

28. HSC - DATABASES

HSC Chemistry can handle two active databases simultaneously, denoted as the **Own** and the **Main** database. The current version of the Main database contains thermochemical data of more than 20000 species, including pure substances and aqueous species. The Own database is reserved for the data specified by the user. It is empty when the user gets the software, but up to 60000 species can be saved into one Own database.

All the calculation options of HSC Chemistry utilize the same databases, and therefore they are an essential part of the program. In the database the enthalpy (H), entropy (S) and heat capacity (C) values of the elements and compounds are saved together with a variety of additional information.

Note that HSC Chemistry primarily uses the Own database, file OwnDB6.HSC, if the same species is found in both files. It is not recommended, therefore, to edit the Main database, file MainDB6.HSC. It would be more convenient to save new data into the Own database. Any valid file names and directories can be used for the OwnDB6.HSC and MainDB6.HSC database files, and both can easily be changed.

All HSC database files may usually be found from \HSC6\Databases folder. Old MainDB3.HSC, MainDB4.HSC and MainDB5.HSC files are included with the new MainDB6.HSC database file. **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 calculation results. See Chapter 31 for details.**

28.1 Database Menu

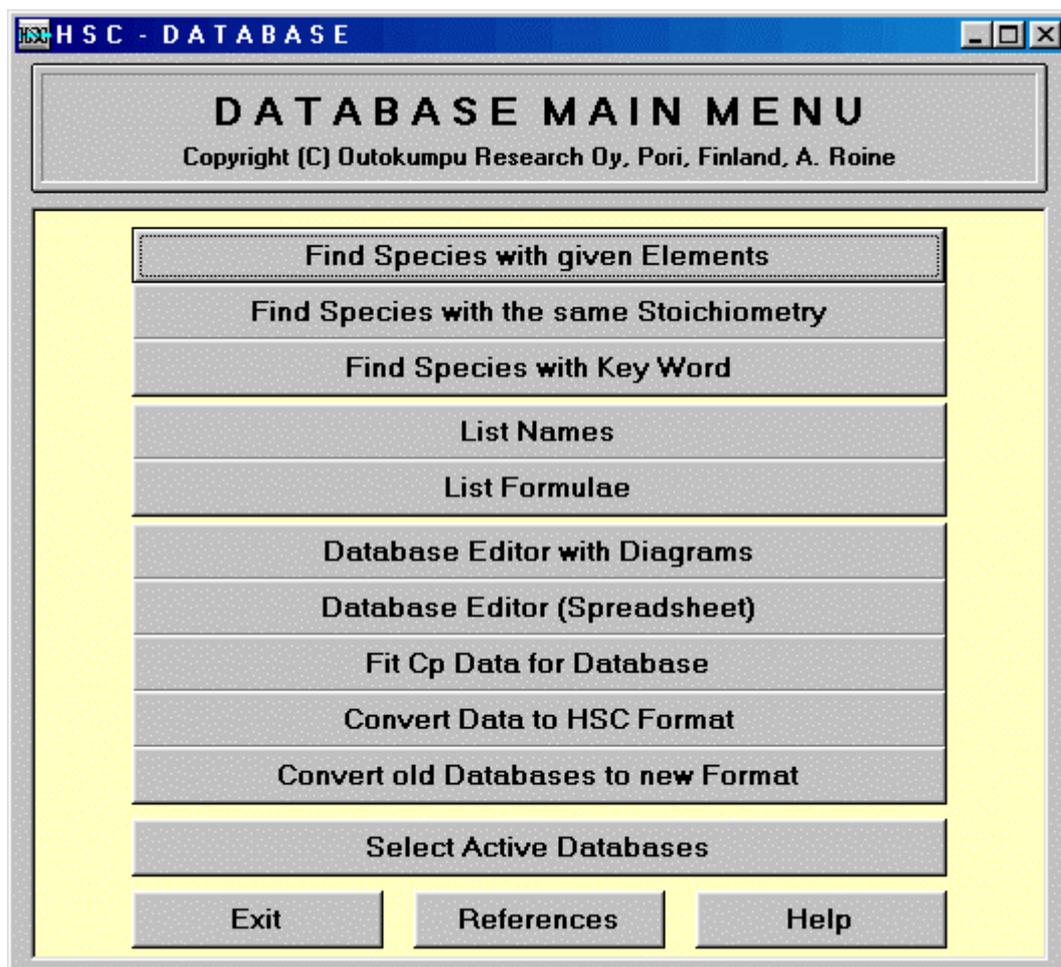


Fig. 1. The Database Menu.

The Database Menu, Fig. 1, makes it possible to search for the species on the basis of given elements, list species, print data, edit old data, save new data, etc. It can also convert thermochemical data to the H, S and Cp formats for saving in the HSC-databases. You can select these options by pressing the appropriate buttons in the Database Menu.

28.2 Notations and Abbreviations used in the Database

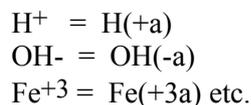
The chemical formulae are written using a standard formalism and as briefly as possible. However, there are some exceptions, because superscripts and subscripts cannot be used. These will be discussed in the following paragraphs in more detail. See also Chapter 34. *Species*, for a complete list of all the species in the Main database.

Thermodynamic data for the solid and liquid phases of a substance is usually saved under the same formula name: for example, the formula Cu contains data for solid (fcc) and liquid copper. Gaseous substances, however, have their own records and their names have the extension (g), for example Cu(g).

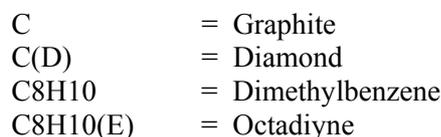
If the extension (l) is added to a chemical formula and such a substance is not found in the database files, HSC automatically searches the records for the liquid phase, extrapolates its H and S to 298.15 K, using the Cp data of the liquid, and saves the results with the extension (l) in the OWNDB6.HSC file. This permits extrapolation of the liquid data to lower temperatures. Be careful, however, when utilizing the extrapolated values as the method is purely mathematical, especially if the temperature of your system is far from the stable liquid temperature range of the species considered.

Exceptions to the normal chemical notation are the formulae, which start with a stoichiometric number. An extra * character (for example *2MgO*SiO2) must be added at the beginning of such a formula.

Because different composition coordinates have been used for aqueous species in the HSC database, they must be distinguished from other species with a similar stoichiometry. This is done using the suffix (ending "a") with uncharged aqueous molecules, radicals and ions, for example:



HSC also calculates the electronic neutrality of the system and therefore the suffix (ending) of an ionized species must also contain the charge, for example H(+a), OH(-a), Fe(+3a), etc. Ionized gaseous species are written using the similar formalism: Ar(+g), H2(+g), etc. Endings can also be used to distinguish compounds with a similar chemical formula, for example, different allotropic forms, organic isomers, etc. Here are some examples:



Note that the endings must be inside parentheses. However, the use of lower-case letters s, l, g or a is not allowed, because they are reserved to distinguish the states of matter, i.e. the solid, liquid, gas and aqueous states.

28.2.1 HSC Formula Syntax

An easy and illustrative specification method of species is needed in thermochemical calculations. In inorganic chemistry this is not usually a problem, because traditional formulae are quite short and illustrative. However, problems arise with some natural minerals with quite long and complicated formulae and especially with many extremely complicated organic species, for example:



Species could be identified using chemical names, but these are very clumsy to use, Chemical Abstract numbers are not illustrative, structural formulae could be very long and cross formulae are not enough. These are the main reasons for the formula syntax which is used in HSC Chemistry 6.0. The basic idea of this syntax is described in the previous Chapter 28.2 and in Fig. 2. More details are given in the following paragraphs as well as in Chapter 29. *Hydrocarbons* for the organic species.

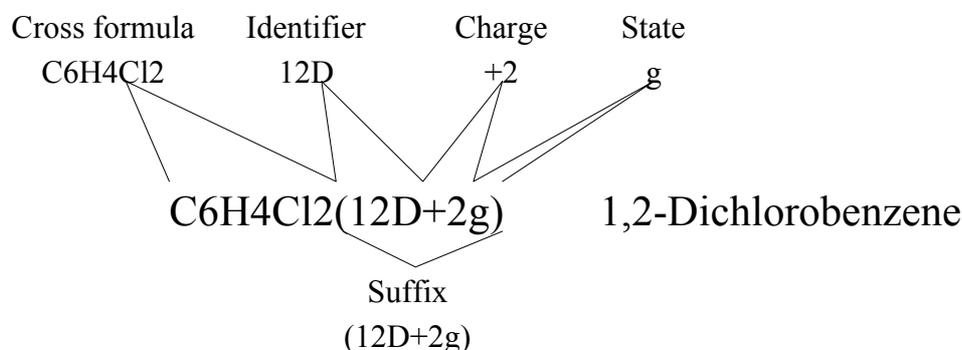


Fig. 2. The chemical formula syntax used in HSC Chemistry 6.0.

1. The maximum length of a formula is 24 characters. With simple inorganic species the traditional formula syntax can be used. However, if the structural formula with suffix is longer than 24 characters, then a cross formula must be used, see Fig. 2.
2. Superscripts and subscripts cannot be used.
3. Inner parentheses are not allowed, for example:
 $\text{H}_2(\text{Sn}(\text{OH})_6)$ is not a valid formula, use $\text{H}_2\text{Sn}(\text{OH})_6$, instead.
4. The last parentheses, at the end of the formula, are always reserved for the suffix, see Fig. 2. Therefore you cannot use the formula $\text{AlO}(\text{OH})$. Please write it in one of the following ways: AlO_2H , AlO^*OH or $\text{AlO}^*(\text{OH})$.
5. The last two characters specify the state if the last character of the formula is “)”. E.g. gas, liquid and aqueous identifiers must be at the end of the suffix. See the following examples and Fig. 2:

As(g)	Monoatomic arsenic gas
O ₂ (g)	Diatomic oxygen gas
Fe(l)	Liquid iron
OH(-a)	Aqueous OH ion (charge = -1)
6. Gaseous species always need the “g)” suffix. The state identifier “s)” is not used for the solid species. Normally the liquid species are also written without the “l)” suffix, but sometimes an “l)” suffix must be added to the formula. See Chapter 28.11 for details, because incorrect selections may cause big errors.

