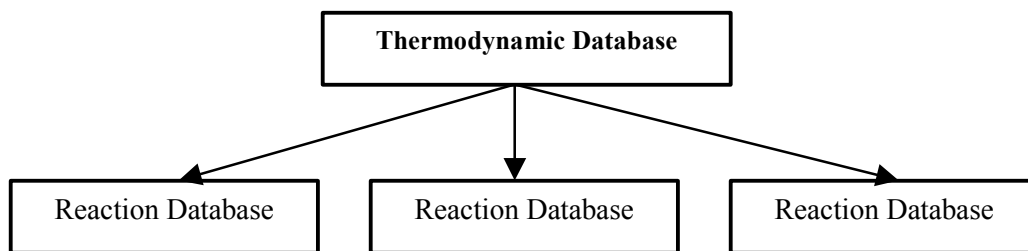


General Description

In Chemked, the thermodynamic data is collected in databases and stored in Microsoft Access file type; the files should have the '.mdb' extension. For each species, the data are presented as seven polynomial coefficients for each of two temperature ranges. The polynomials are used for calculating the specific thermodynamic functions (the heat capacity at constant pressure C_p , the enthalpy H and the entropy S). More information on this subject can be found in the following topics.

In the program the data is displayed in tables and handled via the user interface. You can edit the data, sort and select species with particular properties. Chemked provides numerical and graphical information on the thermodynamic functions. Data and charts can be printed or exported to the clipboard or as a file. The data is checked and if there are problems will display error messages.

You can create and save several thermodynamic (THERMO) databases, but Chemked can be connected with only one at a time. After connection with a thermodynamic database you can process several reaction databases simultaneously.



Relationship between thermodynamic database and reaction databases

When editing a reaction database the information from the connected thermodynamic database is used for checking the reactions. Due to the way the program connects to the thermodynamic database the user needs to follow certain rules:

- 1) To connect the program to another thermodynamic database you should first close the connected thermodynamic database and all reaction databases before proceeding.
- 2) To edit the connected thermodynamic database you should first close all reaction databases.

Note. If you do not need to work with the connected thermodynamic database, you may close it. Chemked remains connected to the closed database and the thermodynamic information will be available in Chemked subroutines.

Text Format of Thermodynamic Data

The specific thermodynamic properties of a species (the heat capacity at constant pressure C_p , the enthalpy H and the entropy S) are presented as a set of polynomial coefficients.

$$C_p / R = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4$$

$$H / RT = a_1 + a_2 T / 2 + a_3 T^2 / 3 + a_4 T^3 / 4 + a_5 T^4 / 5 + a_6 / T$$

$$S / R = a_1 \ln T + a_2 T + a_3 T^2 / 2 + a_4 T^3 / 3 + a_5 T^4 / 4 + a_7$$

where R is the universal gas constant, T is temperature in K, a_1 - a_7 are polynomial coefficients. A set of the seven coefficients is valid for a limited temperature interval. To expand the limits, two coefficient sets for overlapping intervals are used. An example of the thermodynamic data in the CHEMKIN-II text format is shown here.

```
H2O          20387 H   20   1   0   0G   300.00   5000.00   1000.0   1
 2.67214600E+00 3.05629300E-03-8.73026000E-07 1.20099600E-10-6.39161800E-15   2
-2.98992100E+04 6.86281700E+00 3.38684200E+00 3.47498200E-03-6.35469600E-06   3
 6.96858100E-09-2.50658800E-12-3.02081100E+04 2.59023300E+00 0.00000000E+00   4
```

The first line contains species name, reference, elemental composition, phase, temperature ranges for which coefficients apply. In the following lines the polynomial coefficients are placed.

Important. Thermodynamic data is format sensitive and provides errors if not formatted exactly.

