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

![Microsoft Excel - AddInSample.xls](image-url)

<table>
<thead>
<tr>
<th>Functions</th>
<th>Return Values</th>
<th>Arguments</th>
</tr>
</thead>
<tbody>
<tr>
<td>General</td>
<td></td>
<td></td>
</tr>
<tr>
<td>UNTITS(T;E)</td>
<td>C and Mcal</td>
<td>C</td>
</tr>
<tr>
<td>BAL(Equation)</td>
<td>2H2(g) + O2(g) = 2H2O(1)</td>
<td>H2O(1)</td>
</tr>
<tr>
<td>SPECIES(DBNo,Position)</td>
<td>All(CH3COO)2(-a)</td>
<td>2</td>
</tr>
<tr>
<td>Species</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(Species;T)</td>
<td>-93.357</td>
<td>CO2(g)</td>
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<td>S(Species;T)</td>
<td>28.766</td>
<td>H2O(1)</td>
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<tr>
<td>CP(Species;T)</td>
<td>44.245</td>
<td>CH4(g)</td>
</tr>
<tr>
<td>G(Species;T)</td>
<td>11.294</td>
<td>H2(g)</td>
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<tr>
<td>HKG(Species;T)</td>
<td>-0.264</td>
<td>FeS</td>
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<tr>
<td>HNM3 or HCM(Species;T)</td>
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<td>O2(g)</td>
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<tr>
<td>HLAT(Species;T)</td>
<td>0.000</td>
<td>H2O(1)</td>
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<tr>
<td>Reaction equation</td>
<td>Return Value</td>
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<td>S(Equation;T)</td>
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<td>CP(Equation;T)</td>
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<tr>
<td>G(Equation;T)</td>
<td>-107.631</td>
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<tr>
<td>HKG(Equation;T)</td>
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<td>K(Equation;T)</td>
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<td>2H2(g) + O2(g) = 2H2O(g)</td>
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</tbody>
</table>
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.
### Sulfur dioxide, Barin 93, Frenkel 94

<table>
<thead>
<tr>
<th>Species</th>
<th>Temperature K</th>
<th>Temperature K</th>
<th>Reference</th>
<th>Reliability</th>
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<tbody>
<tr>
<td>S2F10(g)</td>
<td>1</td>
<td>268</td>
<td>6000</td>
<td>JANAF 85</td>
</tr>
<tr>
<td>S2O3(g)</td>
<td>1</td>
<td>268</td>
<td>6000</td>
<td>JANAF 85</td>
</tr>
<tr>
<td>S2F4(g)</td>
<td>1</td>
<td>268</td>
<td>6000</td>
<td>JANAF 85</td>
</tr>
<tr>
<td>S2O4(g)</td>
<td>1</td>
<td>268</td>
<td>6000</td>
<td>JANAF 85</td>
</tr>
<tr>
<td>SF2(g)</td>
<td>1</td>
<td>268</td>
<td>3200</td>
<td>Barin 89</td>
</tr>
<tr>
<td>SF6(g)</td>
<td>1</td>
<td>268</td>
<td>550</td>
<td>Phillips 88, Parkrats 95</td>
</tr>
<tr>
<td>S2F6(g)</td>
<td>1</td>
<td>268</td>
<td>550</td>
<td>Phillips 88, Parkrats 95</td>
</tr>
<tr>
<td>S2F10(g)</td>
<td>1</td>
<td>268</td>
<td>3637</td>
<td>Barin 93</td>
</tr>
<tr>
<td>SF4(g)</td>
<td>1</td>
<td>268</td>
<td>1000</td>
<td>Kracke 91</td>
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<td>1</td>
<td>268</td>
<td>400</td>
<td>Kracke 91</td>
</tr>
<tr>
<td>S2O3(g)</td>
<td>1</td>
<td>268</td>
<td>1700</td>
<td>Barin 93</td>
</tr>
<tr>
<td>S2O4(g)</td>
<td>1</td>
<td>268</td>
<td>2000</td>
<td>Barin 89</td>
</tr>
<tr>
<td>H2O(g)</td>
<td>1</td>
<td>268</td>
<td>500</td>
<td>JANAF 85</td>
</tr>
</tbody>
</table>

**File:** C:\HSC5\Gibbs\Fres4.lg

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.
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.
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.
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.
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(2a), 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)
   - 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
   - PuO2(SO4)(-2a) → PuO2(SO4)2(-2a) (Typo in HSC database)
   - SCN(-a) replaced with CNS(-a) (duplicate)
   - Sr (Si2O7) was renamed SrSi2O7 (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.
   - Pie-routine improvement: Enter -key moves forward 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.
10. Maximum number of records in HSC databases was increased from 32767 to 2147483647 records.
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 Recal 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 on 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.
4. Improved calculation reliability and speed in the Equilibrium module.
5. Eh-pH-diagrams with concentration and temperature lines.
8. A new Mineralogy module for fast conversion between mineralogical and elemental compositions.
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 an 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.

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 \( C_p \) 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

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 (Cp) 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. Quite 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, i.e. 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, i.e. 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 formulæ 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, QuickBASIC 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 $C_p$ 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 $C_p$ at constant pressure (specific heat) can be calculated from this data using Eq. (1).

$$C_p = \frac{dH}{dT}_{P,n}$$

Equation (1) allows the calculation of enthalpy as

$$H(T) = H_f(298.15) + \int_{298.15}^{T} C_p \, dT + \Sigma H_{tr}$$

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 kJ 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 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.

\[
S = S(298.15) + \int_{298.15}^{T} \frac{C_p}{T} dT + \sum \frac{H_{tr}}{T_{tr}}
\]

where \(S(298.15)\) is the standard entropy of the substance which can be calculated by integrating \(C_p / T\) 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 \(C_p\)**: 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:

\[
C_p = A + B \cdot 10^{-3} \cdot T + C \cdot 10^{5} \cdot T^{-2} + D \cdot 10^{-6} \cdot T^2
\]

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.

\[
G = H - T \cdot S
\]

**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 \( S^\circ \) 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.
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: $aA + bB + ... = cC + dD + ...$

Enthalpy of reaction: $\Delta H_r = \Sigma v_i H_i(\text{Products}) - \Sigma v_i H_i(\text{Reactants})$

Entropy of reaction: $\Delta S_r = \Sigma v_i S_i(\text{Products}) - \Sigma v_i S_i(\text{Reactants})$

Gibbs energy of reaction: $\Delta G_r = \Sigma n_i G_i(\text{Products}) - \Sigma n_i G_i(\text{Reactants})$

Equilibrium constant: $K = \frac{C^c D^d}{A^a B^b}$

\[ \ln K = \Delta G_r (-RT) \]

where the following abbreviations have been used:

$A = \text{activity or partial pressure of species } A, B, C, \text{ etc.}$

$a = \text{stoichiometric coefficient of species } A \text{ in reaction}$

$\nu = \text{stoichiometric coefficient of a species in reaction (a, b, c, ...)}$

$R = \text{gas constant} = 1.987 \text{ cal (Kmol)} = 8.314 \text{ (Kmol)}$

$T = \text{Temperature in K}$
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.
Fig. 2. Thermodynamic data of Al2O3 (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 compilation¹.

Delta (Formation functions)
\[ \Delta H = H(\text{species}) - \Sigma H(\text{elements}) \]
\[ \Delta S = S(\text{species}) - \Sigma S(\text{elements}) \]
\[ \Delta G = G(\text{species}) - \Sigma G(\text{elements}) \]
\[ \Delta G = G(\text{ions}) - \Sigma G(\text{elements}) + \frac{z}{2} G(H_2(g)) - z G(H(\text{a})) \]
\[ z = \text{charge.} \]

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.
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 $\text{Mg} = \text{Mg(g)}$, 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.

$$K = \frac{p_{\text{Mg}}}{a_{\text{Mg}}} = \frac{p_{\text{Mg}}}{1} = 1$$

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.

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<th>T</th>
<th>C</th>
<th>deltaH</th>
<th>deltaS</th>
<th>deltaG</th>
<th>K</th>
<th>Log(K)</th>
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</thead>
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<td>26.299</td>
<td>-4.056</td>
<td>1.063E-004</td>
<td>-3.974</td>
<td></td>
</tr>
<tr>
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<td>30.533</td>
<td>22.378</td>
<td>-0.193</td>
<td>1.074E+000</td>
<td>0.031</td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>30.210</td>
<td>22.151</td>
<td>-2.422</td>
<td>2.277E+000</td>
<td>0.359</td>
<td></td>
</tr>
<tr>
<td>1300</td>
<td>29.886</td>
<td>21.938</td>
<td>-4.626</td>
<td>4.393E+000</td>
<td>0.643</td>
<td></td>
</tr>
<tr>
<td>1400</td>
<td>29.563</td>
<td>21.739</td>
<td>-6.810</td>
<td>7.715E+000</td>
<td>0.890</td>
<td></td>
</tr>
<tr>
<td>1500</td>
<td>29.239</td>
<td>21.531</td>
<td>-8.974</td>
<td>1.277E+001</td>
<td>1.106</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Formula</th>
<th>FM</th>
<th>Conc.</th>
<th>Amount</th>
<th>Amount</th>
<th>Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>g/mol</td>
<td>100.000</td>
<td>1.000</td>
<td>24.305</td>
<td>13.968 ml</td>
</tr>
<tr>
<td>Mg(g)</td>
<td>g/mol</td>
<td>100.000</td>
<td>1.000</td>
<td>24.305</td>
<td>22.414 ml</td>
</tr>
</tbody>
</table>
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.
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.
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 Introduction.
4. Positive Enthalpy $H$ of the reaction means that the reaction is endothermic, i.e. heat is needed, Equation 7 in Introduction.
5. Delta Format has no effect on the results of reaction equations.
7. Equilibrium constant $K$ is calculated using Equation 11 in Introduction.
11. HEAT AND MATERIAL BALANCE

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 balance 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 . usuario de balance 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 automatically 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 the automatically created sheet names, i.e. the BAL, INx and OUTx sheets, should not be modified.

