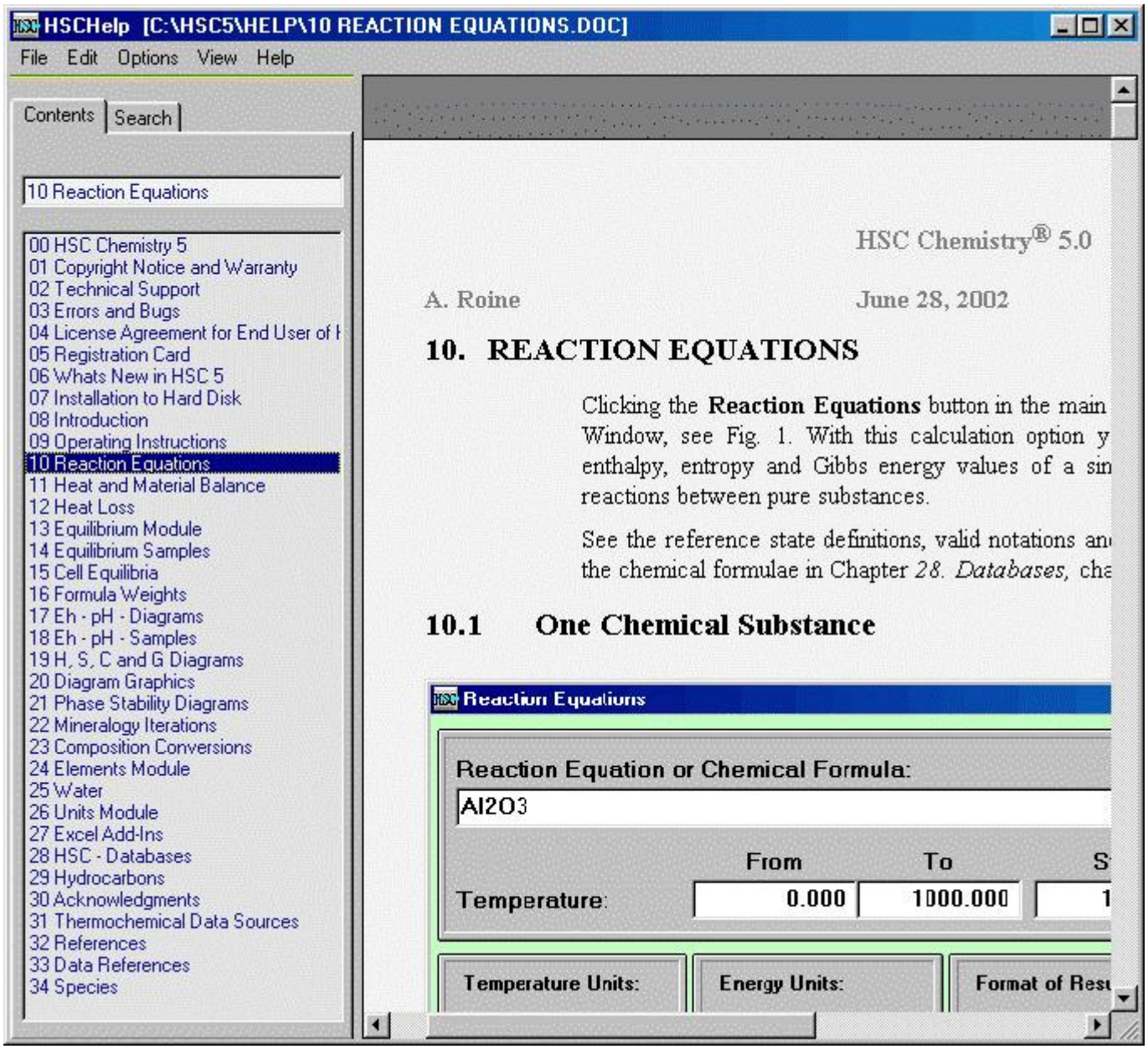
The new Steam Calculator module offers a much more convenient way to estimate enthalpies, entropies and densities of steam, water and ice than the traditional Steam Tables and Mollier Diagrams within 4 - 2273 K and 0.01 - 1000 bar. Steam enthalpies may be needed, for example, when calculating the heat and material balances of boilers or turbines.




Pressure and Temperature Calculator: Peter Björklund, Antti Roine
File Edit Format Show Help
Water / Steam Calculator
H2O
Amount 1.0 kg
MW 18.0152 kg/kmol
Data Limits
T = -200 ... 2000 °C
P = 0.001 ... 1000 bar
Point 1 Point 2 Delta Unit
Temperature -75.000 150.000 225.000 °C
Pressure 10.000 1.000 9.000 bar
Phase Solid (s) Gas (g)
Mixture %
H -16439.695 -13194.209 3245.486 kJ
S 1.716 11.131 9.415 kJ/°C
H specific -574.610 249.226 823.836 kJ
G -16779.665 -17904.145 -1124.480 kJ
Cp 1.531 1.986 0.455 kJ/kg°C
Density 917.000 0.516 -916.484 kg/m³
Exit
Calculate
500
T
[°C]
400
300
200
100
0
-100
0.001 0.01 0.1 1 10 100 1000 P [bar]
Critical point
Gas Steam
Liquid Water
Triple point
Solid Ice
1
2

6.9 New Help Routine

The new Help routine contains all the information, graphics and formulae of the HSC printed manual with convenient search, print, edit and save options.



6.10 Other Improvements

- The new folder structure divides HSC files into logical groups.
- HSC tables now also have Excel 97 and 2000 file support.
- The length of formulas has been increased from 20 to 24 characters in the EpH module.
- Form resize properties have been improved.
- Many small bug fixes and cosmetic adjustments etc.

6.11 New Windows Me, 2000 and XP Compatibility

- New installation routine.
- New compiler and programming tool versions used.

- HSC 5.0 is compatible with Windows 95, 98, NT, Me, 2000 and XP.

6.12 What's New in HSC 5.1 vs. 5.0

1. Database fixes:
- HSC now finds all the F- and r- containing species.
- Database Editor bug which sometimes created empty records to Own Database has been fixed.
- Al(NO3)3(a) - Al(NO3)3(ia)
- AlF(2a), AlF2(a), AlF3(a) added
- AmSO4(-a) - Am(SO4)2(-a) (Typo in HSC database)
- BF4Na S -34.728 replaced with NaBF4 S 34.728 cal mol K
- (Co(NH3)5H2O)Cl3 - Co(NH3)5 H2O Cl3 (Duplicate)
- CrS1.333 H 37.3 - -37.3 kcal mol (Typo in HSC database, Mills 74)
- Cr2NiO4 replaced with NiO Cr2O3 (duplicate)
- FeCr2O4 replaced with Cr2FeO4 (duplicate)
- HFe2O(-a) removed (Typo in Slop 98: HFe2O(-a) - HFeO2(-a)
- H2O Cp constant when T 600 K
- HO(g): typo in H and S values fixed
- HOI(g) - HIO: Reliability Class 1 - 5 (Gas in Pankratz 95). Compare to HIO(g)(Cor 90, Landolt 01)
- I(-3a) - I3(-a) (Typo in HSC database, Fabricius 94)
- K3AlCl9 - K3Al2Cl9 (Typo in Karapet 70)
- K3Al2F6 - K3AlF6 (Typo in Karapet 70)
- MoF2 too stable: Reliability Class 2 - 5 (Ruzinov 75)
- MoO2(2a), CH3COO(-a), CH3COOH added
- Na2O melting point -1405K - 1405 K
- NaAlO2 replaced with Na2O Al2O3 (duplicate)
- Np(4a) data NAGRA 91 - Phillips 88
- Np(OH)3(a) H 313.983 - -313.983 kcal mol (Typo in HSC database)
- Np(H2PO4)(a) - Np(H2PO4)2(a) (Typo in HSC database)
- PbSO4 PbO was removed (Enthalpy value typo in Bard 85)
- (Pt(NH3)4)Cl2 - Pt(NH3)4Cl2
- (Pt(NH3)4)I2 - Pt(NH3)4I2
- Pu(4a) data NAGRA 91 - Phillips 88
- PuO2(SO4)(-2a) - PuO2(SO4)2(-2a) (Typo in HSC database)
- SCN(-a) replaced with CNS(-a) (duplicate)
- Sr r(Si2O7) was renamed Sr rSi2O7 (Huntelaar 95)
- UO2(G) - UO3(G): (Typo in HSC database, Phillips 88)
- UO2.25 replaced with U4O9 (duplicate)
- U3O5 deleted: (Typo in Samsonov 78, data seems to be for U3O8)
- rF2 too stable: Reliability Class 1 - 3 (Barin 77, Glushko 94, Landolt 00)
- Some aqueous (a) species was changed to (ia).
- Some new species
- Small fix in All must exist option in Find Elements dialog.

2. Tpp- Module fixes:
- Scale and Print Dialog bug fixed.
- Diagram Area Color Dialog bug fixed.
- Print and Label dialogs with H, S and Cp diagrams.

3. Water-module:
- Fixed: Small changes in Point 1 did not always effect the Phase option.
- More density values at higher pressures and temperatures.

4. Equilibrium Module:
- Species selection dialog: Sort mode bug fixed.
- Automatic addition of N2(g).
- Warning of SGM limitations.
- Gibbs-routine fix: Diagram button may be pressed before the calculations are ready without crashing application.
- Pic-routine improvement: Enter -key moves forvard after X- and Y-axis species selection.
- Gibbs- and SGM-routines: Problem with phase transition data below 298.15 K fixed.

5. New Key Word Find Option in Database Menu finds, for example, all the species which contain the Key Word benzene .

6. Key Word Find may also be used from Database Peep routine.

7. Clearer option captions in Database Menu

8. More warning dialogs.
- Peep Database dialog: Warning of high number of print pages
- Element Find Dialog: More Tool Tip Text
- Lpp module: Improved Triple Point Outside Range warning.

9. Several small fixes in Help- and Manual- files.

10. Maximum number of records in HSC databases was increased from 32767 to 2147483647 records.

11. HSC DLL Tools opens native HSC functions and database for use in Visual Basic applications and other programming environments.

12. WNDTLS32.DLL could not be found error message bug in HSC Help routine was fixed.

13. Heat and Material Balance Module:
- Stream temperature link refresh bug was fixed.
- Calculate Recalc option clears also columns 0 - S.
- Arrow Graphical Object added.
- New Ideal Gas Density option.

14. Some other small fixes. For example, HSC main menu flicker n some computers was fixed.

Many thanks for the feedback reports to all active HSC users.

6.13 What s New in HSC Chemistry 4.0

The new HSC version 4.0 contains several **new calculation modules**, **new properties** and a **larger database** with a lot of updated data. The familiar HSC style user interface has been maintained in order to minimize the training requirements of current HSC users. The new features can be summarized as follows:

1. The number of substances in the database has been increased from 11000 to more than 15000. A lot of old data has also been updated and extended.
2. Improved graphics, printing and format properties in all modules.
3. Target calculations in the Heat Balance module for automatic iterations.
4. Improved calculation reliability and speed in the Equilibrium module.
5. Eh-pH-diagrams with concentration and temperature lines.
6. A new Tpp-module for stability diagrams with partial pressure and temperature axes.
7. A new Diagram module for H-, S-, Cp-, G-, DH-, DG- T graphics.
8. A new Mineralogy module for fast conversion between mineralogical and elemental compositions.
9. A new Element module with basic data of elements and graphics.
10. A new Units module with a useful units conversion calculator.
11. A lot of small fixes and tuning of properties based on user feedback.
12. New 32-bit HSC version for Windows 95, 98 and NT.

The following sections will give a idea of these new features in more detail.

Installation

The HSC 4.0 installation routine has been updated and is now compatible with Windows® 95, 98 and NT. However, system requirements are still quite reasonable.

Heat and Material Balances

Several new features have been added to the Heat and Material Balance module:

1. The new **Target calculation** feature can be used to iterate sequential variable values in order to reach certain target values. For example, the user can set the zero heat balance as a target and find out the feed amount which satisfies the given target condition.
2. The **graphics feature** enables the user to draw diagrams of heat balance calculation sheets. The user may easily select one variable and range for the x-axis and several others whose values are drawn on the diagram as a function of x-variable change.
3. The user can easily **import additional MS Excel® sheets** to the module. These sheets can be used to calculate input data for the INPUT-sheet or process results of the OUTPUT-sheet. Files can be saved in Excel format for further treatment of results.
4. Several small improvements and new properties. For example, the user can now resize the forms without step values. The printing capabilities have been improved, for example, the final temperature calculation results can also be printed now.

Equilibrium Calculations

Equilibrium Calculations is one of the most used modules in HSC software, therefore a lot of effort has been spent on improving it. For example:

1. The calculation reliability and speed of Gibbs solver is better than in the previous version.
2. The processing of Excel type activity formulae has been improved.
3. The species table form can easily be resized.
4. The diagrams can be printed in any size. A greater number of lines can be visualized simultaneously by increasing the height of the printed diagram.
5. The enthalpy of the reaction can be drawn on the diagram.
6. The maximum number of pure substances in the diagrams has been increased from 99 to 999.
7. This module now makes input-files for ChemSage 2, 3 and 4 versions.
   (ChemSage is a registered trademark of GTT-Technologies)

Formula Weights

The new feature of the formula weight calculator allows the user to specify the amount of the species in kilograms or moles. This enables the module to calculate the amounts of elements in addition to the compositions and formula weights.

Tpp Phase Stability Diagrams

This new module allows you to draw phase stability diagrams with temperature as the x-axis and a selected partial pressure as the y-axis. Diagrams with partial pressures on both axes can also be drawn. Partial pressures of sulfur, oxygen, sulfur dioxide, carbon monoxide, etc. can be used depending on the selected system.

These diagrams can be used, for example, to estimate what kinds of phases prevail in the roasting furnace in different conditions or to evaluate which condensed substances may become stable when the process gas temperature decreases.

Eh - pH - Diagrams

Eh-pH-diagrams are used to estimate the prevailing species in aqueous solutions as a function of pH and chemical potential. A completely new option has been added to this module. The new features can be summarized in the following list:

1. The new routine can be used to combine several diagrams with different concentrations, temperatures or main elements into a single diagram. The traditional concentration diagrams are widely used, but more special temperature and main element diagrams may also give valuable information.
2. The possibility to change the size of printed diagrams is also very useful when there are several small stability areas in the same diagram.
3. The selection of different electrode potential scales is also a useful new feature, where Hydrogen, Calomel and Ag AgCl-scales can be used.
4. Improved calculation reliability.

5. The calculation system specification can easily be modified with the user s own Gibbs energy data. These modifications can be saved for later use.

H, S, C and G - Diagrams

The new diagram module can be used to draw several different types of thermochemical diagrams. The same new versatile graphics and printing features are included as in the other modules. The main features can be summarized as follows:

1. Eight different diagram types can be drawn as a function of temperature:

- H Enthalpy (total)
- H Enthalpy (latent)
- S Entropy
- Cp Heat Capacity
- G Gibbs Energy
- DH
- DS
- DG (Ellingham diagrams)

2. Several species can be selected to the enthalpy diagrams simultaneously to compare total or latent enthalpies.
3. DG diagrams (Ellingham diagrams), offer a very fast way to compare the relative stabilities of substances. For example, you can find out which oxide or chloride compound is the most stable one. This information is useful when comparing the reduction and oxidation tendencies of different elements.
4. This module can also be used to compare the basic thermochemical data from different sources, in order to see the differences and select the best data for subsequent calculations.

Mineralogy Module

Composition conversions between substance (mineralogy) and elemental analyses are often needed in chemical R D work. The new Mineralogy module easily converts mineralogical compositions into elemental compositions.

The conversion of the elemental composition of a substance into a mineralogical one is a more difficult task, for example, due to small analytical errors. This module offers three tools for converting elemental analyzes into mineralogical ones:

1. The **Solve method**, which uses matrix-algebra to solve the mineralogy. It is useful if the given amounts of elements fit the given substances exactly.
2. The **Automatic iterative method**, which fits the given elements to the given substances by changing the species contents to achieve the given elemental compositions.
3. The **Manual iterative method**, which may be needed especially if the same element exists in several species.

Elements Module

The thermochemical behavior of species is based on the properties of elements. The location of the element in the periodic system tells us a lot about its chemical nature. The new Elements Module offers a fast way to compare the basic properties of elements in tabular and graphical format.

The database contains data on 56 different properties of elements. As in other HSC modules, the user is permitted to modify and add new data to this database according to personal requirements.

Units Module

Traditionally, several types of energy, temperature, mass and volume units have been used in thermochemical calculations. Therefore, some inconvenient conversions are needed to compare the results from different sources. The new Units Conversion module is an easy tool for fast unit conversions in thermochemical as well as other engineering fields. The specifications of this module can be summarized as follows:

1. Some 90 different quantities and 444 units are available. The user can easily add his her own units and coefficients into the conversion calculator database.
2. The Units Module also offers data sheets for chemical constants, particle mesh sizes, air humidity and water pressure tables. The user can modify these tables according to personal requirements.

Database

The thermochemical database is an essential part of HSC Chemistry, because the accuracy of the calculation results of all HSC modules depends on the quality of the basic data in the integrated database. Considerable development work has been carried out, which can be summarized as follows:

1. The number of species in the database has been increased from 11000 to more than 15000. This data is not critically evaluated, but gives fast access to data and references, which can be found from literature.
2. The quality of the database has been improved and the number of unnecessary duplicate species has been decreased.
3. Further supporting data, such as structural formulae, chemical names, common names, CAS numbers, melting points, boiling points, etc. have been added to the database.
4. HSC 4 uses the same database format as HSC 3, therefore, the user s own databases can also be used with the new HSC 4.0.
5. The search procedure for species in Database Editor and Show Database windows has been improved. The species lists now show the location of the closest match if the given formula is not found in the database.
6. A direct link to the graphics module has been added to the Cp data-fitting option. This allows the easy comparison of experimental and fitted data.
7. **Important Note**: The main reason for the small differences with HSC 3 and 4 calculation results is the new data in the HSC 4 database.

General improvements

The graphics, printing and format properties as well as resizing capabilities of the table forms have been improved in most calculation modules. This makes it easier to produce high quality hard copies of the results.

Numerous minor improvements and adjustments have been made which are not always visible. However, they will make the life of the HSC user easier. This work has been based mainly on feedback from HSC users.

8. INTRODUCTION

HSC Chemistry is designed for many different kinds of **chemical reactions and equilibrium calculations.** The current version contains 14 calculation options:

1. Reaction Equations
2. Heat and Material Balances
3. Heat Loss Calculations
4. Equilibrium Compositions
5. Electrochemical Cell Equilibria
6. Formula Weights
7. Phase Stability Diagrams (Tpp- and Lpp-versions)
8. Eh - pH – Diagrams with concentration and temperature variables
9. Enthalpy, entropy, heat capacity, Gibbs-energy and Ellingham diagrams.
10. Mineralogy Iterations
11. Composition conversions
12. Water - Steam Tables and Mollier Diagrams
13. Units Conversions
14. Properties of Elements in tabular and graphical format.

The name of the program is based on the fact that all fourteen calculation options automatically utilize the same extensive **thermochemical database** which contains enthalpy (**H**), entropy (**S**) and heat capacity (**C**p) data for more than 17000 chemical compounds. This database is equivalent to more than seventeen thick data books.

The HSC Chemistry software enables the user to simulate chemical reactions and processes on the thermochemical basis. This method does not take into account all the necessary factors, such as rates of reactions, heat and mass transfer issues, etc. However, in many cases a pure thermochemical approach may easily give useful and versatile information for **developing new chemical processes and improving the old ones**.

Perfect simulation for all processes means that any chemical process can be designed completely in the computer without any experimental work. This goal is, however, far in the future, because there is no complete general theory or basic data available which would successfully combine **thermodynamics**, **non-ideality of solutions** as well as **dynamics** (kinetics) for all processes. Nearly perfect simulation may be achieved for a single individual process step by measuring experimentally all the necessary parameters for solution models, kinetic models, as well as for flow and heat transfer models. However, this needs several months or years work to be able to simulate one single process step. uite often a fast mainframe computer is needed.

With HSC Chemistry it is possible to calculate chemical equilibria between pure substances and the ideal and also, to some extent, non-ideal solutions. For these calculations only enthalpy (H), entropy (S) and heat capacity (Cp) data for all prevailing compounds or pure substances is needed. In many cases these calculation results may simulate the real chemical reactions and processes at sufficient accuracy for the practical applications. Important advantage is also that specification of the chemical system, data retrieval and final calculations may be carried out in normal Intel Pentium personal computers within few minutes.

Of course, experimental work is needed to verify the results, because HSC does not take kinetic phenomena into account. However, HSC helps to avoid expensive trial-and-error chemistry, because it quickly and easily gives some kind of clue as to the effects of process parameters on the reaction products and process conditions. Usually, thermochemical calculations at least show what is physically possible and what is impossible, which is highly valuable information when making plans for experimental investigations.

In the thermodynamic equilibrium the rates of reactions and reverse reactions may both be interpreted to have the same rate, ie. this state is only one special case of kinetic phenomena. Of course, some programs are available which also take some kinetic aspects into account. However, these are not general like thermodynamic equilibrium codes are, ie. they are usually valid only for certain geometries and environments.

A number of solution models are available in literature to describe the non-ideality of mixture phases. The practical problem is quite often a lack of valid data for solution parameters. Although solution models have not been installed in the HSC Chemistry, the non-ideality of solutions can be taken into account in the equilibrium calculations to a certain extent by including constant activity coefficients or simple activity coefficient formulae in the Gibbs equilibrium solver.

8.1 Invitation to new Authors

If you have a thermochemical computer program or basic thermodynamic data which may be of more general interest, please send it to the author:

Antti Roine
Outokumpu Research Oy
P.O. Box 60
FIN-28101 PORI, FINLAND
Fax: 358 - 2 - 626 - 5310

We may also add your code to future versions of HSC Chemistry. Connection to the HSC-database and fitting the code and user interface to HSC format can be carried out in Outokumpu Research. Integration is easiest if the original code is written in Visual Basic, uickBASIC or BASIC.

The new thermodynamic data which is saved in OwnDB5.HSC database can easily be transferred to MainDB5.HSC at Outokumpu Research.

8.2 Physical Background of H, S, C and G

Thermochemical calculations are based on enthalpy **H**, entropy **S**, heat capacity **Cp** or Gibbs energy **G** values for chemical species. They can all be mathematically derived from experimental observations. The following presentation gives a brief and simplified but illustrative idea of the thermochemical quantities and methods.

Enthalpy H: Absolute values of enthalpy H of substances cannot be measured, but enthalpy differences between two temperatures can be determined with a calorimeter. Heat capacity Cp at constant pressure (specific heat) can be calculated from this data using Eq. (1).

$$\mathbf{Cp \quad (dH \quad dT)_{P,n}} \qquad \mathbf{1}$$

Equation (1) allows the calculation of enthalpy as

$$\mathbf{H(T) \quad H_f(298.15) \quad \int_{298.15}^{T} Cp \; dT \quad \Sigma H_{tr}} \qquad \mathbf{2}$$

where $H_f(298.15)$ is the enthalpy of formation at 298.15 K and H_{tr} is the enthalpy of transformation of the substance. Calorimetric measurements at different temperatures yield the enthalpy curve of zinc shown in Fig. 2.

The enthalpy scale in Eq. 2 is fixed by defining **H 0 for the elements in their most stable state at 25 C and 1 bar,** mainly because this is convenient for calculations at elevated temperatures. This is called the reference state. (Another fix point could have been H = 0 at 0 K, because the thermal motion of atoms and electrons stops completely at this temperature.)

The ability of a chemical substance to absorb or emit heat depends on the temperature, and therefore the curve in Fig. 2 is not linear. In addition, at phase transformation temperatures the curve is discontinuous, because heat is needed for the phase transformations (ie. for crystal structure changes, as well as for melting and boiling).

The **enthalpy of compounds** also contains their enthalpy of formation DH_f from elements. This is usually measured calorimetrically by letting pure constituent elements react and form the compound at 298.15 K and 1 bar. The enthalpy of the compound is therefore calculated by adding the enthalpy of formation to the experimental enthalpy difference H(T)-H(298), see the solid line in Fig. 3.

The enthalpy values of gaseous zinc can be extrapolated to lower temperatures as shown in Fig. 2 by the dotted line. The reference state for zinc at 25 C and 1 bar is hexagonal crystal. The enthalpy of gaseous zinc is 130.415 k mol larger compared to solid pure zinc at 298.15 K. This amount of heat is needed to evaporate one mole of zinc at 25 C and 1 bar, and is called the enthalpy of formation of zinc gas from solid zinc.

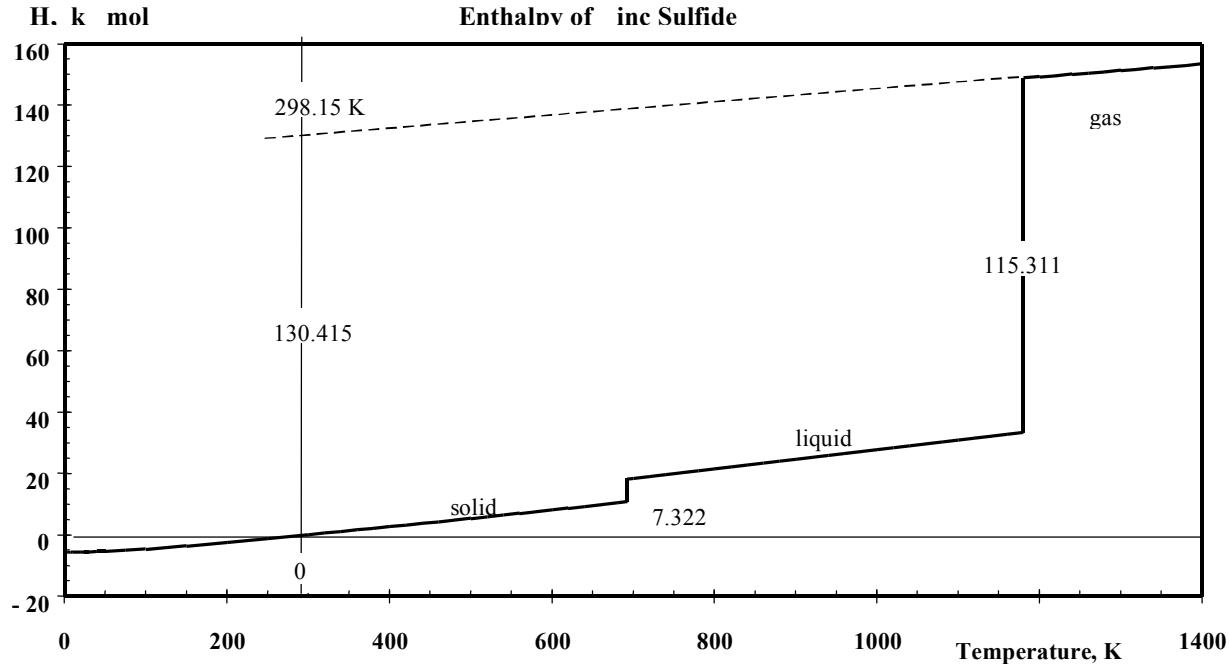


Fig. 2. Enthalpy of pure zinc from 0 K to 1400 K with reference to solid, hexagonal n at 298.15 K.

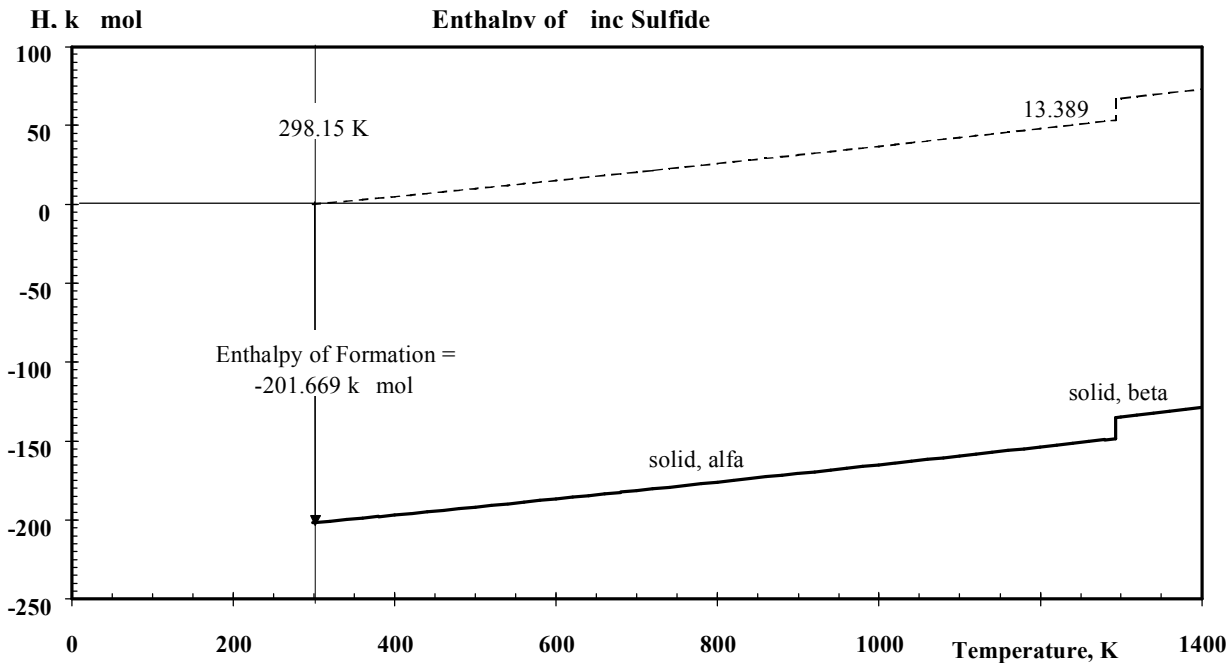


Fig. 3. Enthalpy of zinc sulfide (——). Enthalpy difference H(T)-H(298) (-----) and enthalpy of formation have been measured by calorimeter. Note crystal structure transformation at 1293 K.

Entropy S: Absolute entropy values can be calculated from the experimental heat capacity values using Equation (3) and numerical integration.

$$S \quad S(298.15) \quad \int_{298.15}^{T} (Cp \quad T)\, dT \quad \Sigma H_{tr} \quad T_{tr} \qquad 3$$

where S(298.15) is the standard entropy of the substance which can be calculated by integrating Cp T function from 0 to 298.15 Kelvins, T is temperature and H_{tr} is enthalpy of phase transformation at a temperature T_{tr}, see Fig. 4.

Entropies of crystalline substances approach zero at 0 K. This fundamental experimental observation is compatible with the third law of thermodynamics. If entropy is understood as a measure of disorder, the disorder reaches its minimum at absolute zero and in perfect crystal structures.

Heat Capacity Cp: The absolute heat capacity of substances at constant pressure can be calculated as a first derivative of the enthalpy curve in Fig. 2, using Equation (1). The heat capacity curve is discontinuous at phase transformation temperatures, see Fig. 5. The heat capacity values of crystalline substances in equilibrium approaches zero value at 0 K.

The temperature dependence of heat capacity at elevated temperatures cannot be predicted theoretically by thermodynamics. A fully mathematical correlation is therefore adopted for fitting experimental heat capacities. The Kelley equation is used throughout this program in the following form:

$$Cp \quad A \quad B \cdot 10^{-3} \cdot T \quad C \cdot 10^{5} \cdot T^{-2} \quad D \cdot 10^{-6} \cdot T^{2} \qquad 4$$

where A, B, C and D are coefficients estimated from experimental data.

Gibbs Energy G: The mutual stability of substances (elements, compounds, ions, etc.) cannot be compared using enthalpy, entropy or heat capacity functions solely. It must be done using the Gibbs energy defined by Equation (5). The Gibbs energy of pure zinc has been calculated using this equation and data in Figs. 2 and 4. The results can be seen in Fig. 6.

$$G = H - T \cdot S \qquad 5$$

Experimental Methods: Many experimental and theoretical methods are available for evaluating the basic thermochemical enthalpy, entropy and heat capacity data than it is practical to describe in this context. Usually a critical analysis of the values is based on a thorough simultaneous cross-correlation of thermochemical data from different sources, measurement methods (calorimetric, spectroscopic, electromotive force, solubility, etc.) and theoretical calculations. More information of the assessment methods can be found, for example, in the references mentioned in Chapters 32 and 33.

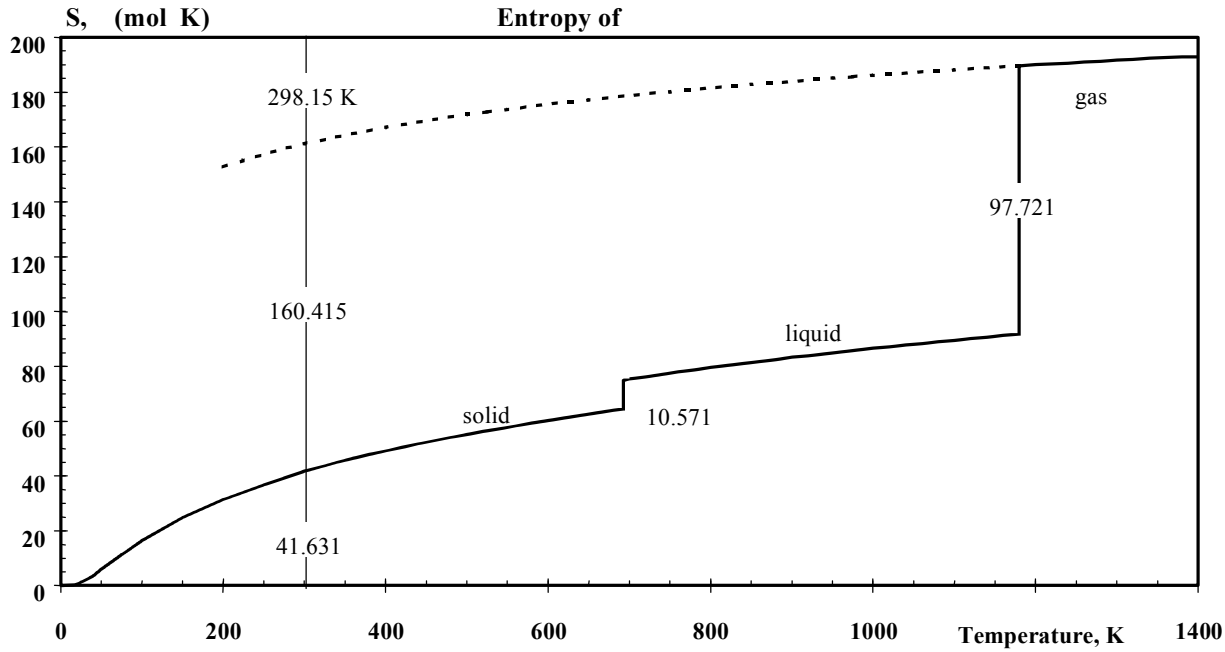


Fig. 4. Entropy of zinc calculated from the experimental heat capacity, by Eq. (3).

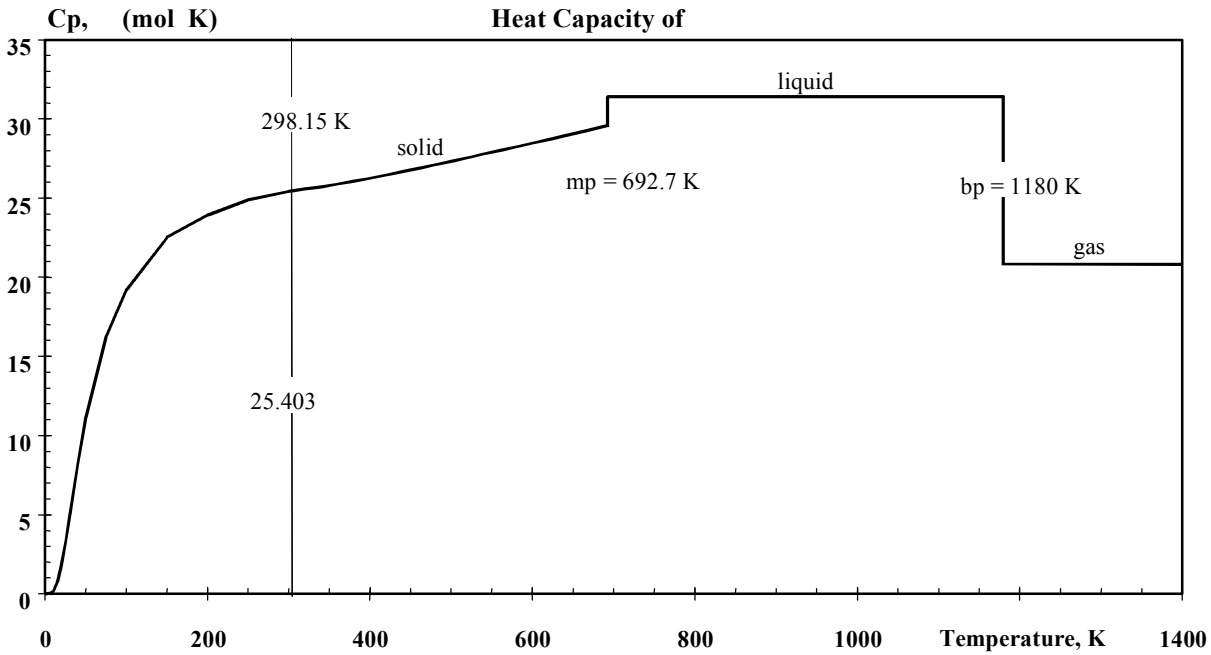


Fig. 5. Heat capacity of zinc from 0 K to 1400 K calculated from calorimetric data, by Eq. (1).

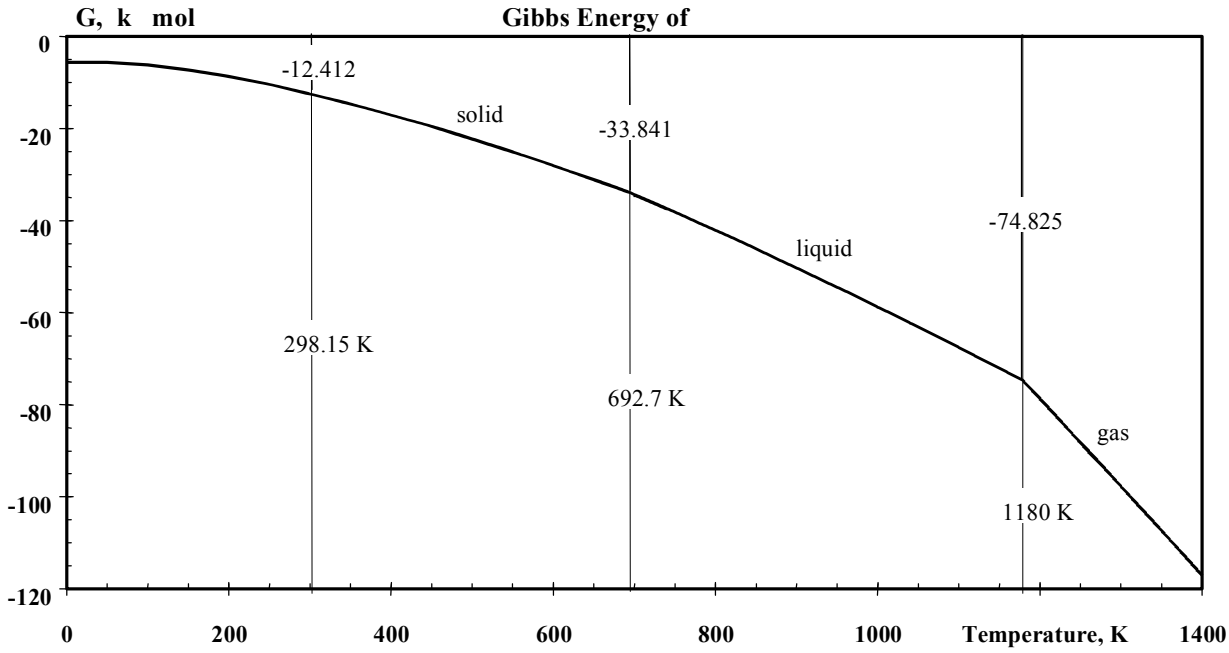


Fig. 6. Gibbs energy of zinc at 0 - 1400 K calculated from the enthalpy and entropy values using Equation (5).

Data Format in the HSC Databases: Traditionally, experimental heat capacity values - see Fig. 5 - have been fitted using the empirical Equation (4). The coefficients A, B, C and D provided in HSC are valid in limited temperature ranges only. Usually the temperature ranges are the same as the stability ranges of solid, liquid and gaseous states of the substances.

The heat capacity coefficients can be saved in the HSC database as data sets for each temperature range, together with the enthalpy and entropy values for formation and transformations. The first data set contains the enthalpy of the formation H_f(298.15), standard entropy S and the coefficients A, B, C and D for the most stable form of the substance at room temperature. The second set contains the enthalpy and entropy of transformation as well as the coefficients for the second temperature range, etc. For further details, see Chapter 28.11.

Table 1 shows the thermochemical data of zinc as printed from the HSC main database. The same enthalpy values can be found in Fig. 2, as well as the entropy values in Fig. 4. The coefficients A, B, C and D have been derived from the experimental heat capacity values, Fig. 5, using curve fitting and Equation (4), see Chapter 28.12.

Note that the data for gaseous substances as n(g) has been saved separately. Such a selection allows, for example, equilibrium calculations with the gaseous substances also below their boiling points.

Species	State	Enthalpy H k mol	Entropy S (mol K)	Heat Capacity Cp A (mol K)	B	C	D	Temperature Range T1 K	T2 K
n	s	0.000	41.631	20.736	12.510	0.833	0.000	298.150	692.655
n	l	7.322	10.571	31.380	0.000	0.000	0.000	692.655	1180.000
n(g)	g	130.415	160.984	20.786	0.000	0.000	0.000	298.150	2000.000

Table 1. Thermochemical data of zinc as printed from the HSC database.

All thermochemical data required in HSC and its modules, including heat capacity, enthalpy, entropy and Gibbs energy of the substances, can be calculated from the basic data in its databases using Equations (1)-(11). HSC Chemistry utilizes the equations automatically whenever needed.

Chemical Reactions: The thermodynamic enthalpy, entropy and Gibbs energy functions for a chemical reaction are calculated as the difference between the products and reactants, using Equations (6) - (9). The commonly needed equilibrium constant K can be calculated using Equation (11). The physical meaning of these functions and values will be described in more detail in Chapters 10.1 - 10.4.

Chemical reaction $aA \quad bB \quad ... \quad cC \quad dD \quad ...$ **6**

Enthalpy of reaction $\Delta H_r \; \Sigma \nu_i H_i(\text{Products}) - \Sigma \nu_i H_i(\text{Reactants})$ **7**

$(c\ H_C \quad d\ H_D \quad ...) - (a\ H_A \quad b\ H_B \quad ...)$

Entropy of reaction $\Delta S_r \; \Sigma \nu_i S_i(\text{Products}) - \Sigma \nu_i S_i(\text{Reactants})$ **8**

$(c\ S_C \quad d\ S_D \quad ...) - (a\ S_A \quad b\ S_B \quad ...)$

Gibbs energy of reaction $\Delta G_r \; S n_i G_i(\text{Products}) - \Sigma \nu_i G_i(\text{Reactants})$ **9**

$(c\ G_C \quad d\ G_D \quad ...) - (a\ G_A \quad b\ G_B \quad ...)$

Equilibrium constant $$K \quad \frac{C^c \quad D^d \quad ...}{A^a \quad B^b \quad ...}$$ **10**

$$\ln K = \Delta G_r \quad (-RT)$$ **11**

where the following abbreviations have been used:

A = activity or partial pressure of species A, B, C, etc.
a = stoichiometric coefficient of species A in reaction
ν = stoichiometric coefficient of a species in reaction (a, b, c, ...)
R = gas constant = 1.987 cal (Kmol) = 8.314 (Kmol)
T = Temperature in K

10. REACTION EQUATIONS

Clicking the **Reaction Equations** button in the main menu shows the Reaction Equations Window, see Fig. 1. With this calculation option you can calculate the heat capacity, enthalpy, entropy and Gibbs energy values of a single species as well as of specified reactions between pure substances.

See the reference state definitions, valid notations and abbreviations for the description of the chemical formulae in Chapter *28. Databases,* chapter 2.

10.1 One Chemical Substance

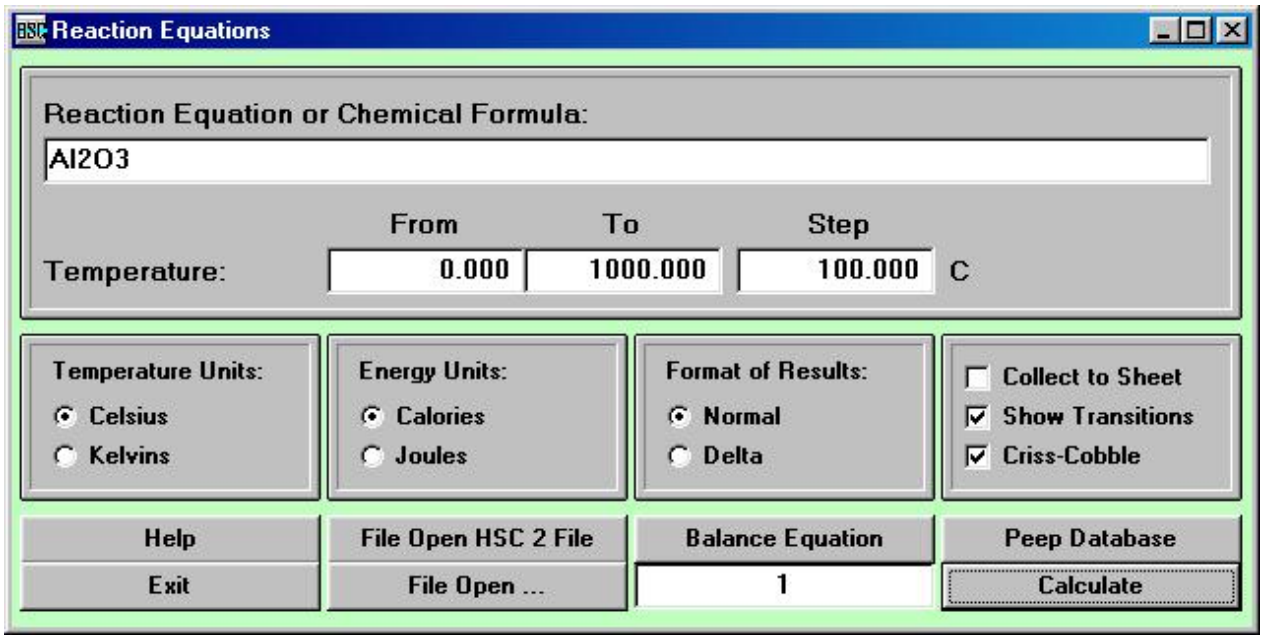


Fig. 1. Reaction Equations Window of HSC Chemistry.

Results

File Edit Format Help

	T	Cp	H	S	G	Reference
1	Al2O3		Aluminum oxide			
2	T	Cp	H	S	G	Reference
3	C	cal/(mol*K)	kcal/mol	cal/(mol*K)	kcal/mol	
4	0.000	17.248	-400.947	10.614	-403.846	Barin 77, JANAF 98
5	100.000	21.600	-398.993	16.671	-405.214	Barin 77, JANAF 98
6	200.000	24.797	-396.665	22.185	-407.162	Barin 77, JANAF 98
7	300.000	26.970	-394.068	27.157	-409.633	Barin 77, JANAF 98
8	400.000	28.161	-391.303	31.601	-412.576	Barin 77, JANAF 98
9	500.000	28.386	-388.468	35.527	-415.936	Barin 77, JANAF 98
10	600.000	29.168	-385.590	39.027	-419.666	Barin 77
11	700.000	29.709	-382.646	42.219	-423.731	Barin 77
12	800.000	30.166	-379.651	45.148	-428.101	Barin 77
13	900.000	30.564	-376.614	47.853	-432.753	Barin 77
14	1000.000	30.916	-373.540	50.368	-437.666	Barin 77
15						
16	Formula	FM	Conc.	Amount	Amount	Volume
17		g/mol	wt-%	mol	g	l or ml
18	A12O3	101.961	100.000	1.000	101.961	25.715 ml
19		g/mol	wt-%	mol	g	l or ml
20						

OK Help Print Clear Copy All Copy Save

Fig. 2. Thermodynamic data of A12O3 (alumina) displayed by the Reaction Equation option of HSC Chemistry.

By entering a single chemical formula into the **Formula** box you will get similar tables of thermochemical data as presented in many thermochemical data books. HSC will, however, provide the results faster and exactly at those temperatures which you really want. Please follow these steps:

1. Write a chemical formula into the box, Fig. 1.
For example: Fe, Na2SO4, Al2O3, SO4(-a), H(a) or SO2(g).
See the valid notation and syntax of chemical formulae in Chapter 21.2.

2. Select the lower limit, upper limit and temperature step.

3. Select the Temperature and Energy Units, by clicking the corresponding buttons.

4. Select the Format of the results.

Normal (Absolute scale)

H(species), S(species) and C(species)

This format is used for example in the famous I. Barin, O. Knacke, and O. Kubaschewski data compilation[1].

Delta (Formation functions)

ΔH = H(species) - ΣH(elements)

ΔS = S(species) - ΣS(elements)

ΔG = G(species) - ΣG(elements)

ΔG = G(ions) - ΣG(elements) z 2 G(H2(g)) - z G(H(a))
z = charge.

This format is used for example in the NBS Tables[NBS 82].

5. The **Collect to Sheet** option will collect several tables on the same spreadsheet.

6. Select the **Show Transitions** option if you also want to see the data at the phase transformation temperatures, such as crystal structure changes and melting.

7. Select the **Criss-Cobble** option if you want a Criss-Cobble extrapolation for the heat capacity of aqueous species, see Chapter 21.4.

8. Press **Calculate** (or Enter) to get the results on the screen.

9. Press **Print** to print the results, see Fig. 2. Note that you can collect several sets of results in the same sheet if you have selected the **Collect to Sheet** option in Fig. 1. You can clear the whole sheet by pressing **Clear**.

10. Press **Copy All** to get all the results into the Clipboard, then you can easily paste the results to other Windows applications, for example, to MS-Excel, see Fig. 2. Using **Copy** it is possible to copy and paste contents of individual cells to other applications.

11. If you want to save the formula and results in an ASCII-file press **Save**, see Fig. 2. You can read these files back to the Reaction module using **File Open**, see Fig. 1. Note that **Save** saves all the selections in Fig. 1, so you can return these using **File Open**. The **File Open HSC 2 File** button reads only old HSC 2.0 files which return only formula, but not the selections nor temperature range.

Note 1. You can easily check the basic data from the database, which has been used in the reaction module calculations. In Fig. 1 select the formula in the Reaction Equation box and press **Peep Database**. The same procedure can be found in Fig. 2 by pressing the right mouse button or selecting **Edit** from the menu.

2. The table in Fig. 2 has some formatting and Copy - Paste functions as do other tables in HSC Chemistry. These features help to create a good printed copy of the results for various purposes.

3. HSC searches for the species data first from the **Own database** (OwnDB5.HSC). If it does not find a species there, it will search from the **Main database** (MainDB5.HSC). Therefore HSC always uses data in the Own database if the same species exists in both Own and Main databases.

4. If you have selected **Delta-format** for the results, HSC will also search for data for the necessary elements and calculate the formation functions of enthalpy, entropy and Gibbs energy. Usually the original experimental data is in this format: however, sometimes the comparison of data in this format may be more difficult because the data sources often use different data for elements.

5. HSC will make a **Criss-Cobble extrapolation** for the heat capacity of aqueous species at elevated temperatures (25 C) if the Criss-Cobble option is selected. The extrapolation is not done if A and B of the heat capacity coefficients A, B, C

and D exist in the HSC Chemistry databases. The extrapolation error increases rapidly at higher temperatures. More information on extrapolation is given in Chapter 28.4.

6. For **aqueous species** it is recommended to set:
Lower temperature = 25 C
Upper temperature = 300 C
Step = 25 C

10.2 One Chemical Substance Results

After pressing the Calculate button in the previous screen, Fig. 1, you will arrive in the results window, Fig. 2. From this results screen you can save and print the results:

1. Press **Save** if you wish to recalculate the results later. The **Save** button will also save the settings used in Fig. 1. You can read these files back to HSC using the **File Open** button, see Fig. 1.
2. Press **Print** if you want a paper copy. If you have selected the **Collect to Sheet** option in Fig. 1, then all results will be collected on the same sheet and can be printed together. **Clear** will clear the results sheet.
3. Press **Copy** to get the results of selected cells into the Clipboard, then you can easily paste the results, for example, to MS -Excel, see Fig. 2.
4. Press **Copy All** to get all the results of the sheet into the Clipboard, then you can easily paste the results, for example, to MS -Excel, see Fig. 2.
5. Press **OK** to return to the previous Window.

10.3 Reaction Equations

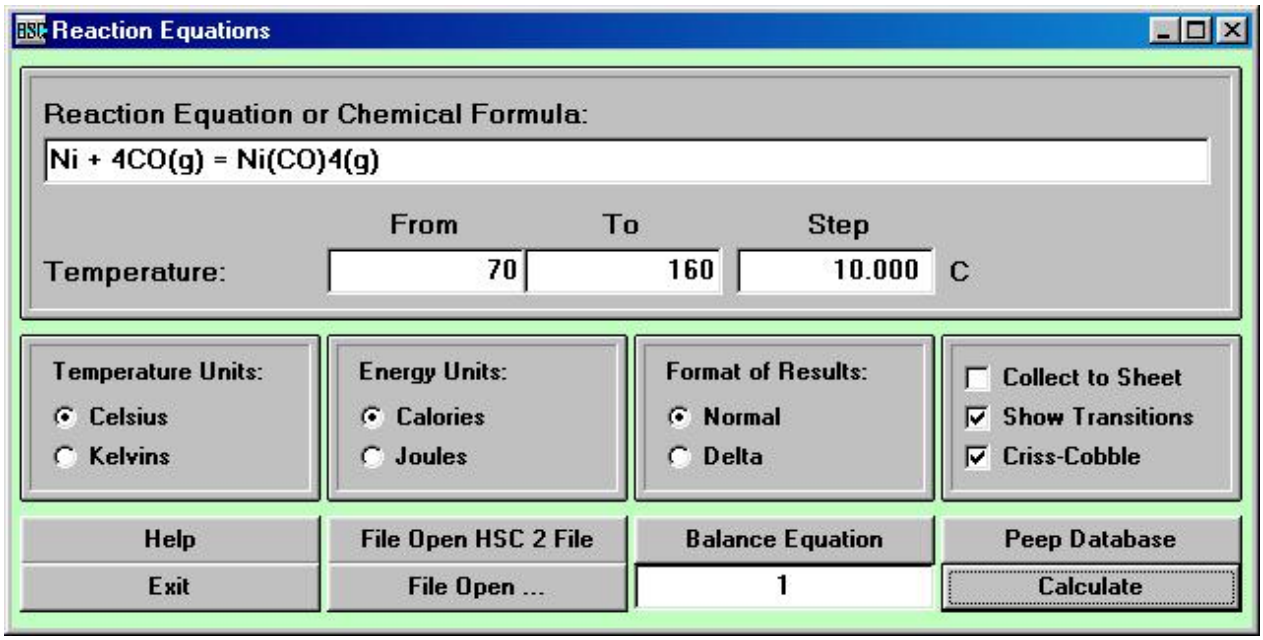


Fig. 3. Input data for Reaction Equation calculations.

Results

File Edit Format Help

	T	Cp	H	S	G	Reference
1	Ni + 4CO(g) = Ni(CO)4(g)					
2	T	deltaH	deltaS	deltaG	K	Log(K)
3	C	kcal	cal/K	kcal		
4	70.000	-38.321	-97.649	-4.813	1.163E+003	3.065
5	80.000	-38.293	-97.569	-3.837	2.369E+002	2.375
6	90.000	-38.264	-97.487	-2.861	5.274E+001	1.722
7	100.000	-38.233	-97.404	-1.887	1.274E+001	1.105
8	110.000	-38.201	-97.318	-0.913	3.319E+000	0.521
9	120.000	-38.167	-97.232	0.059	9.267E-001	-0.033
10	130.000	-38.133	-97.145	1.031	2.760E-001	-0.559
11	140.000	-38.097	-97.057	2.002	8.724E-002	-1.059
12	150.000	-38.060	-96.969	2.972	2.915E-002	-1.535
13	160.000	-38.022	-96.881	3.942	1.026E-002	-1.989
14						
15	Formula	FM	Conc.	Amount	Amount	Volume
16		g/mol	wt-%	mol	g	l or ml
17	Ni	58.700	34.379	1.000	58.700	6.596 ml
18	CO(g)	28.010	65.621	4.000	112.042	89.654 l
19		g/mol	wt-%	mol	g	l or ml
20	Ni(CO)4(g)	170.742	100.000	1.000	170.742	22.414 l

OK Help Print Clear Copy All Copy Save

Fig. 4. Results of Reaction Equation calculations.

You can write almost any kind of reaction equation into the Reaction Equation box of HSC, Fig. 3. Here are some examples of valid equation syntax:

2Cu S = Cu2S
H2O = H(a) OH(-a)
H2(g) = 2H(a) 2e-
H2O = 1 2O2(g) 2H(a) 2e-
Ag = Ag(a) e-
3NO2(-a) 2H(a) = 2NO(g) H2O NO3(-a)
2Al(3a) 3S(-2a) 6H2O = 2Al(OH)3 3H2S(g)

Write the reaction equation into the box, see Fig. 3. If you have not given the stoichiometric coefficients for the species, you can press **Balance Equation** for solving unknown coefficients. The balance button solves the coefficients on the basis of element balance equations. Therefore it cannot solve unknown coefficients if their number is larger than the number of elements in the corresponding reaction.

On the right side of the button you may give a **multiplier**, which will be used to multiply all the coefficients in the reaction equation. The default value is 1, which means that the smallest stoichiometric coefficient in the reaction equation is 1.

You can continue in the same way as in the One Chemical Formula option Chapter 10.1. Note that the **Delta Format** and **Show Transitions** options have no effect on the results, because the enthalpy and Gibbs energy of a reaction are in the Delta format by definition.

HSC calculates the stoichiometry of the reaction given by the user, and points out errors if the element balance is incorrect.

The example in Fig. 3 refers to the Mond-process for refining impure nickel. In the process raw impure nickel is first treated with CO gas at 60 C to evaporate the nickel as a carbonyl gas. In the second stage, the temperature of the gas is increased to 200 C to decompose the nickel carbonyl gas into pure metallic nickel and CO. This process works because the equilibrium of this reaction is on the right side (Equilibrium constant K 1) at lower temperatures and on the left side (K 1) at higher temperatures. The reaction is exothermic (DH is negative) at all temperatures.

Vapor pressures **p** can be calculated by writing the reaction equation for the vaporization reaction concerned. For example, for pure magnesium the equilibrium is Mg = Mg(g), Fig. 5. The activity **a** of pure magnesium is 1 and thus the vapor pressure in bar is equal to the equilibrium constant according to Eq. (10) in Chapter *8. Introduction* and Eq. (1). See also Fig. 6.

K pMg aMg pMg **1**

If a substance vaporizes into several polymers, all of them must be taken into account. The total vapor pressure is then the sum of all the individual partial pressures, if the gas phase behaves ideally.

You can also calculate more complicated reactions. First write the reaction as shown in Fig. 7, then press **Balance** for the coefficients, see Fig. 8 and finally press **Calculate** for the results, see Fig. 9. Note that for aqueous ionic reactions HSC also calculates the electrode potential versus Standard Hydrogen Electrode if electron (e-) is used in the formula.

You can calculate mass balances in moles, grams and liters for any reaction. The species does not need to exist in the HSC databases.

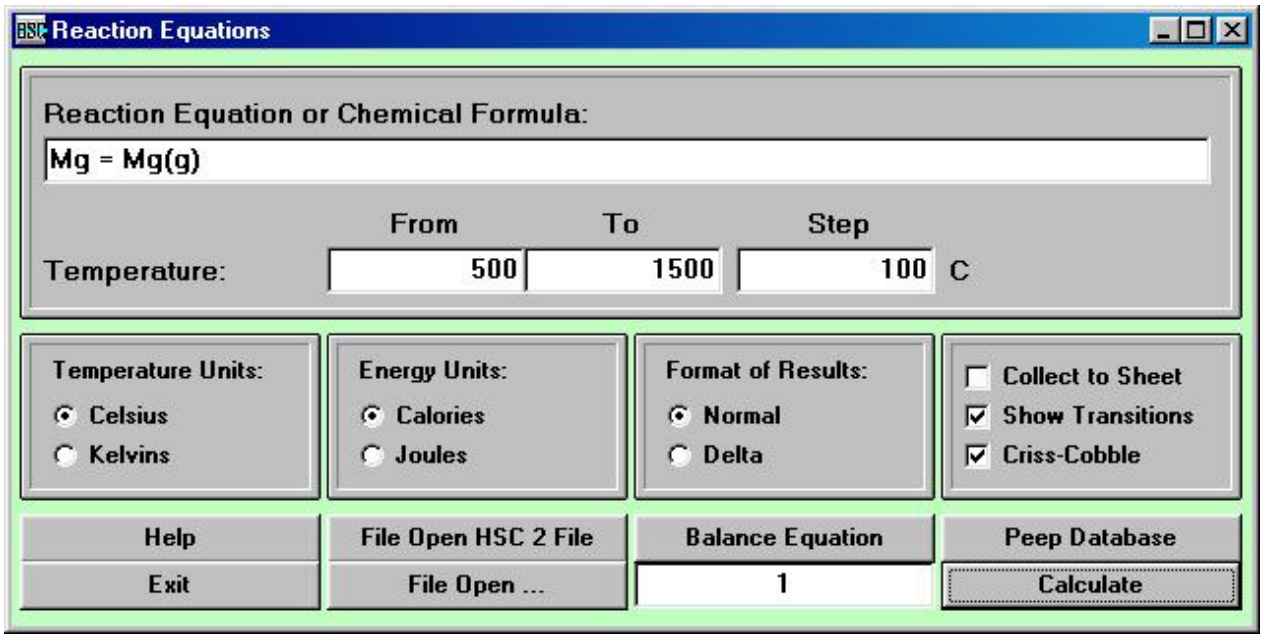
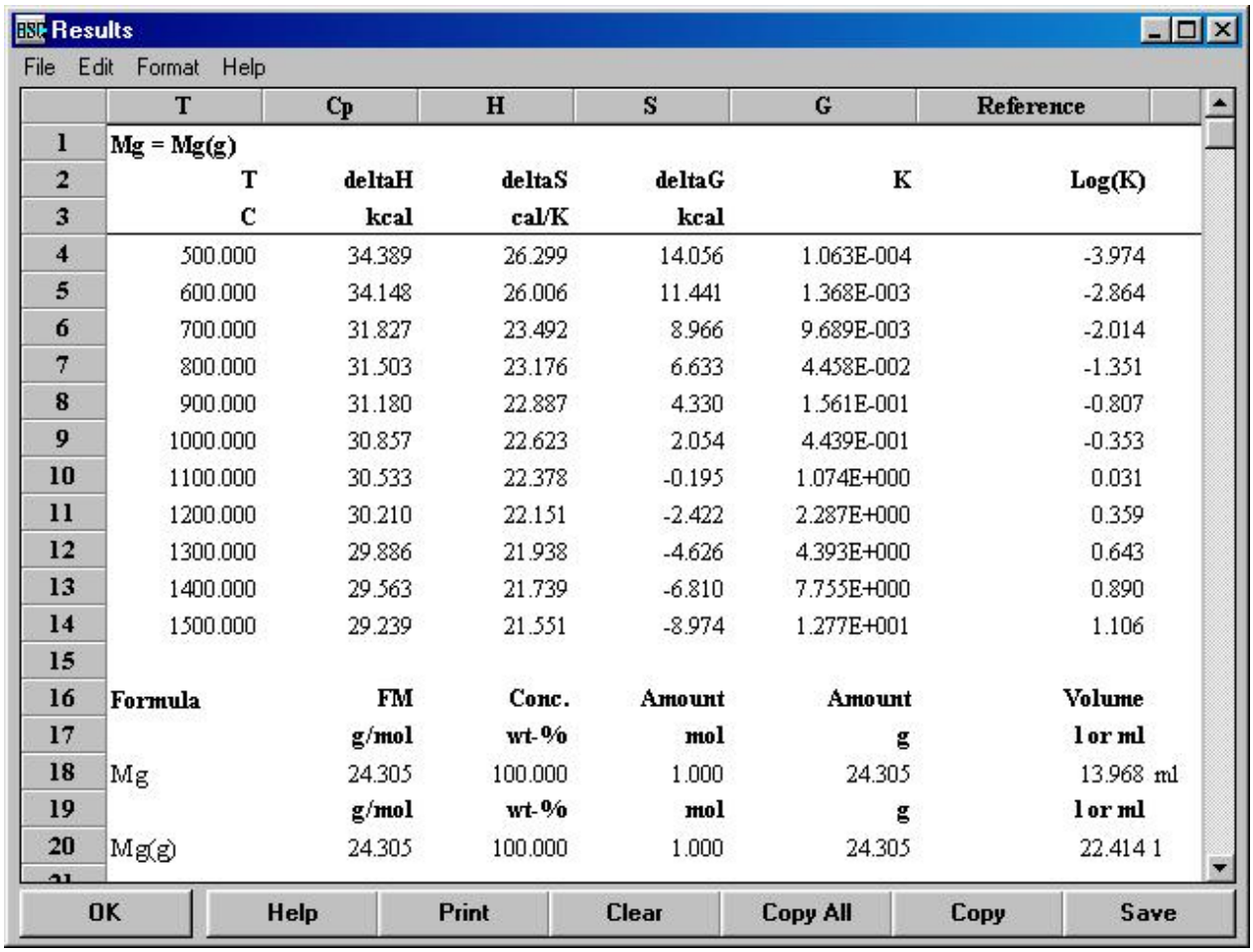


Fig. 5. Input data for Reaction Equation calculations.



	T	Cp	H	S	G	Reference
1	Mg = Mg(g)					
2	T	deltaH	deltaS	deltaG	K	Log(K)
3	C	kcal	cal/K	kcal		
4	500.000	34.389	26.299	14.056	1.063E-004	-3.974
5	600.000	34.148	26.006	11.441	1.368E-003	-2.864
6	700.000	31.827	23.492	8.966	9.689E-003	-2.014
7	800.000	31.503	23.176	6.633	4.458E-002	-1.351
8	900.000	31.180	22.887	4.330	1.561E-001	-0.807
9	1000.000	30.857	22.623	2.054	4.439E-001	-0.353
10	1100.000	30.533	22.378	-0.195	1.074E+000	0.031
11	1200.000	30.210	22.151	-2.422	2.287E+000	0.359
12	1300.000	29.886	21.938	-4.626	4.393E+000	0.643
13	1400.000	29.563	21.739	-6.810	7.755E+000	0.890
14	1500.000	29.239	21.551	-8.974	1.277E+001	1.106
15						
16	Formula	FM	Conc.	Amount	Amount	Volume
17		g/mol	wt-%	mol	g	l or ml
18	Mg	24.305	100.000	1.000	24.305	13.968 ml
19		g/mol	wt-%	mol	g	l or ml
20	Mg(g)	24.305	100.000	1.000	24.305	22.414 l

Fig. 6. The equilibrium constant K is equal to the vapor pressure in atm according to Equation (1) if the activity of magnesium is 1. The boiling point of magnesium is about 1100 C beyond which its vapor pressure exceeds 1 atm.

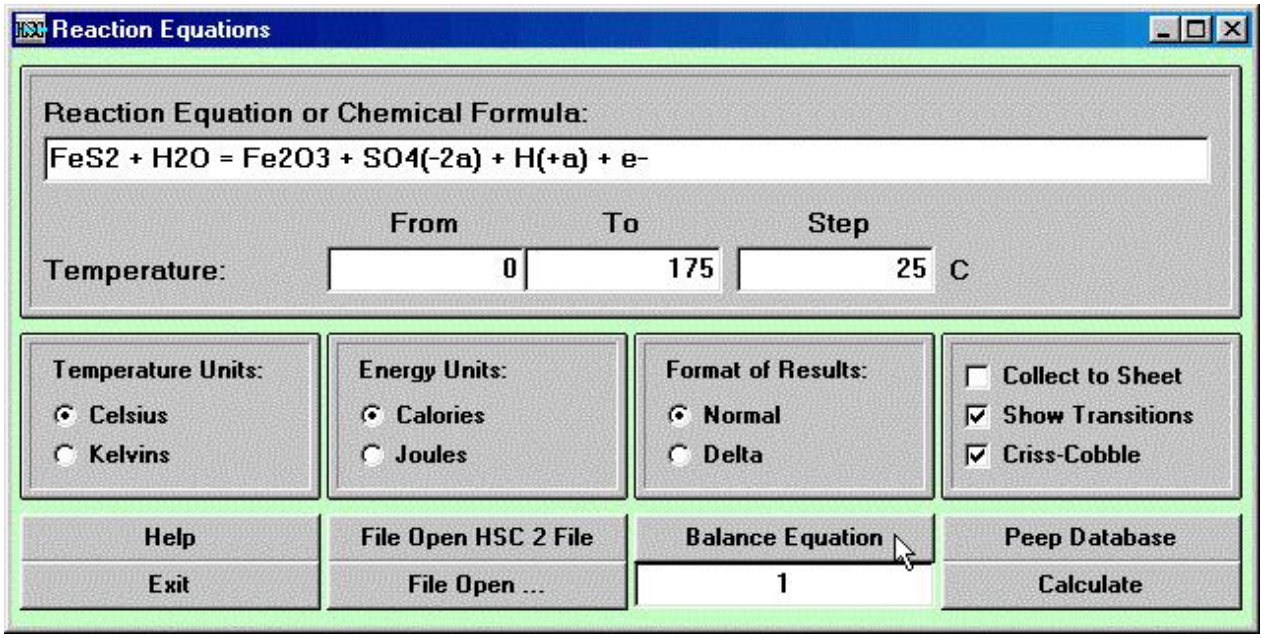


Fig. 7. Write the reaction equation without stoichiometric coefficients and press **Balance Equation**.

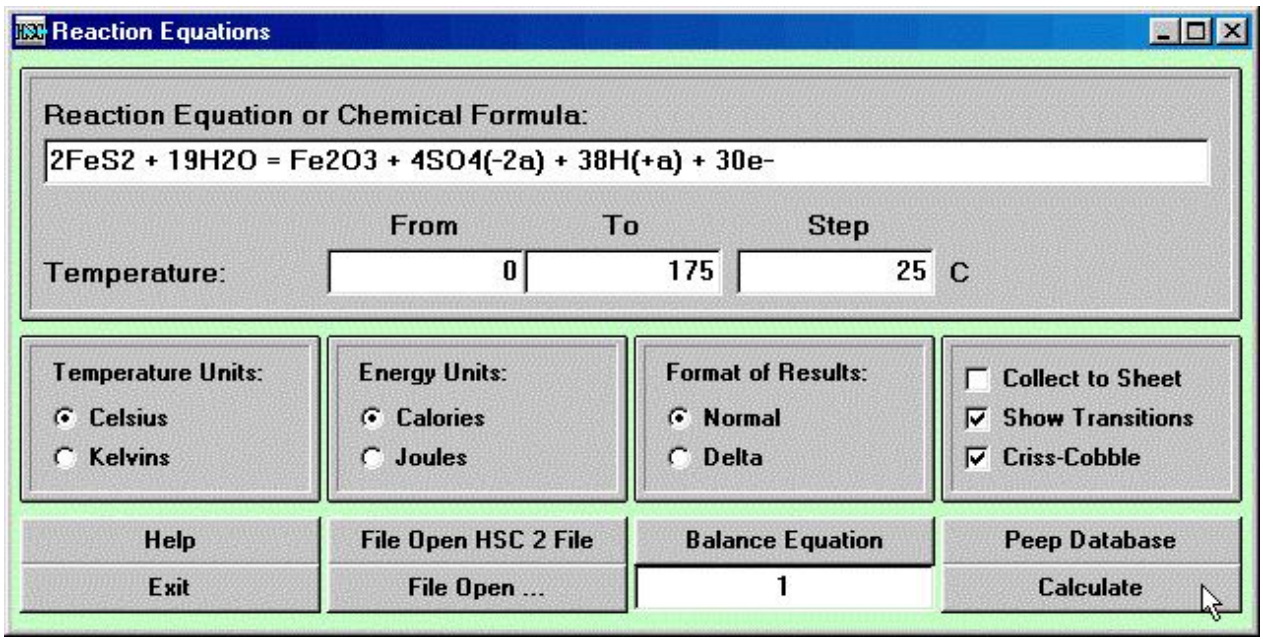


Fig. 8. Press **Calculate** to display the results.

Results

File Edit Format Help

	T	Cp	H	S	G	Reference
1	2FeS2 + 19H2O = Fe2O3 + 4SO4(-2a) + 38H(+a) + 30e-					
2	T	deltaH	deltaS	deltaG	K	E vs. SHE
3	C	kcal	cal/K	kcal		V
4	0.000	354.839	315.127	268.762	8.768E-216	-0.389
5	25.000	313.089	164.432	264.063	2.632E-194	-0.382
6	50.000	301.399	126.758	260.437	7.067E-177	-0.377
7	75.000	290.273	93.592	257.688	1.674E-162	-0.373
8	100.000	278.971	62.250	255.743	1.592E-150	-0.370
9	125.000	266.991	31.187	254.574	1.776E-140	-0.368
10	150.000	253.803	-0.920	254.192	5.050E-132	-0.368
11	175.000	238.836	-35.261	254.638	6.456E-125	-0.368
12						
13	Formula	FM	Conc.	Amount	Amount	Volume
14		g/mol	wt-%	mol	g	l or ml
15	FeS2	119.967	41.210	2.000	239.934	47.796 ml
16	H2O	18.015	58.790	19.000	342.289	373.270 ml
17		g/mol	wt-%	mol	g	l or ml
18	Fe2O3	159.692	27.427	1.000	159.692	30.476 ml
19	SO4(-2a)	96.058	65.992	4.000	384.230	0.000 ml
20	H(+a)	1.008	6.578	38.000	38.300	0.000 ml

OK Help Print Clear Copy All Copy Save

Fig. 9. Results for an aqueous ionic reaction.

The data used to calculate the results can be displayed by selecting one substance in the **Reaction Equation** box, see Fig. 3 and pressing **Peep Database**. The same procedure can be found in the Results window, see Fig. 4, by pressing the right mouse button. The database content is shown in Fig. 10. **Insert** is available for inserting a selected formula into the Reaction Equation box. **Remove** will remove a selected formula from this same box. Note that the selections and editing in Fig. 10 do not have any effect on the HSC databases.

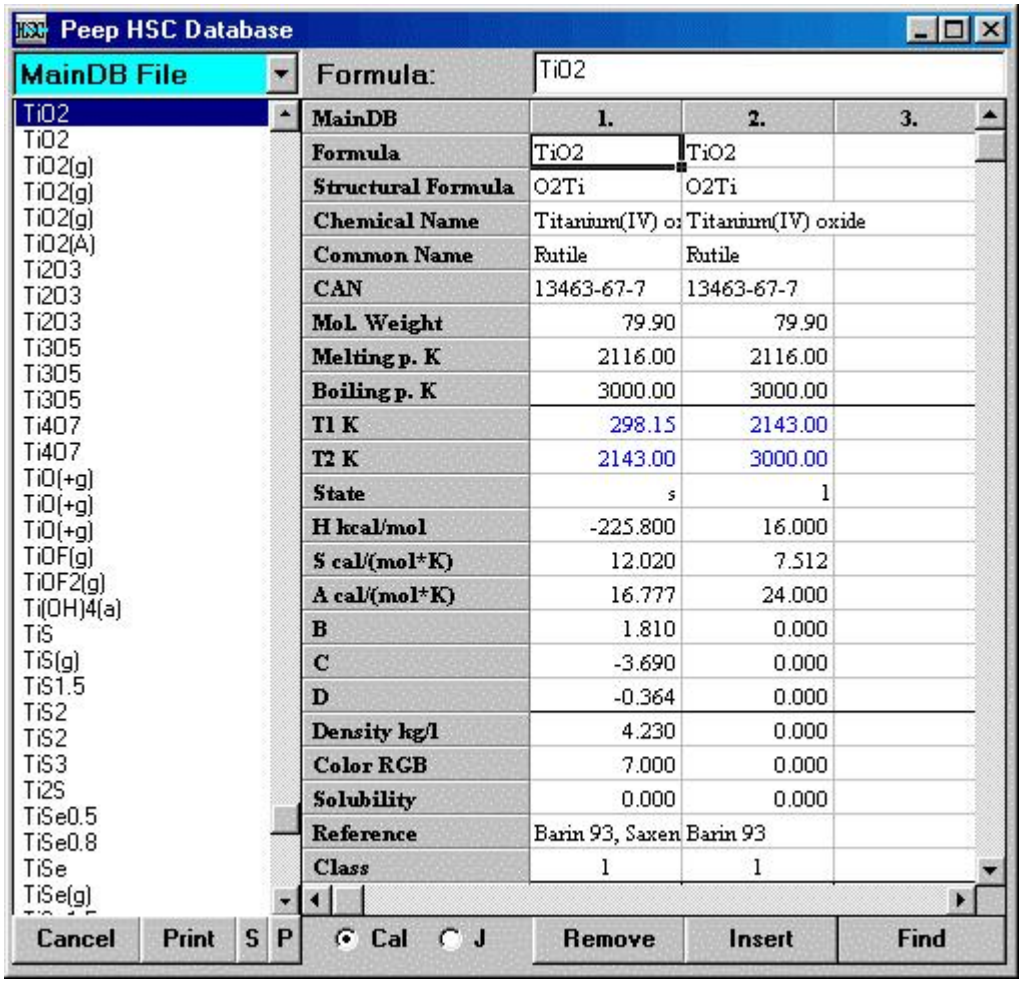


Fig. 10. The database window.

10.4 Reaction Equations Results

The operation of the buttons in Fig. 3 are described in the previous chapter. The meaning of the results can be summarized as the following:

1. If the equilibrium constant K is 1 (or log(K) 0) the reaction goes to the left.
2. If the equilibrium constant K is 1 (or log(K) 0) the reaction goes to the right.
3. Negative Enthalpy H of the reaction means that the reaction is exothermic, i.e. heat is released, Equation 7 in *8. Introduction*.
4. Positive Enthalpy H of the reaction means that the reaction is endothermic, i.e. heat is needed, Equation 7 in *8. Introduction*.
5. Delta Format has no effect on the results of reaction equations.
6. In ionic reactions POTENTIAL E yields the electrochemical potential (in Volts) versus the Standard Hydrogen Electrode.
7. Equilibrium constant K is calculated using Equation 11 in *8. Introduction*.

11. HEAT AND MATERIAL BALANCE

Heat and Material Balance - D:\HSC5\Balance\Cuconv1.bal

File Edit View Insert Delete Format Units Calculate Target Diagram Options Help

A11 EXTRA HEAT:

	INPUT SPECIES (1) Formula	Temper. °C	Amount kmol	Amount kg	Amount Nm³	Latent H MJ	Total H MJ
1	GAS:	25.000	4.386	126.537	99.971	0.000	0.000
2	N2(g)	25.000	3.465	97.066	78.980	0.000	0.000
3	O2(g)	25.000	0.921	29.471	20.991	0.000	0.000
4	FLUX:	25.000	0.215	12.918	0.005	0.000	-195.834
5	SiO2	25.000	0.215	12.918	0.005	0.000	-195.834
6	MATTE:	1250.000	1.040	127.046	0.024	96.296	27.347
7	Cu2S(l)	1250.000	0.500	79.576	0.014	54.919	20.869
8	FeS(l)	1250.000	0.540	47.470	0.010	41.377	6.477
9	COOLING SCRAP:	25.000	0.000	0.000	0.000	0.000	0.000
10	Cu	25.000	0.000	0.000	0.000	0.000	0.000
11	EXTRA HEAT:						0.000
12							
13							
14							
15							
16							
17							

BAL IN1 OUT1

	kmol	kg	Nm³	MJ	MJ
BALANCE (1)	-0.807	0.000	-6.929	209.86	-80.74

Exit

Fig. 1. Heat and Material Balance workbook with IN1, OUT1 and BAL sheets.

Heat balance calculations are usually carried out when developing new chemical processes and improving old ones, because no process can work if too much heat is released or if there is a lack of thermal energy to maintain the reaction temperature. This module calculates the real or constrained heat balances, with given mass-balances as the boundary conditions, but not the theoretical balances at equilibrium conditions.

The heat balance application always contains IN1, OUT1 and BAL sheets. A pair of IN and OUT sheets is called a *a ance area*, which may be considered equivalent to a control volume. A total number of 127 balance areas may be inserted, to create a multiple balance area workbook. Multiple balance area workbooks are explained in more detail in chapter . *u ti e ba ance areas*. For simplicity only the first balance area (IN1, OUT1) will be described in the following chapters.

The basic idea of the heat balance module is that the user specifies the IN1 and OUT1 species, temperatures and amounts and the Heat Balance module *auto atica* calculates the heat and material balances using the BAL sheet. The Heat balance module updates the calculated results on the BALANCE row at the bottom of the form each time the user changes the input data. Please do not modify the BAL sheet.

Since the program uses and creates new balance areas according to the name of the sheets, it is extremely important that *t e auto atica created s eet na es, i.e. t e , I and s eets, s ou d not be odi ied.*

You can also add new sheets for other spreadsheet calculations using the **Insert Sheet** and **Insert Excel Sheet** selections in the menu. The other sheets work very much like MS Excel worksheets, for example, you can:

- rename the sheet name by double clicking the sheet tab
- type formulae into the cells
- use similar cell references as in Excel
- use most of the Excel functions
- link the sheet to IN1 sheet using normal Excel cell references, for example, for converting elemental analysis of the raw material to amounts of the components.
- use the heat balance calculation results in OUT1 sheet as the initial values for other spreadsheet calculations.

In addition the Heat Balance menu provides a wide range of Excel type features, such as: number, font, alignment and border formatting, defined names settings and cell protection. Because they are not necessarily needed in heat balance calculations, these features are not described here in detail.

The new heat balance module offers several ways to calculate heat and material balances:

1. The user types the input and output species, temperatures and amounts into the IN1 and OUT1 sheets respectively. This is a simple way to calculate heat and material balances and was available already in HSC 2.0. However, the problem with the old version was that the user had to manually maintain the material balance when the input feed changed.
2. Materials (species) are given as groups of substances, called *strea s*. These streams can be the same as the phases, but they can also be a mixture of phases.
3. The output amounts can be linked with the input amounts with Excel type cell references, or vice versa.

