

# ThermoChemTool: Tools for the Use of Thermochemical Data

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## 1 Description

Thermochemical calculations or estimations are made in order to get the equilibrium constants of chemical reactions of interest. For most compounds the thermochemical functions of formation from the elements are known and available in data compilations or textbooks. These data let us know under which conditions of concentration, pressure, and temperature an ensemble of materials is in equilibrium or in which direction a chemical process will proceed.

The procedures to obtain information from data found in literature are simple, but frequently not used since one has forgotten how to do this. However, the mathematical routines are no real problem if they are done by this program. You have only to follow the instructions given on top of each form. If it does not work at once you can correct the input and try it again or consult the help files.

The main task of this program is to read thermochemical data of chemical reactions from data files, to show them and the equilibrium constant as a function of temperature in a table or as a curve plot in the units and the style you need, and to save new input data in your personal data files. The program may be a helpful assistance for engineers, scientists, or students who hesitate to use the efficient methods of thermochemistry since they have not enough time to warm up again the knowledge on some simple rules needed to profit by the stock of data available in literature.

## 2 Quickstart

### 2.1 How to Install

**Step1:** Download and unpack the zip archive **ThermoChemTool.zip**

**Step2:** A folder with the same name will be created

**Step3:** Find the executable file "ThermoChemTool" inside

### 2.2 Program Structure

#### 2.2.1 The files of the program are:

- The program file **ThermoChemTool.exe**
- **DataBasis.txt** with data on (H, C, N, O, metal) – systems
- Two empty data files: **TempData.txt** and **PrivData.txt** for input of your own data
- Eight helpfiles .....**H.txt** explaining the actions of the individual forms.

The program needs all these files at run time. They must be available in the same directory as the program file ThermoChemTool.exe.. Thus, you only have to copy this one directory to your computer for installation and to remove it for uninstallation. That is all.

#### 2.2.2 First steps:

When you click the ThermoChemTool.exe file you see the main form of the program with the menus Units, Get data, Show data, Plot, Calculate, Data input, File care. Click Get data and write the symbols of the chemical elements, occurring in the reaction equation into the boxes (O, Al) and push Make system name. You may read, for example, AL O . The style of writing the system name is made by a routine in order to avoid errors. Next, a form shows up where you can choose the file where you expect to find data (DataBasis). Press Input to store and in the list

box you find three reaction equations for AL O. The data sets of these three reactions have been found in the data file and copied to the work store of your present session. You can add more sets or delete some by the same procedures.

### 2.2.3 Forms:

In all forms there is on top a white memo which tells you what you have to do. In the yellow areas are input elements for the change of parameters. Push buttons are grey. The [ESC] key closes the form too. The small [?] button opens a help window for the form.

### 2.2.4 Presentation:

Now, we will have a look at the data. We open the form Show data in the main menu. At first you find the Unit form where you can change the temperature and energy units of presentation. We close it for the moment, but when you want to change units this can be done any time in all menus. Then we select one equation from the list box. The data can be presented in three kinds: As a data sheet, which can be copied for documentation, or as table of the functions stored in the data set as a function of T. The start point and end point of T and delta T can be chosen. Thus, you can get a function value for any T value by making it T<sub>min</sub> or T<sub>max</sub>. The table can be saved also as text file and used as basis for a table in a manuscript typed by your program.

### 2.2.5 Plot:

Now, we will have a look at the Plot menu. At first we have to select one or several reactions from the list box (the first and second) and select the function we want to plot (G or lg K<sub>p</sub>). The next form enables changes of plot parameters. For the moment we accept the parameters proposed by the program and go on. Now, we see a plot with two curves. The fat lines represent the area of definition and the thin lines the extrapolation. We see that the curve for the oxidation of solid Al is given by a fat line below the melting point. In the plot only scale numbers and units are written at the axes but no other text. The white area can be stored as bitmap and used as sketch for a figure in your manuscript when it is finished by the graphic program you use. The points of the curves can also be obtained as [T,F(T)] plot-point file for input in advanced plot programs. You can write comments in the text lines on the right side for the documentation of the plot files when printed as screen copy.

The menus Get data, Show data, and Plot are the menus that demonstrate best which kind of results can be obtained by the program and how they can be adapted to the taste of the user. If you play now a little bit with units and output parameters you may get an idea how easy it is to present data in a specific style.

### 2.2.6 Further menus:

In the menus Calculate and Data input similar routines are provided for data input into files. There, some definitions on standard states have to be considered which are explained in more detail in separate sections below.