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 streams. 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 Nm³. *It is advised to use mol and g because missing density data can cause inaccuracies in the units.*

2. Introduce the output substances (products), temperatures and amounts on the OUT1 sheet. Type amounts in either kmol, kg or Nm³ 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
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:

\[ H_{\text{loss}} = (6.8 + 0.046 \times T_2^2) \times (T_2 - T_1) \times A \]

Where:
- \( A \) = Outer surface area of the reactor (m²)
- \( T_2 \) = 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 Nm³ 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.

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![Fig. 2. Element Balance.](image-url)
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 of 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, MJ 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 reasure 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 formulae/links in temperature cells the temperature cells are not updated if the species are not divided into streams.

Examples of one-phase streams are, for example:

1. Air feed.
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 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.

![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.](image-url)
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 \[ 0.938 \times \text{IN1!C7} \] 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: \[ 0.938 \times (\text{InCu-C12}) \times 2 \] 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.
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.
**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.
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. *You can also enter the cell reference manually in the Target dialog.* Note: Please use only Stream temperature cells as variables for the temperature iterations, i.e. do not use species temperature cells.

4. Select one cell which will be used as first target and select **Set target cell**. This will add the cell reference of this target to the Target dialog in column H. *You may also type names in columns A and F.*

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, i.e. do not use species temperature cells.

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

![Image of BAL sheet](image)

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

In the balance areas it each other is regarded to carry out after each individual balance area or rate of each individual balance area or rate of each. 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 (formulæ) 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 stream temperature in the copied stream is a formulæ 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 streams, 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 circular reference 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.
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 circular references 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.

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. 

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 27. Excel Add-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 stream, instead link them to the stream 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 Object 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 Object 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. *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 transferred 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.

![Heat Loss Calculation Example](image)

Figure 1: Heat Loss calculation example of a smelting reactor wall.

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 arbitrary 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.

![Heat Transfer Calculations](image)
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 highly recommended to start the calculations with a simple wall 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 *manually* or using the database.

   **Manually**
   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<sub>c</sub> and/or h<sub>r</sub>) 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 *unfixed*.

- 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 adjacent layer columns, in this case please make sure that the radiation coefficient is *unfixed*.

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: **Conduction** button.
   - Surface column: **Convection** or **Radiation** button.
   - Enclosure column: **Convection** or **Radiation** 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 table or function sheet. 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 **thickness** 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:

   * **Temperature profile** (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 Flow (press the Heat flow button):
- Specify temperature points using the cursor.
- **0 or 1 point selected** (by cursor position): The whole range 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 between these points will be calculated.
  - Cube or cylinder geometry: The other sheets will not be calculated.
  - The end temperature points in the selection will remain constant.

8. Press the **Drawing 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: \(1.5 \text{ m}^2 \times (700 - 418 \; \text{°C}) \times 0.4 \; \text{W/(mK)} / (0.23 \; \text{m}) = 735 \; \text{W}\)

   Silica brick: \(1.5 \text{ m}^2 \times (418 - 50.63 \; \text{°C}) \times 0.2 \; \text{W/(mK)} / (0.15 \; \text{m}) = 735 \; \text{W}\)

   Air: \(1.5 \text{ m}^2 \times (50.63 - 20 \; \text{°C}) \times 16 \; \text{W/(m}^2\text{K}) = 735 \; \text{W}\)

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.
<table>
<thead>
<tr>
<th>Properties</th>
<th>Units</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column Type:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Material:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface Material:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thickness x</td>
<td>m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface Area A</td>
<td>m²</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>Conduction k (mean)</td>
<td>W/(m·°C)</td>
<td>5.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface Convection h</td>
<td>W/(m²·°C)</td>
<td>261.184</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface Radiation h</td>
<td>W/(m²·°C)</td>
<td>0.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Left (inner) T</td>
<td>°C</td>
<td>40</td>
<td>39</td>
<td>39</td>
</tr>
<tr>
<td>Right (outer) T</td>
<td>°C</td>
<td>39</td>
<td>39</td>
<td>20</td>
</tr>
<tr>
<td>Thermal Resistance</td>
<td>°C/kW</td>
<td>3.829</td>
<td>0.060</td>
<td>11.164</td>
</tr>
<tr>
<td>Heat Flux</td>
<td>kW/m²</td>
<td>0.174</td>
<td>0.174</td>
<td>0.174</td>
</tr>
<tr>
<td>Calculation Grid</td>
<td></td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Distance</td>
<td>m</td>
<td>0.000</td>
<td>0.003</td>
<td>0.003</td>
</tr>
</tbody>
</table>

**Figure 2**: Radiator calculation example.
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: Temperature profiles for the hot water tank.](image)

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: \( \text{H}_2\text{O(g)} \) 11.08 vol-\%, \( \text{CO}_2\text{(g)} \) 11.69 vol-\% and \( \text{SO}_2\text{(g)} \) 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 steel and the convective gas is approximated as air. These can both be found from the database. There is a 10 mm thick plain carbon steel layer surrounding the furnace. It is important to insert a Layer or a Layer contact column to the right of the Surface column, in order to calculate internal 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 steel and in Reactor2 paint, white (acrylic). The convective gas is air 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 twice. 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: Temperature profiles for different inner temperatures.

- Smelting 1600°C, Heat Loss = 5.502 kW
- Smelting 1400°C, Heat Loss = 4.836 kW
- Smelting 1200°C, Heat Loss = 4.251 kW

Water, Copper elements cooling

REXAL 2S EXTRA

Molten metal
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 _try_ to _use_ databases 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

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.

Figure 5

1. Headings area

2. Calculation area
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 ction 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 os u re 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

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

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 $\beta = 1/T$. 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

Figure 8: Thermal Convection database window, Function sheet.

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 $h_c(v) = A v^a + B v^b + \ldots + G v^g$ 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 horizontal 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

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 \( ^\circ C \). 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

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 automatically 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 gas and surface temperatures are known.

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 temperature and or surface temperature are unknown.
### 12.3.8 Particle Radiation Calculator

**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)

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 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 Diagram dialog window. Specifying the 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.
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.
12.3.11 Limitations

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

- The maximum number of calculation 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 own 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 *external* 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 total heat flow in one dimension \((x)\) is

\[
q = A \frac{\partial T}{\partial x},
\]

where \(q\) 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 thermal resistance is defined as

\[
R = \frac{T_2 - T_1}{q_x},
\]

where \(T_1\) and \(T_2\) are the temperature points and \(q_x\) is the heat flow. The thermal conductance is then

\[
G = \frac{1}{R},
\]

where \(R\) is the thermal resistance.

Time-dependent heat flows, where \(q_x = q(x, t)\), and steady 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 thermal diffusivity is defined as

\[
\alpha = \frac{k}{c_p \rho},
\]

where \(k\) is the thermal conductivity, \(c_p\) is the heat capacity at constant pressure and \(\rho\) is the density.

The kinematic viscosity is defined as

\[
\nu = \frac{\mu}{\rho},
\]

where \(\mu\) is the dynamic viscosity.
The Prandtl number describes the ratio of the momentum and thermal diffusivities. This is defined as

\[ \text{Pr} = \frac{\nu}{\alpha}, \]

where \( \nu \) is the kinematic viscosity and \( \alpha \) is the thermal diffusivity.

The thermal expansion coefficient is defined as

\[ \beta = -\frac{1}{\rho} \left( \frac{\partial \rho}{\partial T} \right) \approx -\frac{1}{\rho} \frac{\Delta \rho}{\Delta T}, \]

where \( \rho \) denotes the derivative at constant pressure.

In order to calculate the heat flux, it must be separated into the three main forms: conduction, convection 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

$$\frac{dT}{dx} = \frac{k}{q},$$

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 grid. Hence we can calculate the heat flux by using the following approximate equation that calculates the average heat flux through a layer

$$\frac{\sum_{n=1}^{m} \left( T_{n+1/2} - T_{n-1/2} \right)}{\sum_{n=1}^{m} \Delta x_n} = \frac{2\pi}{\ln \left( \frac{o}{t} \right)},$$

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 $\Delta x_n$ is the thickness of the grid.

In order to be able to calculate other geometries, the $S$ in the total heat rate equation is defined for different geometries according to equations 10 to 12.

For one-dimensional plane and for cube walls, $S$ is defined as

$$S = \frac{A}{x},$$

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

For cylindrical coordinates, $S$ is defined as

$$S = \frac{2\pi}{\ln \left( \frac{o}{t} \right)},$$

where $o$ is the outer radius and $t$ is the thickness of the layer.
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 spherical walls (spherical coordinates), \( S \) is defined as

\[
S = \frac{4\pi x^2}{o - i}. 
\]
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

\[ q_s = h_c (T_s - T_{\infty}) \]

where \( h_c \) is the convection coefficient, \( T_s \) is the surface temperature and \( T_{\infty} \) 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

\[ \frac{h}{\lambda} \times L = Nu_c \]

where \( L \) is the characteristic length 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 equation. Using equation 14 and the appropriate correlation equation the value of \( h_c \) can be calculated. The correlations depend on whether forced or free convection 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 mixed convection, however this is not taken into account in this work. See 3.11 Limitations for a more detailed description of when mixed convection conditions are noticeable.