11.1 Basic Calculation Procedure

The following procedure will describe the most simple way to calculate Heat Balance:

1. Introduce the input substances (raw materials), temperatures and amounts on the IN1 sheet. It is possible to either type amounts in kmol, kg or Nm^3. *It is ad ised to use* ***mol*** *and* ***g*** *because issin densit data a cause inaccurac it units.*
2. Introduce the output substances (products), temperatures and amounts on the OUT1 sheet. Type amounts in either kmol, kg or Nm^3 as preferred.
3. When feeding additional energy (electricity) to the process, enter this amount into the **Total** column in the last empty row of the IN1 sheet. You can also type for example Extra Heat in the first column of this row, see Fig. 20. The Database module will convert the color of all inert text in the first column to green, if this text is not identified in the database as a substance. Notice that:

   1 kWh 3.6 M 0.8604 Mcal (th).

   However, the Balance module will automatically recalculate green text when changing units from the menu. If the green text cell contains a formula, it will

auto atica be c an ed accordin to t e ne unit. For example a change from C to K will add **273.15** to the end of the formula.

4. If heat loss values are known then type them into the last empty row of the OUT1 sheet in the last column (**Total**). A first estimate of heat losses for an air-cooled reactor (natural convection) can easily be calculated using the following formula in **kcal h**:

$$\mathbf{Hloss \quad (6.8 \quad 0.046 \quad T_2) \quad (T_2 - T_1) \quad A} \qquad \mathbf{1}$$

Where: A = Outer surface area of the reactor (m^2)
T_2 = Surface temperature of the reactor (C)
T_1 = Room temperature (C)

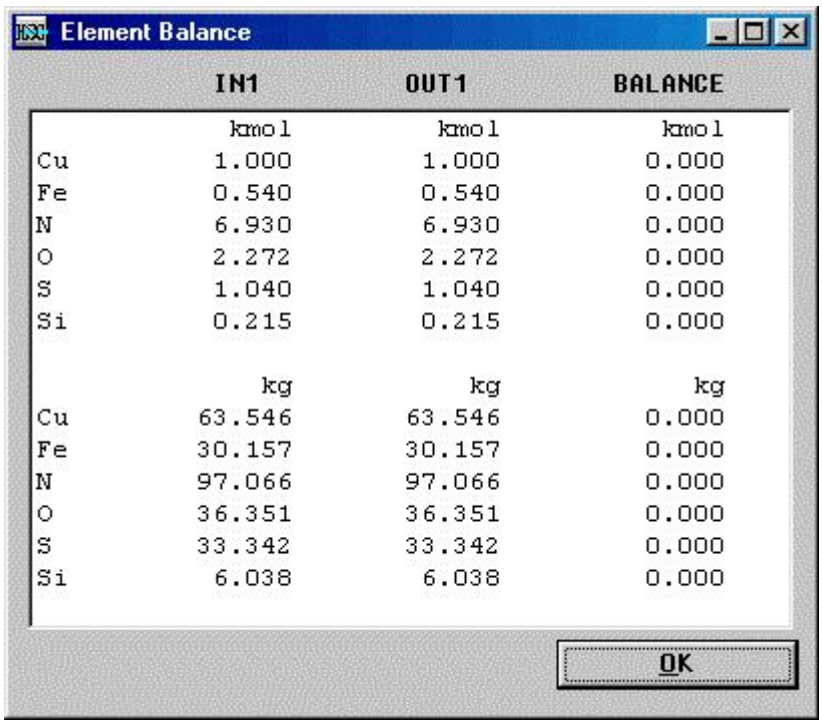
Please use the Heat Loss module if more accurate heat loss approximations are needed.

5. HSC automatically and immediately updates the heat balance on the bottom line as soon as changes to any input data are made.

6. HSC also automatically updates the material amount balances in mol, kg and Nm^3 units. Notice that only the mass balance in kg units on the bottom row should be zero the mole or volume balances can easily change in any chemical process.

7. The element balance can be checked by selecting **Element Balance** from the **Calculate** menu, see Figs. 1 and 2.

8. By selecting **Temperature Balance** from the **Calculate** menu it is possible to see the estimated temperature of the products when the heat balance = 0, see Figs. 1 and 3.



	IN1	OUT1	BALANCE
	kmol	kmol	kmol
Cu	1.000	1.000	0.000
Fe	0.540	0.540	0.000
N	6.930	6.930	0.000
O	2.272	2.272	0.000
S	1.040	1.040	0.000
Si	0.215	0.215	0.000
	kg	kg	kg
Cu	63.546	63.546	0.000
Fe	30.157	30.157	0.000
N	97.066	97.066	0.000
O	36.351	36.351	0.000
S	33.342	33.342	0.000
Si	6.038	6.038	0.000

Fig. 2. Element Balance.

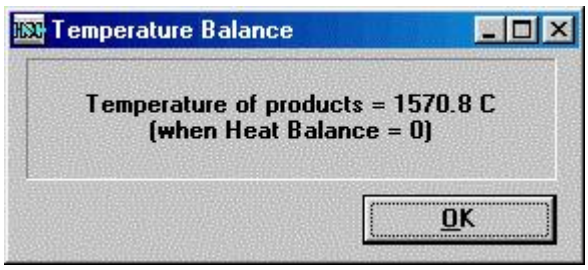


Fig. 3. Temperature of the products (adiabatic process).

9. To insert an empty row in the table, select **Row** from the **Insert** menu or by pressing the right mouse button and selecting **Insert Row** from the popup menu.
10. Rows can be deleted by selecting **Row** from the **Delete** menu or pressing the right mouse button and selecting **Del Row** from the popup menu.
11. You can change the order of the substances by inserting an empty row and using the Copy - Paste method to insert the substance in the new row. The Drag and Drop method can also be used. ***Ho e er it is extremely important to Copy and aste the hole ro not only the orm la beca se o a xiliary data in the hidden col mns on the right side o the and sheets***.

    Please keep the **Copy Mode** selection **on** in the **Edit** menu when rearranging the species, as this will force the program to select the whole row. When formatting the columns and cells, turn the **Copy Mode** selection **off** in the **Edit** menu.
12. Temperature units can be changed by selecting the **C** or **K** from the **Units** menu.
13. Energy units can be changed by selecting **Mcal**, **M** or **kWh** from the **Units** menu.
14. If a paper copy is needed, select **Print** from the **File** menu. This option will copy all the data on the same Print sheet and will also print this sheet on paper if the user presses OK. Notice that you can delete this Print sheet by activating it and then selecting **Sheet** from the **Delete** menu. The **Print Sheet** selection in the **File** menu will print only the active sheet.
15. To save the sheets, select **Save** from the **File** menu. Please save sheets often using different names, because you may wish to make small changes later or to return to the original sheet. Saving sheets is important, because the Undo feature is not available in HSC Chemistry.
16. It is possible to take into account the water steam pressure compensation by moving the cursor to an H2O or H2O(g) species and selecting *Insert ressure correction 2* from the menu. This will open the Pressure and Temperature calculator, where it is possible to specify the pressure for the species. This is useful when calculating for example steam processes.

11.2 Formatting the Worksheet

The heat balance module offers several Excel type formatting possibilities. These may be selected in the **Format** menu:

- Number, Font, Font Default, Alignment, Border, Pattern, Object (for graphical objects), Sheet, Options
- Column Width, Row Height
- Define Names, Refresh Names
- Protection On, Off, Lock all Cells, Unlock all Cells

The window size may also be changed from the **View** menu. The **Normal** selection gives a VGA size window, **Full Height** selection uses the whole height of the screen and **Full Width** fills the whole screen.

11.3 Specification of Substance Groups (Streams)

The new HSC Chemistry 5.0 offers the possibility to specify the input and output substances in streams. These streams can be made of one or several physical phases or species which have the same fixed temperature and elemental composition. Although heat and material balance calculations can be made without using the streams, division into streams helps considerably when changing temperatures and material amounts. Notice that when using *or u ae in s in te erature ce s t e te erature ce s are not u dated i t e s ecies are not di ided into strea s.*

Examples of one-phase streams are, for example:

1. Air feed.
2. Process gas output.
3. Homogenous liquid and solid inputs and outputs.

Examples of multi-phase streams are, for example:

1. Liquid material with solid particles (suspension) as input or output.
2. Solid feed mixture of the process, made of different substances, such as mineral concentrate, coal and sand.
3. Gas feed with liquid droplets or solid powder.

The species rows in the IN1 and OUT1 sheets are divided into separate groups by special stream rows. These rows can be inserted in the sheet using the **Stream** selection in the **Insert** menu or using the same selection in the popup menu from the right mouse button.

The heat balance module *auto atica* makes the following modifications to the sheet when you insert a new stream (group) row in the sheet:

1. Asks for a name for the new group, which you can change later if necessary.
2. Inserts a new empty row above the selected cell with a light blue pattern.
3. HSC assumes that all rows under the new group row will belong to the new group down to the next group row.
4. Inserts Excel type SUM formulae in the new group row for calculating the total amount in the group using kmol, kg and Nm^3 units.

Once the insert procedure is ready, you can edit the group row in the following way:

1. The stream name (label) can be edited directly in the cell.
2. The stream temperature can also be changed directly in the cell and will affect the temperature of all the species in this group.
3. The total material amount of the group can be changed simply by typing a new amount in the group row in kmol, kg or Nm^3 units. This amount can be typed directly over the SUM formula and the program will automatically change the amounts of the species keeping the overall composition constant. The program will then regenerate the original SUM formula after calculating the new amounts.
4. It is important to note that you are unable to type formulae in the amount and enthalpy columns of the stream row, because the SUM formulae must be in the stream row.

To change the amounts of species in a stream using kmol, kg or Nm^3 units, simply type the new amount in the corresponding cell. The program will automatically update the amounts in the other columns, total amount of the stream and the total material and heat balance as well.

An example of the species streams can be seen in Fig. 4. The output species have been divided into four streams. In this example the species in each stream exist in the same phase. **Process Gas** is a gaseous mixture phase, **Slag** is a molten mixture phase and **White Metal** is a pure molten substance.

Heat and Material Balance - D:\HSC5\Balance\Cuconv1.bal

File Edit View Insert Delete Format Units Calculate Target Diagram Options Help

A13 HEAT LOSSES:

	OUTPUT SPECIES (1) Formula	Temper. °C	Amount kmol	Amount kg	Amount Nm³	Latent H MJ	Total H MJ
1	**PROCESS GAS:**	1250.000	4.082	135.121	93.044	174.772	5.292
2	N2(g)	1250.000	3.465	97.066	78.980	135.910	135.910
3	O2(g)	1250.000	0.046	1.477	1.052	1.913	1.913
4	SO2(g)	1250.000	0.571	36.578	13.012	36.949	-132.531
5	**SLAG:**	1300.000	0.283	56.738	0.013	79.874	-274.095
6	*2FeO*SiO2(l)	1300.000	0.215	43.812	0.010	65.949	-247.561
7	Fe3O4(l)	1300.000	0.037	8.490	0.002	9.976	-26.446
8	Cu2O(l)	1300.000	0.031	4.436	0.001	3.949	-0.088
9	**WHITE METAL:**	1250.000	0.469	74.642	0.013	51.514	19.576
10	Cu2S(l)	1250.000	0.469	74.642	0.013	51.514	19.576
11	**METAL:**	1250.000	0.000	0.000	0.000	0.000	0.000
12	Cu(l)	1250.000	0.000	0.000	0.000	0.000	0.000
13	HEAT LOSSES:						0.000
14							
15							
16							
17							

BAL IN1 OUT1

	kmol	kg	Nm³	MJ	MJ
BALANCE (1)	-0.807	0.000	-6.929	209.86	-80.74

Exit

Fig. 4. The OUT1 sheet of the Heat Balance module. The species have been divided into three streams, which are the same as the existing phases.

11.4 Formulae in the Cells

Excel-type formulae and cell references can be used, for example, in order to link the input and output amounts with each other and to maintain the material balance automatically when the input amounts change. The input and output amounts can be linked using two main methods:

1. An Excel-type formula can be typed in the **kmol column**, which expresses the dependence of the output mole amount on the input mole amount. For example, if Cu2S in the cell OUT1 C10 contains 93.8 of copper input then you may type formula **0.938 IN1 C7** in cell OUT1 C10, see Fig 5.

2. The Heat balance module automatically calculates input and output mole amounts for elements. The cell names for input amounts are: InAc, InAg, InAl, InAm and the equivalent for output elements are called OutAc, OutAg, OutAl, OutAm, etc. For balance areas with a higher number (for example the IN2 and OUT2 sheets) the corresponding cell names are simply InAc2, InAc3 and OutAc2, OutAc3, etc. These names can be used in the formulae. The formula in the previous example can also be written: =**0.938 (InCu-C12) 2** using these defined names, see Fig. 5. The cells with element amounts are not visible to the user.

   Please be very careful when using default input and output names simultaneously, because it is very easy to end up with circular references. An indication of a circular reference is that the heat and material balance, which can be seen on the BALANCE row, changes even after a recalculation (**Calculate ReCalc** from the menu). By selecting **Format Options** from the menu and highlighting the **Iteration** checkbox under the **Calculation** tab, it is possible to automatically iterate the circular references. This is, however, not recommended for very large worksheets.

Within the IN1 and OUT1 sheets it is recommended to use formulae only in the kmol column and not in the other Amount columns. You can use the formulae also in other columns, but please be very careful. In the other sheets there are no special limitations for the formulae.

Heat and Material Balance - D:\HSC5\Balance\Cuconv1.bal

File Edit View Insert Delete Format Units Calculate Target Diagram Options Help

C10 =0.938*(InCu-C12)/2

	OUTPUT SPECIES (1) Formula	Temper. °C	Amount kmol	Amount kg	Amount Nm³	Latent H MJ	Total H MJ
1	PROCESS GAS:	1250.000	4.082	135.121	93.044	174.772	5.292
2	N2(g)	1250.000	3.465	97.066	78.980	135.910	135.910
3	O2(g)	1250.000	0.046	1.477	1.052	1.913	1.913
4	SO2(g)	1250.000	0.571	36.578	13.012	36.949	-132.531
5	SLAG:	1300.000	0.283	56.738	0.013	79.874	-274.095
6	*2FeO*SiO2(l)	1300.000	0.215	43.812	0.010	65.949	-247.561
7	Fe3O4(l)	1300.000	0.037	8.490	0.002	9.976	-26.446
8	Cu2O(l)	1300.000	0.031	4.436	0.001	3.949	-0.088
9	WHITE METAL:	1250.000	0.469	74.642	0.013	51.514	19.576
10	Cu2S(l)	1250.000	0.469	74.642	0.013	51.514	19.576
11	METAL:	1250.000	0.000	0.000	0.000	0.000	0.000
12	Cu(l)	1250.000	0.000	0.000	0.000	0.000	0.000
13	HEAT LOSSES:						0.000
14							
15							
16							
17							

BAL IN1 OUT1

	kmol	kg	Nm³	MJ	MJ
BALANCE (1)	-0.807	0.000	-6.929	209.86	-80.74

Exit

Fig. 5. The OUT1 sheet of the Heat Balance module. Copper output has been linked with copper input with a formula and defined name: InCu.

11.5 Elemental Compositions

The elemental compositions of the species groups may be calculated using the **Stream Compositions** selection in the **Calculate** menu, see Fig. 6. This procedure calculates the elemental compositions of each group, creates new In1- and Out1- sheets and prints results on these new sheets in mol- and wt- units.

Notice that a procedure to convert elemental analysis back to species analysis is not yet available in the heat balance module. A general solution to this kind of problem is quite difficult and in many cases impossible. However, a custom-made solution for an individual case is possible with a little effort and normal Excel-type formulae:

1. Create a new sheet using the **Sheet** selection in the **Insert** menu, see Fig. 6.
2. Rename the new sheet by double clicking the tab, for example to **Compositions** . Notice that you can use also the Input- sheet as the starting point as you rename it.
3. Type the elemental and species compositions on the new sheet.
4. Notice that you can insert Formula Weights in this new sheet by selecting the chemical formula cells and then selecting **Mol Weight** from the **Insert** menu.
5. Create Excel-type formulae, which convert the elemental analysis of a group to mole amounts of species using formula weights of the elements and species.
6. Type formulae in the kmol columns of the IN1 sheet, which refer to species amounts in the Compositions sheet.

Heat and Material Balance - D:\HSC5\Balance\Cuconv1.bal

File Edit View Insert Delete Format Units Calculate Target Diagram Options Help

C11 0.938

	OUT1 Compositions	Temper. °C	Amount kmol	Amount kg		Content mol-%	Content wt-%
1	PROCESS GAS:	1250.000	8.735	135.121		100.000	100.000
2	N		6.930	97.066		79.333	71.837
3	O		1.234	19.749		14.130	14.615
4	S		0.571	18.306		6.537	13.548
5	SLAG:	1300.000	1.855	56.738		100.000	100.000
6	Cu		0.062	3.940		3.343	6.944
7	Fe		0.540	30.157		29.116	53.152
8	O		1.038	16.602		55.949	29.261
9	Si		0.215	6.038		11.592	10.643
10	WHITE METAL:	1250.000	1.407	74.642		100.000	100.000
11	Cu		0.938	59.606		66.667	79.856
12	S		0.469	15.036		33.333	20.144
13	METAL:	1250.000	0.000	0.000		0.000	0.000
14							
15							
16							
17							
18							

BAL IN1 OUT1 In1-% Out1-%

	kmol	kg	Nm³	MJ	MJ
BALANCE (1)	-0.807	0.000	-6.929	209.86	-80.74

Exit

Fig. 6. The Out1- sheet of the Heat Balance module. This sheet shows the elemental compositions of the phases, after the Stream Compositions option has been selected from the Calculate menu.

11.6 Additional Sheets

The Heat Balance workbook consists at least of the IN1, OUT1 and BAL sheets. The user may, however, add up to 256 sheets to one workbook. These additional sheets may be used, for example, to convert the elemental compositions of raw materials to amounts of species which are needed in the IN1 sheet. These sheets can also be used to collect the main results from the OUT1 sheet in one summary table. Do not use the reserved names IN1, OUT1, BAL and Target as sheet names.

To add sheets select **Insert Sheet** from the menu. This will add one sheet on the selected location. To rename this new sheet, double click the Tab on the bottom of the form. You can also import Excel sheets by selecting **Insert Excel Sheet** from the menu. This selection allows you first to select the file and then the sheet which you want to insert into the active Heat Balance workbook.

The example in Fig. 7 shows a FEED sheet, which is used to specify the raw materials amounts to the IN1 sheet. The user may give the compositions and amounts in column C, this data will then be used to calculate the amounts of species in column F. The material amounts in IN1 sheet are given using relevant cell references to column F in the FEED sheet. This example can be found from your HSC5 Balance directory under the name CUCONV2.BAL. The user can construct the layout of the additional sheets freely.

The Red Font Shield property is a useful way to prevent accidental modification of the data in the cells. If this property is set using menu selection **Format, Red Font Shield** then only cells with red font can be edited. However, it is recommended to save the work regularly using different names, for example, test1.bal, test2.bal, test3.bal, etc. in order to recover the original situation after harmful modifications.

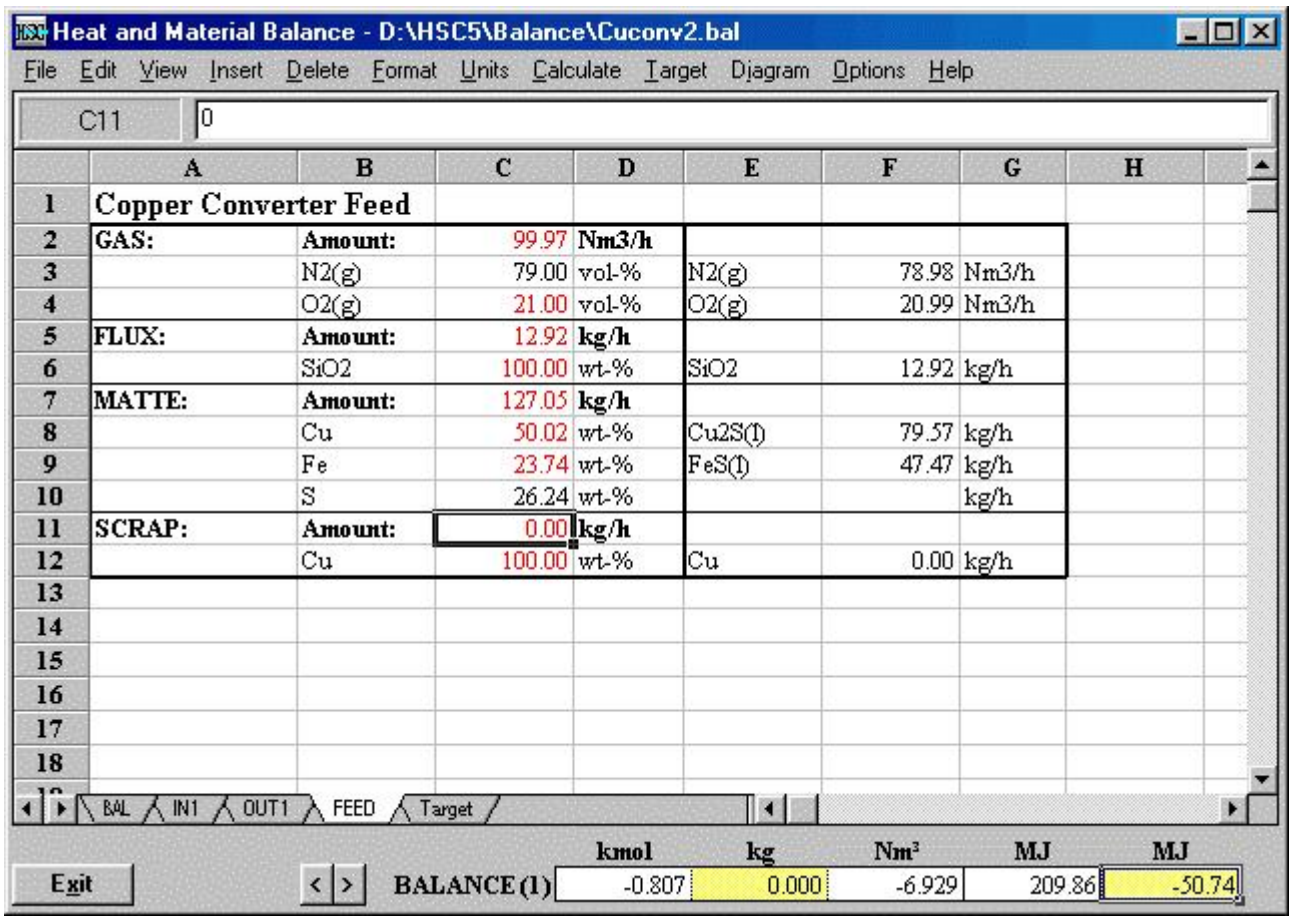


Fig. 7. Additional sheets can be added to the Heat Balance workbook.

11.7 Target Dialog

The user can iterate manually, for example, the fuel amount which is needed to achieve zero heat balance by changing the fuel amount until the heat balance is zero. The Target sheet offers a faster automatic way to carry out these kind of iterations. The following instructions will explain this procedure in more detail:

1. Select **Target Dialog** from the menu. This will also automatically create a Target sheet, which is similar to previous HSC versions.
2. Select one cell on row 4 in the Target dialog if not selected.
3. Select one cell which will be used as a first variable and select **Set variable cell**. This will add the cell reference of this variable to the Target dialog in column B. *ou can a so t e t e ce re erences anua* in the Target dialog. Note: Please use only Stream temperature cells as variables for the temperature iterations, ie. do not use species temperature cells.
4. Select one cell which will be used as first variable and select **Set target cell**. This will add the cell reference of this variable to the Target dialog in column B.
5. Repeat steps 3 and 4 if you want to add more variables and targets.
6. Set valid **Min** and **Max** limits in columns D and E as well as the **Target Value** in column H. You may also type names in columns A and F.

7. Usually it is also necessary to give estimated initial Test Values in column C for the automatic iterations. Iteration ends when the target value (col H) or iteration number (col I) is reached. Accuracy can be improved by increasing the number of decimals used in columns G and H with the **Format Number** selection.
8. Select the rows (3) on the Target sheet which you want to iterate and press **Iterate selected rows** or **F8**. If all rows should be iterated, simply press **Iterate All**.

In the following example, shown in Fig. 8, you can select for example row 4 and press **F8**. This will evaluate the copper scrap amount which is needed to maintain the heat balance in the given conditions. Row 5 can be used to iterate the iron content of the matte in the same conditions and row 6 to achieve a given FeS amount.

Important note: Please use only Stream temperature cells as variables for the temperature iterations, ie. do not use species temperature cells.

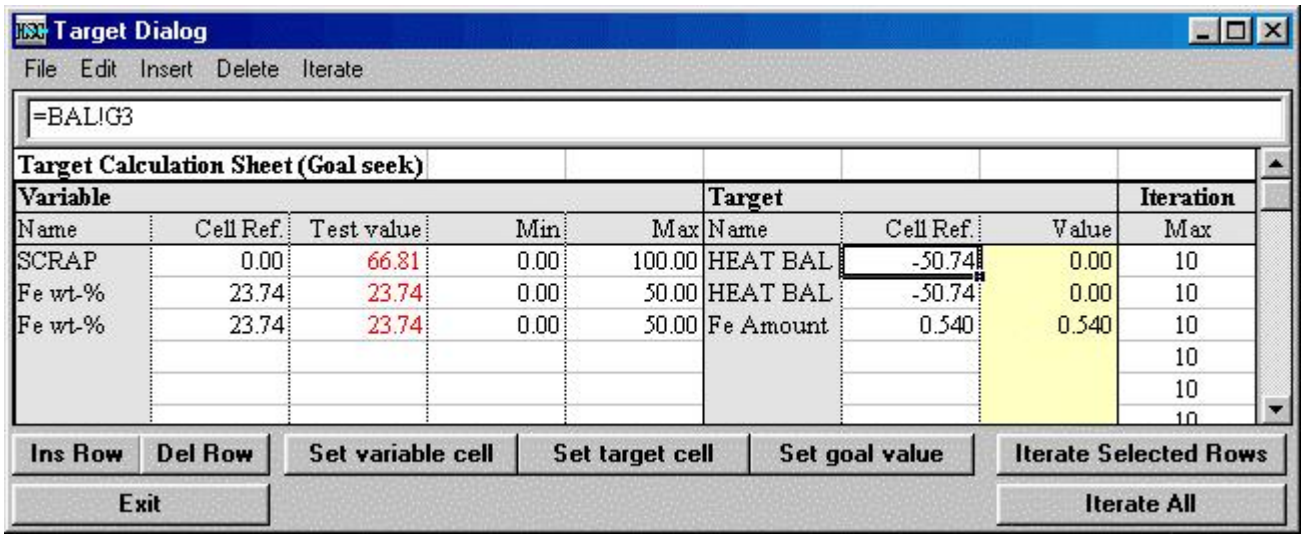


Fig. 8. Target dialog specifies the variables and target cell references.

11.8 Graphics

Occasionally it is useful to see the results, of for example a heat balance calculation, in graphical format. This can be carried out manually by making step by step changes to one variable cell and collecting data from interesting cells, for example, to an Excel sheet. Sometimes further calculations may be required after every step, which can be specified using the Diagram Dialog. Step by step the procedure is as follows:

1. Select **Diagram Diagram Dialog** from the menu.
2. Select the variable cell and press **Set X-cell** from the dialog. Select, for example, cell C11, see Fig. 7.
3. Select a cell for the y-axis and press **Set Y-cell** from the dialog. Select, for example, the Heat Balance cell at the bottom right of the form. You may repeat this step and collect several cells whose values will be drawn to the diagram.
4. If other calculations are required between every step, press **Target iteration** and the Target sheet will automatically open. Select the calculation rows that should be iterated before the Y-row and press **Set Target rows** from the menu. The row data will now be tranferred to the Diagram dialog into columns 4, 5, etc.
5. Fill the Diagram Settings as shown in Fig. 9. You must specify the MIN, MAX and STEP values for the X-Axis. You can also specify the cell references, labels and units manually in this form.
6. Press **Diagram** to create the tabular data for the diagram and **Diagram** once again to see the final diagram, Fig 9.
7. The diagram can be modified, copied and printed in the same manner as other diagrams in HSC Chemistry.
8. **Show Toolbar** shows the drawing menu and **Show Ob ect Editor** shows the object editor, which lets you specify the objects manually.
9. To return to the Heat Balance module, press **Exit** at the bottom left corner of the diagram form.

From the diagram shown in Fig. 9 you can see that roughly 68 kg h of scrap is needed to adjust the heat balance to zero. Notice that the units in the diagram are kg h and kW.

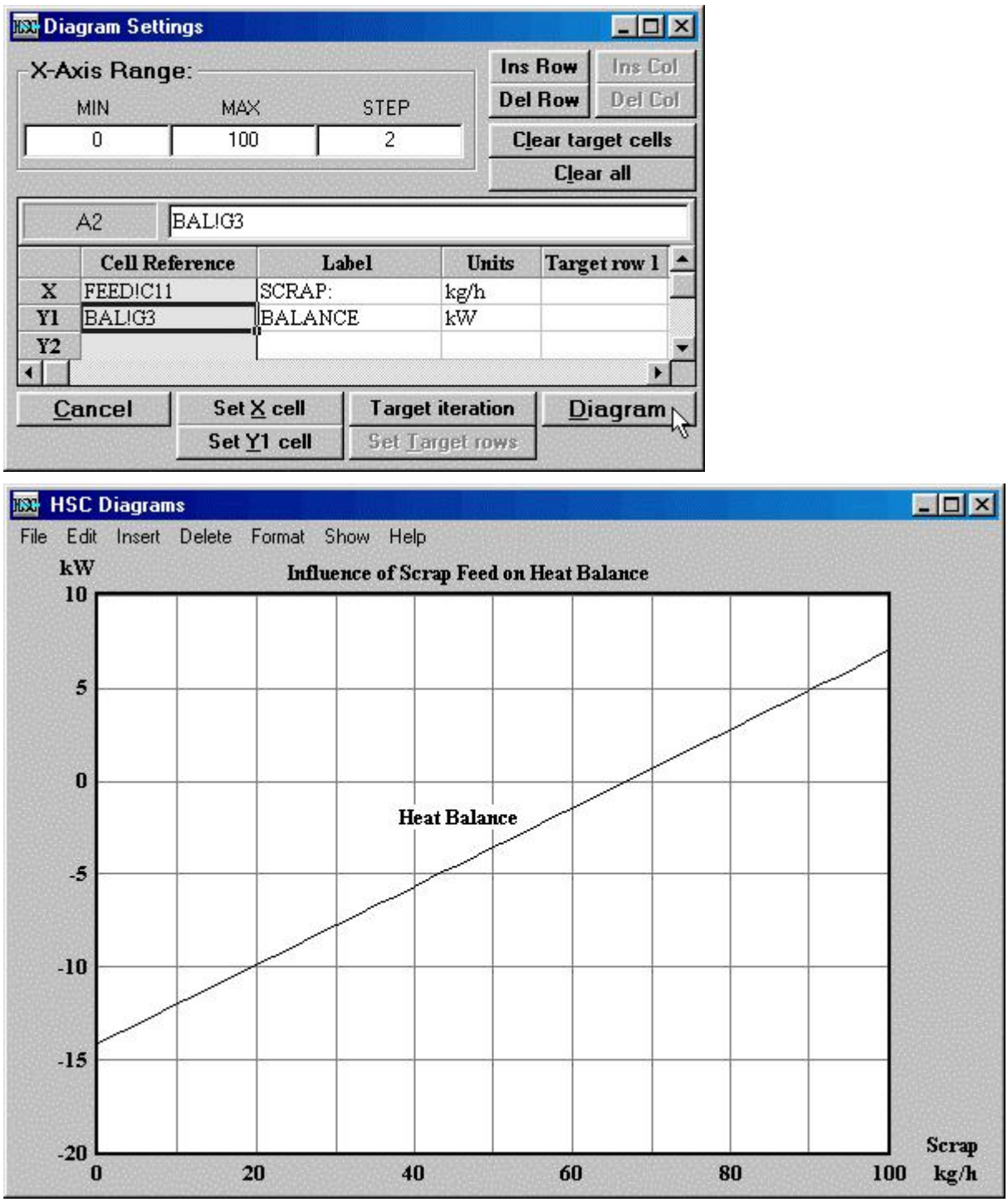


Fig. 9. Simple heat balance diagram.

In the following diagram (Fig. 10) the heat balance is automatically calculated before each step, which is indicated by the number 4 in the **Target row 1** column. This is done by pressing the **Target iteration** button, selecting row 4 on the Target sheet and clicking the **Set Target rows** button. The x-axis now gives the Fe wt- and the y-axis the cooling scrap required. The diagram may then be interpreted as the quantity of cooling scrap required to make the heat balance zero, when the Fe wt- varies from 20 to 25 .

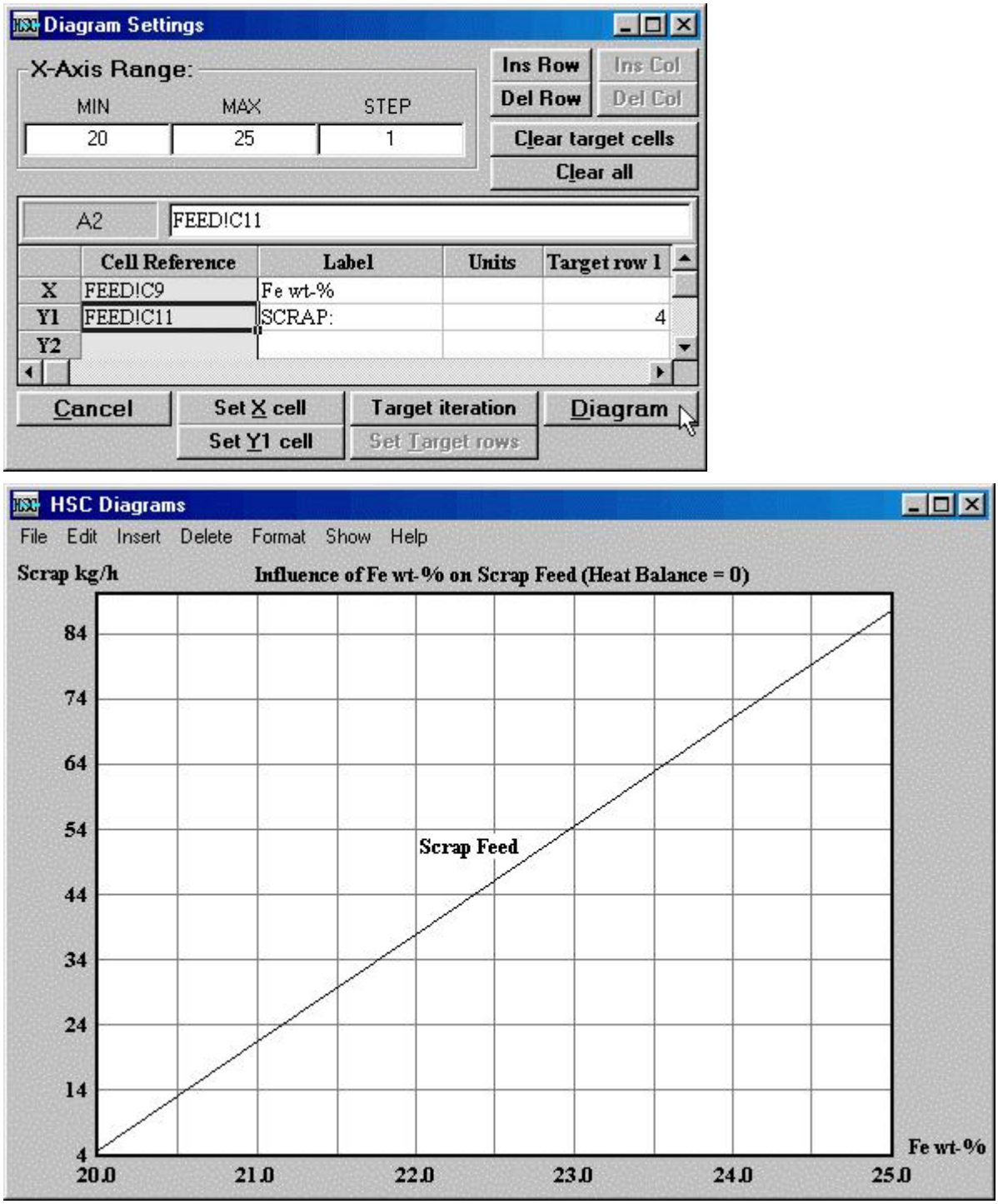
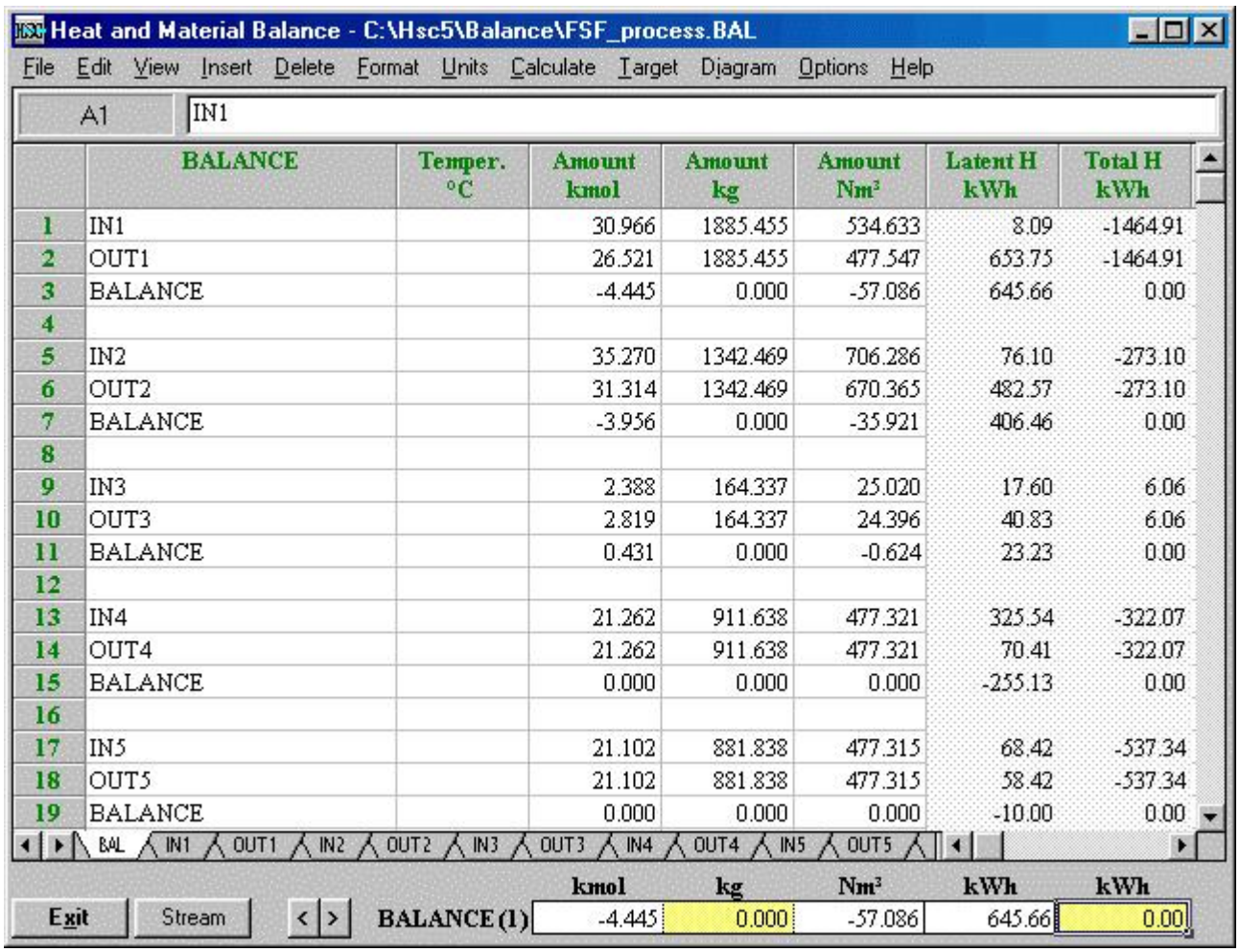


Fig. 10. Diagram where the heat balance is automatically iterated to zero before every calculation step.

11.9 Multiple balance areas

The previous Balance modules up to HSC 4.0 were restricted to one balance area (or control volume) only. Since most processes consist of multiple balance areas, the new Balance module enables the user to create up to 127 multiple balance areas. A balance area consists of an INx and an OUTx sheet, where x denotes the number of the balance area. These can then be connected to each other creating a realistic simulation of a process. The example file **FSF process.BAL** contains a highly simplified multibalance model of an Outokumpu Flash Smelting Furnace process.

A new balance area is created by selecting either **Insert Balance Area to Right** or **Insert Balance Area to Left** from the menu. This will insert a pair of INx and OUTx sheets to the corresponding position. A balance area may easily be deleted by selecting **Delete Balance Area**. Deleting a single sheet of a balance area, for example an INx sheet, is not possible. The balances are all automatically collected into the **BAL** sheet so please do not modify this sheet.



	BALANCE	Temper. °C	Amount kmol	Amount kg	Amount Nm³	Latent H kWh	Total H kWh
1	IN1		30.966	1885.455	534.633	8.09	-1464.91
2	OUT1		26.521	1885.455	477.547	653.75	-1464.91
3	BALANCE		-4.445	0.000	-57.086	645.66	0.00
4							
5	IN2		35.270	1342.469	706.286	76.10	-273.10
6	OUT2		31.314	1342.469	670.365	482.57	-273.10
7	BALANCE		-3.956	0.000	-35.921	406.46	0.00
8							
9	IN3		2.388	164.337	25.020	17.60	6.06
10	OUT3		2.819	164.337	24.396	40.83	6.06
11	BALANCE		0.431	0.000	-0.624	23.23	0.00
12							
13	IN4		21.262	911.638	477.321	325.54	-322.07
14	OUT4		21.262	911.638	477.321	70.41	-322.07
15	BALANCE		0.000	0.000	0.000	-255.13	0.00
16							
17	IN5		21.102	881.838	477.315	68.42	-537.34
18	OUT5		21.102	881.838	477.315	58.42	-537.34
19	BALANCE		0.000	0.000	0.000	-10.00	0.00

Fig. 11. The **BAL** sheet when the worksheet consists of 5 balance areas.

in in t e ba ance areas it eac ot er is reco ended to carr out a ter eac indi idua ba ance areas o erate ro er . Linking may be achieved either manually with formulae or automatically with the **Copy - Paste Stream** combination. Simply place the cursor on a stream row in an OUTx sheet, or on a row that belongs to a stream, and select **Edit Copy**. Then place the cursor on a row in an INx sheet and select **Edit Paste**

Stream. The stream will now be copied here so that the first row of the stream is the cursor position. The **kmol** column of the pasted stream will consist of links (formulae) to the copied stream, so that the material amounts of the streams will remain equal. The other cells are directly copied as values. If the *strea te erature ce* in the copied stream is a formulae then it will not be copied. In this case it is up to the user to decide how the stream temperature for the pasted stream should be calculated.

It is also possible to create *return strea s*, i.e. streams that return to a previous part of the process, thus creating loops in the process. When pasting a stream into an already linked part, a *circu ar re erence* might occur. This is the case when links eventually refer back to each other, i.e. iterations are needed to calculate the worksheet. Automatic iterations may be done by selecting **Format Options** from the menu and highlighting the **Iteration** checkbox under the **Calculation** tab. Please be careful when changing the inputs of a worksheet consisting of circular references. For example if a cell, which is part of a circular reference, shows the message **VALUE** , it will not recover unless the links in the cells are changed thus breaking the circular reference. Saving the worksheet regularly using different names (Test1, Test2, etc.) is thus always recommended.

Heat and Material Balance - C:\Hsc5\Balance\FSF_process.BAL

File Edit View Insert Delete Format Units Calculate Target Diagram Options Help

C14 =OUT4!C11

	INPUT SPECIES (1) Formula	Temper. °C	Amount kmol	Amount kg	Amount Nm³	Latent H kWh	Total H kWh
1	**Concentrate**	25.000	5.589	1000.000	0.255	0.00	-922.73
2	CuFeS2	25.000	4.091	750.800	0.179	0.00	-216.35
3	FeS	25.000	0.669	58.800	0.012	0.00	-18.89
4	FeS2	25.000	0.253	30.400	0.006	0.00	-12.07
5	CaO*Al2O3*2SiO2	25.000	0.575	160.000	0.058	0.00	-675.41
6	**Flux**	25.000	1.573	112.000	0.042	0.00	-462.98
7	SiO2	25.000	1.486	89.264	0.034	0.00	-375.89
8	*2FeO*SiO2	25.000	0.020	4.032	0.001	0.00	-8.13
9	CaO*Al2O3*2SiO2	25.000	0.067	18.704	0.007	0.00	-78.96
10	**Air (oxygen enriched)**	25.000	23.443	712.787	534.323	0.00	0.00
11	O2(g)	25.000	14.067	450.114	320.594	0.00	0.00
12	N2(g)	25.000	9.377	262.673	213.729	0.00	0.00
13	**Flue dust (Boiler return)**	350.000	0.160	29.800	0.006	1.99	-39.86
14	Cu2O	350.000	0.089	12.723	0.002	0.56	-3.66
15	Fe3O4(l)	350.000	0.049	11.370	0.002	0.95	-12.60
16	SiO2	350.000	0.001	0.082	0.000	0.01	-0.34
17	CaO*Al2O3*2SiO2	350.000	0.020	5.625	0.002	0.48	-23.27
18	**Flue dust (ESP return)**	305.021	0.080	14.900	0.003	0.85	-20.08
19	Cu2O	305.021	0.044	6.362	0.001	0.24	-1.87
20	Fe3O4(l)	305.021	0.025	5.685	0.001	0.41	-6.37
21	SiO2	305.021	0.001	0.041	0.000	0.00	-0.17
22	CaO*Al2O3*2SiO2	305.021	0.010	2.812	0.001	0.20	-11.67

BAL IN1 OUT1 IN2 OUT2 IN3 OUT3 IN4 OUT4 IN5 OUT5

	kmol	kg	Nm³	kWh	kWh
BALANCE (1)	-4.445	0.000	-57.086	645.66	0.00

Exit Stream

Fig. 12. The IN1 sheet (Flash Furnace) of the FSF process.BAL example. The stream **Flue dust** is a return stream from the boiler (**Copy Paste stream**), thus creating *circu ar re erences* in the worksheet.

Automatically updated defined names (input and output kmol amounts) vary according to the balance area. For example InAl, InC, OutFe for the first balance area will become InAl2, InC2, OutFe2 for the second etc. Note that the defined names of the first balance area do not have index numbers.

Heat and Material Balance - C:\Hsc5\Balance\FSF_process.BAL

File Edit View Insert Delete Format Units Calculate Target Diagram Options Help

C5 =InCa2*Analysis!L29/100

	OUTPUT SPECIES (2) Formula	Temper. °C	Amount kmol	Amount kg	Amount Nm³	Latent H kWh	Total H kWh
1	**Slag**	1300.000	1.204	255.673	0.058	104.89	-372.70
2	*2FeO*SiO2	1300.000	0.843	171.848	0.040	76.94	-269.73
3	Fe3O4(l)	1300.000	0.304	70.422	0.014	22.99	-60.93
4	Cu2O(l)	1300.000	0.017	2.415	0.000	0.60	-0.01
5	CaO*Al2O3*2SiO2	1300.000	0.039	10.989	0.004	4.37	-42.02
6	**White metal**	1260.000	0.512	81.465	0.015	17.60	6.06
7	Cu2S	1260.000	0.512	81.465	0.015	17.60	6.06
8	**Flue dust**	1260.000	0.095	12.099	0.003	4.01	-19.20
9	Cu2O	1260.000	0.017	2.415	0.000	0.77	-0.03
10	Fe3O4	1260.000	0.028	6.402	0.001	1.95	-6.64
11	SiO2	1260.000	0.049	2.932	0.001	1.16	-11.19
12	CaO*Al2O3*2SiO2	1260.000	0.001	0.351	0.000	0.13	-1.35
13	**Flue gas**	1260.000	29.409	981.134	670.287	352.04	121.94
14	SO2(g)	1260.000	2.791	178.779	63.600	50.62	-179.48
15	N2(g)	1260.000	12.393	347.165	282.477	136.23	136.23
16	O2(g)	1260.000	14.225	455.190	324.210	165.20	165.20
17	**Flue dust (Conv. 1 return)**	1260.000	0.095	12.099	0.003	4.01	-19.20
18	Cu2O	1260.000	0.017	2.415	0.000	0.77	-0.03
19	Fe3O4	1260.000	0.028	6.402	0.001	1.95	-6.64
20	SiO2	1260.000	0.049	2.932	0.001	1.16	-11.19
21	CaO*Al2O3*2SiO2	1260.000	0.001	0.351	0.000	0.13	-1.35
22	Heat loss (Converter I):						10.00

BAL IN1 OUT1 IN2 OUT2 IN3 OUT3 IN4 OUT4 IN5 OUT5

	kmol	kg	Nm³	kWh	kWh
BALANCE (2)	-3.956	0.000	-35.921	406.46	0.00

Exit Stream

Fig. 13. The OUT2 sheet (Converter I), gives the output from the first part of the converter. The formula **InCa2 Analysis L29 100** in cell C5 means that the total Ca is distributed as the percentage given in cell L29 on the Analysis sheet.

Drawing Flowsheets (Flowcharts)

Additional sheets may be used to collect, for example, all the necessary input for the process into one sheet. They may also be used to collect calculated process parameters, for example the amount of Cu in a stream. Figure 14 shows the process layout for the Flash Smelting Furnace process.

Insert, Graphical Object, ... selection gives possibility to draw lines, rectangles, etc. on the additional sheets. However, it is recommended to draw flowsheets using Format, Border, ... and Format, Pattern, ... selection because these properties are more compatible with Excel 95, 97 and 2000. Arrows may be drawn using Insert, Graphical Object, Arrow selection.

HSC graphical objects are compatible only with Excel 95. This means that if you want to get the graphical objects to Excel-files then you should save using File, Save XLS 5 file, ... dialog.

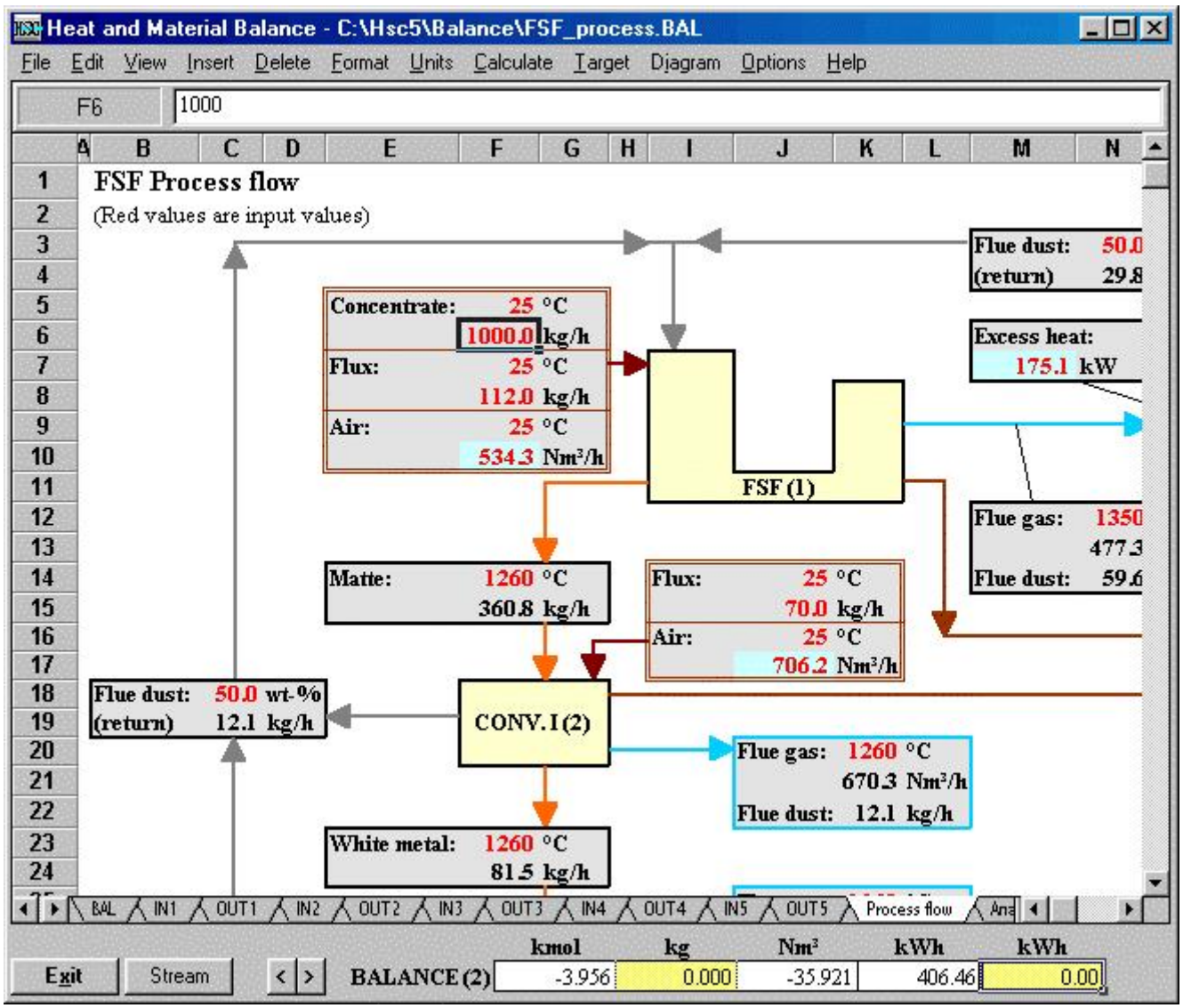


Fig. 14. Process layout and input sheet for the Flash Smelting Furnace process.

Figure 15 provides a more detailed analysis of the process. The model is constructed so that the inputs are given as species analysis and the outputs are calculated. The elemental distributions are also inputs, in other words the user defines the wt- for the elemental distributions into the given species and streams. This is achieved using the automatically defined names, for example InCa and InO2, and thus always keeping the elemental balance at zero. The model may then be used to balance the heat balances of the process, which enables the user to calculate one unknown parameter per balance area. The unknown parameters calculated in the FSF process.BAL example are indicated by a light blue cell background. The calculated parameters may be changed using the Target Dialog option, which is described in further detail in chapter *8. ar et Dia o* .

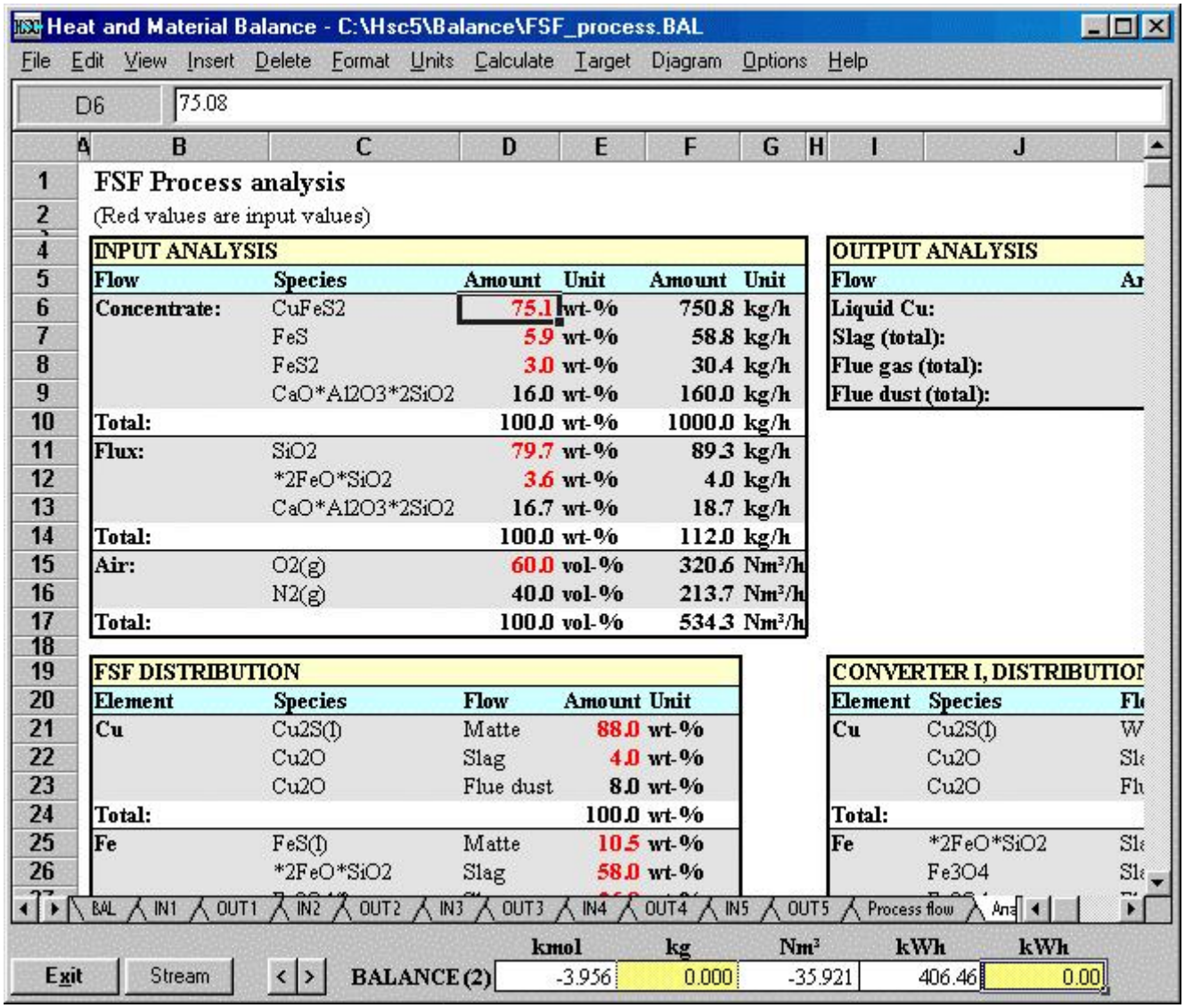


Fig. 15. Detailed analysis of the input and output streams and the elemental distributions into different species. The distributions are given in wt- (weight percentage).

11.10 General Considerations

In the Heat Balance module it is possible to use the new add-in functions provided by HSC 5.0. The functions should be enabled automatically, this may be seen from the **File** selection in the menu. A checked **HSC5.dll On** indicates that the functions are available and a checked **HSC5.dll Off** indicates that they are disabled. Sometimes it is necessary to browse the location of the add-in file manually. This is done by selecting **File Add-Ins** from the menu and then browsing to your Windows system directory (for example c: Windows System in Windows 98) by pressing the **Browse...** button. Select the file HSC5.dll . A more detailed description of the functions available may be found in Chapter *2 . ce dd Ins.* It is, however, not recommended to use add-in functions for very large worksheets, since a complete recalculation of the worksheet is necessary each time a change is made in the worksheet. This is the case *on* when using add-in functions.

Please do not use temperature formulae that are linked to other temperature values *it in a strea* , instead link them to the *strea* temperature cell or any cell in a user sheet. Otherwise the temperatures will be updated only after the next change. Notice also that a change in the temperature value is required for the whole stream to be updated accordingly.

Simple graphical objects may be inserted by selecting **Insert Graphical Ob ect** from the menu. The shapes are: Line, Rectangle, Oval, Arc and Polygon. After inserting, the objects may be modified by first selecting the object and then selecting **Format Ob ect** from the menu.

The **Latent H** column (= specific heat) is used to describe the energy which may be released when the compound is cooled down from the given temperature to 298.15 K. In other words, it contains latent heats (= enthalpies of the possible phase transformations) but also specific heats. The enthalpies given in the **Total H** column contain the values of the Latent H column as well as the heats of formation reactions. These values are used to calculate heat balances.

In **molten mixtures** such as oxide slags, substances can exist in liquid state at lower temperatures than their melting points. In these cases it is possible to use an (l)-suffix at the end of the formulae, see Fig. 1. This will force HSC to use data of the liquid state for species with an (l)-suffix.

The **Red Font Shield** property is sometimes useful if you want to prevent accidental changes to cells. You can activate this property by selecting **Format Red Font Shield** from the menu. After this selection you can edit only those cells which contain red font.

If you have carried out a laboratory or industrial scale experiment or process calculations you usually know:

1. The raw (input) materials and their amounts and temperatures.
2. The product (output) materials and their amounts, temperatures and analysis.
3. The input heat and heat losses can first be estimated as zero, if not available.

In order to calculate a heat balance you must first convert the (elemental) chemical analysis of the raw materials and the products into input and output substances (species). Sometimes this step is the most difficult, so you may choose to carry out this procedure

using the HSC Mineralogy Iterations module, see Chapter *22. inera o iterations*. When this is completed, simply type the input substances (species) into the IN1 Sheet and the output substances into the OUT1 sheet. Immediately after that you will see the heat and material balance on the bottom line. You can also test the procedure described in chapter 5.

It is important to check the element balance by selecting **Calculate Element Balance**, in order to avoid incorrect material and heat balances. This can also be used to check the validity of the chemical analyses and the other amount measurements of the experiment if the user input is based on this data.

When creating a multiple balance area model, selecting **Calculate Total Balance** shows an overview of all balance areas in one window. This is useful for a quick check where the material and or heat balance are not zero. It also shows the total (or net) material and heat balance for all balance areas. It is then easy to see which balance areas produce heat, which require heat, and indications of how the heat could be tranferred within the process.

On the basis of the final results, conclusions can be made as to whether extra energy is needed or increased insulation is required or if the reactor needs cooling on a large scale. The heat losses may also be determined using the HeatLoss module. Combining the two modules provides a powerful way of calculating processes.

It is important to note that this is a real heat balance for engineering purposes, which also takes into account the kinetic aspects if the user input is based on real experimental data. The heat balance, which can be obtained from the equilibrium calculations, is theoretical in this respect. It is valid only if the equilibrium is reached in the real process.

11.11 Heat Balance Examples

See the examples provided by the HSC package by selecting **File Open** from the menu, see Fig. 1, and select some of the ready made files in the directory for editing. HSC 5.0 can read the old HSC 2.0 Heat Balance text-files, but it cannot save them in the old format. The new HSC 5.0 Heat Balance files save all the sheets and formats, not only the text data.

1. Preliminary check for a heat balance (CUSMELT.BAL file)

For some processes based on reaction equations or equilibrium calculations, the heat balance can easily be checked by entering the assumed input and output substances as well as their temperatures and amounts, see example CUCONV.OHE and CUSMELT.OHE, Fig. 1.

2. Adiabatic temperature of the flame (BUTANE.BAL-file)

In an adiabatic process heat losses from and heat input to the system are zero, i.e. there is no heat exchange with the surroundings through the system boundaries. Therefore, the adiabatic temperature equals the highest attainable temperature from a flame or a chemical reaction. By typing the raw materials into the IN1 sheet and the products into the OUT1 sheet it is possible to see the adiabatic temperature by selecting Calculate Temperature Balance from the menu, Fig. 3, see example BUTANE.OHE.

3. Dimensioning of an evaporator (H2O.BAL-file)

The evaporator dimensions can be optimized manually by typing the input substances into the IN1 sheet and the desired output substances, amounts and temperatures into the OUT1 sheet. Once these have been entered, you can start to change the amount or temperature of the input vapor (input heat if heated by electricity) manually, in order to find the optimum values. See example H2O.OHE.

4. Net and gross heat value of coal, fuel oil and natural gas.
(Coal1-, Coal2-, FuelOil1-, FuelOil2-, NatGas1.bal-files)

The Heat balance module makes it possible to calculate the Heat Values (Calorific Values) for different fuels. Examples for coal, fuel oil and natural gas are found in the example files. Notice that the chemical structures of the fuel oil and coal are very complicated, however, heat values based on the elemental analysis will usually give sufficiently accurate results for practical applications.

5. Outokumpu Flash Smelting Furnace process (FSF process.BAL-file).

This highly simplified process case consist of five balance areas linked together.
The balance areas are:
1) Flash Smelting Furnace
2) Converter I
3) Converter II
4) Boiler
5) ESP
The process input values are provided in the **Process flow** sheet and in the **Analysis** sheet. By pressing **F8** or by selecting **Iterate All** from the **Target Dialog**,

the heat balances are calculated. The values calculated are in the **Process flow** sheet and indicated by a light blue cell background.

6. Iron production process (Iron process.BAL file).

The example in this file is a very simplified model of an iron production process consisting of three balance areas:
1) Pelletizing
2) Coking
3) Reduction
The process and its most important parameters are shown in the **Process flow** sheet, with a more detailed analysis available in the **Analysis** sheet. Notice that only the material balances are zero and iterated according to what is set in the Target sheet (or Target dialog). The heat balances are not iterated and therefore not zero.

12. HEAT LOSS

The main use of this module is to estimate total heat loss or draw the temperature profile of a wall or reactor. However, it can also be used to compare different materials and different setups, for example the use of insulation when a material has a critical maximum temperature or when the outside air cannot exceed a certain temperature. The conduction, convection and radiation databases also provide a resource as simple reference tables for material properties. Figure 1 shows an example of a heat loss wall calculation for a smelting reactor with the temperature profile shown in rows 9 and 10.

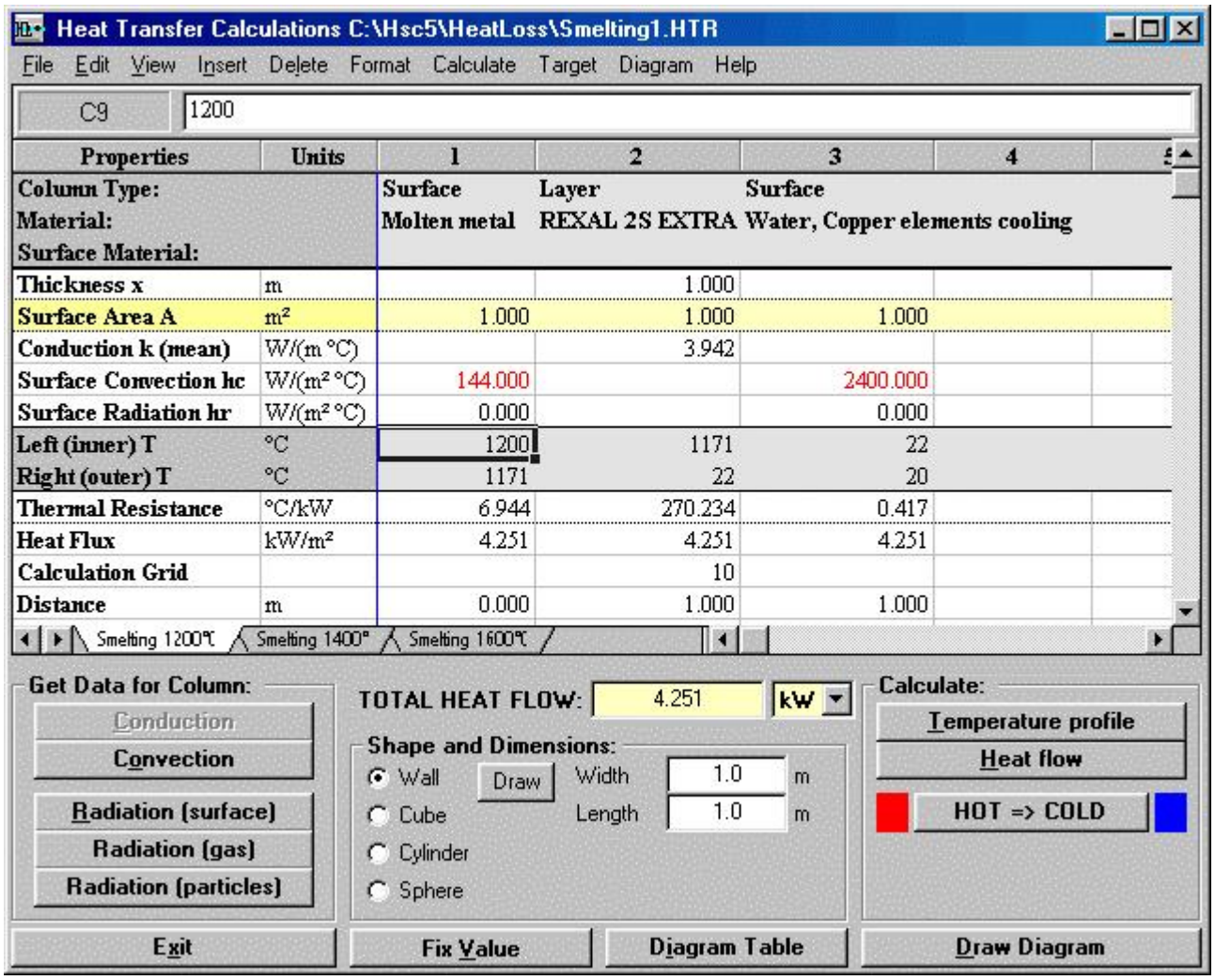


Figure 1 *eat oss ca cu ation e a e o a s e tin reactor a .*

The basic concept of the module is that the user specifies the system setup by selecting the geometry of the object, inserting columns, specifying a material for each column, specifying thicknesses (if any) and entering either one temperature point and a total heat loss or two arbitary temperature points within the same sheet. From these inputs the program can calculate either the temperature profile or the total heat loss. The temperature profile (profiles) can then be plotted graphically.

The main workbook is very similar to Excel-type worksheets in terms of the properties that can be found in the menu and also most of the Excel worksheet functions are available.

The new Heat Loss module may be used, for example, to estimate heat loss values needed in the Balance module. The user must first specify the column types, which can be **Layer**, **Layer contact**, **Surface** and **Enclosure**. The thickness must be specified for **Layer** and **Enclosure** columns, while **Layer contact** and **Surface** columns have zero thickness. Two basic types of calculations may be carried out:

1. **Temperature profile** with fixed heat loss and one temperature point.
2. **Heat Loss** with two fixed temperature points. This will return the heat loss but also the temperature profile.

The calculation routine handles conduction, convection and radiation properties as functions of temperature but fixed values may also be used by selecting the value and pressing the **Fix Value** button. These fixed values are shown in red on the calculation sheet.

Temperature profile as well as some other user specified values may also be presented in graphical form. Target dialog may be used to find, for example, minimum layer thickness. The calculation specifications may be saved to files for later use.

12.1 Basic Calculation Procedure

1. Select geometry.

To select the choice of geometry, click on the desired option button in the frame **Shape and Dimensions**. The available options are wall, cube, cylinder and sphere. *It is i reco ended to start t e ca cu ations it a si e a case* and then to continue with more complicated shapes later.

2. Select dimension.

When selecting the geometry, appropriate dimension textboxes automatically pop up. The dimensions are always *inner* dimensions.

3. Insert new column.

The user may specify the layout of the heat transfer object by selecting **Insert** from the menu bar and then the desired column type. There are four types of columns: **Surface**, **Enclosure**, **Layer** and **Layer contact**. **Surface** columns must be inserted to the left and or to the right of the other columns. **Enclosure** columns must be inserted between two **Layer** columns. Finally **Layer contact**, **Enclosure** and **Layer** columns must all be inserted between **Surface** columns.

4. Specify heat transfer type.

You can select the type of heat transfer to study in two ways: either *anua* or *usin t e database.*

Man ally

1. Write the name of the material gas liquid on the second row of the table in the current column.
2. Select the desired heat transfer factor:
   - Layer column: Enter the mean conductivity for the material (k) on row 6.
   - Surface column: Enter the convection and or the radiation coefficient

(h_c and or h_r) on row 7 and or row 8. It is also possible to specify the emissivities and or absorptivities on rows 20-23, in this case please make sure that the radiation coefficient is *un i ed*.

- Layer contact column: Enter the thermal resistance on row 11.
- Enclosure column: Enter the convection coefficient on row 7 and or the radiation coefficient on row 8. It is also possible to specify the emissivities on the *ad acent a er co u ns*, in this case please make sure that the radiation coefficient is *un i ed*.

3. For each value entered press the **Fix Value** button, unless the value is already fixed. By doing this the program will use these given values, indicated by a red font, when calculating instead of the database values.

sing the database

1. Press the corresponding button in the frame **Get Data for Column**
   - Layer column: *onduction* button.
   - Surface column: *on ection* or *adiation* button.
   - Enclosure column: *on ection* or *adiation* button (radiation for adjacent layer columns).
   - To specify the desired material gas liquid, place the cursor on top of it and press **Select**. Now the data for the material will be transferred automatically to the column on the main sheet where the cursor is located. Note that sometimes several database sheets are available, for example the convection *tab e* or *unction s eet*. You will know that the data has been transferred from the database sheet to the calculation sheet, once the selected material name appears on the material name rows 2 or 3.

5. Specify thicknesses.

Type the *ic ness* on row 4 for every **Layer** and **Enclosure** column. **Surface** and **Layer contact** columns have zero thickness.

6. Repeat steps 3, 4 and 5 until the desired layout is achieved.

7. Calculate results.

To calculate results for a cylinder or cube, first select whether to calculate all sheets or just the active sheet, by pressing the appropriate option button in the **Calculate** frame. By, for example, calculating only the wall sheet of a cylinder, pipe calculations can be obtained. The two basic calculation types are:

emperat re ro ile (press the **Temperature profile** button)

- Specify the total heat loss by selecting the appropriate unit (W, kW or MW) and by typing the heat loss in the textbox.
- Specify *one* fixed temperature point by the cursor.
- For cube or cylinder geometry, specify calculation range by selecting either **Calculate all sheets** (calculates all walls) or **Calculate active sheet** (calculates active wall) from the option buttons.
- Note that when calculating all sheets, the temperature profiles will be iterated so that the temperatures in the first columns (inside temperatures), as well as the outside temperatures, are the same for all sheets.

Heat Flo (press the **Heat flow** button):

- Specify temperature points using the cursor.
- 0 or 1 point selected (by cursor position): The *o e ran e* will be calculated.
  - Cube or cylinder geometry: Specify calculation range by selecting either **Calculate all sheets** (calculates all walls) or **Calculate active sheet** (calculates active wall).
  - sheets will have the same inside and outside temperatures as on the current sheet, once the calculation is completed.
- 2 points selected (by selection): The range *bet een t ese oints* will be calculated.
  - Cube or cylinder geometry: The other sheets will *not* be calculated.
  - The *end te erature oints* in the selection will remain constant.

8. Press the *Dra Diagram* button for a graphical plot of the temperature profile.

12.2 Heat Loss Examples

12.2.1 Examples provided by HSC

See the examples provided by the HSC package by selecting **File Open** from the menu and selecting the appropriate file (examples exist in HSC5 Heatloss -folder).

1. Simple Case with fixed conduction and convection values (SimpleCase.HTR)

In this example the furnace wall is made of two layers, the inside temperature is 700 C and the outer surface is cooled with air (20 C). The conduction and convection values are fixed. In this case the heat flow through each layer and through the surface may easily also be calculated manually:

Firebrick: 1.5 m^2 (700 - 418 C) 0.4 W (mK) (0.23 m) = 735 W
Silica brick: 1.5 m^2 (418 - 50.63 C) 0.2 W (mK) (0.15 m) = 735 W
Air: 1.5 m^2 (50.63 - 20 C) 16 W (m^2K) = 735 W

2. Radiator heat (Radiator.HTR-file)

This example calculates the heat output of a radiator at room temperature (20 C) and at three different water temperatures, when the water flow to the radiator is zero. Select the appropriate sheet according to the inside water temperature (40 C, 50 C or 60 C) and press the **Heat flow** button to view changes in the output heat. Adjustments can also be made to the width or length (height for a vertical wall) of the radiator to examine what influence this has on the result.

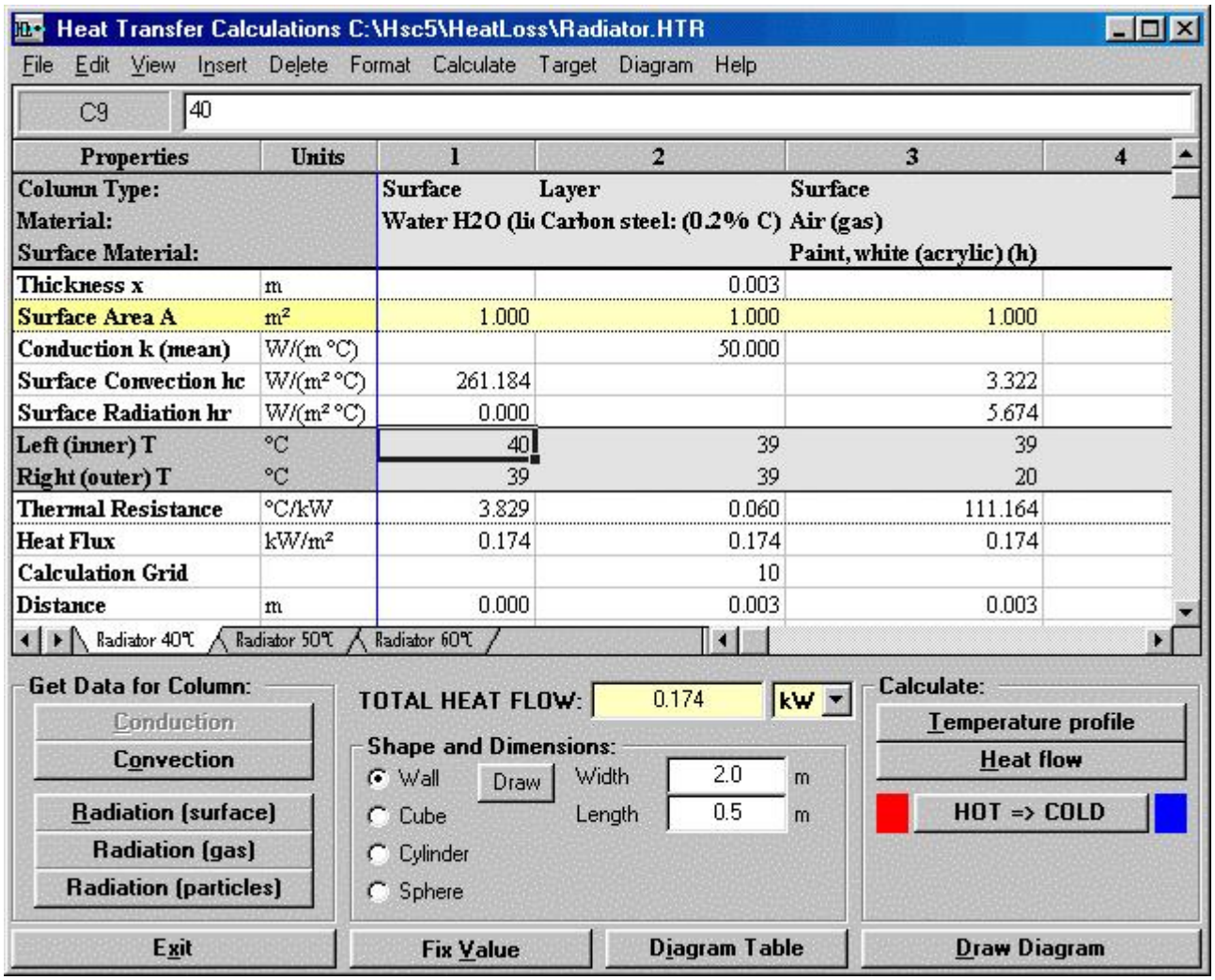


Figure 2 *adiator ca cu ation e a e.*

3. Heat loss from uninsulated pipe at constant T (incropera94 503.HTR file)

This is an example taken from Fundamentals of Heat and Mass Transfer by F. P. Incropera and D. P. DeWitt (page 503 in the 4th edition) 1 . In this example the heat loss from an uninsulated horizontal pipe is calculated with knowledge of the surface temperature (165 C) and the air temperature (23 C).

4. Heat loss from insulated pipe at constant T (incropera94 504.HTR file)

Example 3 above is extended by insulating the pipe with a 25 mm thick urethane layer. Notice how the heat loss decreases significantly.

5. Heat loss from a hot water tank (Hotwatertank.HTR file)

This example is a calculation of heat loss from a hot water tank. By specifying the materials, dimensions, geometry, water and air temperatures the total heat loss for the tank can be calculated. The insulation thickness can easily be increased separately for the top, wall and bottom sides, in order to lower the heat loss from the tank.

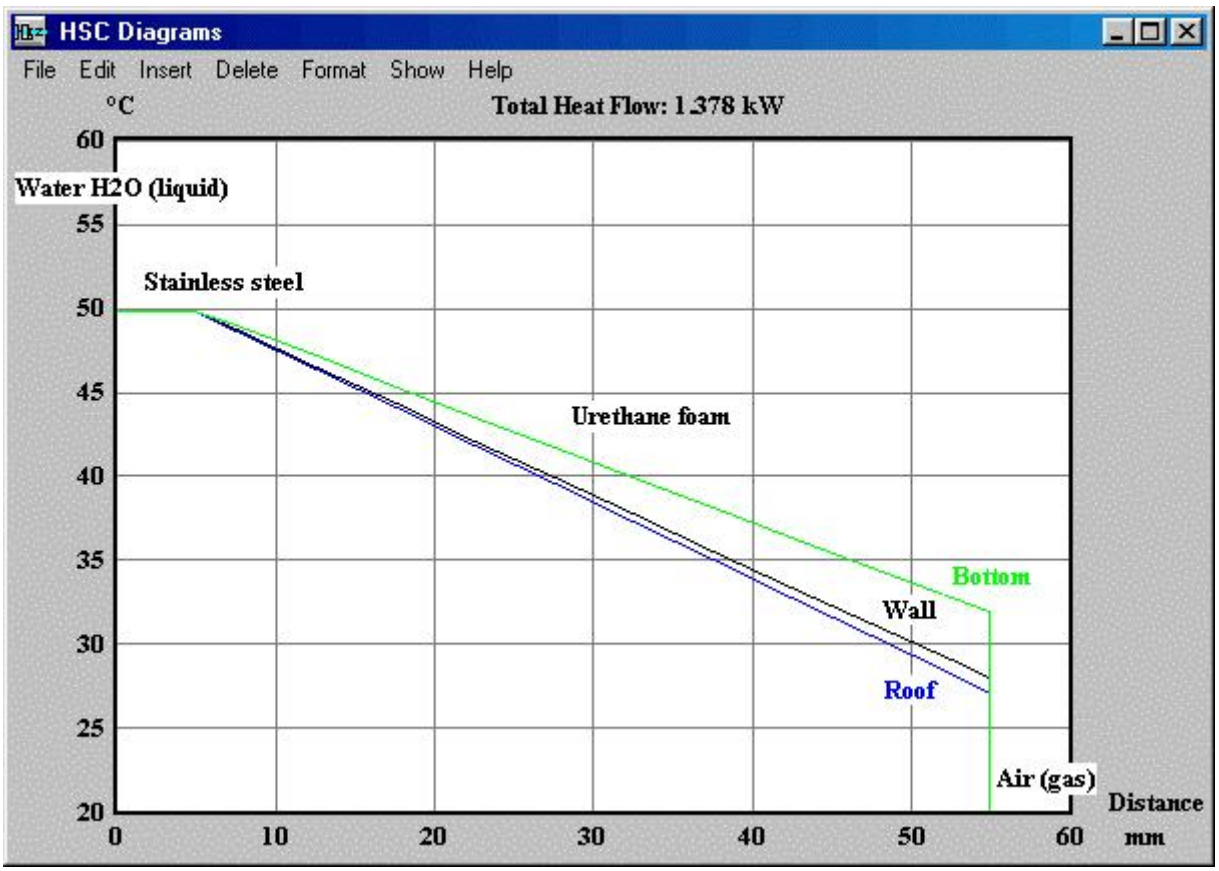


Figure 3 *e erature ro i es or t e ot ater tan .*

6. Oil furnace (OilFurnace.HTR file)

In this example the heat flow due to hot flue gases and internal convection in a furnace is calculated. The flue gas composition can be seen from the **Gas Mixture Radiation** dialog by pressing the **Radiation (gas)** button. The gas contains the following radiating species: $H_2O(g)$ 11.08 vol- , $CO_2(g)$ 11.69 vol- and $SO_2(g)$ 0.05 vol- . This is a typical flue gas composition for fuel oils. The gas temperature

is 1200 C and the wall temperature is 500 C. The wall surface material is *tee s eet it s in due to ro in* and the convective gas is approximated as *ir bar* . These can both be found from the database. There is a 10 mm thick *ain carbon stee* layer surrounding the furnace. It is important to insert a **Layer** or a **Layer contact** column to the *ri t* of the **Surface** column, in order to calculate *interna* radiation (or convection), since the program otherwise assumes *outside* radiation (or convection). By entering a very low thickness value for the **Layer** column (row 4), or by entering zero thermal resistance for the **Layer contact** column (row 11), the inside surface temperature may still be used in the **Layer** or **Layer contact** column.