The user can, but not must, specify the polynomial coefficients. A polynomial is identified as unspecified if the ALL coefficients are zero; otherwise the polynomial is specified. The thermodynamic functions cannot be calculated for species with unspecified polynomials.

```
O3          O   3   0   0   0G   200.00   3000.00   1000.0   1
 0.00000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00   2
 0.00000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00   3
 0.00000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00   4
```

Remark -----

If your reaction mechanism contains species whose thermodynamic functions are unknown, you should include these species in database as species with unspecified polynomials. Elemental compositions of these species are used to check balance of elements in reactions.

Species Name

Species name is a sequence of any characters; a name may have maximum length of 16 characters. The name must be unique. **The species names are case-sensitive.** The names C2H(s) and C2H(S), SiO2 and SIO2 are different.

Some symbols are forbidden for use in the species names. The forbidden symbols inhibit the interpretation of reaction formulas. These symbols are

=, < , > , \$ and blank space.

The sign '+' is used for the positive ion designation. A species name may end with any number of '+'s without parentheses. The use of embedded '+'s in the names is forbidden.

Example.

Correct species names are Ar, C6H8, H, Methane, 1,2-C4H6, C2H(s), C+.
Incorrect species names are C2H<S>, HN=C=NH.

Molecular Formula

Molecular formula states the number and type of chemical elements present in a molecule. This information is placed on the first line after the reference. The maximum number of elements in a chemical compound should not exceed 4. Chemked uses molecular formulas, not names, for checking balance of chemical elements in reactions.

Example.

If you specify species with different names H2O and Water that have the identical molecular formulas H1O2 then the following reactions will be equivalent.

H2O + M = OH + H + M	1.91E+23	-1.83	118500
Water + M = OH + H + M	1.91E+23	-1.83	118500

Creating a New Thermodynamic Database

1. Close all child windows including currently connected thermodynamic database.
2. Choose **File > THERMO Database > New**. The File dialog appears.
3. In the dialog, specify a database file path; click the Open button.

The program connects to the new database and the THERMO window with an empty thermodynamic table opens. The path of this database is saved; the next time Chemked is opened this database will be opened automatically as the default.

Note. We recommend you enter data into the new database immediately. If the database is empty you cannot open any reaction databases!

Connecting the Program to a Thermodynamic Database

Chemked should be always connected to a thermodynamic database. You can change it by choosing another database from existing ones. To do this the following steps should be carried out.

1. Close all child windows including currently connected thermodynamic database.
2. Choose **File > THERMO Database > Connect**. The File dialog appears.
3. In the dialog, select the database file path; click the Open button.

The program connects to this database and the THERMO window opens. The path of this database is saved; the next time Chemked is opened this database will be opened automatically as the default.

Note. Make sure that the database file is not read-only.

Valid and Invalid Properties of Species

A species has **Invalid** property when its name contains forbidden symbols (=, < , > , \$ or blank space) or is not unique (the name is a duplicate). Otherwise the species has the **Valid** property. In the THERMO table, the invalid species are

highlighted. Information from the thermodynamic database is used for checking reactions; the invalid species will be ignored.

Entering Chemical Elements

1. Close all reaction databases and activate the THERMO window.

2. Choose **Edit > Chemical Elements**

or on the toolbar, click the **Chemical Elements** button.

A window with the chemical element table appears.

3. In fields of the table, enter or remove the chemical element names and atomic weights; click OK.

The changes are written to the database and the element window closes.

No	Ele...	El. weight
1	H	1.00794
2	O	15.9994
3	N	14.00674
4	C	12.0107
5	S	32.066
6	AR	39.948
7		0.
8		0.
9		0.
10		0.

To enter an element type the element name and the element weight in the corresponding fields, click OK. To remove an element, delete its name, click OK.

Important. If an element is removed from the table, all species from the THERMO table, containing this element, will be removed as well.

OK Cancel

Chemical element table

Important. If an element is removed from the element table, all species containing this element will be also removed from the THERMO table.

Remark -----

The maximum number of chemical elements is 10. The element name should consist of 1 or 2 letters.

Each thermodynamic database has an own element table.

Entering Species

Paste Data

This method can be used when data is available in an electronic form, for example, as a text file. You should copy the data to the clipboard and then carry out the following steps.