- The charge of an ion must be written just before the state identifier with the correct plus or minus sign. For example: H(+a), SO₄(-2a), O₂(-g), etc., see Fig. 2. The phase code **ao** is used in the database for undissociated aqueous species (ions) and **ai** for aqueous electrolyte (neutral), which are formed from undissociated aqueous species. Note that the suffix “ia)” is used for the **ai** species and “a)” for **ao** ones.
- Identical cross formulae must be separated from each other using the identifier just before the charge and state identifiers, see Fig. 2. These identifiers should be constructed from the name of the substance. Substances with the same composition, but different crystal structure, can easily be separated from each other using only one character identifier. Note that the most common form of the substance is written without any suffix. For example:

C	Carbon
C(D)	Diamond
FeS ₂	Pyrite
FeS ₂ (M)	Marcasite

The situation with organic substances is not as simple because there are a number of substances with the same cross formula. Therefore longer identifiers must be used, but it is recommended to keep the length of the identifier to three characters, see Fig. 2. In many cases the identifier must be longer, for example:

C ₇ H ₆ N ₂ O ₄ (26DNTg)	2,6-Dinitrotoluene
C ₇ H ₆ N ₂ O ₄ (34DNTg)	3,4-Dinitrotoluene

Numbers can also be used in the identifier, but the last character of the identifier cannot be a number, because it might be confused with a charge, for example: CH₂ClBr(CBM+2g), where +2 is a charge, see also Fig. 2 and Chapter 29. *Hydrocarbons*.

- The formula before the suffix can be written in many ways, usually the same syntax as in the original data source is used in the main database of HSC. However, in some cases there is no established and settled syntax for all the formulae and therefore sometimes a different syntax has been used in the HSC 6.0 database, for example:

CaMgSiO ₄	=	CaO*MgO*SiO ₂	Calcium magnesium silicate
MgTi ₂ O ₅	=	MgO*2TiO ₂	Magnesium dititanium pentaoxide

The new **Find** option in the database menu can be used to display all the formulae with the same elements and stoichiometry, see Fig. 1. The formula can be written using nearly any conventional syntax to find the species with the same stoichiometry.

Another useful feature, which is in nearly all the calculation modules, is the possibility to check the name of any species in the database as well as collect formulae directly from the database, see Chapter 10. *Reaction equations*, Fig. 10.

- The formula cannot start with a number character. For example, 2MgO*SiO₂ is not a valid formula, because the reaction equation module may confuse the first “2” character with the stoichiometric coefficient in a reaction. Please add an asterisk “*” character onto the beginning of such a formula: i.e. *2MgO*SiO₂.

Please note that you can easily check the name and other data of a species in most of the HSC modules by double clicking the formula in the list or using the right mouse button.

28.3 Reference States

The reference state used in the databases is the most stable phase of the pure elements at 298.15 K and 1 bar. The enthalpy and entropy scales of the **elements** are therefore fixed in HSC Chemistry by defining:

$$H^\circ = 0 \text{ at } 25 \text{ }^\circ\text{C and 1 bar.}$$

$$S^\circ = 0 \text{ at } 0 \text{ K and 1 bar (absolute entropy scale, third law scale).}$$

Previously the standard pressure was one atm, but more recently 1 bar has been adopted. This has negligible effect on H, S and C_p values at 298.15 K.

The data of aqueous species is given for a theoretical 1 mol/kg H₂O solution at 25 °C and 1 bar, which is extrapolated from an infinite dilution on a molality scale. The aqueous ions have been saved using the conventions traditionally used in aqueous chemistry. The scale is fixed assuming that the enthalpy, entropy and heat capacity values, for a hydrogen ion (H⁺) at all temperatures, are zero in a hypothetical ideal, one molal solution (1 mol/kg H₂O), i.e.:

$$DH^\circ(\text{H}^+) = 0 \quad DS^\circ(\text{H}^+) = 0 \quad Cp(\text{H}^+) = 0$$

The different scales between aqueous ions and other substances in HSC database do not, however, cause inconveniences in the calculations, because HSC Chemistry makes the scale conversions automatically, if you remember to use the "a"-extension with the aqueous species, with the proper integer and sign for the charge, i.e., (+a), (-2a), etc. Note however that the phase code **ao** is used in the database for undissociated aqueous species (ions) and **ai** for aqueous electrolyte (neutral), which are formed from undissociated aqueous species.

28.4 Aqueous Ions

The thermodynamic properties of aqueous ions are traditionally given only at 25 °C, which limits the use of calculations to room temperatures. Therefore HSC Chemistry extrapolates the heat capacity values of such ions to higher temperatures by an empirical correlation, the Criss-Cobble method, if the **Criss-Cobble** option is selected. This method has been described in the following references¹¹⁻¹⁴.

The Criss-Cobble method is only used if the temperature coefficients of the heat capacity function are not given in the HSC database. It is not used if B, C and/or D are given together with A. By using this method, it is possible to extrapolate the heat capacity and estimate their values up to 300 °C. According to previous references in literature¹¹⁻¹⁴, the extrapolated C_p values have been found to be quite consistent with the experimental data available.

HSC Chemistry makes some modifications to the data of aqueous ions:

- The entropy scale of aqueous ions is changed to the "normal" absolute (Third law) entropy scale by subtracting 5 cal/(mol*K) from the hydrogen ion scale at 25 °C. This is "the experimental entropy value for hydrogen ions" in the absolute scale¹⁴. This conversion is needed for Criss-Cobble extrapolation and it is invisible for the user.
- The entropy values of aqueous ions contain the mixing entropy to a 1 molal solution. Therefore the entropy change $R \cdot \ln x_i = 1.987 \cdot \ln(1/55.51) = 7.981$ (cal/mol*K) may be subtracted from the entropy if a mole fraction scale is used for the aqueous solution. HSC introduces hypothetical "pure ion" entropies in the GIBBS-program, if the **Mixing Entropy Conversion** option is selected, Chapter 13.3 of the *Equilibrium module*, Fig. 5

There are two types of **neutral aqueous species** in the HSC 6.0 database:

1. **"ao"** as phase code: Data may not be calculated from the species.
2. **"ai"** as phase code: Data may be directly calculated from the species.

Phase code "ao" is used for undissociated aqueous species (usually ions) and "ai" for aqueous electrolyte (neutral) which is formed of undissociated aqueous species. The "ai" species has suffix "ia" in the HSC 6.0 database but suffix "a" in HSC 2.0 database. The number of "ai" species in HSC database is very small and most of them are from NBS 82 data source.

In the HSC Chemistry 6.0 these species may easily be separated without checking the Phase code from the database, because the "ai" species has a suffix "ia" in the MainDB6.HSC database. For example, MnCl₂(a) name has changed to MnCl₂(ia) because it's phase code in the database is "ai".

The enthalpy and entropy values of "ai" species may be calculated as a sum of its dissociated components, for example, enthalpy for MgSO₄(ia) is:

$$\text{MgSO}_4(\text{ia}) = \text{Mg}(+2\text{a}) + \text{SO}_4(-2\text{a}) = -465.960 + (-909.602) = 1375.562 \text{ kJ/mol}$$

This calculation procedure may not give exactly the same results as given for "ao" species in the HSC database due to the different original data sources for species. The H and S values for "ao" species such as MgSO₄(a) can not be calculated in the same way. **Note: It is recommended to use only "ao" species in the calculations.**

The reason for the differences in H, S and Cp values are usually because the HSC database is collected from 900 different data sources and there is lot of small differences with the original data for the same species in these sources. For example: HF(a), HF(ia), H(+a), F(-a) are from different sources.

28.5 Search Option

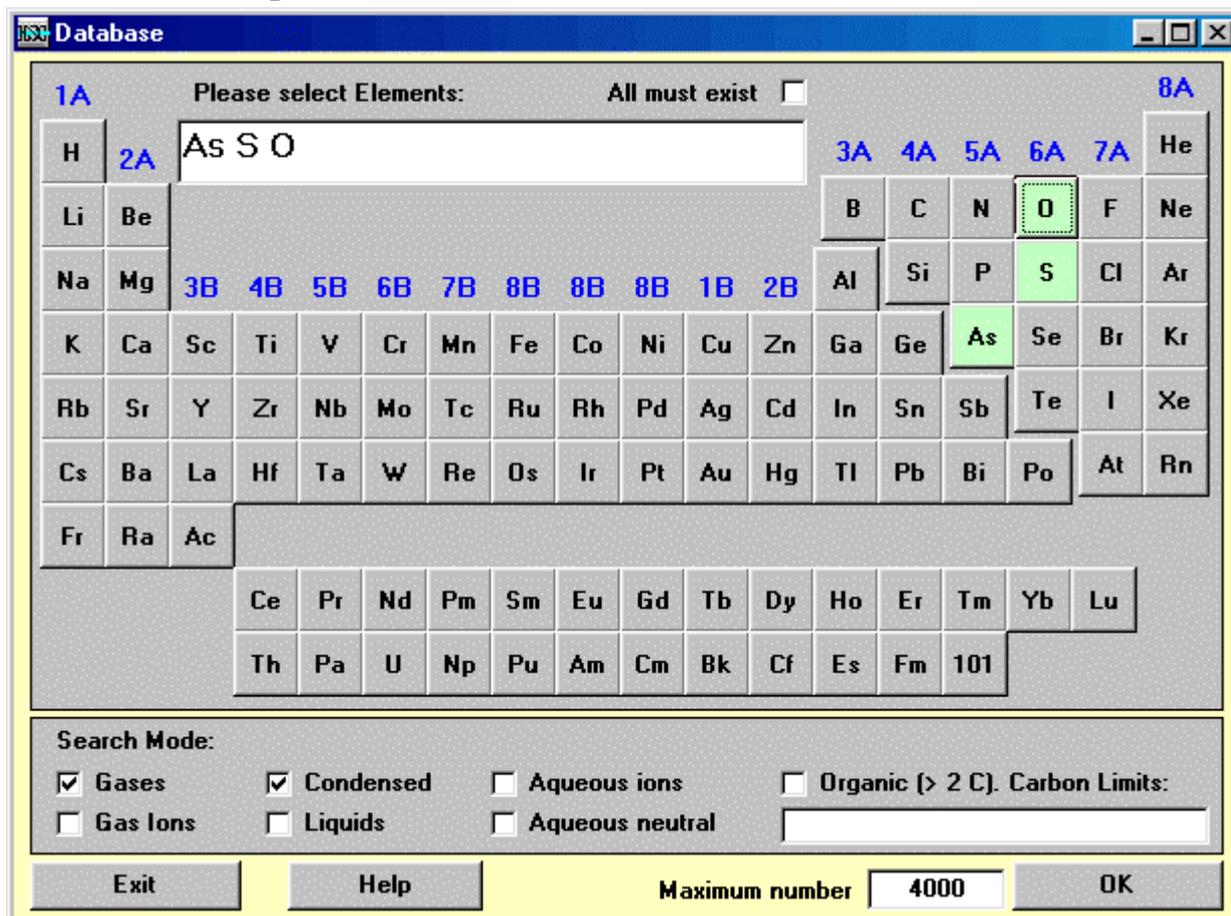


Fig. 3. Search for species containing given elements.