Finally, in the program menu Filecare manipulations of data files and the data sets in data files are possible or personal files can be created, deleted or renamed. It is very easy to handle these procedures under control of the program definitions.

## 3 User's Guide

### 3.1 General structure of the program

#### 3.1.1 Files

The program is a 32 bit Windows application. All files used in addition to the program file are text files. As filter in file save and file load processes we use: Data.txt for data files, H.txt for

help files and Plot.txt for [T,F(T)] point data. Thus, the user is not troubled if Microsoft changes again the formats and he has direct access to these files to change or manipulate them, of course on his personal responsibility. You have not to use the filter names for personal files, but the program runs smoother if you do this.

The table of functions is printed also as text file with the old-fashioned courier type font in order to remain independent of changes of font standards. If the table has to be inserted correctly into a manuscript it may be no big problem to do this by the text program used.

The curve plots are printed as bitmap files. They can serve as a sketch for a figure in a manuscript and further optimized by the text or graphic program.

The data files are textfiles, too. Each data set is written in a line with this structure:

System[Tab]Reaction[Tab]Ref[Tab]Tmin[Tab]Tmax[Tab]H[Tab]S[Tab]a[Tab]b[Tab]c[Tab]d[Tab]l.

The numeric values are defined as double and written as string variable, too.

### 3.1.2 Data set of thermochemical functions:

The data set for reactions of H, C, N, and O with metals, offered in the program file DataBasis.txt, is used as standard set of the program and has been chosen according to conventions used also in many data compilations. H means  $\Delta H$ , i.e.  $H_o$  at 298.16 K of reaction products minus reactants. S means  $\Delta S$ , i.e.  $S_o$  at 298.16 K of reaction products minus reactants. cp means  $\Delta c_p$ , i.e.  $c_p$  at 298.16 K of reaction products minus reactants.  $c_p(T)$  is given as:

$$c_p = a + b \cdot 10^{-3} \cdot T + c \cdot 10^5 / T^2 + d \cdot 10^{-6} \cdot T^2.$$

By this definition we get (for details read a textbook on thermochemistry):

$$H(T) = H_o(T_o) + a(T - T_o) + 1/2 \cdot b \cdot 10^{-3} \cdot (T^2 - T_o^2)$$

$$- c \cdot 10^5 \cdot (1/T - 1/T_o) + 1/3 \cdot d \cdot 10^{-6} \cdot (T^3 - T_o^3)$$

$$S(T) = S_o + a(\ln T - \ln T_o) + b \cdot 10^{-3} \cdot (T - T_o)$$

$$- 1/2 \cdot c \cdot 10^5 \cdot (1/T^2 - 1/T_o^2) + 1/2 \cdot d \cdot 10^{-6} \cdot (T^2 - T_o^2),$$

Tmin is used as  $T_o$  in the program.

Tmin, Tmax define the temperature range, given by the authors. Thus, the complete data set consists of:

System name, reaction equation, references, Tmin, Tmax, H, S, a, b, c, d, and l as a zero string available for the user.

The selection of data is made by the system name which consists of the symbols of the chemical elements occurring in the reaction equation. The elements are written as capitals and in alphabetic order. A system name has the following structure:

SystemName = 'E1' [+ 'E2' [+ 'E3' [+ 'E4' [+ 'E5' [+ 'E6']]]] + ' '

The reaction equation specifies the individual reaction and references or comments are given in variable Ref.

In most cases the factors a to d are zero, since only the two most important quantities H and S are known and suffice for realistic estimations within the error of the experimental data they rely on. The factors a to d are included in the program to assist more detailed thermochemical

analyses sometimes made by experts.

In the data sets temperatures are given in K and energies in Joule.

### 3.1.3 Menus

The menus control the data input and output.