Convection can also be subdivided into internal and external 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 convection

The correlation describing the nature of the flow for free convection is called the Rayleigh number and is defined according to

\[ a = \frac{\beta (s - \omega)}{\nu \alpha} \]

where \( g \) is the acceleration due to gravity and \( \beta \) the thermal expansion coefficient.

Sometimes the Grashof number, which describes the ratio of buoyancy forces to viscous forces, is used in correlations and is defined as

\[ r = \frac{\beta (s - \omega)}{\nu^2} = \frac{a}{\Pr} \]

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

Wall vertical position \( \theta_v = 0 \ 1 \)

- Surface:
  - Characteristic length: \( L = z \)
  - Laminar flow (\( \text{Ra}_L < 10^9 \)):
    \[ \overline{u} = 0.68 + \frac{0.670}{\left[ 1 + (0.492 \frac{a}{r})^{9/16} \right]^{4/9}} \]
    \[ \text{Ra}_L \]
  - Turbulent flow (\( \text{Ra}_L \geq 10^9 \)):
    \[ \overline{u} = \left\{ 0.825 + \frac{0.387}{\left[ 1 + (0.492 \frac{a}{Pr})^{9/16} \right]^{8/27}} \right\}^2 \]

- Enclosure:
  - Characteristic length: \( L = \) thickness of wall enclosure
  - \( H = z \) (height of enclosure)
  - \( H/L = 2 \):
    \[ \overline{u} = 0.18 \left( \frac{r}{0.2 + a} \right)^{0.29} \]
    \[ \text{Valid when:} \]
    \[ 1 \leq H/L \leq 2 \]
    \[ 10^3 \leq \text{Pr} \leq 10^5 \]
    \[ 10^3 \leq \text{Ra}_L \Pr (0.2 \text{ Pr}) \]
  - \( 2 \leq H/L \leq 10 \):
    \[ \overline{u} = 0.22 \left( \frac{r}{0.2 + a} \right)^{0.28} \left( \frac{r}{a} \right)^{1/4} \]
    \[ \text{Valid when:} \]
    \[ 2 \leq H/L \leq 10 \]
\[ \frac{Pr}{10^5} \quad \frac{Ra}{10^{10}} \]

- \( H/L \geq 10 \)

\[ \frac{u}{H/L} = 0.42 \ a^{1.4} \ r^{0.012} \left( \frac{a}{L} \right)^{-0.3} \]

- Valid when:
  - \( 10 \leq H/L \leq 40 \)
  - \( 1 \leq Pr \leq 2 \times 10^4 \)
  - \( 10^4 \leq Ra \leq 10^7 \)

Wall, horizontal position \( \theta_v = 90 \degree \)

- Surface:
  - Characteristic length: \( L = A/P \), i.e. the surface area divided by the perimeter
  - Hot upper surface or cold lower surface:
    \[ \frac{u}{H/L} = 0.27 \ a^{1.4} \]

- Cold upper surface or hot upper surface:
  - \( Ra \leq 10^7 \):
    \[ \frac{u}{L} = 0.54 \ a^{1.4} \]
  - \( Ra \geq 10^7 \):
    \[ \frac{u}{L} = 0.15 \ a^{1.3} \]

- Enclosure:
  - Characteristic length: \( L = \) thickness of wall enclosure
  - Hot lower surface:
    - \( Ra \leq 1708 \):
      \[ \frac{u}{L} = 1 \) (pure conduction)
    - \( Ra \geq 1708 \):
      \[ \frac{u}{L} = 0.069 \ a^{1.3} \ r^{0.074} \]
  - Cold lower surface:
    - \( u = 1 \) (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
  - \(\text{Nu}_{\text{roof}}\) and \(\text{Nu}_{\text{bottom}}\) according to equation \(22\), \(23\) or \(24\)
- Enclosure:
  - Same as for wall depending on horizontal or vertical cube enclosure

**Cylinder, vertical \(\theta_v = 0^\circ\)**

- 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:
        \[D \geq 35 (aPr)^{1/4}\]
    - Roof and bottom:
      - Characteristic length: \(L = A/P = D/4\), i.e. the surface area divided by the perimeter
      - \(\text{Nu}_{\text{wall}}\) according to equation \(17\) or \(18\)
      - \(\text{Nu}_{\text{roof}}\) and \(\text{Nu}_{\text{bottom}}\) according to equation \(22\), \(23\) or \(24\)

- Enclosure:
  - As vertical wall enclosure

**Cylinder, horizontal \(\theta_v = 90^\circ\)**

- 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: \(L = D_o\)
\[ u_D = \left\{ 0.60 + \frac{0.387 \ a_D^6}{\left[ 1 + (0.559 \ \text{Pr}^{9/16}) \right]^{27}} \right\}^2 \]

- Valid when: \( \text{Ra}_D \leq 10^{12} \)
- Roof and bottom:
  - Characteristic length: \( L = r_o \sqrt{\text{Pr}} \), i.e. square with same area
  - \( \text{Nu}_{\text{roof}} \) and \( \text{Nu}_{\text{bottom}} \) according to equation 17 or 18

- Enclosure:
  - Characteristic length \( L = \) thickness of cylinder enclosure
  - \( h_\text{c} \) calculated directly, not through the Nusselt number (\( \text{Nu}_L \))

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

- \( \text{Ra}_c \) 100:

\[
\epsilon = \frac{n(D_o - D_i) \cdot D_i}{2}
\]

- \( \text{Ra}_c \) 100:

\[
\epsilon = 0.386 \left( \frac{r}{0.861 + r} \right)^4 \left( a_c \right)^4.
\]

\[
\epsilon = \frac{n(D_o - D_i) \cdot D_i}{2}
\]

- valid when: \( \text{Ra}_c \leq 10^{7} \)

### 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: \( L = D_o \)

\[
\frac{1}{u_D} = 2 + \frac{0.589 \ a_D^4}{\left[ 1 + (0.469 \ \text{Pr}^{9/16}) \right]^{8/9}}
\]

- Valid when:
  - \( \text{Ra}_D \leq 10^{11} \)
  - \( \text{Pr} \geq 0.7 \)
- Enclosure:
  - Characteristic length: \( L = \) thickness of the sphere enclosure
  - \( h_\text{c} \) calculated directly, not through the Nusselt number (\( \text{Nu}_L \))
\[ a_s = \frac{a}{(D_o D_i)^4 \left( D_i^{-7.5} + D_o^{-7.5} \right)^5} \]

- **\( \text{Ra}_a \) 100:**
  \[ c = \pi \frac{D_i D_o}{r} \]

- **\( \text{Ra}_a \) 100:**
  \[ c = 0.74 \left( \frac{r}{0.861 + r} \right)^4 \left( a_s \right)^4 \]
  \[ c = \pi \frac{D_i D_o}{r} \]

- Valid when:
  \[ 10^2 \text{ Ra}_a \leq 10^4 \]
Forced convection

Forced convection is here assumed to be external only. The correlation number describing the nature of the flow for forced convection is called the Reynolds number, which describes the ratio of inertia forces to viscous forces of a flow and is defined as

\[ \text{Re} = \frac{u_\infty}{\nu} \]

where \( u_\infty \) is the speed of the fluid gas. Note that the direction of the flow is assumed to be horizontal in this program and that forced convection inside enclosures is not taken into consideration.

**Wall 1**

- Laminar flow, \( \text{Re}_L \leq 5 \times 10^5 \):
  \[ \text{Nu} = 0.664 \text{Re}^{1/2} \text{Pr}^{1/3} \]
  Valid when: \( \text{Pr} \geq 0.6 \)
- Turbulent flow (flow separation), \( \text{Re}_L \geq 5 \times 10^5 \):
  \[ \text{Nu} = (0.037 \text{Re}^{4/5} - 871) \text{Pr}^{1/3} \]
  Valid when: \( 0.6 \leq \text{Pr} \leq 60 \)
  \( 5 \times 10^5 \leq \text{Re}_L \leq 10^8 \)

**Cube 1**

- Tangential horizontal flow on all sides assumed
- Cube walls:
  - Characteristic length front and back wall: \( L = x_0 \)
  - Characteristic length left and right wall: \( L = y_0 \)
  - Nusselt number calculated as 37 or 38
- Roof and bottom:
  - Characteristic length: \( L = y_0 \)
  - Nusselt number calculated as 37 or 38

**Cylinder 1**

- Cylinder wall:
  - Characteristic length: \( L = D_0 \)
  \[ \text{Nu} = 0.3 + 0.62 \frac{e_D^{1/2}}{r^{1/3}} \left[ \frac{e_D^{1/2}}{r^{1/3}} \right]^{1/4} + \left( \frac{e_D}{282000} \right)^{5/8} \]
  Valid when: \( \text{Re}\text{DPr} \geq 0.2 \)
- Roof and bottom:
Characteristic length: $L = r_0 \sqrt{\pi}$, i.e. square with same area

Nusselt number calculated as \[37\] or \[38\]

Sphere 1, 2

Characteristic length: $L = D_0$

$$
\overline{u_D} = 2 + (0.4 \text{Re}_D^{1.2} + 0.06 \text{Re}_D^{2.3}) \text{Pr}^{0.4} \left( \frac{\mu_\infty}{\mu_s} \right)^{1.4},
$$

where $\mu_\infty$ is the dynamic viscosity at the fluid/gas temperature and $\mu_s$ is the dynamic viscosity at the surface temperature.

valid when:

- $0.71 \leq \Pr \leq 380$
- $3.5 \leq \text{Re}D \leq 7.6 \times 10^4$
- $1.0 \leq (\mu_\infty/\mu_s) \leq 3.2$
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. This spectrum includes both visible light as well as infrared radiation. Radiation heat transfer between two points occurs when waves are emitted at one point and absorbed at another. Sometimes the wave is reflected or transmitted 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: Surface radiation, as radiation and combined as and artice radiation. These are described more closely below.