7. Reactor heat loss calculation (Reactor1.HTR and Reactor2.HTR)

In this example the total heat loss of a reactor is estimated. The given input data are the dimensions of the reactor, the surface temperature and the surrounding temperature (room temperature). The surface material in the Reactor1 example is *tee s eet it rou o ide a er* and in Reactor2 *aint, ite acr ic* . The convective gas is *ir bar* in both examples. Since the surface emissivity is lower in Reactor2, the heat loss is smaller.

8. Smelting reactor calculation (Smelting1.HTR, Smelting2.HTR and Smelting3.HTR files)

In this example the temperature profiles and heat losses of three different types of smelting reactors are calculated. The default input values given in this example have not been taken from any specific reactor type, however the input values may easily be changed in order to achieve a more realistic situation.

12.2.2 Simple Step-by-step Example (creating Smelting1.HTR)

The following steps describe how to create the Smelting1.HTR example from the very beginning. The final example can be used to approximate heat losses through a smelting reactor wall. The temperature profiles for different inside temperatures can be plotted using the Draw Diagram button.

1. Select **File New** from the menu.

2. Select **Insert Surface column** and press the **Convection** button.

3. From the Convection window (to the left), select the **Function** sheet.

4. Select **Water, Copper elements cooling** by moving the cursor to row 10.

5. Press the **Select** button.

6. Select **Insert Layer column** in the main sheet and press the **Conduction** button.

7. Type **REXAL 2S EXTRA** in the yellow textbox in the Conduction window and press the **Find** button. The cursor will now automatically move to the correct position in the database.

8. Press the **Select** button.

9. Type **1** as the layer thickness on row 4 in the main window.

10. Select **Insert Surface column** and press the **Convection** button.

11. Select the **Function** sheet from the Convection window.

12. Select **Molten metal** by moving the cursor to row 4.

13. Click the **Forced Convection** option button and type **0.02** (= 2 cm s) in the speed textbox.

14. Press the **Select** button.

15. Type **1200** as the inside temperature in cell C9 and **20** as the outside temperature in cell E10.

16. Press the **Heat loss** button.

Heat Loss will now calculate the total heat loss from a 1x1 m square of the reactor wall. The inside and outside convection coefficients, calculated from the Function sheet, are based on generalized empirical data. They can, however, be used up to a reasonable accuracy for **smelting reactor** walls with **corresponding cooling methods**. The temperature profile may be plotted graphically by pressing the **Draw Diagram** button. The following procedure describes how it is possible to compare several temperature profiles within the same diagram.

1. Select **Insert Wall sheet** from the menu *t ice*. Two copies of the reactor wall are created.

2. Select **Wall2** sheet and type **1400** as the inside temperature (cell C9).

3. Press the **Heat loss** button.

4. Select **Wall3** sheet and type **1600** as the inside temperature (cell C9).

5. Press the **Heat loss** button.

6. Press the **Draw Diagram** button.

Now the temperature profiles for three different inner temperatures (1200 C, 1400 C and 1600 C) are plotted. After modifying the diagram labels and their positioning, the final diagram might look similar to the enclosed diagram (Figure 4). The setup should now also be similar to that of the Smelting1.HTR example.

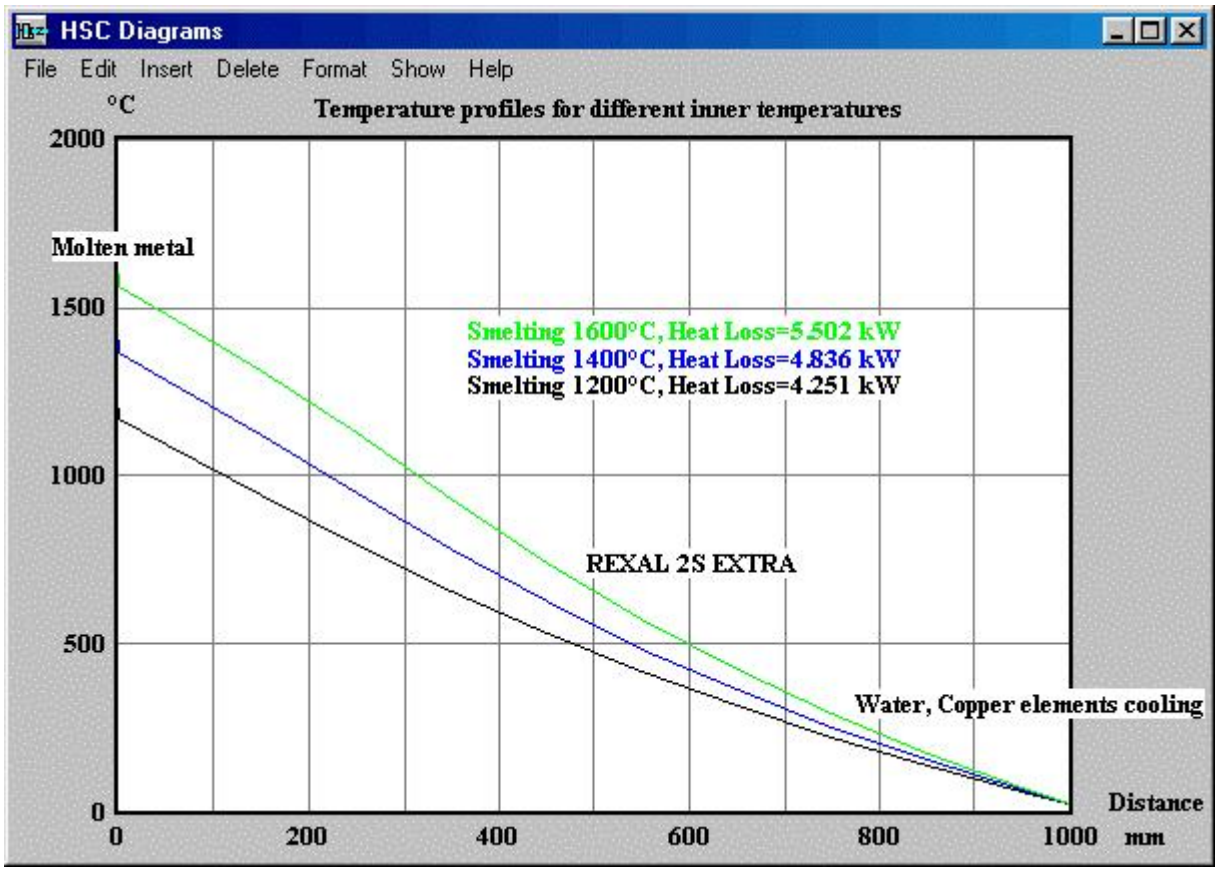


Figure 4 *e erature ro i es or e tin . ca cu ation e a e.*

12.3. Detailed Description of the Program

12.3.1 Using the Fix Value Button and the logic behind it

Once the **Fix Value** button is activated the user is able to fix values manually to make these a direct input for the calculation. A fixed value is indicated by **red font** and the caption on the button changing to **Unfix Value**. If, for example, the user wishes to specify the convection coefficient h_c directly, the specified value must be fixed (and the fluid name typed manually), otherwise the program will iterate the value using the database for the selected fluid. The program will always *irst oo or i ed a ues* and if the value is unfixed then it will use iterative methods and the databases. In the end the iteration result will be returned to the cell, for example the h_c-value. Using fixed values significantly improves the calculation speed, however these values are not always available. As a rule of thumb, the accuracy of the result will improve if it is possible to accurately specify and fix values, for example the convection and the radiation coefficients. The cells on rows 6-8 and 20-23 can be fixed, as well as row 11 if the column is of **Layer contact** type.

12.3.2 Main Window

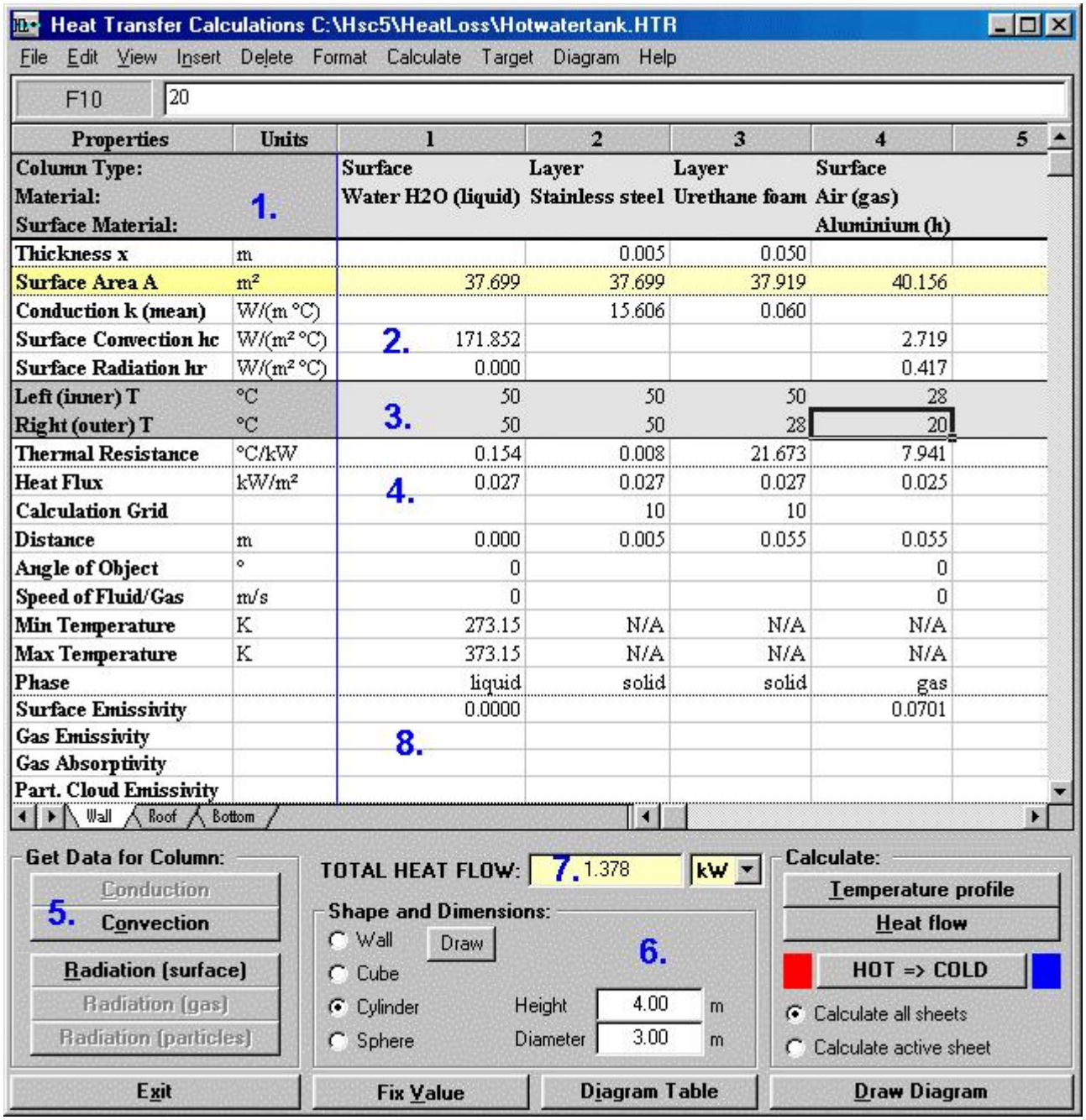


Figure 5 *ain indo a out.*

1. Headings area

This is the headings area and it cannot be altered, except for the second and third row if the material is user-specified.

2. Calculation area

The main inputs are entered in this area, with the thickness of a layer or enclosure column being mandatory. The surface area row is automatically calculated from the geometry and layer thicknesses.

3. Temperature inputs results

In this area the temperature points are entered. In order to calculate the temperature profile **one** temperature point must be specified. In order to calculate the heat loss **two** points must be specified. For three-dimensional objects (**cube and cylinder**), the user can select **Calculate all sheets** (calculate the whole object simultaneously) or **Calculate active sheet** (calculate only the active wall), by selecting the appropriate option button from the **Calculation** frame. It is also possible to select a calculation area by selecting a temperature range with the mouse. In this case *on t e ran e it in t is se ection* will be calculated. An example of this would be to select the range between C9 and F10 in figure 5.

4. Detailed information

Here you can find more detailed information about the setup. If more precise layer calculations are required, the **Calculation grid** (row 13) value may be changed. By default this is set to 10, i.e. the layer is divided into 10 elements. Note that the calculation time increases with an increasing grid size. **Speed** (row 16) indicates the speed of the fluid for forced convection. If this is zero, free convection is assumed. The **minimum** and **maximum temperatures** (rows 17-18) give the valid range for a certain material N A indicates that the limit is not available from the database. If a temperature point in the calculation result exceeds one of these points, it will be indicated by a warning message box.

5. Available data (frame)

These buttons are enabled disabled depending on the column type the cursor is placed on.

Conduction *a er co u n*

Convection *ur ace co u n* or *nc osure co u n*

Radiation (surface) *ur ace co u n* or *a er co u n* (adjacent to an Enclosure column only)

Radiation (gas) *ur ace co u n*, left of a Layer or Layer contact column (internal radiation)

Radiation (particles) *ur ace co u n*, left of a Layer or Layer contact column (internal radiation)

6. Geometry input

The option box selects the geometry and the appropriate dimension textboxes. Note that when changing from a **wall** or **sphere** (one sheet calculations) to a **cube** or **cylinder** (one or multiple sheets calculations) the wall sheet will be copied to the joining sheets of the cube or cylinder. This is useful if all walls consist of the same materials, since the user thus only has to specify the layout of one wall and then change to the correct geometry. The **Draw** button draws a simple drawing of the current geometry.

7. Heat loss input result

This can be used both as input or output data. If calculating the temperature profile the total heat loss must be entered here, but when calculating heat loss, this can also be used as a starting approximation to achieve faster calculations. The starting approximation has a maximum value of 10 MW. If a higher value is specified, the maximum value is simply inserted in the textbox by default.

8. Radiation inputs results

Rows 30-349 consist of Convection and Conduction data and rows 350- of Radiation data. These are automatically collected from the database sheet when pressing the **Select** button and these should not be changed.

12.3.3 Conduction Database

Conduction C:\HSC5\Database\HeatCond.XLS

File Edit Insert Delete Format View

Aluminium Al

	B	C	D	E	F	G
1	Thermal	Data				
2	Conduction					
3	Database	Property	Units	T1	T2	T3
4	**Aluminium Al**	**Temperature**	K	100	200	300
5	(pure)	**Thermal conductivity**	W/m K	302	237	237
6	**Aluminium 2024-T6**	**Temperature**	K	100	200	300
7	(4.5%Cu, 1.5%Mg, 0.6%Mn)	**Thermal conductivity**	W/m K	65	163	177
8	**Aluminium 195, cast**	**Temperature**	K	300	400	600
9	(4.5%Cu)	**Thermal conductivity**	W/m K	168	174	185
10	**Antimony Sb**	**Temperature**	K	293.15		
11		**Thermal conductivity**	W/m K	21		
12	**Beryllium Be**	**Temperature**	K	100	200	300
13		**Thermal conductivity**	W/m K	990	301	200
14	**Bismuth Bi**	**Temperature**	K	100	200	300
15		**Thermal conductivity**	W/m K	16.5	9.69	7.86
16	**Boron B**	**Temperature**	K	100	200	300
17		**Thermal conductivity**	W/m K	190	55.5	27
18	**Cadmium Cd**	**Temperature**	K	100	200	300
19		**Thermal conductivity**	W/m K	203	99.3	96.8
20	**Chromium Cr**	**Temperature**	K	100	200	300
21		**Thermal conductivity**	W/m K	159	111	93.7

Table

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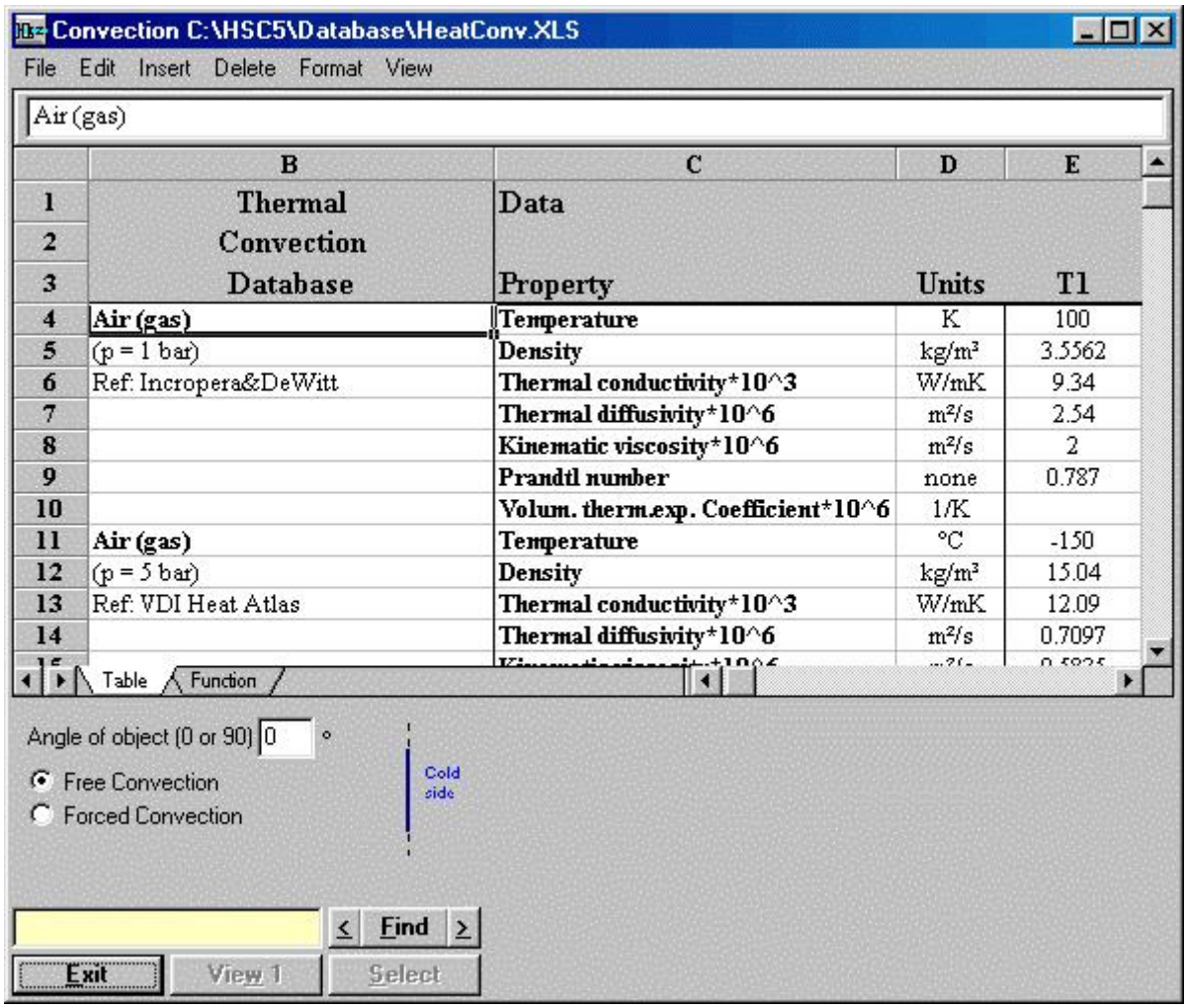
Exit View 1 Select

Figure 6 *er a onduction database indo .*

The conduction database can be edited by selecting **Edit Conduction Database** from the menu bar. Since the files are of XLS type you can also edit them directly from Excel. It is important to notice that when editing or adding new materials it is very important to follow the same pattern and syntax as the rest of the table. Temperature units can be entered in either **K** or **C** and the program will automatically calculate accordingly. The maximum and minimum temperatures are available in column A and are always given in Kelvin. This window is used when selecting the layer material by pressing the **Conduction** button.

12.3.4 Convection Database, Table sheet

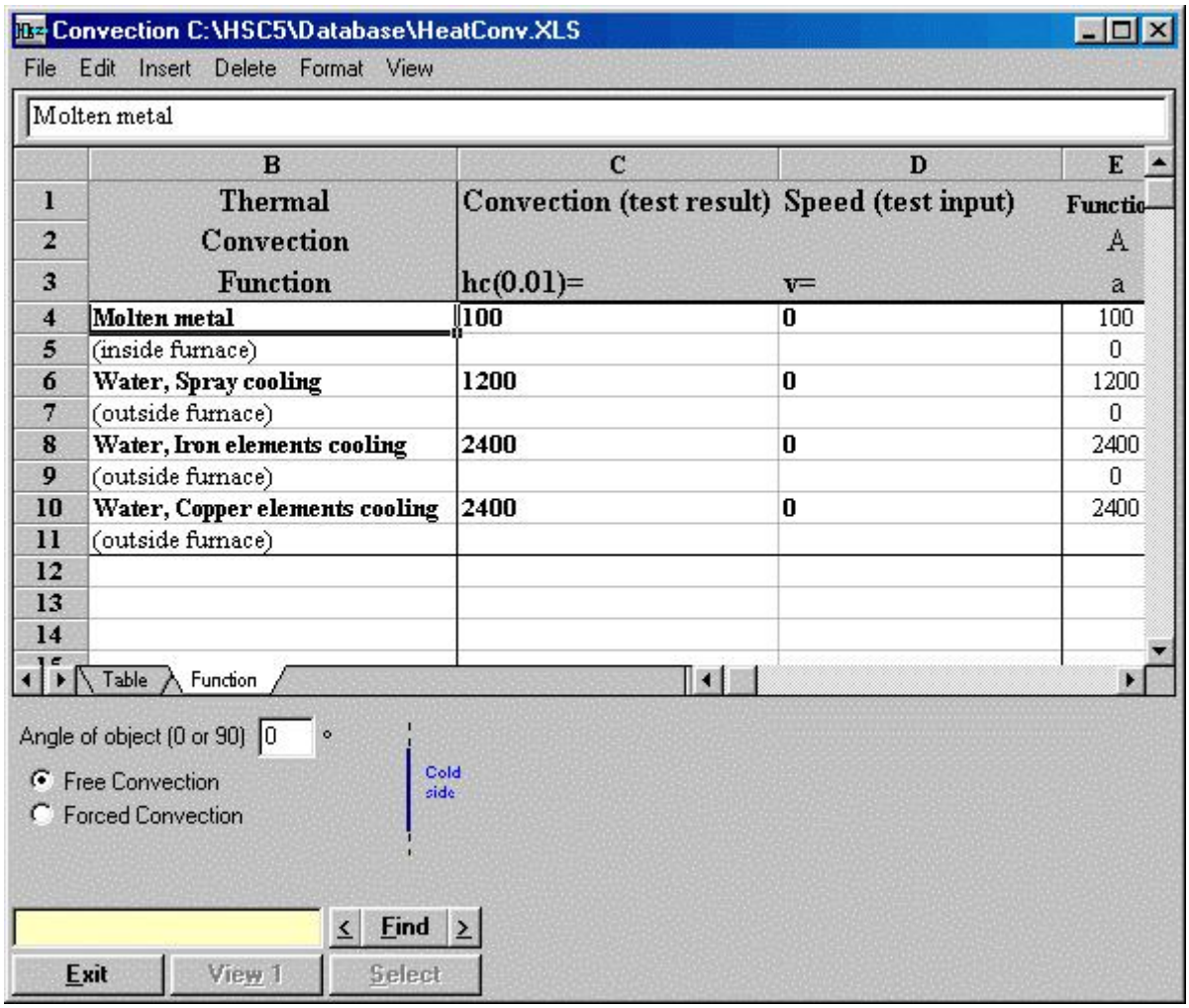


	B	C	D	E
1	Thermal	Data		
2	Convection			
3	Database	Property	Units	T1
4	Air (gas)	Temperature	K	100
5	(p = 1 bar)	Density	kg/m³	3.5562
6	Ref: Incropera&DeWitt	Thermal conductivity*10^3	W/mK	9.34
7		Thermal diffusivity*10^6	m²/s	2.54
8		Kinematic viscosity*10^6	m²/s	2
9		Prandtl number	none	0.787
10		Volum. therm.exp. Coefficient*10^6	1/K	
11	Air (gas)	Temperature	°C	-150
12	(p = 5 bar)	Density	kg/m³	15.04
13	Ref: VDI Heat Atlas	Thermal conductivity*10^3	W/mK	12.09
14		Thermal diffusivity*10^6	m²/s	0.7097

Figure 7 *er a on ection database indo , ab e s eet.*

The convection database can be edited by selecting **Edit Convection Database** from the menu bar. Since the files are of XLS type you can also edit them directly from Excel. Temperature units available are **K** and **C**. The density is not a key requirement, although it can be used in order to calculate the other properties. If the thermal expansion coefficient is not given, the program will assume that the material is an ideal gas and calculate the coefficient as $\beta = 1\ T_\infty$. The maximum and minimum temperatures are in the hidden column A and are always given in Kelvins. This window is used when selecting the surface or enclosure material and pressing the **Convection** button.

12.3.5 Convection Database, Function sheet



	B	C	D	E
1	Thermal	Convection (test result)	Speed (test input)	Functio
2	Convection			A
3	Function	hc(0.01)=	v=	a
4	**Molten metal**	**100**	**0**	100
5	(inside furnace)			0
6	**Water, Spray cooling**	**1200**	**0**	1200
7	(outside furnace)			0
8	**Water, Iron elements cooling**	**2400**	**0**	2400
9	(outside furnace)			0
10	**Water, Copper elements cooling**	**2400**	**0**	2400
11	(outside furnace)			
12				
13				
14				

Figure 8 *er a on ection database indo , unction s eet.*

The function sheet can be used for special cases of forced convection. For example, the **Molten metal** selection is an approximation of h_c based on a **polynomial function** of the speed of the molten metal inside a smelting reactor. The database uses a function of the type $h_c(v) = Av^a + Bv^b + \ldots + Gv^g$ where v is m s . The coefficients (A-G) are located between column E and K and the exponents (a-g) in the cells directly underneath these. This sheet can also be used if the convection coefficient is considered constant: simply type the constant value in column E and a zero underneath. This is shown in rows 6, 8 and 10.

For a wall or cylinder it is possible to specify an angle of 0 or 90 , which means either a **hori ontal** or a **vertical** object. When selecting the **Forced Convection** option button, a textbox for the fluid gas speed appears under the option buttons.

12.3.6 Surface Radiation Database

Surface Radiation C:\HSC5\Database\HeatRadi.XLS

File Edit Insert Delete Format View

Ideal black surface

	B	C	D	E	F	G	H
1	Thermal	Data	(h)=hemispherical emissivity, (n)=normal emissivity				
2	Radiation						
3	Database	Property	Units	T1	T2	T3	T4
4	**Ideal black surface**	**Temperature**	K	273.15			
5	(absorbs all radiation)	**Emissivity**	none	1			
6	**Aluminium (h)**	**Temperature**	K	100	200	300	400
7	(highly polished, film)	**Emissivity**	none	0.02	0.03	0.04	0.05
8	**Aluminium (h)**	**Temperature**	K	100	200	300	
9	(foil, bright)	**Emissivity**	none	0.06	0.06	0.07	
10	**Aluminium (h)**	**Temperature**	K	300	400		
11	(anodized)	**Emissivity**	none	0.82	0.76		
12	**Chromium (n)**	**Temperature**	K	100	200	300	400
13	(polished or plated)	**Emissivity**	none	0.05	0.07	0.1	0.12
14	**Copper (h)**	**Temperature**	K	300	400	600	800
15	(highly polished)	**Emissivity**	none	0.03	0.03	0.04	0.04
16	**Copper (h)**	**Temperature**	K	600	800	1000	
17	(stably oxidized)	**Emissivity**	none	0.5	0.58	0.8	
18	**Gold (h)**	**Temperature**	K	100	200	300	400
19	(highly polished or film)	**Emissivity**	none	0.01	0.02	0.03	0.03
20	**Gold (h)**	**Temperature**	K	100	200	300	
21	(foil, bright)	**Emissivity**	none	0.06	0.07	0.07	

Table

< Find >

Exit View 1 Select

Figure 9 *er a adiation database indo .*

The radiation database can be edited by selecting **Edit Radiation Database** from the menu bar. Since the files are of XLS type you can also edit them directly from Excel. Temperature units available are **K** and **C**. An (n) after the material indicates that the emissivities are normal emissivities and an (h) indicates that they are hemispherical emissivities. Note that the emissivity for a material can vary a lot depending on the surface, for example, a polished surface emits much less radiation than an unpolished one. This window is used when selecting the surface material and pressing the **Radiation** button.

12.3.7 Gas Mixture Radiation Calculator

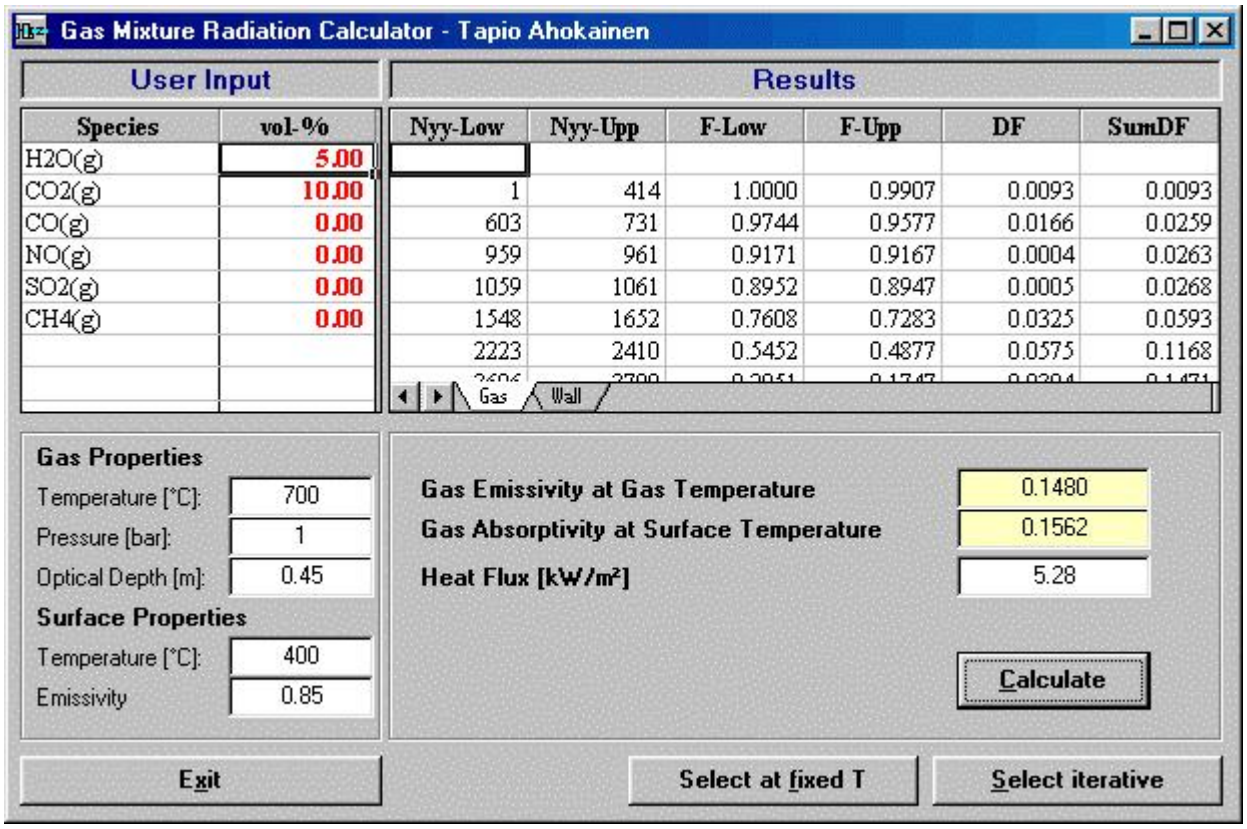


Figure 10 *er a radiation ro a as i ture.*

Using this window it is possible to calculate the gas emissivity and absorptivity by specifying the **volume fractions** (indicated by a red font), **pressure**, **gas temperature** and **surface (wall) temperature**. If the object is a cube, cylinder or sphere the **optical depth** is *auto atica* calculated accordingly, although it can still be changed in the textbox. See Table 1 for examples of optical depths for simple geometries.

The **Calculate** button calculates using the specified inputs. The **Gas** sheet shows the detailed results for the gas emissivity at the gas temperature and the **Wall** sheet shows the detailed results for the gas absorptivity at the wall temperature.

There are two ways of using the results from the calculation in the main sheet:

Select at fixed T: By selecting this the gas temperature, surface temperature and surface emissivity will be used directly in the main sheet. This is a fast way of calculating if the *as and sur ace te eratures are no n.*

Select iterative: By selecting this the program iterates emissivity and absorptivity values in the range 0 C – 3000 C for every 50 C step. The results are transferred to the main sheet for use in iterative calculations. Outside this range the values will be extrapolated. This is useful when the *as te erature and or sur ace te erature are un no n.*

12.3.8 Particle Radiation Calculator

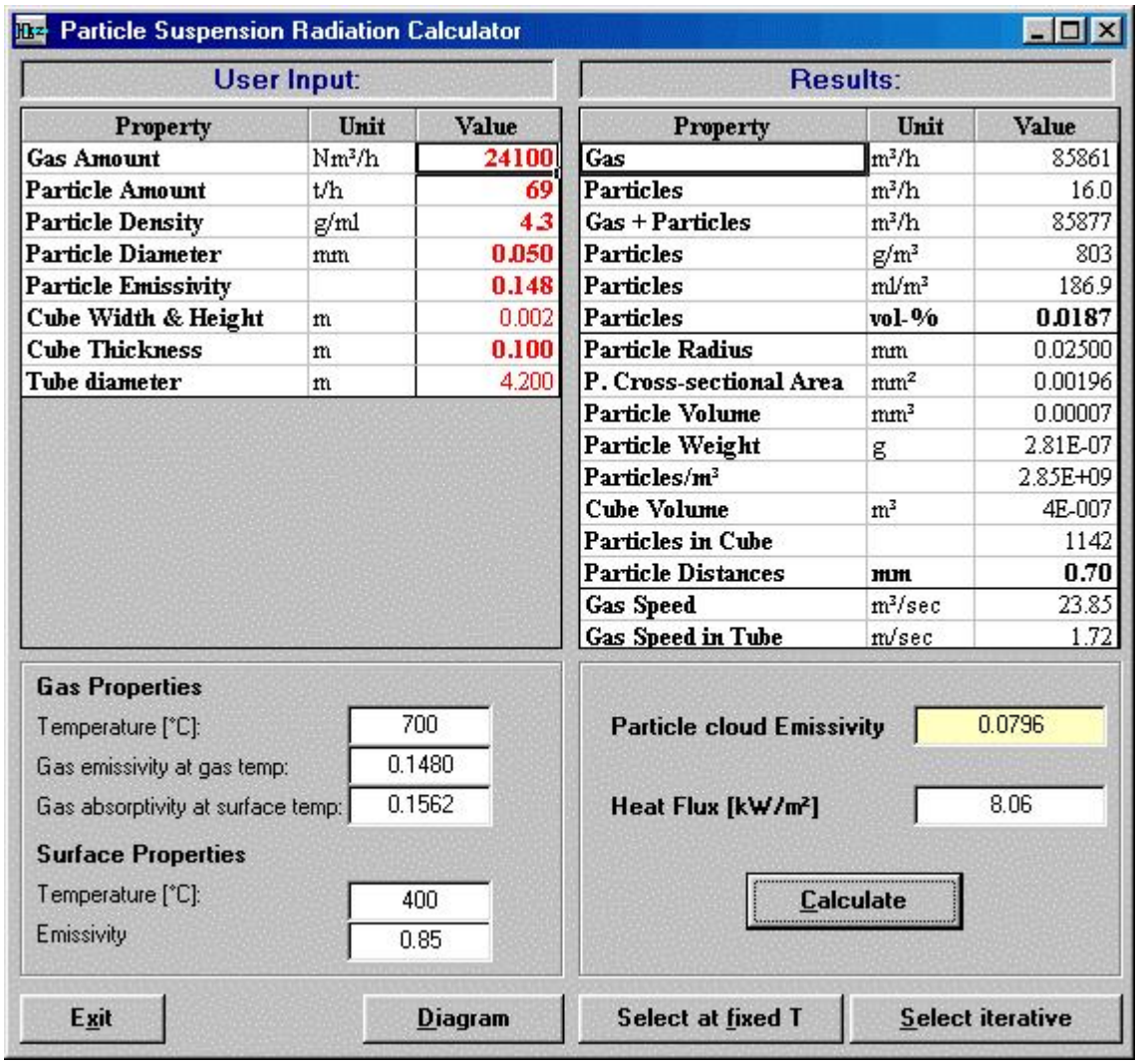


Figure 11 *artic e radiation indo .*

Using this window it is possible to calculate a particle cloud emissivity when some detailed data about the particles and the geometry of the container are known. The results can also be used at a fixed T or iteratively as in the **Gas Mixture Radiation** dialog. The **Diagram** button shows a simple drawing of a particle distribution in the container. The Gas emissivity at gas temperature and the gas absorptivity at surface temperature are automatically taken from the **Gas Mixture Radiation** dialog when available.

12.3.9 Target Calculations (Target Dialog)

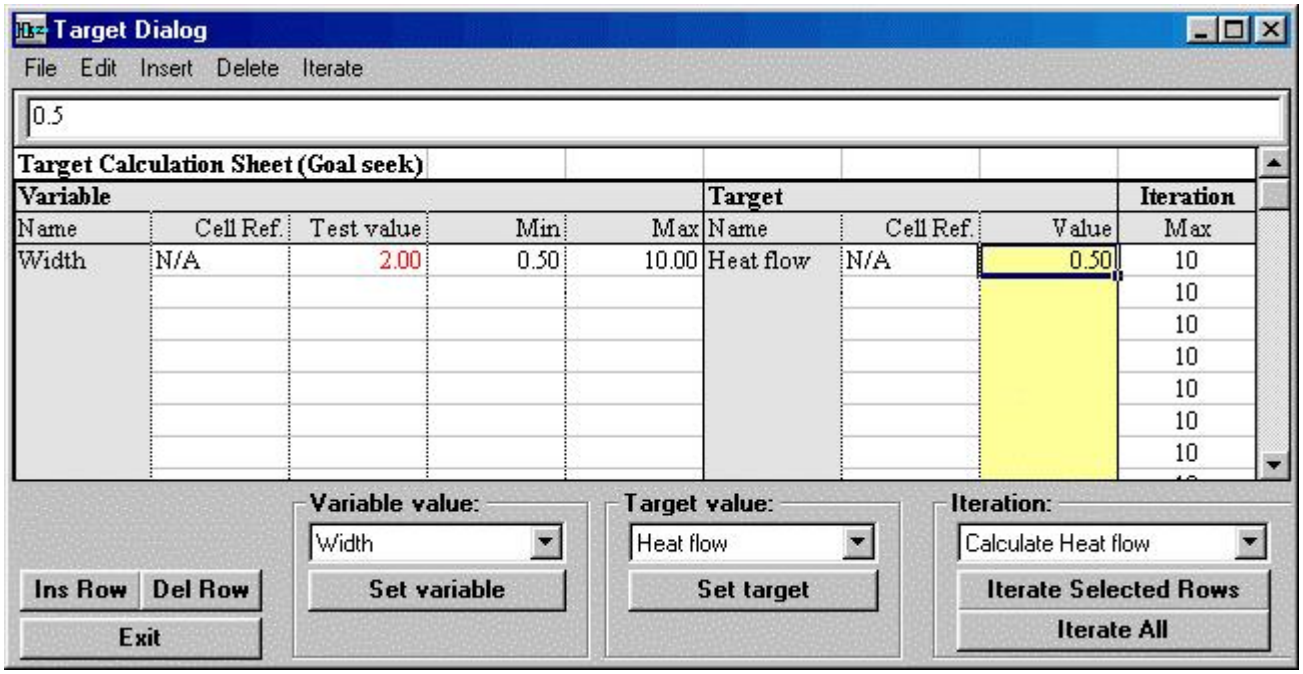


Figure 12 *ar et Dia o indo .*

The **Target Dialog** extends the calculation possibilities of Heat Loss. For example it is possible to calculate the required insulation thickness to achieve a certain heat loss or, as the example in Figure 12, the required width of a radiator to achieve a heat loss (in this case heat output) of 0.5 kW. The following step-by-step procedure describes how the Target dialog can be used for this iteration.

1. Open the file **Radiator.HTR** from the **Hsc5 HeatLoss** directory.
2. Select **Target Target Dialog** from the menu.
3. Choose **Width** from the drop-down box in the **Variable value** frame.
4. Press **Set variable**, which sets the width of the radiator as the variable value.
5. Choose **Heat flow** from the drop-down box in the **Target value** frame.
6. Press **Set target**, which sets the Heat loss of the radiator (heat output) as the target value.
7. Choose **Calculate Heat flow** (calculation method) from the drop-down box in the **Iteration** frame.
8. Write **1** in the Min column, **10** in the Max column and **0.5** in the Value column. This specifies the minimum and maximum widths and the goal value for the heat loss (heat output).
9. Press **Iterate Selected Rows**, which calculates the required width for a heat output of 0.5 kW. The required width of the radiator is 5.747 m, as can be seen from the main window.

If the **Worksheet cell** option in a drop-down box is selected, any worksheet cells in the main window may be used as either a variable or target value. An example of this could

be to iterate the required thickness of a layer (row 4) in order to achieve a certain heat loss.

12.3.10 User-specified Diagrams (Diagram Dialog)

Instead of only iterating a certain goal value, the **Diagram Dialog** may be used for graphically plotting the whole range. In the example below (Figure 13), the influence of the inside water temperature on the heat flow (in this case the radiator heat output), is shown. Step-by-step the diagram may be achieved in the following manner:

1. Open **Radiator.HTR** from the **Hsc5 HeatLoss** directory.
2. Select **Diagram Diagram Dialog** from the menu.
3. Select **Worksheet cell** from the drop-down box in the **X-value** frame.
4. Move to cell C9 in the main window (inner temperature) and press **Set X value** in the dialog box.
5. Select **Heat loss** from the drop-down box in the **Y-value** frame and press **Set Y1 value**.
6. Select **Calculate Heat loss** from the drop-down box in the **Diagram** frame.
7. Type **90** in the MAX textbox and **5** in the STEP textbox. This means that the inner temperature will range from 30 C to 90 C calculated every 5 C. The dialog box should now look similar to Figure 13.

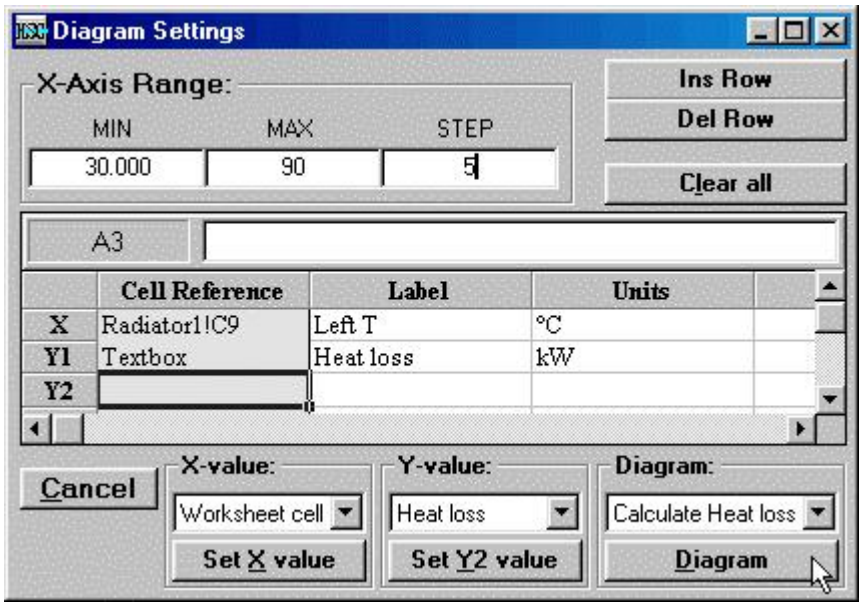


Figure 13 *Dia ra dia o indo . eci in t e dia ra .*

8. Press **Diagram**.
9. In the **Diagram Table** window, it is possible to specify properties in detail. However, if this is not necessary just press **Diagram** here too. The resulting diagram is shown in Figure 14.

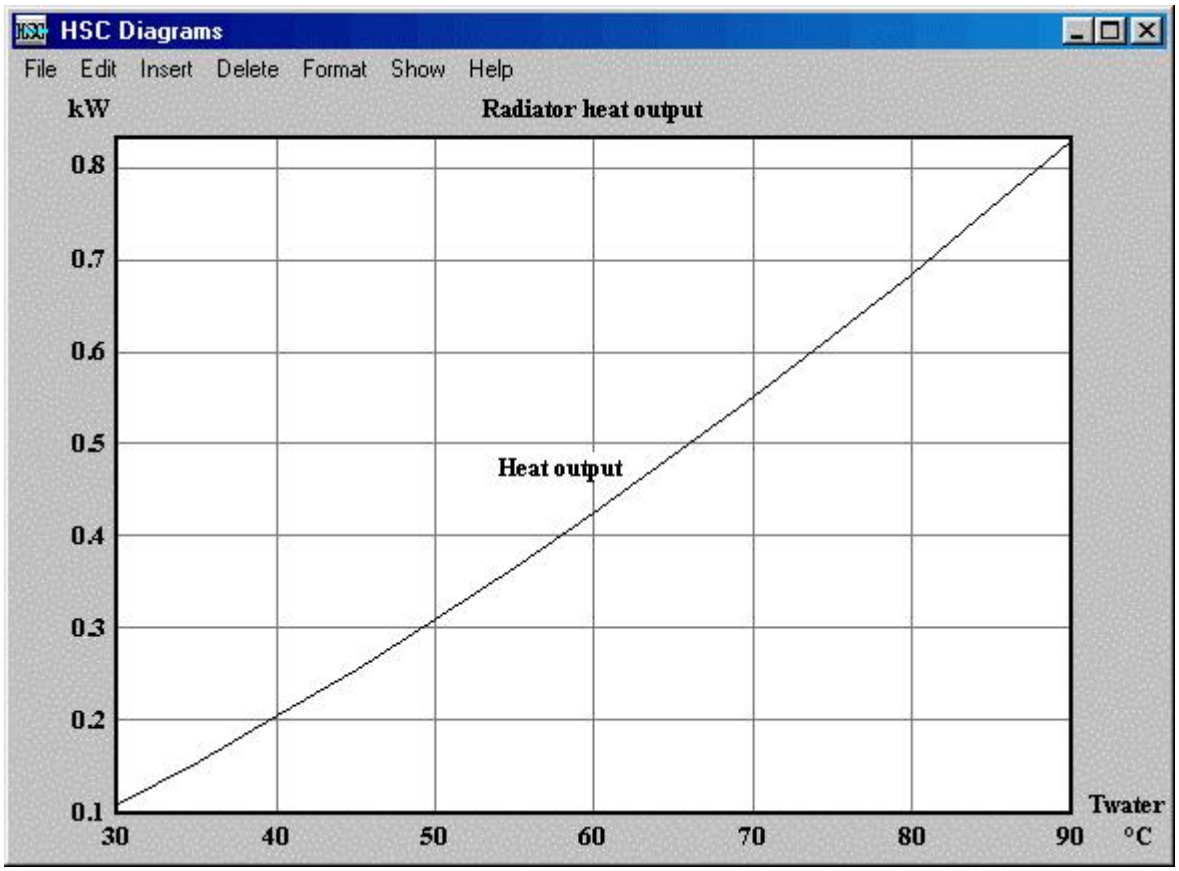


Figure 14 *Dia ra s o in t e in uence o t e inside te erature on t e radiator eat out ut.*

Another useful diagram would be to study the optimum insulation thickness of a cylinder geometry (for example a pipe or a cylindrical tank). An optimum thickness is available due to an increasing outside surface area, thus increasing convective and radiative heat loss. The following step-by-step instructions show how this diagram may be created:

1. Open **Hotwatertank.HTR** from the **Hsc5 HeatLoss** directory.

2. Select **Diagram Diagram Dialog** from the menu.

3. Select **Worksheet cell** from the drop-down box in the **X-value** frame.

4. Move to cell E4 in the main window (urethane insulation thickness) and press **Set X value** in the dialog box.

5. Select **Heat loss** from the drop-down box in the **Y-value** frame and press **Set Y1 value**.

6. Select **Calculate Heat loss** from the drop-down box in the **Diagram** frame.

7. Type **0.2** in the MIN textbox, **0.5** in the MAX textbox and **0.02** in the STEP textbox. This means that the insulation thickness varies from 0.2 m to 0.5 m and is calculated every 0.02 m.

8. Press **Diagram**. Notice that the calculation time may be significant on slow computers.

9. Press **Diagram** again in the **Diagram table** window. The final diagram should look similar to Figure 15. The theoretical optimum insulation thickness is now roughly 33 cm.

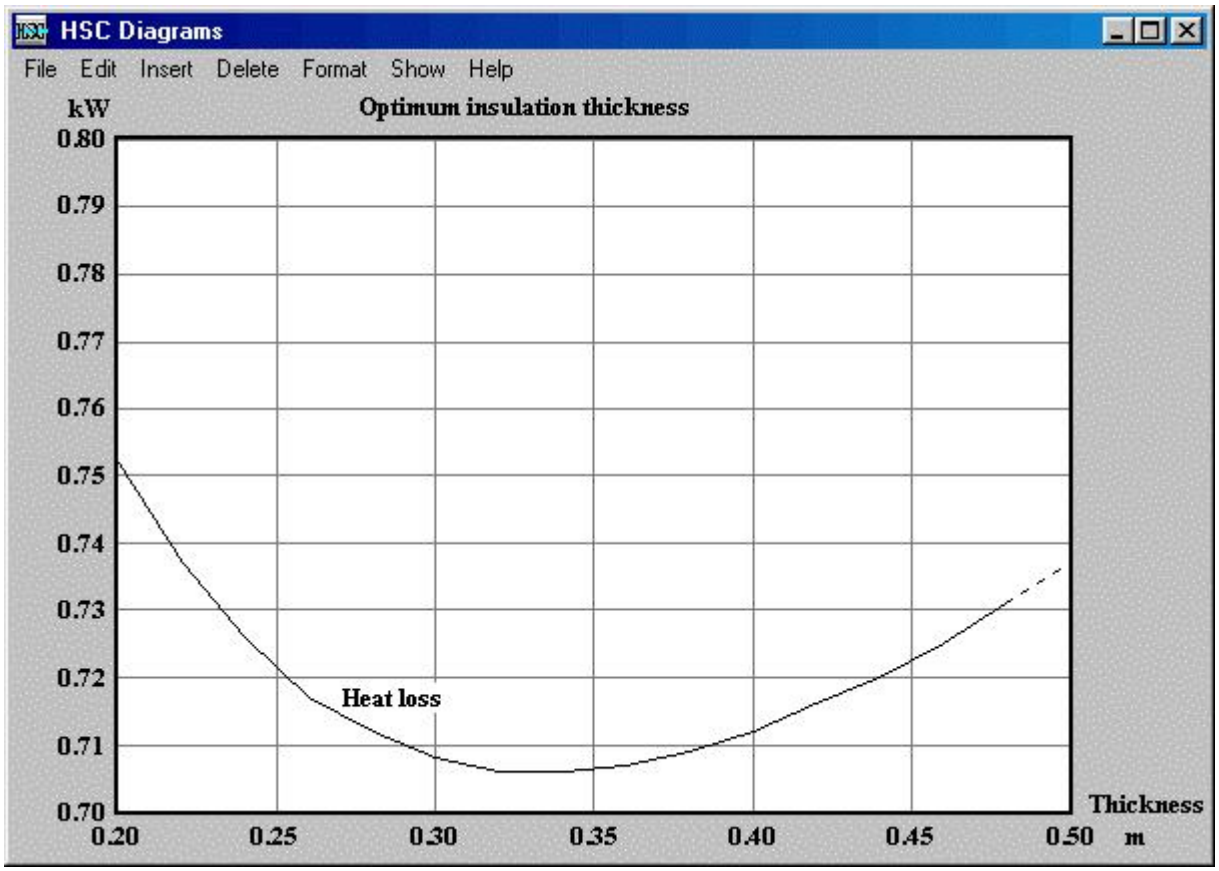


Figure 15 *Dia ra s o in t e t eoretica o ti u side a insu ation t ic ness or a c indrica ot ater tan .*

12.3.11 Limitations

The current version of Heat Loss has some limitations, some of which are listed below.

- The maximum number of *ca cu ation* sheets for the wall and the sphere is ten, for the cube four and the cylinder three. It is possible to insert up to 255 *o n* sheets.
- Inaccuracy increases with thick walls for the cube and cylinder, since the roof and bottom layers are stretched to overlap the walls. Please use surface columns only if the outer surface temperature is known, see examples Reactor1.HTR and Reactor2.HTR.
- If minimum and or maximum temperatures are not entered into the database, or directly on the sheet on rows 17 and or 18, then the extrapolated heat transfer coefficients (k, h_c and h_r) may be inaccurate.
- The convection correlations are not valid for all ranges and the results cannot be trusted outside these ranges. Detailed specifications of the valid ranges are given in Chapter 12.4.
- Inaccuracy increases with convection for small geometries.
- Forced convection cannot be used for internal calculations (gas liquid to surface) with a cube, cylinder and sphere, since the correlations are only valid for forced

external convection. Instead the heat convection coefficient h_c must be specified manually or using the **Function** sheet in the **Conduction Database**.

- If only surface columns are given for a cube, cylinder or sphere, then *e terna* convection is assumed.
- If the speed of a fluid is very low and the **Table** sheet is selected as input, the combined free and forced convection plays an important role, however this is not taken into account in this module.
- Radiation from a surface to the surroundings (or vice versa): the surface is considered gray and diffuse, that is $\alpha(T) = \varepsilon(T)$ only, this is however a valid approximation for most cases.
- Radiation emissivities for surfaces in the database are given as either normal (n) or hemispherical (h).
- The minimum temperature is –200 C and the maximum is 8000 C, however data for extreme temperatures such as these are seldom available.
- Sometimes the program is not able to iterate the answer correctly. If this happens try using a different starting heat loss (better starting approximation) and recalculate. Make sure that the minimum or maximum temperature is not exceeded.
- When calculating temperature profiles it is advised to fix the outer (cooler) temperature and let the program calculate the inner temperature. The reverse selection may easily lead to temperatures lower than 0 K if the heat loss specified is too high.

12.4. Basic Theory behind Heat Transfer

This chapter explains the basic theory of heat transfer used by the module. The equations and theory given are utilized within the program.

The *tota eat o* in one dimension (x) is

$$= \quad , \qquad 1$$

where is the heat flux and A is the unit area. It is often practical to use an analogy between heat transfer and Ohm's law in electricity. The *t er a resistance* is defined as

$$= \frac{_1 - _2}{} , \qquad 2$$

where T_1 and T_2 are the temperature points and q_x is the heat flow. The *t er a conductance* is then

$$= \frac{1}{} , \qquad 3$$

where R is the thermal resistance.

i e de endent heat flows, where $q_x = q(x, t)$, and *stead state* non-time-dependent heat flows $q_x = q(x)$ are two basic ways of identifying heat transfer problems. This program is concerned only with steady-state non-time-dependent conditions, which means that the condition is valid for infinite t.

A number of dimensionless parameters are used in this chapter. Some of them are only material-specific and can be listed in a table, while others are geometry-specific or directly related. Equations 4 to 7 show the most important ones.

The *t er a di usi it* is defined as

$$\alpha = \frac{}{c \ \rho} , \qquad 4$$

where k is the thermal conductivity, c_p is the heat capacity at constant pressure and ρ is the density.

The *ine atic iscosit* is defined as

$$\nu = \frac{\mu}{\rho} , \qquad 5$$

where μ is the dynamic viscosity.

The *randt nu ber* describes the ratio of the momentum and thermal diffusivities. This is defined as

$$\mathrm{Pr} = \frac{\nu}{\alpha}, \qquad 6$$

where ν is the kinematic viscosity and α is the thermal diffusivity.

The *t er a e ansion coe icient* is defined as

$$\beta = -\frac{1}{\rho}\left(\frac{\partial\rho}{\partial}\right) \approx -\frac{1}{\rho}\frac{\Delta\rho}{\Delta}, \qquad 7$$

where p denotes the derivative at constant pressure.

In order to calculate the heat flux, it must be separated into the three main forms: *conduction*, *con ection* and *radiation*. A more detailed description of these forms will be given in the following chapters.

12.4.1 Conduction

Heat transfer due to conduction occurs between points inside a material or materials connected to each other. Thermal conductivity is very dependent on the phase the material is in and on the temperature of the material materials. Therefore accurate calculations with a simple non-iterative formula are sometimes impossible. The use of a numerical technique such as an element method can be applied in order to achieve more accurate results.

The conduction heat flux for one dimension (Fourier's law) is calculated as

$$= - \frac{d}{d}, \qquad 8$$

where dT dx is the temperature derivative in x-direction. The function k = k(T) is generally not expressed the same way as the heat capacity function $c_p = c_p(T)$, which is a fitted equation in other parts of HSC, i.e. the Kelley equation. Instead the values of k are known at certain temperature points and linear interpolation and extrapolation may be used for temperatures outside these points. When calculating the heat flux (or flow) the distance between the two temperature points is divided into a *rid*. Hence we can calculate the heat flux by using the following approximate equation that calculates the average heat flux through a layer

$$= \frac{-\sum_{n=1} {}_{n} \cdot \left({}_{n+1\ 2} - {}_{n-1\ 2} \right)}{\cdot \sum_{n=1} \Delta {}_{n}}, \qquad 9$$

where $k_n = k_n (T_n)$ is the heat conduction coefficient at T_n (middle of the grid), m is a grid step (the amount of steps the distance x is divided into), n is the point in the middle of one grid step, $T_{n\ 1\ 2}$ is the temperature point between grid n and grid n 1, $T_{n-1\ 2}$ is the temperature point between grid n and grid n-1 and Δx_n is the thickness of the grid.

In order to be able to calculate other geometries, the *s a e actor* S in the total heat rate equation = = *Δ* is defined for different geometries according to equations 10 to 12 .

For one-dimensional plane *a s* and for *cube* walls, S is defined as

$$= \quad , \qquad 10$$

where A is the unit area for the layer and x is the thickness of the layer.

For c *indrica a s* (cylindrical coordinates), S is defined as

$$= \frac{2\pi}{\ln\left({}_{o} \quad {}_{i} \right)}, \qquad 11$$

where h is the height of the cylinder, x_o the outer radius of the layer and x_i the inner radius of the layer.

For s *erica* *a s* (spherical coordinates), S is defined as

$$= \frac{4\pi \quad {}_i \quad {}_o}{{}_o - {}_i} . \qquad 12$$

12.4.2 Convection

Heat transfer due to convection occurs between two points, where one is on a surface and the other in a fluid gas. Convection cannot normally be solved mathematically except for some laminar cases. Therefore convection calculations are mostly based on empirical equations or correlations and the uncertainty, or the margin of error in these calculations can be as high as ±20 . In the literature these correlations can also vary and the validity of the result is mostly limited to some range of one or more thermophysical properties of the fluid gas. The correlation equations used in the program are taken from references 1 and 2 .

The heat flux due to convection is calculated as

$$= {}_{c}\left({}_{s} - {}_{\infty}\right), \qquad 13$$

where h_c is the convection coefficient, T_s is the surface temperature and T_∞ is the fluid gas temperature. The mathematical models for h_c, based on experimental data, are given in dimensionless form using the Nusselt number, which is defined as

$$\overline{u} = \frac{{}_{c}}{}, \qquad 14$$

where L is the *c aracteristic en t* for the prescribed geometry.

The Nusselt number can be related through empirical data to other properties of the convective gas fluid. These properties are normally temperature and pressure dependent, hence the film temperature, $T_f = (T_s \ T_\infty)\ 2$, should be used when determining these properties. The task is then simply to describe the problem as accurately as possible and to select the appropriate correlation. Using equation 14 and the appropriate correlation equation the value of h_c can be calculated. The correlations depend on whether *orced* or *ree natura con ection* is studied. In forced convection the motion of the fluid is due to an external pressure gradient caused by a fan or a pump. In free convection the fluid motion is due to buoyancy forces only, such as gravitational or centrifugal forces. In some forced convection cases when the speed of the fluid is low there is a mixture of forced and free convection called *i ed con ection*, however this is not taken into account in this work. See . *i itations* for a more detailed description of when mixed convection conditions are noticeable.

Convection can also be subdivided into *interna* and *e terna* flow, which means that the fluid is either contained inside an enclosure or flowing freely outside a geometry. Flow in pipes is an example of a forced internal flow that has been studied thoroughly. Forced internal flow is more difficult to examine due to, for instance, the influence of centrifugal forces inside reactors. The convection coefficient are also dependent on the way the fluid is put into motion, for example, different types of propellers give different coefficients. In some cases simple experimental correlations for the convection coefficient in the form $h_c = h_c(u_\infty)$ may be used. External flow has also been studied extensively and listed below are the different correlations, which may be used for different cases. Note that for a plane wall the internal convection is equivalent to the external convection.

Free con ection

The correlation describing the nature of the flow for free convection is called the *a ei nu ber* and is defined according to

$$a = \frac{\beta(\ _s - \ _\infty)\ ^3}{\nu\alpha}, \qquad 15$$

where g is the acceleration due to gravity and β the thermal expansion coefficient.

Sometimes the *ras o nu ber,* which describes the ratio of buoyancy forces to viscous forces, is used in correlations and is defined as

$$r = \frac{\beta(\ _s - \ _\infty)\ ^3}{\nu^2} = \frac{a}{\mathrm{Pr}} \qquad 16$$

A description of how to calculate the free convection Nusselt number, defined in equation 14, for different geometries is explained below.

Wall vertical position θ_V 0 1

- Surface:
  - Characteristic length: L = z
  - Laminar flow (Ra_L 10^9):

$$\overline{u} = 0.68 + \frac{0.670\ a^{1\ 4}}{\left[1 + (0.492\ r)^{9\ 16}\right]^{4\ 9}} \qquad 17$$

  - Turbulent flow (Ra_L 10^9):

$$\overline{u} = \left\{0.825 + \frac{0.387\ a^{1\ 6}}{\left[1 + (0.492\ \mathrm{Pr})^{9\ 16}\right]^{8\ 27}}\right\}^2 \qquad 18$$

- Enclosure:
  - Characteristic length: L = thickness of wall enclosure
  - H = z (height of enclosure)
  - H L 2:

$$\overline{u} = 0.18\left(\frac{r}{0.2 + \ r}\ a\right)^{0.29} \qquad 19$$

    - Valid when:
      1 H L 2
      10^{-3} Pr 10^5
      10^3 (Ra_LPr) (0.2 Pr)

  - 2 H L 10:

$$\overline{u} = 0.22\left(\frac{r}{0.2 + \ r}\ a\right)^{0.28}\left(\frac{\ }{\ }\right)^{-1\ 4} \qquad 20$$

    - Valid when:
      2 H L 10

Pr 10^5
10^3 Ra_L 10^{10}

- H L 10:

$$\overline{u} = 0.42 \quad a^{1 \ 4} \quad r^{0.012}\left(\frac{}{}\right)^{-0.3} \qquad 21$$

- Valid when:
  10 H L 40
  1 Pr 2 10^4
  10^4 Ra_L 10^7

Wall, hori ontal position θ_V 90 1 , 2

- Surface:
  - Characteristic length: L = A P, i.e. the surface area divided by the perimeter
  - Hot upper surface or cold lower surface:

$$\overline{u} = 0.27 \quad a^{1 \ 4} \qquad 22$$

  - Cold upper surface or hot upper surface:
    - Ra_L 10^7:

$$\overline{u} = 0.54 \quad a^{1 \ 4} \qquad 23$$

    - Ra_L 10^7:

$$\overline{u} = 0.15 \quad a^{1 \ 3} \qquad 24$$

- Enclosure:
  - Characteristic length: L = thickness of wall enclosure
  - Hot lower surface:
    - Ra_L 1708:

$$\overline{u} = 1 \text{(pure conduction)}$$

    - Ra_L 1708:

$$\overline{u} = 0.069 \quad a^{1 \ 3} \quad r^{0.074} \qquad 25$$

      - Valid when:
        3 10^5 Ra_L 7 10^9
  - Cold lower surface:
    - $\overline{u} = 1$ (pure conduction)

Cube 1

- Surface:
  - Internal flow:
    - Characteristic length: L = z_i
    - Nusselt number according to equation 17 or 18 for all walls
    - The flow is assumed to cool down at the walls (downflow), thus creating a circulating flow with an upflow through the center of the cube.
    - Not valid for small cubes
  - External flow:
    - Cube walls:
      - Characteristic length: L = z_O

- Nusselt number according to equation 17 or 18
- Roof and bottom:
  - Characteristic length: L = A P, i.e. the roof bottom surface area divided by the perimeter
  - Nu_{roof} and Nu_{bottom} according to equation 22 , 23 or 24
- Enclosure:
  - Same as for wall depending on horizontal or vertical cube enclosure

Cylinder, vertical θ_v 0 1

- Surface:
  - Internal flow:
    - Characteristic length: $L = z_i$
    - Nusselt number according to equation 17 or 18 for wall, roof and bottom
    - The flow is assumed to cool down at the walls (downflow), thus creating a circulating flow with an upflow through the center of the cylinder
    - Not valid for small cylinders
  - External flow:
    - Cylinder wall:
      - Characteristic length: $L = z_o$
      - Nusselt number according to equation 17 or 18
        - Valid when:

$$D \geq 35 \ (\ a \ \ \mathrm{Pr})^{1\ 4}$$

    - Roof and bottom:
      - Characteristic length: L = A P = D 4, i.e. the surface area divided by the perimeter
      - Nu_{wall} according to equation 17 or 18
      - Nu_{roof} and Nu_{bottom} according to equation 22 , 23 or 24
- Enclosure:
  - *ro i ated* as vertical wall enclosure

Cylinder, hori ontal θ_v 90 1

- Surface:
  - Internal flow:
    - Characteristic length: $L = D_i$
    - Nusselt number calculated according to equation 17 or 18
    - The flow is assumed to cool down at the walls (downflow), thus creating a circulating flow with an upflow through the center of the cylinder
    - Not valid for small cylinders
  - External flow:
    - Cylinder wall:
      - Characteristic length: $L = D_o$

$$\overline{u}_D = \left\{ 0.60 + \frac{0.387 \quad a_D^{1\ 6}}{\left[1 + (0.559 \quad \mathrm{Pr})^{9\ 16}\right]^{8\ 27}} \right\}^2 \qquad 26$$

- Valid when:
  $Ra_D \leq 10^{12}$
- Roof and bottom:
  - Characteristic length: $L = r_o \sqrt{\pi}$, i.e. square with same area
  - Nu_{roof} and Nu_{bottom} according to equation 17 or 18
- Enclosure:
  - Characteristic length L = thickness of cylinder enclosure
  - h_c calculated directly, not through the Nusselt number (Nu_L)

$$a_c = \frac{\left[n(D_o \quad D_i)\right]^4}{{}^3\left(D_i^{-3\ 5} + D_o^{-3\ 5}\right)^5} \quad a \qquad 27$$

- Ra_c 100:

$$_c = \frac{}{n(D_o \quad D_i) \cdot D_i \quad 2} \qquad 28$$

- Ra_c 100:

$$_e = 0.386\left(\frac{r}{0.861 + \quad r}\right)^{1\ 4} \left(\quad a_c\right)^{1\ 4} \cdot \qquad 29$$

$$_c = \frac{_e}{n(D_o \quad D_i) \cdot D_i \quad 2} \qquad 30$$

- valid when:
  10^2 Ra_c 10^7

Sphere 1

- Surface:
  - Internal flow:
    - Characteristic length: $L = z_i$
    - Nusselt number according to equation 17 or 18
    - The flow is assumed to cool down at the walls (downflow), thus creating a circulating flow with an upflow through the center of the sphere
    - Not valid for small spheres
  - External flow:
    - Characteristic length: $L = D_O$

$$\overline{u}_D = 2 + \frac{0.589 \quad a_D^{1\ 4}}{\left[1 + (0.469 \quad \mathrm{Pr})^{9\ 16}\right]^{4\ 9}} \qquad 31$$

    - Valid when:
      $Ra_D \leq 10^{11}$
      $Pr \geq 0.7$
- Enclosure:
  - Characteristic length: L = thickness of the sphere enclosure
  - h_c calculated directly, not through the Nusselt number (Nu_L)

$$a_s = \frac{a}{(D_o D_i)^4} \frac{}{\left(D_i^{-7\ 5} + D_o^{-7\ 5}\right)^5} \qquad 32$$

- Ra_s 100:

$$_c = \pi \frac{D_i D_o}{} \qquad 33$$

- Ra_s 100:

$$_e = 0.74\left(\frac{r}{0.861 + r}\right)^{1\ 4} \left(a_s \right)^{1\ 4} . \qquad 34$$

$$_c = {}_e \pi \frac{D_i D_o}{} \qquad 35$$

- Valid when:
  10^2 Ra_s 10^4

Forced con ection

Forced convection is here assumed to be *e terna* only. The correlation number describing the nature of the flow for forced convection is called the *e no ds nu ber*, which describes the ratio of inertia forces to viscous forces of a flow and is defined as

$$\mathrm{Re} = \frac{u_\infty}{\nu} \qquad 36$$

where u_∞ is the speed of the fluid gas. Note that the direction of the flow is assumed to be *ori onta* in this program and that forced convection inside enclosures is not taken into consideration.

Wall 1

- Laminar flow, $\mathrm{Re}_L \le 5\cdot10^5$:

$$\overline{u} = 0.664\,\mathrm{Re}^{1/2}\,\mathrm{Pr}^{1/3} \qquad 37$$

  - Valid when:
    $\mathrm{Pr} \ge 0.6$
- Turbulent flow (flow separation), $\mathrm{Re}_L \ge 5\cdot10^5$:

$$\overline{u} = (0.037\,\mathrm{Re}^{4/5} - 871)\,\mathrm{Pr}^{1/3} \qquad 38$$

  - Valid when:
    $0.6 \le \mathrm{Pr} \le 60$
    $5\cdot10^5 \le \mathrm{Re}_L \le 10^8$

Cube 1

- Tangential horizontal flow on *a* sides assumed
- Cube walls:
  - Characteristic length front and back wall: $L = x_O$
  - Characteristic length left and right wall: $L = y_O$
  - Nusselt number calculated as 37 or 38
- Roof and bottom:
  - Characteristic length: $L = y_O$
  - Nusselt number calculated as 37 or 38

Cylinder 1

- Cylinder wall:
  - Characteristic length: $L = D_O$

$$\overline{u}_D = 0.3 + \frac{0.62\ e_D^{1/2}\ r^{1/3}}{\left[1+(0.4\ r)^{2/3}\right]^{1/4}}\left[1+\left(\frac{e_D}{282000}\right)^{5/8}\right]^{4/5} \qquad 39$$

  - Valid when:
    $\mathrm{Re}_D\cdot\mathrm{Pr} \ge 0.2$
- Roof and bottom:

- Characteristic length: $L = r_o\sqrt{\pi}$, i.e. square with same area
- Nusselt number calculated as 37 or 38

Sphere 1 , 2

- Characteristic length: $L = D_O$

$$\overline{u}_D = 2 + (0.4\,\mathrm{Re}_D^{1/2} + 0.06\,\mathrm{Re}_D^{2/3})\,\mathrm{Pr}^{0.4}\left(\frac{\mu_\infty}{\mu_s}\right)^{1/4}, \qquad 40$$

where μ_∞ is the dynamic viscosity at the fluid gas temperature and μ_s is the dynamic viscosity at the surface temperature.

- valid when:
  $0.71 \le \mathrm{Pr} \le 380$
  $3.5 \le \mathrm{Re}_D \le 7.6\cdot10^4$
  $1.0 \le (\mu_\infty\ \mu_S) \le 3.2$

12.4.3 Radiation

Heat transfer due to radiation occurs in the range of approximately 0.4 μm to 1000 μm of the electromagnetic wavelength spectrum 3 . This spectrum includes both visible light as well as infrared radiation. Radiation heat transfer between two points occurs when waves are *e itted* at one point and *absorbed* at another. Sometimes the wave is *re ected* or *trans itted* and thus there is no radiation heat transfer between these two points. However, the wave can be absorbed at another point thus creating a heat flow between these new points instead. Since radiation consists of electromagnetic waves it is therefore not dependent on the medium, in fact radiation heat transfer through a vacuum is higher than through other mediums since almost no radiation is absorbed there. Radiation plays a significant role at high temperatures and radiation heat transfer is in this instance much higher than convection heat transfer. This can be seen from equations 41 , 44 and 52 , with temperatures raised to a power of four.

Radiation heat transfer can be subdivided into three types: S*ur ace radiation*, *as radiation* and *co bined as and artic e radiation*. These are described more closely below.

S r ace radiation

Surface radiation means that the heat flux is due to a surface (at temperature T_s) that radiates to the outside environment (at temperature T_∞), which is assumed to be very large compared to the radiating surface. A typical case could be the walls of a big room. The net heat flux is calculated according to

$$= \varepsilon_s \sigma \left({}_s^4 - {}_\infty^4 \right), \qquad 41$$

where ε_s is the surface emissivity, which is a function of the surface temperature, $\varepsilon_s = \varepsilon_s (T_s)$ and σ is the Stefan-Boltzmann constant. The surface is assumed to be gray, which means that the surface absorptivity is equal to the surface emissivity ($\alpha_s(T) = \varepsilon_s (T)$).

For easier comparison with the convection heat rate, we can define the heat radiation coefficient as

$$_r = \varepsilon_s \sigma \left({}_s + {}_\infty \right) \left({}_s^2 + {}_\infty^2 \right) \qquad 42$$

and by using equations 41 and 42 the heat rate can be expressed as

$$= {}_r \left({}_s - {}_\infty \right) \qquad 43$$

which is of the same form as equation 13 . The surface emissivity can be found from tables in the literature. The *nor a e issi it* (ε_n) or the *e is erica* or *tota e issi it* (ε_h) may be listed depending on the material. The normal emissivity is the normal directional emissivity while the hemispherical emissivity is the averaged value for all solid angles passing through a hemisphere centered over the surface element 3 .

Gas radiation

The heat flux due to radiation from a gas to a surface is calculated as 4

$$= \frac{\varepsilon_s + 1}{2} \sigma \left(\varepsilon \quad {}^4 - \alpha \quad {}_s^4 \right), \qquad 44$$

where ε_s is the surface emissivity, $\varepsilon_g = \varepsilon_g (T_g)$ is the gas emissivity at the *as* temperature and $\alpha_g = \alpha_g (T_g, T_s)$ is the gas absorptivity as a function of both the *as and sur ace* temperatures. It is natural that α_g also depends on T_s as this defines the spectrum of incoming radiation and this is clear because T_g defines the state of the gas and therefore its thermal properties. The surface is also here assumed to be gray. The coefficient (ε_s 1) 2 is an approximation for the effective emissivity of the solid.

The heat radiation coefficient is now

$$_r = \frac{(\varepsilon_s + 1)\sigma \left(\varepsilon \quad {}^4 - \alpha \quad {}_s^4 \right)}{2\left(\quad - \quad {}_s \right)}. \qquad 45$$

In order to calculate ε_g and α_g the *e onentia ide band ode* proposed in 5 can be used. This model has been optimized and made more efficient computationally in 6 . The model can treat mixtures containing H_2O, CO_2, CO, NO, SO_2 and CH_4 in, for example, a non-radiating nitrogen gas. The model also takes into account the pressure and the optical depth of the geometry. The gas emissivity function is

$$\varepsilon \quad = \varepsilon \left(\quad , \quad , \quad , \quad {}_2 , \quad {}_2 , \quad , \quad , \quad {}_2 , \quad {}_4 \right), \qquad 46$$

where p is the pressure, L is the optical depth and x is the molar fraction of the individual gas species. Note that the sum of the radiating gases can be smaller than one, $\sum x_{sp} \leq 1$, since the rest of the mixture can consist of non-radiating gases.

This model is applicable for the temperature range T = 300 K to 2500-3000 K and the pressure range p = 0.5 to 20 bar. The optical depth L depends on the geometry and is listed in the following table for the most common geometries 7 . All surfaces are assumed to be able to absorb radiation.

Geometry	Characteristic dimension	Optical depth (L)
1. Sphere	Diameter (D)	0.63D
2.1 Cylinder (h = 0.5D)	Diameter (D)	0.45D
2.2 Cylinder (h = D)	Diameter (D)	0.6D
2.3 Cylinder (h = 2D)	Diameter (D)	0.73D
3.1 Cube (1x1x1)	Any side (x)	0.6x
3.2 Cube (1x1x4)	Shortest side (x)	0.81x
3.3 Cube (1x2x6)	Shortest side (x)	1.06x

Table 1 *a es o o tica de t s or si e eo etries*

For dimensions not listed in Table 1 the optical depth coefficient can be interpolated or extrapolated. A simple example is:

Calculate the optical depth for a cube with the dimensions 1x4x7.

1. Extrapolated as a 1x1x7 cube using geometries 3.1 and 3.2 gives
   $L_{1x1x7} = 0.6\ (0.81-0.6)\cdot (7-1)\ (4-1) = 1.02$
2. Extrapolated as a 1x2.5x7 cube using geometries 3.2 and 3.3 gives
   $L_{1x2.5x7} = 0.81\ (1.06-0.81)\cdot (2.5-1)\ (2-1) = 1.185.$
3. These two results can then be used again to extrapolate into the 1x4x7 cube which gives $L_{1x4x7} = 1.02\ (1.185-1.02)\cdot (4-1)\ (2.5-1) = 1.35$. This is the answer since the shortest side is x = 1.

The gas absorptivity at the surface temperature can be calculated using the same model if two temperature correction factors are introduced. The function then becomes

$$\alpha = \varepsilon\ (\ ,\ ,\ \cdot\left(\frac{\ }{s}\right)^{1.5},\ 2,\ 2,\ ,\ ,\ 2,\ 4)\cdot\left(\frac{\ }{s}\right)^{0.5} \qquad 47$$

and as seen from the correction factors, the surface temperature T_s is now also needed as an input. For further information and detail on this model references 5 and 6 should be consulted. The gas radiation calculation code used by HSC is based on code made by *a io o ainen*.

Combined gas and particle radiation

A particle cloud emissivity can be calculated when the mean size of the particles and the particle cloud geometry are known, according to 4

$$\varepsilon_c = 1 - e^{-\varepsilon\ n}\ , \qquad 48$$

where ε_p is the emissivity of a single particle, n_p is the number of particles per unit volume of cloud, L is the thickness of the cloud and A_p is the average cross-sectional area of the particle. If the particles in the cloud are not uniform in size, then the surface mean diameter can be used according to

$$= \frac{\pi d_s^2}{4} = \frac{\pi}{4}\frac{\sum_{i=1}^{n} n_i d_i^2}{\sum_{i=1}^{n} n_i}, \qquad 49$$

where d_s is the surface mean diameter and n_i is the number of particles of the same diameter d_i. The total gas and particle cloud emissivity can then be approximated as 7

$$\varepsilon_{+c} = \varepsilon\ + \varepsilon_c - \varepsilon\ \varepsilon_c, \qquad 50$$

where ε_c is the particle cloud emissivity and ε_g is the gas emissivity calculated according to the model behind equation 46 . The total gas and particle cloud absorptivity can be approximated as

$$\alpha_{+c} = \alpha\ + \varepsilon_c - \alpha\ \varepsilon_c, \qquad 51$$

where α_g is the gas absorptivity calculated according to the model behind equation 47 .