1. In the THERMO table select a row.
2. Choose **Edit > Paste**
or on the toolbar, click the Paste button.

The data will be pasted in the THERMO table below the selected row.

Remark -----

If you need to enter a large volume of data (more than a few hundred species), we recommend you to enter the data in parts.

In the CHEMKIN standard representation the data is written as a sequence of lines where the first and last lines contain the key words THERMO and END respectively. To use this data you should copy all the text between, not including, the key words. An error will occur if the data contains key words, such as SPECIES, THERMO, END, or another auxiliary information.

Paste Special

Sometimes values of the common temperature of temperature intervals are omitted in the descriptions, as shown here.

```
iC4H7          P11/94C    4H    7    0    0G    300.000  3000.000          1
 0.74491956E+01 0.22630504E-01-0.88095014E-05 0.14336478E-08-0.73247269E-13 2
 0.11196182E+05-0.11947779E+02 0.34512660E+01 0.24686039E-01 0.52359514E-05 3
-0.16130826E-07 0.53881687E-11 0.12783361E+05 0.11080150E+02          4
```

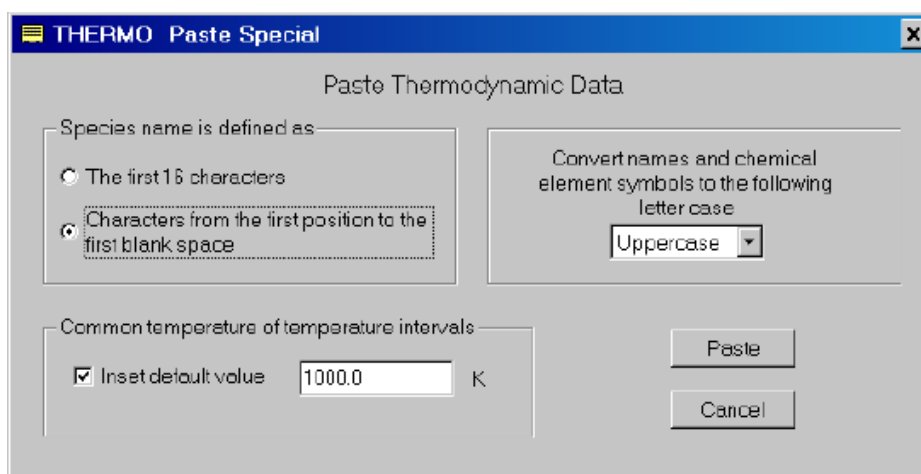
There are also special cases when the reference is too long and it must be placed in the name field as it shown in this example.

```
oh          7/13/ 0 rucich    1o    1    0    0g    300.000  5000.000 1710.000    01
2.85376040e+00 1.02994334e-03-2.32666477e-07 1.93750704e-11-3.15759847e-16    2
3.69949720e+03 5.78756825e+00 3.41896226e+00 3.19255801e-04-3.08292717e-07    3
3.64407494e-10-1.00195479e-13 3.45264448e+03 2.54433372e+00          4
```

The following procedure can be used to input these types of data. As previously detailed you should first copy the data to the clipboard. The descriptions of the species can contain or not contain the common temperature. Then carry out the following steps.

1. In the THERMO table select a row.
2. Choose **Edit > Paste Special**. The Paste Special dialog appears.
3. In the frame 'Common temperature of temperature intervals', check 'Insert default value', and type the default value in the text box.
4. In the frame 'Species name is defined as' chose the option 'Characters from the first position to the first blank spac'
5. Change the letter case of names of species and chemical elements if it is needed.
6. Click the Paste button.

The species will be pasted into the THERMO table below the selected row. The default value of the common temperature will be inserted in the species where these values were absent.