Surface 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

\[ q_s = \varepsilon_s \sigma \left( T_s^4 - T_¥^4 \right), \]

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

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

\[ r = \varepsilon_s \sigma \left( T_s^2 + T_¥^2 \right) \]

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

\[ q_s = r \left( T_s - T_¥ \right) \]

which is of the same form as equation 13. The surface emissivity can be found from tables in the literature. The normal emissivity (\( \varepsilon_n \)) or the hemispherical or total emissivity (\( \varepsilon_h \)) 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.
Gas radiation

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

\[ q_a = \frac{\varepsilon_s + 1}{2} \sigma \left( \varepsilon^4 - \alpha_s^4 \right), \]

where \( \varepsilon_s \) is the surface emissivity, \( \varepsilon_g = \varepsilon_g(T_g) \) is the gas emissivity at the gas temperature and \( \alpha_g = \alpha_g(T_g, T_s) \) is the gas absorptivity as a function of both the gas and surface temperatures. It is natural that \( \alpha_g \) 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 \( (\varepsilon_s + 1)/2 \) is an approximation for the effective emissivity of the solid.

The heat radiation coefficient is now

\[ r = \frac{(\varepsilon_s + 1)\sigma(\varepsilon^4 - \alpha_s^4)}{2} \]

In order to calculate \( \varepsilon_g \) and \( \alpha_g \), 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 \( \text{H}_2\text{O}, \text{CO}_2, \text{CO}, \text{NO}, \text{SO}_2 \) and \( \text{CH}_4 \) 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

\[ \varepsilon_g = \varepsilon(\text{H}_2\text{O}, \text{CO}_2, \text{CO}, \text{NO}, \text{SO}_2, \text{CH}_4), \]

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, \( \sum x_s \leq 1 \), since the rest of the mixture can consist of non-radiating gases.

This model is applicable for the temperature range \( T = 300 \text{ K} \) to \( 2500-3000 \text{ K} \) 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.

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

Table 1  a e 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
   \[ L_{1x1x7} = 0.6 \times (7-1) / (4-1) = 1.02 \]

2. Extrapolated as a 1x2.5x7 cube using geometries 3.2 and 3.3 gives
   \[ L_{1x2.5x7} = 0.81 \times (2.5-1) / (2-1) = 1.185 \]

3. These two results can then be used again to extrapolate into the 1x4x7 cube which gives
   \[ L_{1x4x7} = 1.02 \times (1.185-1.02) / (4-1) = 1.35 \] 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

\[
\alpha = \varepsilon \left( \frac{L}{L_p} \right)^{0.5} 
\]

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 Tapio Ahokaine.

**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

\[
\varepsilon_c = 1 - e^{-\varepsilon n} 
\]

where \( \varepsilon_p \) 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

\[
\frac{\pi d_s^2}{4} = \sum_{i=1}^{n} n_i d_i^2 / 4 \sum_{i=1}^{n} n_i 
\]

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

\[
\varepsilon_{p+c} = \varepsilon_g + \varepsilon_c - \varepsilon_g \varepsilon_c 
\]

where \( \varepsilon_c \) is the particle cloud emissivity and \( \varepsilon_g \) is the gas emissivity calculated according to the model behind equation 46. The total gas and particle cloud absorptivity can be approximated as

\[
\alpha_{p+c} = \alpha_g + \varepsilon_c - \alpha_g \varepsilon_c 
\]
where $a_g$ 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

\[ q = \frac{\varepsilon_s}{\alpha_{sc} + \varepsilon_s - \alpha_{sc}\varepsilon_s} \sigma \left( \varepsilon_{sc}^4 - \alpha_{sc}\varepsilon_s^4 \right) \]  

and the heat radiation coefficient as

\[ r = \frac{\varepsilon_s \sigma \left( \varepsilon_{sc}^4 - \alpha_{sc}\varepsilon_s^4 \right)}{\left( \alpha_{sc} + \varepsilon_s - \alpha_{sc}\varepsilon_s \right) \left( \varepsilon_s^4 - \alpha_{sc}\varepsilon_s^4 \right)} \]
References


13. EQUILIBRIUM MODULE

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. 

   \[ \text{ote t at t is e ui ibru so er is not inc uded in} \]

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. 

   \[ \text{ote t at t is e ui ibru ro ra is not inc uded in} \]

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.](image)

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

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

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

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

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

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

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

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

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

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

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

Use the (l)-suffix for a species only if you want to use the data of liquid phases at temperatures below its melting point. For example, type SiO$_2$(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 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 (FeS$_2$), calcium carbonate (CaCO$_3$), etc. might form their own pure phases.

One of the most common mistakes is to insert a large amount of relatively inert 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.

\[
a = \frac{p_{\text{over solution}}}{p_{\text{pure}}} \quad 1
\]

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

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

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

\[
\begin{align*}
\ln(f) &= 8495 - 2.653 \\
\ln(f) &= 0.69 + 56.8 \times 24 - 5.45 \times 25 \\
\ln(f) &= -3926 \\
\ln(f) &= -1.21 \times 7 - 2.44 \times 8 \\
\end{align*}
\]

where:

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

Formulae are written using the same syntax as in Excel, the defined names $T$ and $P$ are available for temperature and pressure. Mole fractions are given as cell references to
column X. Please note that the returning values of the formulae are insignificant, because the mole fraction values in column X are zero, see Figs. 16 - 17.

7. Heading

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

8. Equilibrium Temperature

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

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

9. Equilibrium Pressure

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

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

\[
\begin{align*}
a_i &= P \times x_i \\
F_i &= a_i \times 1 \text{ bar}
\end{align*}
\]

10. Number of Steps

If you have defined increments (steps) for raw material species or specified a temperature or a pressure range then you should also give the Number of Steps required, see Fig. 5

The maximum number of steps in Gibbs solver is 251 and for Solgasmix the maximum available is 51. Usually 21 - 51 steps give quite smooth curves in the equilibrium diagram. A large number will only give more points to the picture and a longer calculation time.

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

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

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

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

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

### 12. GIBBS, SOLGASMIX and ChemSAGE File Format

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

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

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

### 13. Pure Substances (Invariant phases)

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

### 14. File Save and File Open

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

### 15. Exit

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

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

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

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

3. If you are calculating, for example, the dissolution of 1 mole of CaCO₃ into water and you have stoichiometric raw material amounts, please also add a small amount of O₂(g) to the gas phase, for example, 1E-5 moles. If you have stoichiometric NaCl in the system please add a minor amount of Cl₂(g) to the gas phase (1E-5 mol). These tricks help the GIBBS and SOLGASMIX solvers to find the equilibrium composition in cases of fully stoichiometric overall compositions.

4. HSC converts the entropy values of aqueous components from the molality scale to mole fraction scale if the Mixing Entropy scale if the Mixing Entropy option is selected, Fig. 33. Therefore, the entropy values in the input files are not the same as in the HSC database. Identical results will be achieved if the Raoultian activity coefficients of the aqueous species are changed to 55.509 X(H₂O) which converts the Raoultian activity scale to the aqueous activity scale.

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

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

\[ H_2O \quad H( +a) \quad OH(−a) \quad K \quad 1.020E-14 \quad 5 \]

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.

\[ K = \frac{H( +a) \times OH(−a)}{H_2O} = \frac{4.735E-13 \times 2.159E-2}{55.468/55.509} = 1.023E-14 \quad 6 \]
HSC Chemistry® 5.0

A. Roine
June 28, 2002

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>MOLE FRACT</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>H2O</strong></td>
<td>5.5500E 01</td>
</tr>
<tr>
<td><strong>CO3(-2a)</strong></td>
<td>0.0000E 00</td>
</tr>
<tr>
<td><strong>C2O4(-2a)</strong></td>
<td>0.0000E 00</td>
</tr>
<tr>
<td><strong>Ca(2a)</strong></td>
<td>1.0000E 00</td>
</tr>
<tr>
<td><strong>CaOH(a)</strong></td>
<td>0.0000E 00</td>
</tr>
<tr>
<td><strong>H(a)</strong></td>
<td>0.0000E 00</td>
</tr>
<tr>
<td><strong>HCO2(-a)</strong></td>
<td>0.0000E 00</td>
</tr>
<tr>
<td><strong>HCO3(-a)</strong></td>
<td>0.0000E 00</td>
</tr>
<tr>
<td><strong>HO2(-a)</strong></td>
<td>0.0000E 00</td>
</tr>
<tr>
<td><strong>OH(-a)</strong></td>
<td>2.0000E 00</td>
</tr>
<tr>
<td><strong>Total:</strong></td>
<td>5.8500E 01</td>
</tr>
</tbody>
</table>
13.4 General Considerations

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

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

1. Before any calculations are made, the system components (elements in HSC Chemistry) and substances must be carefully defined in order to build up all the species and substances as well as mixture phases which may be stable in the system. Phase diagrams and solubility data as well as other experimental observations are often useful when evaluating possible stable substances and phases.