The HSC database menu offers two ways to find species from the databases. The first search option finds all the species, which contain *some* of the given elements, and species types can also be used as the search criteria. The second search option collects only those species, which contain *all* the given elements.

The first search option makes it possible to find all the species, which contain given elements in the HSC Chemistry's Own and Main databases. Use the following steps:

1. Select one or more **elements**, Fig. 3. Press the element buttons or type directly into the text box. Try for example As, S, O.
2. Select the substance groups, which you are interested in, from **Search Mode**. If you do not select the "**Organic**" option, all the species containing hydrogen together with more than 2 atoms of carbon will be ignored in the search. You can also set a limit for the number of carbon atoms in the species, for example 4, 6, 7 (up to 9 numbers may be specified).
Warning: In some cases inorganic species may also contain hydrogen and more than 2 atoms of carbon.
3. Press **OK** and you will see the species found, see Fig. 7.

28.6 Finding Species with the same Stoichiometry

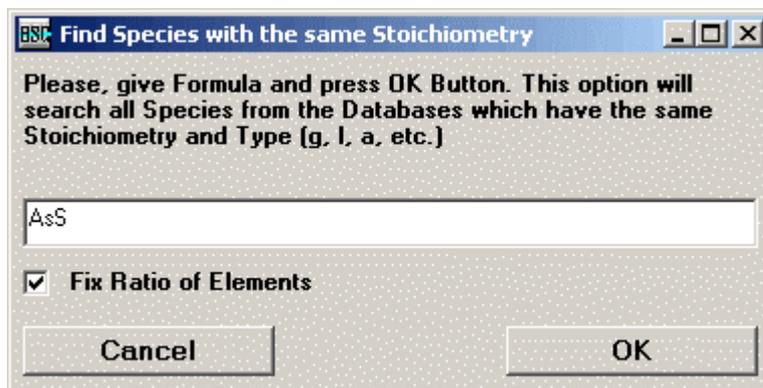


Fig. 4. Finding species from the databases.

This search option finds only those species, which contain all the given elements in the same proportion as in the given formula. This means that you can type the formula nearly any way you like, and elements can be written in any order. For example, if you type **SiO4FeFe** then you get the following species as a result:

*2FeO*SiO2	Fayalite
Fe2SiO4(B)	Beta fayalite
Fe2SiO4(G)	Gamma fayalite

If the **Fix Ratio of Elements** option is selected, Fig. 2, the program searches all the species with the same stoichiometry ratios. For example, if you type formula **AsS** into the input box, you might also get **As2S2**, **As3S3**, etc., see Fig. 5. If you do not select this option you get only **AsS**, **AsS(l)**, **AsS(g)**, etc.

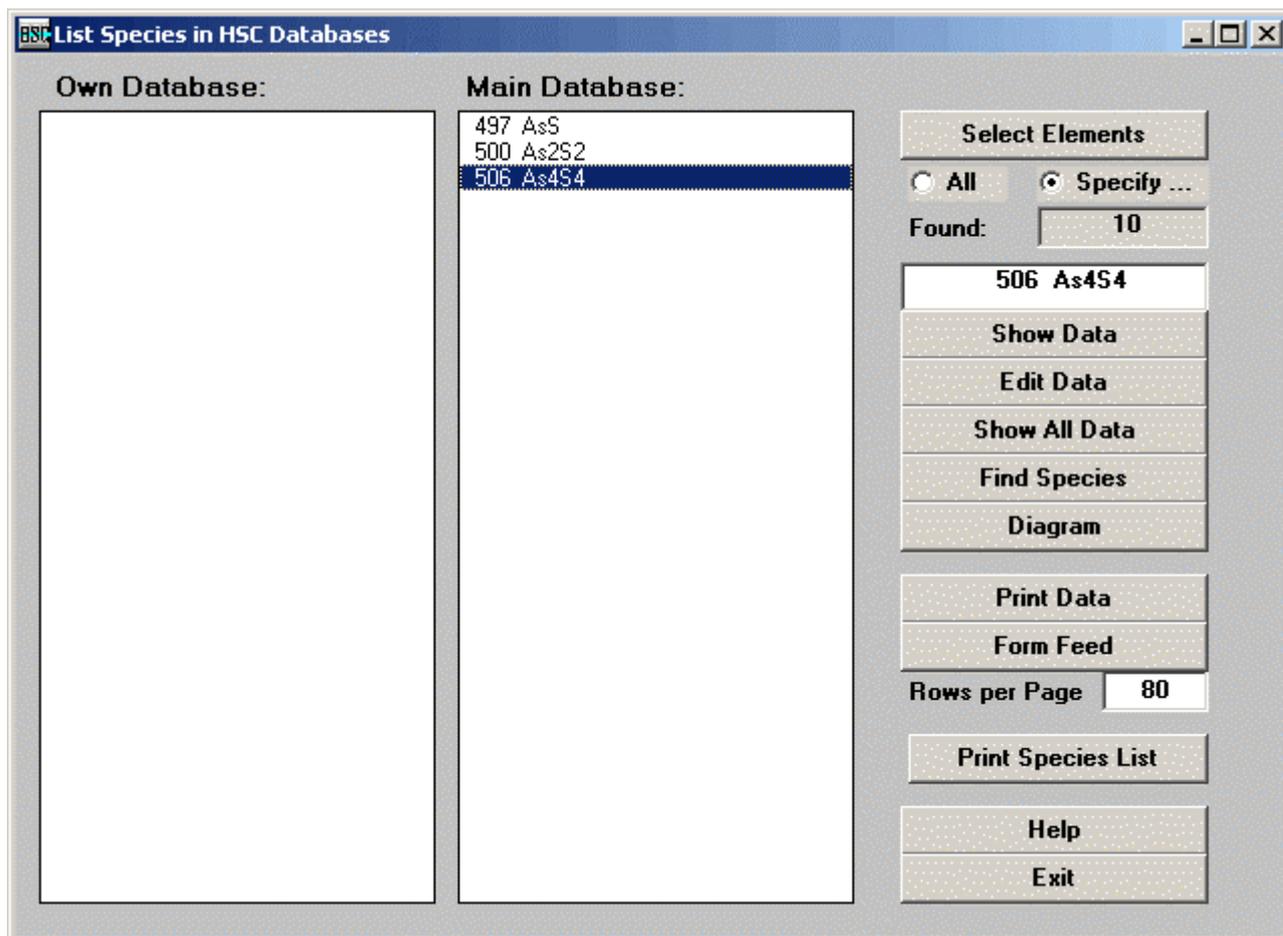


Fig. 5. Results of a search using AsS key word (formula). Note that you can see the names and data of the species by double clicking the species formulae.

28.7 Listing Species Names

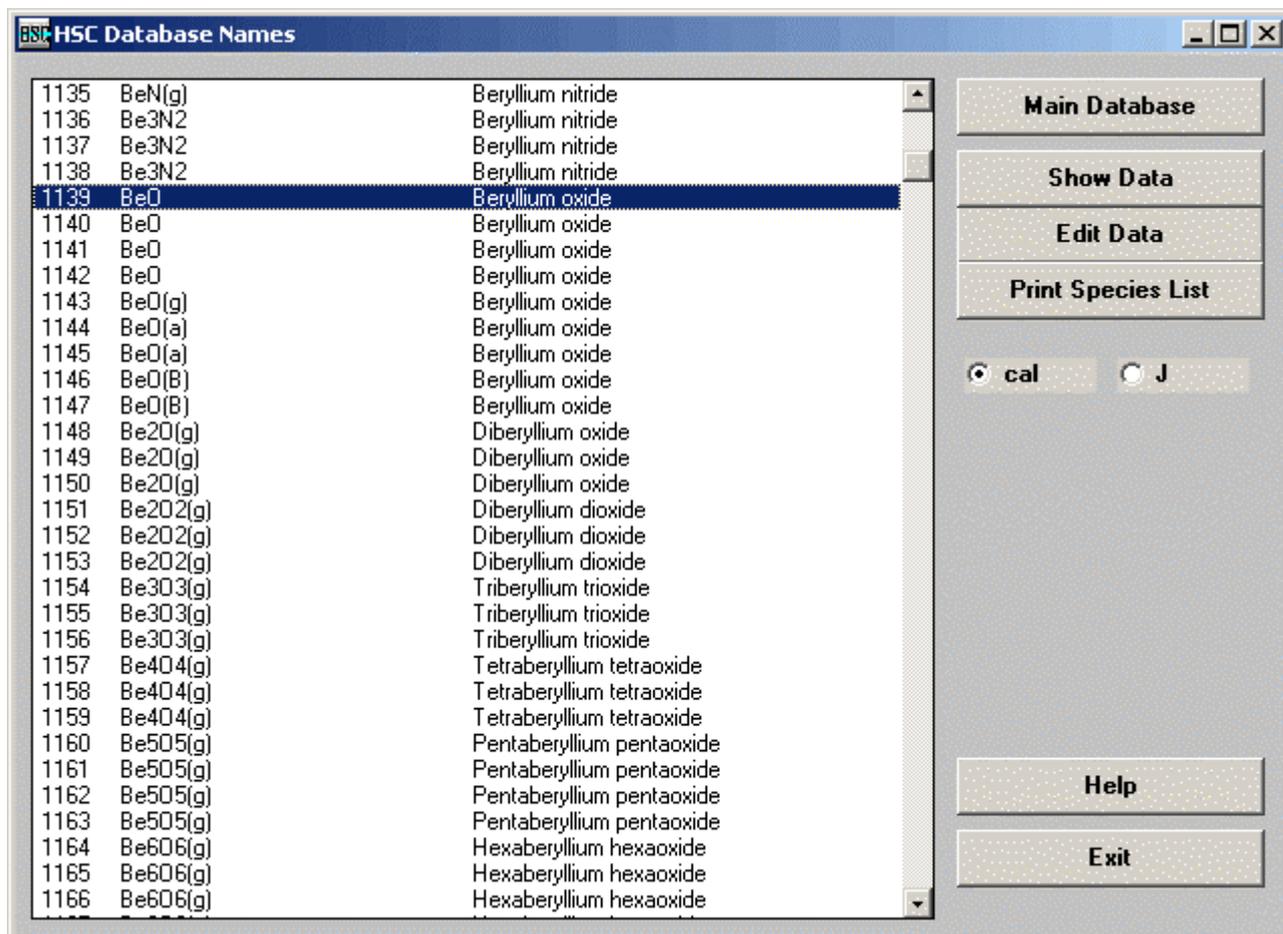


Fig. 6. List Species Names option.