Finally, the heat flux due to radiation from a gas and particle cloud to a surface is then calculated according to 7

$$= \frac{\varepsilon_s}{\alpha_{+c} + \varepsilon_s - \alpha_{+c}\varepsilon_s} \sigma\left(\varepsilon_{+c}{}^{4} - \alpha_{+c}{}_{s}^{4}\right) \qquad 52$$

and the heat radiation coefficient as

$$_{r} = \frac{\varepsilon_s \sigma\left(\varepsilon_{+c}{}^{4} - \alpha_{+c}{}_{s}^{4}\right)}{\left(\alpha_{+c} + \varepsilon_s - \alpha_{+c}\varepsilon_s\right)\left(- {}_{s}\right)}. \qquad 53$$

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13. EQUILIBRIUM MODULE

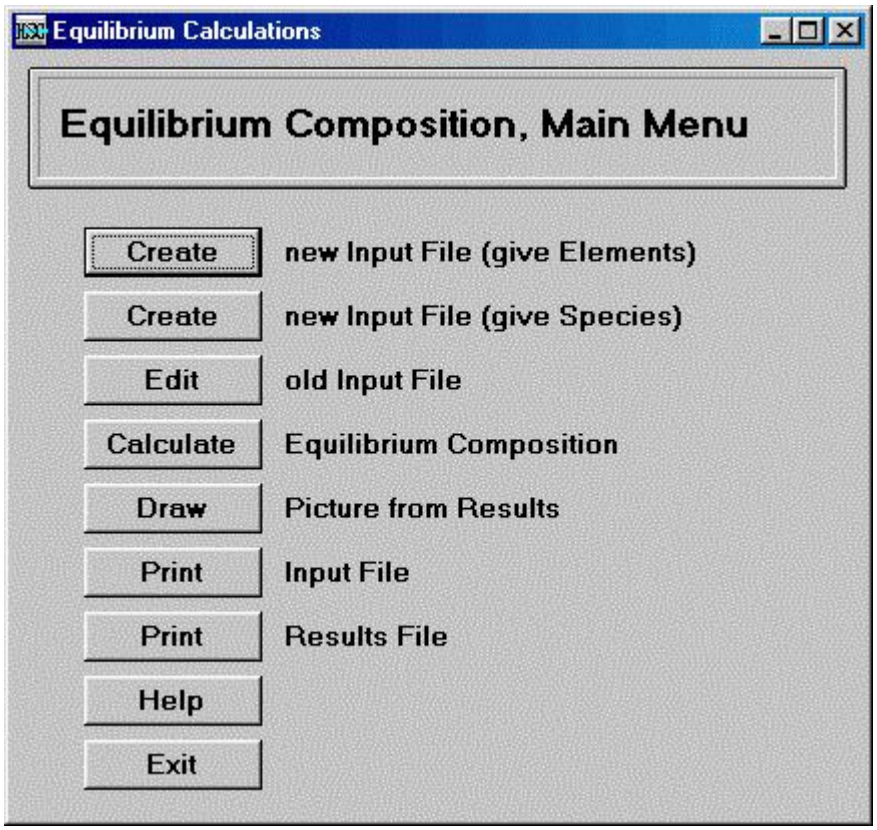


Fig. 1. Equilibrium Module Menu.

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

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

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

The Equilibrium module reads and writes the following file formats:

1. **.GEM-File Format**

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

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

2. **.IGI-file Format**

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

3. **.ISG-file Format**

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

4. **.DA2-file Format**

   This file format contains the data for calculations for the ChemSAGE 2.0 only. The equilibrium module also reads .DA2-files, but not if solution model parameters have been added to the file manually. *ote t at t is e ui ibriu so er is not inc uded in . .*

5. **.DAT-file Format**

   This file format contains the data for calculations for ChemSAGE 3.0 and 4.0 only. The equilibrium module also reads .DAT-files, but not if solution model parameters have been added to the file manually. *ote t at t is e ui ibriu ro ra is not inc uded in . .*

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

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

1. Press the **top button** in the menu, see Fig. 1. Then specify the elements which are present in your system, see Fig. 2. The HSC-program will search for all the available species in the database and divide them, as default, into gas, condensed and aqueous phases. The user can then edit this preliminary input table.

2. Press the **second button** of the menu if you already know for sure the possible substances and the phases of the system, see Fig. 1.

3. Press **Edit Old Input File** if you already have an input file which can be used as a starting file. Edit the input table and save it using a different name, see Fig. 1.

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

13.1 Starting from defining the Elements

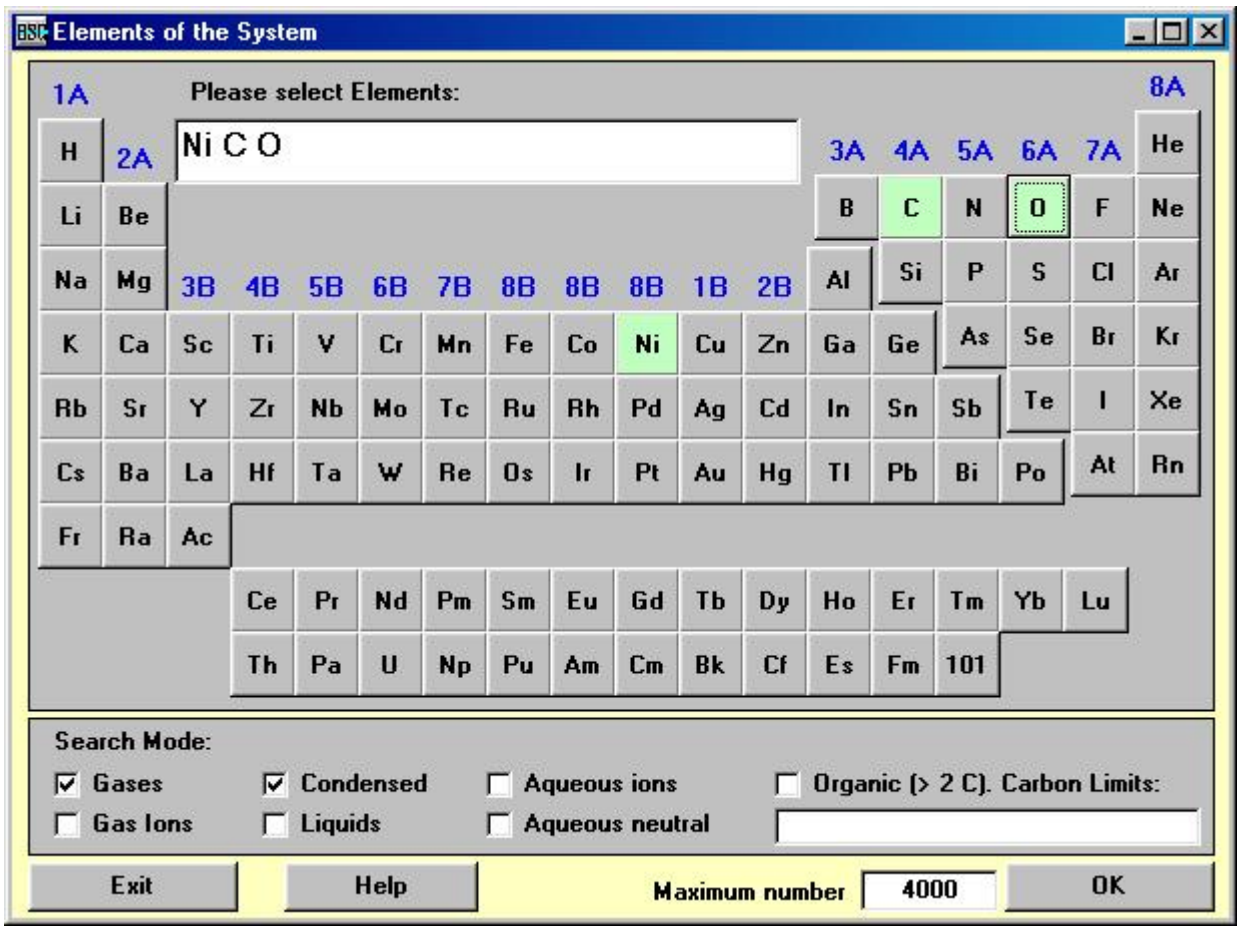


Fig. 2. Specifying the elements of the system.

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

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

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

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

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

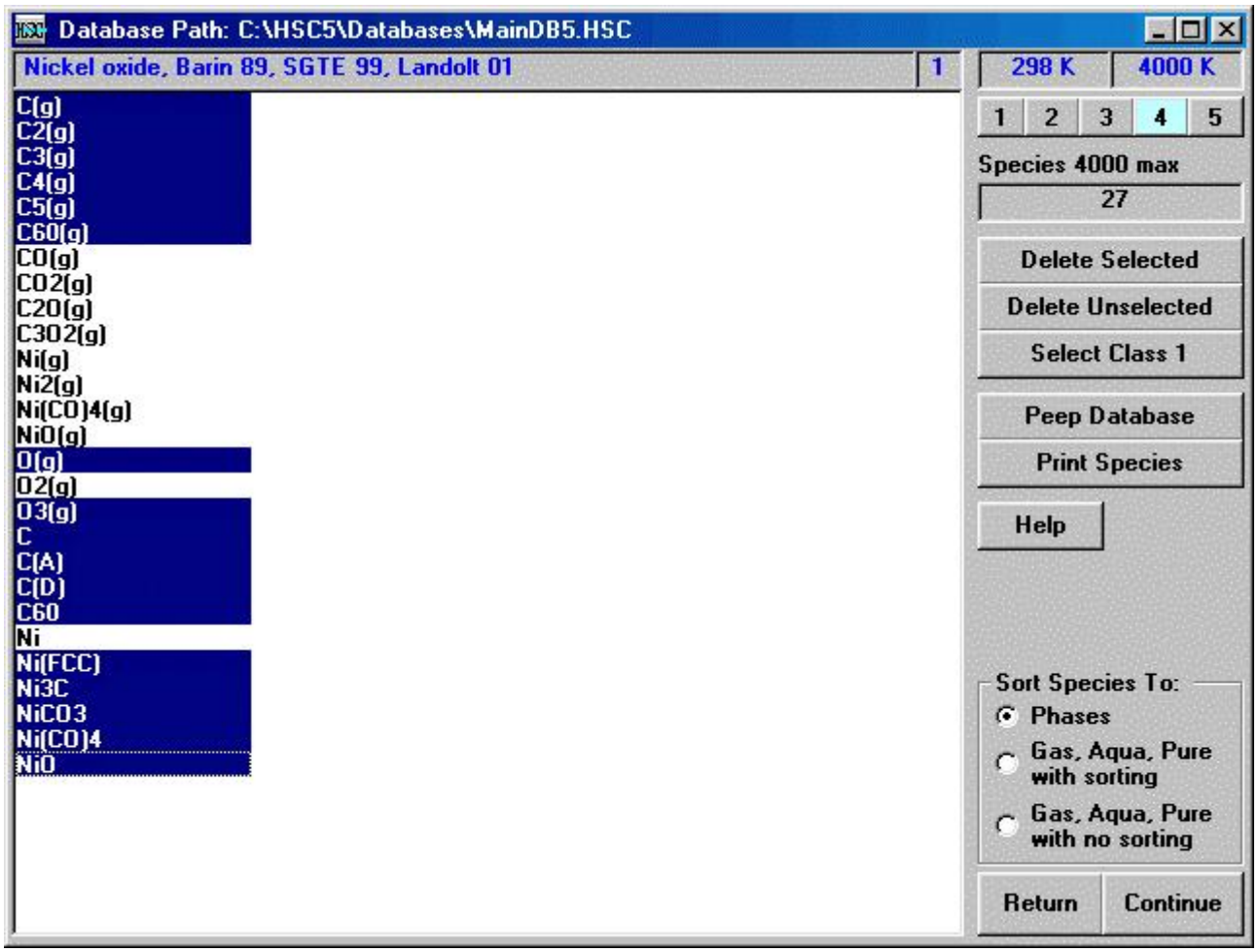


Fig. 3. Deleting undesired species.

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

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

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

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

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

13.2 Giving Input Data for Equilibrium Calculations

Equilibrium Calculations C:\Hsc5\Gibbs\Nico.igi

File Edit View Insert Delete Format Units Calculate Help

C11 1

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

Species Options

Exit Ins Phase Del Phase Ins Row Del Row Open C:\Hsc5\Gibbs\Nico.igi Save Gibbs

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

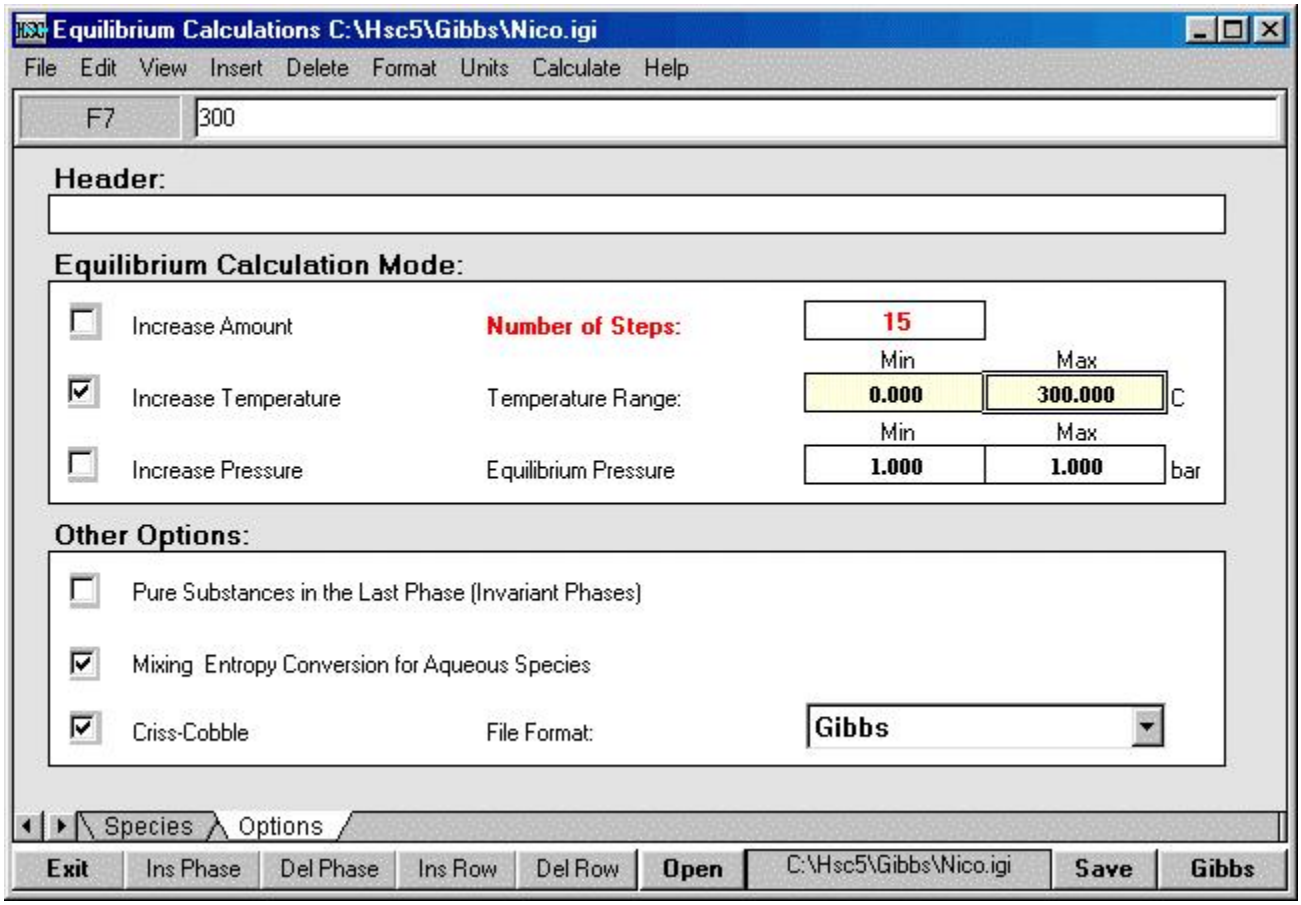


Fig. 5. Specification of the calculation mode.

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

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

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

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

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

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

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

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

You can change the order of the substances by inserting an empty row and using the copy - paste method to insert substance in the new row. The drag and drop method can also be used. ***Ho e er it is extremely important to mo e the hole ro beca se there is a lot o a xiliary data in the hidden col mns on the right side o the sheet***.

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

Use the (l)-suffix for a species only if you want to use the data of liquid phases at temperatures below its melting point. For example, type **SiO2(l)** if SiO_2 is present in a liquid oxide phase at temperatures below the melting point of pure SiO_2. See Chapter 28.2.

2. Phases

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

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

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

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

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

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

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

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

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

3. Input Temperatures of the Species

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

4. Amount of the Species

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

You may choose between kmol or kg Nm^3 units by selecting **mol** or **kg** from the **Units** menu. Note that kilograms refer to condensed substances and standard cubic meters (Nm^3) to gaseous substances, see Fig. 4.

5. Amount Step for Raw Materials

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

You may give step values for several species simultaneously. For example, if you want to add air to the system give a step value for both $O_2(g)$ and $N_2(g)$. Please do not forget to specify the number of steps, if a diagram is to be drawn from the results.

6. Activity Coefficients (in Gibbs-solver)

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

a p(over solution) p(pure) 1

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

f a x 2

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

Ln(f)	=	8495 T-2.653
Ln(f)	=	0.69 56.8 X24 5.45 X25
Ln(f)	=	-3926 T
Ln(f)	=	-1.21 X7 2-2.44 X8 2

where:

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

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

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

7. Heading

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

8. Equilibrium Temperature

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

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

9. Equilibrium Pressure

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

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

$$a_i \quad P \quad x_i \qquad (3)$$

$$F_i \quad a_i \quad 1\ \text{bar} \qquad (4)$$

10. Number of Steps

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

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

11. Criss-Cobble and Mixing Entropy of Aqueous Species

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

A) It is necessary to select the Mixing Entropy option for the GIBBS and SOLGASMIX routines. In this case, the activities of the results will be presented on the Raoultian scale which is based on mole fractions, see Chapter 13.3.

B) It is not recommended to select the Mixing Entropy option for the ChemSAGE or for the SOLGASMIX if the conventional activity coefficients of aqueous species are to be given in the FACTOR subprogram.

If the Criss-Cobble and Mixing Entropy options are not selected for the GIBBS or SOLGASMIX programs, then the activity coefficients of aqueous species may be set to 55.509 X(H2O), which will convert the Raoultian activity scale to the aqueous activity scale. This trick will also give the activities of the results on an aqueous scale, where the concentrations units are expressed as moles per liter of H_2O (mol l).

12. GIBBS, SOLGASMIX and ChemSAGE File Format

With this option you can select the input file formats accepted by the GIBBS, SOLGASMIX[3] or ChemSAGE[4] Gibbs energy minimization routines, Fig. 5

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

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

13. Pure Substances (Invariant phases)

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

14. File Save and File Open

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

15. Exit

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

13.3 Aqueous Equilibria

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

1. Always remember to add water to the aqueous phase. For example, 55.509 mol (= 1 kg) is a good selection if the amount of ions is some 0.01 - 5 moles.

2. Add some charged species (electrons) to the system, for example, by 0.001 mol OH(-a) and the same amount of H(a). Be sure to maintain the electronic neutrality of the system if you will carry out the calculations with the Gibbs solver.

3. If you are calculating, for example, the dissolution of 1 mole of $CaCO_3$ into water and you have stoichiometric raw material amounts, please also add a small amount of O_2(g) to the gas phase, for example, 1E-5 moles. If you have stoichiometric NaCl in the system please add a minor amount of Cl_2(g) to the gas phase (1E-5 mol). These tricks help the GIBBS and SOLGASMIX solvers to find the equilibrium composition in cases of fully stoichiometric overall compositions.

4. HSC converts the entropy values of aqueous components from the *o a it sca e* to *o e raction* scale if the **Mixing Entropy** option is selected, Fig. 33. Therefore, the entropy values in the input files are not the same as in the HSC database. Identical results will be achieved if the Raoultian activity coefficients of the aqueous species are changed to 55.509 X(H_2O) which converts the Raoultian activity scale to the aqueous activity scale.

5. For some aqueous species only G values are available at 25 C. These can be saved in the database as H values if S = 0. Note, however, that these can only be used in the calculations at 25 C.

6. You may check the equilibrium results by doing simple element balance checks or comparing the equilibrium constants. For example, you can calculate the equilibrium constant for reaction 18 using the Reaction Equations option at 25 C, see Fig. 12:

H_2O H(a) OH(-a) K 1.020E-14 5

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

$$K = \frac{H(a) \quad OH(-a)}{H_2O} = \frac{4.735E\text{-}13 \quad 2.159E\text{-}2}{55.468 \quad 55.509} = \mathbf{1.023E\text{-}14} \qquad 6$$

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

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

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

13.4 General Considerations

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

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

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

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

materials and you have NaCl as the pure substance, all raw materials may fit into NaCl due its high stability. The routines meet difficulties in calculations, because the amounts of all the other phases and species, except the stoichiometric one, go to zero. You can avoid this situation by giving an additional 1E-5 mol $Cl_2(g)$ to the gas phase, see Fig. 46.

9. uite often the most simple examples are the most difficult ones for the Gibbs energy minimization routines due to matrix operations. However, the new GIBBS 4.0 version usually finds the solution for the simple systems too, such as the two phase $H_2O(g)$ - H_2O -system between 0 - 200 C.

10. Sometimes a substance is very stable thermodynamically, but its amount in experiments remains quite low, obviously due to kinetic reasons. You may try to eliminate such a substance in the calculations in order to **simulate the kinetic (rate) phenomena,** which have been proven experimentally.

11. It is also important to note that different basic thermochemical data may cause differences to the calculation results. For example, use of HSC MainDB4.HSC or MainDB5.HSC database files may lead to different results.

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

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

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

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

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

The Na2SO4.IGI example in the HSC5 GIBBS directory shows the effect of temperature on Na_2SO_4 reduction with coal the same example can be seen also in the HSC color brochure, page 3. The calculated compositions are not exactly the same as found experimentally, but from these results we can easily see that at least 900 C will be needed to reduce the Na_2SO_4 to Na_2S, which has also been verified experimentally.

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

13.5 Limitations

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

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

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

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

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

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

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

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

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

13.6 Calculation Routines

13.6.1 GIBBS Equilibrium Solver

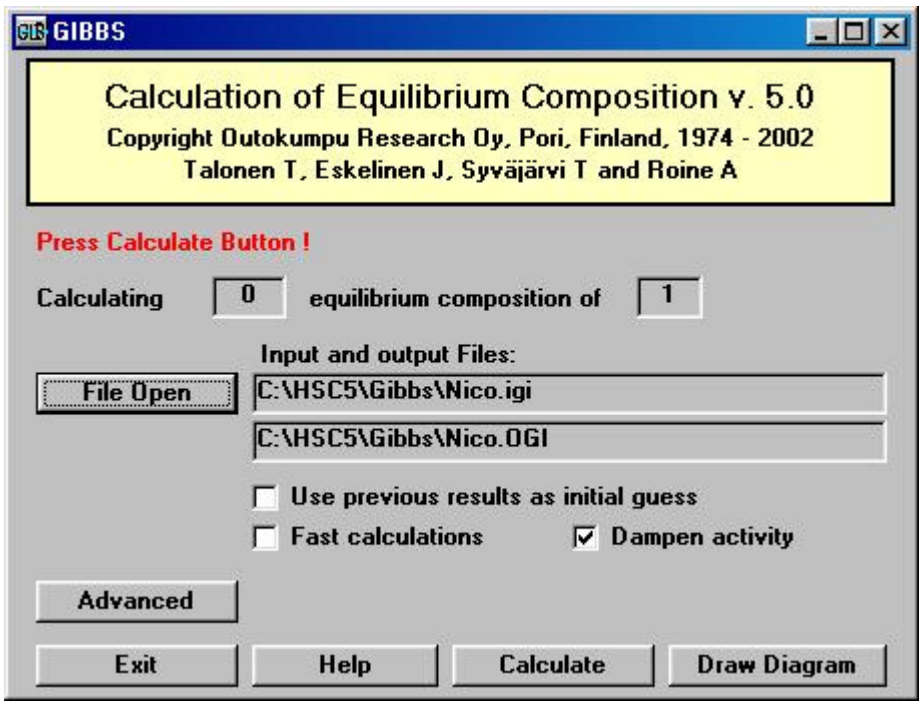


Fig. 6. GIBBS equilibrium solver.

Equilibrium calculations in the GIBBS routine are made using the Gibbs energy minimization method. The GIBBS program finds the most stable phase combination and seeks the phase compositions where the Gibbs energy of the system reaches its minimum at a fixed mass balance (a constraint minimization problem), constant pressure and temperature. This method has been described in detail elsewhere[5].

Operation Instructions

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

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

13.6.2 SOLGASMIX Equilibrium Solver

Fig. 7. Message box of the SOLGASMIX program.

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

The SOLGASMIX routine uses a similar Gibbs energy minimization calculation method as the GIBBS program. All its mixture phases can be defined as non-ideal mixtures in the FACTOR subroutine, but this option is not supported by HSC interface. For further reference, the original input guide and the thesis of Gunnar Eriksson should be consulted[6].

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

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

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

13.7 Drawing Equilibrium Diagrams

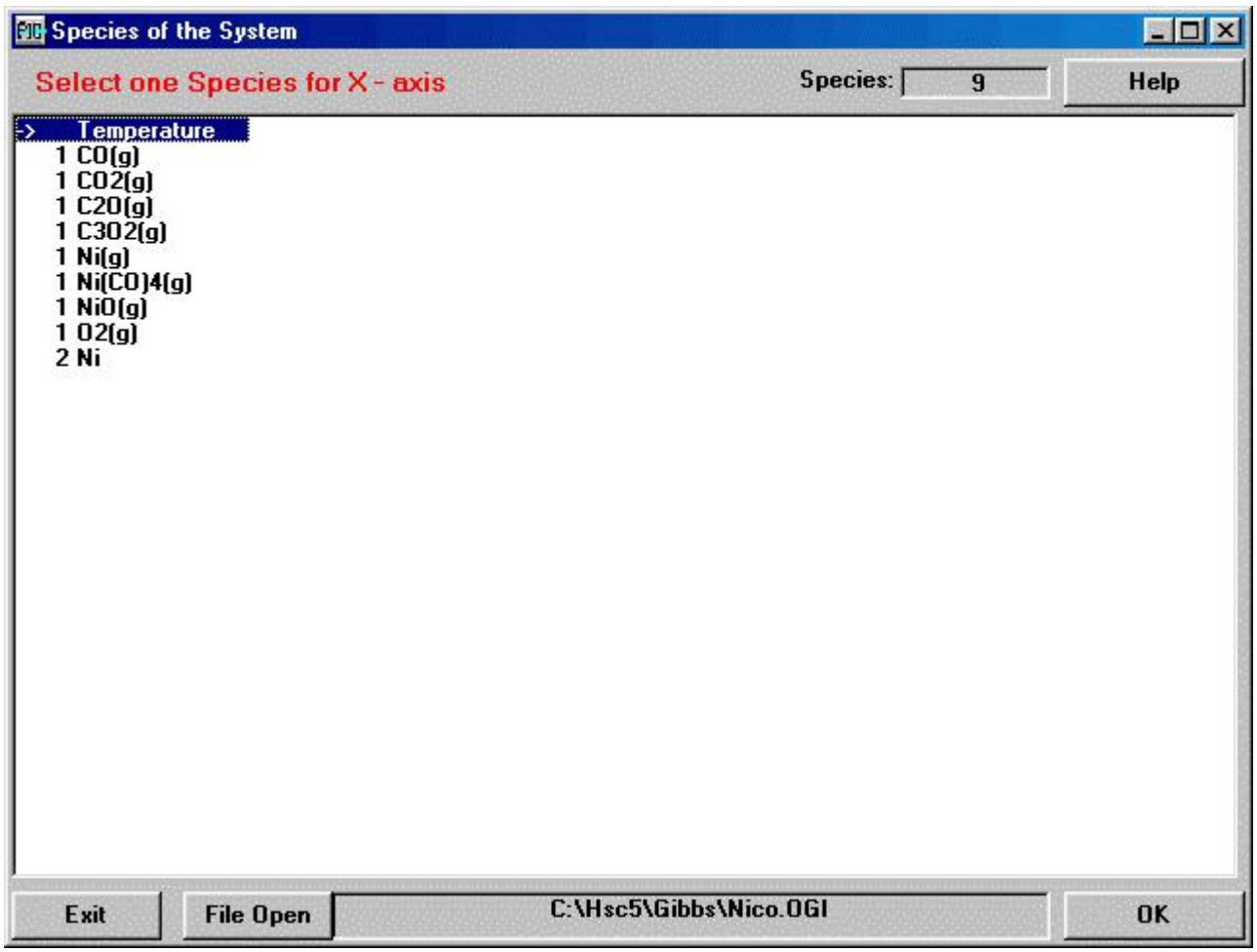


Fig. 8. Selecting the x-axis for an Equilibrium Diagram.

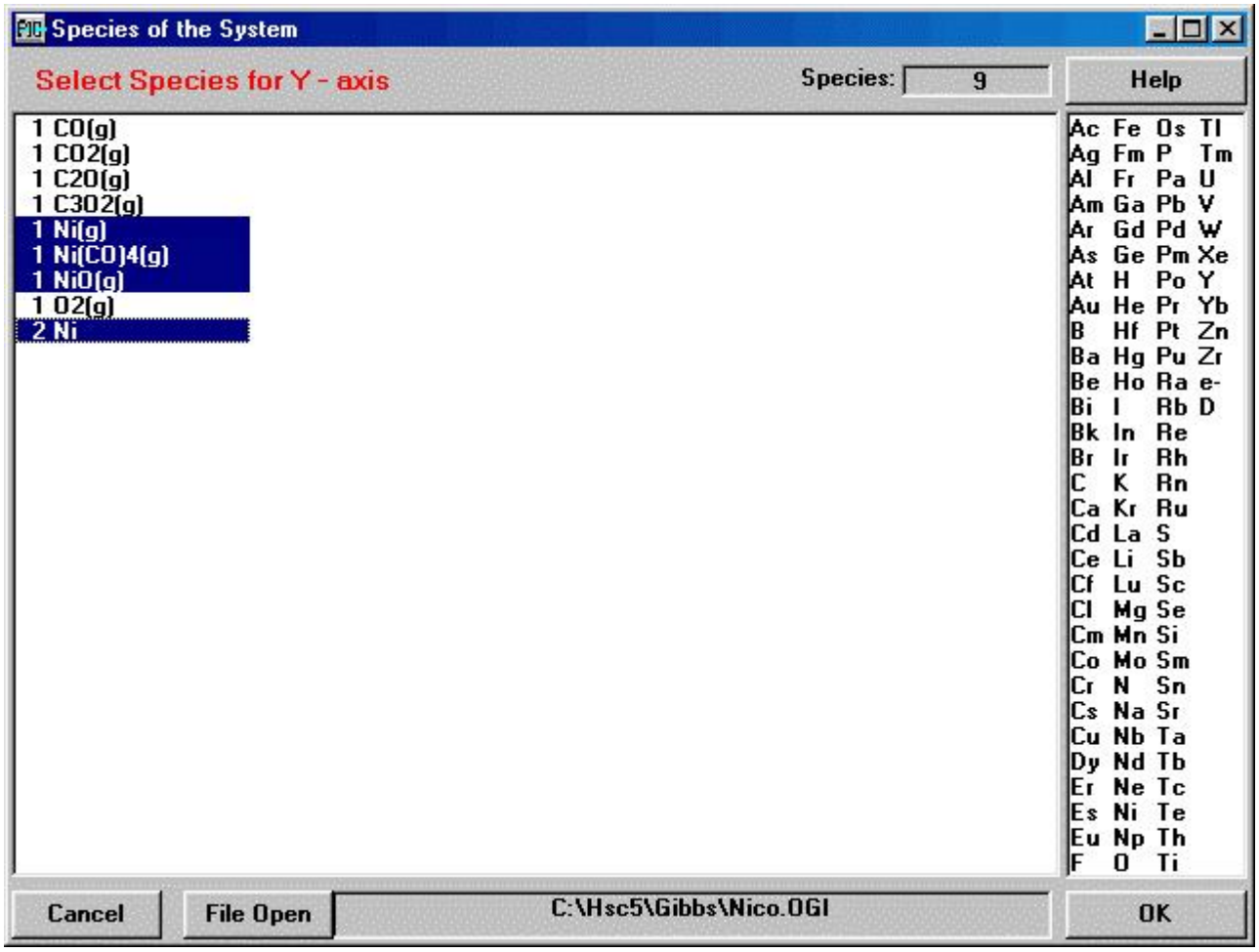


Fig. 9. Selecting the x-axis for an Equilibrium Diagram.

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

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

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

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

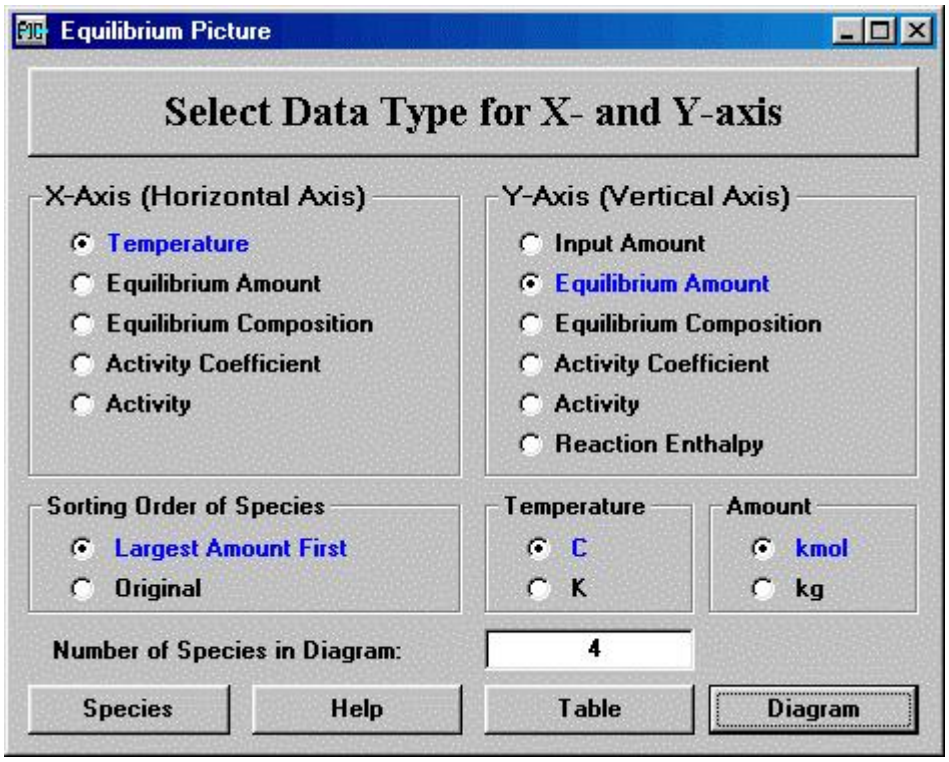


Fig. 10. Selecting data type for the x- and y-axis.

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

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

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

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

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

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

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

13.7.2 Result Graphics (Equilibrium Diagram)

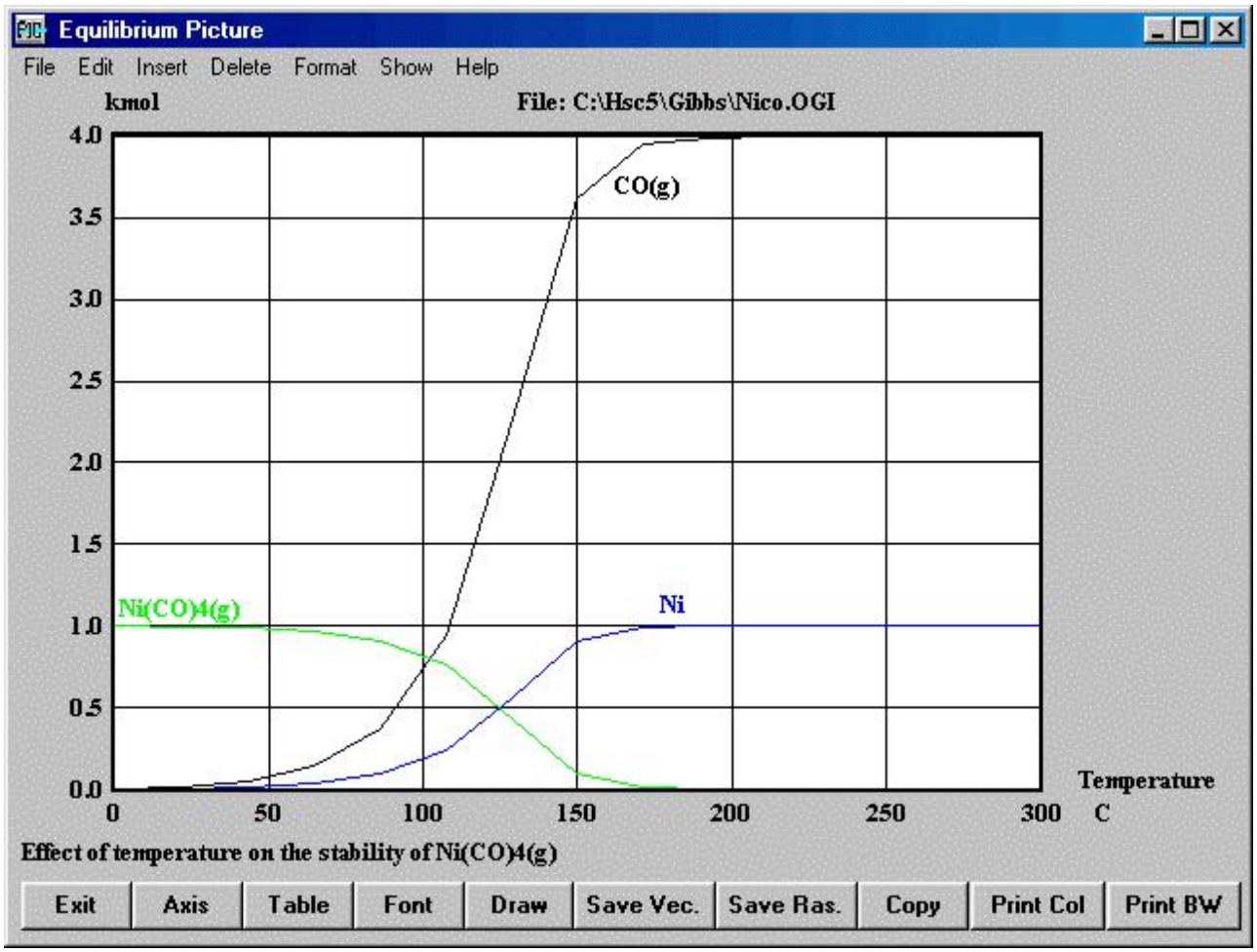


Fig. 11. Equilibrium Diagram.

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

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

1. Double click the x- or y-scale numbers or select **X-Axis** or **Y-Axis** from the **Format** menu to change, for example, the minimum and maximum values of the X- and Y-axis, see Fig. 12. In some cases it is also advantageous to change the y-axis to logarithmic scale in order to display the large variations in amounts or concentrations.

   From the same window you can change the number format of x- and y-axis numbers as well as their font size, color, etc.

2. When the scales are OK, you can relocate any **label** (species, x- and y-axis heading, etc.) by mouse using the drag and drop method. First select the label, keep

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

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

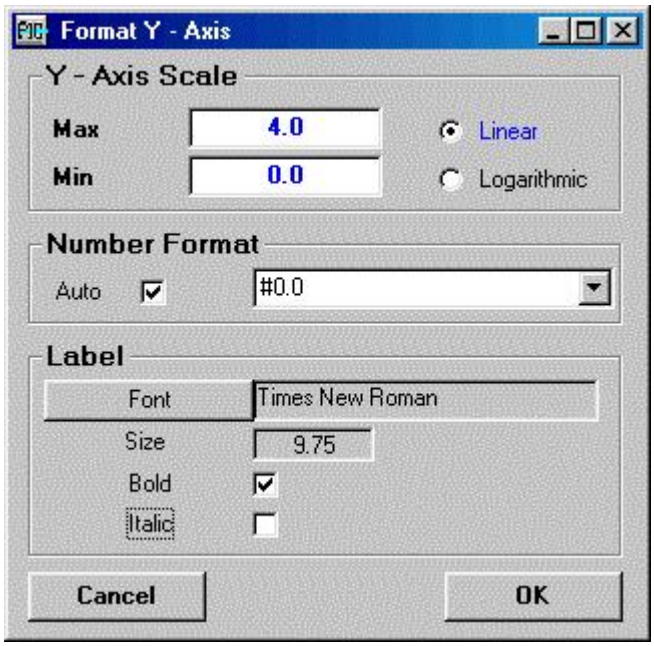


Fig. 12. Changing scales, scale number format and font settings.

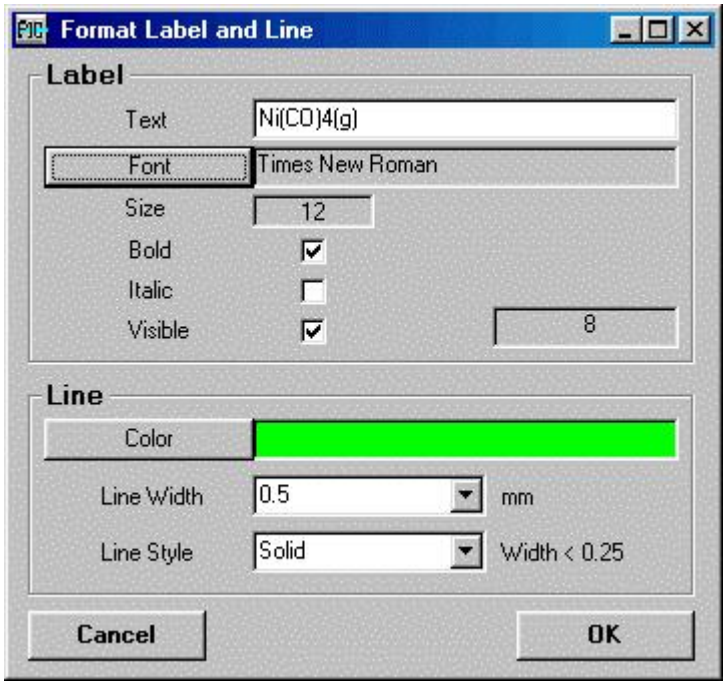


Fig. 13. Changing label and line specifications.

4. You can edit any label and heading on the screen by simply clicking the text in the label by mouse and starting to edit. For example you can change the label Ni to a non-abbreviated form Nickel .

5. You can create new labels by selecting **Label** from the **Insert** menu. These new labels can be deleted using the Label selection in the Delete menu. Default labels cannot be deleted, and the only possibility is to remove all text from them.

6. The first time you use HSC Chemistry it may be necessary to change the default fonts by selecting the **Default Font** from the **Format** menu, because the available fonts vary from one computer to another. Usually Times New Roman, bold, size 11 font is a good selection. The selection will be automatically saved in the HSC.INI-file in your Windows directory.

7. When you are satisfied with the diagram you can print it by pressing **Print B W**. If you have a color printer press **Print Col**. The print dialog gives several useful options for a hard copy, see Fig. 14.

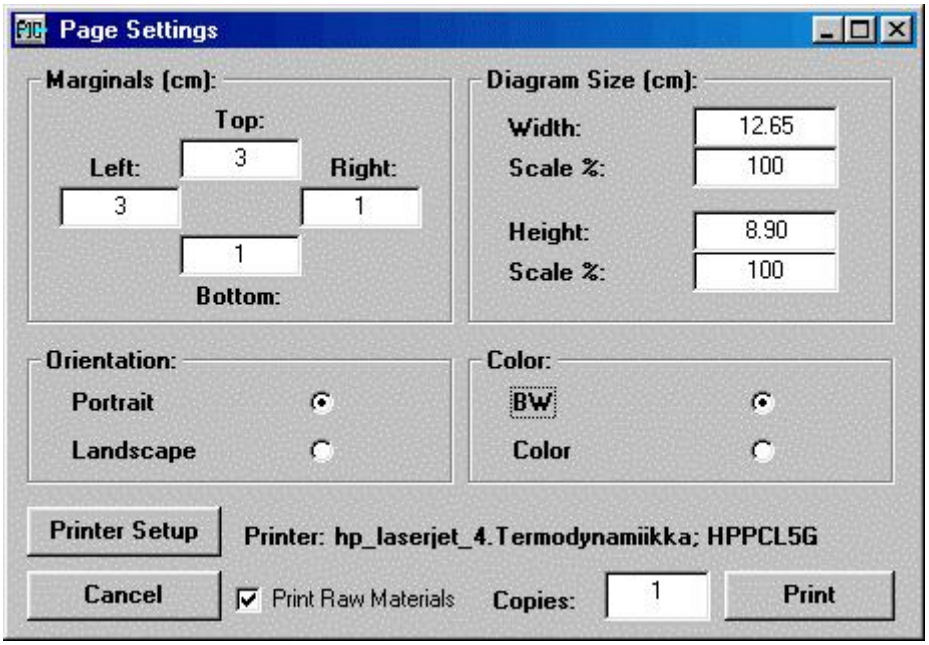


Fig. 14. HSC print dialog for graphics.

8. If you want to see the diagram in a tabular format or use the data of the diagram in other programs, such as MS Excel, press **Table**.

9. You can copy the diagram to the Clipboard by pressing **Copy**, and paste the diagram to other Windows programs. The **Copy** command uses the Windows Metafile format, which enables you to resize the diagram in other Windows applications in full resolution.

10. With **Save** you can save the diagram into a file using the Windows Metafile format.

11. Press **Axis** to return to the previous Axis menu, Fig 10.

12. Press **Exit** to return the Species window, Fig. 8, or to exit the PIC program.

13.7.3 Equilibrium Diagram Table

Equilibrium Results

File Edit View Insert Delete Format Help

A16

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

Species Format

Axis Print Copy All Diagram

Fig. 15. Equilibrium Diagram Table.

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

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

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

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

13.8 Non-ideal mixture GaAs Example with Activity formulae

Equilibrium Calculations C:\Hsc5\Gibbs\Gaas.igi

File Edit View Insert Delete Format Units Calculate Help

G2 =((1-X2)^2)*(-25503.6-4.3109*T+5174.7*(1-4*X2))/(8.31431*T)

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

Species Options

Exit Ins Phase Del Phase Ins Row Del Row Open C:\Hsc5\Gibbs\Gaas.igi Save Gibbs

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

LOGf(1) =((1-X1) 2) (-25503.6-4.3109 T 5174.7 (1-4 X1)) (8.31431 T)
LOGf(2) =((X1) 2) (-25503.6-4.3109 T 5174.7 (3-4 X1)) (8.31431 T)

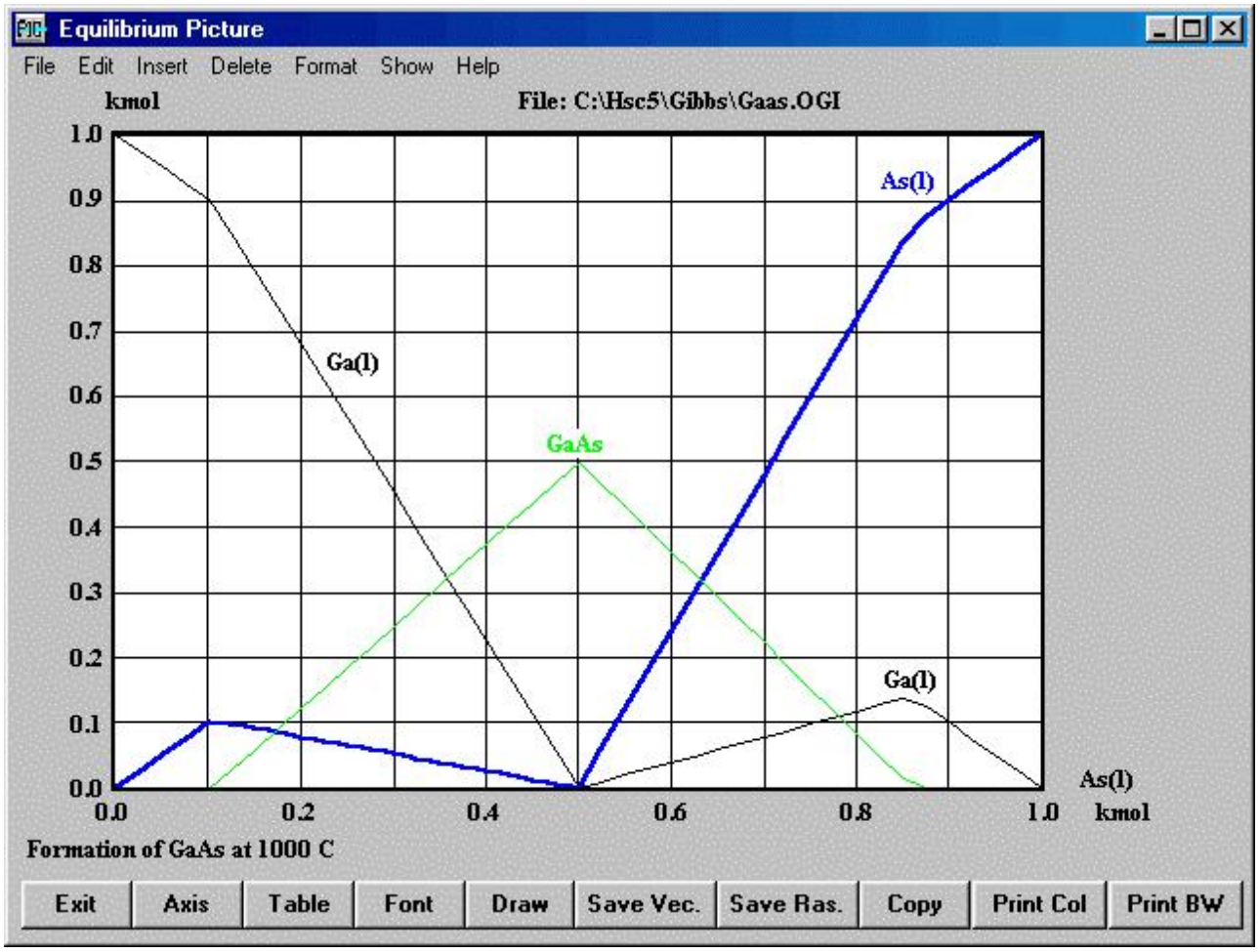


Fig. 17. Results as a function of arsenic amount. Different colors have been used for species, but these do not show up well in this B W copy.

13.9 CaCO3 Example (Aqueous solution exists)

Equilibrium Calculations C:\Hsc5\Gibbs\Caco3.igi

File Edit View Insert Delete Format Units Calculate Help

C4 1E-005

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

Species Options

Exit Ins Phase Del Phase Ins Row Del Row Open C:\Hsc5\Gibbs\Caco3.igi Save Gibbs

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

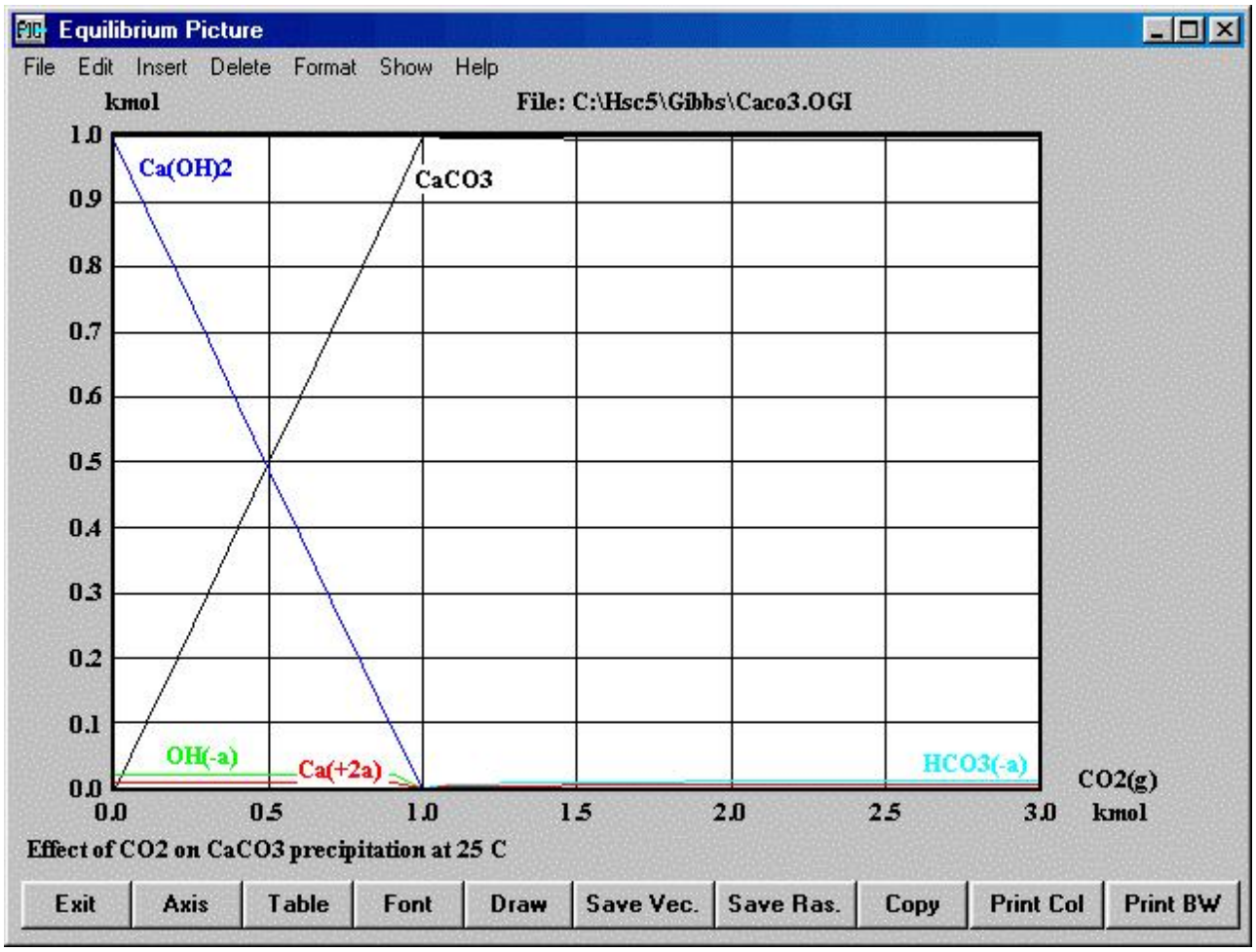


Fig. 19. Results as a function of added $CO_2(g)$. Different colors have been used for the species, but these do not show up well in this B W copy.

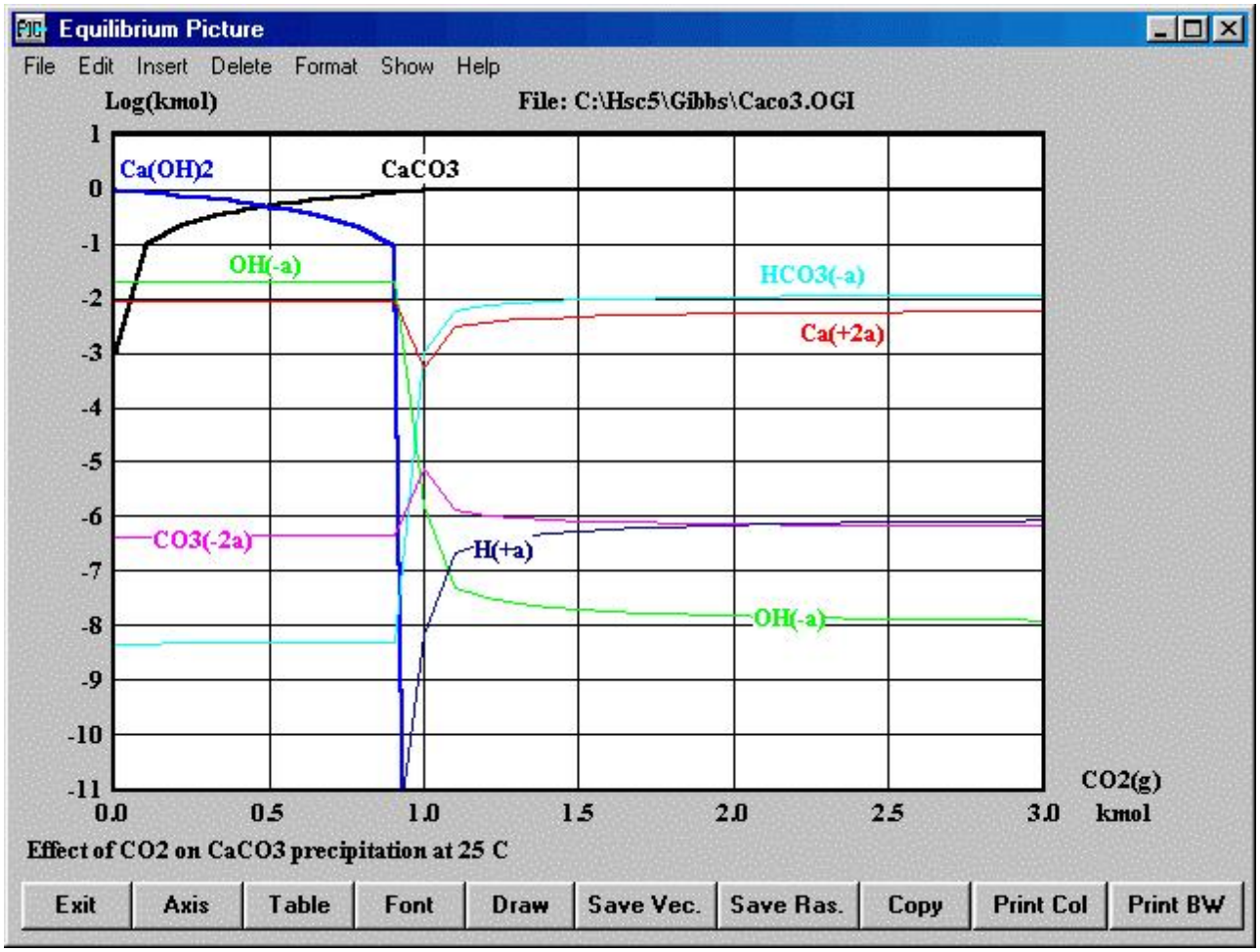


Fig. 20. Results on logarithmic scale, the default example is shown in Fig. 19.

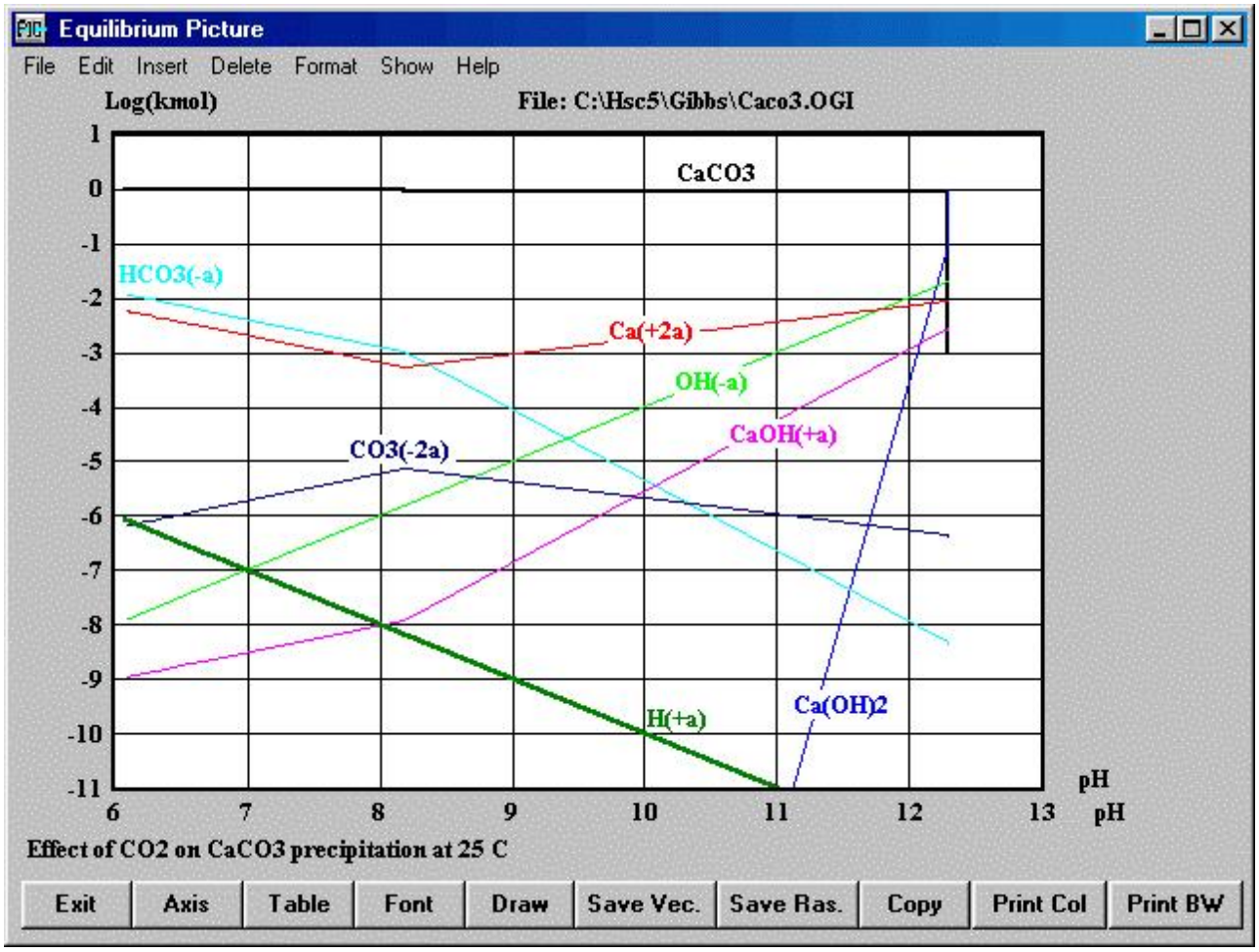


Fig. 21. Results as a function of pH, the default example is shown in Fig. 19.

13.10 Vapor Pressures

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

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

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

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

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

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

File Edit View Insert Delete Format Units Calculate Help

C17 1

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

Species Options

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

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

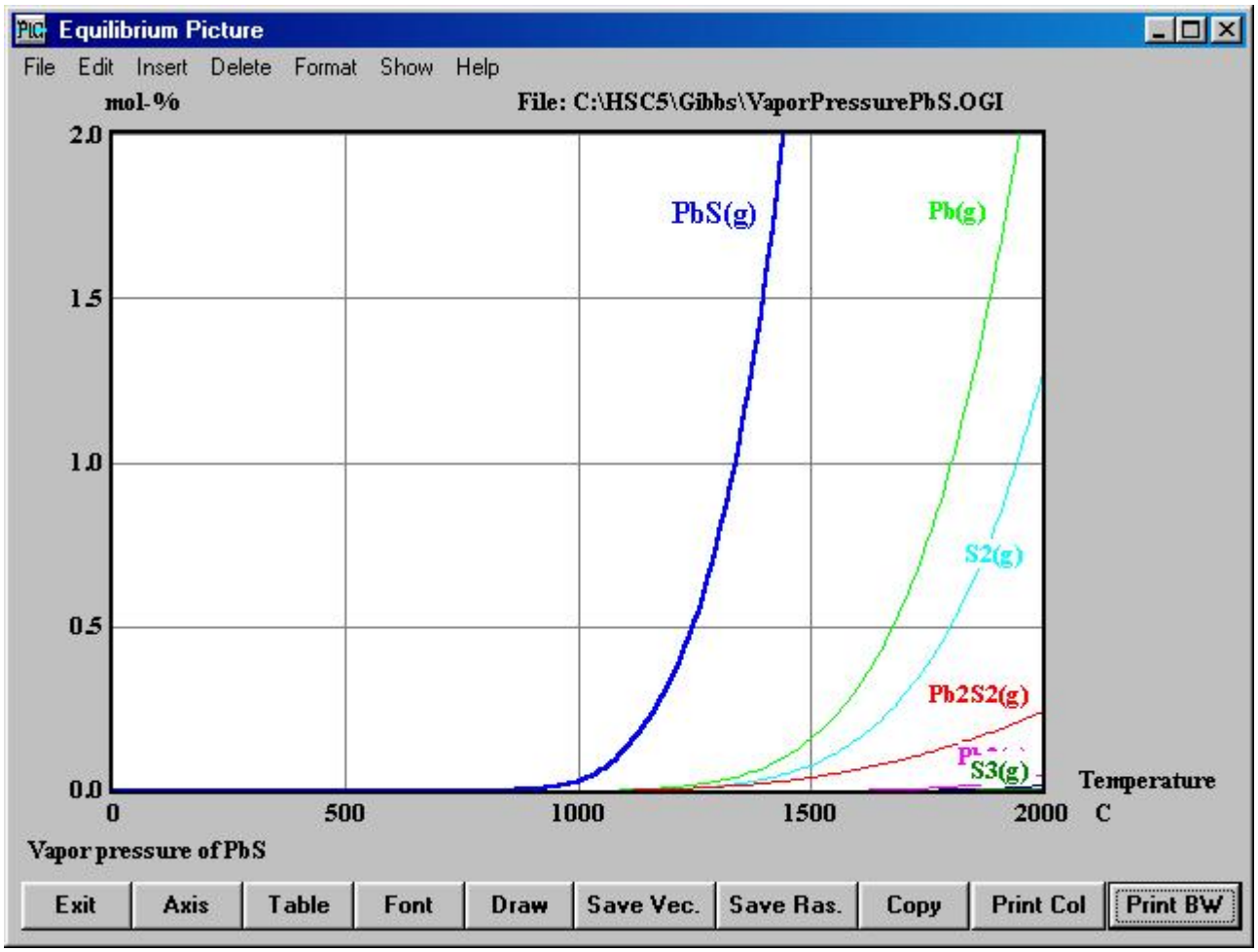


Fig. 23. Results of PbS vapor pressure calculations.

14. HSC EQUILIBRIUM MODULE SAMPLES

Contents of an Input File for GIBBS Program

```
§Copper Smelting at 1300 C                  ' Heading
   1                                        ' 0 = results to screen, 1= results to file
   6   4   0   3   3   2   1                ' Elements, phases, inv. phases, and
                                            ' ^ number of components / phase 1., etc.
 'N2(g)              '  2.00  0.00  0.00  0.00  0.00  0.00          ' stoichiomet.
 'O2(g)              '  0.00  2.00  0.00  0.00  0.00  0.00          ' matrix
 'SO2(g)             '  0.00  2.00  1.00  0.00  0.00  0.00
 '*2FeO*SiO2(l)      '  0.00  4.00  0.00  2.00  1.00  0.00
 'SiO2(l)            '  0.00  2.00  0.00  0.00  1.00  0.00
 'Cu2O(l)            '  0.00  1.00  0.00  0.00  0.00  2.00
 'Cu2S               '  0.00  0.00  1.00  0.00  0.00  2.00
 'FeS                '  0.00  0.00  1.00  1.00  0.00  0.00
 'Cu                 '  0.00  0.00  0.00  0.00  0.00  1.00
 4
1573.150                                    ' Equilibrium temperature (K)
  0.000000E+00  1.916105E+02  3             ' H, S, number of temperature intervals
  2.919177E+01 -1.121312E-03  0.000000E+00  4.091976E-06  0.000000E+00  0.000000E+00
   400.000      0.000000E+00                ' ^ A, B, C, D, E, F (J/(mol*K))
  2.255176E+01  1.320889E-02  3.129632E+05 -3.389040E-06  0.000000E+00  0.000000E+00
  1600.000      0.000000E+00                ' Temperature (K), H (J/mol)
  3.684012E+01  2.594080E-04 -5.478948E+06  0.000000E+00  0.000000E+00  0.000000E+00
  0.000000E+00  2.051470E+02  1             ' H (J/mol), S (J/(mol*K)), ()
  3.132312E+01  3.893657E-03 -3.105337E+05 -3.349854E-07  0.000000E+00  0.000000E+00
 -2.968130E+05  2.482210E+02  3
  1.734500E+01  7.922700E-02  2.646000E+05 -4.563100E-05  0.000000E+00  0.000000E+00
   700.000      0.000000E+00
  5.164756E+01  6.297887E-03 -2.158751E+06 -1.367747E-06  0.000000E+00  0.000000E+00
  2000.000      0.000000E+00
  6.665800E+01 -4.478000E-03 -1.128930E+07  8.430000E-07  0.000000E+00  0.000000E+00
 -1.458188E+06  9.729792E+01  1
  2.405800E+02  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00
 -9.275245E+05  9.310607E+00  1
  8.577200E+01  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00
 -1.302203E+05  9.640145E+01  1
  9.991399E+01  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00
 -8.117000E+04  1.161520E+02  4
  4.793800E+01  9.717300E-02  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00
   376.000      3.619000E+03
  1.184100E+02 -5.818200E-02  7.920001E+04  2.231700E-05  0.000000E+00  0.000000E+00
   720.000      1.172000E+03
  8.372372E+01 -1.253259E-03  2.450114E+05 -6.180060E-07  0.000000E+00  0.000000E+00
  1400.000      1.284500E+04
  8.966300E+01  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00
 -1.016710E+05  6.032100E+01  4
 -2.732690E+02  7.791840E-01  8.124200E+06  0.000000E+00  0.000000E+00  0.000000E+00
   411.000      1.665000E+03
  7.235800E+01  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00
   598.000      3.970000E+02
  9.458400E+01 -8.366901E-02  1.411000E+05  4.794300E-05  0.000000E+00  0.000000E+00
  1465.000      3.246400E+04
  6.255100E+01  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00
  0.000000E+00  3.316400E+01  2
  4.057800E+01 -1.132500E-02 -3.284000E+05  9.800000E-06  0.000000E+00  0.000000E+00
  1358.000      1.313800E+04
  3.284400E+01  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00
 5  1  2  5  7  8                           ' Raw materials, and their serial numbers
   298.150    298.150    298.150    298.150    298.150
 2                                          ' ^ Temperatures of the raw materials (K)
 13                                         ' Number of equilibria to be calculated
 3 3 3 2 2                                  ' 2 = constant input amount, 3 = increases
 1.0000000E-03 1.8850000E+00                ' Amount of raw material 1., step (mol)
 1.0000000E-03 5.0000000E-01                ' Amount of raw material 2., step (mol)
 1.0000000E-03 1.2500000E-01                ' Amount of raw material 5., step (mol)
 1.0000000E+00                              ' Amount of raw material 7. (mol)
 2.0000000E+00                              ' Amount of raw material 8. (mol)
 10                                         ' Exit
                                            ' 9 = Activity Coefficients if values other than 1
```

Input File for SOLGASMIX Program (Amounts in moles)

```
§Copper Smelting at 1300 C                  ' Heading
   0                                        ' 0 = mole mode, 1= gram mode
   6   4   1   3   3   2                   ' Elements, phases, inv. phases, and
                                            ' ^ number of components / phase 1., etc.
 'N2(g)                '  2.00  0.00  0.00  0.00  0.00  0.00            ' stoichiomet.
 'O2(g)                '  0.00  2.00  0.00  0.00  0.00  0.00            ' matrix
 'SO2(g)               '  0.00  2.00  1.00  0.00  0.00  0.00
 '*2FeO*SiO2(l)        '  0.00  4.00  0.00  2.00  1.00  0.00
 'SiO2(l)              '  0.00  2.00  0.00  0.00  1.00  0.00
 'Cu2O(l)              '  0.00  1.00  0.00  0.00  0.00  2.00
 'Cu2S                 '  0.00  0.00  1.00  0.00  0.00  2.00
 'FeS                  '  0.00  0.00  1.00  1.00  0.00  0.00
 'Cu                   '  0.00  0.00  0.00  0.00  0.00  1.00
 4
1573.150                                    ' Equilibrium temperature (K)
  0.000000E+00  1.916105E+02  3             ' H, S, number of temperature intervals
  2.919177E+01 -1.121312E-03  0.000000E+00  4.091976E-06  0.000000E+00  0.000000E+00
   400.000      0.000000E+00                ' ^ A, B, C, D, E, F (J/(mol*K))
  2.255176E+01  1.320889E-02  3.129632E+05 -3.389040E-06  0.000000E+00  0.000000E+00
  1600.000      0.000000E+00                ' Temperature (K), H (J/mol)
  3.684012E+01  2.594080E-04 -5.478948E+06  0.000000E+00  0.000000E+00  0.000000E+00
  0.000000E+00  2.051470E+02  1             ' H (J/mol), S (J/(mol*K)), ()
  3.132312E+01  3.893657E-03 -3.105337E+05 -3.349854E-07  0.000000E+00  0.000000E+00
 -2.968130E+05  2.482210E+02  3
  1.734500E+01  7.922700E-02  2.646000E+05 -4.563100E-05  0.000000E+00  0.000000E+00
   700.000      0.000000E+00
  5.164756E+01  6.297887E-03 -2.158751E+06 -1.367747E-06  0.000000E+00  0.000000E+00
  2000.000      0.000000E+00
  6.665800E+01 -4.478000E-03 -1.128930E+07  8.430000E-07  0.000000E+00  0.000000E+00
 -1.458188E+06  9.729792E+01  1
  2.405800E+02  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00
 -9.275245E+05  9.310607E+00  1
  8.577200E+01  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00
 -1.302203E+05  9.640145E+01  1
  9.991399E+01  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00
 -8.117000E+04  1.161520E+02  4
  4.793800E+01  9.717300E-02  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00
   376.000      3.619000E+03
  1.184100E+02 -5.818200E-02  7.920001E+04  2.231700E-05  0.000000E+00  0.000000E+00
   720.000      1.172000E+03
  8.372372E+01 -1.253259E-03  2.450114E+05 -6.180060E-07  0.000000E+00  0.000000E+00
  1400.000      1.284500E+04
  8.966300E+01  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00
 -1.016710E+05  6.032100E+01  4
 -2.732690E+02  7.791840E-01  8.124200E+06  0.000000E+00  0.000000E+00  0.000000E+00
   411.000      1.665000E+03
  7.235800E+01  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00
   598.000      3.970000E+02
  9.458400E+01 -8.366901E-02  1.411000E+05  4.794300E-05  0.000000E+00  0.000000E+00
  1465.000      3.246400E+04
  6.255100E+01  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00
  0.000000E+00  3.316400E+01  2
  4.057800E+01 -1.132500E-02 -3.284000E+05  9.800000E-06  0.000000E+00  0.000000E+00
  1358.000      1.313800E+04
  3.284400E+01  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00
 5  1  2  5  7  8  ' Raw materials, and their row numbers in the stoichiometry matrix
   298.150    298.150    298.150    298.150    298.150
 2                                          ' ^ Temperatures of the raw materials (K)
 13                                         ' Number of equilibria to be calculated
 3 3 3 2 2                                  ' 2 = constant input amount, 3 = increases
 1.0000000E-03 1.8850000E+00                ' Amount of raw material 1., step (mol)
 1.0000000E-03 5.0000000E-01                ' Amount of raw material 2., step (mol)
 1.0000000E-03 1.2500000E-01                ' Amount of raw material 5., step (mol)
 1.0000000E+00                              ' Amount of raw material 7. (mol)
 2.0000000E+00                              ' Amount of raw material 8. (mol)
 10                                         ' Exit
```

Input File for SOLGASMIX (Input amounts in grams)

```
§Copper Smelting at 1300 C                    ' Heading
   1                                          ' 0 = mole mode, 1= gram mode
   6   4   1   3   3   2  ' Elements, phases, inv. phases, and number of components   phase 1...
 'N2(g)                '  2.00  0.00  0.00  0.00  0.00  0.00            ' stoichiomet.
 'O2(g)                '  0.00  2.00  0.00  0.00  0.00  0.00            ' matrix
 'SO2(g)               '  0.00  2.00  1.00  0.00  0.00  0.00
 '*2FeO*SiO2(l)        '  0.00  4.00  0.00  2.00  1.00  0.00
 'SiO2(l)              '  0.00  2.00  0.00  0.00  1.00  0.00
 'Cu2O(l)              '  0.00  1.00  0.00  0.00  0.00  2.00
 'Cu2S                 '  0.00  0.00  1.00  0.00  0.00  2.00
 'FeS                  '  0.00  0.00  1.00  1.00  0.00  0.00
 'Cu                   '  0.00  0.00  0.00  0.00  0.00  1.00
14.007                                        ' N Mol. Weight g/mol
15.999                                        ' O
32.060                                        ' S
55.847                                        ' Fe
28.086                                        ' Si
63.546                                        ' Cu
 4
1573.150                                      ' Equilibrium temperature (K)
  0.000000E+00  1.916105E+02  3               ' H, S, number of temperature intervals
  2.919177E+01 -1.121312E-03  0.000000E+00  4.091976E-06  0.000000E+00  0.000000E+00
   400.000      0.000000E+00                  ' ^ A, B, C, D, E, F (J/(mol*K))
  2.255176E+01  1.320889E-02  3.129632E+05 -3.389040E-06  0.000000E+00  0.000000E+00
  1600.000      0.000000E+00                  ' Temperature (K), H (J/mol)
  3.684012E+01  2.594080E-04 -5.478948E+06  0.000000E+00  0.000000E+00  0.000000E+00
  0.000000E+00  2.051470E+02  1               ' H (J/mol), S (J/(mol*K)), ()
  3.132312E+01  3.893657E-03 -3.105337E+05 -3.349854E-07  0.000000E+00  0.000000E+00
 -2.968130E+05  2.482210E+02  3
  1.734500E+01  7.922700E-02  2.646000E+05 -4.563100E-05  0.000000E+00  0.000000E+00
   700.000      0.000000E+00
  5.164756E+01  6.297887E-03 -2.158751E+06 -1.367747E-06  0.000000E+00  0.000000E+00
  2000.000      0.000000E+00
  6.665800E+01 -4.478000E-03 -1.128930E+07  8.430000E-07  0.000000E+00  0.000000E+00
 -1.458188E+06  9.729792E+01  1
  2.405800E+02  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00
 -9.275245E+05  9.310607E+00  1
  8.577200E+01  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00
 -1.302203E+05  9.640145E+01  1
  9.991399E+01  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00
 -8.117000E+04  1.161520E+02  4
  4.793800E+01  9.717300E-02  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00
   376.000      3.619000E+03
  1.184100E+02 -5.818200E-02  7.920001E+04  2.231700E-05  0.000000E+00  0.000000E+00
   720.000      1.172000E+03
  8.372372E+01 -1.253259E-03  2.450114E+05 -6.180060E-07  0.000000E+00  0.000000E+00
  1400.000      1.284500E+04
  8.966300E+01  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00
 -1.016710E+05  6.032100E+01  4
 -2.732690E+02  7.791840E-01  8.124200E+06  0.000000E+00  0.000000E+00  0.000000E+00
   411.000      1.665000E+03
  7.235800E+01  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00
   598.000      3.970000E+02
  9.458400E+01 -8.366901E-02  1.411000E+05  4.794300E-05  0.000000E+00  0.000000E+00
  1465.000      3.246400E+04
  6.255100E+01  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00
  0.000000E+00  3.316400E+01  2
  4.057800E+01 -1.132500E-02 -3.284000E+05  9.800000E-06  0.000000E+00  0.000000E+00
  1358.000      1.313800E+04
  3.284400E+01  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00
 5  1  2  5  7  8            ' Raw materials, and their row numbers in the stoichiometry matrix
   298.150    298.150    298.150    298.150    298.150
 2                                            ' ^ Temperatures of the raw materials (K)
 13                                           ' Number of equilibria to be calculated
 3 3 3 2 2                                    ' 2 = constant input amount, 3 = increases
 2.8013401E-02 5.2805256E+01                  ' Amount of raw material 1., step (g)
 3.1998802E-02 1.5999400E+01                  ' Amount of raw material 2., step (g)
 6.0084306E-02 7.5105376E+00                  ' Amount of raw material 5., step (g)
 1.5915201E+02                                ' Amount of raw material 7. (g)
 1.7581400E+02                                ' Amount of raw material 8. (g)
 10                                           ' Exit
```

Case 1 Hydration of Magnesia Chrome Bricks

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, which 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 to the Equilibrium module from the database. The following ideas were used to specify the system (see Fig 2):

- Metallic substances were removed, as they are not needed in these conditions.
- Gas species (16) were inserted in 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, Cr2O3 and Fe2O3 raw materials were added according to their amount in the brick: MgO 60, Cr2O3 18 and Fe2O3 14 kg.
- Water gas was added to the gas phase. The amount was set slightly higher than needed to hydrate all species in the brick.
- A small amount of nitrogen was added to the gas phase.

The results of the calculations are shown in Fig. 1. 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.

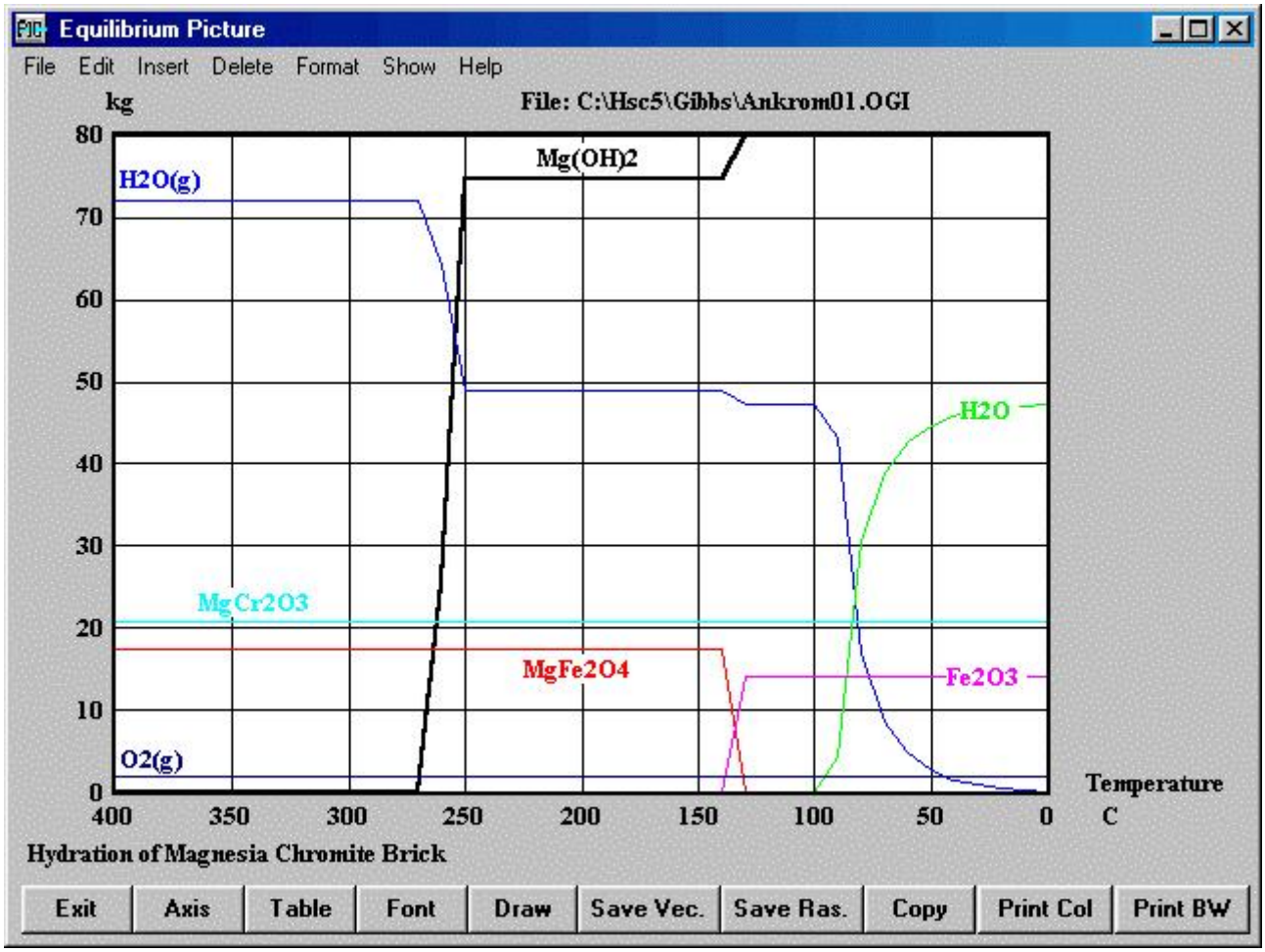


Figure 1. Calculation results for hydration of magnesia chrome brick.