2. Defining all the phases for the calculation, which may stabilize in the system, is as important as the selection of system components. You may also select a large number of potential phases just to be sure of the equilibrium configuration, but it increases the calculation time and may also cause problems in finding the equilibrium.

3. The definition of mixtures is necessary because the behavior of a substance (species) in a mixture phase is different from that in the pure form. The microstructure or activity data available often determines the selection of species for each mixture. Many alternatives are available even for a single system, depending on the solution model used for correlating the thermochemical data.

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

4. If you expect a substance to exist in the pure form or precipitate from a mixture as a pure substance, define such a species in the system also as a pure (in a riant phase. This is often a valid approximation although pure substances often contain some impurities in real processes. All species in the last phase can be set to be pure substances using the Pure Substances in the Last Phase option, see Fig. 5.

5. The raw materials must be given in their actual state (s, l, g, a) and temperature if the correct enthalpy and entropy values for equilibrium heat balance calculations are required. These do not affect the equilibrium compositions.

6. Gibbs energy minimization routines do not always find the equilibrium configuration. You may check the results by a known equilibrium coefficient or mass balance tests. SOLGASMIX provides a note on error in such cases. It is evident that results are in error if you get random scatter in the curves of the diagram, see Figs. 11, 17 and 19. You can then try to change species and their amounts as described in Chapter 13.2 (2. Phases, 4. Amount of Species).

7. Sometimes when calculating equilibria in completely condensed systems it is also necessary to add small amounts of an inert gas as the gas phase, for example, Ar(g) or N2(g). This makes calculations easier for the equilibrium programs.

8. It may also be necessary to avoid stoichiometric raw material atom ratios by inserting an additional substance, which does not interfere with the existing equilibrium. For example, if you have given 1 mol Na and 1 mol Cl as the raw
materials and you have NaCl as the pure substance, all raw materials may fit into NaCl due its high stability. The routines meet difficulties in calculations, because the amounts of all the other phases and species, except the stoichiometric one, go to zero. You can avoid this situation by giving an additional 1E-5 mol Cl2(g) to the gas phase, see Fig. 46.

9. Quite often the most simple examples are the most difficult ones for the Gibbs energy minimization routines due to matrix operations. However, the new GIBBS 4.0 version usually finds the solution for the simple systems too, such as the two phase H2O(g) - H2O -system between 0 - 200 °C.

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

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

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

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

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

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

For example, the user might only want to know at which temperature Na2SO4 can be reduced by coal to Na2S, or how much oxygen is needed to sulfatize zinc sulfide, etc.: The Na2SO4.IGI example in the HSC5 GIBBS directory shows the effect of temperature on Na2SO4 reduction with coal the same example can be seen also in the HSC color brochure, page 3. The calculated compositions are not exactly the same as found experimentally, but from these results we can easily see that at least 900 C will be needed to reduce the Na2SO4 to Na2S, which has also been verified experimentally.
The real Na-S-O-C-system is quite complicated. In order to describe this system precisely from 0 to 1000 C, solution models for each mixture phase would be needed to describe the activities of the species. Kinetic models would also be necessary at least for low temperatures. To find the correct parameters from the literature for all these models might take several months. However, with HSC Chemistry the user can get preliminary results in just minutes. This information is often enough to design laboratory and industrial scale experiments.
13.5 Limitations

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

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

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

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

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

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

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

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

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

13.6.1 GIBBS Equilibrium Solver

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.

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

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.

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

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

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

Fig. 8. Selecting the x-axis for an Equilibrium Diagram.
Fig. 9. Selecting the x-axis for an Equilibrium Diagram.
The PIC post-processor draws diagrams on the basis of the output files of the GIBBS program (*.OGI-files), as well as from the SOLGASMIX (*.OSG) and ChemSAGE (*.RES) result files. These diagrams can be drawn, for example, as a function of a specified reactant amount or equilibrium temperature. Start the PIC program by pressing **Draw** in Fig. 6 or 7 and follow these instructions:

1. Select the *.OGI file for diagram by pressing **File Open** if not yet selected, see Fig. 8. This file contains the results of the equilibrium program.

2. Select the species or temperature for the **x-axis** by clicking the desired item in the list box using the mouse. The program shows the recommended selection with an arrow, which is the variable used in the calculations, see Fig. 8.

3. Press **OK**.

4. Select the species for the **y-axis** by keeping **Ctrl Key** down and clicking with the mouse. Sometimes it is convenient to select only those species, which contain the same element, for example Ni, for one diagram. This can easily be done using the element list, see Fig. 9. In standard cases you can get more illustrative diagrams by drawing all gaseous species on one diagram and all other species on another.

The number of selected species is not limited. All species included in the calculation can be selected to the diagram.

5. Press **OK**.

6. Note: You can return to HSC by pressing **Cancel** or **Exit**.
13.7.1 Selecting Data Type for the X- and Y-axis

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.

Fig. 10. Selecting data type for the x- and y-axis.
13.7.2 Result Graphics (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.

![Format Y-Axis](image1)

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

![Format Label and Line](image2)

**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.

![Page Settings](image)

**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

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

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

\[
\text{LOG} f(1) = ((1-X_1)^2) \cdot (-25503.6 - 4.3109 \cdot T + 5174.7 \cdot (1 - 4 \cdot X_1)) / (8.31431 \cdot T)
\]

\[
\text{LOG} f(2) = (X_1)^2 \cdot (-25503.6 - 4.3109 \cdot T + 5174.7 \cdot (3 - 4 \cdot X_1)) / (8.31431 \cdot T)
\]
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](image)

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

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>Formula</th>
<th>Temp. °C</th>
<th>Amount kmol</th>
<th>Amount %</th>
<th>Step kmol</th>
<th>Step %</th>
<th>Activity Coeff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PHASE 1:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>N₂(g)</td>
<td>25.000</td>
<td>1.000</td>
<td>100.000</td>
<td>0.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>CO₂(g)</td>
<td>25.000</td>
<td>1.000</td>
<td>100.000</td>
<td>0.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>O₂(g)</td>
<td>25.000</td>
<td>1.000</td>
<td>100.000</td>
<td>0.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>CaO(g)</td>
<td>25.000</td>
<td>1.000</td>
<td>100.000</td>
<td>0.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>PHASE 2:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>H₂O</td>
<td>25.000</td>
<td>55.200</td>
<td>94.872</td>
<td>1.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>CO³(-2a)</td>
<td>25.000</td>
<td>1.000</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>C₂O₄(-2a)</td>
<td>25.000</td>
<td>1.000</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Ca²⁺(2a)</td>
<td>25.000</td>
<td>1.000</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>CaOH⁺(a)</td>
<td>25.000</td>
<td>1.000</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>H⁺(a)</td>
<td>25.000</td>
<td>1.000</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>HCO₃⁻(a)</td>
<td>25.000</td>
<td>1.000</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>HCO₃⁻(a)</td>
<td>25.000</td>
<td>1.000</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>H₂O⁺(a)</td>
<td>25.000</td>
<td>1.000</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>OH⁻(a)</td>
<td>25.000</td>
<td>2.000</td>
<td>3.419</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>PHASE 3:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>CaCO₃</td>
<td>25.000</td>
<td>1.000</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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 it 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, i.e. 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 substance (not N2(g)).
Fig. 22. Chemical system specification for PbS vapor pressure calculations.

<table>
<thead>
<tr>
<th>SPECIES Formula</th>
<th>Amount knol</th>
<th>Amount %</th>
<th>Step %</th>
<th>Activity Coeff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbS(g)</td>
<td>25.000</td>
<td>0.100</td>
<td>100.000</td>
<td>1.000</td>
</tr>
<tr>
<td>PbS2(g)</td>
<td>25.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>PbS2S2(g)</td>
<td>23.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>S(g)</td>
<td>25.000</td>
<td>1.000E-20</td>
<td>0.000</td>
<td>1.000</td>
</tr>
<tr>
<td>S2(g)</td>
<td>25.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>S3(g)</td>
<td>25.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>S4(g)</td>
<td>25.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>S5(g)</td>
<td>25.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>S6(g)</td>
<td>25.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>S7(g)</td>
<td>25.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>S8(g)</td>
<td>25.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
</tbody>
</table>
Fig. 23. Results of PbS vapor pressure calculations.
5 Copper Smelting at 1300 C

Contents of an Input File for GIBBS Program

§Copper Smelting at 1300 C

1
6 4 0 3 3 2 1

'HSC EQUILIBRIUM MODULE SAMPLES

Heading
0 = results to screen, 1= results to file
Elements, phases, inv. phases, and
^ number of components / phase l., etc.