With the List Names option you can retrieve a list of the species names, which exist in the Own or Main database. You may switch between the Own and Main database by pressing **Main Database**.

If you press **Show Data** you will see the thermochemical data of the species selected, see Fig. 6. You can also go directly to the edit option by pressing **Edit Data**, see Fig. 7. **Print Species List** enables you to print the list of the database species on paper.

An easy way to check the name and data of a species is to double click the formulae in the list using the mouse. This quickly shows the information of the species, see Chapter 10. *Reaction equations*, Fig. 10.

By pressing **Exit** you return to the Database Menu, see Fig. 1.

28.8 Listing Species Formulae

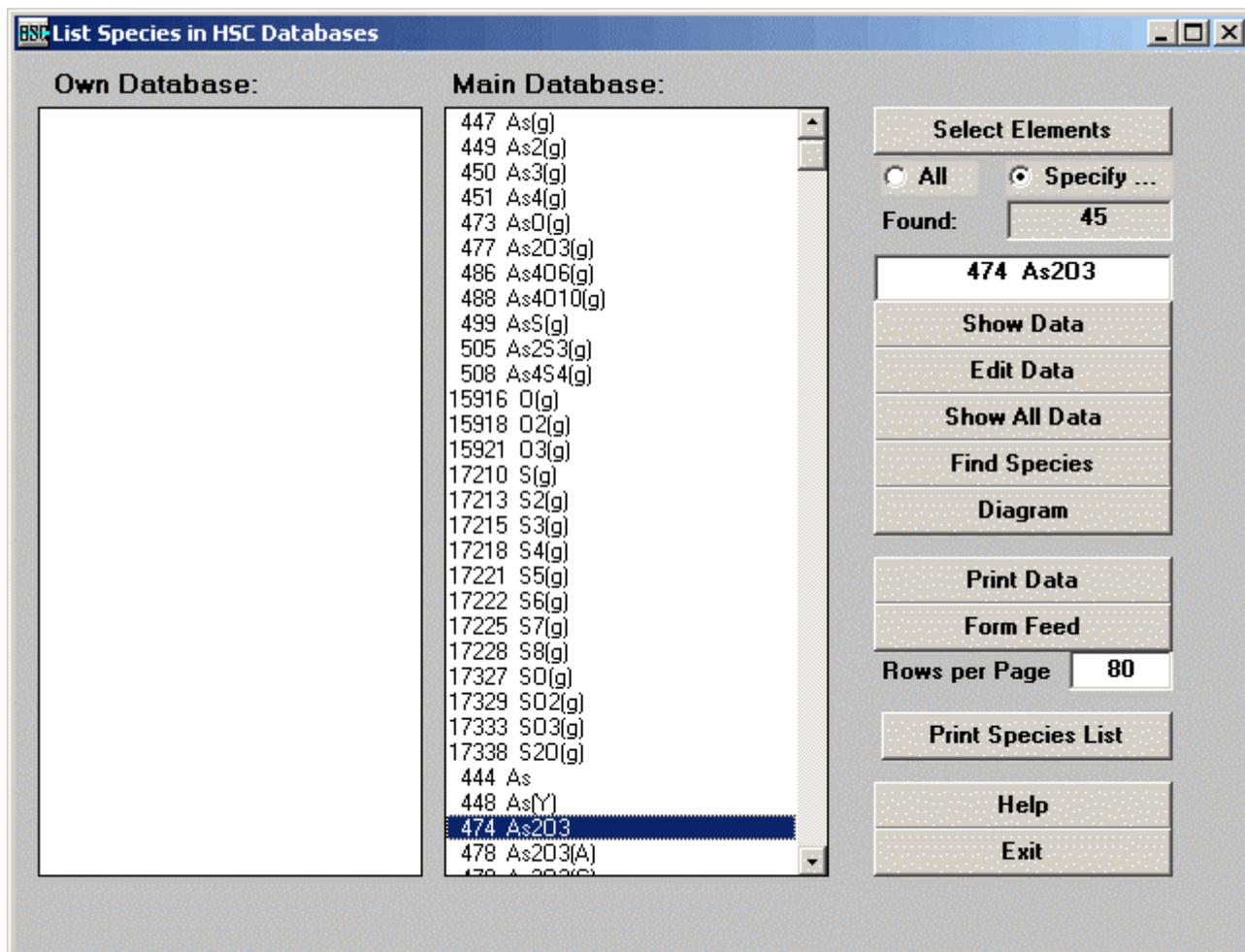


Fig. 7. Results of the species search made in Fig. 3.

With the **List Formulae** option you can get a list of all the species formulae, which exist in the Own and Main Database or only of those, which contain the given elements. This example, Fig. 7, shows the results of the species search made in Fig. 3. All As, S and O containing species exist in the Main Database. No such species were found in the Own Database.

Using **Select Elements** you may specify the elements for the search, whereas if you select the **All** option the list of all species in the databases will be displayed.

If you press **Show Data** you can see the thermochemical data of the selected species, see Fig. 8. You may also go directly to the edit option by pressing **Edit Data**, see Fig. 9.

Print Data will print the database content for the selected species on paper and by using **Form Feed** you will get the copy from the printer. You can also define how many **Rows per Page** you want. **Print Species List** makes it possible to print a list of database species formulae on paper. You can switch between the Own and Main databases.

An easy way to check the name and data of a species is to double click the formulae in the list using the mouse. This will quickly show the information required, see Chapter 10. *Reaction equations*, Fig. 10.

By pressing **Exit** you can return to the Database Menu, Fig. 1.

28.9 Listing Species Data in the Own and Main Database

Find Data with Key Word

As2O3 All **Find**

Find What:

- Formula
- Structural Formula
- Chemical Name
- Common Name
- Chem. Abs. Number

Search From:

- Main Database
- Own Database

Criss-Cobble

Heat Capacity Formula: $C_p = A + B \cdot 10^{-3} \cdot T + C \cdot 10^5 \cdot T^{-2} + D \cdot 10^{-6} \cdot T^2$

Units:

- Calories
- Joules

As ₂ O ₃		Arsenic(III) oxide				1327-53-3		197.841 g/mol	
	H	S	A	B	C	D	T1	T2	
	kcal/mol	cal/(mol*K)	cal/(mol*K)				K	K	
s	-156.500	27.964	21.045	17.368	-2.728	0.000	298.150	585.000	
l	5.400	9.231	36.500	0.000	0.000	0.000	585.000	734.000	
	Density	Color	Solubility	Reference			Melting P. K	Boiling P. K	
s	3.738	0.000	0.000	Barin 93			588.000	0.000	
l	0.000	0.000	0.000	Barin 93					

Exit Help Print Setup Clear **Print** Print All Copy List

Fig. 8. List of existing data in main database for As₂O₃.

The **Find Species with Key Word** option displays the data, which exist in the Own or Main database. First, select the database from the **Search From** options in which you are interested. Then type the element or compound formula in the Formula box and press **Enter** key or **Find** to see the data.

You may search data using Formula, Structural Formula, Chemical Name, Common Name or Chemical Abstract Number as a key word. You can make this selection in the **Find What** option list. Then you may type the key word and press **Enter** key or **Find** to see the data.

If the **All** check box is highlighted, a complete list of all the entries containing the keyword will be displayed in a new window to the left. From this list it is possible to select the desired species by simply clicking on them. Only the first entry will be shown if the checkbox is empty. By clicking the **Criss-Cobble** check box, you can see the effect of the Criss-Cobble extrapolation on the heat capacity of *aqueous ions* if the heat capacity data is not available in the database, see Chapter 28.4.

Antti Roine

August 10, 2006

06120-ORC-T

Press **Print** to get a paper copy. Press **Form Feed** to get the paper out of the printer. With **Copy** you can copy the data into the Windows Clipboard and then paste it onto other Windows programs. Note that you must first select the copy area using the mouse and that you must select at least one cell.

With **Copy** you can copy the data into the Windows Clipboard and then paste it onto other Windows programs. Note that you must first select the copy area using the mouse and that you must select at least one cell.

If you press **List** you can see a list of all the species in the database and you may select any species to display its thermochemical data. By pressing **Exit** you will return to the Database Menu, see Fig. 1.

28.10 Editing Data in Own and Main Database

Temp. Range:	1.	2.	3.	4.	5.
T1 K	298.15	1511.00			
T2 K	1511.00	1800.00			
Phase	s	l			
H kcal/mol	-21.236	21.000			
S cal/(mol*K)	15.030	13.898			
A cal/(mol*K)	11.636	14.100			
B	0.534	0.000			
C	-0.610	0.000			
D	1.024	0.000			
Density kg/l	5.318	5.317			
Color RGB	18	0			
Solubility in H2O g/l	0.000	0.000			
Reference	Chatillon 1990 KKH 1990				
Reliability Class	2	2			

Fig. 9. Editing data in the own and main databases.

This option lets you view data in the Own and Main database easily by clicking the species formula in the list on the left side of the window. You can swap between the Own and Main Databases using the Option list in the top left corner of the window.

You can edit any value and text if you have more accurate data available, you can also add or delete temperature ranges. However, you can save the new edited data only in the active Own Database file. If you want to save the data in the Main Database file, you may select this file to the Own Database file, see Fig. 18. The following lines give only brief instructions, for details see the next Chapter 28.11.

1. Select **Own** or **MainDB File** from the option list at the top left corner. It is not a good idea to edit the original Main database. Instead, you can save the same species with more accurate data in your Own Database. HSC Chemistry always uses the data from the Own Database when available.
2. Type the formula into the Formula box and press **Read from:** to select the source database. **Find Formula** will search the closest match if the species does not exist in the database.

Antti Roine

August 10, 2006

06120-ORC-T

3. Edit the data. You can type directly into the cell.
4. Press **Save to:** to save the edited data. It is recommended to save the new data in the Own Database.
5. Press **Exit** to exit from the Editing Window. You can return to the Formula List option by pressing **List**.

Note that you can delete species from both databases by pressing **Delete**. You can toggle between calories and Joules with the **Calories** and **Joules** options.