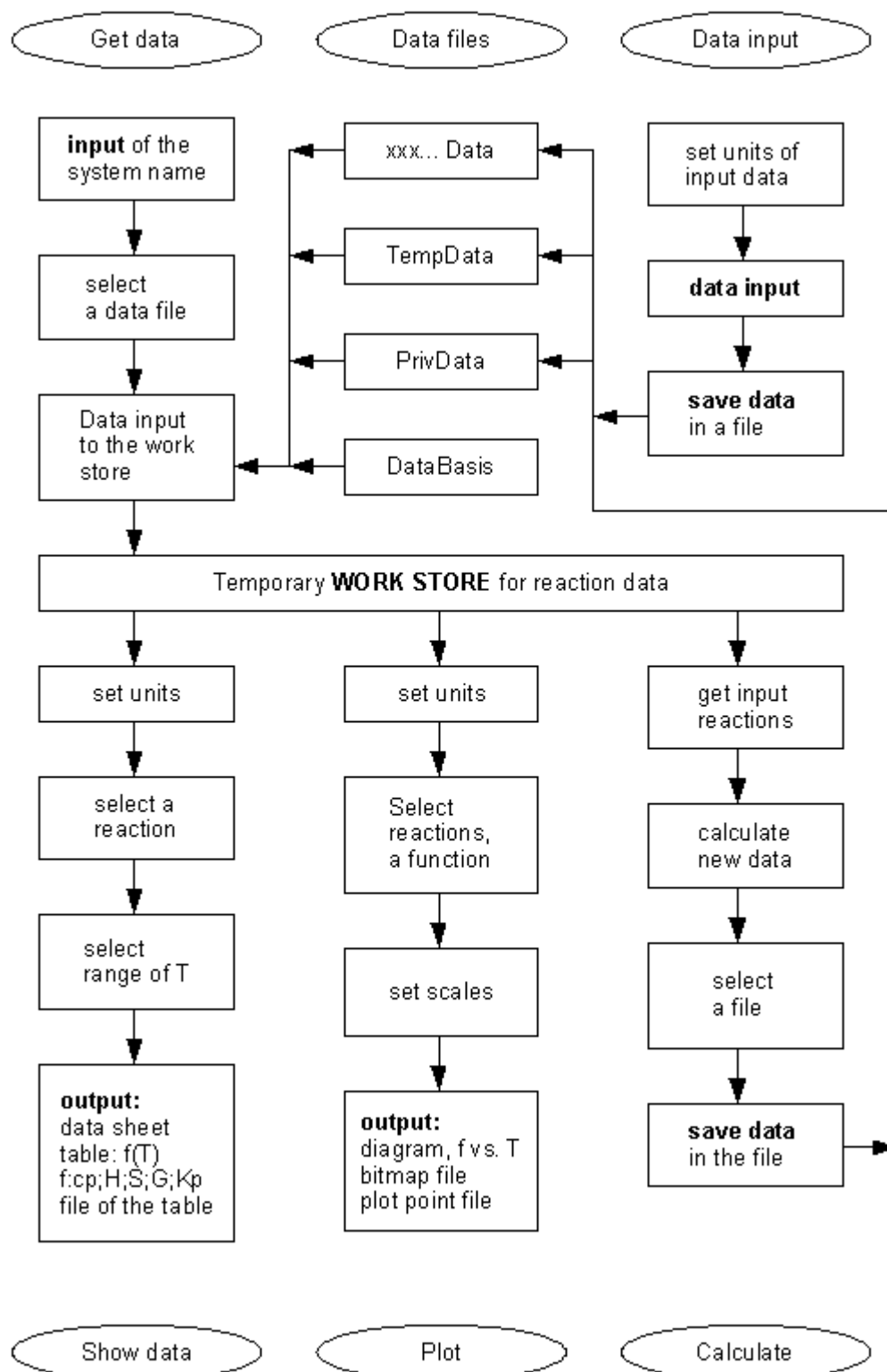
Data input is made by the menu Get data by selection of the data sets beginning with the system name chosen, and their transfer from the data file to the work store opened for the present session.

The input of data found in the literature to the work store requires two steps. They must first be filled into a private data file (TempData.txt, PrivData.txt or another one, \_\_\_\_Data.txt) by the menu Data input. Then you can use the menu Get data and have them available in the work store for output procedures.

Data output is performed by the menus Show data and Plot. The conversion of units are only active in the output procedures and in the menu Data input where correct data sets must be produced before they can be saved in the data files.

The menu Calculate produces data sets of new reactions by addition of data sets available in the work store which are multiplied by factors chosen by the user. This data set must then be written into one of the private data files and then filled into the work store by Get data. Only then you can use the new data in output procedures.

By the menu File care you can look into the files and delete one data set or all sets in a data file. The data file 'DataBasis.txt' with the evaluated data on (H-C-N-O-Me) systems is write protected and should not be changed unless a backup is made. If a user has made a file with his own basic reactions he can save it as DataBasis.txt after he has renamed the original file DataBasis.txt for further use.