' stoichiomet.

matrix

N2(g) 2.00 0.00 0.00 0.00 0.00 0.00
O2(g) 0.00 2.00 0.00 0.00 0.00 0.00
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

1573.150

Equilibrium temperature (K)
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H, S, number of temperature intervals
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Temperature (K), H (J/mol)
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H (J/mol), S (J/(mol*K)), ()
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1600.000 0.000000E+00

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200.000 0.000000E+00

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Raw materials, and their serial numbers

^ Temperatures of the raw materials (K)

Number of equilibria to be calculated
2 = constant input amount, 3 = increases

Amount of raw material 1., step (mol)
Amount of raw material 2., step (mol)
Amount of raw material 5., step (mol)
Amount of raw material 7. (mol)
Amount of raw material 8. (mol)
Exit
9 = Activity Coefficients if values other than 1
Input File for SOLGASMIX Program (Amounts in moles)

%Copper Smelting at 1300 C

0 6 4 1 3 3 2

' Heading
' 0 = mole mode, 1= gram mode
' Elements, phases, inv. phases, and
' ^ number of components / phase 1., etc.

' stoichiomet.
' matrix

1573.150

H, S, number of temperature intervals

A, B, C, D, E, F (J/(mol*K))

Equilibrium temperature (K)

Raw materials, and their row numbers in the stoichiometry matrix

Temperatures of the raw materials (K)

Number of equilibria to be calculated

' Amount of raw material 1., step (mol)

' Amount of raw material 2., step (mol)

' Amount of raw material 3., step (mol)

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' Amount of raw material 6., step (mol)

' Amount of raw material 7. (mol)

' Amount of raw material 8. (mol)

' Exit
Input File for SOLGASMIX (Input amounts in grams)

% Copper Smelting at 1300 C

Elements, phases, inv. phases, and number of components / phase 1...

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'O2(g) ' 0.00 2.00 0.00 0.00 0.00
'SO2(g) ' 0.00 2.00 1.00 0.00 0.00
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14.007

'N Mol. Weight g/mol

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'O

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'S

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'Fe

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'Si

63.546

'Cu

1573.150

'Equilibrium temperature (K)

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1.60000

'Temperature (K), H (J/mol)

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5.164756E+01 -2.158751E+06 0.000000E+00 0.000000E+00

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-0.000000E+00 2.051470E+02 1

0.000000E+00 0.000000E+00 0.000000E+00 0.000000E+00

2

5 1 2 5 7 8

'Raw materials, and their row numbers in the stoichiometry matrix

A. Roine

June 28, 2002

02103-ORC-T
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

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**Increase Temperature:** 101 Steps  
**Criss-Cobble On:**  
**Temperature Range:** 1000.000 0.000 °C  
**Pressure Range:** 1.000 1.000 bar

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_Figure 2._ Specification of phases and species in the Magnesia Chrome brick example.
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:

\[ \text{N}_2(g) + 3 \text{H}_2(g) \rightarrow 2\text{NH}_3(g) \]

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

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**Figure 4.** Specification of phases and species in ammonia synthesis example.
Case 3  Decomposition of MgCl₂  6H₂O

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 MgCl₂ 6H₂O compound which decomposes according to the reaction:

MgCl₂ 6H₂O - MgCl₂ 4H₂O  2H₂O(g)
MgCl₂ 4H₂O - MgCl₂ 2H₂O  2H₂O(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 Cl₂(g) and O₂(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.

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Figure 5. Specification of phases and species in MgCl₂ 6H₂O example.
Figure 6. Calculation results for MgCl$_2$·6H$_2$O decomposition example.
Figure 7. Vapor composition at a total pressure of 1 bar.
Case 4 Decomposition of FeSO$_4$·7H$_2$O (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$_2$O. 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 O$_2$(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.

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<th>Step kmol</th>
<th>Step %</th>
<th>Activity Coeff.</th>
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Figure 8. The specification of phases and species for the equilibrium calculations.
Figure 9. The result of the calculated decomposition of FeSO$_4 \cdot 7$H$_2$O.

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$_2$O 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 FeSO₄·7H₂O.
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$_2$O$_3$ 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.
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</table>

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 Nm³ 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 20. Diagram Graphics.

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:

<table>
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<th>Species</th>
<th>Oxidation number of e-(Pt)</th>
<th>Oxidation number of O2(g)</th>
<th>Discharge amount: F (mol)</th>
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<td>-4</td>
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</tr>
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<td>17</td>
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</table>

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 \(2 \times (-2) = -4\). 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:

\[
Q = \text{Amount of electricity in As (charge)}
\]

\[
F = \text{Faraday's constant, } 96487 \text{ As/mol}
\]

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\textsuperscript{7,8}.

15.1 Cell Module

![Cell program](image)

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 EQUATION. 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.
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, H₂O, 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
   - O₂(g) Oxygen gas
   - Fe(l) Liquid iron
   - OH(-a) Aqueous OH ion
   - C Carbon
   - C(D) Diamond
   - FeS₂ Pyrite
   - 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. 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. Huang, at Montana Tech., USA.

17.1 Introduction

Eh-pH-diagrams are also known as Pourbaix Diagrams according to author of the famous Pourbaix diagram handbook. The most simple type of these diagrams is based on a chemical system consisting of one element and water solution, for example, the Mn-H2O-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 + H2O2 = CuO + H2O). 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. **Horizontal 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:

\[ 2 \text{H}_2\text{O} = \text{O}_2(g) \quad 4 \text{H}(\text{a}) \quad 4 \text{e}^- \]

The lower stability limit is based on hydrogen formation on the cathode. It is specified by the reaction:

\[ 2 \text{H}(\text{a}) \quad 2 \text{e}^- = \text{H}_2(g) \]

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 H₂O. 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**: condensed =

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 database11, 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

The Eh-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 EhP diagrams or **Combine** for combined diagrams. Usually at the beginning, 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 EhP 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 t e s c e i t r a m a t e r a t e s e r r e d r o t e s t e s e c i t a t i o n s e e t t e d i a r a n e u, 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

\[ \Delta \text{G} = - n \cdot F \cdot E, \]

where \( n \) is the charge transferred in the cell reaction, \( F \) is the Faraday constant \((23045 \text{ cal/(V mol)})\) 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 rows.

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 H₂O are automatically calculated on the basis of the selected temperature and pressure. The calculation of Dielectric Constant is based on experimental values and water vapor pressure, 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 H₂O 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-H2O-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

The Eh pH diagrams show only those species which 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-H2O diagram and Fig. 4 for the S-Cu-H2O-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-H₂O-system at 25 °C using Cu as the main element. The molalities of Cu and S are 1 mol kg H₂O.
Fig. 4. Eh-pH-diagram of S-Cu-H\textsubscript{2}O-system at 25 °C using S as the main element. The molalities of Cu and S are 1 mol/kg H\textsubscript{2}O.

The **Format H\textsubscript{2}O 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$_2$O-System

The Cu-S- and S-Cu-H$_2$O-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.
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 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 strongly recommended to use only one variable, 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-H2O-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-H2O-system for an Eh-pH-diagram.
Fig. 8. Specification of a combined diagram layout for an Fe-S-H2O 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-H2O 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-H2O-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-H2O-system at 25 °C. The Fe molality values 1, 10^{-3}, and 10^{-6} have been used as parameter.
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

\[ D = \sum_{i=1}^{d} 2^{(n-i)} , \]

where \( n \) is the data set number.

For example, \( 6 = 2^{(2-1)} \cdot 2^{(3-1)} \) 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

<table>
<thead>
<tr>
<th>Element</th>
<th>Molality</th>
<th>Pressure</th>
</tr>
</thead>
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1.0000, 1.0000
-2, 2, 0, 14

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SO₃(G) -89.7786 -86.7094
Cu⁺²⁺ 15.6300 15.7317
Cu⁺⁺ 11.9450 11.0901
Cu₂(SO₄)²⁻ 162.3104 155.7567
Cu₂(SO₃)²⁻ 92.2243 87.8581
Z₂O   -6.5160 -6.1670
Z₂O₂⁻ 2.9113 4.2276
Z₂O₃   -128.5529 -125.6145
Z₂O₄⁻ 177.9474 171.0575
Z₃O₃⁻ 126.1208 122.2317
Z₃O₄⁻ 180.6580 175.4083
Z₃O₅⁻ 175.2501 169.3171
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SO₅⁻ 188.0263 180.6896
SO₇⁻ 231.6000 223.3179
SO₈⁻ 266.4866 257.3452
SO₉⁻ 244.8178 236.2948
**EpH Case 1: Metal Corrosion in Fe-H₂O-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-H₂O-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:

1. **Corrosion area**: Formation of ions means that metal dissolves into an aqueous solution. For example, Fe( 3a), Fe( 2a), FeO₂⁺(a) and HFeO₂⁻(a)-ions in an Fe-H₂O-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 Al₂O₃ on aluminium or TiO₂ 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-H₂O-system for EpH-diagram at 25 °C.
Fig. 2. Eh-pH Diagram of Fe-H₂O-system at 25 °C. Molality of Fe is 10⁻⁶ M.
EpH Case 2: Corrosion Inhibitors in Fe-Cr-H$_2$O-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$_3$O$_4$), hematite (Fe$_2$O$_3$) and chromic oxide (Cr$_2$O$_3$).