28.11 Saving Data in Own Database

The screenshot shows the HSC Database Editor window with the title bar 'Database Editor: C:\HSC5\Database\OwnDB5.HSC'. The menu bar includes File, Edit, Insert, Delete, Format, Fit, and Help. The 'OwnDB File' dropdown is selected, showing a list of species: Al(l), NaCN(l), Na2CO3(l), Na2S(l), and 0. The 'Find Formula' field contains 'Cu2S'. The right side of the window displays the data for Copper(I) sulfide, including its chemical name, common name, CAS number (22205-45-4), molecular weight (159.152), melting point (1373.00 K), and boiling point (0.00 K). A table of thermodynamic data is shown for five temperature intervals (1-5 K), with columns for H, S, Cp, and G. The 'H kcal/mol' row is highlighted, showing values: -19.400, 0.865, 0.280, 3.070. At the bottom, there are buttons for 'Delete Species', 'Exit', 'Read from:' (set to 'OwnDB File'), 'Save to:' (set to 'OwnDB File'), 'Print', 'List', and 'Fit Cp Data'.

Temp. Range:	1.	2.	3.	4.	5.
T1 K	298.15	376.00	720.00	1400.00	
T2 K	376.00	720.00	1400.00	2000.00	
Phase	s	s	s	l	
H kcal/mol	-19.400	0.865	0.280	3.070	
S cal/(mol*K)	27.761	2.300	0.389	2.193	
A cal/(mol*K)	11.457	28.301	20.010	21.430	
B	23.225	-13.906	-0.300	0.000	
C	0.000	0.189	0.586	0.000	
D	0.000	5.334	-0.148	0.000	
Density kg/l	5.600	0.000	0.000	0.000	
Color RGB	31	31	31	0	
Solubility in H2O g/l	0.000	0.000	0.000	0.000	
Reference	Barin 89	Barin 89	Barin 89	Barin 89	
Reliability Class	1	1	1	1	

Fig. 10. Saving new data in the active Own Database.

The HSC database editor can be used to show and edit species data of the active Own and Main Databases. The data can be selected for editing using two procedures:

- The editor will show the data of a selected species in the list on the left side of the editor window, selection can be made using the mouse. Select the database by using the option list box at the top left corner of the editor window, see Fig. 10.
- Another way is to type the formula of the species in the Formula box in the upper row of the window and press **Read from:**. The editor will show the data if it is found from the selected database, which is shown on the right side of the button.

The user can also type the new data directly in the blank database editor window. It is recommended to save the data of a new species or the edited data of an old species in the Own database. The saving must be done using **Save to:** on the bottom row of the editor. This button will save the data into the database, which is displayed on the right side of this button.

In HSC-databases, the data is given as sets of temperature intervals. One H, S and Cp data set is valid only within a certain temperature range, which normally corresponds to a

thermodynamic phase. Follow these steps when you save new data in the HSC Own Database. The most important steps have been underlined:

1. Clear input fields

First clear the Database Editor by selecting **Clear All** from the **Edit** menu.

2. Units (Essential)

You must decide which energy units you want to use; make this selection with the **Calories** and **Joules** options. Kelvins must always be used as temperature.

3. Formula (24 Characters, Essential)

The formula must always be given. The valid formula syntax is described in Chapter 28.2.1. The database editor will automatically calculate the molecular weight when you type the formula and press **Enter**.

The use of the correct state identifier (g, l, a, etc.) is extremely important, because the calculation modules handle the species in different ways. The state identifier “g)” must always be used for a gaseous species and “a)” for an aqueous species. Solid species must be given without the state identifier “s”. Liquid species and different structural forms can be specified in two ways:

A. One formula for liquid and solid phases

This format is traditionally used for inorganic species, see example in Fig. 10. Solid and liquid copper sulfides, as well as its different crystallographic forms, have the same formula Cu₂S in the database. It is extremely important to note that:

The enthalpy H value in the first temperature range must be the heat of formation of solid Cu₂S at 298.15 K and 1 bar.

The entropy S value in the first temperature range must be the standard entropy of solid Cu₂S at 298.15 K and 1 bar.

The enthalpy H value in the following temperature ranges must be the heats of phase transformation at the phase transformation temperature. The following phase transformations can be seen in Fig. 10:

- 376 K: Orthorombic a-Cu₂S -> hexagonal b-Cu₂S
- 720 K: Hexagonal b-Cu₂S -> cubic g-Cu₂S
- 1400 K: Cubic g-Cu₂S -> liquid Cu₂S

The entropy S values in the following temperature ranges are the entropy changes in the phase transformations. Note that D_{tr}S can be calculated from the corresponding D_{tr}H values using equation (1) at the transition temperature T_{tr}. One must keep in mind that this relation is not valid for the heat of formation and standard entropy values at 298.15 K.

$$D_{tr}S = D_{tr}H / T_{tr} \quad [1]$$

B. Different formulae for liquid and solid phases

The same data can also be given using different formulae for each substance. The copper sulfide data in Fig. 10 may be divided into four separate phases: Cu₂S(A), Cu₂S(B), Cu₂S(C) and Cu₂S(l). It is, however, extremely important to note that for each phase:

The H value in the first temperature range must always be the heat of formation of solid Cu₂S(A), Cu₂S(B), Cu₂S(C) or liquid Cu₂S(l) at 298.15 K and 1 bar.

The S value in the first temperature range must always be the standard entropy of solid Cu₂S(A), Cu₂S(B), Cu₂S(C) or liquid Cu₂S(l) at 298.15 K and 1 bar, respectively.

The enthalpy and entropy change values for phase transformations cannot be used. The heat of formation and standard entropy values for each state must be extrapolated from the normal stability range down to 298.15 K.

Quite often the heat of formation and standard entropy values for organic species are given for gas, liquid and solid phases separately at 298.15 K. These values can easily be saved in the HSC database. However, different formulae must be used for each phase. See, for example, solid Tert-butyl alcohol C₄H₁₀O(TBA), liquid C₄H₁₀O(TBAI) and gaseous C₄H₁₀O(TBAG) in the HSC Main Database.

4. Structural Formula (32 Characters max)

The structural formula is not utilized by the calculation modules, but it can be used to specify the species. It may also be used to save normal formula synonyms.

5. Chemical Name (52 Characters max)

The chemical name is not needed in thermochemical calculations, but it is very useful when selecting species for the calculations. Please use lower case characters, but start with an upper case character, see example in Fig. 10.

6. Common Name (32 Characters max)

Usually substances have a short common name, which is used instead of the long chemical name. Mineralogical, trade, etc. names as well as synonyms can be used. Please try to use the most common ones in the HSC databases. Please use lower case characters, but start with an upper case character.

7. Chemical Abstract Number (12 Characters max)

The Chemical Abstract number is one precise way to specify substances. However, this number is not usually available in the original references of the HSC database, therefore this data is partly defective in HSC 6.0. However, this data field gives the user the possibility to use CAN numbers in his Own Databases.

8. Molecular Weight (Number, Essential)

You can type the molecular weight in this data field. However, this is usually not necessary, because the Database Editor calculates the value automatically if you press **Enter** in the Formula field. The molecular weight must be given, because the calculation modules use the MW values in the amount unit conversions.

9. Melting and Boiling points (Number)

This data is not used by the calculation modules. However, the values can help a lot when analyzing the calculation results. **Negative values mean that the substance decomposes before the melting or boiling point.**

10. Temperature Range T1 - T2 (Number, Essential)

The valid temperature range must always be given for the H, S and Cp data, because calculation modules use these temperatures in nearly all calculations. The basic idea

of temperature ranges is described in the previous Formula paragraph. Remember also that:

- The first limit T1 is the lowest temperature where the Cp data A, B, C and D are valid. Traditionally the first temperature range starts from 298.15 K (= T1). However, other temperatures may be used.
- The second temperature T2 is the highest temperature where the Cp data A, B, C and D are valid.
- Quite often the upper limit T2 is the phase transformation temperature. However, sometimes the heat capacity temperature dependence of a phase is so complicated that it has been divided into several ranges. In these cases the phase transformation enthalpy and entropy values are zero (0).
- The temperature ranges of a substance and formula must be continuous. No discontinuities are allowed.

11. Phase (2 Characters, Essential)

The correct state code must be given for the species: **g** for gases, **l** for liquids and **s** for solids. The code **ao** is used for undissociated aqueous species (usually ions) and **ai** for aqueous electrolyte (neutral), which are formed from undissociated aqueous species. The ai species has suffix “ia” in HSC database.

The enthalpy and entropy values of **ai** species may be calculated as a sum of its dissociated components, for example enthalpy for MgSO4(ia) is:

$$\text{MgSO}_4(\text{ia}) = \text{Mg}(+2\text{a}) + \text{SO}_4(-2\text{a}) = -465.960 + (-909.602) = 1375.562 \text{ kJ/mol}$$

This calculation may not give exactly the same results as given for **ao** species in the HSC database due to different original data sources. The H and S values for **ao** species such as MgSO4(a) can not be calculated in the same way. It is recommended to use only **ao** species in the calculations.

12. H (Number, Essential)

The first enthalpy value at 298.15 K and 1 bar must always be **the heat of formation** of the same state as described in the formula and phase fields. If there are several temperature ranges, the other H values are the heats of transformations at the phase transformation temperatures. Note that the heat of formation for elements is zero at 298.15 K.

13. S (Number, Essential)

The first entropy value at 298.15 K and 1 bar must always be the **standard entropy** of the same state as described in the formula and phase fields. If there are several temperature ranges, the other S values are the entropies of phase transformations at the transformation temperatures.

14. A, B, C and D (Numbers)

These values are the coefficients of the heat capacity function, see Chapter 8. *Introduction*, equation 4. These coefficients are not needed if thermochemical calculations are done at 298.15 K or near that temperature. At other temperatures it is essential to know this data.

Quite often A, B, C and D coefficients are not available, and the heat capacity values are listed as a function of temperature only. These values can easily be converted to A, B, C and D coefficients using the **Cp Fitting** option of the database menu.

Sometimes the coefficients A, B, C and D are given for other heat capacity functions than used in HSC Chemistry. Their coefficients can also be converted to HSC format using the **Cp fitting** option of the database menu.

15. Density (Number)

The calculation modules use density values in the mol - kg - Nm³ - conversions. However, missing density values do not usually cause too much trouble. **Kg/l** units have been used for the condensed species and **g/l** for gases.

16. Color (Number)

Color of the substances is given using the color code. See Chapter 28.18 for color codes. "0" - value means that data is not available.

17. Solubility (Number)

These values are not yet available in HSC 6.0. This field is provided in order to guarantee the compability of the database with future versions of HSC.

18. Reference (36 Characters)

It is always recommended to also give the original reference of the data. There are only 36 characters available for the references and therefore abbreviations must be used. The abbreviations are formed using the author name and the year of publication. The Main Database abbreviations are given in alphabetical order in Chapter 33. *Data references*.