Hydration of Magnesia Chromite Brick						
File Format		GIBBS		C: Hsc5 Gibbs Ankrom01.igi		
Pure Substances in the Last Phase		YES				
Increase Temperature	101	Steps		Criss-Cobble On		
Temperature Range	1000.000	0.000	C			
Pressure Range	1.000	1.000	bar			
SPECIES Formula	**Temper. C**	**Amount kmol**	**Amount**	**Step kmol**	**Step**	**Activity Coeff.**
PHASE 1		5.000	100.000			
N2(g)	25.000	1.000	20.000			1.000
H2O(g)	25.000	4.000	80.000			1.000
H2(g)	25.000					1.000
O2(g)	25.000					1.000
Cr(g)	25.000					1.000
CrO(g)	25.000					1.000
CrO2(g)	25.000					1.000
CrO3(g)	25.000					1.000
Fe(g)	25.000					1.000
FeO(g)	25.000					1.000
Fe(OH)2(g)	25.000					1.000
Mg(g)	25.000					1.000
Mg2(g)	25.000					1.000
MgH(g)	25.000					1.000
MgO(g)	25.000					1.000
MgOH(g)	25.000					1.000
Mg(OH)2(g)	25.000					1.000
PURE SUBSTANCES		1.695	100.000			
Cr2FeO4	25.000					1.000
Cr2MgO4	25.000					1.000
CrO2	25.000					1.000
CrO3	25.000					1.000
Cr2O3	25.000	0.118	6.988			1.000
Cr5O12	25.000					1.000
Cr8O21	25.000					1.000
Cr(OH)2	25.000					1.000
Cr(OH)3	25.000					1.000
Fe2MgO4	25.000					1.000
Fe0.945O	25.000					1.000
Fe0.947O	25.000					1.000
FeO	25.000					1.000
FeO1.056	25.000					1.000
Fe2O3	25.000	0.088	5.173			1.000
Fe3O4	25.000					1.000
Fe(OH)2	25.000					1.000
Fe(OH)3	25.000					1.000
Fe2O3 H2O	25.000					1.000
H2O	25.000					1.000
MgCr2O3	25.000					1.000
MgFe2O4	25.000					1.000
MgO	25.000	1.489	87.839			1.000
MgO2	25.000					1.000
Mg(OH)2	25.000					1.000

Figure 2. Specification of phases and species in the Magnesia Chrome brick example.

Case 2 Ammonia Synthesis (by Panu Talonen)

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

$N_2(g)$ 3 $H_2(g)$ - $2NH_3(g)$

The number of gas moles decreases in this reaction and therefore high pressure may be assumed to favor the synthesis. The equilibrium calculation may be carried out as described in Chapter 13. The chemical system specification and other calculation parameters are shown in Fig. 2. 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. 3. It is easy to see that at normal 1 bar pressure it is quite impossible to produce high amounts of ammonia. It also seems that synthesis should be done 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.

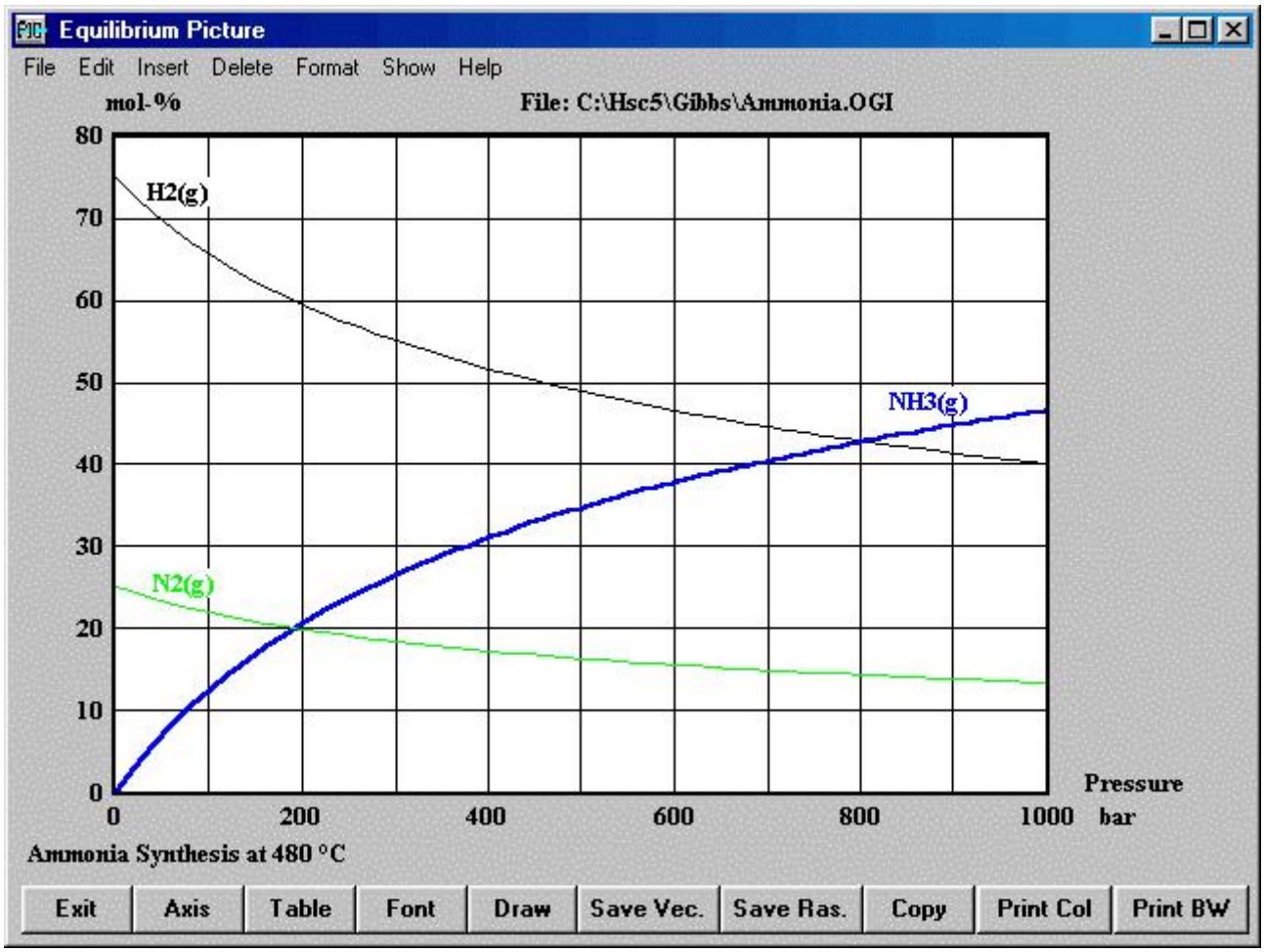


Figure 3. Calculation results for ammonia synthesis example.

Ammonia Synthesis at 480 C						
File Format		GIBBS		C: Hsc5 Gibbs Ammonia.igi		
Pure Substances in the Last Phase		YES				
Increase Pressure	51	Steps		Criss-Cobble On		
Temperature Range	480.000	480.000	C			
Pressure Range	0.001	1000.001	bar			
SPECIES Formula	**Temper. C**	**Amount kmol**	**Amount**	**Step kmol**	**Step**	**Activity Coeff.**
PHASE 1		4.001	100.000			
H(g)	25.000					1.000
H2(g)	25.000	3.000	74.981			1.000
HN3(g)	25.000					1.000
N(g)	25.000					1.000
N2(g)	25.000	1.001	25.019			1.000
N3(g)	25.000					1.000
NH(g)	25.000					1.000
NH2(g)	25.000					1.000
NH3(g)	25.000					1.000
N2H2(g)	25.000					1.000
N2H4(g)	25.000					1.000
N3H(g)	25.000					1.000
NH(H3)2(g)	25.000					1.000
PURE SUBSTANCES						
NH4N3	25.000					1.000

Figure 4. Specification of phases and species in ammonia synthesis example.

Case 3 Decomposition of $MgCl_2$ $6H_2O$

All compounds will decompose if the temperature is high enough. Especially substances with combined water will decompose at quite low temperatures. The decomposition temperatures may be found from many different handbooks, but they may also be calculated with the HSC Equilibrium module if the basic data is available in the HSC database. Magnesium chloride forms a $MgCl_2$ $6H_2O$ compound which decomposes according to the reaction:

$MgCl_2$ $6H_2O$ - $MgCl_2$ $4H_2O$ $2H_2O(g)$

$MgCl_2$ $4H_2O$ - $MgCl_2$ $2H_2O$ $2H_2O(g)$, etc.

The decomposition temperature as well as the decomposition vapor pressure may be calculated using the chemical system specification shown in Fig. 5. The user must specify all possible condensed phases as well as a gas phase. **Please note**: A) Small nitrogen amount stabilize the gas phase, B) small $Cl_2(g)$ and $O_2(g)$ amounts shift the material balance out from stoichiometric one and C) Mg(g) allows magnesium to enter the gas phase also.

The results of the calculations are shown in Figs. 6 and 7. The decomposition seems to start at 100 C, see Fig. 6. The vapor composition is drawn in Fig. 7 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.

Decomposition of MgCl2 6H2O at 1 bar						
File Format		GIBBS		C: Hsc5 Gibbs Mgcl2.igi		
Pure Substances in the Last Phase		YES				
Increase Temperature	81	Steps		Criss-Cobble On		
Temperature Range	0.000	400.000	C			
Pressure Range	1.000	1.000	bar			
SPECIES Formula	**Temper. C**	**Amount kmol**	**Amount**	**Step kmol**	**Step**	**Activity Coeff.**
PHASE 1		0.100	100.000			
N2(g)	25.000	0.100	99.980			1.000
Cl2(g)	25.000	0.000	0.010			1.000
HCl(g)	25.000					1.000
H2O(g)	25.000					1.000
O2(g)	25.000	0.000	0.010			1.000
H2(g)	25.000					1.000
Mg(g)	25.000					1.000
PURE SUBSTANCES		1.000	100.000			
MgCl2 6H2O	25.000	1.000	100.000			1.000
MgCl2 4H2O	25.000					1.000
MgCl2 2H2O	25.000					1.000
MgCl2 H2O	25.000					1.000
MgCl2	25.000					1.000
Mg(OH)Cl	25.000					1.000
MgO	25.000					1.000
H2O	25.000					1.000

Figure 5. Specification of phases and species in $MgCl_2$ $6H_2O$ example.

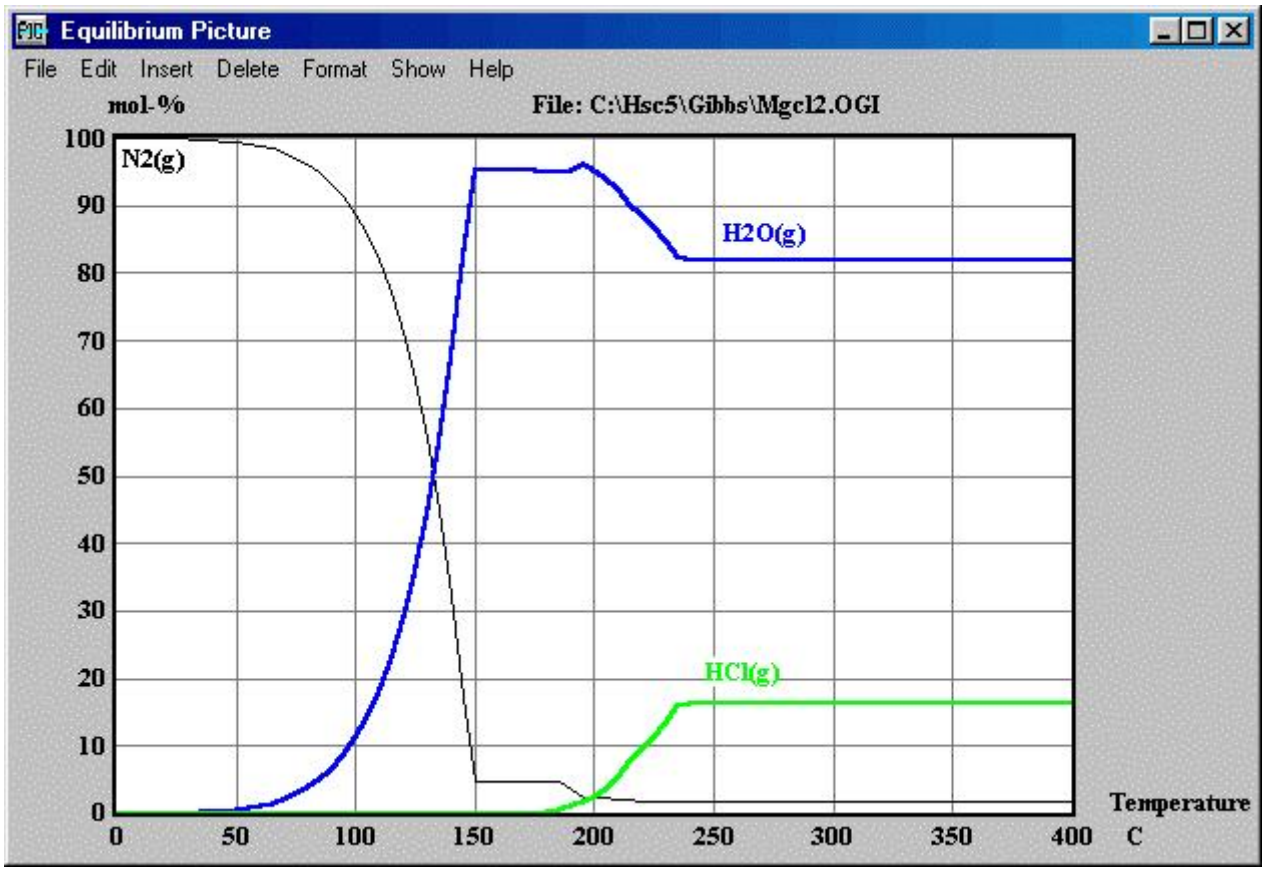


Figure 6. Calculation results for $MgCl_2$ $6H_2O$ decomposition example.

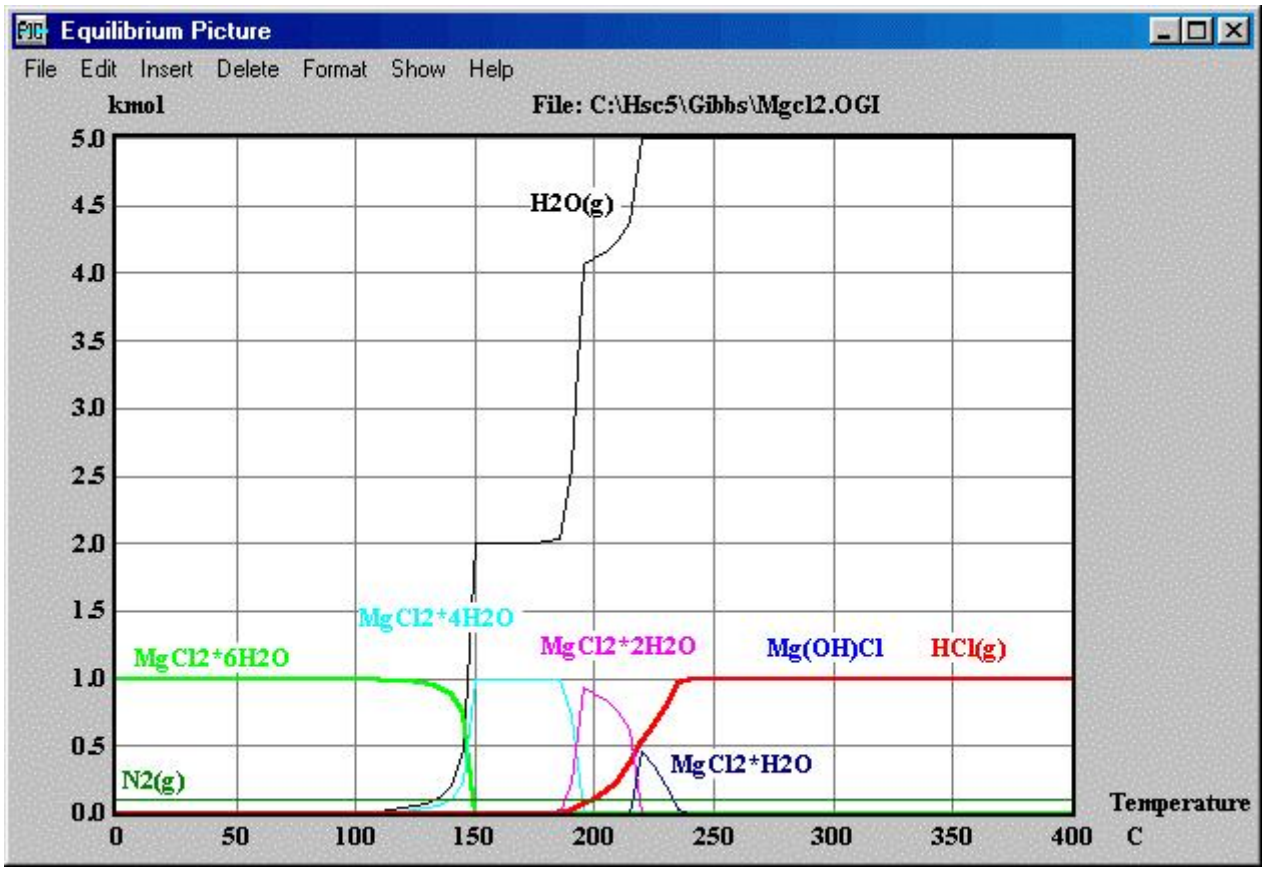


Figure 7. Vapor composition at a total pressure of 1 bar.

Case 4 Decomposition of $FeSO_4$ $7H_2O$ (by Ben Karlemo)

Thermal decomposition of a chemical compound will sometimes give valuable information of its behaviour 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 $FeSO_4$ $7H_2O$. The chemical system specifications for the HSC equilibrium module are shown in Fig. 8. **Please note** (see Chapter 13.4): A) The small amount of nitrogen stabilizes the gas phase, B) the small amount 1E-5 kmol of O2(g) shifts the material balance away from the stoichiometric one, C) Fe(g) allows iron to enter the gas phase also, and D) Solgasmix routine has been used. The results are shown in Fig. 9.

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. 10. The TG curve shows the actual weight change and the DSC curve shows the enthalpy change compared to the reference test.

Decomposition of FeSO4 7H2O at 1 bar						
File Format		GIBBS		C: Hsc5 Gibbs Feso4.igi		
Pure Substances in the Last Phase		YES				
Increase Temperature	100	Steps		Criss-Cobble On		
Temperature Range	0.000	1600.038	C			
Pressure Range	1.000	1.000	bar			
SPECIES Formula	**Temper. C**	**Amount kmol**	**Amount**	**Step kmol**	**Step**	**Activity Coeff.**
PHASE 1		0.004	100.000			
N2(g)	25.000	0.004	99.990			1.000
O2(g)	25.000	0.000	0.010			1.000
SO2(g)	25.000					1.000
S2(g)	25.000					1.000
H2S(g)	25.000					1.000
H2O(g)	25.000					1.000
H2(g)	25.000					1.000
Fe(g)	25.000					1.000
PURE SUBSTANCES		0.360	100.000			
FeSO4 7H2O	25.000	0.360	100.000			1.000
FeSO4 4H2O	25.000					1.000
FeSO4 H2O	25.000					1.000
Fe2(SO4)3	25.000					1.000
FeSO4	25.000					1.000
FeO OH	25.000					1.000
FeO	25.000					1.000
Fe2O3	25.000					1.000
Fe3O4	25.000					1.000
H2O	25.000					1.000

Figure 8. The specification of phases and species for the equilibrium calculations.

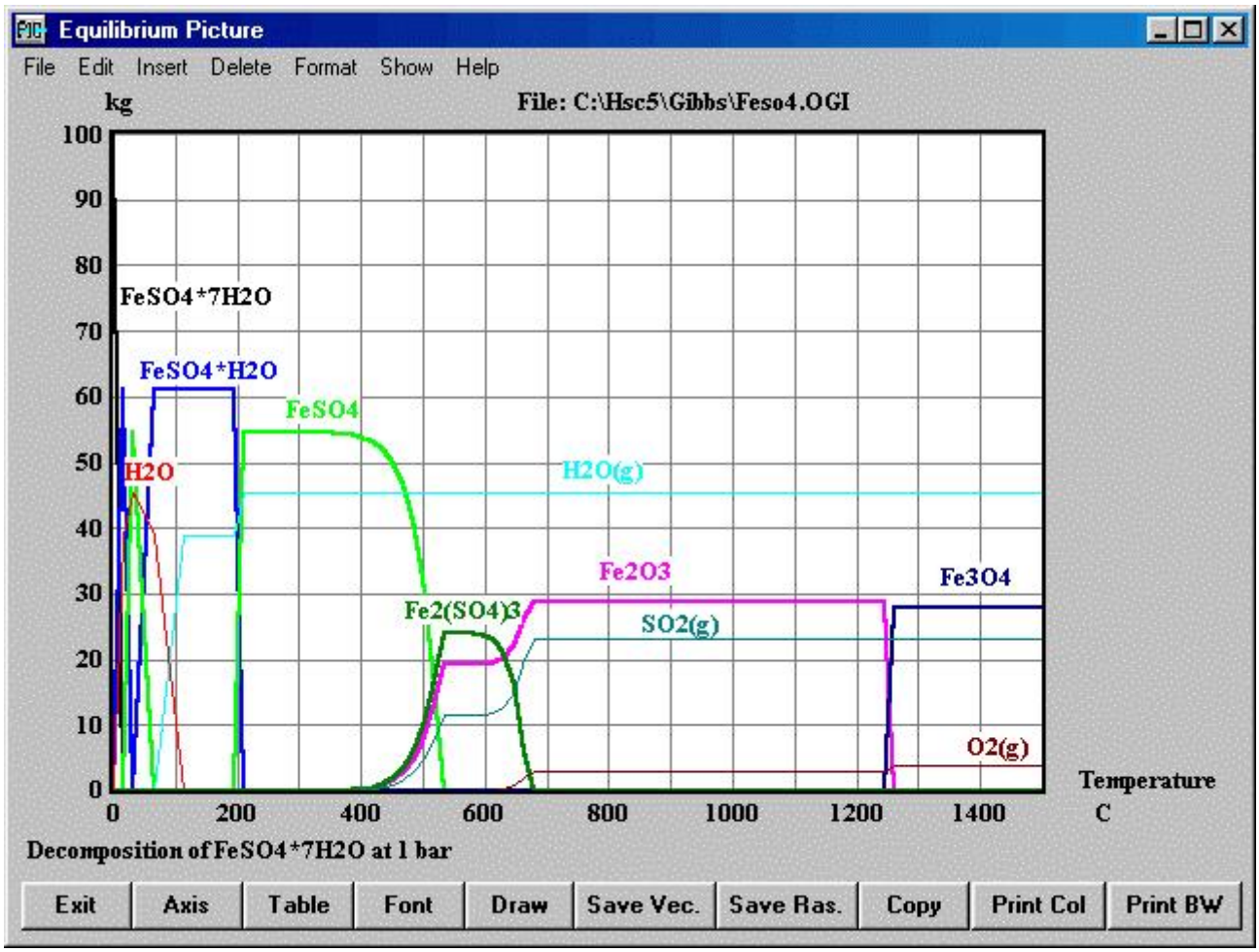


Figure 9. The result of the calculated decomposition of $FeSO_4$ $7H_2O$.

The theoretical and experimental weight change curves are compared in Fig. 11, 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.

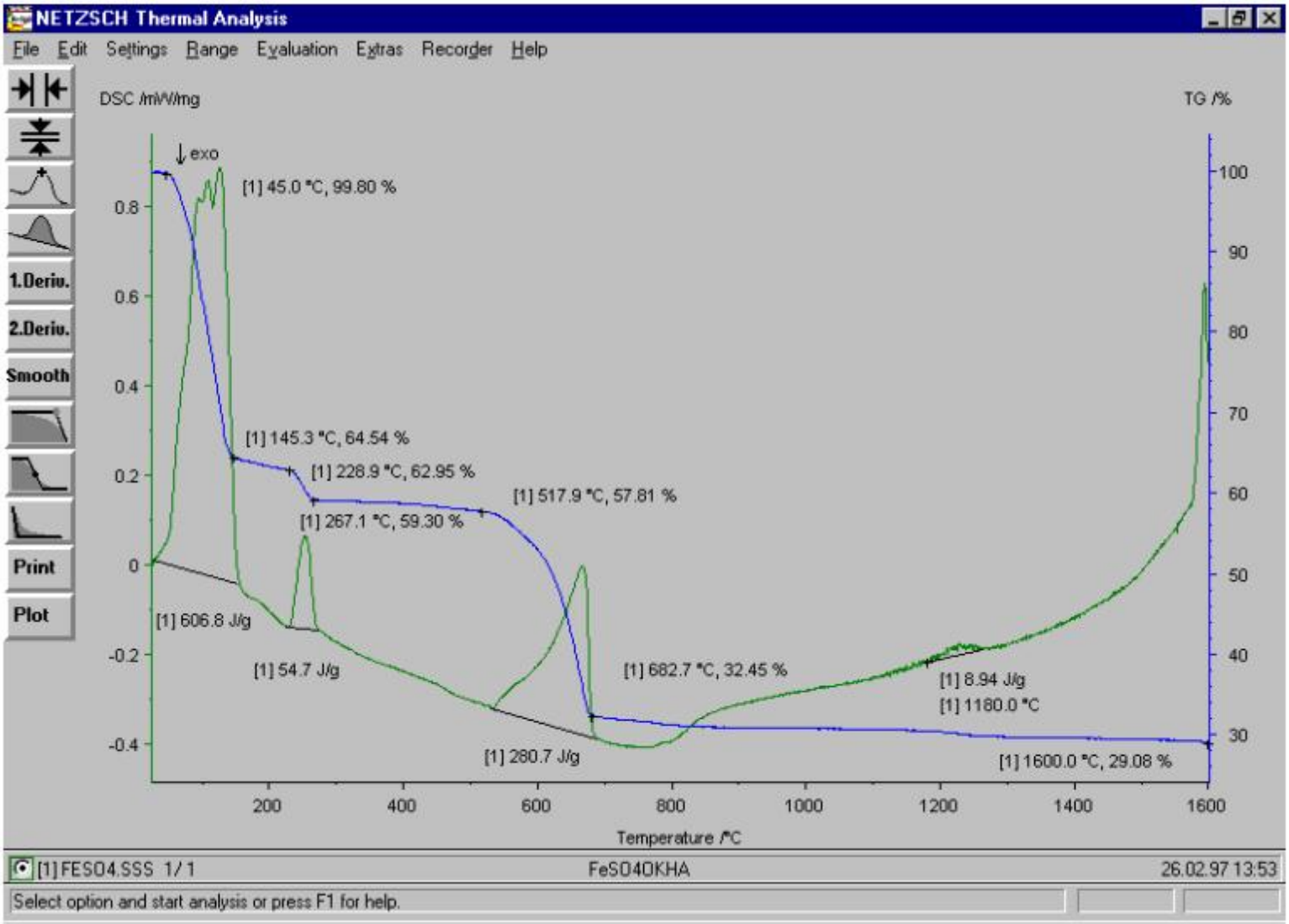


Figure 10. Results of $FeSO_4$ $7H_2O$ run on NETSCH TG-DSC analyzer under nitrogen atmosphere showing TG and DSC curves. Heating rate was 5 C min.

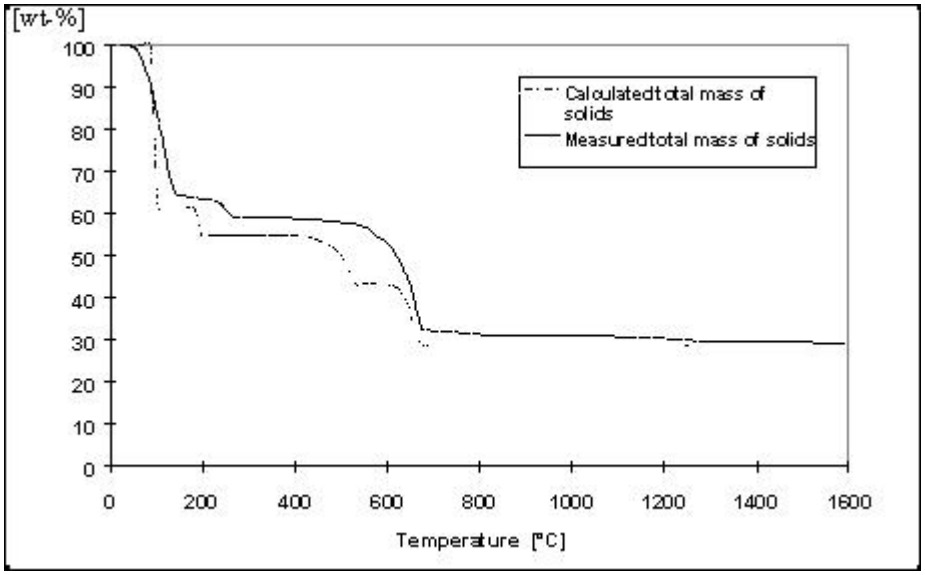


Figure 11. The comparison of the measured and calculated mass change of $FeSO_4$ $7H_2O$.

Case 5: Alkali circulation in Blast Furnace (by Riku Sarkkinen)

Alkali metals tend to enrich in the iron blast furnace. The alkali content in raw materials (pellets, sinter and coke) is not so high, but they evaporate at the bottom part of the furnace (1500 C) and do not exit with the products (slag, iron) easily. Neither 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. 13. The raw material amounts are based on the following assumptions: Coke ash analysis (main components): SiO_2 53, CaO 3, MgO 2, and Al_2O_3 27 wt . Process gas is formed by air reaction with coke, the main components in the gas phase are CO(g), CO_2(g) and N_2(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. 12. 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 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 downwards 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.

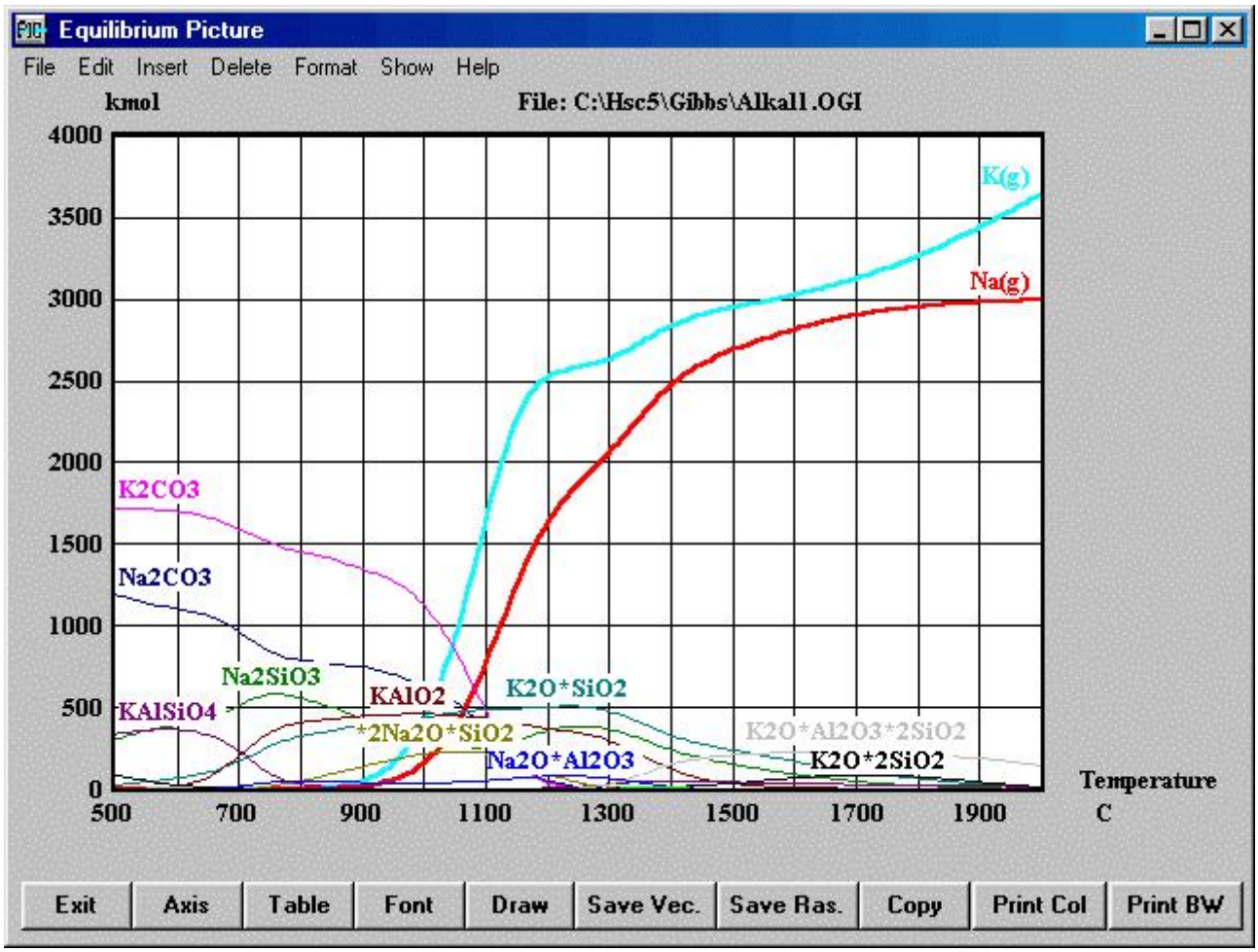


Figure 12. Equilibrium results of alkalis and slag components as a function of temperature.

File Format		GIBBS		C: Hsc5 Gibbs Alkal1.igi		
Pure Substances in the Last Phase		YES				
Increase Temperature	200	Steps		Criss-Cobble On		
Temperature Range	500.000	2000.062	C			
Pressure Range	1.000	1.000	bar			
SPECIES Formula	**Temper. C**	**Amount kmol**	**Amount**	**Step kmol**	**Step**	**Activity Coeff.**
PHASE 1		197000.000	100.000			
AlO(g)	25.000					1.000
CO(g)	25.000					1.000
CO2(g)	25.000					1.000
Ca(g)	25.000					1.000
K(g)	25.000	4000.000	2.030			1.000
K2(g)	25.000					1.000
K2CO3(g)	25.000					1.000
KNa(g)	25.000					1.000
KO(g)	25.000					1.000
Mg(g)	25.000					1.000
MgO(g)	25.000					1.000
N2(g)	25.000	150000.000	76.142			1.000
Na(g)	25.000	3000.000	1.523			1.000
Na2(g)	25.000					1.000
NaO(g)	25.000					1.000
O(g)	25.000					1.000
O2(g)	25.000	40000.000	20.305			1.000
SiO(g)	25.000					1.000
PHASE 2		1417.000	100.000			
AlO	25.000					1.000
Al2O3	25.000	300.000	21.171			1.000
Al2O3 SiO2(D)	25.000					1.000
Ca2Al2SiO7	25.000					1.000
Ca3Al2Si3O12	25.000					1.000
CaO	25.000	60.000	4.234			1.000
Ca2SiO4(A)	25.000					1.000
KAlO2	25.000					1.000
KAlSiO4	25.000					1.000
K2CO3	25.000					1.000
K2O	25.000					1.000
K2O Al2O3 2SiO2	25.000					1.000
K2O SiO2	25.000					1.000
K2O 2SiO2	25.000					1.000
MgO	25.000	57.000	4.023			1.000
MgSiO3	25.000					1.000
Na2CO3	25.000					1.000
Na2O	25.000					1.000
Na2O Al2O3	25.000					1.000
2Na2O SiO2	25.000					1.000
Na2SiO3	25.000					1.000
SiO2	25.000	1000.000	70.572			1.000
PHASE 3						
Al	25.000					1.000
Ca	25.000					1.000
K	25.000					1.000
Mg	25.000					1.000
Na	25.000					1.000
Si	25.000					1.000
PURE SUBSTANCES		70000.000	100.000			
C	25.000	70000.000	100.000			1.000
Al4C3	25.000					1.000
Na2C2	25.000					1.000
SiC	25.000					1.000

Figure 13. Specification of phases and species in the Blast Furnace example.

15. CELL EQUILIBRIA

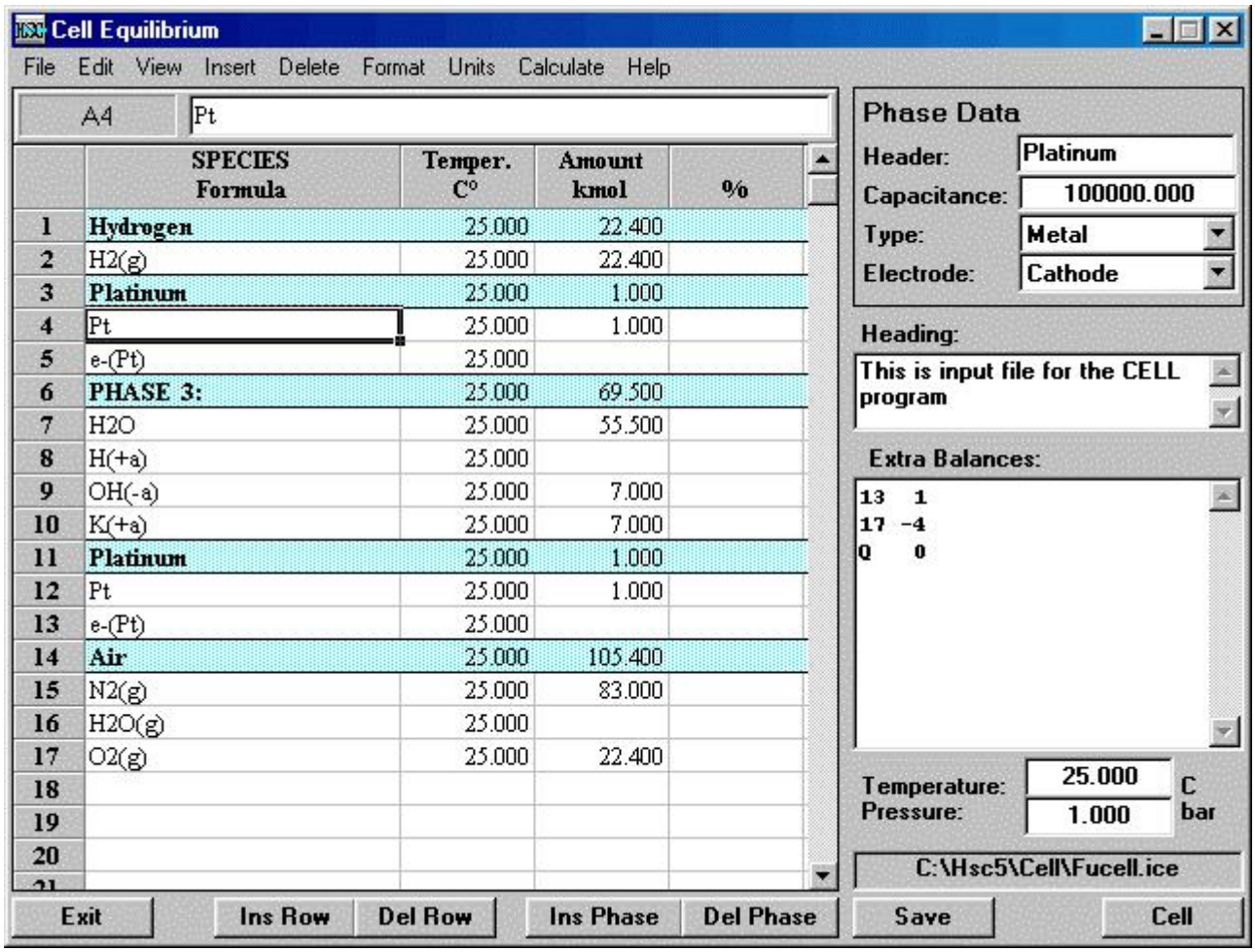


Fig. 1. Input data for the Cell program.

The CELL module calculates the equilibrium composition of an electrochemical cell using the same calculation method as the GIBBS-solver. However, the CELL module is especially designed for electrochemical cell calculations.

In addition to the phase compositions it also gives the electrochemical potentials of the electrodes. The user gives input data for the CELL program in the Cell Equilibrium window, see Fig. 1.

Brief Instructions

In the Cell Equilibrium window you can give the input data required for the calculations and save the input data for the CELL program. You can see examples of the data by selecting **Open** from the **File** menu. Please do this before making your own input files for CELL.

1. You can move in the spreadsheet using the mouse or arrow keys.

2. If you want to edit the cell double click with the mouse or simply start typing. Use **Esc key** to undo typing.
3. When you are satisfied with the formula or number, press **Enter**, **Down** or **Up keys**. You can also click another cell with the mouse.
4. Type the name of the first species into the Species column. Note that you must start filling in the spreadsheet from the first row.
5. You can first type all species and then edit the temperature and amount values, or you can give these values after every species name input.
6. You can toggle between degrees Celsius and Kelvins by selecting **C** or **K** from the Units menu and from moles to kilograms (or Nm^3 for gases) by the **mol** selection.
7. You must divide the species into phases in the same way as described in normal equilibrium calculations, see examples in Chapter 15.2.
8. Every phase must have its own phase row. All species under this phase row until the next phase row belong to this same phase.
9. For every phase you must at least specify its **Type** (Gas, Liquid, ...). You must also specify the Anode and Cathode phases. You can also give a name and capacitance for the phases.
10. If you want to change the order of species, simply use **Insert Row**, Copy and Paste or the Drag and Drop technique described in Chapter *2 . Dia ra ra ics*.
11. You can also insert and delete rows by pressing **Ins Row** and **Del Row**.
12. You can give **Extra Balances** as a table or matrix in the Extra Balances Box. For example:

13	**1**	Species 13: Oxidation number of e-(Pt)
17	**-4**	Species 17: Oxidation number of O2(g)
Q	**0**	Discharge amount: F (mol)

Extra Balances makes it possible to calculate potentials of electrodes and chemical compositions of phases at different discharge states of an electrochemical cell.

You must first define the species numbers, which react at the anode or cathode, as well as their oxidation numbers. In the example oxygen gas O2(g) is decomposed on a cathode, its oxidation number is 2 (-2) = -4. The oxidation number of an electron is always 1.

The discharge amount defines the amount of electricity, which is transferred from anode to cathode in the equilibrium. By changing the discharge amount you can calculate potentials and compositions at different discharge states of the cell. Note:

= Amount of electricity in As (charge)

F = Faraday s constant, 96487 As mol

13. When you are satisfied with the data, save it by pressing **Save**.
14. After saving you can go to the CELL-program by pressing **Cell**.

Additional Information

You can obtain more information on the CELL program and the thermodynamics in the background using **Help** as well as from the original publications of the authors[7,8].

15.1 Cell Module

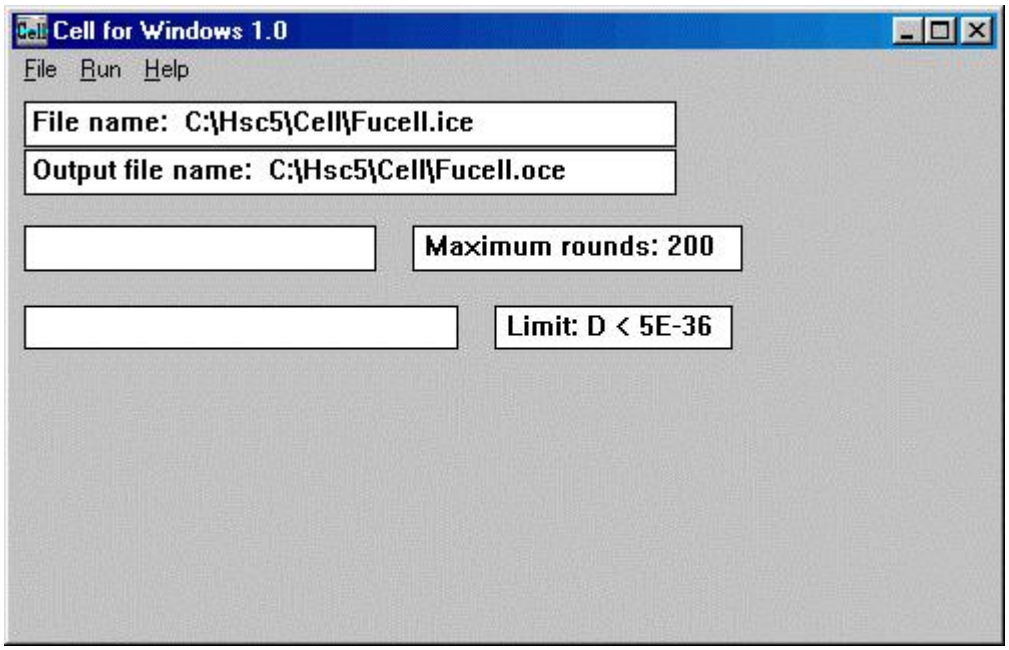


Fig. 2. Cell program.

The CELL-program calculates the equilibrium configuration of chemical and electrochemical systems and cells, half cells, fuel cells, as well as secondary and primary batteries.

For a complete cell with two or more electrodes, the total charge and the amount of atoms present in the system are not sufficient conditions of equilibrium. The additional constraint used in the CELL routine is the so-called DISCHARGE E UATION. This 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, see the example fucell.ice. These constraints can be defined in the **Extra Balances** box, see Fig. 1.

Running the program

1. Open input data file with the option **File Open**...
2. Select the option **Run Calculate** . The program will then calculate the equilibrium state. If you want to change the number of iterations, choose the Run Maximum rounds option which gives the new number of iterations. The default value is 200. You may interrupt the calculation by pressing any key or the mouse button.

3. Answer YES to the question Do you want to save equilibrium data if you want to save results in input data file format on the file Equil.ice . Otherwise select NO.
4. You can return to the HSC Main menu by selecting **File Exit** .

With the options **File View** input file and **File View** output file you can view the input file and output file, respectively. You may also send files to the printer with the **Print** option in the viewing window.

16. FORMULA WEIGHTS

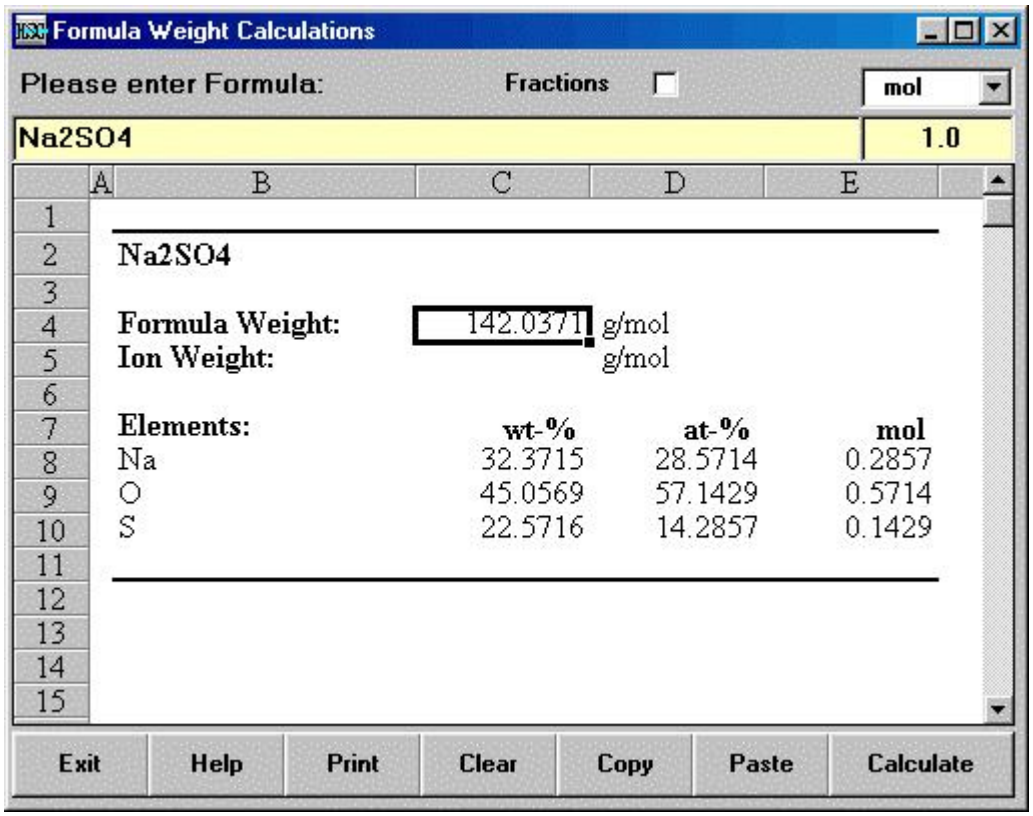


Fig. 1. Formula Weights.

This simplest calculation option of HSC Chemistry is a versatile routine for calculating formula weights. As input, it accepts almost any form of chemical formula using conventional organic or inorganic expressions. Typical entries may be:

NaBO3 4H2O, H2Sn(OH)6, (C2H5)2O, Fe0.998O, etc.

You can collect several results on the sheet. **Clear** will clear the whole sheet. You can print the results using **Print**. The Formula Weight option uses the same routine for calculating the formula weights and elemental composition as all other calculation options in the HSC. Therefore you can test the correct formula formats in this option. **Copy** will copy the results into the clipboard. Note that you can copy and paste cell ranges also.

You can select mol or kg units for column E as well as the total amount from the box at top right corner of the form. By pressing mouse right button you can, for example, modify number format.

Limitations

1. Superscripts and subscripts are not allowed.
2. Inner parentheses are not allowed, for example:
   H2(Sn(OH)6) is not a valid formula. Use H2Sn(OH)6 instead.
3. Last parentheses are always reserved for species type declarations, for example:

As(g)	Arsenic gas	C	Carbon
O2(g)	Oxygen gas	C(D)	Diamond
Fe(l)	Liquid iron	FeS2	Pyrite
OH(-a)	Aqueous OH ion	FeS2(M)	Marcasite

If you want to write the following formula please write it in one of the following ways: (Last parenthesis are reserved for suffix)

AlO(OH)	Not valid
AlO2H	Valid
AlO (OH)	Valid
AlO OH	Valid

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

Eh-pH-diagrams show the thermodynamic stability areas of different species in an **aqueous solution**. Stability areas are presented as a function of pH and electrochemical potential scales. Usually the upper and lower stability limits of water are also shown in the diagrams with dotted lines. Traditionally these diagrams have been taken from different handbooks[12]. However, in most handbooks these diagrams are available only for a limited number of temperatures, concentrations and element combinations.

The Eh-pH module of HSC Chemistry allows the construction of diagrams in a highly flexible and fast way, because the user can draw the diagrams exactly at the selected temperature and concentration.

The Eh-pH-module is based on STABCAL - Stability Calculations for Aqueous Systems - developed by H.H. Haung, at Montana Tech., USA[9,10].

17.1 Introduction

Eh-pH-diagrams are also known as **Pourbaix Diagrams** according to author of the famous Pourbaix diagram handbook[12]. The most simple type of these diagrams is based on a chemical system consisting of one element and water solution, for example, the Mn-H_2O-system. The system can contain several types of species, such as dissolved ions, condensed oxides, hydroxides, oxides, etc. The Eh-pH-diagram shows the **stability areas** of these species in the redox potential-pH-coordinates.

Usually the **redox potential** axis is based on the Standart Hydrogen Electrode (SHE) scale designated Eh, but other scales can also be used. The redox potential of the system represents its ability to change electrons. The system tends to remove electrons from the species when the potential is high (Eh 0). These conditions may exist near the anode in the electrochemical cell, but can also be generated with some oxidizing agents (Cu H_2O_2 = CuO H_2O). In reducing conditions, when potential is low (Eh 0), the system is able to supply electrons to the species, for example, with a cathode electrode or with some reducing agents.

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

Usually a large amount of different species exist simultaneously in the aqueous mixtures in fixed Eh-pH-conditions. The Pourbaix diagrams simplify this situation a lot by showing only the predominant species which content is highest in each stability areas. The **lines** in the diagrams represent the Eh-pH-conditions where the content of the adjacent species is the same in the equilibrium state. However, these species always exist in small amounts on both sides of these lines and may have an effect on practical applications.

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

1. **Hori ontal lines**. These lines represent reactions that are involved with electrons, but are independent of pH. Neither H(a)-ions nor OH(-a)-ions participate to these reactions.
2. **Diagonal lines** with either positive or negative slope. These lines represent reactions that are involved with both electrons and H(a)-and OH(-a)-ions.

3. **Vertical lines**. These lines represent reactions that are involved either with H(a)- or OH(-a)-ions, but are independent of Eh. In other words, electrons do not participate with these reactions.

The chemical **stability area of the water** is shown in the Eh-pH-diagrams with dotted lines. The upper stability limit of water is based on the potential when the oxygen generation starts on the anode. It is specified by the reaction:

$$2\ H_2O = O_2(g) \quad 4\ H(\ a) \quad 4\ e^-$$

The lower stability limit is based on hydrogen formation on the cathode. It is specified by the reaction:

$$2\ H(\ a) \quad 2\ e^- = H_2(g)$$

The construction of the diagrams with HSC Chemistry EpH module is quite a simple task. However, several aspects must be taken into account when specifying the chemical system and analyzing the calculation results, for example:

1. **A basic knowledge** of chemistry, aqueous systems and electrochemistry or hydrometallurgy is always needed in order to draw the correct conclusions.
2. The EpH module carries out the calculations using **pure stoichiometric substances**. In practice minerals may contain impurity elements and the composition may deviate slightly from the stoichiometric one.
3. There are always some **errors** in the basic thermochemical data of the species. This may have significant effect on the results, especially if the chemical driving force of the reaction is small. Usually small differences between Pourbaix diagrams from different sources can be explained by the slightly different basic data used.
4. Sometimes data for all existing **species is not available** from the HSC database or from the other sources. This will distort the results if the missing species are stable in given conditions. The missing unstable species will have no effect on the results.
5. The EpH module does not take into account **the non-ideal** behavior **of aqueous solutions**. However, in many cases these ideal diagrams give a quite good idea of the possible reactions in aqueous solutions, especially if the driving force of the reactions is high.
6. Thermochemical calculations do not take into account the **speed of the reactions** (kinetics). For example, the formation of the SO4(-2a) ion may be a slow reaction. In these cases metastable diagrams created by removing such species from the system may give more consistent results with the experimental laboratory results.

The HSC user must be very careful when drawing conclusions from Eh-pH-diagrams due to these limitations and assumptions. However, these diagrams may offer extremely valuable information when combining the results with the experimental work and with a good knowledge of aqueous chemistry. There is no universal kinetic or thermochemical theory available, which could entirely substitute traditional experimental laboratory work with pure theoretical calculation models.

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

17.2 Chemical System Specifications

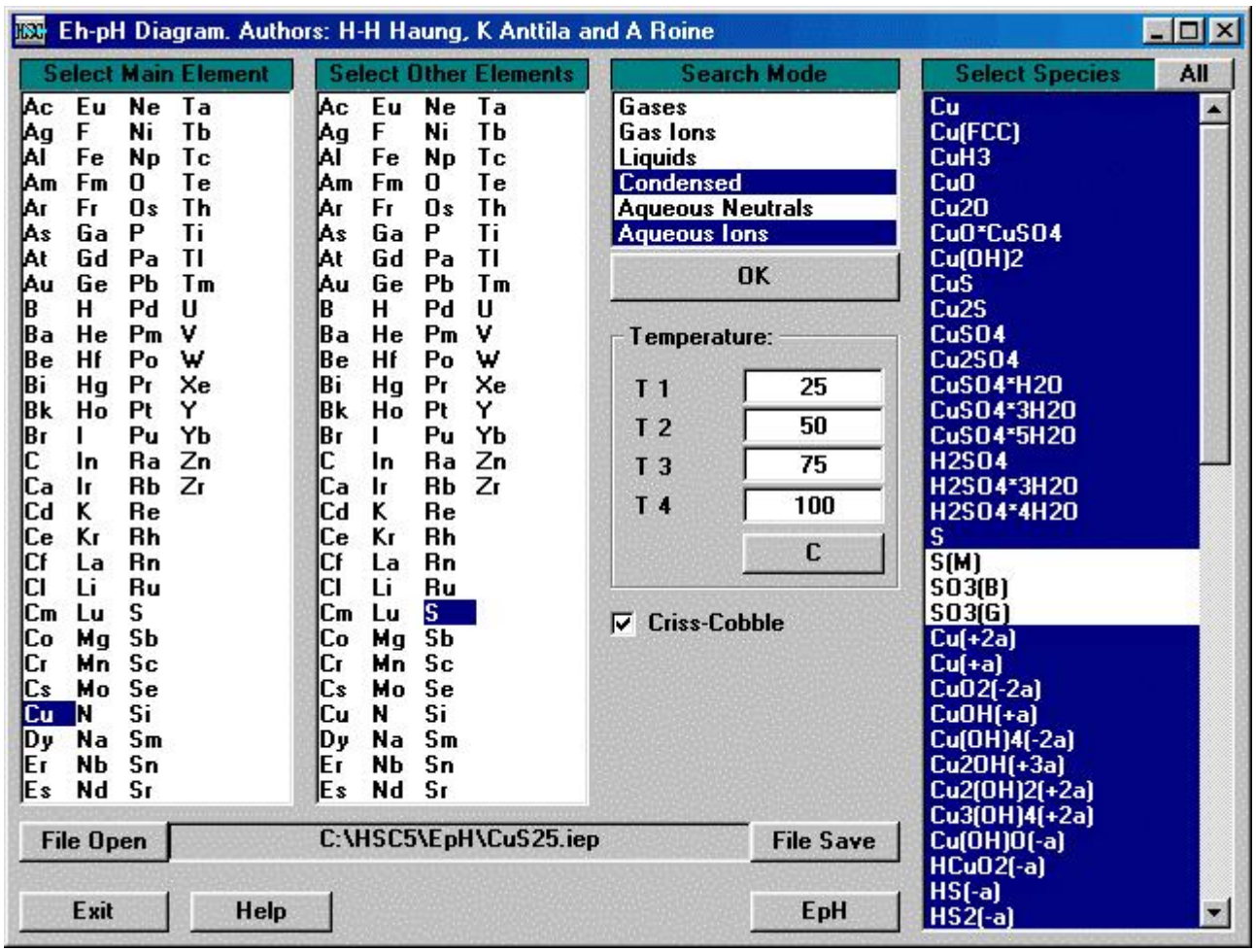


Fig. 1. Selecting elements and species for the Eh - pH - diagram.

The EpH Diagram selection in the HSC main menu will show the EpH-form, Fig. 1. The user must specify the chemical system, which will be used to calculate the diagram in this form. Assume that system contains Cu, S and H_2O. The following steps should be specified in order to create the diagram:

1. **Select Main Element**: Select one element from the list. This element will be used as the main element in the first diagram, i.e. all species, which are shown in the diagram, will contain this element. The user can easily change the main element selection later on in the diagram form, see Fig. 3. The **Cu** has been selected in this example, but **S** may be selected to main element by pressing S button in Fig. 3.

2. **Select Other Elements**: Select other elements to the system. Up to 7 elements can be selected but it is recommended to use less, because large amount of elements and species increase calculation time and could cause some other problems. **S** has been selected in this example. **Note**: It is not necessary to select **H** and **O**, because these are always automatically included.

3. **Search Mode**: This selection specifies the type of species, which will be collected from the database. It is recommended to use default selections. **Note**: *ondensed* =

solid substances, *ueous eutra s* =dissolved species without charge, *ueous Ions* = dissolved ions, *ases* = gaseous species without charge, *as Ions* = gaseous ions, and *i uids* = liquid species.

4. **OK**: Press OK to start the search from the database.

5. **Select Species**: Usually you can select all species to the diagram by pressing **All**. In some cases, however, it is useful to remove unnecessary species from the system. This will decrease calculation time and simplify diagrams. Note: A) By pressing simultaneously **Ctrl-key** and clicking with the mouse it is easy to make any kind of selection. B) By double clicking the species it is possible to see more information of the species. Load CUS25.IEP file to see the selected species of this example.

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

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

6. **Temperature**: The user must specify at least one temperature for the diagram. Up to four temperatures may be specified in order to draw combined diagrams, which show the effect of temperature. The temperatures 25, 50, 75 and 100 C have been selected in this example, Figs. 1 and 2.

7. **Criss-Cobble**: This option enables HSC to extrapolate the heat capacity function of the aqueous species if this data is not given in the database[11], see Chapter 28.4.

8. **EpH**: Press EpH to start the File Save dialog and Calculation of the diagram. You can also press **File Save** in order to save the data for later use without running the calculation procedure.

9. **Diagram**: Pressing the EpH button will show the Diagram specification form, see Chapter 17.3 and Fig 2. By pressing **Diagram** in Fig. 2 you will see the default diagram.

17.3 Eh - pH - Diagram Menu

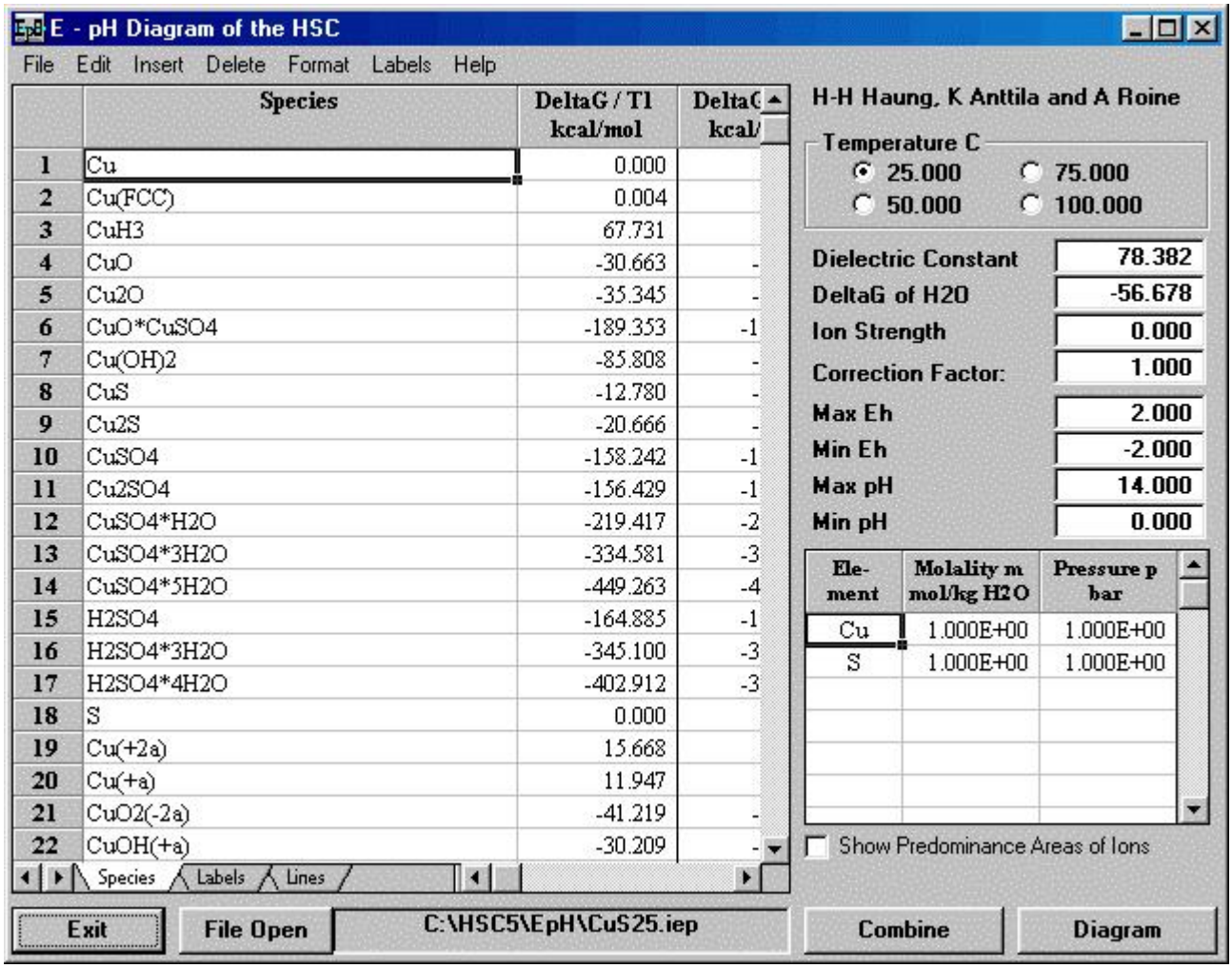


Fig. 2. Default values for the Eh - pH - diagram.

The EpH-diagram menu shows a summary of the chemical system specifications as well as selected default values for the diagram. The fastest way to go forward is to accept all the default values and press **Diagram** for simple EpH diagrams or **Combine** for combined diagrams. Usually at the begining, there is no need for modifications to the default values. However, it is important to understand the meaning of these settings because they may have strong effect on the diagram. The details of the diagram menu options are explained in the following paragraphs.

1. File Open

The EpH module can also be used as an independent application, in these cases the data for the diagram may be read from .IEP files by pressing **File Open**. *or a t e s ste s eci ications are auto atica trans erred ro t e s ste s eci ication s eet to t e dia ra enu, i . 2.*

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

2. Species and ΔG-data workbook

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

A. The published Pourbaix diagrams are often based on **ΔG-data** which is given in the original papers. This ΔG-data can be used in the Species sheet to replace the default values based on the HSC database if necessary. Note that these ΔG-values can also be calculated from the standard potential values using equation 1

$$\Delta \quad = - n \cdot \quad \cdot \mathrm{E}, \qquad 1$$

where n is the charge transferred in the cell reaction, F is the Faraday constant (23045 cal (V mol)) and E is the standard electrode potential in volts. **Note**: Give ΔG-data for the selected temperatures, usually these values are only available at 25 C.

B. Sometimes all necessary species are not available in the HSC database. These **missing species** can be added to the chemical system specification if the user has the ΔG-values or chemical potential data for these species. The new species may be added by inserting empty row with **Insert Row** selection and typing formula and ΔG-values to this row.

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

C. In some cases it is necessary to remove certain species from the system, e.g. if some kinetic barriers are found to slow down the reaction rate in the experiments. Such species can be removed by **Delete Row** selection.

The **Labels** and **Lines** sheets are in the programs internal use and it is not necessary to make any modifications to these sheets. The **Labels** sheet contains format data for the labels such as text, area number, coordinates, font name and properties, and labels visibility and orientation. The **Lines** sheet contains format data of the equilibrium lines of the diagram: Species names, line area numbers, line endpoint coordinates, and line properties.

3. Temperature

The Pourbaix-diagrams are drawn at a constant temperature. The user must select one temperature for the diagram from the list of temperatures, Fig. 2. The actual temperature values can only be changed from the system specification form, Fig. 1. No temperature selection is needed here for the Combined diagrams.

The default ΔG-values in the Species sheet in columns 2 – 5 are calculated at the given temperatures. The ΔG-values at column 2 are calculated using the first temperature, column 2 using the second temperature, etc.

4. Other parameters

The default values for **Dielectric Constant** and **ΔG of H_2O** are automatically calculated on the basis of the selected temperature and pressure. The calculation of Dielectric Constant is based on experimental values[15] and water vapor pressure[16], which are valid from 0 to 373 C, and from 1 to 5000 bar. Outside this range the Dielectric Constant will be extrapolated.

The **Ion Strength** and **Correction Factor** constants are automatically calculated by the program and usually they do not need to be modified by the user.

5. Potential and pH scale ranges

The user may change the default range (**Max Eh** and **Min Eh**) for the potential scale as well as the range of pH scale (**Max pH** and **Min pH**). The scale settings can also be changed by clicking the x- or y-axis on the diagram form. The minimum difference between Min and Max values is 0.2 and there is no upper limit for the difference.

6. Molality and Pressure

The diagrams are calculated using constant molalities (concentrations) for all the elements. The default values may be changed in the table in the bottom right corner of the diagram menu, see Fig. 2. **Molality** values are given in mol kg H_2O units.

The total pressure of the system is also given in the Molality table. The EpH module uses maximum value given in the **Pressure** column as the chemical system total pressure. It is not possible to select a smaller pressure value than water vapor pressure at the selected temperature. In other words, the total pressure must always be bigger than the water vapor pressure at the selected temperature. The default value for the pressure is 1 bar.

7. Show Predominance Areas of Ions

The **Show Predominance Areas of Ions** selection causes the EpH-module to calculate two diagrams for the same system. The first one is a normal Eh-pH-diagram with all species, and the second one is the predominance diagram with only aqueous species. Both diagrams are drawn into the same figure the first diagram in black and the second one in blue. This option is recommended for use only with normal Eh-pH-diagrams (see Chapter 17.4).

8. Diagram and Combine Buttons

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

9. Other options

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

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

the **Format** menu, which contains dialogs for column width, row height, font, alignment and number formats.

Press **Exit** or select **File Exit** when you want to return back to the system specifications form, Fig. 1. The **Help** menu opens the HSC Help dialog.

10. Example of Normal Pourbaix-Diagrams (Cu-S-H_2O-system)

Accept all the default values and press **Diagram**. Continue from Chapter 17.4.

17.4 Normal Eh-pH-Diagrams

The calculated Eh-pH-diagrams are shown in Fig. 3. In the Diagram window it is possible, for example, to modify the layout and format of the diagram. The solid black lines show the stability areas of the most stable species on the pH- and Eh-scales. The dotted cyan lines show the upper and lower stability areas of water, see Chapter 17.1. The stability areas of ions are shown with blue dotted lines if the **Show Predominance Areas of Ions** option has been selected, see Fig. 2.

1. Main Elements

he Eh pH diagrams sho only those species hich contain the selected main element. The default main element (Cu) must be selected in the system specification form, Fig. 1. However, the active main element can easily be changed in the diagram form by pressing **Element buttons** on the upper right side of the diagram form, see Fig. 3 for the Cu-S-H_2O diagram and Fig. 4 for the S-Cu-H_2O-diagram. Usually it is useful to check all the diagrams with different main elements to get a better idea of the equilibria.

2. Labels and Lines

The EpH-module locates the area labels automatically on the widest point of the stability areas. You can easily **relocate** the labels by dragging with the mouse cursor if necessary. The text of the labels and headings can be **modified** by inserting the cursor into the correct location within the text row and then by starting to type. You can start the **Label Format** dialog by double clicking the label or by the **Format Label** selection. This dialog makes it possible to change text and lines properties, such as font, type, size, line width, color, etc.

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

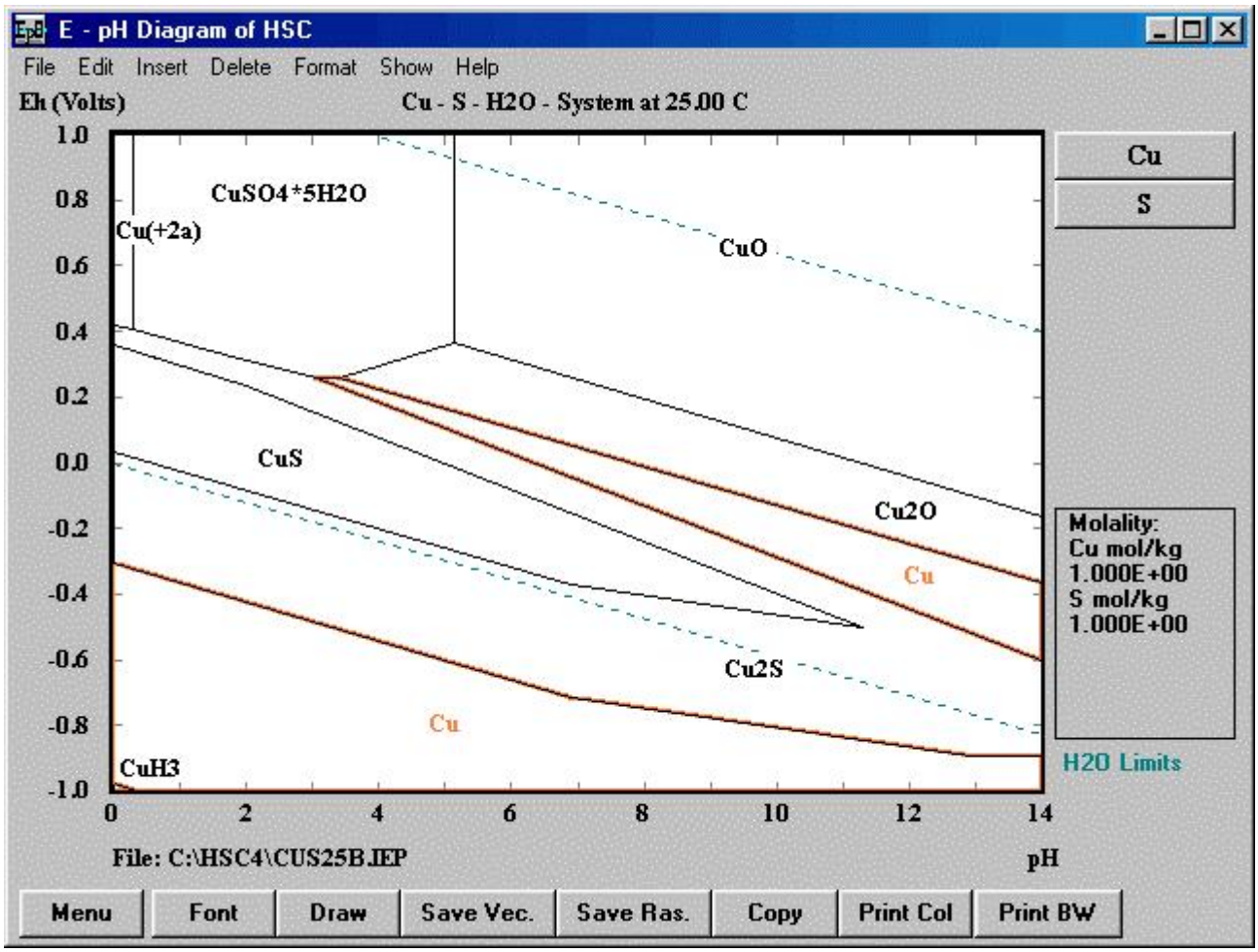


Fig. 3. Eh-pH-diagram of Cu-S-H_2O-system at 25 C using Cu as the main element. The molalities of Cu and S are 1 mol kg H_2O.

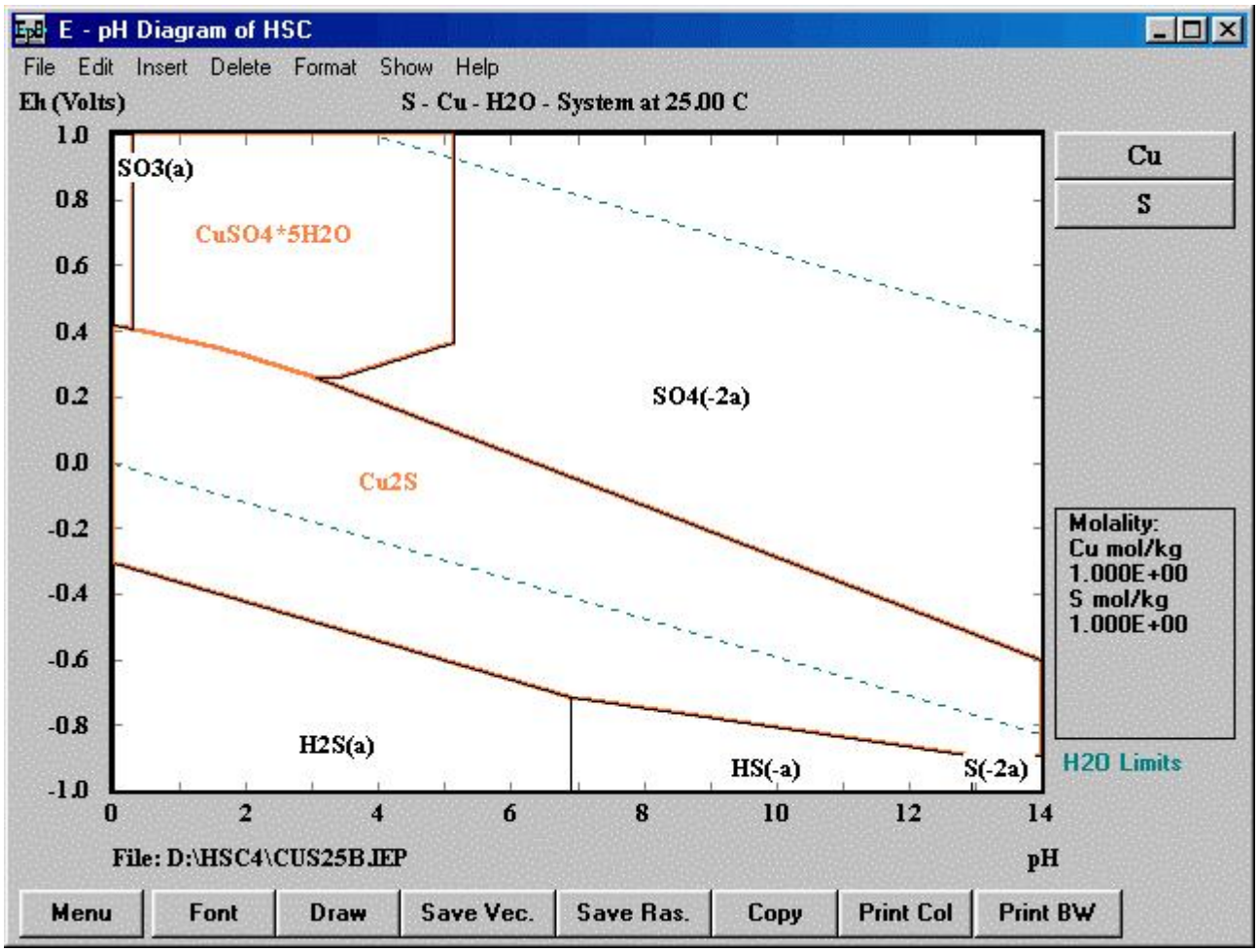


Fig. 4. Eh-pH-diagram of S-Cu-H_2O-system at 25 C using S as the main element. The molalities of Cu and S are 1 mol kg H_2O.

The **Format H2O Stability Lines** selection opens the format dialog, which makes it possible to modify the water stability lines formats and properties. This dialog can not be opened by double clicking the water stability lines.

3. Scales

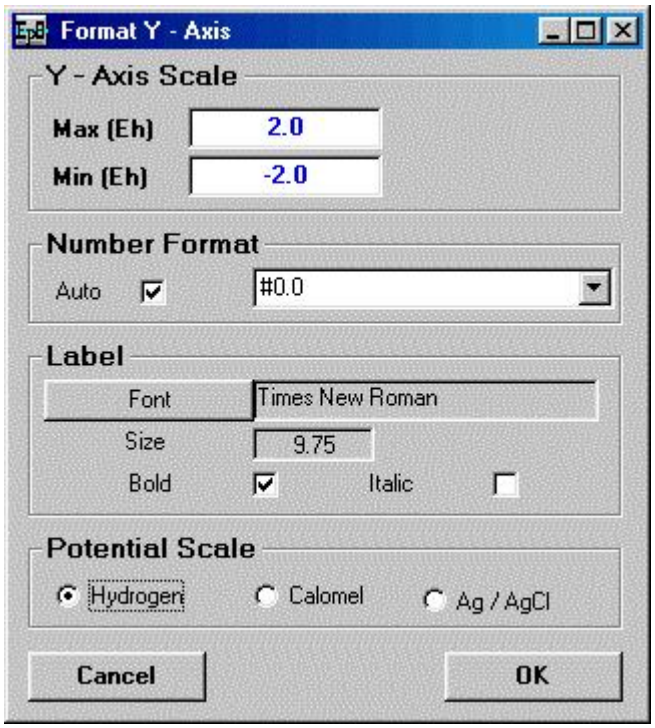


Fig. 5. Menu for formatting y-axis, note the different potential scale options.

The scale format dialog can be opened by double clicking the axis numbers, see Fig. 3, or by the **Format Scale** selection, see Fig. 5. A special feature of the Eh-pH-diagram scale dialog is the scale unit option. You can select between the Hydrogen, Saturated Calomel and Ag AgCl scales. The default scale is Hydrogen, which is used in the calculations. The difference between the Min and Max values must be at least 0.2 units.

4. Printing

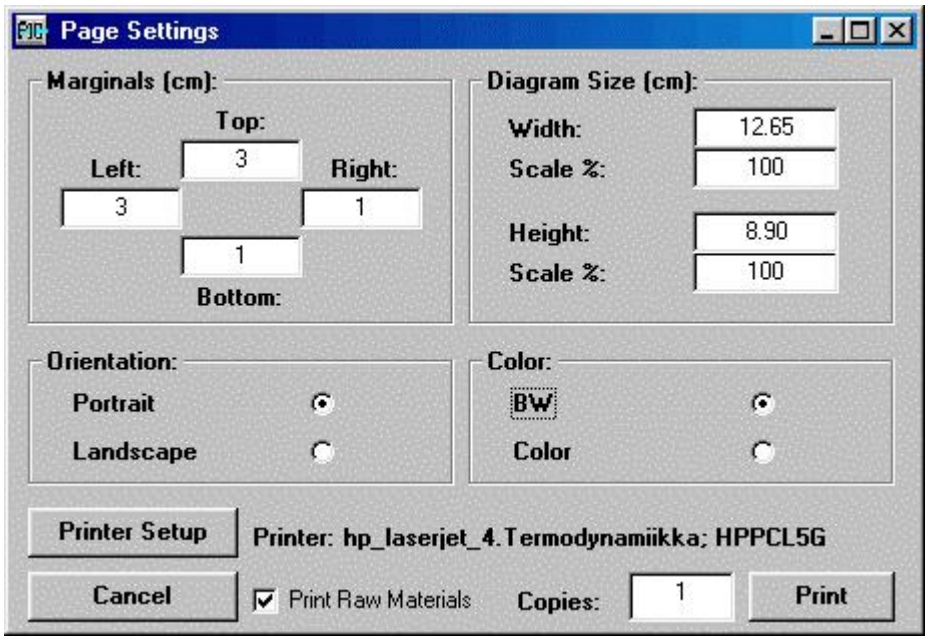


Fig. 6. EpH-Diagram Print Dialog.

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

5. Other Options

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

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

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

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

6. Example Cu-S-H_2O-System

The Cu-S- and S-Cu-H_2O-diagrams are shown in Figs. 3 and 4. These diagrams may give a lot of valuable information. For example, the dissolution behavior of copper can easily be estimated from Fig. 3. It is easy to see that in neutral and caustic solutions metallic copper is stable near zero potential values. It will form oxides in anode conditions (Eh 0) and sulfides in cathode conditions (Eh 0). However, it will dissolve as Cu(2a) in acid conditions at anode (Eh 0) and precipitate on a cathode (Eh 0) in metallic form.