Paste Special dialog

Comments

Lines with the exclamation mark (!) in the first position are comments; they will be written in the Comment field of the THERMO table. The comment for a species may have maximum length of 256 characters. An example of the comment is shown here:

```
h2o2          120186h   2o   2           g  0300.00   5000.00   1000.00      1
  0.04573167e+02 0.04336136e-01-0.01474689e-04 0.02348904e-08-0.01431654e-12      2
-0.01800696e+06 0.05011370e+01 0.03388754e+02 0.06569226e-01-0.01485013e-05      3
-0.04625806e-07 0.02471515e-10-0.01766315e+06 0.06785363e+02      4
! Review and release date: May 19, 2004
! 4/16/04 version 1a
```

Remark -----

In the following example, the data have the CHEMKIN format and are recognized by CHEMKIN. Nevertheless, the error occurs if you will attempt to input the data

in Chemked. The C5H10 description contains 5 elements N, AR, C, H and O; only 4 elements are allowable.

C5H10	000000N	0AR	0C	5H	100	0G	300	5000	1000	1
4.62768794E+00	3.99163471E-02	-1.76584355E-05	2.94527974E-09	0.00000000E+00						2
-5.90930391E+03	3.39515508E+00	-1.36099451E+00	5.87684877E-02	-3.93332993E-05						3
1.36933176E-08	-1.93663167E-12	-4.42142034E+03	3.36502744E+01							4

In this case, you receive the message 'Error in temperature intervals'.

Manual input

1. In the THERMO table, select a row.
2. Choose **Edit > Insert New Row**
or on the toolbar, click the **Insert New Row** button
or right click mouse on the selected row and choose **Insert New Row** from the pop-up menu.
A new row will be created below the selected row.
3. Double click the new row; the input window appears.
4. Type the data into the text boxes of the input window; click OK.

The image shows two screenshots of the 'THERMO Input Window' dialog box, labeled 'No 6'.

The left screenshot shows the 'General' tab. It contains the following fields:

- Species Name:
- Molecular Formula:
- Molecular Weight:
- Phase:
- Electronic Charge:

At the bottom are 'OK' and 'Cancel' buttons.

The right screenshot shows the 'Elements' tab. It contains a table titled 'Elemental content (positive integers)'.

Element	Content	Blank	Blank
H	<input type="text" value="2"/>	-	<input type="text"/>
O	<input type="text" value="1"/>	-	<input type="text"/>
N	<input type="text"/>	-	<input type="text"/>
AR	<input type="text"/>	-	<input type="text"/>
-	<input type="text"/>	-	<input type="text"/>

At the bottom are 'OK' and 'Cancel' buttons.

Input window of the THERMO table, the features for entering species name and molecular formula

Editing Data

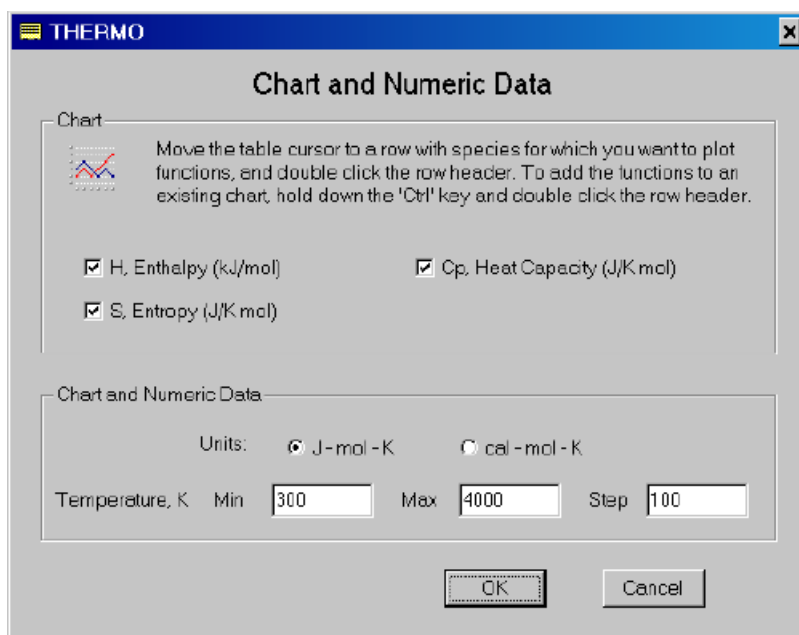
1. Double click the field of the THERMO table with a value you want to change. The input window appears.
2. In the corresponding text box of the input window, change the value; click OK.