19. Reliability Class (Number)

The data in the HSC Main database have been collected from a large number of sources. Especially in some old sources, the accuracy of the H, S and Cp data does not seem to be so good. However, all this data has been included in the Main database, because in some cases small errors in the basic thermochemical data are not critical.

The Reliability class gives a rough estimate of the reliability of the data. The best reliability code is 1 and worst is 10. Usually, new data books⁷ have a reliability class of 1. The user can easily edit the reliability class of different references using the **Class** option in the Edit menu. The reliability class offers one additional key word, which can be used to sort species.

You can insert and delete temperature ranges with the **Column** options in the **Insert** and **Delete** menus. You can switch between calories and Joules with **cal**. However, all values are saved as calories in the database. By using **List** you can go directly to the List Formulae option. With the Fit Cp Data button you can go to the Cp Fitting module. With **Exit** you can return to the Menu.

Save to: will save the data shown in the database editor in the database shown on the right side of this button. You can get a paper copy of the data with **Print** and **Form Feed** options in the **File** menu.

If you save new data in your Own database, please send your OwnDB.HSC file with its literature references to Outotec Research (address on the first page). We can then later add this novel pure substance data to the Main database and distribute it to other HSC users.

28.12 Fitting Cp Data

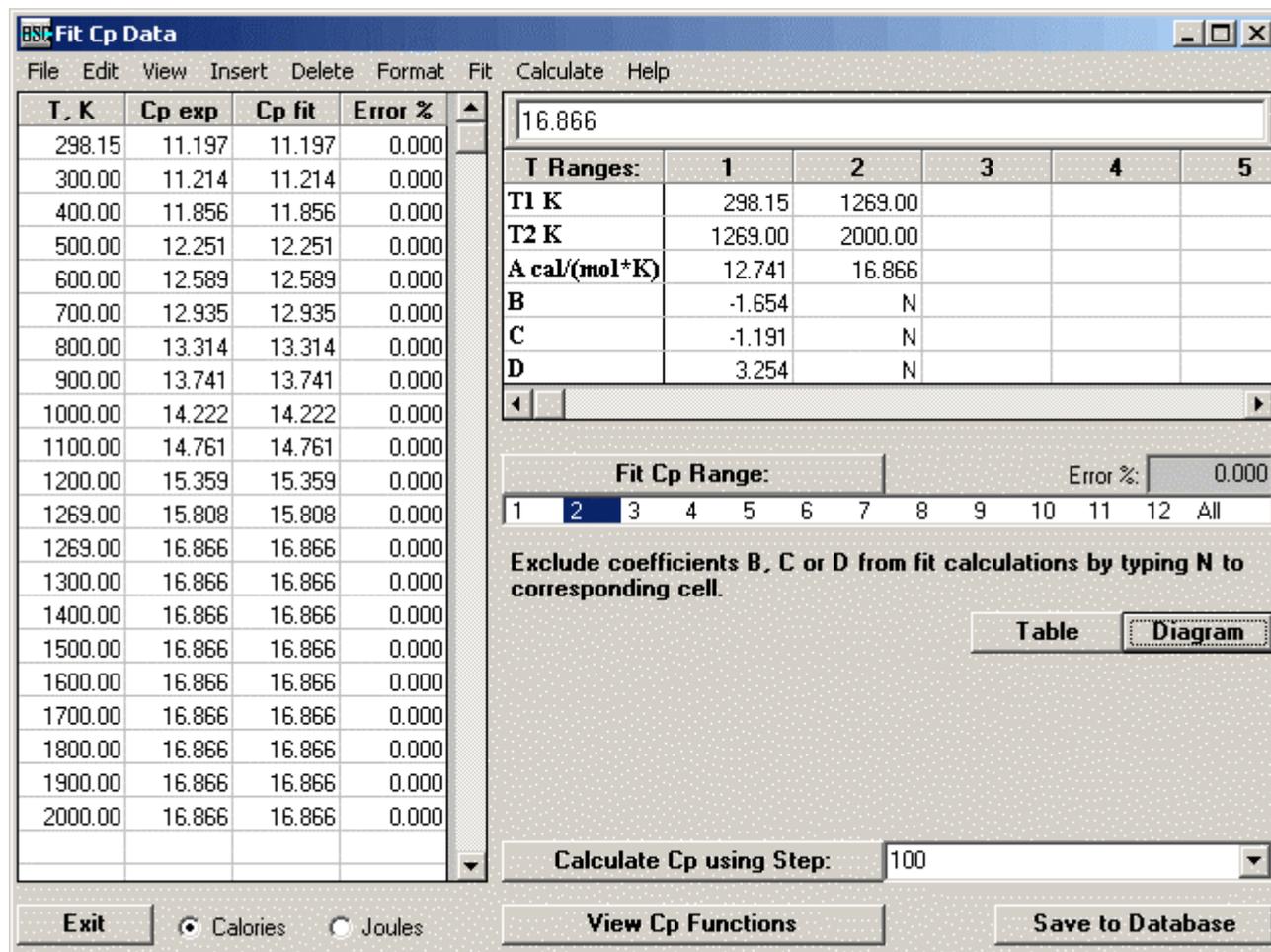


Fig. 11. HSC database Cp Fitting module with NaF Cp data.

Quite often only the heat capacity values at different temperatures are available. You can convert these data to A, B, C and D coefficients using the following procedure:

1. Select **Calories** or **Joules**.
2. Select **Clear All** from the **Edit** menu.
3. Type the lower and upper limits of the temperature ranges to the **T1** and **T2** cells, for example: 298.15 and 1265 K, 1265 and 2000 K.
4. Press **Calculate Cp using Step**:. This will automatically calculate the temperatures to the T - Cp - table on the left side of the window using the given temperature step. Note that you can also type and edit these temperatures manually.
5. Type the heat capacity values to the **Cp exp** column.
6. Select the Cp Range which you want to fit, from the list under **Fit Cp Range**:. If you only want to fit some of the coefficients then type "N" to other cells. See the example in Fig. 11.
7. Press **Fit Cp Range**:.

- You will get the fitted A, B, C and D coefficients to the table on the right side of the window. The fitting option will also calculate the Cp data using the fitted coefficients in the **Cp fit** column. It will also calculate the difference (**Error %**) between the “experimental” and the calculated value.

Usually the Cp ranges are the same as the phase stability ranges. However, if the error % is too high, then you can try to divide the temperature range into even smaller parts. **Diagram** will show the results in a graphical format.

- When all the ranges have been fitted, you may copy the coefficients to the database by pressing **Save to Database**, see Chapter 28.11.

28.13 Converting Cp Functions

The screenshot shows the 'Fit Cp Data' window with a table of experimental and fitted Cp data. The table has columns for Temperature (T, K), Experimental Cp (Cp exp), Fitted Cp (Cp fit), and Error (%). The data points are as follows:

T, K	Cp exp	Cp fit	Error %
298.15	17.214	17.204	0.058
418.34	18.317	18.349	-0.173
538.52	18.870	18.865	0.023
658.71	19.177	19.158	0.096
778.89	19.362	19.347	0.078
899.08	19.482	19.478	0.023
1019.26	19.564	19.570	-0.031
1139.45	19.622	19.635	-0.064
1259.63	19.665	19.677	-0.063
1379.82	19.697	19.701	-0.019
1500.00	19.722	19.707	0.073

The right side of the window shows a formula editor with the equation: $A + B*((C/T)/\sinh(C/T))^2 + D*((E/T)/\cosh(E/T))^2$. Below this is a table for defining Cp ranges and coefficients:

T Ranges:	1	2	3	4	5
Cp Funct.	$A + B*((C/T)/\sinh(C/T))^2 + D*((E/T)/\cosh(E/T))^2$				
Units	J(kmol*K)				
T1 K	298.15				
T2 K	1500.00				
A	4.34E+04				
B	3.97E+04				
C	4.17E+02				
D	2.40E+04				
E	2.01E+02				
F					
G					

At the bottom, there are buttons for 'Exit', 'Calories' (selected), 'Joules', 'View Cp Fit', and 'Save to Database'. A 'Set Cp Formula for Cp Range' button is also present, along with a 'Table' and 'Diagram' view selector.

Fig. 12. Converting Cp functions to the HSC format.

In some references the Cp coefficients A, B, C, D, etc. are based on another Cp-expression than that used in HSC Chemistry. The coefficients cannot be saved into the HSC databases. They can be converted to the HSC format using the following procedure:

- Select **Calories** or **Joules** for the converted A, B, C and D, i.e. for the results.
- Select **Clear All** from the **Edit** menu.
- Select the Cp formula from the list under the **Set Cp Formula for Cp Range** and press **Set Cp Formula for Cp Range** or type the formula manually into the **Cp Funct.** cell.

Antti Roine

August 10, 2006

06120-ORC-T

4. Type the unit string in the **Units** row, for example J/(kmol*K), i.e. the units of original coefficients.
5. Type the lower and upper limits of temperature ranges into **T1** and **T2** cells, for example: 298.15 and 1500 K.
6. Type the Cp function coefficients A, B, C, D, etc. into the correct Cp Range column.
7. Press **Convert Cp Functions to HSC Format**. This will automatically divide the given Cp Range into 10 parts and calculates the Cp values at these temperatures. Then the conversion procedure continues in the same way as in Chapter 28.12. The results will be shown in the same way as in Fig. 11.
8. When all the ranges have been converted, you may copy the coefficients to the database by pressing **Save to Database** and continue as described in Chapter 28.11.

28.14 Converting Thermochemical Data to H, S and Cp format.

Convert Gibbs energy temperature function to enthalpy, entropy and heat capacity values which can be saved to HSC database:

Delta G(T) = $h + sT^E-3 + aT\ln T^E-3 + bT^2^E-6 + cT^{-1} + dT^3$ (kcal/mol)

h	s	a	b	c	d	G(298.15 K)
-14.394	-86.625	13.574	-17.817	-185.3	0	

Convert

Formula: Criss-Cobble

Reaction:

Enthalpy kcal/mol	Entropy cal/(mol*K)	C(T) = A + B*10 ⁻³ *T + C*10 ⁵ *T ⁻² + D*10 ⁻⁶ *T ² cal/(mol*K)				
Delta H	Delta S	Delta A	Delta B	Delta C	Delta D	Delta G
-18.100	4.252	-13.574	35.634	3.706	0.000	-19.368

H	S	A	B	C	D	G
-18.100	27.766	5.053	35.014	2.136	4.684	-26.378

Calories Joules

Fig. 13. Converting G(T)-function to H, S and Cp format.