17.5 Specifications for Combined Diagrams

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

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

1. Chemical System Specifications

The chemical system specifications for the combined diagrams are made exactly in the same manner as for normal diagrams, see Chapter 17.2. The Fe-S-H_2O-system is used here as an example when the combined diagrams approach and properties are described. The selections are shown in Fig. 7. The available temperatures must be specified in the system specifications form, Fig 1.

2. Eh-pH-Diagram Menu

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

3. Combine Menu

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

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

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

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

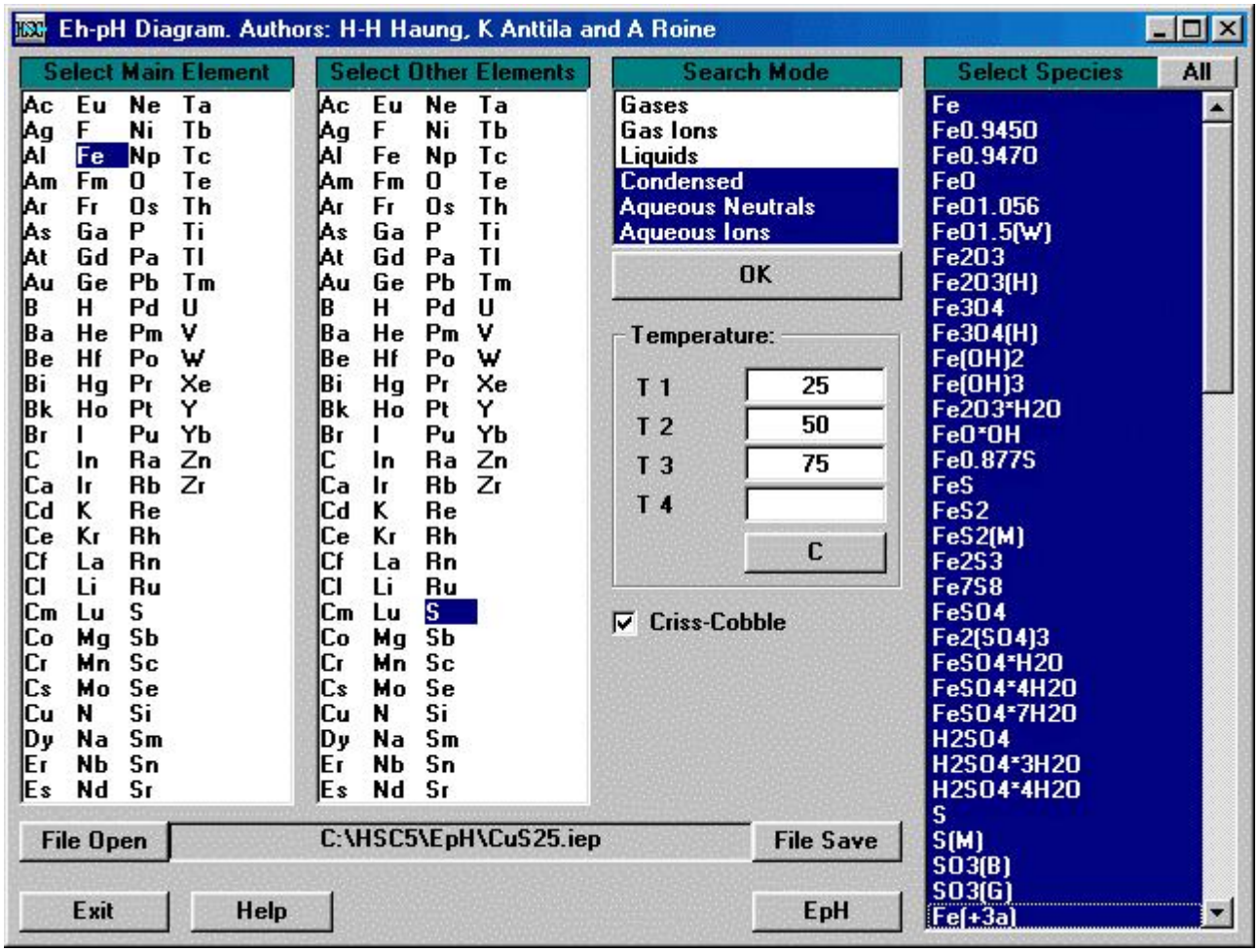


Fig. 7. Specification of an Fe-S-H_2O-system for an Eh-pH-diagram.

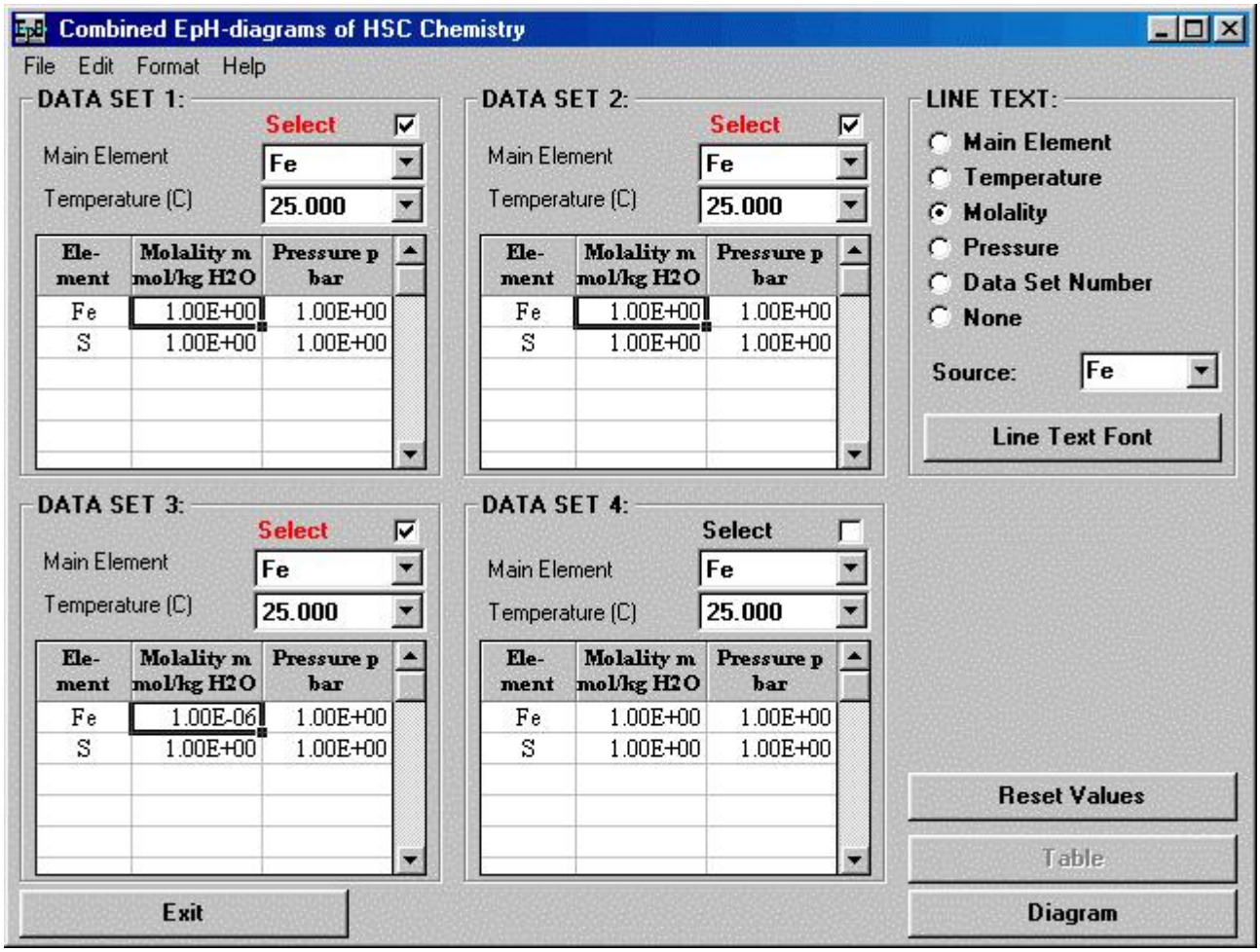


Fig. 8. Specification of a combined diagram layout for an Fe-S-H_2O system.

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

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

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

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

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

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

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

17.6 Combined Eh-pH-Diagrams

The calculation basis and appearance of the combined diagrams is the same as for the normal Eh-pH-diagrams discussed in previous chapters. The combined diagrams are reduced to normal diagrams if only one data set is selected, see Fig. 8. However, there are some differences which will be discussed in this chapter. The combined diagram of the Fe-S-H_2O example is shown in Fig. 9.

The main element selection of the combined diagrams is made in the four Data Sets options, Fig. 8. The selected main element can be seen from the heading of the diagram. The first element in the heading Fe-S-H_2O-system at 25 C is always the main element. **Table** shows all the calculation results, which are used to draw the final diagram, see Chapter 17.7 for details.

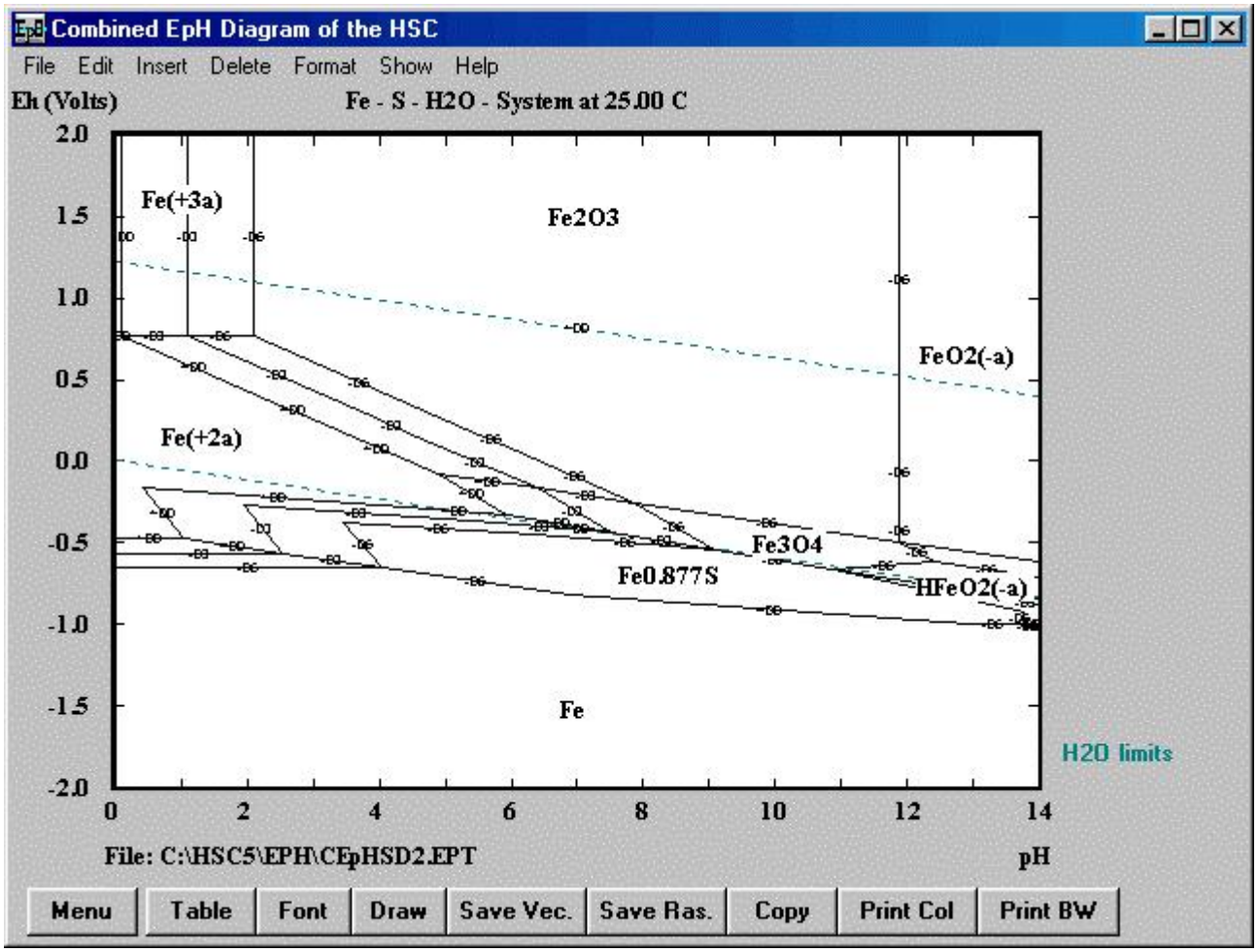


Fig. 9. Combined Eh-pH-diagram for an Fe-S-H_2O-system at 25 C. The Fe molality values 1, 10^{-3}, and 10^{-6} have been used as parameter.

Results for Composite EpH diagram

	Lines	Area No	X1 pH	Y1 V	X2 pH	Y2 V	Width	Style	Color	Data-set	Sl
1	Fe - S - H2O - System at		0.00000	-2.00000	14.00000	2.00000	1	0	0		
2	C:\HSC5\EPH\FES25.IEP						0	0	0		
3	pH						0	0	0		
4	Eh (Volts)						0	0	0		
5	X-heading 2						0	0	0		
6	X-axis Grid						0	0	0		
7	Y-axis Grid						0	0	0		
8							0	0	0		
9	O2 Formation		0.00000	1.22880	14.00000	0.40061	0	2	8421376	1	-0.
10	H2 Formation		0.00000	0.00000	14.00000	-0.82819	0	2	8421376	1	-0.
11	Fe	1	1.04340	-0.47426	2.54340	-0.56299	0	0	0	1	-0.
12	Fe	1	0.00000	-0.47426	1.04340	-0.47426	0	0	0	1	0.
13	Fe	1	6.89225	-0.82026	12.94450	-0.99927	0	0	0	1	-0.
14	Fe	1	13.66000	-0.99927	14.00000	-0.99927	0	0	0	1	0.
15	Fe	1	0.00000	-2.00000	0.00000	-0.47426	0	0	0	1	0.
16	Fe	1	14.00000	-0.99927	14.00000	-2.00000	0	0	0	1	0.
17	Fe	1	0.00000	-2.00000	14.00000	-2.00000	0	0	0	1	0.
18	Fe	1	2.54340	-0.56299	4.04340	-0.65173	0	0	0	2	-0.
19	Fe	1	0.00000	-0.56299	2.54340	-0.56299	0	0	0	2	0.
20	Fe	1	0.00000	-2.00000	0.00000	-0.56299	0	0	0	2	0.
21	Fe	1	14.00000	-0.99927	14.00000	-2.00000	0	0	0	2	0.
22	Fe	1	4.04340	-0.65173	6.89225	-0.82026	0	0	0	3	-0.
23	Fe	1	0.00000	-0.65173	4.04340	-0.65173	0	0	0	3	0.
24	Fe	1	13.66000	0.00927	14.00000	1.02044	0	0	0	3	0

DS1 DS2 DS3 DS4 Labels Lines

Exit Print

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

17.7 Calculation Results of Combined Diagrams

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

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

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

$$D = \sum_{n=1}^{4} 2^{(n-1)}, \qquad 2$$

where n is the data set number.

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

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

17.8 Eh - pH - Diagrams in Practice

The HSC EpH module enables fast and easy creation of Pourbaix diagrams for the required chemical system in user-specified conditions. These diagrams contain the basic information of the aqueous system in a compact and illustrative form. These diagrams have found many applications in corrosion engineering, geochemistry and hydrometallurgy since the publication of the famous Pourbaix Atlas handbook[12].

In hydrometallurgy, the Eh-pH-diagrams may be used, for example, to specify the conditions for selective leaching or precipitation. In corrosion engineering, they may be used to analyze the dissolution and passivation behavior of different metals in aqueous environments. These diagrams may also be used to illustrate the chemical behavior of different ions in aqueous solutions.

Geochemists use the Pourbaix diagrams quite commonly to study the weathering process and chemical sedimentation. The weathering process is used to predict what will happen to a mineral, which is exposed to acid oxidizing conditions at high temperature and pressure. Pourbaix diagrams can also be used to estimate the conditions, which were needed to form certain sediments and other minerals[17] in the geological past.

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

18. Ep pH - Samples

EpH module: **Input File for EpH Module**

```
E  - p  -  iagram 4.0 '    iagram t pe        ' Heading
 2                                             ' Number of Elements
Cu                                             ' Name of a Element
      1.0000        1.0000                     ' Molality and pressure of this Element
S
      1.0000        1.0000
 2                                             ' Number of temperatures
      25.000        75.000                     '  alues of Temperatures in  C
N                                              ' Show stability areas of ions ( /N)
-56.6781  -54.7567                             ' Δ  values of H2O for all temperatures
1.0000  1.0000                                 ' Dielectric Constant
 0                                             '  on strenght
-2  2  0  14                                   '  imits of the diagram
Cu                          0.0000        0.0000 ' Name of a species and ΔG values for all temperatures
Cu 3                       67.7313       68.0470
CuO                       -30.6627      -29.5533
Cu2O                      -35.3446      -34.4294
CuO*CuSO4                -189.3533     -183.9282
Cu(O )2                   -85.8077      -82.4437
CuS                       -12.7800      -12.7952
Cu2S                      -20.6662      -20.8844
CuSO4                    -158.2417     -153.8574
Cu2SO4                   -156.4294     -152.5214
CuSO4*3 2O               -334.5808     -323.1528
CuSO4*5 2O               -449.2635     -433.1954
 2SO4                    -164.8848     -159.9397
 2SO4*3 2O               -345.1000     -334.0907
 2SO4*4 2O               -402.9123     -389.9613
S                           0.0000        0.0000
S( )                        0.0190        0.0068
SO3( )                    -89.4025      -86.2283
SO3( )                    -89.7786      -86.7094
Cu(+2a)                    15.6300       15.7317
Cu(+a)                     11.9450       11.0901
Cu(O )2(a)                -59.5596      -53.6263
CuSO4(a)                 -162.3104     -155.5767
Cu2SO3(a)                 -92.2243      -87.8581
 2S(a)                     -6.5160       -6.1670
 S(-a)                      2.9113        4.2276
 2SO3(a)                 -128.5529     -125.6145
 2SO4(a)                 -177.9474     -171.0575
 SO3(-a)                 -126.1208     -122.2317
 SO3(-2a)                -121.3430     -116.7342
 SO4(-a)                 -180.6580     -175.4083
 SO4(-2a)                -175.2501     -169.3171
 SO5(-a)                 -152.3532     -147.0925
S(-2a)                    20.5471       22.6438
S2(-2a)                   19.0406       21.0895
S3(-2a)                   17.6446       19.6504
SO2(a)                    -71.8354      -71.1981
SO3(a)                   -125.6315     -121.1608
SO3(-2a)                 -116.2971     -110.0146
SO4(-2a)                 -177.9474     -171.1338
S2O3(-2a)                -123.9775     -118.6055
S2O4(-2a)                -143.5482     -137.2786
S2O5(-2a)                -188.0263     -180.6896
S2O6(-2a)                -231.6077     -223.3179
S2O8(-2a)                -266.4866     -257.3452
S3O6(-2a)                -244.8178     -236.2948
```

EpH Case 1: Metal Corrosion in Fe-H_2O-system

Eh-pH-diagrams may be used to estimate corrosion behavior of different metals in aqueous solutions. The most common corrosion phenomenon is rust formation on the iron surfaces. The corrosion rates and types depend on the chemical conditions in the aqueous solution. The Eh-pH-diagram of an Fe-H_2O-system may easily be created as described in Chapter 17. The chemical system specification is shown in Fig.1 and the calculated diagram in Fig. 2.

The stability areas may be divided into three groups[13]:

1. **Corrosion area**: Formation of ions means that metal dissolves into an aqueous solution. For example, Fe(3a), Fe(2a), FeO_2(-a) and $HFeO_2$(-a)-ions in an Fe-H_2O-system.
2. **Passive area**: Formation of oxides or some other condensed compounds may create tight film (impermeable) on the metal surface which passivates the surface, good examples are Al_2O_3 on aluminium or TiO_2 on titanium surfaces. If the oxide layer is not tight enough (porous) to prevent oxygen diffusion into the metal surface, corrosion may continue. This is the case with the most of the iron oxides but they may also cause passivation in favourable conditions.
3. **Immunity area**: All metals are stable if the electrochemical potential is low enough. Most noble metals are stable even at zero potential, but at least –0.6 volts are needed at the cathode for iron to precipitate, see Fig. 2.

The stability areas of water are shown by dotted blue lines in Eh-pH-diagrams, see Fig. 2, the colors can not be seen in this B W copy. Usually it is difficult to exceed these limits due to the formation of oxygen at the upper limit and hydrogen at the lower limit. In some solutions these limits may be exceeded due the necessary overpotential of hydrogen and oxygen formation. On the basis of Fig. 2 it seems that hydrogen formation occurs on cathode before the metallic iron comes stable.

The Eh-pH-diagrams may be used in several ways, for example,

- to find pH, potential and temperature regions which prevent corrosion.
- to find out which compounds are the corrosion reaction products.
- to find immune materials which can be used as protective coating.
- to find out a metal which may corrode instead of the constructive material. For example, the zinc layer on a steel surface.

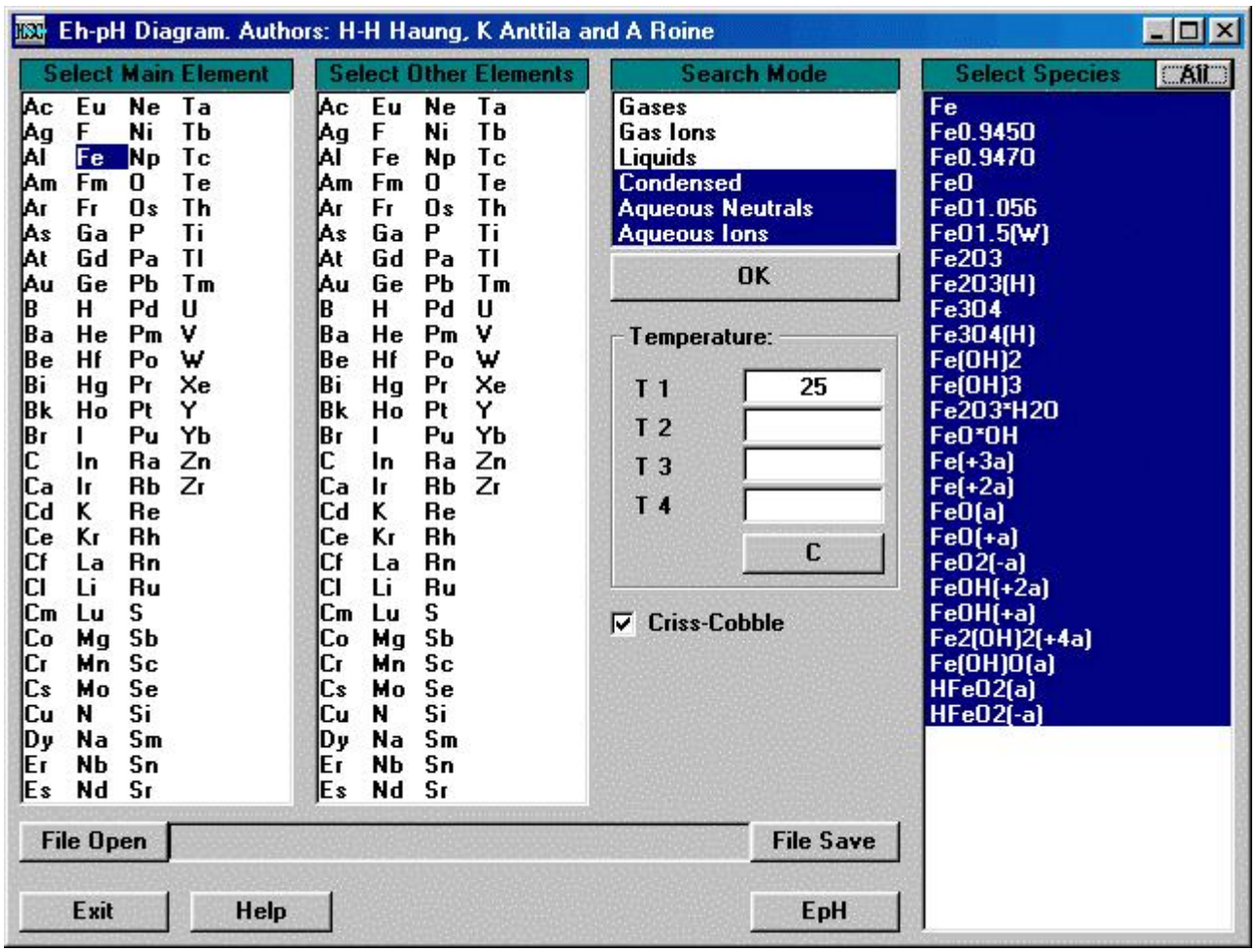


Fig. 1. Specification of Fe-H_2O-system for EpH-diagram at 25 C.

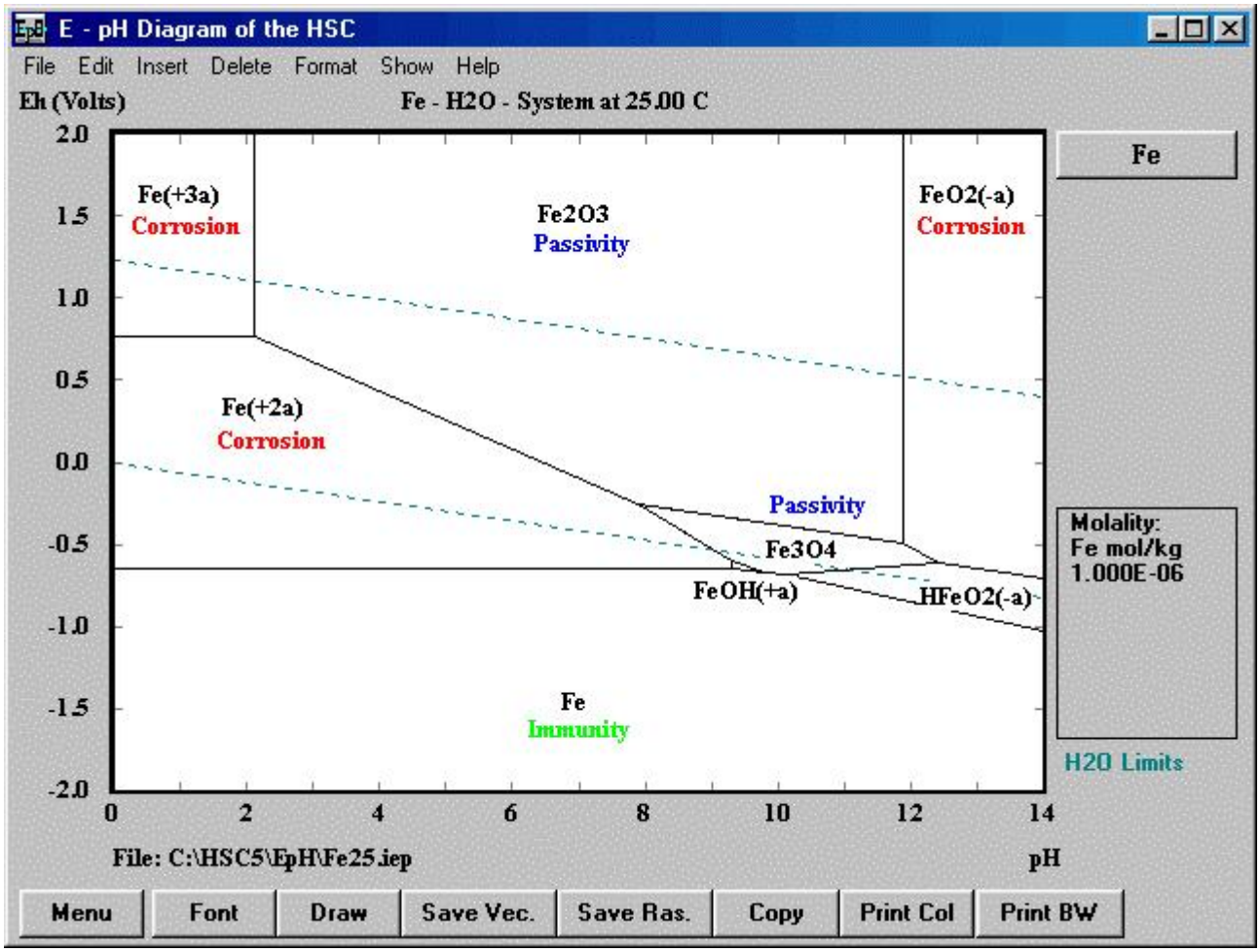


Fig. 2. Eh-pH Diagram of Fe-H_2O-system at 25 C. Molality of Fe is 10^{-6} M.

EpH Case 2 Corrosion Inhibitors in Fe-Cr-H_2O-system

Some elements or compounds may prevent corrosion even at very low content in the chemical system. These substances are called corrosion inhibitors and they can be divided into anodic and cathodic inhibitors. The anodic inhibitors primarily prevent the anodic reaction and passivate metals in this way, the latter ones suppress the corrosion rate by preventing the cathodic reaction or by reducing the cathodic area [13].

Chromate and dichromate ions are well known anodic corrosion inhibitors. Small amounts of chromates will create a tight complex oxide film on the steel surface which prevents corrosion. The oxide film is mainly formed of magnetite (Fe_3O_4), hematite (Fe_2O_3) and chromic oxide (Cr_2O_3).

The inhibitor behavior of chromates may be illustrated with Eh-pH-diagrams. The Fe-Cr-H_2O-system specifications are shown in Fig. 3. The calculation results for Fe-H_2O and Fe-Cr-H_2O-systems are shown in Figs 4 and 5. As shown in the diagrams, a large area in the corrosion region of iron Fe(2a), Fig. 4, is covered by the Cr_2O_3 and Cr_2FeO_4 stability areas and thus protected from corrosion, Fig. 5.

It is easy to create Eh-pH-diagrams with the EpH module. However, you should remember that this type diagram greatly simplifies the real situation. They do not take into account, for example, the kinetic aspects or non-ideality of real solutions. Small errors in the basic thermochemical data may also have a visible effect on the location of the stability areas. In any case, these diagrams give valuable qualitative information of the chemical reactions in aqueous systems in brief and illustrative form.

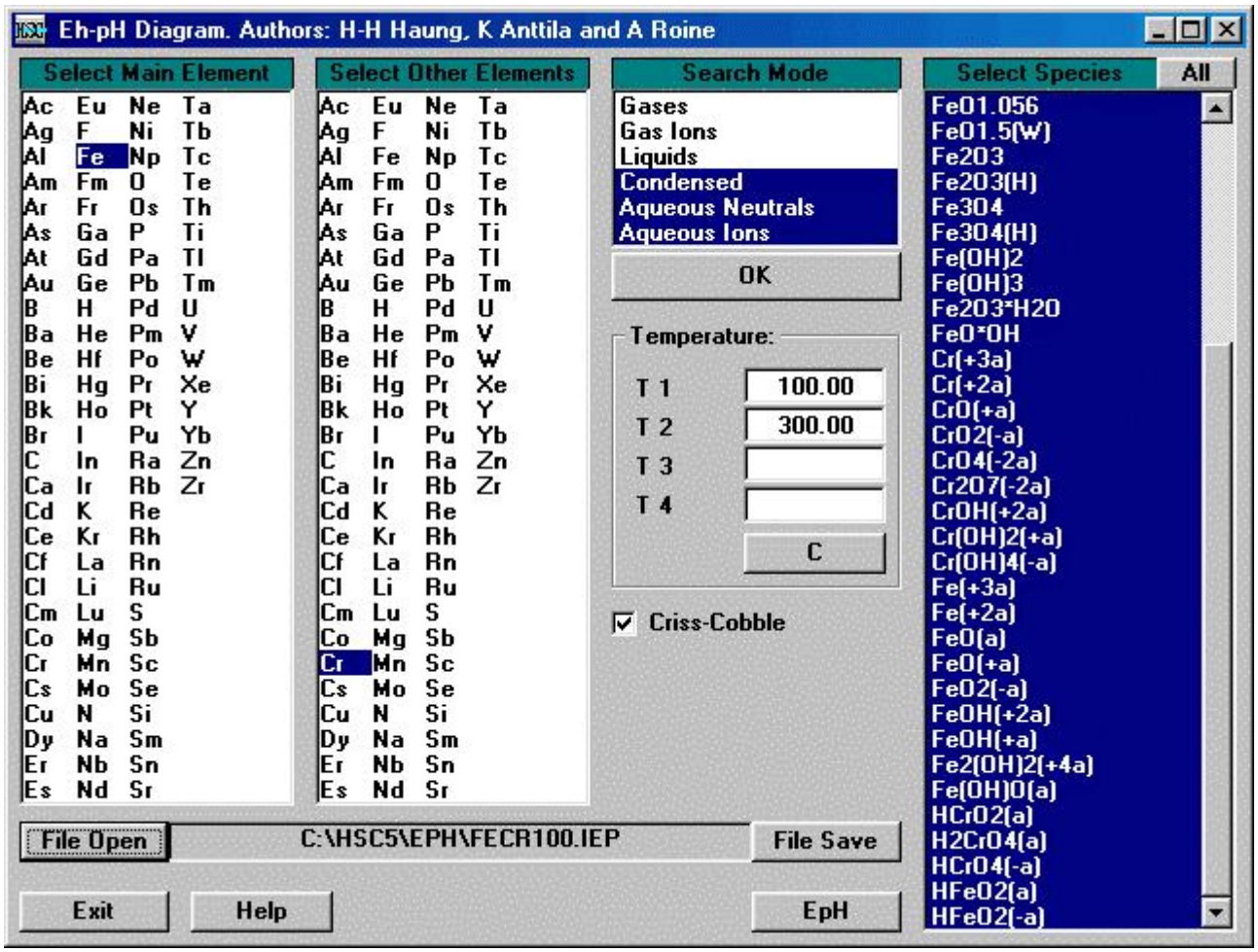


Fig. 3. Specification of Fe-H_2O-system for EpH-diagram at 100 and 300 C.

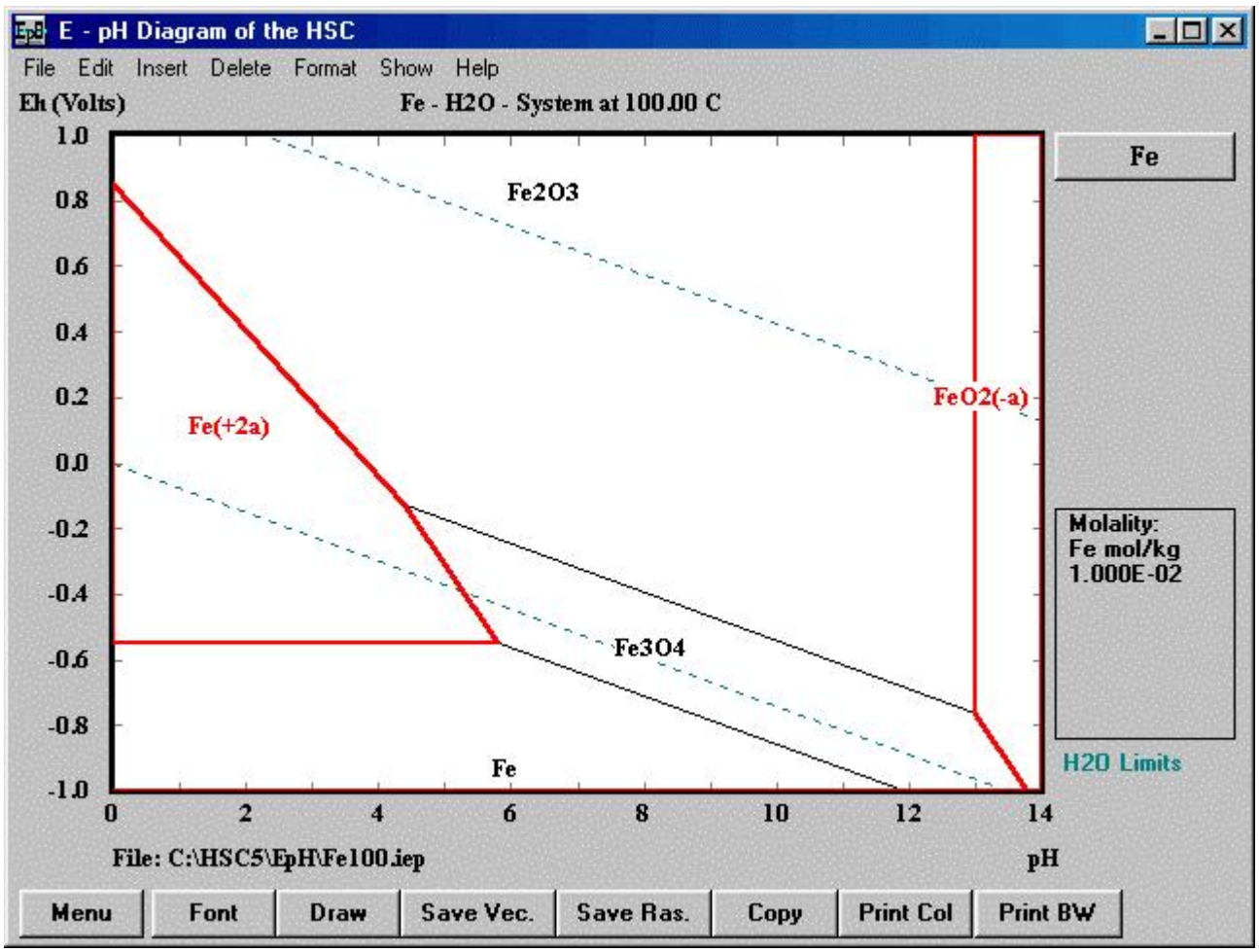


Fig. 4. Fe-H_2O-system at 100 C. Molality: Fe 10^{-2} M, pressure 1 bar.

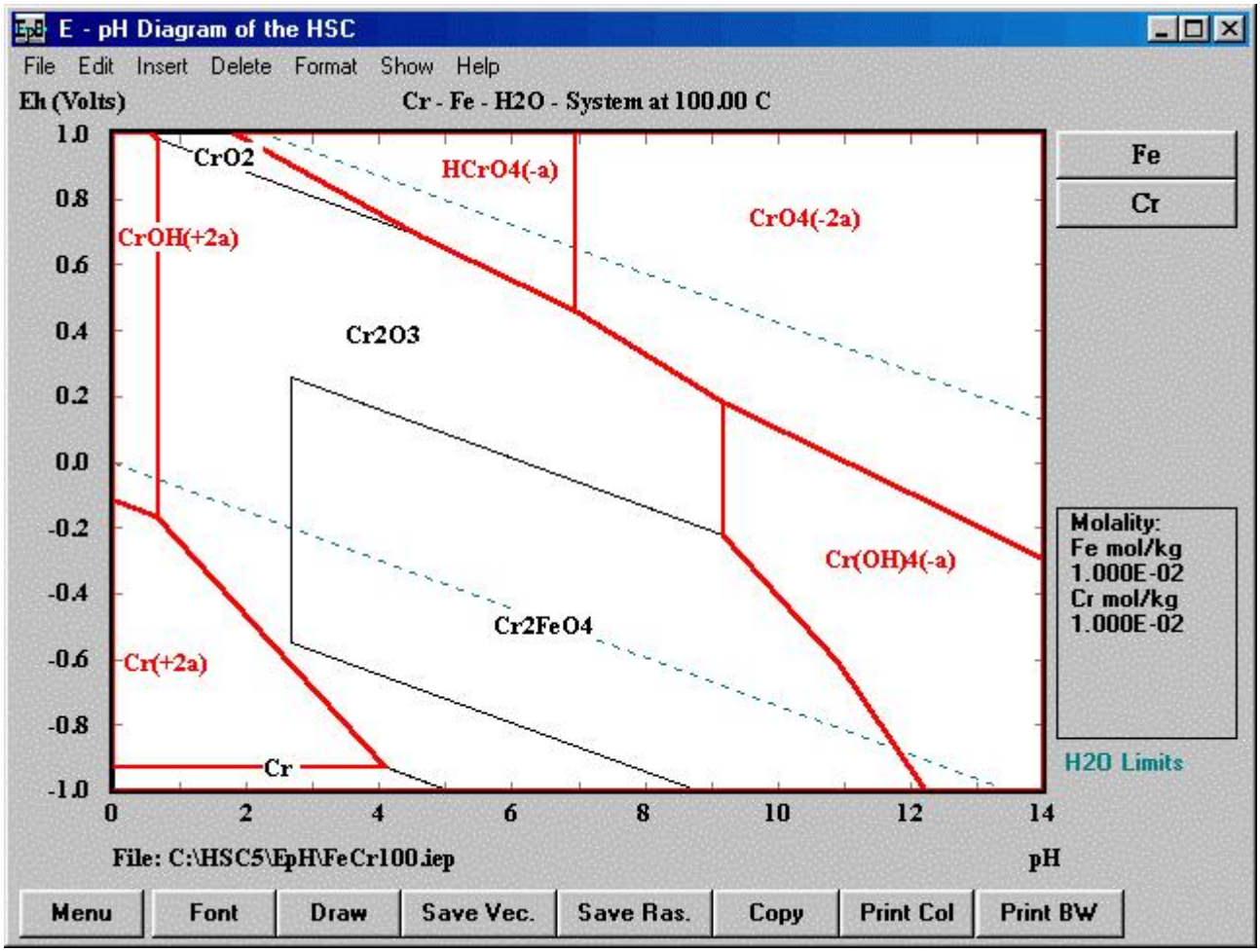


Fig. 5. Fe-Cr-H_2O-system at 100 C. Molalities: Fe and Cr 10^{-2} M, pressure 1 bar.

EpH Case 3 Selection of Leaching Conditions

The first step in a hydrometallurgical process is usually leaching or dissolution of the raw materials in aqueous solution. The aim is to select the most suitable leaching conditions so that the valuable metals dissolve and the rest remain in the solid residue. The leaching conditions may easily be estimated with Eh-pH-diagrams. In favorable leaching conditions the valuable metals must prevail in solution as aqueous species and the others in solid state.

Roasted zinc calcine is the most common raw material for the hydrometallurgical zinc process. It contains mainly zinc oxide. An example of Eh-pH-diagrams application in zinc oxide leaching is shown in Fig. 7, see Fig. 6 for chemical system specifications. It can be seen from the diagram that acid or caustic conditions are needed to dissolve the nO into solution[19].

In acid conditions the pH of the solution must be lowered below a value of 5.5. In practical processes the pH must be even lower because the relative amount of zinc in the solution increases if the pH is adjusted farther from the equilibrium line between the nO and n(2a) areas. The dissolution of the nO consumes hydrogen ions as can be seen from reaction (1). Therefore acid must continuously be added to the solution in order to maintain favorable leaching conditions.

nO 2 H(a) = n(2a) H_2O 1

In caustic conditions zinc may be obtained in solution by the formation of the anion complex nO2(-2a). The leaching reaction may be described by equation (2).

nO H_2O = nO_2(-2a) 2H(a) 2

The leaching conditions change, for example, if sulfur is included in the chemical system. The effect of sulfur can be seen in Fig. 10. Much smaller pH values are need to dissolve nS which has wide stability area. This will lead to the formation of hydrogen sulfide gas and ions according to reaction (3).

nS 2H(a) = n(2a) H_2S(g) 3

In oxidizing conditions a number of different aqueous species may result from the leaching reactions such as (4), (5) and (6), see Fig. 6. In these reactions it is important to note that the consumption of reagents as well as generation of reaction products continuously change the solution conditions. These conditions must be regulated by feeding more acid and or removing reaction products in order to the maintain optimum conditions.

nS = n(2a) S 2e- 4

nS $4H_2O$ = n(2a) HSO_4(-a) 7H(a) 8e- 5

nS $4H_2O$ = n(2a) SO_4(-2a) 8H(a) 8e- 6

The HSC database contains a lot of species which may have a long formation time. *or a it is ise to se ect on suc s ecies ic are identi ied in rea so utions or c e ica s ste s eci ications*. A system specification with only common species included is shown in Fig. 8 and another one with all the species in Fig. 9. The selected species may have a visible effect on the diagrams as can be seen by comparing Figs. 10 and 12 as well as Figs. 11 and 13. In some cases, diagrams with all the species selected into the calculation system may give also valuable information, Figs. 12 and 13.

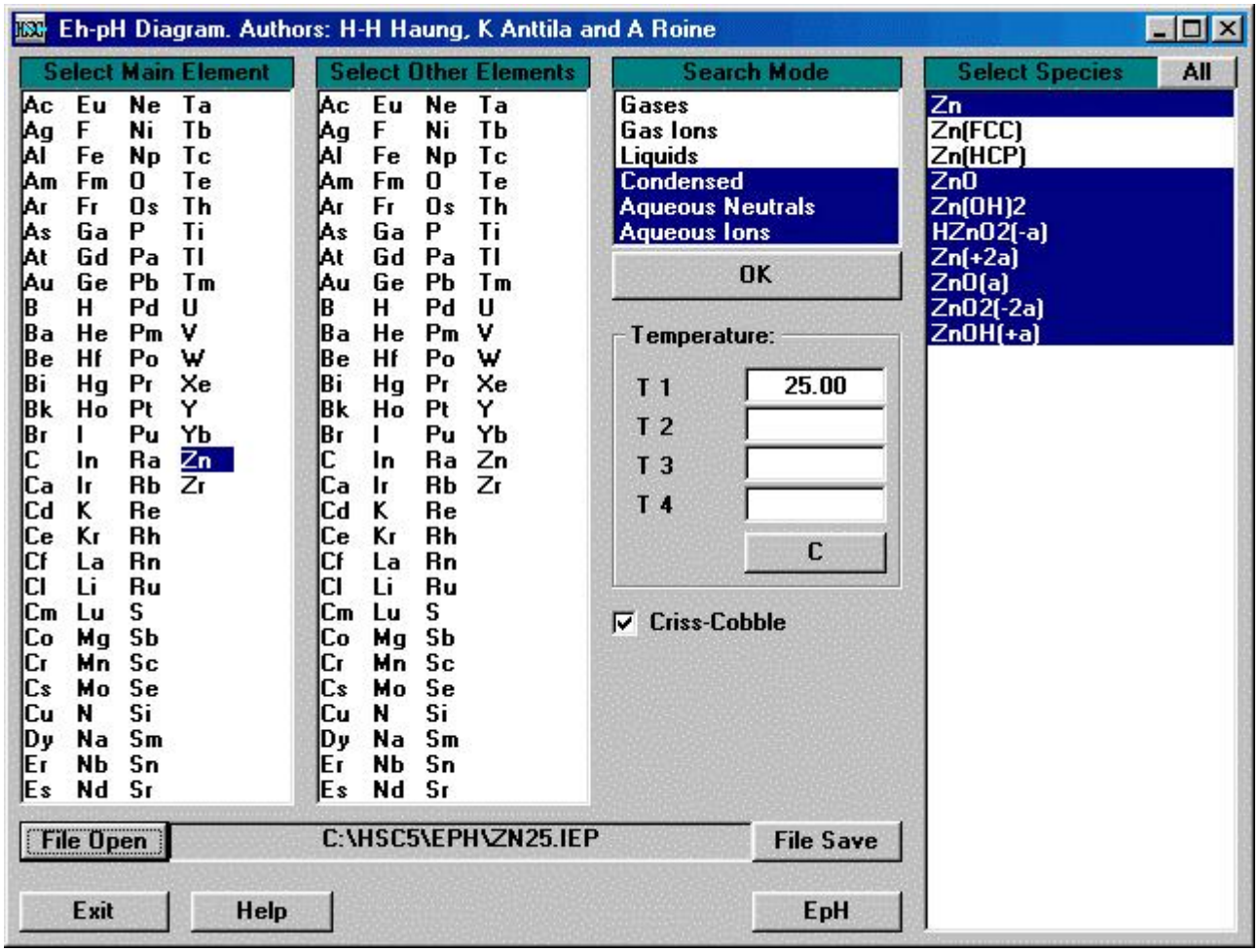


Fig. 6. n-H_2O-system specifications.

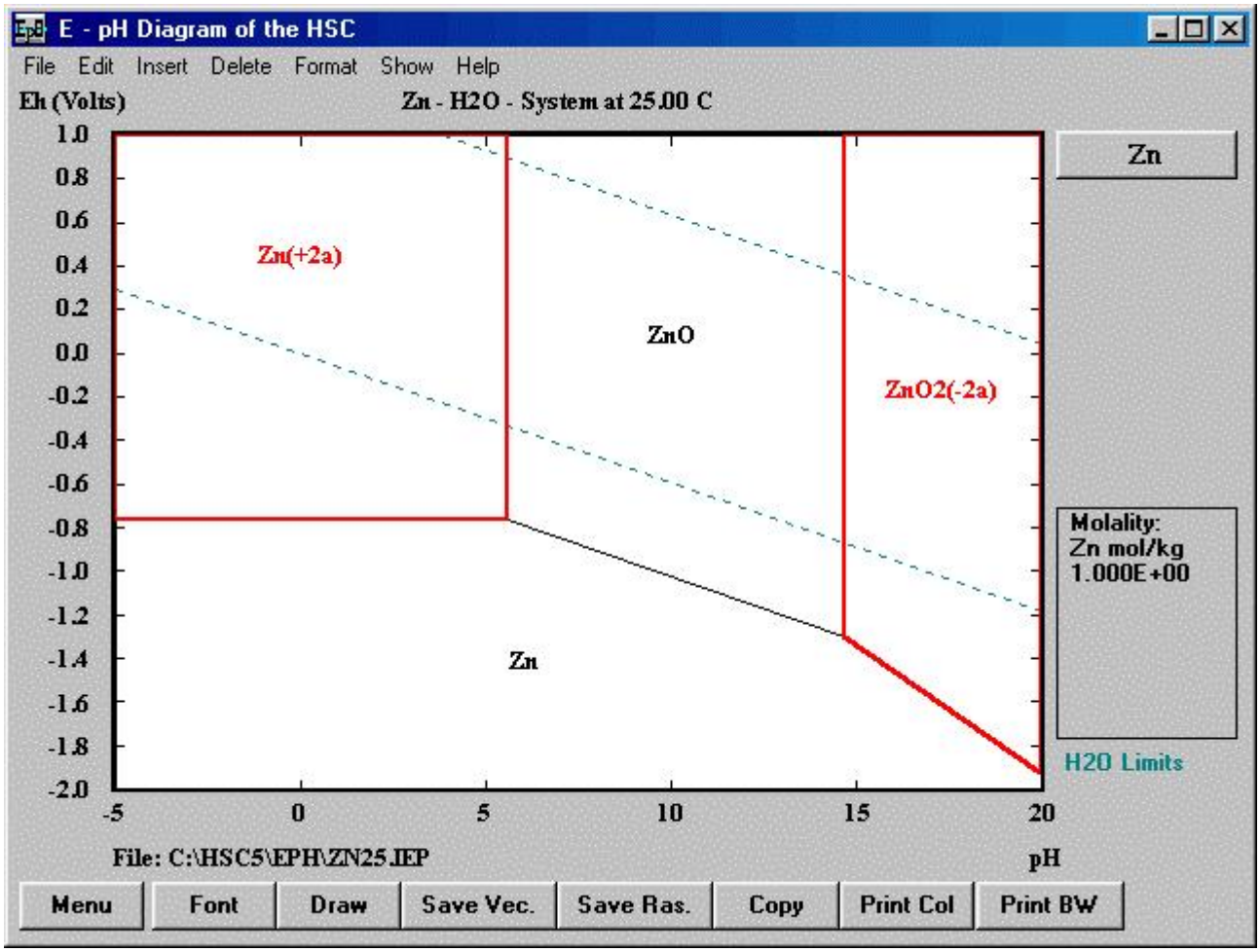


Fig. 7. n-H_2O-system at 25 C. Diagram is based on specifications in Fig. 6.

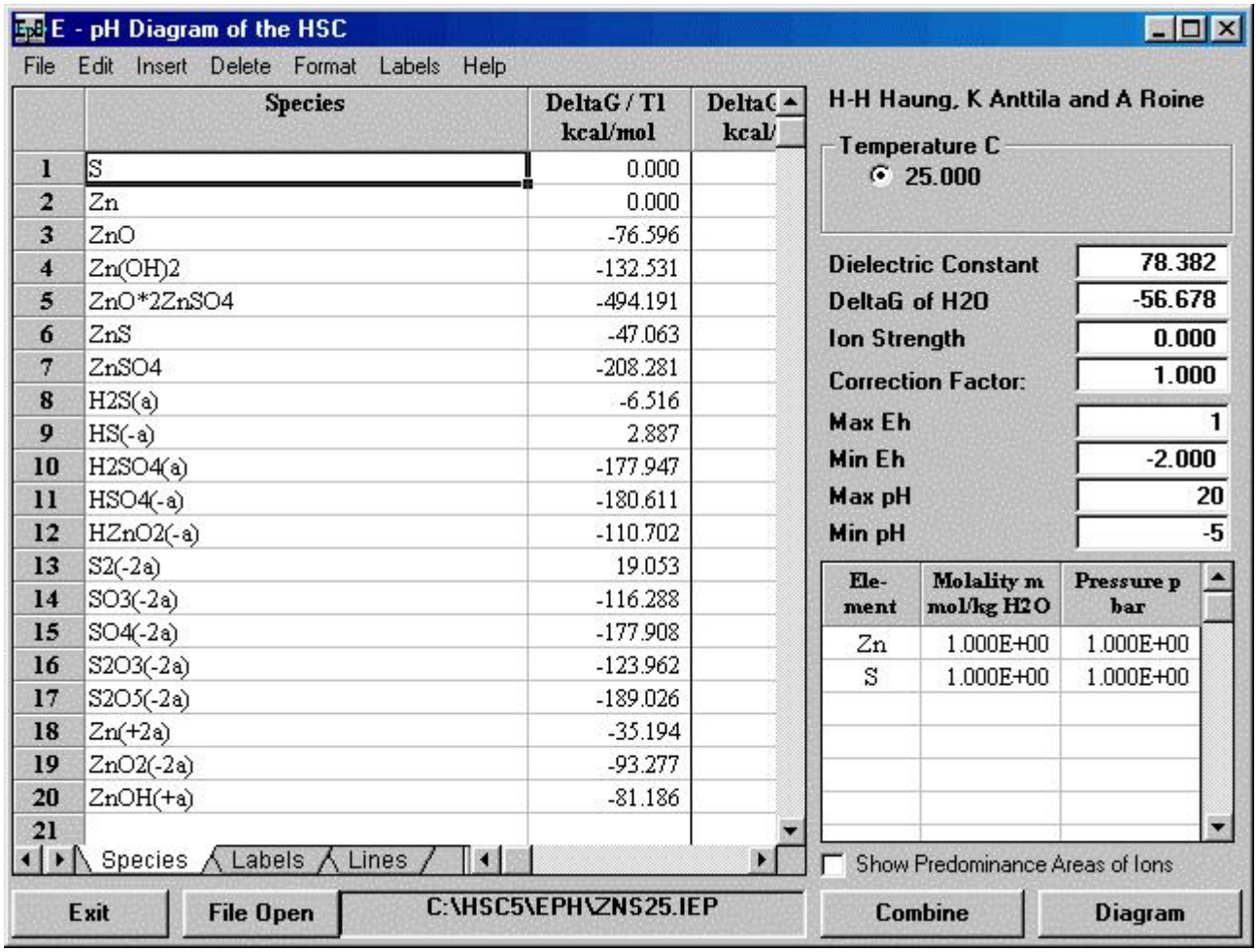


Fig. 8. n-S-H_2O-system specifications, only identified species included

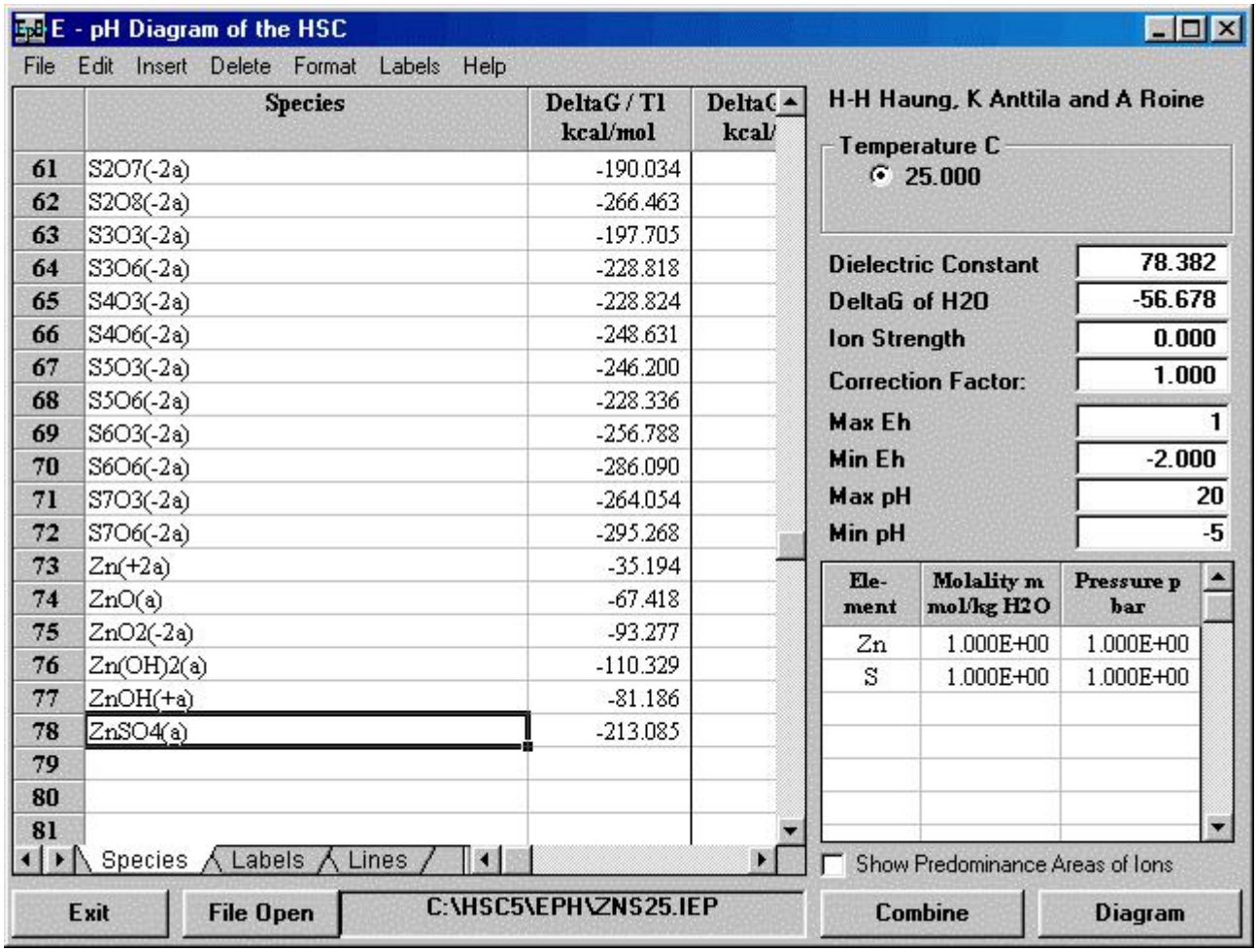


Fig. 9. n-S-H_2O-system specifications, all species included.

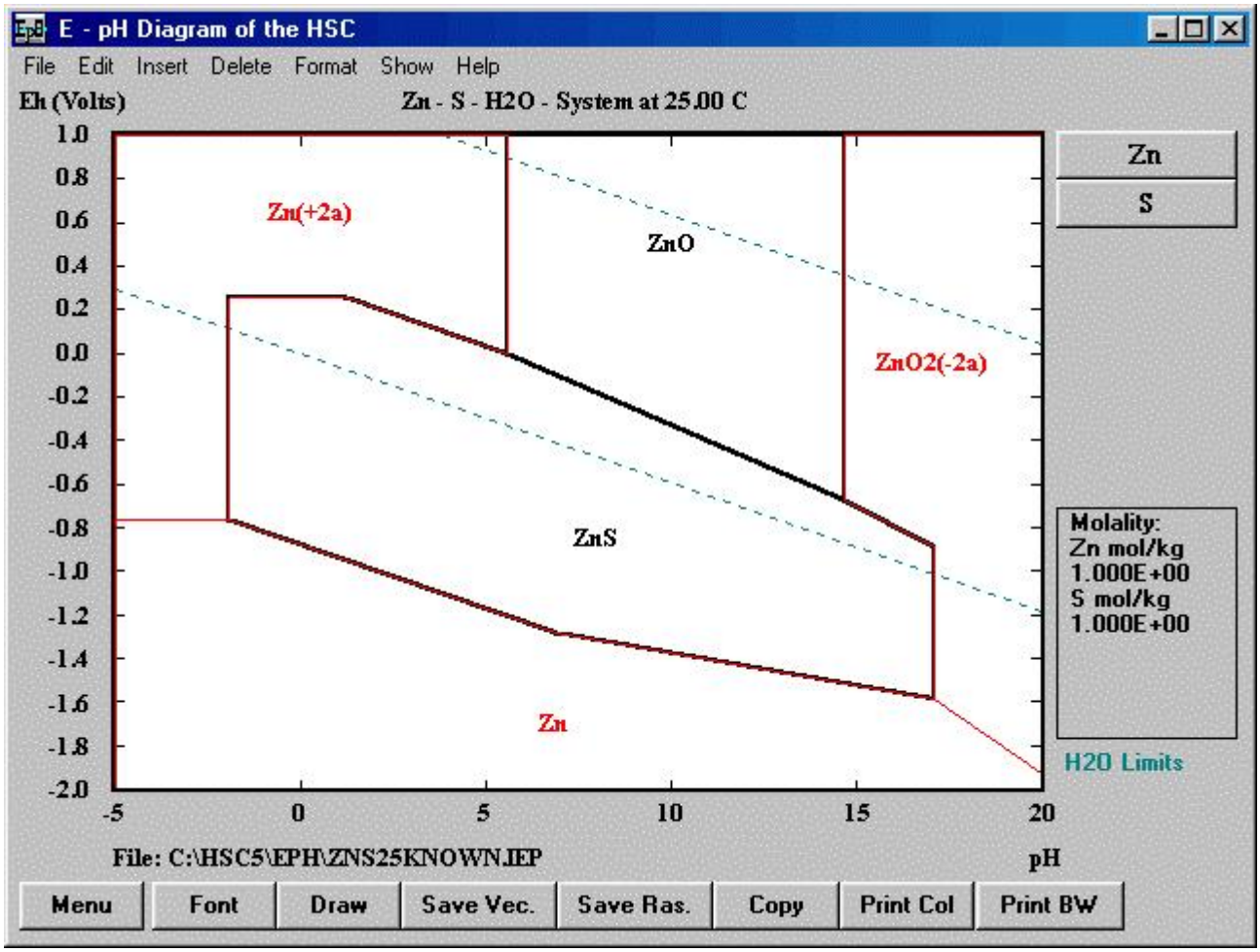


Fig. 10. n-S-H_2O-system at 25 C based on specifications in Fig. 8.

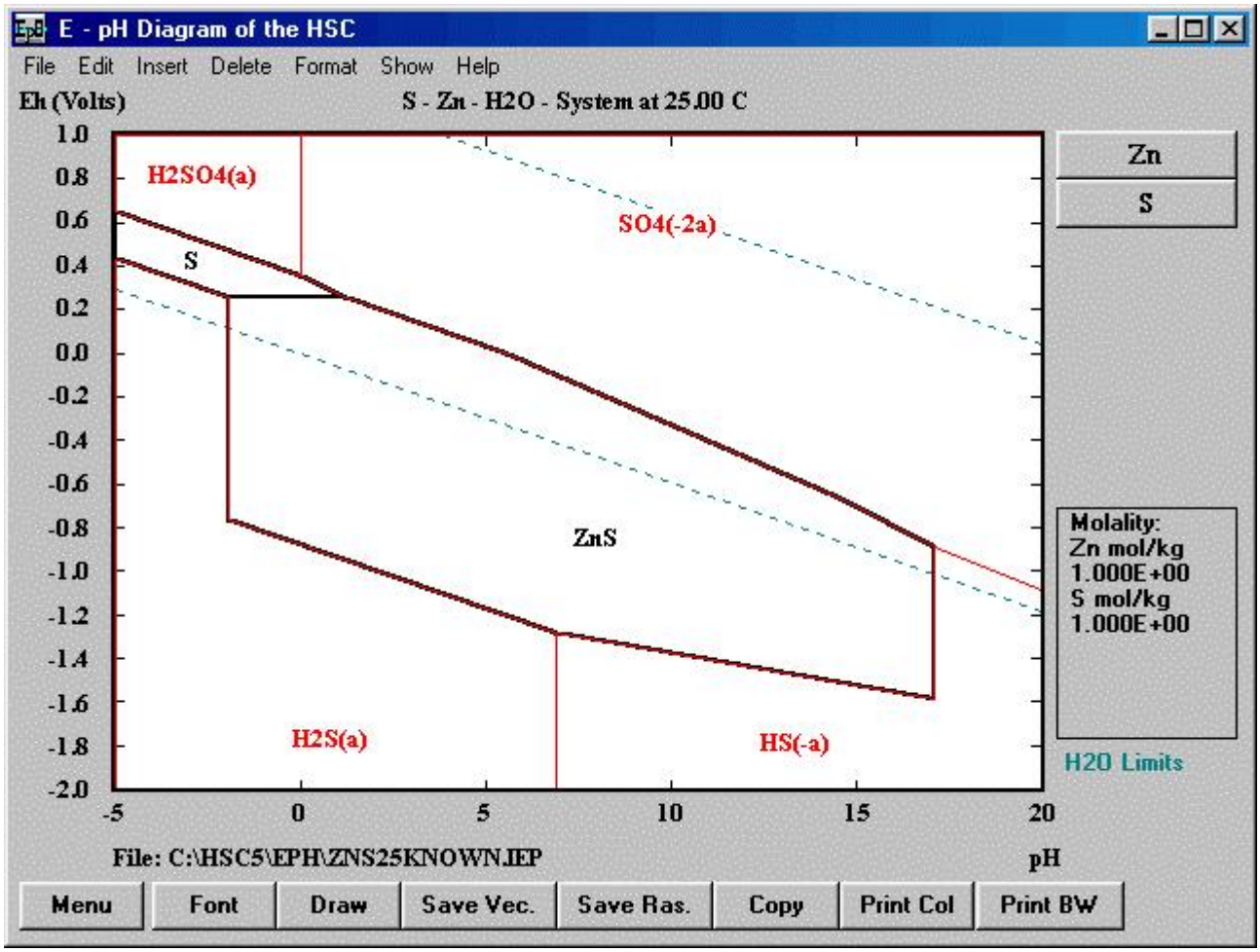


Fig. 11. S- n-H_2O-system at 25 C based on specifications in Fig. 8.

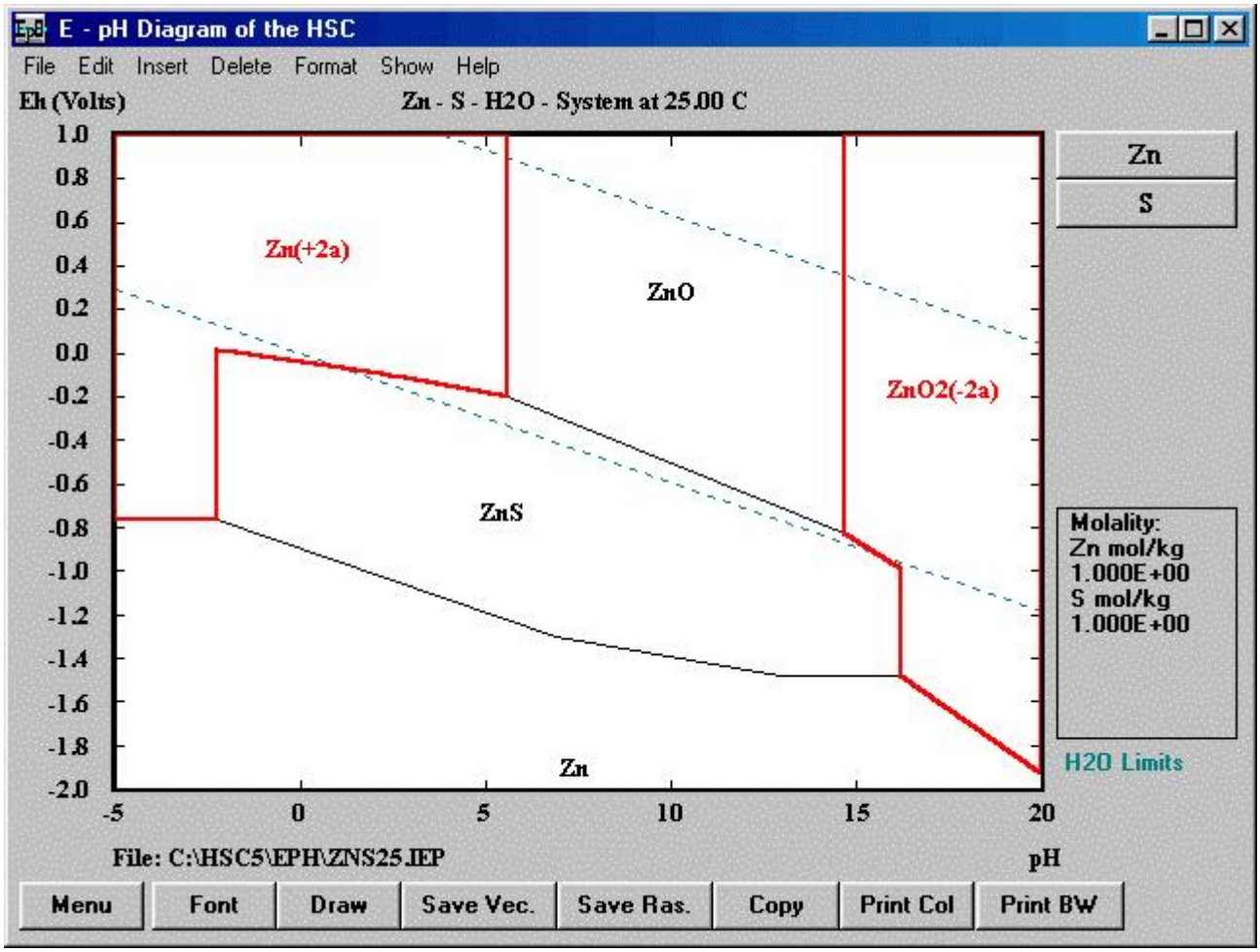


Fig. 12. n-S-H_2O-system at 25 C based on specifications in Fig. 9.

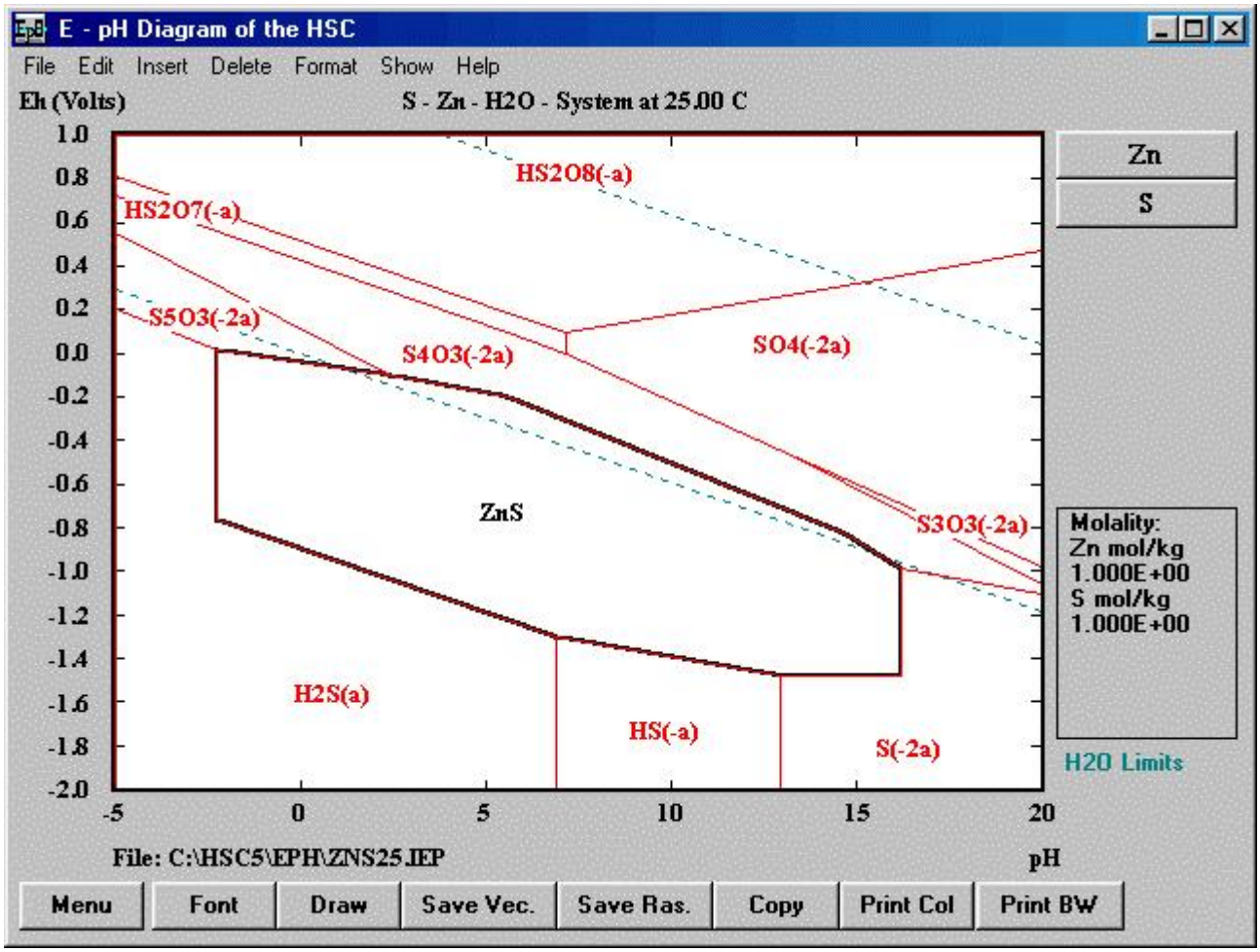


Fig. 13. S- n-H_2O-system at 25 C based on specifications in Fig. 9.

19. H, S, C AND G DIAGRAMS

The diagram module presents the basic thermochemical data for the given species in graphical format. Eight different diagram types can be drawn as a function of temperature:

- H Enthalpy (total)
- H Enthalpy (latent)
- S Entropy
- Cp Heat Capacity
- G Gibbs Energy
- DH
- DS
- DG (Ellingham diagrams)

The basic steps for drawing a diagram for all types is quite the same, except the small difference with the DG-diagrams. These steps are described in more detail in following lines, see example in Fig. 1:

1. Type the **species** formulae to the first column of the **X-data** sheet. There is no need to open the other sheets, because these are in the programs internal use only.

2. Select the diagram type from **Diagram Type** list, in this example H Enthalpy (latent) has been selected, see Fig. 1.

3. **DG-diagrams only**: Select an element from the list (for example: O for oxides, S for sulfides, Cl for chlorides, etc.) and press **Balance Element Amount**.

4. Press **Read Data from Database**. This will search the data from the database for the given ranges. You can force the HSC to use its own or main database by setting 1 or 2 to the **Database No** column. Without this setting, the diagram module looks for the data first from HSC own database and then from the main database.

5. Press **Diagram** to draw the diagram. You can also modify all the default settings such as x- and y-axis ranges and units. However, you must always press **Read Data from Database** after these modifications before you can press the **Diagram**.

An example of a diagram is shown in Fig. 2. The **solid lines** show the values, which are based on data in the database, and the **dotted lines** show the extrapolated values. Sometimes the extrapolated data may behave irregularly because the Cp-function extrapolates incorrectly outside the given range. The scales, lines and labels can be edited in the same manner as in the other graphics routines.

The DG-diagrams (Ellingham) show the relative stability of various oxides, sulfates, chlorides etc. These diagrams must contain only the same type of substances, such as oxides, sulfides, chlorides, etc. The species amounts must be balanced to contain exactly the same amount of the main element, such as oxygen in oxides and sulfur in sulfides.

An example of Ellingham diagram settings is given in Fig. 3. The results in Fig. 4 show, for example, that iron oxides can be reduced with carbon at higher temperatures than 700 C, i.e. FeO C - Fe CO(g). Metals whose oxide DG is smaller at a selected temperature, Fig. 4, can be used to reduce those oxides where the DG is higher. The most stable oxides (Cr_2O_3, MgO) are located at the bottom of the diagram.

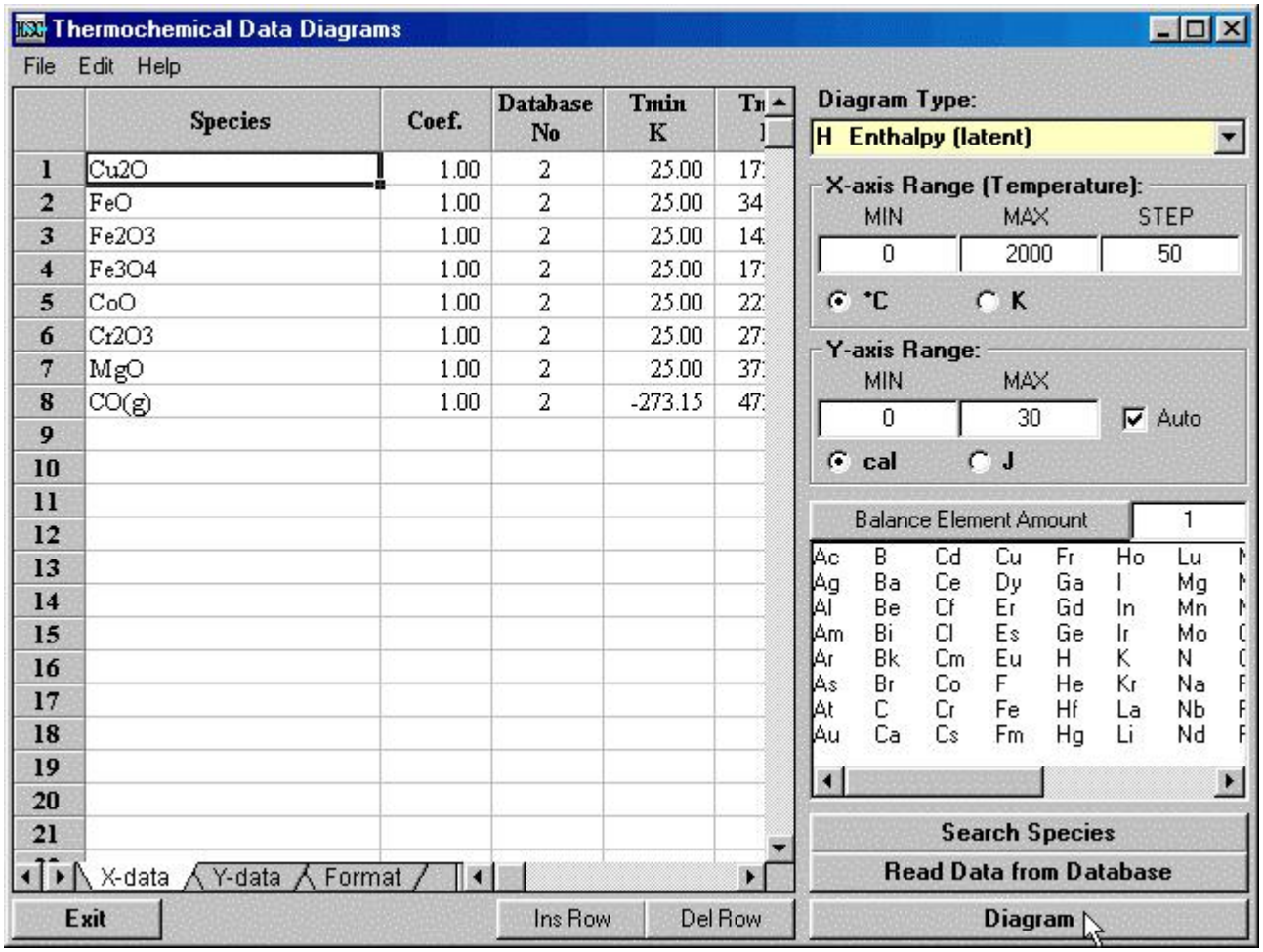


Fig. 1. The diagram menu. Enthalpy diagram type selected.

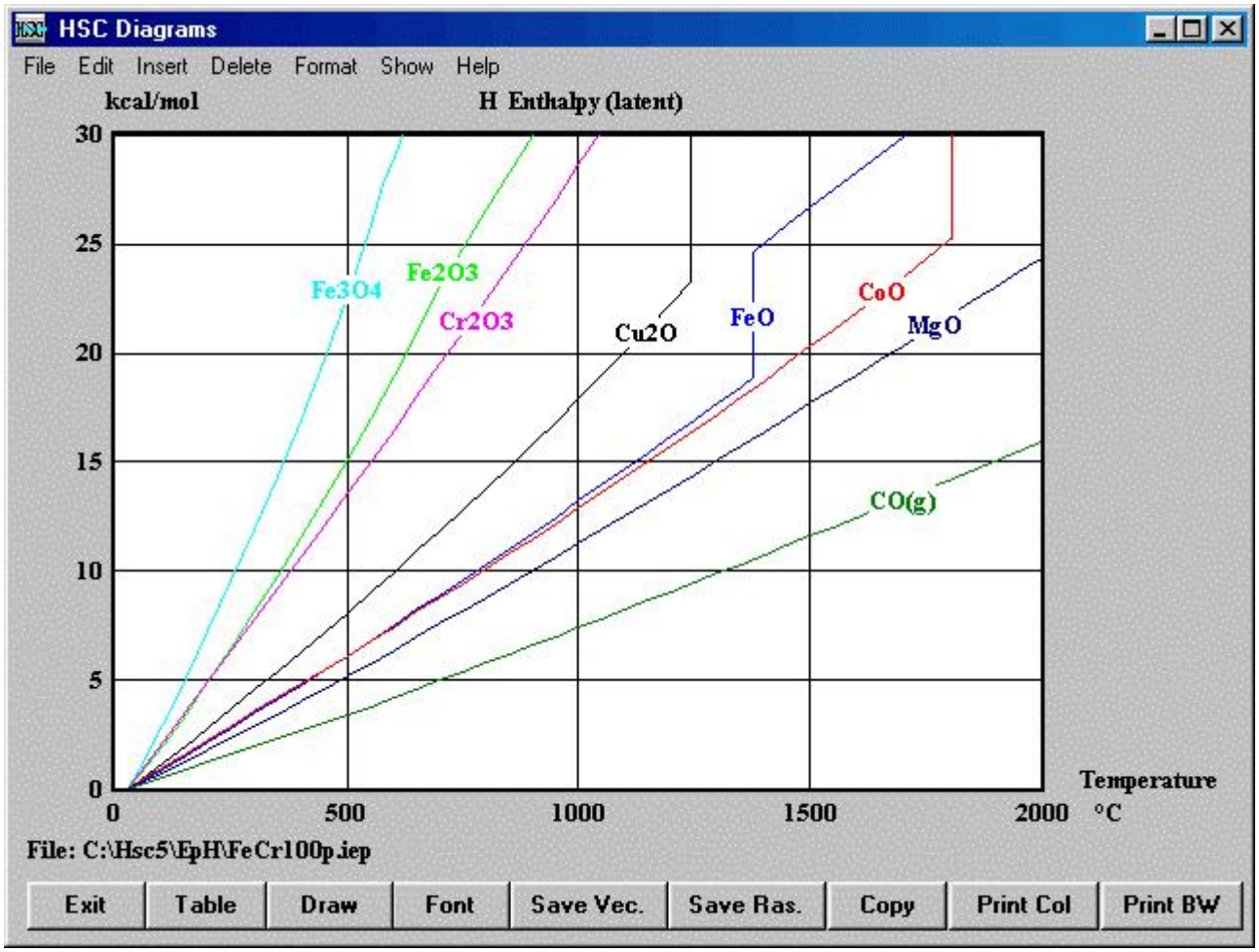


Fig. 2. The Enthalpy (latent) diagram based on the settings in Fig. 1.