Creating Charts and Viewing Numeric Data

You can create charts and view numeric data of the following thermodynamic functions: enthalpy, entropy and heat capacity at constant pressure.

Selecting Functions

1. Choose **View > Chart and Numeric Data Dialog** or on the toolbar, click the **Chart and Numeric Data Dialog** button. The dialog appears.
2. In the dialog, select the functions you want to view, and specify the interval and step of temperature; click OK.

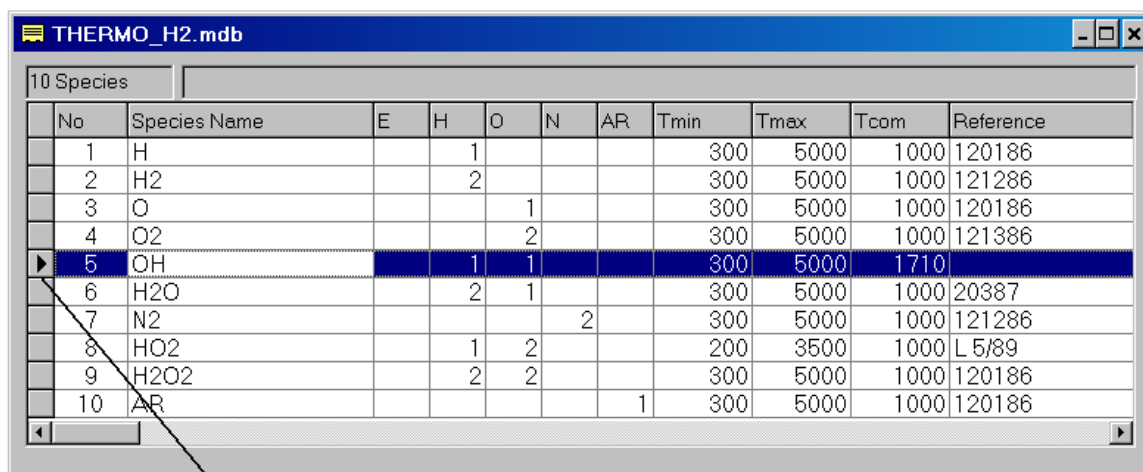


Dialog for selecting thermodynamic functions

Plotting Functions

1. In the THERMO table, select a species whose functions you want to plot.
2. Double click the row header; curves of the chosen functions appear in Temporary Chart.

If this procedure is repeated for different species the existing curves will be replaced with new ones. If you want to add curves to existing Temporary Chart, hold down the Ctrl key and then double click the corresponding row header.



No	Species Name	E	H	O	N	AR	Tmin	Tmax	Tcom	Reference
1	H			1			300	5000	1000	120186
2	H2			2			300	5000	1000	121286
3	O				1		300	5000	1000	120186
4	O2				2		300	5000	1000	121386
5	OH			1	1		300	5000	1710	
6	H2O			2	1		300	5000	1000	20387
7	N2					2	300	5000	1000	121286
8	HO2			1	2		200	3500	1000	L 5/89
9	H2O2			2	2		300	5000	1000	120186
10	AR					1	300	5000	1000	120186

Double click here to plot the functions

Saving Temporary Chart

Temporary Chart is deleted when the program closes. To save the chart you should carry out the following steps.

1. Activate the Temporary Chart window.
2. Choose **File > Save As**. The File dialog appears.
3. In the dialog, specify a file path; click the Save button.

Important. The file name should have the '.pg' extension.

Viewing Numeric Data

1. In the THERMO table select a species whose numeric data you want to view.
2. Choose **View > Numeric Data of Current Species**
or right click mouse on the selected species and choose **Numeric Data of Current Species** from pop-up menu.

Numeric data of the thermodynamic functions will appear in a text window. You can print this or save it to a file.