For some substances only Gibbs energy G values are available in the literature as a function of temperature. You must convert these values to H, S as well as to Cp coefficients A, B, C and D if you want to save them in HSC Chemistry databases. Conversion is simple:

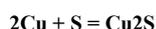
1. First select **Calories** or **Joules** from the option boxes.
2. Then select Delta G(T) or G(T) format, depending on your original data, with **Delta G(T)**.
3. If you have selected the Delta format, please write the corresponding formula in the **Formula** box, i.e. Cu₂S.
4. Type the coefficients of the G(T)-function in the upper boxes of the window.
5. Press **Convert** to get the corresponding Delta H, S, A, B, C and D in the lower boxes.
6. Press **Delta to Normal** to convert the delta H, S, A, B, C and D to the "normal" values, which can be saved in the HSC database.
7. Press **Save HSC** to transfer the data into the Database Editor.

With the **Convert** option you may also calculate $\Delta_f H$ and $\Delta_f S$ values as well as the Cp-coefficients of a reaction, ΔA , ΔB , ΔC and ΔD , to the enthalpy of formation $H_f(298.15)$,

standard entropy $S^\circ(298.15)$ and C_p coefficients A, B, C and D for saving in the HSC database. You must only give the **Formula** and delta values, as the **Delta to Normal** button automatically creates the correct chemical reaction for the formation.

You can copy the data to other Windows programs with **Copy**. With **Print** and **Form Feed** you will get a paper copy of the data. The **Clear** option clears all the cells. With **Find from HSC Database** you can read data from the HSC databases onto the screen if you have first given the chemical formula. The **Criss-Cobble** option forces HSC to extrapolate the C_p values of aqueous ions using the Criss-Cobble method, see Chapter 28.4.

The conversion of ΔH , S, A, B, C and D to normal values can also be done manually. Calculations have been carried out in the following example. The reaction for formation of Cu_2S , with pure copper and condensed sulfur as the raw materials will be:



$$\Delta G_r = -14.394 - 86.625e-3T + 13.574e-3T \ln T - 17.817e-6T^2 - 185.3T^{-1}$$

h	s	a	b	c	d
-14.394	-86.625	13.574	-17.817	-185.3	0

Press the **Convert** button, Fig. 13:

Delta H	Delta S	Delta A	Delta B	Delta C	Delta D	Delta G
kcal/	cal/	cal/				
mol	mol*K	mol*K				
-18.100	4.252	-13.574	35.634	3.706	0.000	-19.368

From these ΔH , ΔS and ΔC_p values you must solve the H, S and C_p values of Cu_2S . You can find the H, S and C_p data of Cu and S in the HSC database:

$$H(Cu_2S) = \Delta H_r + 2H(Cu) + H(S) = -18.100 + 2*0 + 0 = -18.100 \text{ kcal/mol}$$

$$S(Cu_2S) = \Delta S_r + 2S(Cu) + S(S) = 4.252 + 2*7.926 + 7.662 = 27.766 \text{ cal/(mol*K)}$$

	A	B	C	D
ΔC_p	= 1*	(-13.574	35.634	3.706 0)
$C_p(Cu)$	= 2*	(7.308	-2.707	-0.785 2.342)
$C_p(S)$	= 1*	(4.011	4.794 0 0)	
<hr/>				
$C_p(Cu_2S)$	=	5.053	35.014	2.136 4.684 cal/(mol*K)

These "normal" $H(Cu_2S)$, $S(Cu_2S)$ and $C_p(Cu_2S)$ values can be saved in the OwnDB.HSC database.

28.15 Convert Database File Format

The screenshot shows a window titled "HSC Database - C:\HSC5\DATABASE\MAINDB3.HSC". The menu bar includes File, Edit, View, Insert, Delete, Format, Convert, Sort, Search, Calculate, and Help. The main area displays a table with the following columns: Formula, Structural Formula, Chemical Name, Common Name, em. Abs. I, and MW. The table lists various chemical species, including Actinium and Silver compounds, with their respective molecular weights.

	Formula	Structural Formula	Chemical Name	Common Name	em. Abs. I	MW
1	Formula	Structural Formula	Chemical Name	Common Name	em. Abs. I	MW
2		Synonym Formula				g/mol
3	Ac		Actinium			227.02
4	Ac		Actinium			227.02
5	Ac(g)		Actinium			227.02
6	AcBr3(g)		Actinium bromide			466.74
7	AcCl3		Actinium trichloride			333.38
8	AcCl3		Actinium trichloride			333.38
9	AcF3		Actinium trifluoride			284.02
10	AcF3		Actinium trifluoride			284.02
11	Ac2O3		Actinium sesquioxide			502.05
12	Ac2O3		Actinium sesquioxide			502.05
13	Ag		Silver			107.86
14	Ag		Silver			107.86
15	Ag(g)		Silver			107.86
16	Ag2(g)		Silver			215.73
17	Ag(+2a)		Silver			107.86
18	Ag(+a)		Silver			107.86
19	Ag(+g)		Silver			107.86
20	Ag3AsO4		Silver arsenate			462.52
21	Ag3AsO4(a)		Silver orthoarsenate			462.52
22	AgAt		Silver astatine			317.86
23	AgBr		Silver bromide	Bromyrite		187.77

Fig. 14. Database manipulation module.

This module is intended only for advanced HSC Chemistry users, who work with database development. This module offers tools for combining databases, sorting species in the databases, recalculating molecular weights, file conversions, etc. These kinds of operations are not needed at all with normal HSC calculations.

One important option is the database sorting routine in the **Sort** menu. *The species must be in descending alphabetical order according to elements in the formula.* Usually HSC 6.0 keeps this order automatically in the database, but if you have old HSC 2.0 databases converted to HSC 6.0 format or data file made by convert module, Fig. 14, you must sort these files in alphabetical order using the **Sort** option, see Fig. 15.

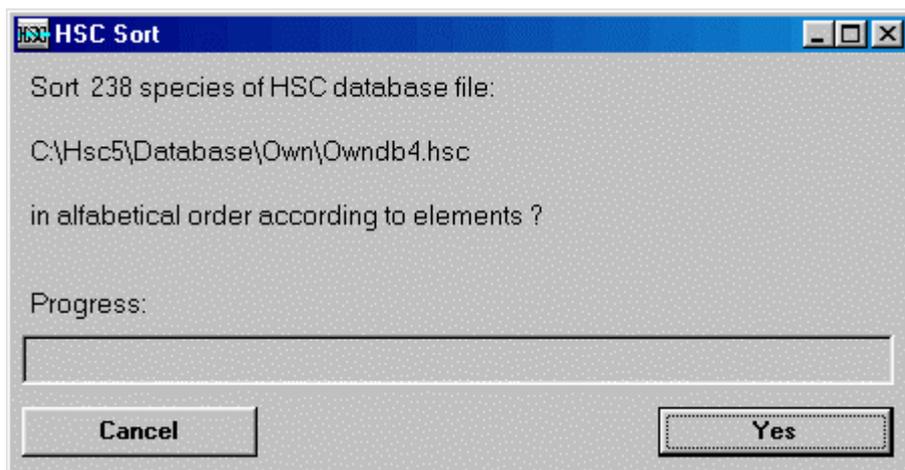


Fig. 15. Sorting an old HSC database file in alphabetical order according to elements. Please note that you have to convert this file first to HSC 6.0 format before applying the sorting option.

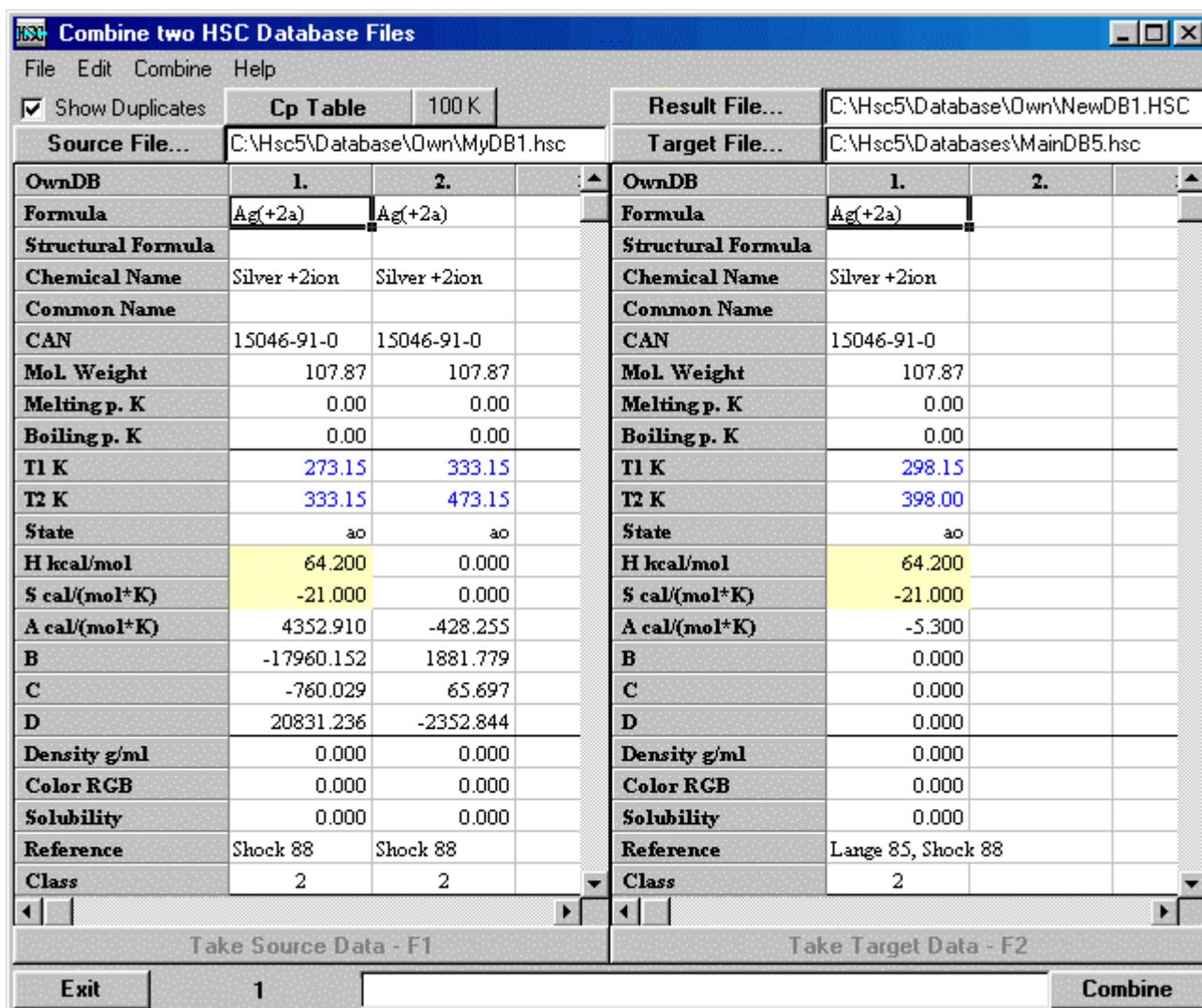


Fig. 16. Combining two HSC database files.