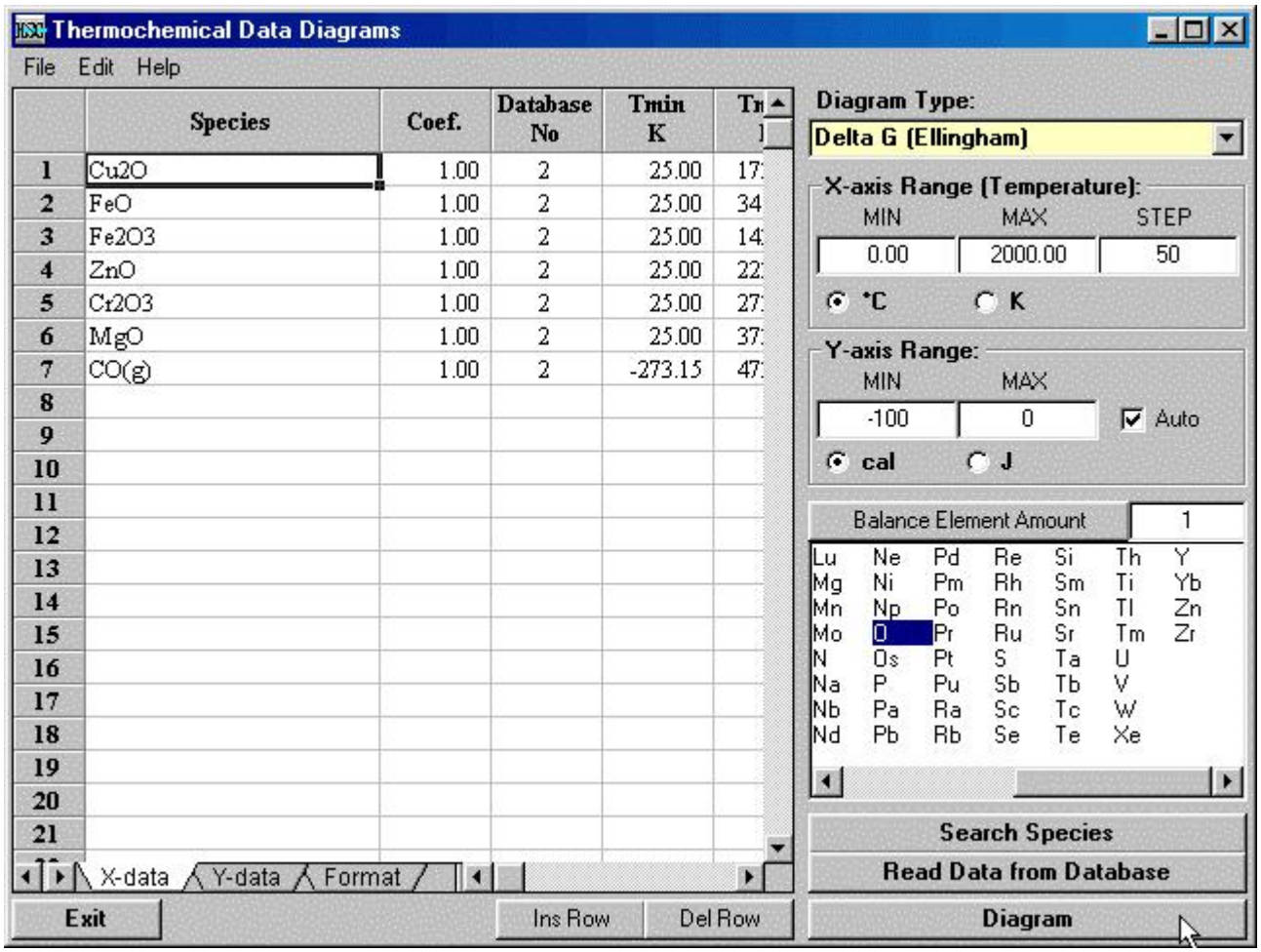


Fig. 3. Diagram settings of the Ellingham diagram for oxides.

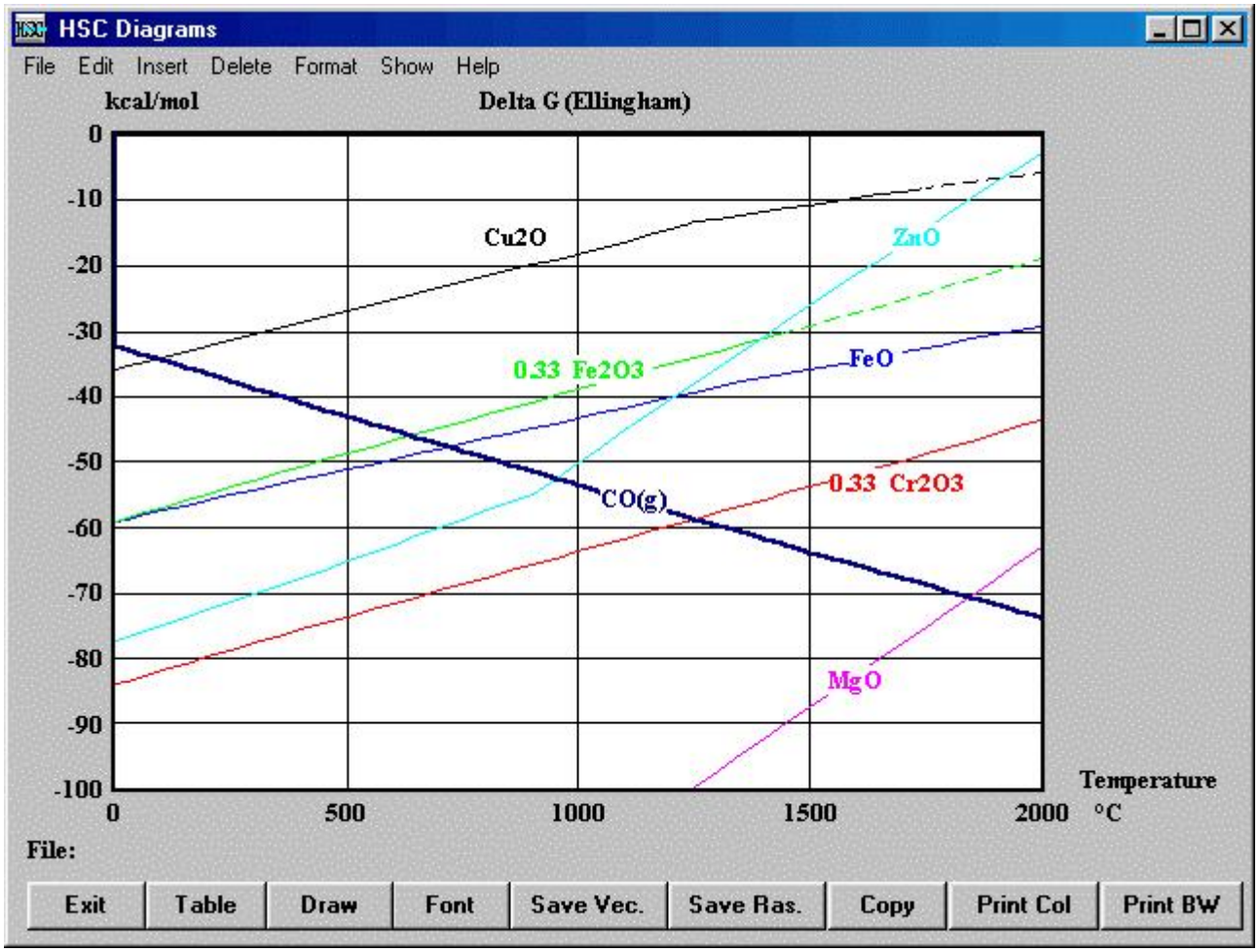


Fig. 4. Ellingham diagram of oxides based on the settings in Fig. 3.

20. DIAGRAM GRAPHICS

20.1 Graphical Ob ects

The new Drawing Toolbar can be used to draw basic graphical objects (lines, arrows, rectangles, ellipses) in HSC diagrams. These shapes may be used, for example, to illustrate experimental conditions. Versatile formatting options enable the user to edit lines, fill color, line widths and styles.

Drawing Objects can be created and edited with the mouse or the Object Editor, which enables very precise editing using numerical values as inputs. Drawing Objects can also be fixed so that they can be used in all diagrams or saved for later use.

User-specified graphics may be added to diagrams in two ways:
1. Using the Toolbar (**Show Toolbar** from the Diagram menu)
2. Using the Object Editor (**Show Ob ect Editor** from the Diagram menu)

1. Using the Toolbar

The Toolbar provides a standard drawing interface for drawing simple shapes and for inserting text. The same functions are also available from a popup menu by clicking the right mouse button. In Figure 1 the example file **incropera 92 494.HTR** in the Heat Loss module has been used to compare the convection and radiation coefficients, when the characteristic length (vertical length) varies from 0.2m to 0.8m.

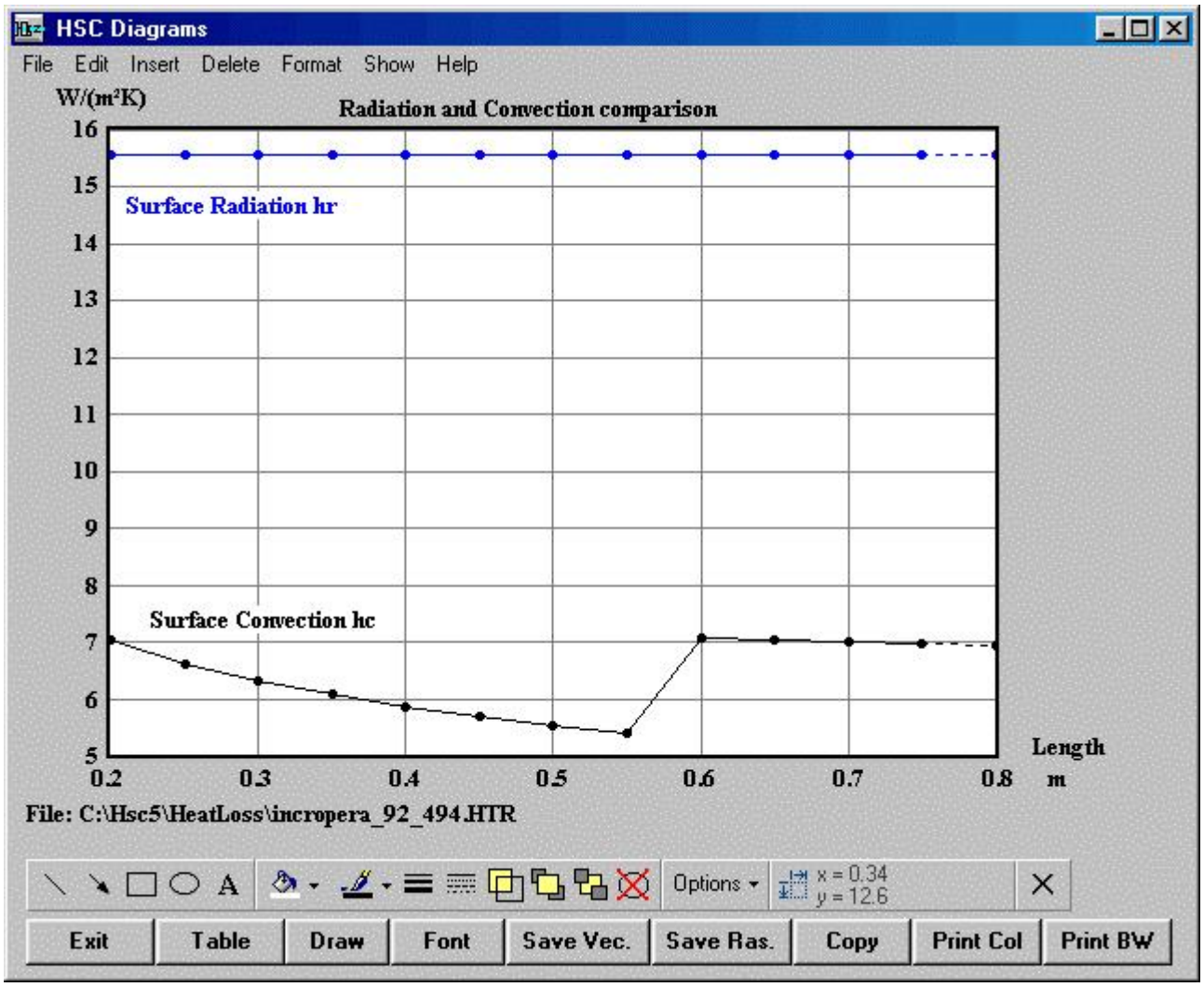


Figure 1 *e dra in too bar, s o n ere ro t e eat oss odu e.*

The first five buttons are used for drawing lines, arrows, rectangles, ellipses and text. The next eight buttons are used for modifying the objects, for example the line thickness. These options are also available from the **Options** drop-down box. The x- and y-coordinates for the mouse cursor are shown on the toolbar. In Figure 2 a simple arrow is inserted and moved around using the mouse. All objects can be moved around the diagram using the drag-and-drop technique.

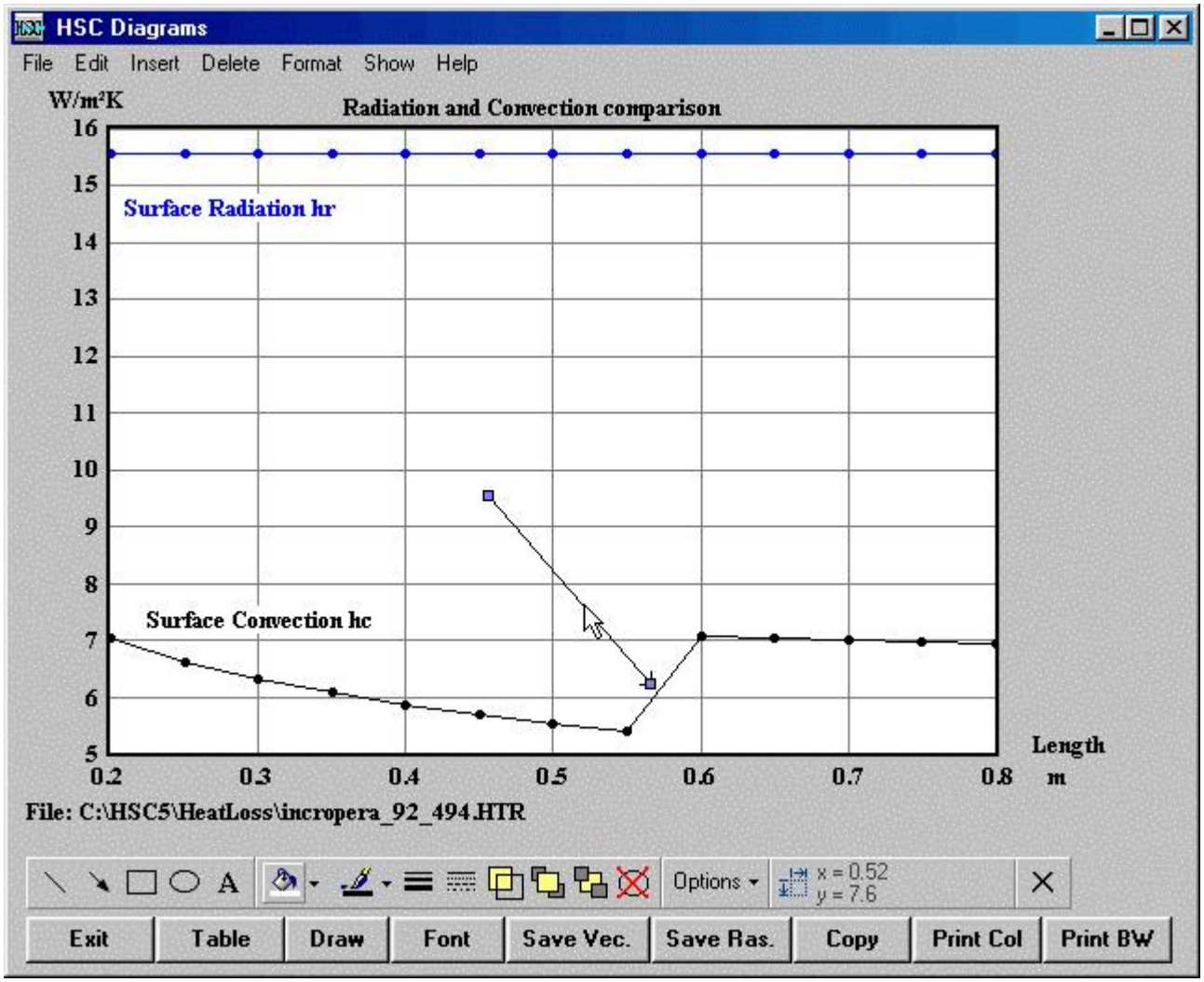


Figure 2 *Dra in an arro and o in it around usin dra and dro tec ni ue.*

2. Using the Ob ect Editor

Another method of creating and modifying objects is to use the Object Editor (**Show Ob ect Editor** from the menu). The Object Editor consists of three sheets: *ines*, *a es* and *abe s*. The Lines sheet contains all lines and arrows, the Shapes sheet contains all rectangles and ellipses and the Labels sheet contains all the labels.

The cells with a *b ue ore round co or*, may be changed manually by typing directly in the cell, for example, the coordinates of a rectangle. The cells with a *b ac ore round co or*, may be changed by double-clicking on the cell. The appropriate property window for the cell will then appear. For example, by double-clicking on the Color column, the color property window appears. In Figure 3 the color of a rectangle, which demonstrates the approximate transition region in the diagram, is changed using the object editor.

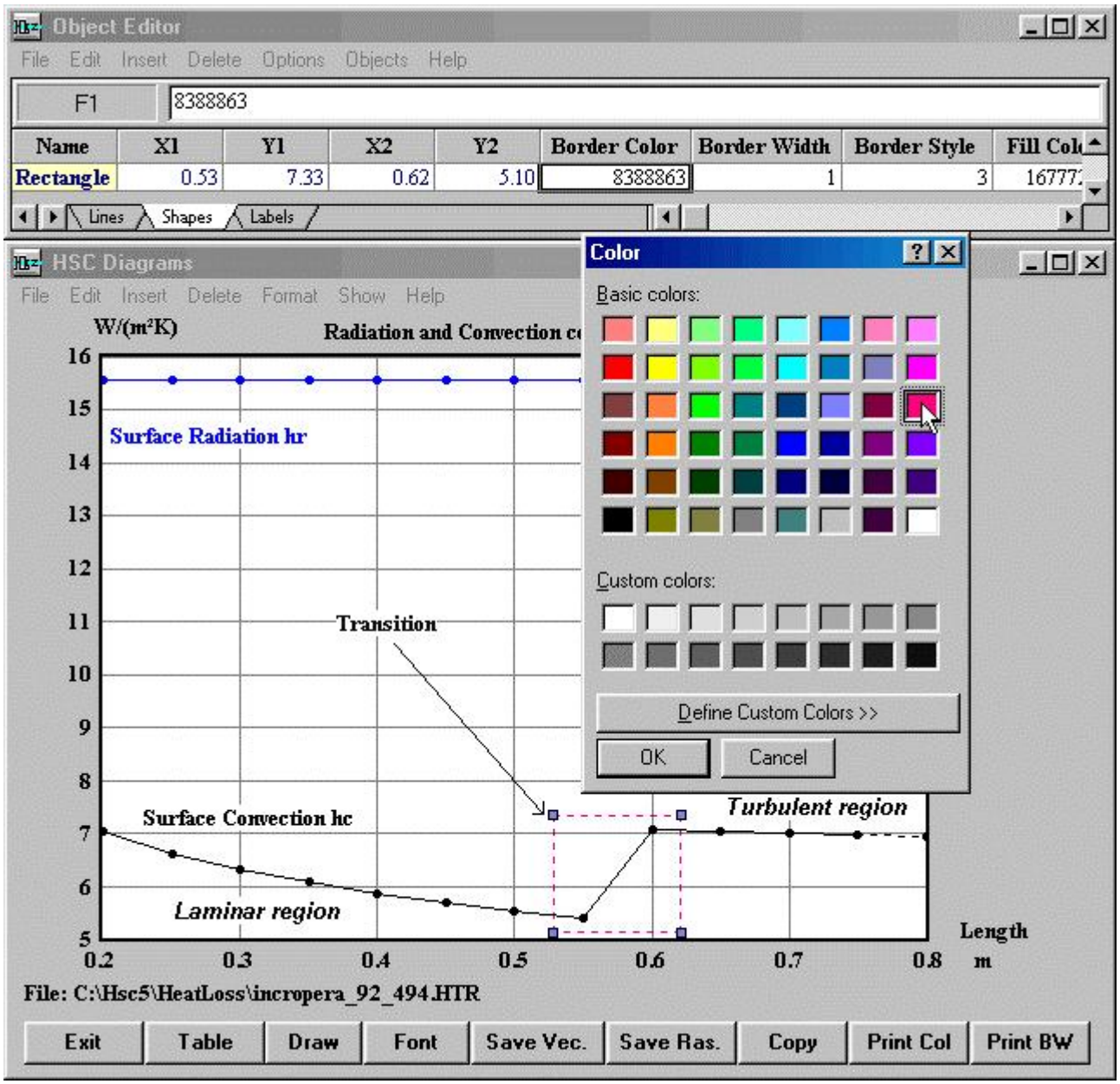


Figure 3 *sin t e b ect ditor to c an e t e ob ect ro erties.*

A created graphical layout may be useful in future diagrams too, therefore HSC 5.0 allows the user to save the layout as an *ob ect i e* (.OBE file), which may be imported to any diagram within HSC 5.0. By selecting **File Save** from the object editor menu, all the current objects in the diagram will be saved in a file for later use, see Figure 4.

Notice that the objects in the HSC Object editor use the same coordinate system as the diagram, i.e. the same x- and y-scales. Therefore the location of the objects will be changed on the screen if the x- or y-scale minimum or maximum values are changed. For example, in MS Excel charts the objects use screen coordinates.

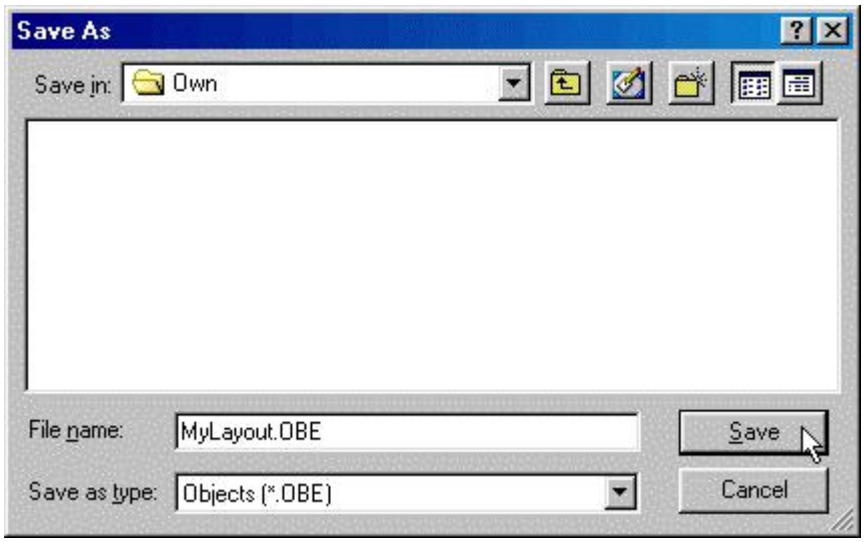


Figure 4 *a in t e current dia ra ob ects.*

20.2 Formatting the Diagram

Most of the diagram formatting options are available within all HSC diagram routines. The following paragraphs give a summary of these options:

1. Calculation points will be drawn on the graph if the menu option **Show Markers** is checked. If the menu option **Show Lines** is unchecked, the connecting lines between the calculation points will not be drawn. The markers are not drawn by default and the connecting lines are drawn by default.
2. X- and y-scales may be formatted by double clicking the x- or y-scale numbers or by selecting **X-Axis** or **Y-Axis** from the **Format** menu. For example, the minimum and maximum values may be changed, see Figure 5. In some cases it is also advantageous to change the y-axis to logarithmic scale in order to display the large variations in amounts or concentrations. Notice that the logarithmic y-axis is not available in all modules. From the same window you can also change the number format of x- and y-axis numbers as well as their font size, color, etc.

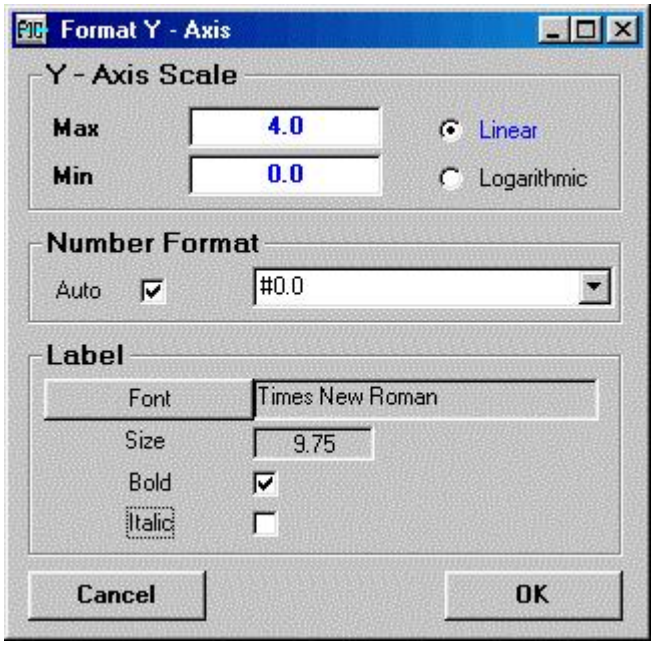


Figure 5 *an in sca es, sca e nu ber or at and ont settin s.*

3. Gridlines can be edited by selecting **Format Gridlines** from the diagram menu and different settings can be specified for the x- and the y-axis. The gridline properties include: color, line width, line style and disabled. Depending on the type of printer in use, different gridline settings may be required in order to produce a desirable printout. An example of a gridline setting is shown in Figure 6, where three different temperature profiles are drawn using the example file **Smelting2.HTR** from the HeatLoss module.

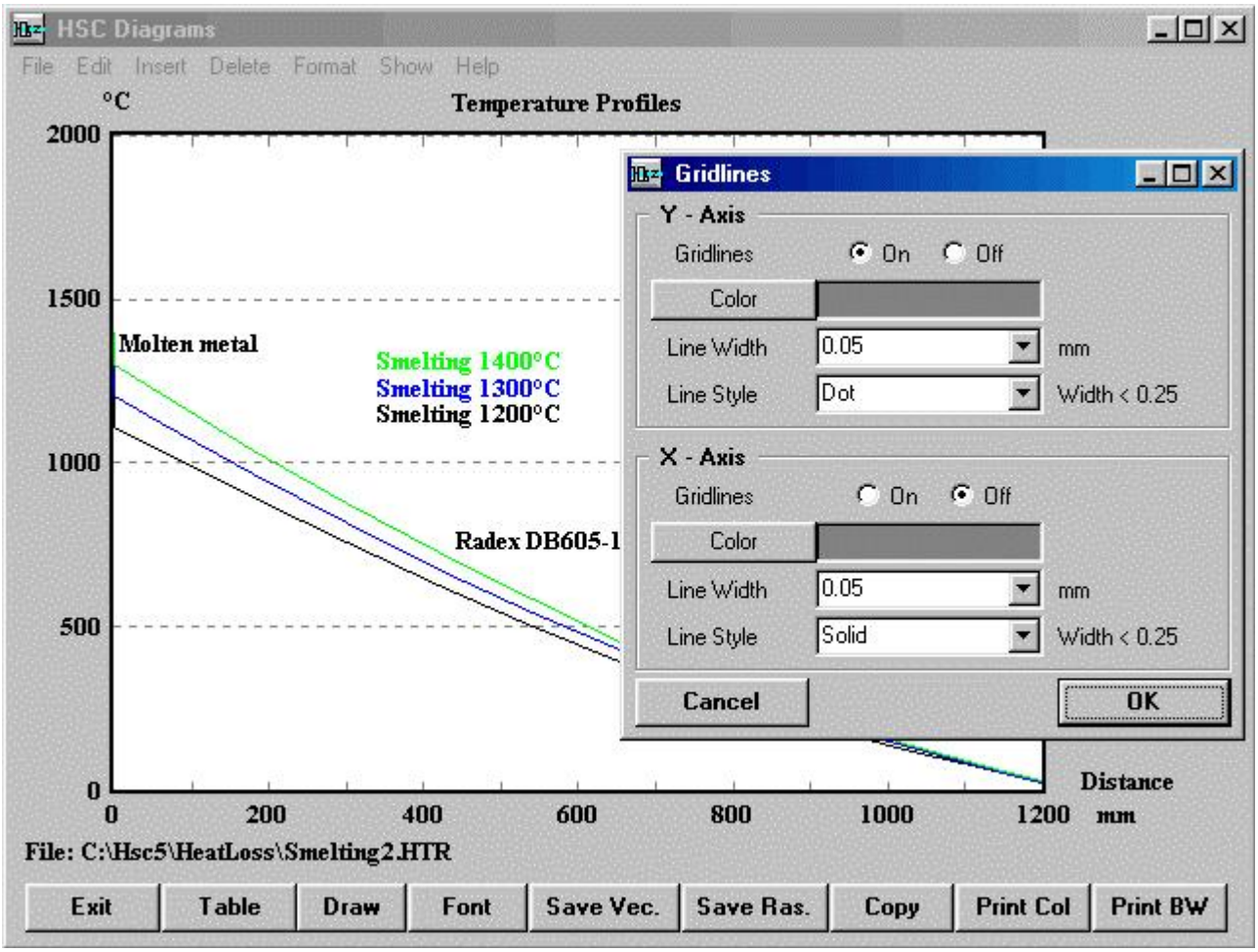


Figure 6 *ditin rid ines.*

4. The **line width** of curves, species label font and other graphical properties may be changed by either double clicking on the species labels or by selecting the label with the mouse and choosing **Format Label** from the menu. This function is not possible by double clicking on the curve. In the label and curve editing window, shown in Figure 7, the thickness of the curve named Smelting 1200 C is changed. Notice that alternative line styles to solid are available only for line widths smaller than 0.3 mm.

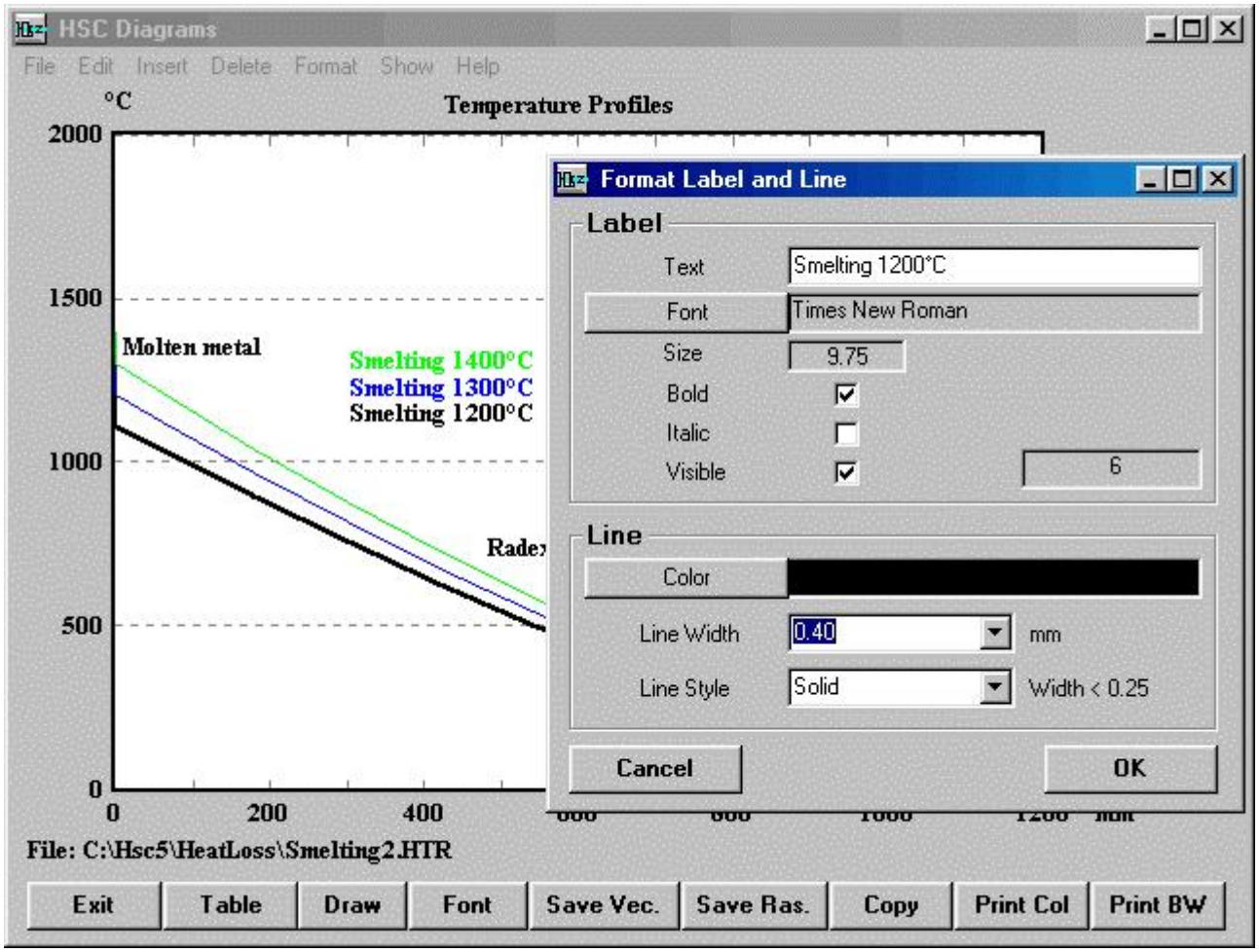


Figure 7 *an in abe and ine s eci ications.*

5. The Plot Area can be modified by selecting **Format Plot Area** from the menu. The background and border colors can be changed, as well as the border line style and thickness. Changing the border line properties may be necessary in order to view a curve that is on a border line.

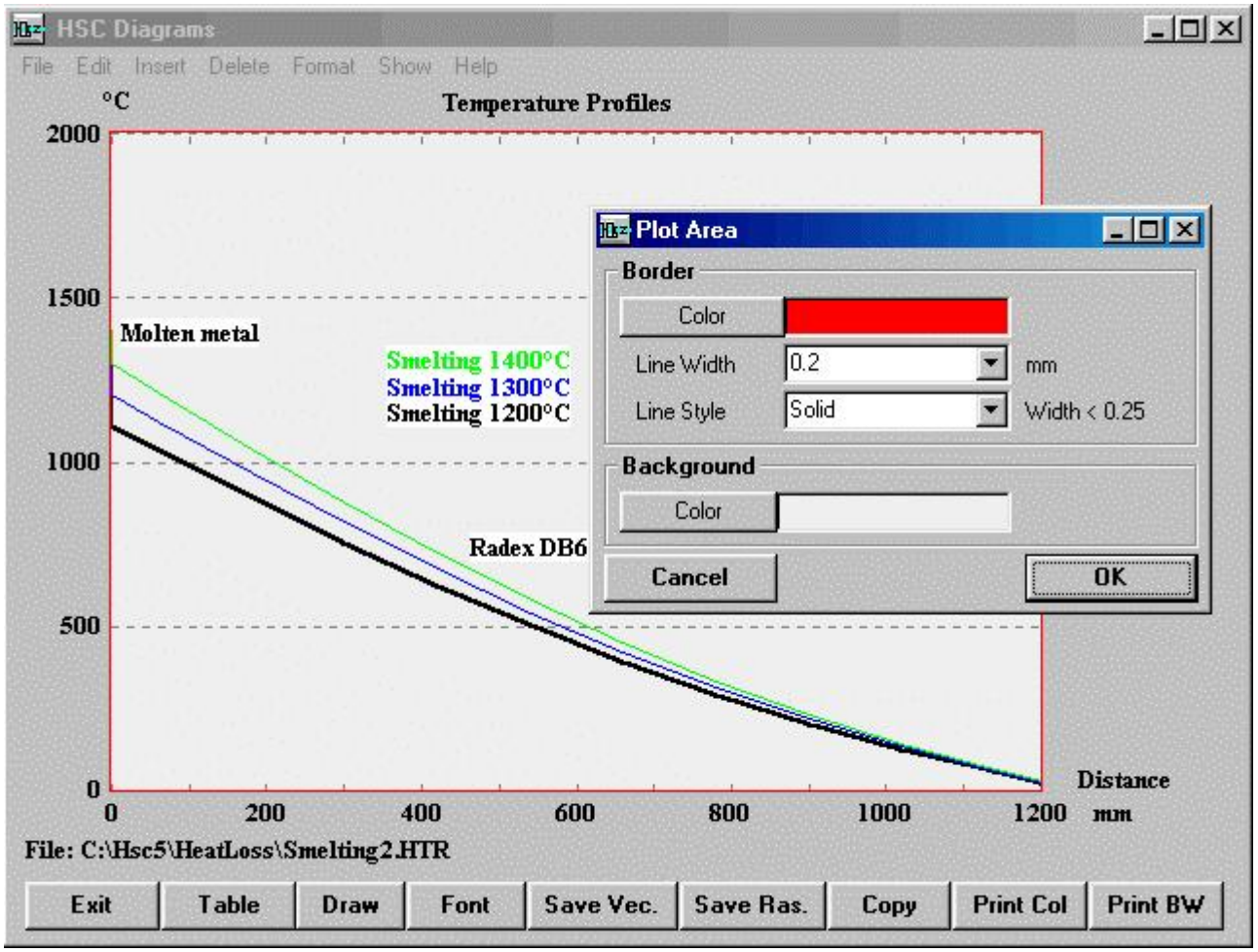


Figure 8 *an in ot area s eci ications.*

6. To edit any label and heading on the screen, simply click the text in the label with the mouse and start to edit.
7. To create new labels, select **Label** from the **Insert** menu. New labels can be deleted using the **Label** selection in the **Delete** menu. Default labels cannot be deleted, it is only possible to remove the text from them.
8. When using HSC Chemistry for the first time it may be necessary to change the default fonts, because the available fonts vary from one computer to another. This is achieved by selecting the **Default Font** from the **Format** menu. Usually Times New Roman, bold, size 11 font is the recommended selection. The selection made will automatically be saved in the HSC.INI-file in your Windows directory.
9. Once satisfied with the diagram, you can print it by pressing **Print BW**. If a color printer is available press **Print Col**. The print dialog provides several useful options for a hard copy, see Figure 9.

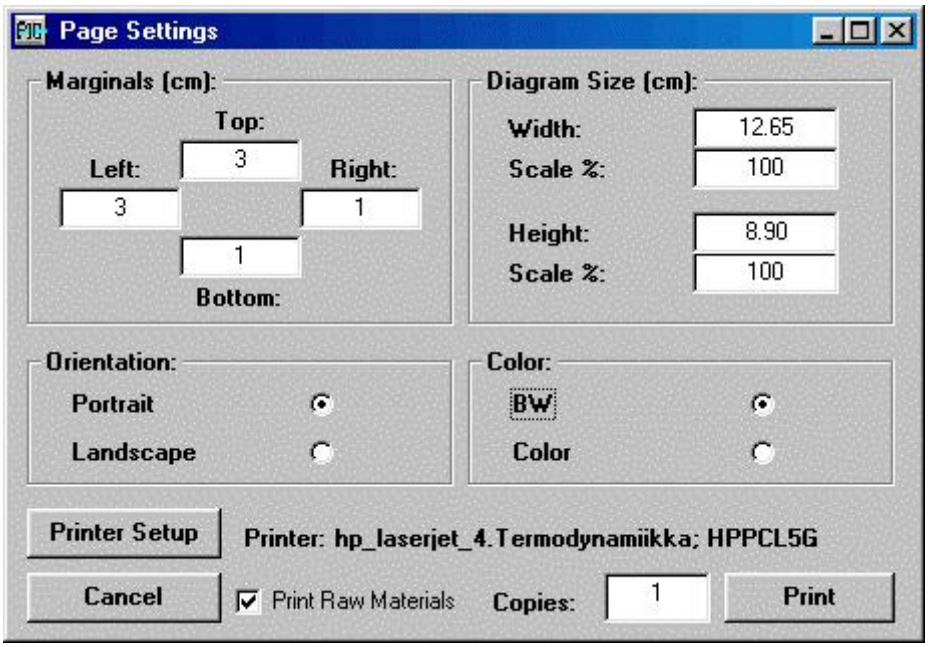


Figure 9 *rint dia o or ra ics.*

10. To view the diagram in a tabular format or use the data of the diagram in other programs, such as MS Excel, press **Table**. Press **Diagram** to return back to the diagram.
11. To copy the diagram to the Clipboard press **Copy**, and paste the diagram to other Windows programs. The **Copy** command uses the Windows Metafile format, which enables you to resize the diagram in other Windows applications in full resolution.
12. The **Save Vec.** button saves the diagram using the Windows Metafile format (.WMF).
13. The **Save Ras.** button saves the diagram in raster format. There are a number of formats available as well as several editing possibilities. See Chapter *2 . ditin and o binin Dia ra s* for a more detailed description.
14. Press **Exit** to return the main module.

20.3 Editing and Combining Diagrams

Whereas the previous HSC Chemistry 4 was only able to save diagrams using a WMF format, now more than 30 file formats are available, such as PG and BMP. HSC diagrams can now be saved in *ector* (.WMF Windows Meta File) and *raster* formats. The image dialog may be opened by pressing the **Save Ras.** button or by selecting **File Save as Raster File** from the diagram menu.

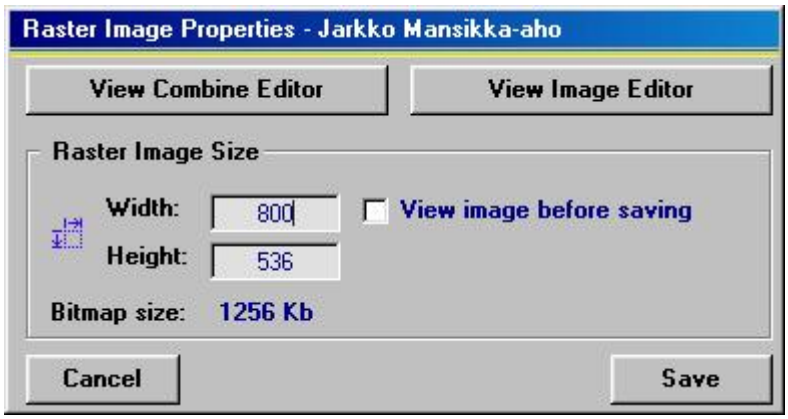


Figure 10 *aster i a e ro erties dia o .*

It is now also possible to *co bine dia ra s* (press **View Combine Editor**) using the new HSC Image Combiner, if the same x- and y-scales have been used. Another new feature is the possibility to *edit dia ra s* (press **View Image Editor**) using the new HSC Image Editor.

1. Editing diagrams (HSC Image Editor)

There are a number of functions in the edit mode, for example filtering techniques, rotating, scaling, tilting, copy paste etc. Once the changes have been made it is easy to save the picture in a number of different formats by selecting **File Save** from the menu. Any saved pictures can be used in other programs. Figure 11 shows the editing of a phase stability diagram created with the Lpp module.

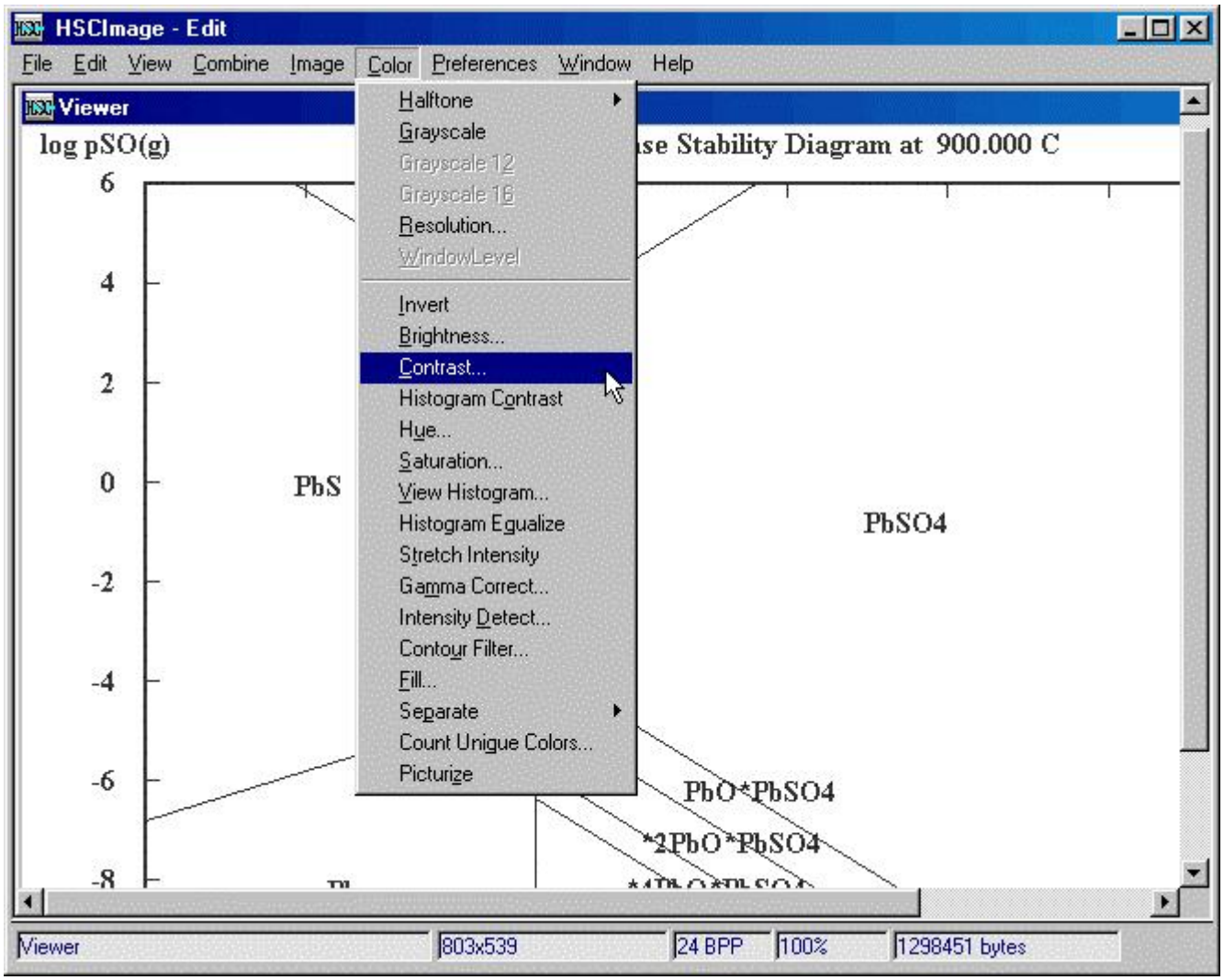


Figure 11 *ditin t e icture usin t e I a e ditor.*

2. Combining diagrams (HSC Combine Editor)

Several diagrams can be combined with the new HSC Image Combiner if the same x- and y-scales have been used. It is also possible to open the Image Combiner from the Image Editor by selecting **Combine** from the Image Editor menu. Figure 12 shows the combination of two phase stability diagrams created with the Lpp module.

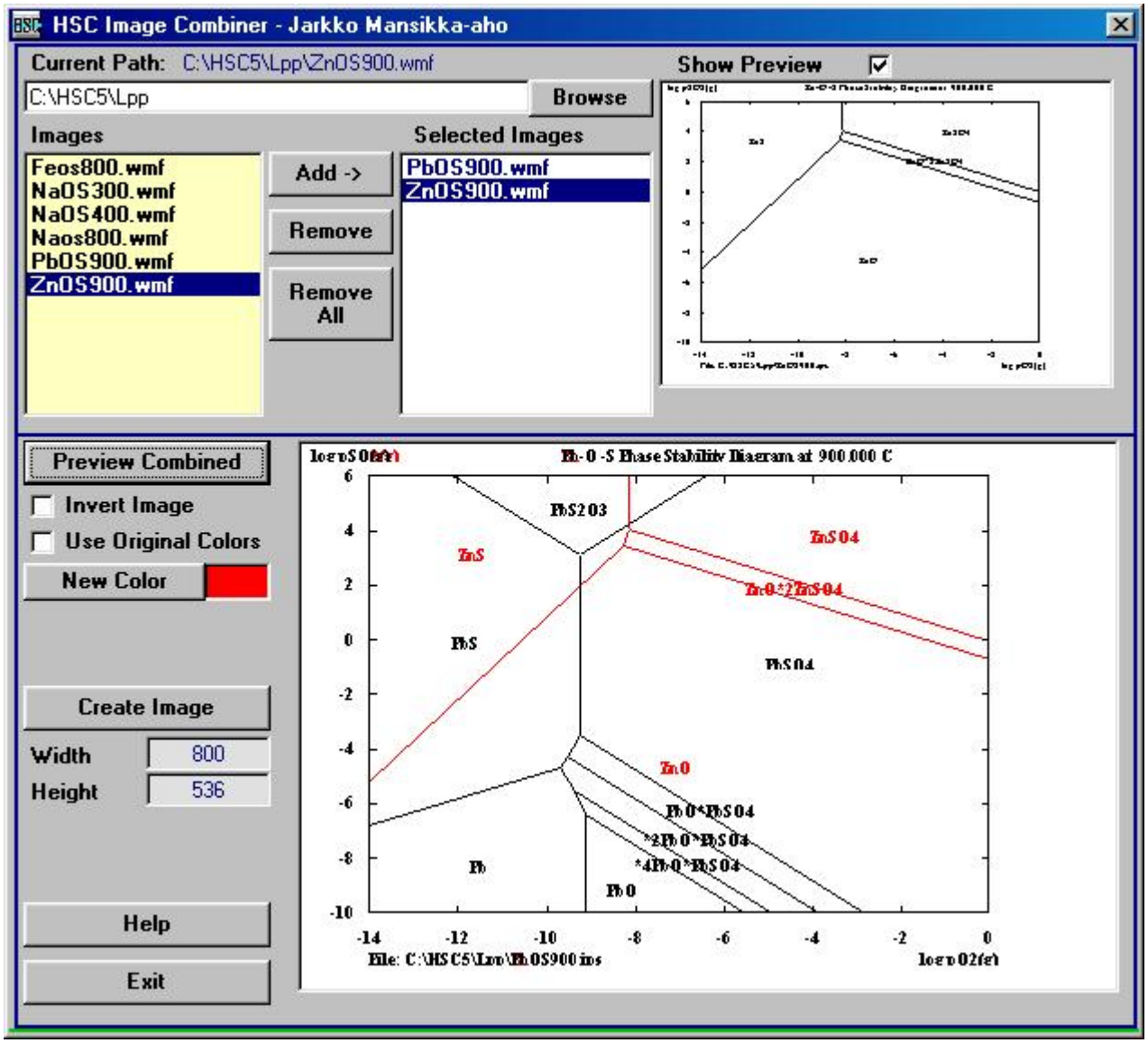


Figure 12 *o binin dia ra s usin t e o bine ditor.*

21. PHASE STABILITY DIAGRAMS

The phase stability diagrams show stability (*redo inance*) areas of condensed phases in a ternary system as a function of temperature or in isothermal conditions, with the remaining constraints as the other axis. These diagrams are very useful when a fast estimation of the prevailing phases is needed. It is assumed that all phases are pure substances. Mixture phases are not taken into account in basic phase stability diagrams.

The new HSC Chemistry 5.0 can draw two types of phase stability diagrams. The new **Tpp Diagram** module calculates the diagrams on the basis of minimum Gibbs energy (area graphics) and the old **Lpp Diagram** module calculates the phase stability boundaries as lines based on the reaction equations (vector graphics). These two modules have their own option buttons in the HSC main menu, i.e. Tpp and Lpp Diagram buttons.

The Tpp diagram module draws temperature partial pressure diagrams (T-p-diagrams) as well as p-p-diagrams with partial pressures on both axes. The old Lpp module draws only diagrams with selected partial pressures on both axes. These both modules offer slightly different benefits and limitations for example, the old Lpp module gives exact coordinates for the phase boundaries but the new Tpp module gives illustrative painted area diagrams and also a versatile T-p-axis option.

A common limitation for both the diagram modules is that only three elements can be selected simultaneously in the calculation system. Another basic feature is that only two variables can be selected for the diagram, i.e.:

1. If partial pressures are selected for both axes then the temperature must be fixed.
2. If the temperature is selected for the x-axis and partial pressure for the y-axis, then one partial pressure must be fixed. The partial pressure species may not contain more elements than the species selected for the y-axis.

The partial pressure $\mathbf{p_i}$ of gas **i** in a gas mixture is defined by equation (1):

$$\mathbf{p_i \quad x_i \quad P} \qquad \mathbf{1}$$

where $\mathbf{x_i}$ is the mole fraction of **i** in the mixture and **P** is the total pressure. The HSC phase stability diagrams use logarithmic scales for partial pressures, which are expressed in bar units (1 bar = 100 kPa = 0.987 atm).

21.1 Tpp Diagram Module

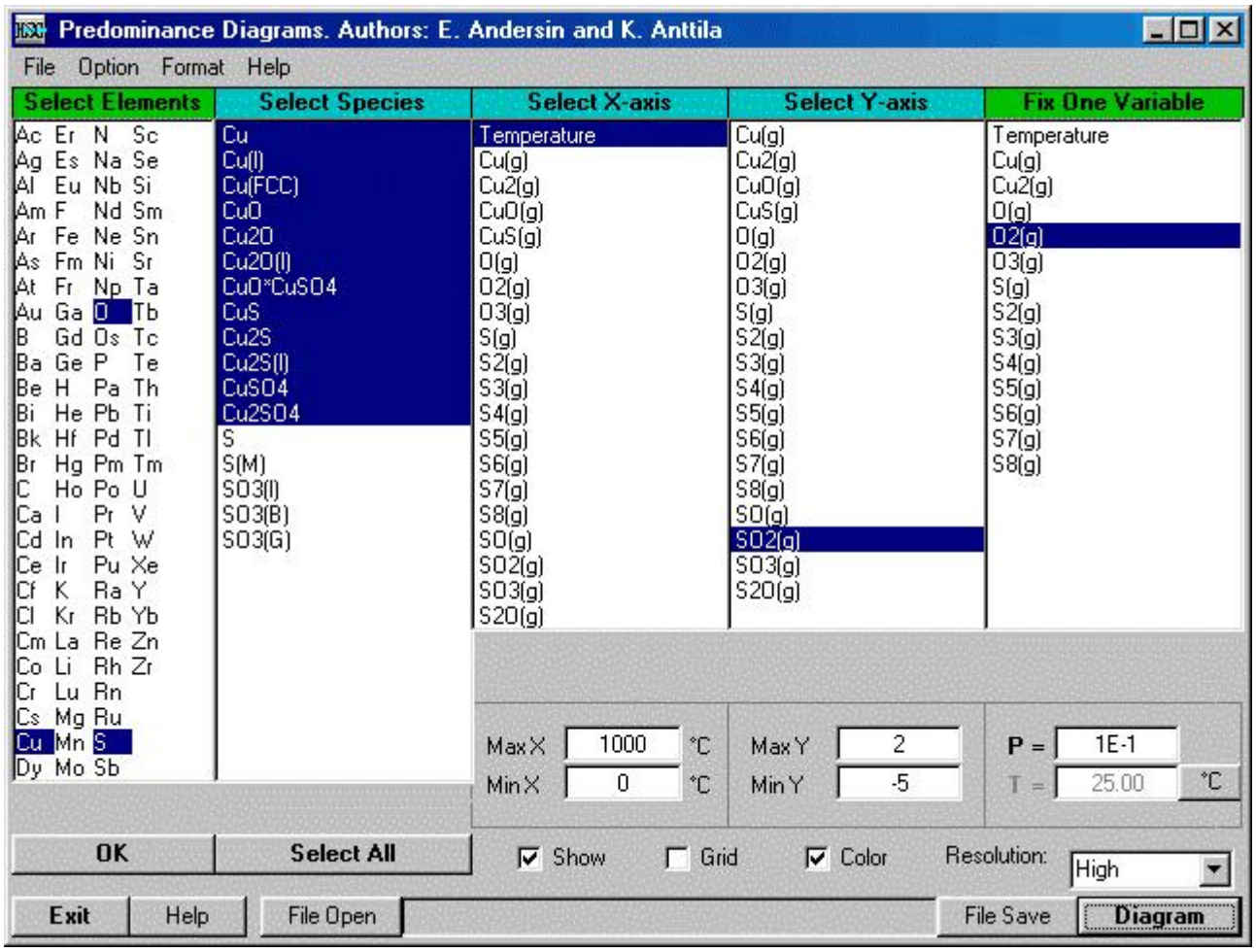


Fig. 1. Input data for Tpp phase stability diagrams.

The Tpp Diagram module calculates phase stability diagrams using partial pressures on both axis or temperature on the x-axis and partial pressure on the y-axis. This module calculates the diagram on the basis of minimum Gibbs energy. However, it does not check each x- and y-point in order to decrease calculation time. The calculation is made recursively using the preset resolution and a specific logout algorithm.

The user interface of the Tpp module is shown in Fig. 1 with an example of a Cu-S-O-system. The diagram may be drawn using the following steps:

1. Select **three elements** from the element list and press **OK**.
2. Select the species to diagram one by one or by pressing **Select All**. Keep **the Ctrl-key** down if you want to remove some species from the selection.
3. Select the x-axis species and the range for the x-axis. This selection will always reset the default x-range settings.
4. Select the y-axis species and the range for the y-axis. This selection will always reset the default y-range settings.

5. Set one variable, either temperature in p-p-diagrams or one partial pressure in T-p-diagrams. Please also remember to give a value for temperature or a selected partial pressure. The default value for partial pressure is 1E-20 and for temperature 25 C. Both C and K units can be used.

6. Make a selection for the diagram lay-out options if needed:
   – **Show**: Show calculation progress.
   – **Grid**: Show grid on diagram
   – **Color**: Paint areas with colors
   – **Resolution**: Low - coarse resolution diagram, fast calculations. High - high resolution diagram, long calculation time. This setting sets the size of the smallest calculated detail. Each step into a higher resolution will halve the size of the smallest visible detail.

7. Press **Diagram**.

The system specifications can be saved using the **File Save TPP** selection for later use. These files can be read back to the Tpp module using **File Open TPP** selection.

The Tpp module uses different colors for each stability area if the **Color** option is selected. The user can modify the default color palette with the **Format Color Palette** selection. This will open the color palette dialog, see Fig. 2. The colors can be modified by double clicking the colors in the **Color** column or by typing the corresponding RGB values to the **Color Code** column.

This modified palette can be saved for later use by pressing **Save Palette**. The Tpp automatically loads the palette file, which is named PPTCOL.PAL, but you can also use other names. These palettes can be reloaded by the **File Load User Palette** selection.

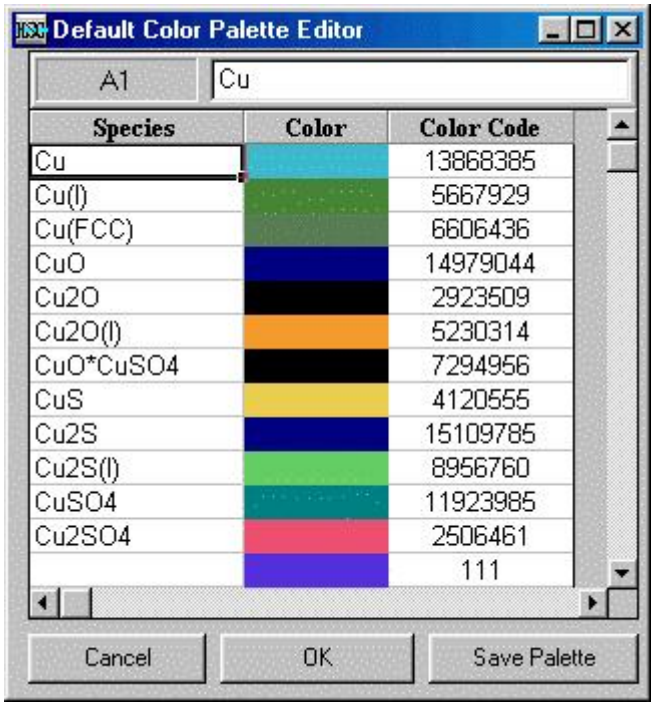


Fig. 2. The color palette dialog for the Tpp module.

21.2 Tpp Diagrams

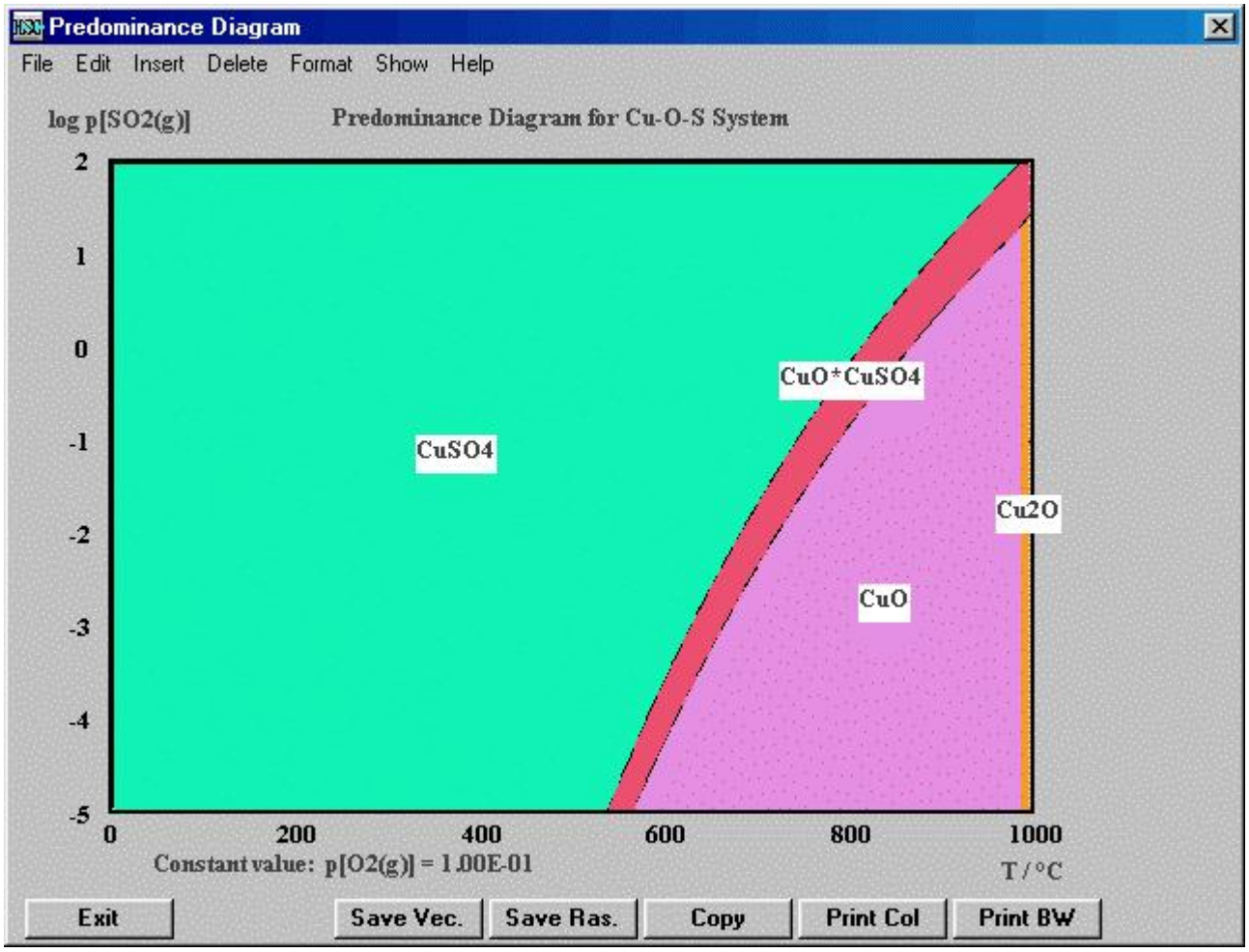


Fig. 3. Tpp phase stability diagrams based on data in Fig. 1.

The Tpp phase stability diagram is shown in Fig. 3, and the corresponding calculation system specifications are shown on the previous page. In this diagram we can see, for example, that copper oxide flue dust in a hot process gas tends to sulfatize, when the flue dust temperature decreases. It is also very easy to see that when the oxygen pressure decreases, the sulfates are reduced first into oxides and finally into metal form.

These diagrams can be modified in the same way as other HSC diagrams:

1. X- and y-axis scales and formats can be edited by double clicking the axes with the mouse.
2. The labels and headings can be edited by double clicking the labels.
3. The diagrams can be copied to the Clipboard by pressing **Copy**.
4. Diagrams can be printed by pressing **Print**. The printing dialog gives several options for hard copies. The new resize option is very useful if there are several small stability areas in the diagram.

21.3 Lpp Diagram Module

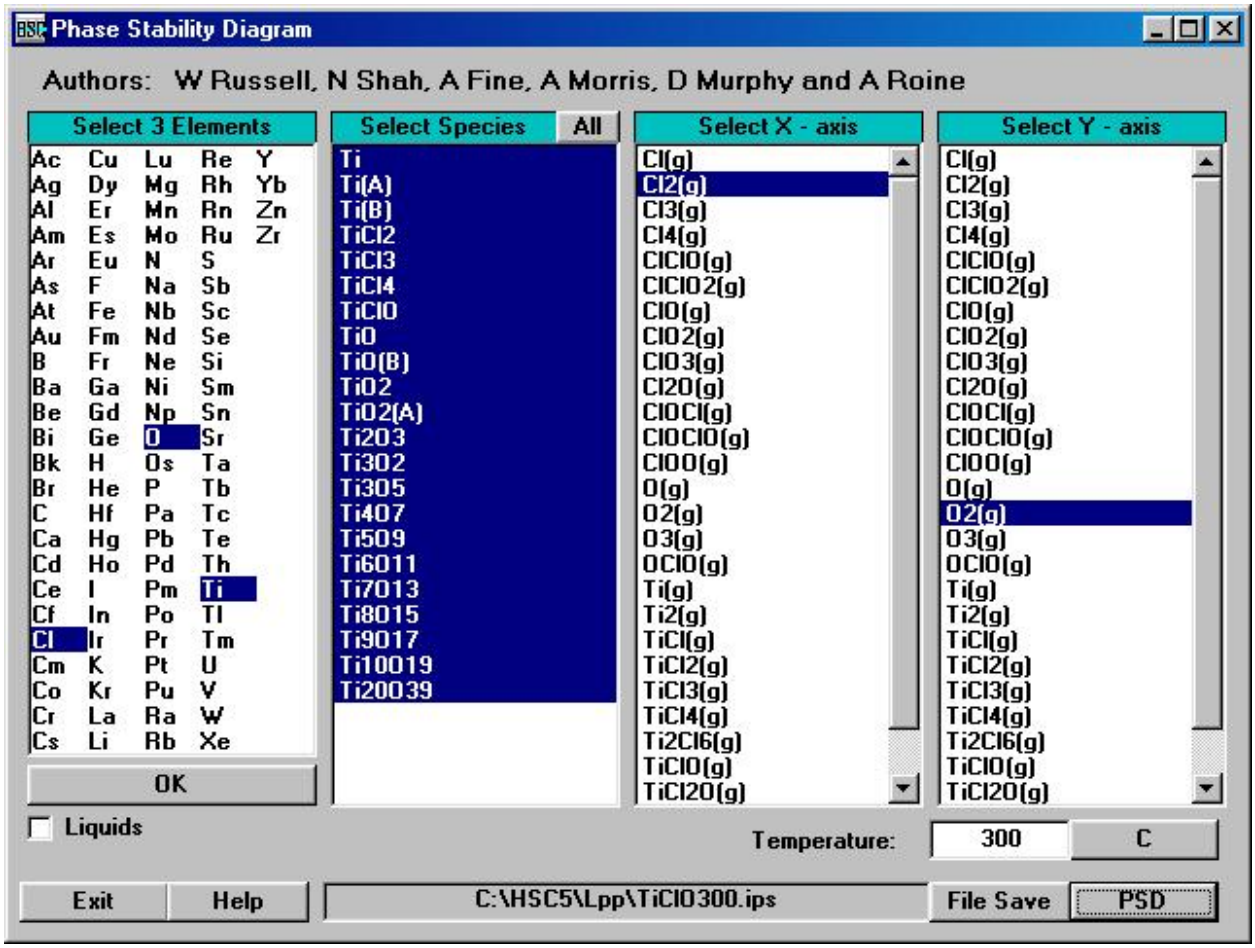


Fig. 4. Input data for phase stability diagrams.

The Lpp Diagram module draws isothermal phase stability diagrams of three element systems, also known as predominance area diagrams or Kellogg-diagrams. An example, shown in Figs. 4-6, is a diagram of the Ti-Cl-O-system, which shows the stability areas of titanium containing substances as a function of Cl_2(g)- and O_2(g)-pressures in the atmosphere. Follow these steps to draw the diagram:

1. Select three elements with the mouse and press **OK**, in this case Ti, Cl and O.
2. Wait a while until HSC displays the substances from the databases. Press **All** or select at least three substances (species) for the diagram. Please select only Ti-containing substances.
3. Select one gas species for the x-axis, for example Cl_2(g). You may select any species for the x-axis except those which contain Ti.
4. Select one gas species for the y-axis, for example O_2(g). You may select any species for the y-axis except those which contain Ti.
5. Change the temperature if needed, in this example 300 C. You may choose between C and K by pressing the button.
6. Press **File Save** and accept the name (TiClO700.IPS) for the input file. The PSD program draws the diagram on the basis of this file. It may be a good idea to save all .IPS-files in a separate HSC PSD directory if available.

7. Press **PSD** and wait a minute to see the diagram. You can return to HSC by pressing **Exit**.
8. You can check the name and data of the species by double clicking the list.

PSD diagrams offer an easy way to evaluate stabilities of different condensed substances as a function of gas pressures, typically $O_2(g)$, $S_2(g)$, $SO_2(g)$, $Cl_2(g)$, etc. These diagrams can be used, for example, to find the best conditions for oxidizing or sulfatizing reactions, etc.

Limitations

Note that all selected substances must contain the main element, for example Ti in the Ti-Cl-O system, but the species selected for the x- and y-axis should not contain this main element (Ti)

If you have more than one substance with the same overall composition (stoichiometry) in the species list, for example NaS and Na_2S_2, FeO and FeO(l), etc., please select only one such substance for the diagram. In any case HSC will automatically omit substances with identical stoichiometry. The user can make this selection himself in order to select exactly those substances which he wants to be taken into account.

21.4 Lpp Diagram Menu

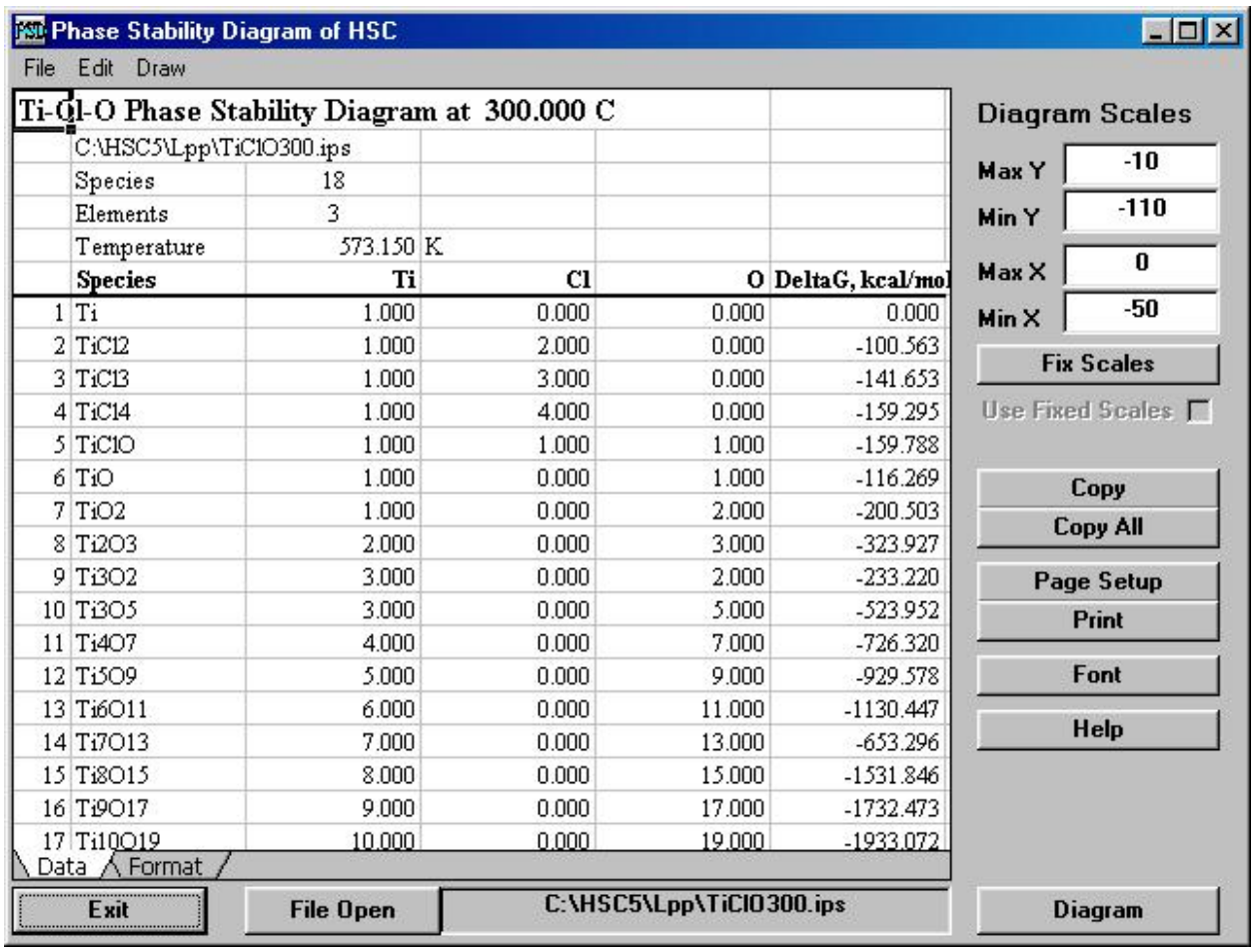


Fig. 5. Changing the default settings of the Phase Stability Diagram.

On the **Data** sheet of the PSD Menu you can see the calculated data of the PSD diagram in a tabular form. The **Format** sheet contains formatting settings of the diagram. It is not recommended to change these. HSC evaluates the default values automatically for Max Y, Min Y, Max X and Min X for the axes.

You can calculate and display the diagram in the following way

1. Select the .IPS file for the diagram by pressing **File Open** if not already selected. This file contains the DG values for the selected species at a given temperature.
2. You will automatically get the diagram on the screen.

Change the default settings of the diagram in the following way

1. You may change the minimum and maximum values for the x- and y-axis simply by clicking the value using the mouse and by starting to edit.
2. Press **Diagram** to display the diagram.
3. Press **Print** to get a paper copy of the tabular results. HSC will draw the diagram at the best resolution of any MS Windows - supported printer.
4. Press **Copy** to paste the data onto other Windows programs.
5. Press **Exit** to return to HSC or to exit the PSD program.

21.5 Lpp Module Diagram

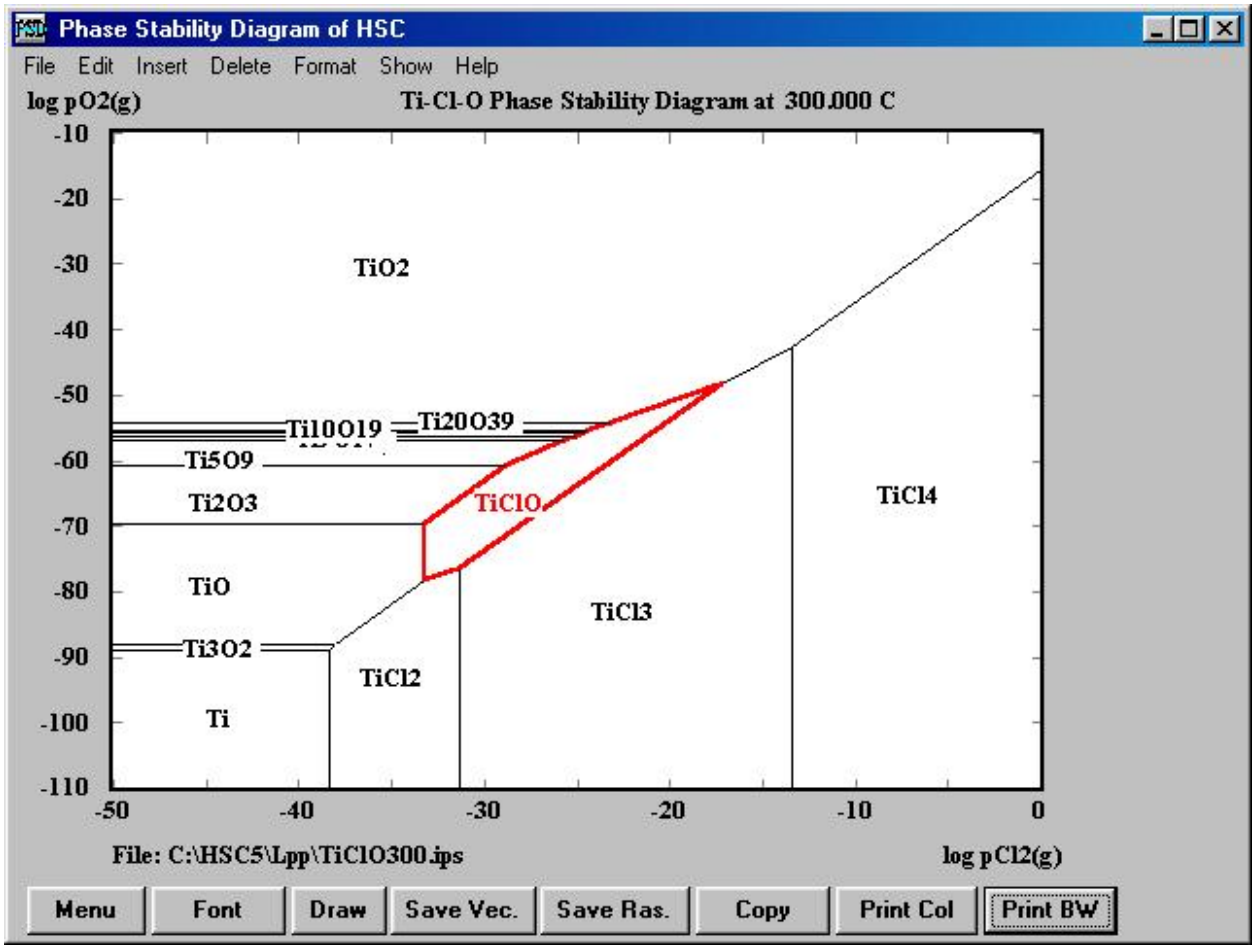


Fig. 6. Phase Stability Diagram of the Ti - Cl - O - system at 300 C.

The phase stability diagram window shows the results of the PSD program in graphical form. In this diagram it is easy to see the stability areas of different pure substances under the prevailing conditions.

You can edit this diagram in the following ways

1. Press **Menu** to change the scales of the axes.
2. When you are satisfied with the scales, you can relocate all the **labels** by mouse with the drag and drop method. First select the label, keep the left mouse button down and drag the label to the right location, release the mouse button and the label will drop into the new location.
3. You can edit the text in the labels by simply clicking the text using the mouse and typing the new text. You can edit the format of the labels and lines by double-clicking the label, see Fig. 6.
4. The x- and y-scales can be changed by double clicking the axis numbers.
5. The first time you use HSC Chemistry it may be necessary to change the fonts by pressing **Font**, because the fonts available vary from one computer to another. Usually Times New Roman, bold, size 11 points is a good selection. The selection will be automatically saved in the HSC.INI-file.

6. When you are satisfied with the diagram you may print it by pressing **Print** at the best resolution of your printer.
7. Using **Copy** you may paste the diagram into other Windows programs using the Windows Metafile format.
8. Press **Menu** to return to HSC or to exit the PSD program.

22. MINERALOGY ITERATIONS

Composition conversions, between substance (mineralogy) and elemental analyzes, are often needed in chemical R D work. *e inera o odu e easi con erts inera o ica co ositions into e e enta ones, but is not a a s ab e to a e re erse con ersion*. Conversion can be made using the following procedure, see Fig. 1:

1. Type the species formulae into column A, use rows 4. The species do not need to exist in the HSC database. However, you must use the HSC formula syntax.
2. Type the compositions in column D.
3. The elemental composition can be seen on row 4.

You can also give the total amount for the material in cell C4 as well as name in cell A1. Note that the user may edit only the cells with red fonts if **Format Red Font Shield** has been selected.

The conversion of the elemental composition of a substance into a mineralogical one is a more difficult task, for example due to small analytical errors. This module offers three tools for converting elemental analyzes into mineralogical ones.

1. Solve Method

The Solve method uses matrix-algebra to solve the mineralogy. It is useful if the given amounts of elements fit exactly to the given substances. The number of unknown compositions must also be the same as or less than the number of element balance columns.