The inhibitor behavior of chromates may be illustrated with Eh-pH-diagrams. The Fe-Cr-H$_2$O-system specifications are shown in Fig. 3. The calculation results for Fe-H$_2$O and Fe-Cr-H$_2$O-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$_2$O$_3$ and Cr$_2$FeO$_4$ 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$_2$O-system for EpH-diagram at 100 and 300 $^\circ$C.
Fig. 4. Fe-H₂O-system at 100°C. Molality: Fe 10⁻² M, pressure 1 bar.
Fig. 5. Fe-Cr-H$_2$O-system at 100°C. Molalities: Fe and Cr 10$^{-2}$ M, pressure 1 bar.
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 \( \text{nO} \) 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 \( \text{nO} \) and \( \text{n( 2a)} \) areas. The dissolution of the \( \text{nO} \) 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.

\[
\text{ZnO} + 2\text{H}(\text{a}) \rightarrow \text{Zn}(\text{2a}) + \text{H}_2\text{O}
\]

In caustic conditions zinc may be obtained in solution by the formation of the anion complex \( \text{nO}_2(-2a) \). The leaching reaction may be described by equation (2).

\[
\text{ZnO} + \text{H}_2\text{O} = \text{nO}_2(-2a) + 2\text{H}(\text{a})
\]

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 \( \text{nS} \) which has wide stability area. This will lead to the formation of hydrogen sulfide gas and ions according to reaction (3).

\[
\text{ZnS} + 2\text{H}(\text{a}) \rightarrow \text{Zn}(\text{2a}) + \text{H}_2\text{S(g)} + 2\text{e}^-
\]

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.

\[
\text{ZnS} + 4\text{H}_2\text{O} = \text{nS} + \text{HSO}_4(-\text{a}) + 7\text{H}(\text{a}) + 8\text{e}^-
\]

\[
\text{ZnS} + 4\text{H}_2\text{O} = \text{nS} + \text{SO}_4(-2\text{a}) + 8\text{H}(\text{a}) + 8\text{e}^-
\]

The HSC database contains a lot of species which may have a long formation time. Normally it is wise to select only such species which are identified in real solutions for chemical system specifications. 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-H2O-system specifications.
Fig. 7. Zn-H$_2$O-system at 25 °C. Diagram is based on specifications in Fig. 6.
Fig. 8. n-S-H₂O-system specifications, only identified species included
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Fig. 9. n-S-H$_2$O-system specifications, all species included.
Fig. 10. $\text{n-S-H}_2\text{O-system at 25 }^\circ\text{C based on specifications in Fig. 8.}$
Fig. 11. S–H$_2$O-system at 25 °C based on specifications in Fig. 8.
Fig. 12. Zn-S-H$_2$O-system at 25 °C based on specifications in Fig. 9.
Fig. 13. S-n-H₂O-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 (Cr₂O₃, 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 Objects**

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 Object 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.
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.
2. Using the Object Editor

Another method of creating and modifying objects is to use the Object Editor (Show Object Editor from the menu). The Object Editor consists of three sheets: lines, shapes and labels. 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 blue foreground color, may be changed manually by typing directly in the cell, for example, the coordinates of a rectangle. The cells with black foreground color, 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.
A created graphical layout may be useful in future diagrams too, therefore HSC 5.0 allows the user to save the layout as an object (.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.
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.
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.
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.
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.
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.
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 20.3. Editing and Combining Diagrams 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 vector (.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.

![Image Properties Dialog](image.png)

Figure 10: Raster image properties dialog.

It is now also possible to **combine diagrams** (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 diagrams** (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.
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: Combining diagrams using the HSC Combine Editor.
21. PHASE STABILITY DIAGRAMS

The phase stability diagrams show stability (predominance) 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 $p_i$ of gas $i$ in a gas mixture is defined by equation (1):

$$ p_i = x_i \cdot P $$

where $x_i$ 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

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.

Fig. 1. Input data for Tpp phase stability diagrams.
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.](image)

### 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 O₂(g), S₂(g), SO₂(g), Cl₂(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 Na₂S₂, 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

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. 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.
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.
**Fig. 2.** Calculation of the species composition in column D using the elemental composition in row 3 by Solve.
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.
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$_2$O$_3$, 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.

Quite 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.
### Fig. 5. Calculation of the mixture composition of three raw materials.

<table>
<thead>
<tr>
<th>Species</th>
<th>Element</th>
<th>Target Amount (kg)</th>
<th>Content wt.%</th>
<th>Al wt.%</th>
<th>As wt.%</th>
<th>Ca wt.%</th>
<th>Co wt.%</th>
<th>Cu wt.%</th>
<th>Fe wt.%</th>
<th>Ni wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuFeS2</td>
<td>Cu</td>
<td>3.62</td>
<td>100.00</td>
<td>3.18</td>
<td>0.61</td>
<td>2.61</td>
<td>0.32</td>
<td>14.03</td>
<td>34.27</td>
<td>0.82</td>
</tr>
<tr>
<td>NiS2S3</td>
<td>Ni</td>
<td>15</td>
<td>100.00</td>
<td>3.18</td>
<td>0.61</td>
<td>2.61</td>
<td>0.32</td>
<td>14.03</td>
<td>34.27</td>
<td>0.82</td>
</tr>
<tr>
<td>CoS</td>
<td>Co</td>
<td>5</td>
<td>100.00</td>
<td>3.18</td>
<td>0.61</td>
<td>2.61</td>
<td>0.32</td>
<td>14.03</td>
<td>34.27</td>
<td>0.82</td>
</tr>
<tr>
<td>As2S3</td>
<td>As</td>
<td>1.00</td>
<td>1.00</td>
<td>0.32</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnS</td>
<td>Zn</td>
<td>2.00</td>
<td>1.00</td>
<td>0.32</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>Ca</td>
<td>3.63</td>
<td>2.61</td>
<td>0.32</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al2O3</td>
<td>Al</td>
<td>6.00</td>
<td>3.18</td>
<td>0.32</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO2</td>
<td>Si</td>
<td>7.00</td>
<td>3.18</td>
<td>0.32</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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 some cases, preliminary guess values are needed to help the iteration routine to find the correct answer.

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.*

![Composition conversions](image)

**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.
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

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 11. Heat and Material Balance), 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 process points, point 1 being the starting point and point 2 the end point. The calculator then calculates the absolute values for the two points and then the difference 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 "Line" from the menu. However, this line does not necessarily represent the actual process path, 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 first 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 first 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 first 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 "Restart all" 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 dry 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 \( T = 25 \, ^\circ C \) and \( p = 1 \) bar. This differs from what is normally found in steam tables, where the reference point is \( T = 0.01 \, ^\circ C \) and \( p = 0.0061 \) bar (triple point for water). This means that only the differences in enthalpy and entropy are important, since they are independent of the choice of reference points. Point 2 is therefore described as the triple point, 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 \( 25 \, ^\circ C \) at constant pressure. Therefore the specific enthalpy is zero at \( 25 \, ^\circ C \).

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.

**Other important terms**

1. **Isentropic process**
   If the entropy is constant through a process, i.e. the entropy difference is zero, the process is called *isentropic*. 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 *compressor* or *pump* is defined as
   \[
   \eta_{c,p} = \frac{\Delta_h}{\Delta_s},
   \]
   where \( \Delta_h \) is the *real* difference and \( \Delta_s \) is the *isentropic* difference. The isentropic efficiency for a *turbine* is defined as
   \[
   \eta_{s,t} = \frac{\Delta_s}{\Delta_s}.
   \]
   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

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 total mixture is liquid water. The enthalpy difference is 290 kJ and the process therefore endothermic. The entropy difference is 1.079 kJ/°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

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 total 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: Steam turbine process.

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, $\eta_{is} = \frac{-10633}{-12903} = 0.82$. 
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 $S(X_{\text{bar}}P)$, where $S$ denotes the species, $X$ the pressure (partial) in bars and $P$ 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 $H_2O(0.01\text{bar})$, $H_2O(0.01\text{barg})$, $H_2O(100\text{bar})$, $H_2O(100\text{barg})$, etc. Note that if the phase is not specified, it may be either solid or liquid depending on the temperature. For $su\ erecritica\ stca$ , that is for $T \mu_373.946^\circ\ C$, a gaseous phase is used for $p \leq 220.64\ \text{bar}$ and a liquid phase for $p \geq 220.64\ \text{bar}$, although the two phases are impossible to separate in reality.

Table 1 shows the pressure-corrected water species currently found in the HSC database.

<table>
<thead>
<tr>
<th>Pressure  bar</th>
<th>Solid liquid species (ice water)</th>
<th>Gaseous species (steam)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>$H_2O(0.01\text{bar})$</td>
<td>$H_2O(0.01\text{barg})$</td>
</tr>
<tr>
<td>0.05</td>
<td>$H_2O(0.05\text{bar})$</td>
<td>$H_2O(0.05\text{barg})$</td>
</tr>
<tr>
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<td>$H_2O(0.1\text{bar})$</td>
<td>$H_2O(0.1\text{barg})$</td>
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<tr>
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<td>$H_2O(0.5\text{barg})$</td>
</tr>
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</tr>
<tr>
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<tr>
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</tr>
<tr>
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</tr>
<tr>
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<td>$H_2O(30\text{bar})$</td>
<td>$H_2O(30\text{barg})$</td>
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</tr>
<tr>
<td>100</td>
<td>$H_2O(100\text{bar})$</td>
<td>$H_2O(100\text{barg})$</td>
</tr>
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<td>$H_2O(200\text{bar})$</td>
<td>$H_2O(200\text{barg})$</td>
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<tr>
<td>300</td>
<td>$H_2O(300\text{bar})$</td>
<td>$H_2O(300\text{barg})$</td>
</tr>
<tr>
<td>400</td>
<td>$H_2O(400\text{bar})$</td>
<td>$H_2O(400\text{barg})$</td>
</tr>
<tr>
<td>500</td>
<td>$H_2O(500\text{bar})$</td>
<td>$H_2O(500\text{barg})$</td>
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<td>$H_2O(800\text{bar})$</td>
<td>$H_2O(800\text{barg})$</td>
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<tr>
<td>900</td>
<td>$H_2O(900\text{bar})$</td>
<td>$H_2O(900\text{barg})$</td>
</tr>
<tr>
<td>1000</td>
<td>$H_2O(1000\text{bar})$</td>
<td>$H_2O(1000\text{barg})$</td>
</tr>
</tbody>
</table>

Supercritical pressures

Table 1 pressure corrected species currently found in the database.