**Fig. 1** - Actions of the menus in the program ThermoChemTool

#### 3.1.4 Units

In practical use there are two big chances for making mistakes.

- 1.) Errors in the conversion of energy and temperature units.
- 2.) The use of incompatible standard states for the activity  $a$  in thermochemical functions.

This program avoids to large extend errors of type 1.) by the routines available. The data stored in the data files and transferred from there to the work store for a specific session are given in units Joule and K. Also the input of new data to personal data files by the user is converted to

these units.

The output procedures providing data sheets, tables, or curve plots begin with the input of these standard data from files to the work store. The data selected can then be presented for temperature in K, C, F, and for energy in cal/mol, Joule/mol, eV/molecule.

### 3.1.5 Standard states

The problem of avoiding type 2.) errors with respect to the standard state unfortunately has to remain in the responsibility of the user. It is the problem of definition of the units for the activity  $a$  in the entropy terms ( for details consult textbooks of thermochemistry ). However, the definitions for  $a$  in the data sets of the file DataBasis are given below.

The pressure standard state of hydrides, nitrides and oxides in the DataBasis file uses as pressure unit 1 atm. The solution reactions for H, N, O use as standard state the ideal diluted solution model with  $p$  in atm and the concentration  $x$  of the dissolved atoms  $x$  in mole fraction, (not in wt % or at% !). The problem of choosing compatible standard states for calculation is described in more detail below in the menu Calculation.

## 3.2 Help files of the menus

### 3.2.1 Units

This menu provides the procedures for unit conversion of data input and output. One can change units by this menu any time. The user is reminded to check units also when entering some of the other menus.

In the lower part there is an input for three constants to adapt the presentation of the equilibrium constant  $\lg K_p$ . This enables the user to plot a pressure or concentration term as a function of temperature.

The following examples shall demonstrate this:

The reaction  $2\text{Al} + 3/2 \text{O}_2 \rightarrow \text{Al}_2\text{O}_3$  gives an equilibrium constant

$$\lg K_p^\circ = \lg (a(\text{Al}_2\text{O}_3) / \{a(\text{Al})^2 * p(\text{O}_2)^{3/2}\}) = -G / (RT \ln 10).$$

$a(\text{Al}_2\text{O}_3)$  and  $a(\text{Al})$  are 1 by definition and  $p(\text{O}_2)$  is given in atm. If you wish to plot the dissociation pressure of  $\text{Al}_2\text{O}_3$  as a function of  $T$  you have to change the  $\lg K_p^\circ$  function to

$$\lg K_p = (-3/2) * \lg K_p^\circ + 0, \quad (A : = -3, B : = 2, C : = 0).$$

With  $C$  you can change the pressure units. E.g.  $C : = 3$  gives millibar.

The reaction  $1/2 \text{H}_2 \rightarrow \text{H}(\text{in Ti})$  has the equilibrium constant

$$\lg K_p^\circ = \lg (a(\text{H in Ti}) / p(\text{H}_2)^{1/2}) = -G / (RT \ln 10).$$

$a(\text{H in Ti})$  is given in mol fraction. If you wish to plot the concentration of

$\text{H}(\text{dissolved in titanium at 1 atm})$  in at% you have to set  $C : = 2$ .

If you need the equilibrium  $\text{H}_2$  pressure for 1 at%  $\text{H}$  you set

$$A : = -2, B : = 1, C : = -4.$$

The input of  $A$  and  $B$  requires integers, decimals are removed.  $\lg$  is common logarithm,  $\ln$  natural logarithm,  $a$  are activities. For elements and stoichiometric compounds

$a = 1$  holds and the solution reactions in the DataBasis file is defined as an ideal diluted solution with  $a(\text{H in Ti}) = n(\text{H atoms}) / [n(\text{H atoms}) + n(\text{Ti atoms})]$  in mol fraction  $x$ .  $\lg K_p^\circ$  is the standard equilibrium constant of the reaction as defined by the data set.

### 3.2.2 Get data:

This routine is responsible for finding relevant data in the files by the input of a *system name*. The *system name* is the alphabetic sequence of the elements occurring in the reaction equation. Correct writing is very important and checked carefully by the program.

Existence and correct writing of each element symbol is checked when leaving its edit box. Confirm the end of input by pushing the buttons *Make system name* and *Insert data to store*.

The data available in a file belonging to the same system name are given to the work store and characterized in the list of content by the reaction equation. The input of data from various files finally provides the set of data required for presentation or calculation.