An example of the Solve method is shown in Fig. 2 (file Example1.mnr). You can create this example from the previous one with the following procedure:

1. Press **Copy Row 4 to 3** button to copy elemental compositions from row 4 to 3.
2. **Type 1** to cells D5-D8, in order to wipe out the original compositions.
3. Press **Solve**. The results will be shown in column D. Usually the elements do not fit exactly to the given species, in these cases the Solve method may add some element rows to the system. These rows can be deleted by **Delete Row** selection.

2. Automatic Iterative Method

The Automatic iterative method fits the given elements to the given substances by changing the species contents in order to reach the given element compositions. To carry out this conversion follow these steps, see Fig. 4:

1. Type species formulae to column A, use rows 4.
2. Type elemental analyze to row 3, use columns D.
3. Type the target elements, which will be used to iterate the species, into column B. Please do not use the same element for several species, otherwise manual iteration may be needed.
4. Press **Iterate All** to start iterations. Sometimes it is necessary to press this button several times in order to reach sufficient accuracy.

3. Manual Iterative Method

Sometimes the given elemental analysis does not fit with the given elements. In this case the user may search the approximate composition manually by changing the contents in column D, in order to reach a satisfactory match with the elemental analyzes in rows 3 and 4. **Iterate Sel** can be used to iterate individual rows.

Elemental and Mineralogical Composition Conversions

File Edit View Insert Delete Format Calculate Help

D8 15

	A	B	C	D	E	F	G	H	I	J	K
1	Substance Name	Target	Amount	Content	Ca	Cl	Cu	Na	O	S	Zn
2	Species	Element	kg	wt-%	#wt-%	#wt-%	#wt-%	#wt-%	#wt-%	#wt-%	#wt-%
3	Target =>			7.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
4	Result =>		200	100.00	5.42	9.58	23.96	16.19	23.51	17.33	4.02
5	Na2SO4		100	50.00				16.19	22.53	11.29	
6	Cu2S		60	30.00			23.96			6.04	
7	ZnO		10	5.00					0.98		4.02
8	CaCl2		30	15.00	5.42	9.58					
9											
10											
11											
12											
13											
14											
15											
16											
17											
18											
19											
20											
21											

Substance

Exit Help Set Last Row Copy Row 4 to 3 Solve Iterate Sel. 10 Iterate All

Fig. 1. Calculation of the elemental composition of a material mixture. The user has given the species names in column A and the contents in column D. The calculated result is shown on row 4.

Mineralogy Conversions C:\Hsc5\Content\Example1.mnr

File Edit View Insert Delete Format Calculate Help

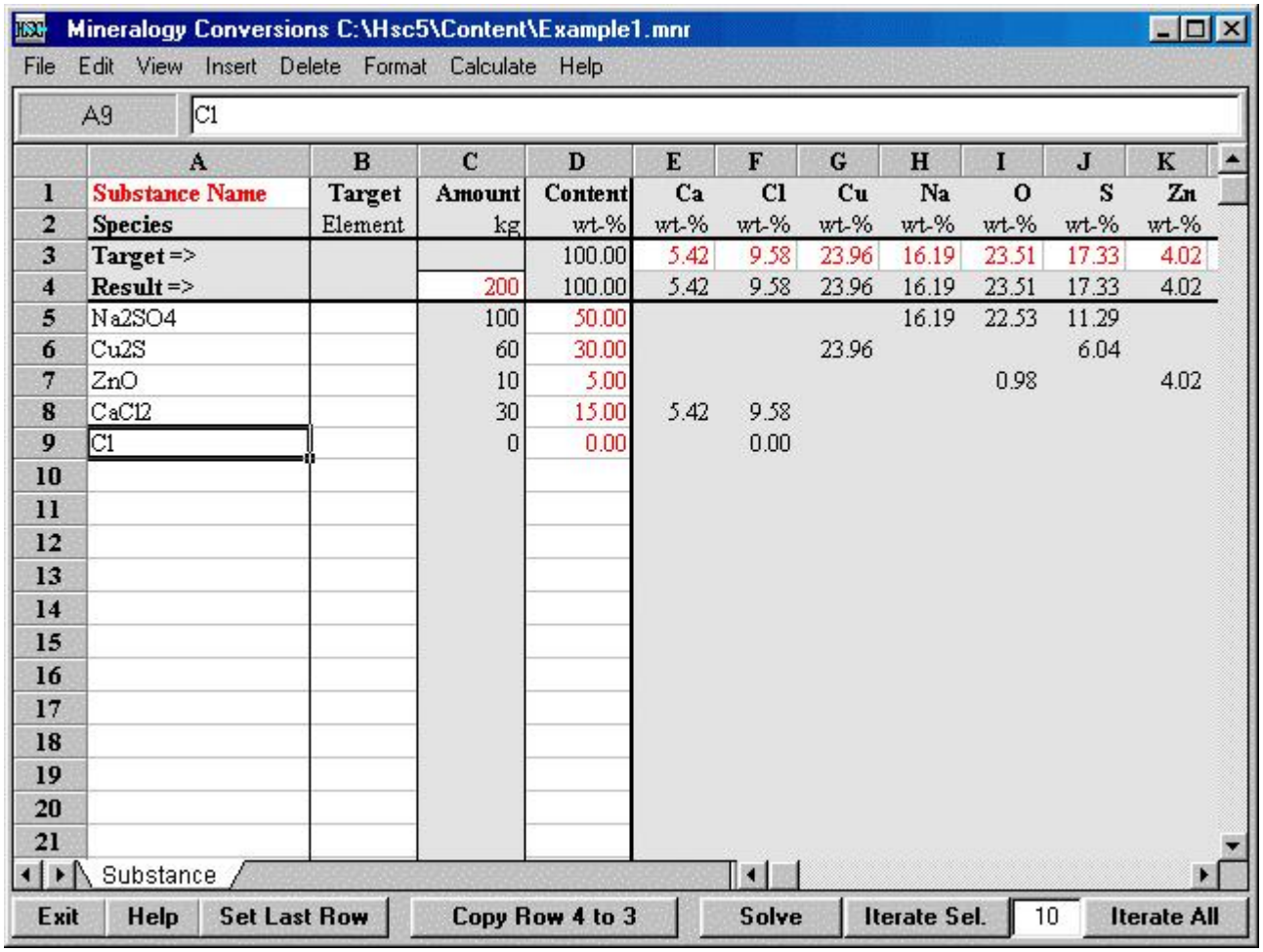
A9 C1

	A	B	C	D	E	F	G	H	I	J	K
1	Substance Name	Target	Amount	Content	Ca	Cl	Cu	Na	O	S	Zn
2	Species	Element	kg	wt-%	wt-%	wt-%	wt-%	wt-%	wt-%	wt-%	wt-%
3	Target =>			100.00	5.42	9.58	23.96	16.19	23.51	17.33	4.02
4	Result =>		200	100.00	5.42	9.58	23.96	16.19	23.51	17.33	4.02
5	Na2SO4		100	50.00				16.19	22.53	11.29	
6	Cu2S		60	30.00			23.96			6.04	
7	ZnO		10	5.00					0.98		4.02
8	CaCl2		30	15.00	5.42	9.58					
9	Cl		0	0.00		0.00					
10											
11											
12											
13											
14											
15											
16											
17											
18											
19											
20											
21											

Substance

Exit | Help | Set Last Row | Copy Row 4 to 3 | Solve | Iterate Sel. | 10 | Iterate All

Fig. 2. Calculation of the species composition in column D using the elemental composition in row 3 by **Solve**.



	A	B	C	D	E	F	G	H	I	J	K
1	Substance Name	Target	Amount	Content	Ca	Cl	Cu	Na	O	S	Zn
2	Species	Element	kg	wt-%	wt-%	wt-%	wt-%	wt-%	wt-%	wt-%	wt-%
3	Target =>			100.00	5.42	9.58	23.96	16.19	23.51	17.33	4.02
4	Result =>		200	100.00	5.42	9.58	23.96	16.19	23.51	17.33	4.02
5	Na2SO4		100	50.00				16.19	22.53	11.29	
6	Cu2S		60	30.00			23.96			6.04	
7	ZnO		10	5.00					0.98		4.02
8	CaCl2		30	15.00	5.42	9.58					
9	Cl		0	0.00		0.00					

Fig. 3. Calculation of the elemental composition of a sulfide material. The user has given the species names in column A and the contents in column D. The result is on row 4.

Mineralogy Conversions C:\Hsc5\Content\Example2.mnr

File Edit View Insert Delete Format Calculate Help

A37

	A	B	C	D	E	F	G	H	I	J	K
1	Substance Name	Target	Amount	Content	Al	As	Ca	Co	Cu	Fe	Ni
2	Species	Element	kg	wt-%	wt-%	wt-%	wt-%	wt-%	wt-%	wt-%	wt-%
3	Target =>			100.00	3.18	0.61	2.14	0.32	22.51	27.66	0.82
4	Result =>		200	100.00	3.18	0.61	2.14	0.32	22.51	27.66	0.82
5	CuFeS2	Cu	130	65.00					22.51	19.78	
6	FeS	Fe	16	8.01						5.09	
7	FeS2	S	12	5.99						2.79	
8	Ni2S3	Ni	3	1.50							0.82
9	CoS	Co	1	0.50				0.32			
10	As2S3	As	2	1.00		0.61					
11	ZnS	Zn	4	2.00							
12	CaO	Ca	6	3.00			2.14				
13	Al2O3	Al	12	6.00	3.18						
14	SiO2	Si	14	7.00							
15											
16											
17											
18											
19											
20											
21											

Substance

Exit | Help | Set Last Row | Copy Row 4 to 3 | Solve | Iterate Sel. | 10 | Iterate All

Fig. 4. Iteration of species compositions in column D on the basis of the elemental compositions in row 3 with **Iterate All**. The target elements in column B must be specified by the user.

Set Last Row

Pressing **Set Last Row** will set the last row which is used in the calculations. All compositions below this row are kept constant. This property can be used, for example, if the contents of some species, such as SiO_2, Al_2O_3, etc., are available.

Calculate Mixture Composition

The user can insert new sheets into the mineralogy workbook with the **Insert Sheet** selection. This will create an identical sheet on the right side of the selected sheet. The new sheet can be cleared with the **Edit Clear All** selection. These identical sheets may also be used for mixture calculations.

uite often the feed of a chemical process consists of several raw materials. The compositions of these materials are fixed, but the ratios change from time to time. The total composition of the mixture may be calculated with the Mineralogy module and by following these steps, see Fig. 5 (file name of this example is **Example3.mnr**):

1. Start from Example 2, shown in Fig. 4 and Select **Insert Sheet**.
2. Double click the sheet 1 tab and rename the sheet as Raw1. Rename sheet 2 in the same way as Raw2, you can also use real names for the materials.
3. Type or solve the compositions for each individual sheet as described before in this chapter. Do not add or remove species from the list, the species list must be identical in each sheet. Give the amounts for each material in the C4 cells.
4. Select **Calculate Mixture Composition**. This will add a mixture sheet and calculate the mixture composition for all the raw materials and give the total amount of the feed in cell C4.

Mineralogy Conversions C:\Hsc5\Content\Example3.mnr

File Edit View Insert Delete Format Calculate Help

C4 968

	A	B	C	D	E	F	G	H	I	J	K
1	Mixture	Target	Amount	Content	Al	As	Ca	Co	Cu	Fe	Ni
2	Species	Element	kg	wt-%	wt-%	wt-%	wt-%	wt-%	wt-%	wt-%	wt-%
3	Target =>			100.00	3.18	0.61	2.61	0.32	14.03	34.27	0.82
4	Result =>		968	100.00	3.18	0.61	2.61	0.32	14.03	34.27	0.82
5	CuFeS2	Cu	392	40.52					14.03	12.33	
6	FeS	Fe	246	25.46						16.17	
7	FeS2	S	120	12.38						5.76	
8	Ni2S3	Ni	15	1.50							0.82
9	CoS	Co	5	0.50				0.32			
10	As2S3	As	10	1.00		0.61					
11	ZnS	Zn	19	2.00							
12	CaO	Ca	35	3.65			2.61				
13	Al2O3	Al	58	6.00	3.18						
Last	SiO2	Si	68	7.00							
15											
16											
17											
18											
19											
20											
21											

Raw1 Raw2 Raw3 Mixture

Exit Help Set Last Row Copy Row 4 to 3 Solve Iterate Sel. 10 Iterate All

Fig. 5. Calculation of the mixture composition of three raw materials.

Copy Row 4 to 3

This button will copy all the elemental composition values from row 4 to row 3.

Number of Iterations

The default number of iterations is 10, but it can be changed in the cell left of the **Iterate All** button. The program carries out a maximum of 10 iterations each time **Iterate All** is pressed. You can decrease the number of necessary iterations by giving some preliminary guess values into column D. *In so e cases re i inar uess a ues are needed to e t e iteration routine to ind t e correct ans er.*

Other Properties

The same type of formatting properties as in other HSC modules are available, such as **Format Number**, **Insert Row**, **Edit Copy**, etc.

The user can also save the workbook for later use by selecting **File Save** and read it back with the **File Open** selection. It is recommended to save the files quite often with different names such as Feed1, Feed2, etc. in order to recover the original settings in case of mistakes. The files can also be saved and opened using Excel 5 format.

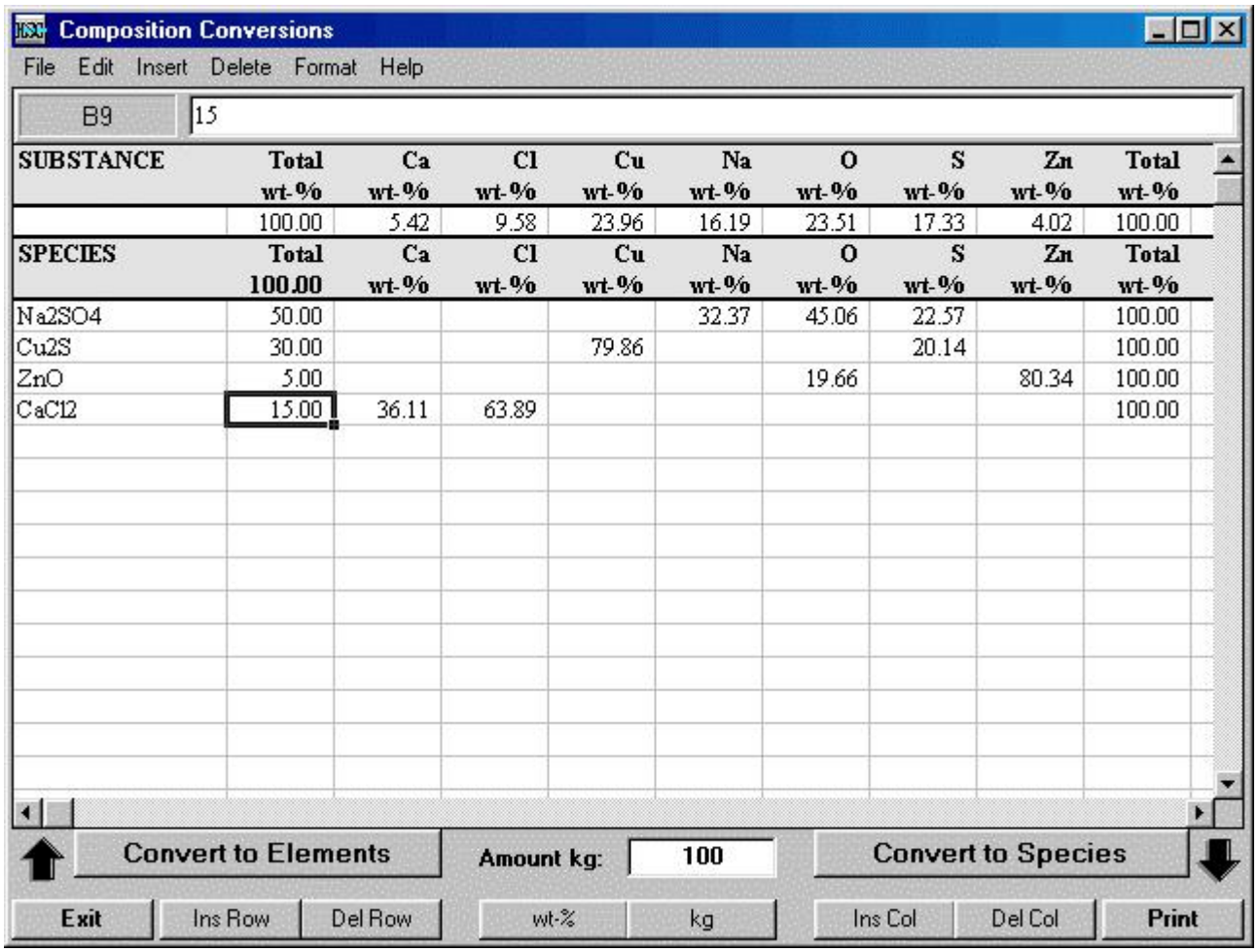
23. COMPOSITION CONVERSIONS

The Composition Conversion module is a simplified version of the Mineralogy iteration module. It is included in HSC Chemistry because the Composition Conversion module easily gives the compositions and amounts of the species in wt- and kg units.

The user may type the names of the species into the first column and the compositions into the second column. You can use also other species than those in the HSC database, however, you must use HSC formula syntax. The module automatically calculates the elemental compositions of the species and the total composition of the mixture by pressing **Convert to Elements**. The reverse conversion is made by pressing **Convert to Species**.

The Composition Conversion is made using the same program routines, which are used in the Mineralogy routine. Therefore the limitations are also the same.

An example is shown in Fig. 1. The same results can be obtained with the Mineralogy module, see Fig.1. in Chapter *22. inera o Iterations.*



SUBSTANCE	Total wt-%	Ca wt-%	Cl wt-%	Cu wt-%	Na wt-%	O wt-%	S wt-%	Zn wt-%	Total wt-%
	100.00	5.42	9.58	23.96	16.19	23.51	17.33	4.02	100.00
SPECIES	**Total 100.00**	**Ca wt-%**	**Cl wt-%**	**Cu wt-%**	**Na wt-%**	**O wt-%**	**S wt-%**	**Zn wt-%**	**Total wt-%**
Na2SO4	50.00				32.37	45.06	22.57		100.00
Cu2S	30.00			79.86			20.14		100.00
ZnO	5.00					19.66		80.34	100.00
CaCl2	15.00	36.11	63.89						100.00

Fig. 1. Composition conversions.

24. ELEMENTS MODULE

The basic chemical and physical properties of the elements have a decisive effect on the thermochemical properties of compounds. For example, the electronegativity values of the elements have a strong effect on the chemical bonds between the elements in all chemical compounds. Therefore the periodic system of elements sets the base for thermochemistry.

The Elements module offers an element database in spreadsheet format with some 56 different properties of the elements. The user may easily add his own data to this table in the same way as in MS Excel applications. This data may be saved for later use by the **File Save** selection. The default name of the workbook is Element4.ele.

Diagram enables the user to draw illustrative diagrams on the basis of the selected property row. Density row 7 has been selected in the example of Fig. 1 and the diagram, shown in Fig. 2, may be drawn by pressing **Diagram**.

The diagram shows at a glance the greatest and smallest values in the periodic system. The exact number values behind the spheres may be shown by double clicking the element square or label in the diagram. The diameter of the sphere shows the magnitude of the value compared to the maximum value. The maximum value creates a sphere, which fits exactly to the element box in Fig. 2.

The **Fix Left 2 Columns** selection, Fig. 1, fixes the two left columns. This makes it possible to see the property headings and units for all the elements, when scrolling the element sheet.

The normal copy and paste properties as well as format and printing functions are available as in other HSC modules. The workbook form may be resized by dragging the form boundaries using the mouse or from the icons at the top right corner of the form.

Elements C:\HSC5\DATABASE\Element4.ELE

File Edit Insert Delete Format Help

C7 0.0899

	Property	Units	H	He	Li	Be
1	Atomic Number		1	2	3	4
2	Symbol		H	He	Li	Be
3	Name		Hydrogen	Helium	Lithium	Beryllium
4	Atomic Weight	g/mol	1.0079	4.0026	6.9410	9.0122
5	Oxidation States, Most Stable		1	-	1	2
6	Oxidation States		1	-	1	2
7	Density	g/ml	0.0899	0.1787	0.53	1.85
8	Electron Configuration		1s1	1s2	1s22s1	1s22s2
9	Melting Point	K	14.025	0.95	453.7	1560
10	Melting Point Pressure	atm	1	26	1	1
11	Boiling Point	K	20.268	4.215	1615	2745
12	Electronegativity		2.2	-	0.98	1.57
13	Heat of Vaporization	kJ/mol	0.44936	0.0845	145.92	292.4
14	Heat of Fusion	kJ/mol	0.05868	-	3	12.2
15	Electrical Conductivity	E6/(ohm*c	-	-	0.108	0.313
16	Thermal Conductivity	W/(cm*K)	0.001815	0.00152	0.847	2
17	Specific Heat Capacity	J/(g*K)	14.304	5.193	3.6	1.82
18	First Ionization Potential	V	13.598	24.587	5.392	9.322
19	Atomic Volume	ml/mol	14.4	-	13.1	5
20	Atomic Radius	Å	0.79	0.49	2.05	1.4
21	Covalent Radius	Å	0.32	0.93	1.23	0.9
22	Crystal Structure		hexagonal	hexagonal	ody centered	hexagonal
23	Acid-Base Properties		amphoteric		basic	amphoteric

Exit ☑ Fix Left 2 Columns Diagram

Fig. 1. The Elements module contains several basic properties of the elements. The selected property may be illustrated in graphical format by pressing **Diagram**.

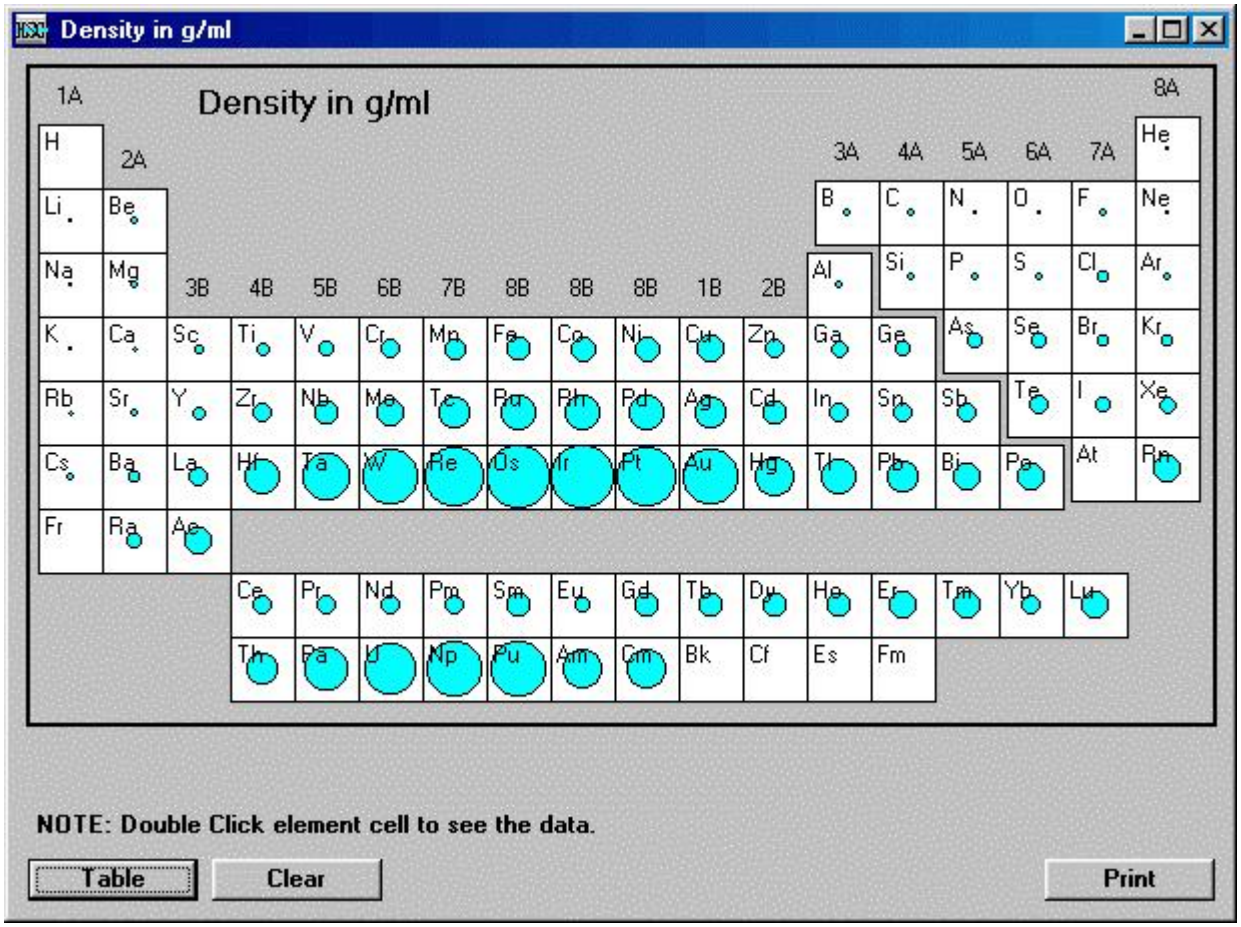


Fig. 2. The properties of the elements may be illustrated in graphical format. The values of the properties may be shown by double clicking the element.

25. WATER

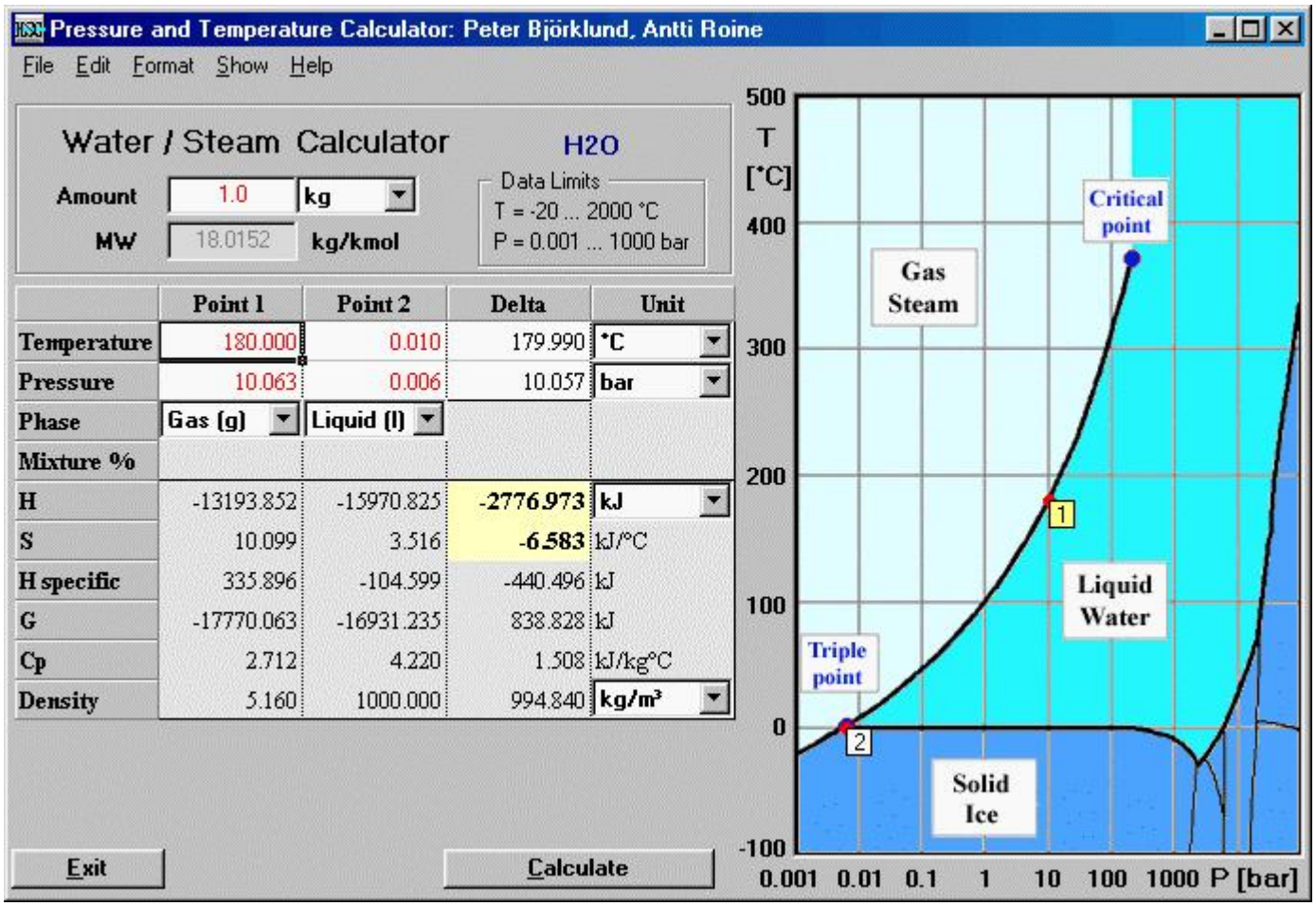


Figure 1 *ressure e erature ca cu ator or ater.*

The Pressure and Temperature calculator enables a complete thermodynamic description for a species, by allowing the user to specify not only the temperature, but also the pressure (partial). This calculator is currently only available for water, since the properties of steam in particular, deviate significantly from those of the ideal gas, i.e. the heat capacity is purely a temperature-dependent function. In letting the user specify water steam pressure, cases where pressure is of extreme importance can easily be calculated.

This calculator is a very useful replacement for **steam table books** and **Mollier diagrams**. By directly typing the pressure and temperature of the process points, or by simply clicking on the diagram, the process enthalpy and entropy are calculated along with several other useful thermodynamic data. The module is also available through the Heat and Material Balances module (Chapter . *eat and ateria a ance*), where the pressure correction may be inserted into the worksheet as a cell formula.

25.1 Basic Calculation Procedure

The calculator lets the user specify two *rocess oints* point 1 being the starting point and point 2 the end point. The calculator then calculates the *abso ute a ues* for the two points and then the *di erence* between them. The absolute values are mostly useful for density and heat capacity data, whereas the difference or delta values are useful for enthalpy and entropy data. A line between the two points may be drawn by selecting *o ine* from the menu. However, this line *does not necessari re resent t e actua rocess at* , instead it makes the visualization of the two points easier. There are two basic ways, which may also be combined, of specifying the process points:

Specifying points using the mouse

1. Specify the appropriate units from the comboboxes and the amount (kmol or kg) in the textbox.

2. Activate one of the points by clicking on the appropriate box in the diagram. A yellow box indicates the active point and a white box the inactive point.

3. Click on a position in the diagram and the selected point will move to that position and the data will automatically be recalculated. Note that if a *saturated state* is selected, the point will jump to the appropriate saturated curve if possible. It is also possible to use the drag-and-drop technique to move the selected point.

4. Repeat steps 2 and 3 for the other point.

5. If a point is on a saturated curve, the user may specify the Mixture , i.e. the percentage of the *irst* of the two phases in the mixture shown in the combobox on row 3 of the worksheet. The default value is 50 .

Specifying points manually

1. Specify the appropriate units from the comboboxes and the amount (kmol or kg) in the textbox.

2. Specify pressures and temperatures for the two points by simply typing them into the cells on columns 1 and 2. Note that if a *saturated state* is selected, the temperature or pressure will automatically be calculated. The values that are automatically calculated are indicated in a black font.

3. If a point is on a saturated curve, the user has to specify the Mixture , i.e. the percentage of the *irst* of the two phases in the mixture given in the combobox on row 3. The default value is 50 .

4. If a point is on a saturated curve, the user may specify the Mixture , i.e. the percentage of the *irst* of the two phases in the mixture shown in the combobox on row 3 of the worksheet. The default value is 50 .

Explanation of the p,T-diagram

The p,T-diagram to the right of the window contains a few labels. These are explained in the following points:

1. Triple Point

The triple point refers to the point where all three phases of water may exist simultaneously. This point is at T = 0.01 C and p = 0.0061 bar. Most steam tables use this as the reference point, i.e. the absolute enthalpy and absolute entropy are set to zero. By selecting *dit oint 2 ri e oint* from the menu, the second process point will automatically be set to the triple point, which is also the default setting. This means that

the enthalpy and entropy differences will have the same values as those found in most steam tables if the phase is set to *i uid* at the triple point.

2. Critical Point

When the temperature rises above the critical point, it is no longer possible to clearly distinguish between the liquid and the gaseous phase. Such a condition is referred to as *su ercritica* . The critical point for water is at T = 373.946 C and p = 220.64 bar. It is important to know that above this point the program still specifies the phase of the point, although there are no longer any actual phase transitions between the phases.

3. Saturated Curves

There are three saturated curves in the diagram. These are *as i uid*, *as so id* and *i uid so id*. A point located on any one of these curves indicates that the two phases are in equilibrium. The three curves join at the *tri e oint*, which is where all three phases can exist simultaneously. The user may force a point onto the saturated curve by selecting either **Sat. (g,l)**, **Sat. (g,s)** or **Sat. (l,s)** from one of the phase comboboxes on row 3.

4. Solid Ice

A stability area consisting of several solid ice phases, with different crystal structures, of which some are shown on the diagram. Data is not, however, available for the high pressure solid phases.

Calculation worksheet

The calculation worksheet is to the left of the window. The first four rows are input rows and the last six rows show the results. The input rows are explained in the following points:

1. Temperature

The temperature unit may be either in **C** or in **K**, depending on the temperature unit combobox. The temperature is automatically calculatad when the **Sat. (l,s)** state is selected.

2. Pressure

The pressure unit may be either in **bar** or in **MPa**, depending on the pressure unit combobox. The pressure is automatically calculatad when the **Sat. (g,l)** or the **Sat. (g,s)** state is selected.

3. Phase

There are three different pure phases available for water: **Solid (s)**, **Liquid (l)** and **Gas (g)**. These three phases may be combined on the *saturated cur es* and they are specified as: **Sat. (g,l)**, **Sat. (g,s)** and **Sat. (l,s)**. At the triple point a mixture of all of these is possible, however, only a mixture of two is possible in this module. When a *ure ase* is selected, the actual phase is automatically selected according to the user input (manually or with the mouse). When a *saturated state* is selected, the temperature or pressure is automatically calculated, which is then indicated in a black font. For the gas liquid and gas solid mixtures the pressure is automatically calculated and for the liquid solid mixture the temperature is automatically calculated. Note that when moving outside the limits of the saturation curve, the phase will automatically change into the corresponding pure phase of the specified point.

4. Mixture

It is possible here to enter the mixture percentage of the saturated state. This is the same as the *dr ness ercenta e* of steam when the point is on the saturated gas liquid curve. The percentage always refers to the amount of the first phase in the total mixture, e.g. the gas percentage in a gas liquid mixture. This is set to 50 by default and only visible when a saturated state is specified.

The results of the calculation are shown in the same table below the input. The data calculated includes:

1. Enthalpy (H) and Entropy (S)
The enthalpies and entropies for the two process points are calculated using the reference point T = 25 C and p = 1 bar. This differs from what is normally found in steam tables, where the reference point is T = 0.01 C and p = 0.0061 bar (triple point for water). This means that only the *di erences in ent a and entro are o i ortance*, since they are independent of the choice of reference points. Point 2 is therefore *b de au t set to t e tri e oint*, which means that the enthalpy and entropy differences, indicated by a yellow background, give the values normally found in steam tables.

2. Specific Enthalpy (H specific)
The specific enthalpies are the enthalpies when the phase transformations are ignored. In other words the enthalpy released gained when water is cooled heated to 25 C at constant pressure. Therefore the specific enthalpy is zero at 25 C.

3. Gibbs Energy (G)
These cells show the Gibbs Energy for the two points.

4. Heat Capacity (Cp)
These cells show the specific heat capacity at constant pressure for the two points.

5. Density
These cells give the densities for the two points. The densities are interpolated or extrapolated from the Excel file H2O.XLS located in the . HSC5 PTCalc directory. Please do not modify this file.

<u>Other important terms</u>

1. Isentropic process
If the entropy is constant through a process, i.e. the entropy difference is zero, the process is called *isentro ic*. An isentropic process is an ideal process and real processes are often compared to the corresponding isentropic process.

2. Isentropic efficiency
An isentropic process generates no entropy and may therefore be considered an ideal process. It is useful to compare real processes to that of the isentropic through the isentropic efficiency. The isentropic efficiency for a *co ressor* or *u* is defined as

$$\eta_{s,c} = \frac{\Delta \quad s}{\Delta}, \qquad 1$$

where Δh is the *rea ent a di erence* and Δh_s is the *isentro ic ent a di erence*. The isentropic efficiency for a *turbine* is defined as

$$\eta_{s,t} = \frac{\Delta}{\Delta \quad s}. \qquad 2$$

An isentropic process is always *adiabatic*, however, an adiabatic process is not necessarily isentropic.

25.2 Calculation examples

25.2.1 Ice melting at high pressure

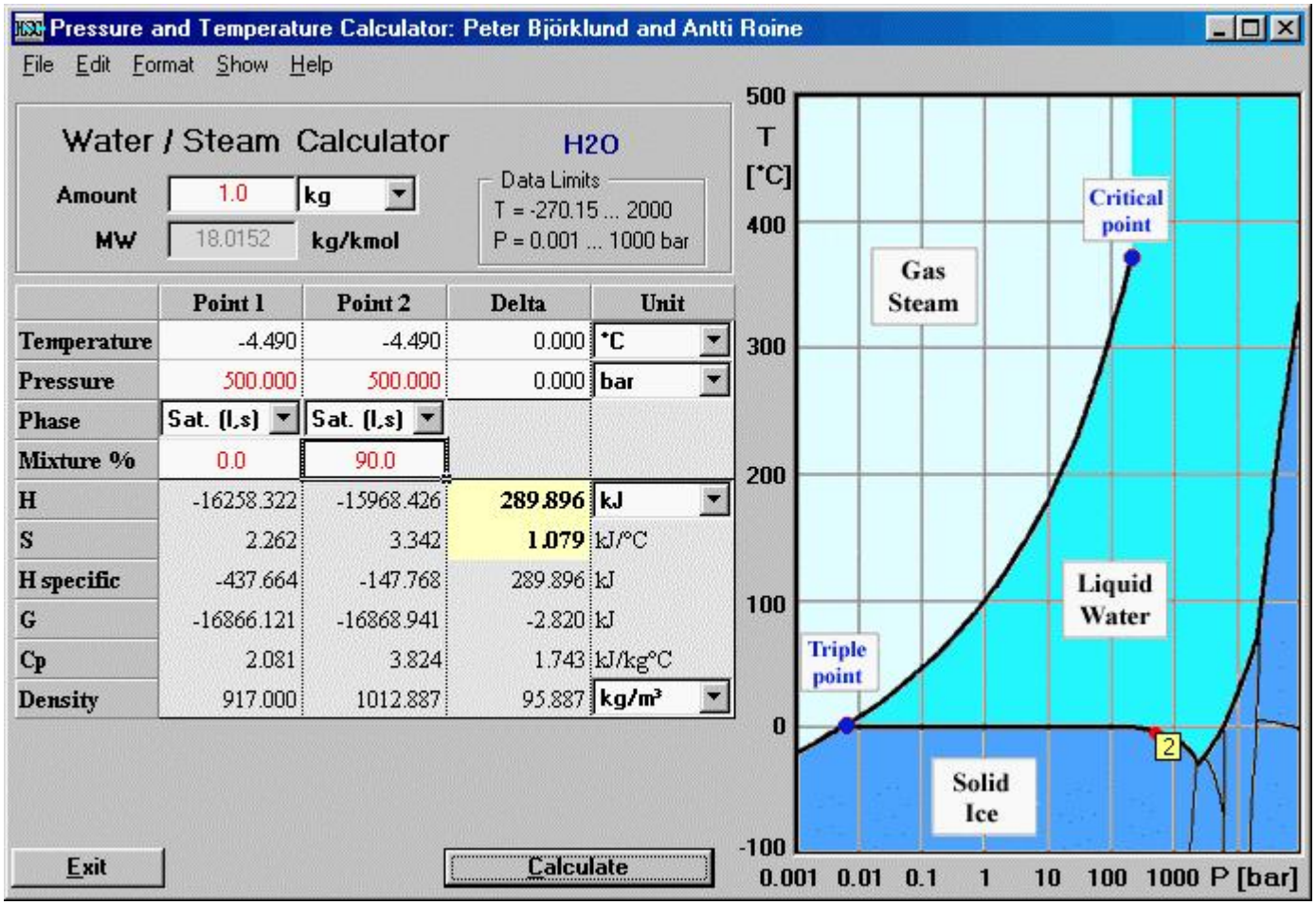


Figure 2 *e tin o ice at a ressure o bar.*

The example in Figure 2 shows the enthalpy and entropy change of 1 kg solid ice melting at a constant pressure of 500 bar, until 90 of the *tota* mixture is liquid water. The enthalpy difference is 290 k and the process therefore endothermic. The entropy difference is 1.079 k C and the process therefore generates entropy. The melting point of ice at 500 bar is automatically calculated, since the point is on the saturated liquid solid curve, and it is roughly –4.5 C. This pressure is achieved, for example, when pressing a sharp object against an icy surface, which then melts due to the decreased melting point temperature.

25.2.2 Evaporation process in a heat recovery boiler

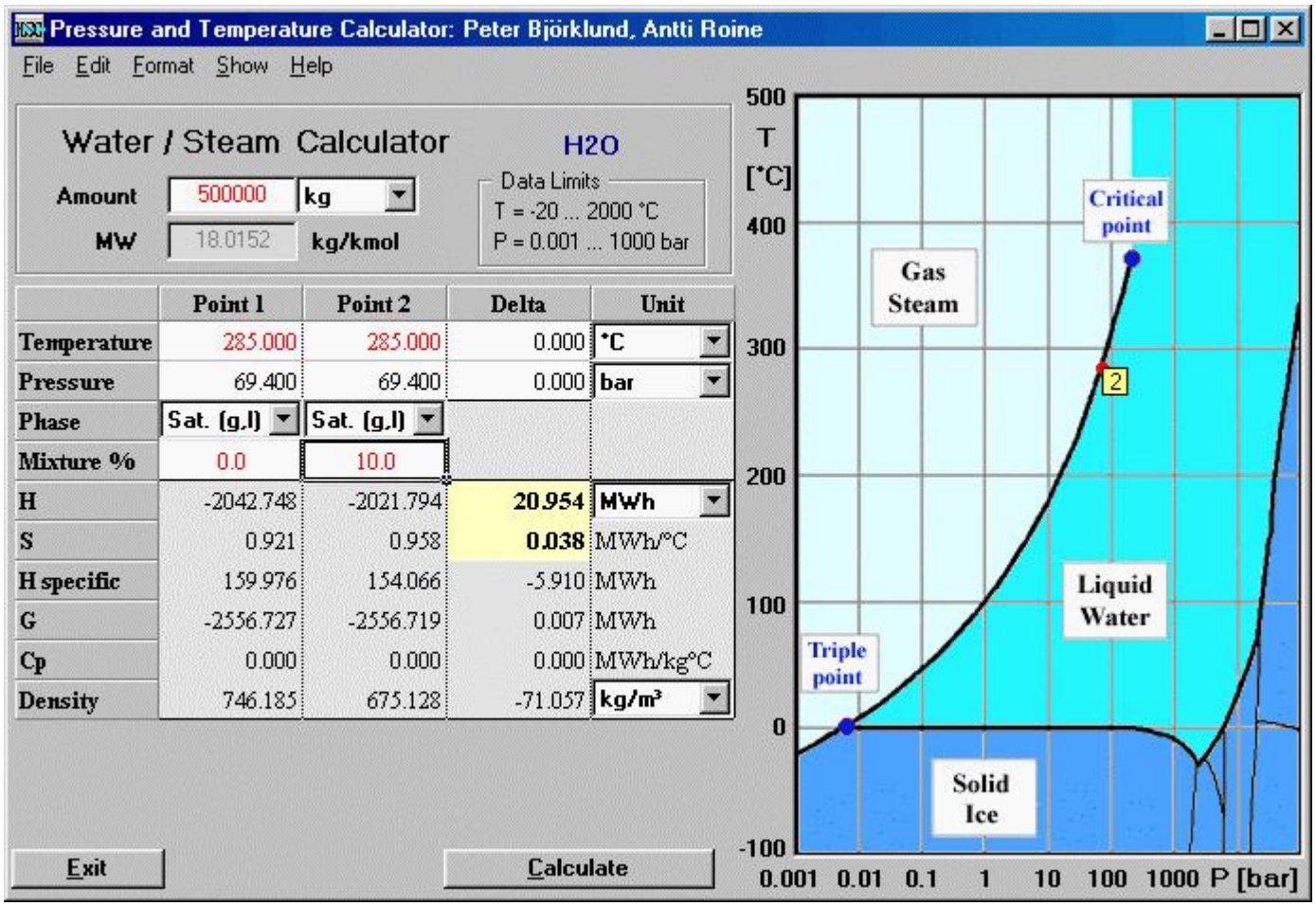


Figure 3 *a oration rocess.*

The example in Figure 3 shows the evaporation process in a heat recovery boiler, when the mass flow is 500 t h (Amount: 500000 kg, Unit: MWh). The temperature is 285 C and the pressures are automatically calculated, since the saturated gas liquid state is selected. The transferred heat is 21 MW, when 10 of the *tota* water flow evaporates. This is equivalent to a water steam ratio of 90 10 = 9. The entropy generation of 0.038 MW C indicates that the process is not isentropic.

25.2.3 Steam turbine process

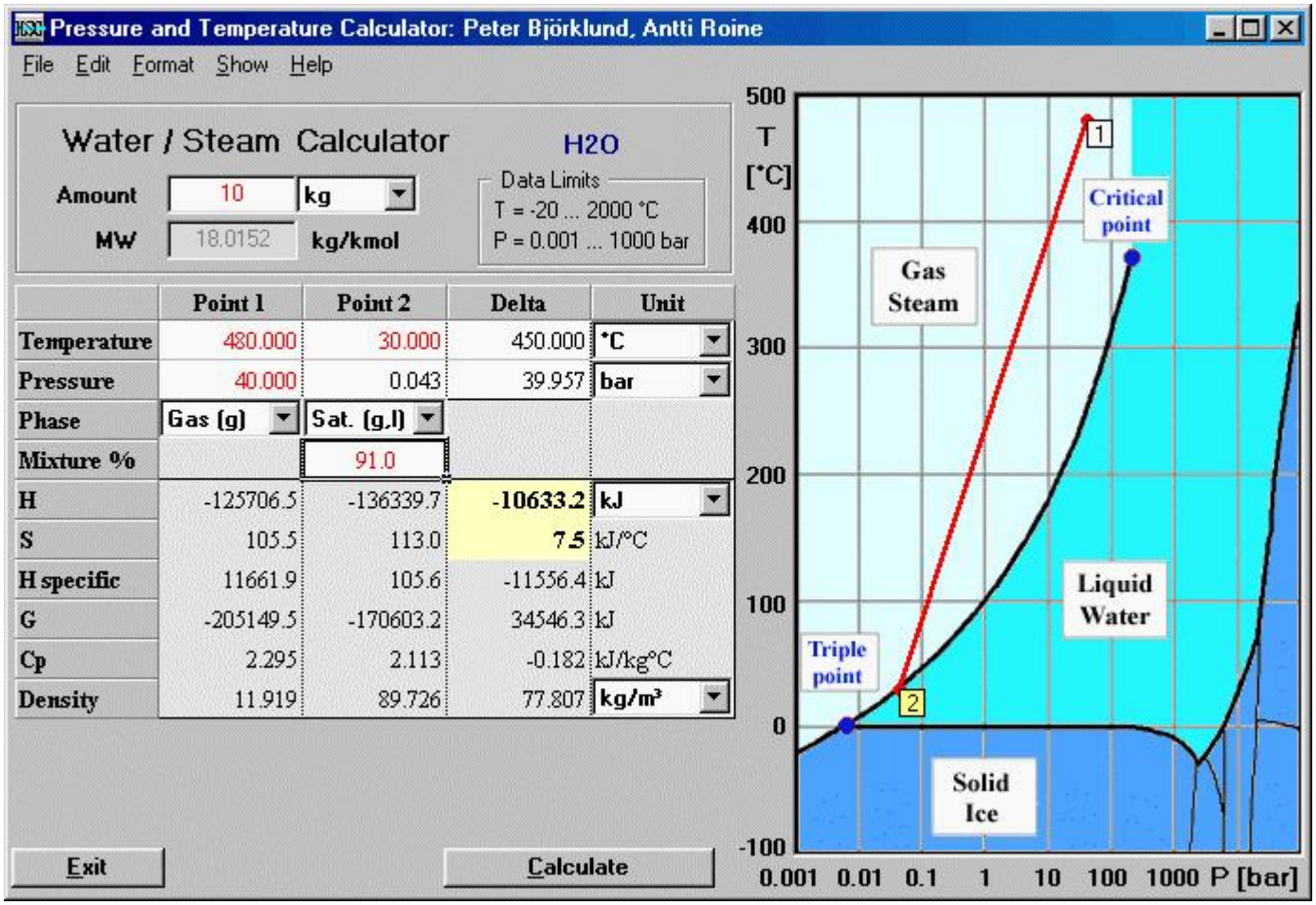


Figure 4 *tea turbine rocess.*

A simple steam turbine process is shown in Figure 4. The calculation shows that the net enthalpy for a mass flow of 10 kg s is –10633 kW and thus exothermic, i.e. the enthalpy is released in the form of work on the shaft. The entropy generation is 7.5 kW C and the process is therefore not isentropic. By decreasing the Mixture (in this case 81.7) the process may be compared with the ideal isentropic process for which there is no entropy generation. The enthalpy released in the isentropic process is –12903 kW and the isentropic efficiency is therefore, according to equation 2, $\eta_{s,t}$ = -10633 kW -12903 kW λ 0.82.

25.3 Detailed Description

25.3.1 Pressure correction in the database

The pressure-corrected calculations are based on new pressure-specific species in the database. They are of the form ***S***(bar), where ***S*** denotes the species, the pressure (partial) in bars and the phase. The phase is only specified for gaseous species. The only currently available species is H_2O (water), and the pressure-corrected species are found in the database as H2O(0.01bar), H2O(0.01barg), H2O(100bar), H2O(100barg), etc. Note that if the phase is not specified, it may be either solid or liquid depending on the temperature. For *su ercritica stea* , that is for T µ 373.946 C, a gaseous phase is used for p 220.64 bar and a liquid phase for p µ 220.64 bar, although the two phases are impossible to separate in reality.

Table 1 shows the pressure-corrected water species currently found in the HSC database.

Pressure bar	Solid liquid species (ice water)	Gaseous species (steam)
0.01	H2O(0.01bar)	H2O(0.01 barg)
0.05	H2O(0.05bar)	H2O(0.05 barg)
0.1	H2O(0.1bar)	H2O(0.1 barg)
0.5	H2O(0.5bar)	H2O(0.5 barg)
1	H2O(1bar)	H2O(1 barg)
5	H2O(5bar)	H2O(5 barg)
10	H2O(10bar)	H2O(10 barg)
20	H2O(20bar)	H2O(20barg)
30	H2O(30bar)	H2O(30barg)
40	H2O(40bar)	H2O(40barg)
50	H2O(50bar)	H2O(50barg)
60	H2O(60bar)	H2O(60barg)
70	H2O(70bar)	H2O(70barg)
80	H2O(80bar)	H2O(80barg)
90	H2O(90bar)	H2O(90barg)
100	H2O(100bar)	H2O(100barg)
200	H2O(200bar)	H2O(200barg)
300	H2O(300bar)	
400	H2O(400bar)	
500	H2O(500bar)	
600	H2O(600bar)	
700	H2O(700bar)	
800	H2O(800bar)	
900	H2O(900bar)	
1000	H2O(1000bar)	

Supercritical pressures

Table 1 *ressure corrected s ecies current a ai ab e in t e database.*

Since water is in a liquid form at the reference temperature of 25 C for pressures higher than 0.032 bar, the Cp functions for steam follow the *saturated stea cur e* below the boiling point. This means that *t e ressure is not e t constant be o t is oint* and thus the pressure value in the species name, i.e. **X** in H2O(**X**barg), is no longer valid for these temperatures. This may be seen from Figure 5, where the Cp functions of steam at different pressures are shown. When the temperature drops below the boiling point the Cp functions follow the saturation curve, where the partial pressure also reduces with the temperature. This also means that the *tota ent a* and *entro* curves below the boiling point will not join as expected and therefore these curves are *co arab e it eac ot er on or a ues abo e or e ua to t e boi in oint*. This is, however, not an issue when studying only one

pressure-corrected species at a time since the enthalpy entropy differences are then still valid. Naturally this is never a problem in the Pressure and Temperature calculator, since it automatically chooses the liquid phase when the temperature drops below the boiling point for a constant pressure.

For the solid liquid phases, i.e. H2O(Xbar), this reference point does not cause any problems, since at least one of the two phases (liquid and or solid) exist below 25 C and at pressure X. They can therefore easily be extrapolated up to 25 C when necessary. Extrapolation above the boiling sublimation points at different pressures are shown as dotted curves in diagrams, which also means that the liquid solid phase does not exist at these temperatures.

Figure 5 also shows that the ideal gas approximation, indicated by the label H2O(g), is generally more accurate for low pressures and high temperatures. The ideal gas curve can be seen below the constant pressure curves. The rule of thumb is that the accuracy of the ideal gas approximation increases the further away you move from the critical point.

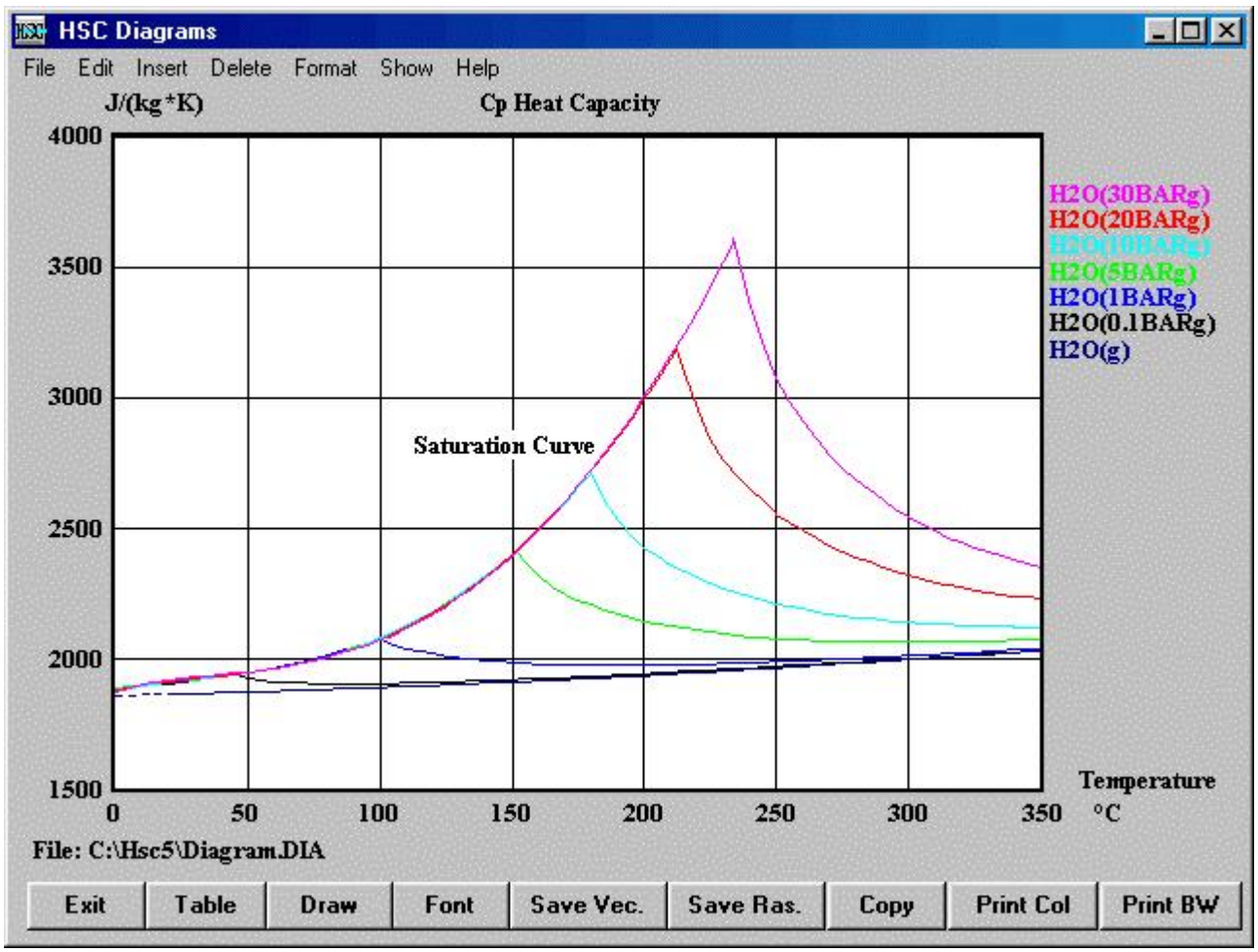


Figure 5 *unctions or stea at di erent ressures.*

25.3.2 Basic theory

In order to calculate the enthalpy and entropy at different pressures, slight modifications have to be made to the enthalpy of formation and standard entropy at 25 C, i.e. the H_f - term of equations 1 and 3 in Chapter *8. Introduction*. Most steam tables use the *tri e oint* of water (T = 0.01 C, p = 0.0061 bar), instead of the standard reference point used in HSC (T = 25 C, p = 1 bar), therefore the *abso ute* enthalpies and entropies will be different from those found in steam tables. However, since point 2 is by default set to the triple point, the enthalpy and entropy differences (cells C5 and C6) are the same as the absolute values found in steam tables and diagrams. This is achieved by selecting *dit oint 2 ri e oint* from the menu and choosing the *i uid* phase.

The pressure corrected enthalpy at temperature T and pressure p is calculated as

$$, = 298.15 , + \int_{298.15} (,)d + \sum_{tr} , \qquad 3$$

where H'_f (298.15K, p) is the modified enthalpy of formation at pressure p and H_{tr} is the enthalpy of a phase transformation. The entropy at pressure p may be calculated in a similar manner as

$$, = {}_0 298.15 , + \int_{298.15} \frac{(,)}{}d + \sum \frac{tr}{tr} , \qquad 4$$

where S'_0 (298.15K, p) is the modified standard entropy at pressure p and H_{tr} is the enthalpy of a phase transformation at temperature T_{tr}.

The Cp function still utilizes the Kelley equation, but the coefficients are now pressure-dependent according to

$$(,) = ( ) + ( )\cdot 10^{-3} + ( )\cdot 10^{5}\cdot {}^{-2} + D( )\cdot 10^{-6}\cdot {}^{2}, \qquad 5$$

where A(p), B(p), C(p) and D(p) are the coefficients fitted at different pressures p. See Table 1 for a list of the current pressures available.

The temperature or pressure of a saturated curve is calculated through either one of the equations 6-8. The pressure for a saturated *as i uid i ture* is

$$= 0.1\cdot e \quad (11.78(- 372.79) (- 43.15)), \qquad 6$$

where T is the temperature in K and p the pressure in MPa. The pressure for a saturated *as so id i ture* is

$$= 10^{10.5380997 - 2663.91 (T \quad 0.01)} \quad 10000, \qquad 7$$

where T is the temperature in K and p the pressure in MPa. The temperature for a saturated *i uid so id i ture* is

$$= -0.009 \quad + 273.16, \qquad 8$$

where T is the temperature in K and p the pressure in MPa. These equations correspond to the saturated curves in the p,T-diagram and are utilized in the module whenever a saturated state is selected.

In order to calculate the influence of pressure on the enthalpy and entropy below the freezing point, a pressure correction term is used. The correction term is

$$\Delta \quad _{=const} = \left(1 - \quad \alpha \quad _{,ice}\right)\nu_{ice}\left(\quad - \quad _{0}\right), \qquad 9$$

where T_f is the temperature at the freezing point, p_f is the pressure at the freezing point, $\alpha \quad _{,ice}$ is the coefficient of thermal expansion and ν_{ice} is the specific volume.

25.4 Limitations

- The current pressure range is –200 C to 2000 C and 0.001 bar to 1000 bar.
- Accuracy in c_p-values and density values decreases close to the critical point.
- Accuracy in saturated liquid gas pressure decreases close to the critical point.
- Uncertainties in c_p-values for ice at different pressures.
- The high temperature and pressure region (800 C - 2000 C and 100 bar - 1000 bar) is extrapolated.
- The low pressure region (0.001 bar - 0.01 bar) is extrapolated.

26. UNITS MODULE

Traditionally, several types of energy, temperature, mass and volume units have been used in thermochemical calculations. Therefore, some inconvenient conversions are needed to compare the results from different sources. The new Units Conversion module is an easy tool for fast unit conversions in thermochemistry as well as in other engineering fields. The specifications of this module can be summarized as follows.

1. Some 90 different quantities and 444 units are available. The user can easily add own units and coefficients into the conversion calculator database.
2. The Units Module also offers data sheets for chemical constants, particle mesh sizes, air humidity and water pressure tables. These tables can be modified by the user according to personal requirements.

Units Conversions (Convert Sheet)

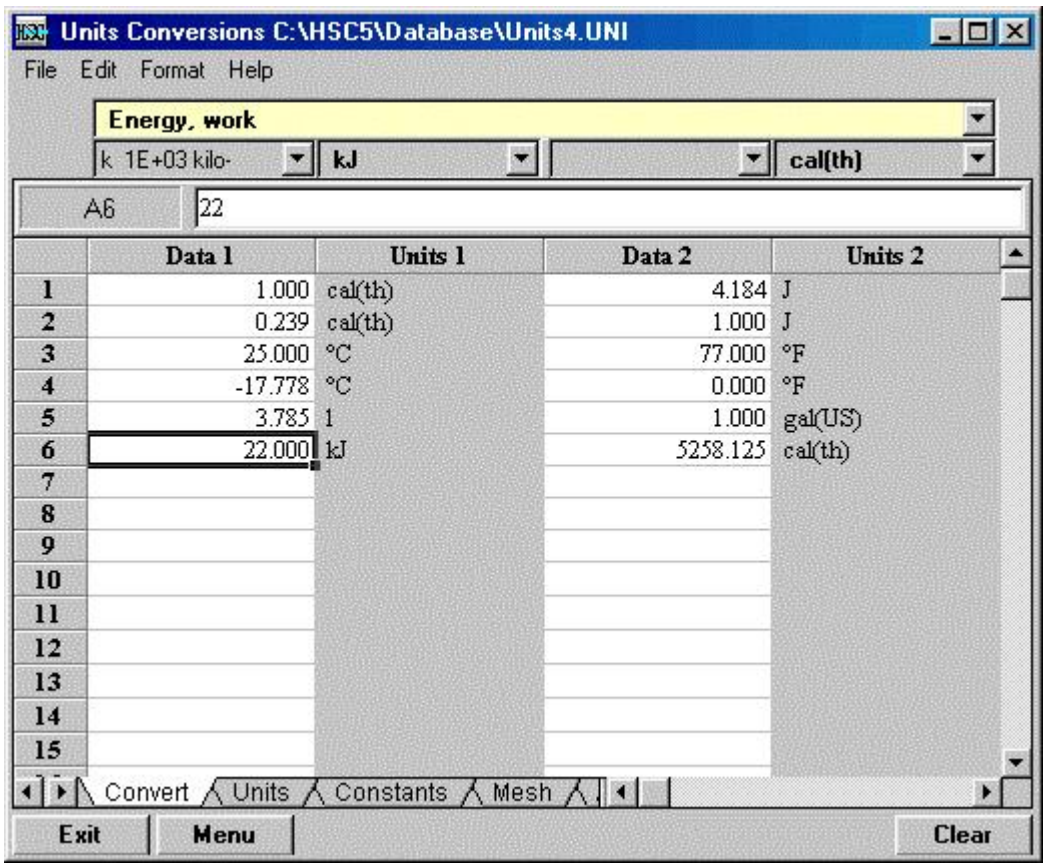


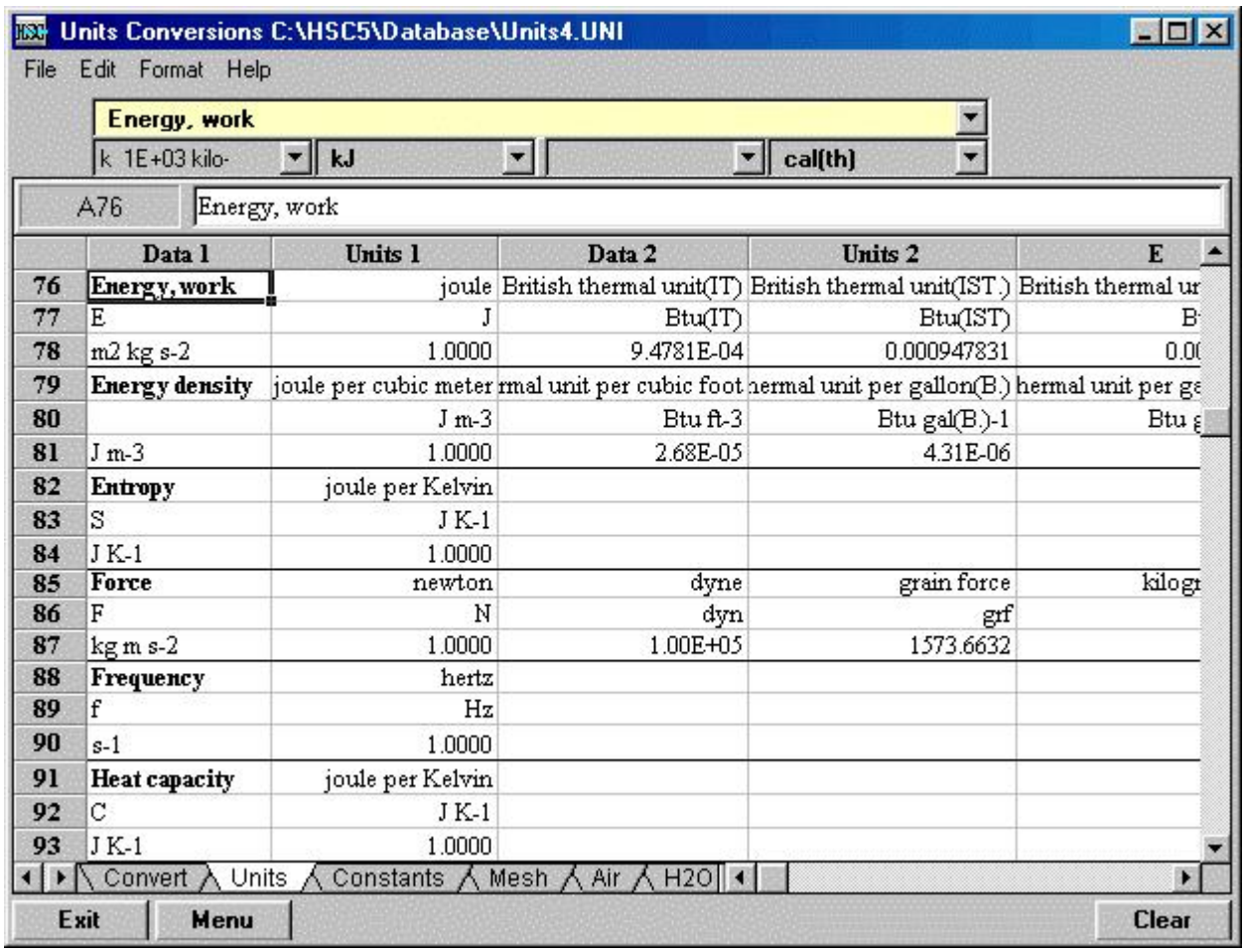
Fig. 1. Units Conversion module.

The user interface of the Units module is shown in Fig. 1. All the data is given in the workbook, which consists of six sheets. The first Convert sheet works as a simple units conversion calculator, which is used in the following manner:

1. Select the quantity you are interested in, for example, **Energy**.
2. Select the unit and prefix to be used in columns 1 and 2.
3. Select the unit and prefix to be used in columns 3 and 4.

4. Type the values into column 1 or 3. This will automatically show the converted value using the selected units. You can change the quantities, units and prefixes whenever you want, as seen in Fig. 1.

Units Database (Units Sheet)



	Data 1	Units 1	Data 2	Units 2	E
76	**Energy, work**	joule	British thermal unit(IT)	British thermal unit(IST.)	British thermal ur
77	E	J	Btu(IT)	Btu(IST)	B
78	m2 kg s-2	1.0000	9.4781E-04	0.000947831	0.0
79	**Energy density**	joule per cubic meter	rmal unit per cubic foot	hermal unit per gallon(B.)	hermal unit per ga
80		J m-3	Btu ft-3	Btu gal(B.)-1	Btu g
81	J m-3	1.0000	2.68E-05	4.31E-06	
82	**Entropy**	joule per Kelvin			
83	S	J K-1			
84	J K-1	1.0000			
85	**Force**	newton	dyne	grain force	kilogr
86	F	N	dyn	grf	
87	kg m s-2	1.0000	1.00E+05	1573.6632	
88	**Frequency**	hertz			
89	f	Hz			
90	s-1	1.0000			
91	**Heat capacity**	joule per Kelvin			
92	C	J K-1			
93	J K-1	1.0000			

Fig. 2. Database sheet for unit coefficients.

The unit calculator on the Convert sheet reads all the quantities and unit coefficients from the Units sheet, see Fig. 2. Three rows are reserved for one quantity, and up to 255 units in the columns can be used for one quantity. The name of the quantity is given in the first column, the quantity first row gives the name of the unit, the second one the abbreviation and the third one the conversion coefficient.

The user may easily add own quantities and units to this sheet. However, remember to save the worksheet if you want to use this new data later on.

Other Sheets

The Units workbook also contains other sheets:

1. **Constants sheet**: Chemical and physical constants.
2. **Mesh sheet**: Particle sizes in mesh and mm units.
3. **Air sheet**: Air composition and humidity tables.
4. **H2O sheet**: Water vapor pressure tables.

The user may also modify these sheets as well as add new sheets. The workbook must be saved with the **File Save** selection in order to use the new data later on.

Nearly all the same format, edit and printing properties, as well as resizing of the form, are available in the Units module.

27. Excel Add-In Functions

27.1 Getting started

With HSC 5.0 Add-In Functions it is possible to use the HSC 5.0 database directly under MS Excel 2000 and in that way carry out several thermochemical calculations. In order to use these functions in Excel they must, however, first be activated. Three stages may be needed to activate HSC functions in Excel. The number of stages needed depends on the computer settings and Windows and Excel versions.

Activation Stage 1

1. Open Excel 2000 (NOTE: *dd Ins do not or under ear ier ce ersions*)
2. Select **Tools, Add-Ins...** from the menu.
3. Select **Browse** and locate HSC5.xla from your **HSC5 AddIns** folder.
4. Select **HSC 5.0 Functions** and press **OK** , see Figure 1. It may be necessary to restart Excel in order for the add-in functions to work.

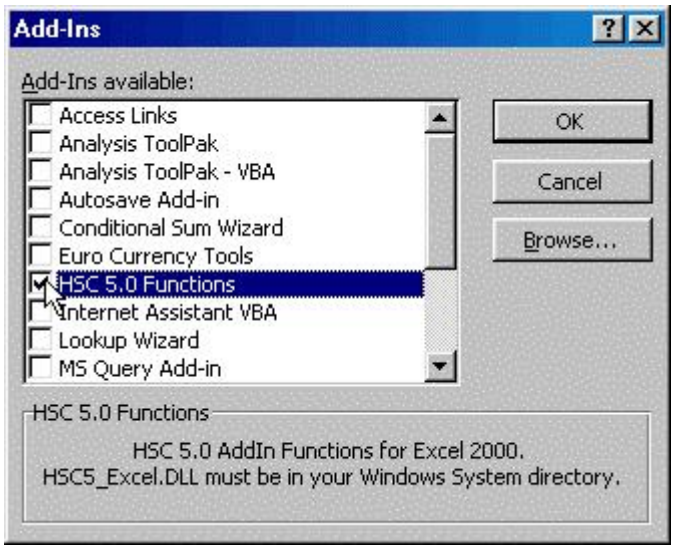


Figure 1 *ddin re o in . unctions under ce .*

Activation Stage 2

If the installation is unsuccessful, the following steps may help:

1. Start the VBA Editor by pressing Alt F11.
   (or select Tools, Macro, Visual Basic Editor, ...)
2. Select **Tools, References** from the menu.
3. Select **Browse** and locate **HSC5 Excel.dll** from your Windows System directory (for example C: Windows System HSC5 Excel.dll). It may be necessary to restart Excel in order for the add-in functions to work.
4. See also stage 3 in Chapter 27.2 if needed.

The HSC installation routine automatically takes care of the DLL registration.

27.2 Opening and Moving Files that use HSC 5.0 Functions

Once installed, as above, you are ready to start using the add-in functions. Sometimes it may be essential to change the links of a worksheet in order for Excel to find the HSC5.xla file. This may be the case if opening a file that uses HSC 5.0 functions for the first time or when moving these files from one computer to another. These steps should then be carried out:

Activation Stage 3

1. During opening, answer **No** when prompted by Excel to update all linked information (automatic link updates do not work due to some bug in MS Excel).
2. Select **Edit, Links** from the menu.
3. Choose the path containing **HSC5.xla** from the listbox and press **Change Source** .
4. Browse to your **HSC5 AddIns** folder and choose **HSC5.xla**.

Alternatively, it is also possible to first remove **HSC 5.0 Functions** under **Tools, AddIns** , see Figure 1, and then by adding them again, to force an update of the worksheet links. If the cells conatining the functions return a **VALUE** error message, please save the file and restart Excel in order to make the functions work. Try opening the test example AddInSample.xls , where all available functions are demonstrated. To turn the add-in feature off, simply deselect it using the **Tools, Add-Ins...** dialog from the main menu.

27.3 Brief Description of the Functions

The add-in functions are used the same way as functions in general under MS Excel. For example by writing **H(A1 A2)** the enthalpy for the species in cell A1 and at the temperature in cell A2, is returned. To view all existing functions simply select **Insert, Function** from the main menu and then choose **User Defined** from the left listbox. The right listbox will now give show all available HSC functions and their arguments. A complete description of the functions is given in the following table (Table 1).

General Functions

UNITS(T E)	Changes the current units, T= C K and E= Mcal M kWh . Sheet NOT recalculated
BAL(Equation)	Balances given equation.
SPECIES(DBNo, Position)	Returns species in database DBNo and given position.

Species Functions

H(Species T)	Returns the enthalpy (per mol) of the species at T (temperature).
S(Species T)	Returns the entropy (per mol) of the species at T.
CP(Species T)	Returns the heat capacity at constant pressure (per mol) of the species at T.
G(Species T)	Returns the Gibbs energy (per mol) of the species at T.
HKG(Species T)	Returns the enthalpy (per kg) of the species at T.
HNM3 or HCM(Species T)	Returns the enthalpy (per Nm) of the species at T.
HLAT(Species T)	Returns the latent enthalpy (per mol) of the species at T.

Reaction Equation Functions

H(Equation T)	Returns the enthalpy (per mol) of the reaction equation at T.
S(Equation T)	Returns the entropy (per mol) of the reaction equation at T.
CP(Equation T)	Returns the heat capacity difference (per mol) of the reaction equation at T.
G(Equation T)	Returns the Gibbs energy (per mol) of the reaction equation at T.

HKG(Equation T)	Returns the enthalpy (per kg) of the reaction equation at T.
K(Equation T)	Returns the equilibrium constant of the reaction equation at T.

Iteration (reverse) Functions

TATH(Species H)	Returns the temperature of the species with given enthalpy (per mol).
TATS(Species S)	Returns the temperature of the species with given entropy (per mol).
TATCP(Species CP)	Returns the temperature of the species with given heat capacity (per mol).
TATG(Species G)	Returns the temperature of the species with given Gibbs energy (per mol).

Flow Functions

FLOWH(Species Amount T)	Returns the enthalpy of a flow (Species and Amount as ranges) at T.
FLOWS(Species Amount T)	Returns the entropy of a flow (Species and Amount as ranges) at T.
FLOWCP(Species Amount T)	Returns the heat capacity of a flow (Species and Amount as ranges) at T.
FLOWG(Species Amount T)	Returns the Gibbs energy of a flow (Species and Amount as ranges) at T.

Temperature-independent Functions

STRUCT(Species)	Returns the structural formula of the species.
CHNAME(Species)	Returns the chemical name of the species.
CONAME(Species)	Returns the common name of the species.
CAN(Species)	Returns the chemical abstract number of the species.
MW(Species)	Returns the molecular weight of the species.
DE(Species)	Returns the density of the species.
MP(Species)	Returns the melting point of the species.
BP(Species)	Returns the boiling point of the species.
PHASE(Species)	Returns the phase of the species.
RGBCOLOR(Species)	Returns the RGB color of the species.
REF(Species)	Returns the database reference of the species.
REL(Species)	Returns the reliability class of the species.

Percentage Functions

MOLP(Species1 Species2)	Returns the mol- of Species1 in Species2.
WTP(Species1 Species2)	Returns the wt- of Species1 in Species2.

Cp Data Functions

CPFUNCTION(Species)	Returns the complete heat capacity (c_p) polynomial function (as a string) of the given species.
CPA(Species)	Returns the A-coefficient (as a number) of the c_p-function.
CPB(Species)	Returns the B-coefficient (as a number) of the c_p-function.
CPC(Species)	Returns the C-coefficient (as a number) of the c_p-function.
CPD(Species)	Returns the D-coefficient (as a number) of the c_p-function.
TMIN(Species)	Returns the minimum valid temperature of the c_p-function.
TMAX(Species)	Returns the maximum valid temperature of the c_p-function.

Table 1 *Descri tion o a current a ai ab e add in unctions.*

A useful Excel example file is located in the catalogue AddIns in your HSC installation directory. The example, called AddInSample.xls , can be viewed after the add-ins have been made available (described in Chapter 27.1). Figure 2 shows what the example file should look like using MS Excel 2000.

Microsoft Excel - AddInSample.xls

E11 = 100

	A	B	C	D	E	F	
2	HSC Chemistry 5.0 add-in functions in MS Excel 2000						
3		Examples		Red values are argument (input) values.			
5		Functions	Return Values	Arguments			Descrip
6		General	Return Value	Argument 1	Arg. 2	Arg. 3	Descripti
7		UNITS(T;E)	C and Mcal	C	Mcal		Changes
8		BAL(Equation)	2H2(g) + O2(g) = 2H2O(	H2(g)+O2(g)=H2O(g)			Balanced
9		SPECIES(DBNo,Position)	Al(CH3COO)2(+a)	2	200		Species f
10		Species	Return Value	Argument 1	Arg. 2	Arg. 3	Descripti
11		H(Species;T)	-93.357	CO2(g)	100		Enthalpy
12		S(Species;T)	20.766	H2O(l)	100		Entropy (
13		CP(Species;T)	44.245	CH4(a)	100		Heat cap
14		G(Species;T)	-11.294	He(g)	100		Gibbs en
15		HKG(Species;T)	-0.264	FeS	100		Enthalpy
16		HNM3 or HCM(Species;T)	0.023	O2(g)	100		Enthalpy
17		HLAT(Species;T)	0.000	H2O(l)	25		Enthalpy
18		Reaction equation	Return Value	Argument 1	Arg. 2	Arg. 3	Descripti
19		H(Equation;T)	-115.952	2H2(g) + O2(g) = 2H2O(g)	100		Enthalpy
20		S(Equation;T)	-22.299	2H2(g) + O2(g) = 2H2O(g)	100		Entropy c
21		CP(Equation;T)	-4.744	2H2(g) + O2(g) = 2H2O(g)	100		Heat cap
22		G(Equation;T)	-107.631	2H2(g) + O2(g) = 2H2O(g)	100		Gibbs en
23		HKG(Equation;T)	-3.218	2H2(g) + O2(g) = 2H2O(g)	100		Enthalpy
24		K(Equation;T)	1.106E+63	2H2(g) + O2(g) = 2H2O(g)	100		Equilibriu
25		Iteration (reverse)	Return Value	Argument 1	Arg. 2	Arg. 3	Descripti
26		TATH(Species;H)	410.037	CO2(g)	-90		Temparat
27		TATS(Species;S)	430.915	CO2(g)	60		Returns t
28		TATCP(Species;CP)	144.756	CO2(g)	10		Temparat
29		TATG(Species;G)	224.503	CO2(g)	-120		Temparat
30		Flow	Return Value	Argument 1	Arg. 2	Arg. 3	Descripti
31		FLOWH(Species;Amount;T)	0.524	N2(g)	0.78	100	Enthalpy

Sheet1 / Sheet2 / Sheet3

Draw AutoShapes

Ready NUM

Figure 2 *a e inc udin a a ai ab e ce add in unctions ddIn a e. s .*

The functions are all collected in the column Function and their return values under Return value . A red font indicates the input values with a short description of every function shown to the right. This example provides an easy method for testing the functions and also provides practice in learning how to use them.

27.4 More about registering DLL Files

The HSC 5.0 installation routine should take care of all necessary DLL registrations. When selecting deselecting the HSC 5.0 add-in using Excel, HSC5 Excel.dll is automatically registered unregistered. However, it is also possible to register unregister the HSC5 Excel.dll and HSC5.dll (used by the Heat and Material Balances module) files manually. The program to achieve this is called Regsvr32.exe) and registration is completed using the following method:

1. Select **Start, Run...** from the Windows menu.
2. Type **regsvr32 HSC5 Excel.dll** for registering Excel 2000 add-in functions.
3. Type **regsvr32 HSC5.dll** for registering HSC 5.0 add-in functions.

Alternatively it can be achieved using the following method:

1. Double-click the file **HSC5 Excel.dll** in your Windows System directory.
2. If the file is *not* registered automatically, which is indicated by an **Open With** - dialog box, choose **Other** in the dialog window.
3. Select **Regsvr32.exe** from your Windows System directory. Now double-click the file again and it should register automatically.

When unregistering files follow the same procedure, but add the **u** switch before the file name, i.e. **regsvr32 u HSC5 Excel.dll** for unregistering HSC5 Excel.dll.

Description of Regsvr32.exe

To add .ocx and certain .dll files, it will be necessary to run REGSVR32.EXE from the Run option in the Start menu. The following are the commands and switches needed: *re s r 2* u s n i :cmdline *d na e* or *oc na e*

u (unregistered server)
s (silent display no message boxes)
c (console output)
i Call dll or ocx install passing it an optional cmdline
when used with u calls dll or ocx uninstall
n Do not call dll RegisterServer this option must be used with i

27.5 Unactivation of Excel Add-In Functions

To remove HSC 5.1 Functions completely from the Add-Ins list, simply highlight the checkbox again and Excel will ask whether you want to remove the Add-Ins from the list.