Since water is in a liquid form at the reference temperature of $25^\circ\ C$ for pressures higher than $0.032\ \text{bar}$, the Cp functions for steam follow the saturated steam curve below the boiling point. This means that it is not constant below this point and thus the pressure value in the species name, i.e. $X$ in $H_2O(X\text{barg})$, 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 total and entropy curves below the boiling point will not join as expected and therefore these curves are not comparable with each other only for values above or equal to the boiling point. 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**: Cp functions for steam at different pressures.
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 triple point 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 absolute 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

$$H' = H_f + \int_{298.15}^{T} \left( \frac{H}{T} \right) dT + \sum_{tr} H'_{tr},$$

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

$$S' = S_0 + \int_{298.15}^{T} \left( \frac{S}{T} \right) dT + \sum_{tr} S'_{tr},$$

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

$$C_p = A(p) + B(p) \cdot 10^{-3} + C(p) \cdot 10^{-5} \cdot T^2 + D(p) \cdot 10^{-6} \cdot T^2,$$

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

$$p = 0.1 \cdot e^{(11.78(173.279) - 43.15)}$$

where $T$ is the temperature in K and $p$ the pressure in MPa. The pressure for a saturated as so id i ture is

$$p = 10^{(0.5380997 \cdot 2663.91 \cdot 0.01)} \cdot 10000,$$

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

$$T = -0.009 + 273.16,$$
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

$$\Delta H_{\text{const}} = \left(1 - \alpha_{\text{ice}}\right)\nu_{\text{ice}} \left(T - T_f\right),$$

where $T_f$ is the temperature at the freezing point, $p_f$ is the pressure at the freezing point, $\alpha_{\text{ice}}$ is the coefficient of thermal expansion and $\nu_{\text{ice}}$ 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)

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.

Fig. 1. Units Conversion module.
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)**

![Units Database](image)

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: Add Ins do not or under ear ier ce versions)
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.

![Add-Ins](image)

**Figure 1** Add-ins activated under Excel.

**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 containing 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  \( \text{H(A1;A2)} \) 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).

<table>
<thead>
<tr>
<th>General Functions</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>UNITS(T;E)</td>
<td>Changes the current units, T= C, K and E= Mcal, M, kWh.</td>
</tr>
<tr>
<td>BAL(Equation)</td>
<td>Balances given equation.</td>
</tr>
<tr>
<td>SPECIES(DBNo, Position)</td>
<td>Returns species in database DBNo and given position.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Species Functions</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(Species T)</td>
<td>Returns the enthalpy (per mol) of the species at T (temperature).</td>
</tr>
<tr>
<td>S(Species T)</td>
<td>Returns the entropy (per mol) of the species at T.</td>
</tr>
<tr>
<td>CP(Species T)</td>
<td>Returns the heat capacity at constant pressure (per mol) of the species at T.</td>
</tr>
<tr>
<td>G(Species T)</td>
<td>Returns the Gibbs energy (per mol) of the species at T.</td>
</tr>
<tr>
<td>HKG(Species T)</td>
<td>Returns the enthalpy (per kg) of the species at T.</td>
</tr>
<tr>
<td>HNM3 or HCM(Species T)</td>
<td>Returns the enthalpy (per Nm) of the species at T.</td>
</tr>
<tr>
<td>HLAT(Species T)</td>
<td>Returns the latent enthalpy (per mol) of the species at T.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reaction Equation Functions</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(Equation T)</td>
<td>Returns the enthalpy (per mol) of the reaction equation at T.</td>
</tr>
<tr>
<td>S(Equation T)</td>
<td>Returns the entropy (per mol) of the reaction equation at T.</td>
</tr>
<tr>
<td>CP(Equation T)</td>
<td>Returns the heat capacity difference (per mol) of the reaction equation at T.</td>
</tr>
<tr>
<td>G(Equation T)</td>
<td>Returns the Gibbs energy (per mol) of the reaction equation at T.</td>
</tr>
</tbody>
</table>
HSC Chemistry® 5.0

Peter Bjorklund  June 28, 2002

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
CPFUNTION(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  Description of all currently available HSC add-in functions.

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.
### Figure 2

![Excel Add-in Example](image.png)

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.

<table>
<thead>
<tr>
<th>Functions</th>
<th>Return Value</th>
<th>Arguments</th>
<th>Arg. 1</th>
<th>Arg. 2</th>
<th>Arg. 3</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>General</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UNITS(E;E)</td>
<td></td>
<td>C</td>
<td></td>
<td></td>
<td></td>
<td>Changes</td>
</tr>
<tr>
<td>BAL(Equation)</td>
<td>2H₂(g) + O₂(g) = 2H₂O(l)</td>
<td>C</td>
<td>Mca1</td>
<td></td>
<td></td>
<td>Balanced</td>
</tr>
<tr>
<td>SPECIES(Equation;I)</td>
<td>Al(CH₃COO)₂(t=+)</td>
<td>2</td>
<td>200</td>
<td></td>
<td></td>
<td>Species f</td>
</tr>
<tr>
<td><strong>Species</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(Species;I)</td>
<td>-93.357</td>
<td>CO₂(g)</td>
<td></td>
<td>100</td>
<td></td>
<td>Enthalpy</td>
</tr>
<tr>
<td>S(Species;I)</td>
<td>20.766</td>
<td>H₂O(l)</td>
<td></td>
<td>100</td>
<td></td>
<td>Entropy</td>
</tr>
<tr>
<td>CP(Species;I)</td>
<td>44.245</td>
<td>CH₄(g)</td>
<td></td>
<td>100</td>
<td></td>
<td>Heat capt</td>
</tr>
<tr>
<td>G(Species;I)</td>
<td>-11.294</td>
<td>H₂(g)</td>
<td></td>
<td>100</td>
<td></td>
<td>Gibbs sm</td>
</tr>
<tr>
<td>HKG(Species;I)</td>
<td>-0.264</td>
<td>FeS</td>
<td></td>
<td>100</td>
<td></td>
<td>Enthalpy</td>
</tr>
<tr>
<td>HNM3 or HCM(Species;I)</td>
<td>0.023</td>
<td>O₂(g)</td>
<td></td>
<td>100</td>
<td></td>
<td>Enthalpy</td>
</tr>
<tr>
<td>HLAT(Species;I)</td>
<td>0.000</td>
<td>H₂O(l)</td>
<td></td>
<td>25</td>
<td></td>
<td>Enthalpy</td>
</tr>
<tr>
<td><strong>Reaction equation</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(Equation;I)</td>
<td>-115.952</td>
<td>2H₂(g) + O₂(g) = 2H₂O(l)</td>
<td>100</td>
<td></td>
<td></td>
<td>Enthalpy</td>
</tr>
<tr>
<td>S(Equation;T)</td>
<td>-22.259</td>
<td>2H₂(g) + O₂(g) = 2H₂O(l)</td>
<td>100</td>
<td></td>
<td></td>
<td>Entropy c</td>
</tr>
<tr>
<td>CP(Equation;I)</td>
<td>-4.744</td>
<td>2H₂(g) + O₂(g) = 2H₂O(l)</td>
<td>100</td>
<td></td>
<td></td>
<td>Heat capt</td>
</tr>
<tr>
<td>G(Equation;I)</td>
<td>-107.631</td>
<td>2H₂(g) + O₂(g) = 2H₂O(l)</td>
<td>100</td>
<td></td>
<td></td>
<td>Gibbs sm</td>
</tr>
<tr>
<td>HKG(Equation;I)</td>
<td>-3.218</td>
<td>2H₂(g) + O₂(g) = 2H₂O(l)</td>
<td>100</td>
<td></td>
<td></td>
<td>Enthalpy</td>
</tr>
<tr>
<td>K(Equation;I)</td>
<td>1.106E+63</td>
<td>2H₂(g) + O₂(g) = 2H₂O(l)</td>
<td>100</td>
<td></td>
<td></td>
<td>Equilibrium</td>
</tr>
<tr>
<td><strong>Iteration (reverse)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TATH(Species;H)</td>
<td>410.037</td>
<td>CO₂(g)</td>
<td></td>
<td></td>
<td></td>
<td>Temporal</td>
</tr>
<tr>
<td>TATS(Species;S)</td>
<td>430.915</td>
<td>CO₂(g)</td>
<td></td>
<td></td>
<td></td>
<td>Temporal</td>
</tr>
<tr>
<td>TATCP(Species;CP)</td>
<td>114.756</td>
<td>CO₂(g)</td>
<td></td>
<td></td>
<td></td>
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<td>CO₂(g)</td>
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<td>Temporal</td>
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<td></td>
<td>0.78</td>
<td>100</td>
<td>Enthalpy</td>
</tr>
</tbody>
</table>
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:

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.