Data not needed can be deleted.

### 3.2.3 Show data:

With this menu you can look at the data of a reaction selected from the work store.

The *data sheet* shows the data set read from the file in the units chosen. You can get a screen copy of the sheet.

The *table* shows the values of thermochemical functions calculated from these data for various temperatures. The values for  $T_{\min}$  and  $T_{\max}$  and the temperature steps are proposed by the program, but you can choose also other numbers. If you need function values at specific temperatures you can insert these  $T$  values as  $T_{\min}$  or  $T_{\max}$ . The table shown can be printed as screen copy or saved as a text file for further use in personal documents.

### 3.2.4 Plot

With this menu the thermochemical functions  $c_p$ ,  $H$ ,  $S$ ,  $G$ ,  $\lg K_p$  of one or several reactions can be plotted vs. temperature or  $1/T$ , respectively. The units of the plot can be chosen optionally. The length and scales of the axes are at first proposed by the program according to the temperature range given in the data set, but they can be changed to fit the taste of the user.

In the plot  $\lg K_p$  vs.  $1/T$  dashes at the top can be printed at  $T$  values  $n \cdot 500\text{K}$ ,  $n \cdot 200\text{K}$ ,  $n \cdot 100\text{K}$ ,  $n \cdot 50\text{K}$ , or  $n \cdot 10\text{K}$  by pushing a button and plotting it again.

The plotted data points ( $T$ ,  $\text{function}(T)$ ) of the curves can also be stored in a text file of data points for further use in other plot programs. The lines have this structure:

$T + ' + \text{function}(T) + ' + \text{'fat/thin'}$ .

fat means data within the limits of definition, thin means extrapolation.

A bitmap of the curves can be stored, too, for further use.

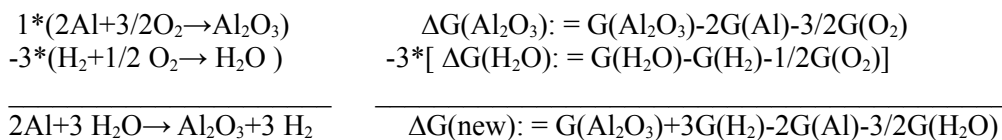
Finally, a screen copy can be printed. The comments written can remind details of the reactions or curves and, in addition, the names of the file or bitmap can be read from the printed copy.

### 3.2.5 Calculate

In compilations of thermochemical data the values for the formation of compounds from the elements are found. The  $\Delta c_p$ ,  $\Delta H$  and  $\Delta S$  values of these reactions can be combined by



multiplying with a factor and addition or subtraction in exactly the same way as the chemical symbols in order to form a new reaction equation. The result of this procedure gives the reaction data of the new reaction.

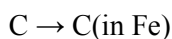


This example for G demonstrates how the data set of the new reaction is obtained by multiplication of the second data set by a factor of -3 and addition. The pointers in the equations on the left hand defines: The reactants on the left side of the equation form the reaction products on the right side. Using -1 and 3 as factors yields the backward reaction with opposite signs of the energy terms in the new data set.

One problem is left to the care of to the user, the problem of *compatible standard states*.

The activity for *stoichiometric compounds* is defined to be 1 and for *gases* the pressure is normally defined to be 1 atm. That is no real problem.

For *diluted solutions* (mole fraction  $x < 0.03$ ) one can write a reaction equation



and define the activity as  $a = x$ . This has the consequence that we define a new artificial standard state, carbon in iron with the concentration  $x = 1$ . The reaction energy and entropy values represent the difference between these two standard states. This sounds somehow crazy. However, also for the solution of gases,  $\text{H}_2 \rightarrow 2\text{H}(\text{in Fe})$  we obtain a clear definition for the Sievert's constant  $x^2/p = K_p(T)$ . The "heat of solution", the enthalpy change of this reaction, is a very informative term for such type of reactions. The data file DataBasis.txt contains a collection of solution data for H, C, N, and O in metals using these standard states.

Whenever data of solutions, mixtures or alloys are used in calculations one has to check carefully the standard states with respect to  $p$  and  $a$  (i.e. pressure and concentration units). The definition of the activity of an element as an element in a mixture defines also the standard state of  $\Delta S$  of a reaction. Big mistakes can arise in this corner. A look at relevant chapters in a text book may be helpful to avoid drastic errors caused by mixing incompatible standard states in calculations.