Antti Roine

August 10, 2006

06120-ORC-T

One important routine is the **HSC1 to HSC2 file** option in the **Insert** menu. This option will insert a species in one database, for example, HSC1.HSC to a second database HSC2.HSC. It will overwrite the species in the HSC2-database if the same species exists in both databases, see Fig. 16. Both files must be in sorted into alphabetical order with the **Sort** selection before the **Insert** procedure is selected.

If the **Show Duplicates** option is selected, Fig. 16, the program will show the data for the duplicate species for both files and you have an opportunity to select better data with **Take Source Data** or **Take Target Data**. You can also edit data before the final selection is made.

File menu offers several options, which can be used to read and save the HSC database files in different file formats. The same kind of file conversions can also be done using the **Convert** menu.

28.16 Converting old HSC 2.0 Databases to HSC 4.0 Format

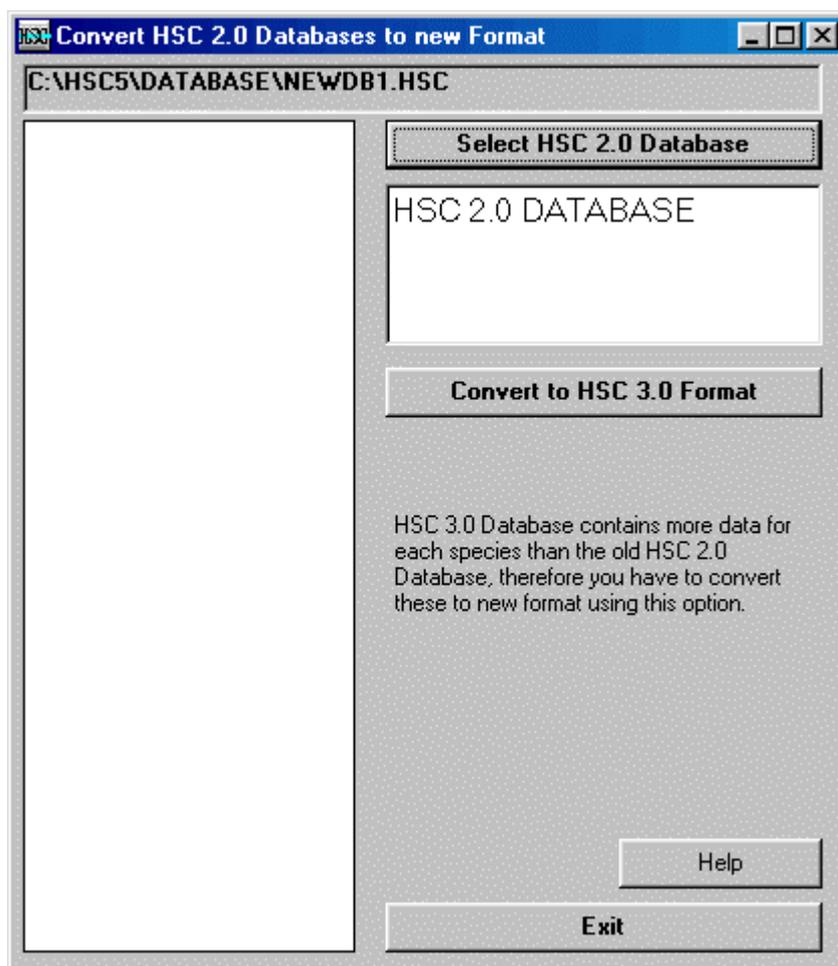


Fig. 17. Converting old HSC 2.0 Main database to HSC 6.0 format.

You cannot use HSC 2.0 databases directly in HSC 6.0. You must first convert them to HSC 6.0 format. If you select **Convert old Databases to new Format** in the Database Menu, see Fig. 1, you will get to the Convert window, see Fig. 17.

You must first select the old HSC 2.0 database file by pressing **Select HSC 2.0 Database** and then you must press **Convert to HSC 3.0 Format** to carry out the conversion.

28.17 Selecting Active Databases

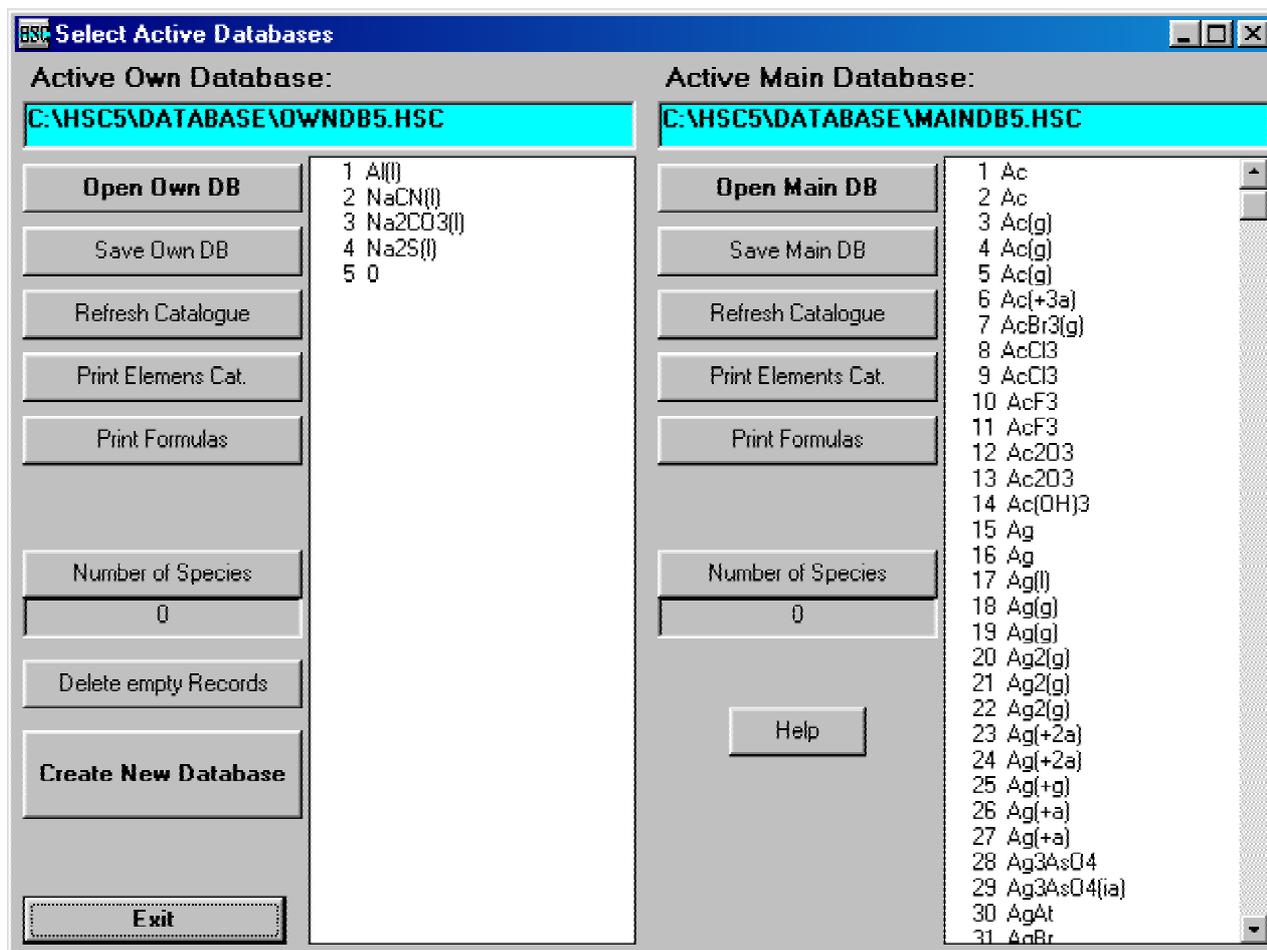


Fig. 18. Changing the active database.

Two databases can be open at the same time. They are called the Own and the Main database. Nearly any valid file name and directory can be used. However, the suffix (type) of these files must be *.HSC (Note: Awdb4.HSC file is in HSC internal use). *HSC Chemistry calculation modules primarily use the data in the Own database. If a species is not found from the Own database the HSC tries to find it from the Main database.*

Active databases can be changed at any time by pressing **Select Active Databases** in the Database Menu, see Fig. 1. The active databases can be selected using **Open Own DB** and **Open Main DB**. Sometimes, especially when working with old HSC 2.0 files it is recommended to also press **Refresh Catalogue** after opening the file. This will make a separate *.CAT file which helps HSC Chemistry to find the correct species in the database. **Print Catalogue** will print this *.CAT file.

Active databases can be saved using different names using **Save Own DB** and **Save Main DB**. You can easily create a new empty HSC 6.0 database file using **Create New Database**.

Number of Species will give the number of different species in the database. The number of species is usually smaller than the number of temperature ranges in the file, because some species have several temperature ranges.

28.18 Color Codes

The color of the substances is given for some species with the following color codes in HSC 6.0 main database:

0. No data available
1. Blue
2. Green
3. Cyan
4. Red
5. Magenta (blue-red)
6. Brown
7. White
8. Dark Grey
9. Light Blue
10. Light Green
11. Light Cyan
12. Light Red
13. Light Magenta
14. Light Yellow
15. Bright White
16. Colorless
17. Yellow
18. Grey
19. Black
20. Orange
21. Yellow-grey
22. Yellow-brown
23. Red-brown
24. Orange-yellow
25. Yellow-green
26. Black-brown
27. White brown
28. Orange-green
29. Blue-green
30. Dark-green
31. Blue-black
32. Red-orange
33. Yellow-orange
34. Green-yellow
35. Brown-black
36. Green-blue
37. Orange-red
38. Brown-yellow
39. Dark-red
40. Brown-violet
41. Red-violet
42. Violet-black

Antti Roine

August 10, 2006

06120-ORC-T

43. Yellow-black
44. Blue-white
45. Red-black
46. Green-black
47. Purple-black
48. Grey-brown
49. Brown-red
50. Gold-brown
51. Gold-yellow
52. Blue-grey
53. Orange-brown