Another point one has to consider when using literature data is to check whether the term  $G(\text{Al}_2\text{O}_3)$  means  $\Delta G$ , i.e. the reaction Gibbs free energy of formation from the elements, like in this program, or the absolute value of  $G$ . An example how to handle this problem is discussed in the menu *Data input* [2,3].

### 3.2.6 Data Input

With this menu you make new data sets in the style of this program and save them in data files, e. g. in the files PrivData.txt or TempData.txt already existing, or in any other file with a new name \_\_\_\_Data.txt.

At first you are asked to define the units of input data and the *system name* of the reaction. Then you have to enter the type of data presentation you found in the literature and have to write the reaction equation and the reference or other comments.

Then a data sheet is shown which contains already the system name, the reaction equation and reference and the units of the data, you are inserting now. The sheet asks for Tmax and Tmin of the data. Tmin is frequently 298 or 300 K and Tmax the melting point of a compound or the highest temperature of experiments.

The types of data presentation accepted by the program are:

1) Ho, So : In many data collections these most important constants of a reaction are found. Since the values at To (mostly 298 K) are only slightly affected by the cp value of the reaction these data give very reliable estimations, in most cases reliable within the error of experiments [4-7]. In many more professional data compilations the H and S values are tabulated as a function of temperature. Since both quantities are not strongly temperature dependent one can get average values for a temperature range of interest from such tables for the input of H and S.

2) The book of Kubaschewski et al., Metallurgical Thermochemistry [1], uses three constants A, B, C, which define Ho, So, and a constant Δcp value, which is represented in our system by the constant a.

A detail for the insider:

With the approximations  $cp = a$  and  $To = Tmin$  one can write:

$$G = (H - a \cdot Tmin) - T \cdot (S - a \cdot (1 + \ln Tmin)) - a \cdot T \cdot \ln T \\ = A + B \cdot T \cdot \lg T + C \cdot T.$$

Thus:  $a = -B / \ln 10$ ;  $H = A + a \cdot Tmin$  ;

$S = -C + a \cdot (1 + \ln Tmin)$ ;

3) This data set is based on the compilation of Barin/Knacke[2,3] with the additional constants a, b, c, d, which describe the temperature dependence of cp(T) and of H(T) and S(T). This very precise description of thermochemical data is included for the use by experts and has to be handled with care. When using the data from the book of Barin/Knacke a problem arises from the fact that they give not the reaction data (delta values) but data of the components of the reaction equation.

$$\text{delta value}(2Al + 3/2 O_2 \rightarrow Al_2O_3) = \text{data}(Al_2O_3) - 2 \cdot \text{data}(Al) - 3/2 \cdot \text{data}(O_2)$$

To stay within the system of this program one has to perform at first this transformation before the input of reaction delta values is done, either by hand or by the menus *input* and *calculate*.

4.) Sometimes only an equilibrium constant is available for a reaction. If we use the equation  $\Delta Go[J] = -RT \cdot \ln Kp(T) = -19.144 \cdot T \cdot \lg Kp(T)$ , the Go value at two temperatures of interest can be obtained. This gives us an average H and S value and a data set which is as reliable as the set obtained by style 1.) data [4,5]. Of course, the standard state with respect to pressure (p in atm) and concentration (x mol fraction for ideal dilute solutions) must be the same as for the other reaction data used to yield correct results in the *calculate* menu.

The input of data to the temporary file, just to have a look at them or to get a plot or a table, is not critical. However, if one needs a data set for more detailed thermochemical analysis or for calculations, the compatibility of the standard state of the new data set with the data in the permanent files should be controlled carefully.

#### References:

- 1) O Kubaschewski, C.B.Alcock, P.J.Spencer, Materials Thermochemistry, 6th Ed., Pergamon, Oxford 1993
- 2) I. Barin, O. Knacke, Thermochemical Properties of Inorganic Substances, Springer Berlin 1973

- 3) O. Knacke, O. Kubaschewski, K. Kesselmann, Thermochemical Properties of Inorganic Substances, Springer Berlin 1991
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- 5) E.Fromm, H.Jehn, G.Hoerz, H.Speck, W. Hehn, Gases and Carbon in Metals, Pt 1-22, Physics Data, H. Behrens, G.Ebel eds. Fachinformationszentrum Energie, Physik, Mathematik, Karlsruhe 1976-1984
- 6) E. Fromm, G.Hoerz, Gases and carbon in metals (Rev. 259), International Metals Reviews, TMS,ASM London,1980, Nos.5 and 6
- 7) E.T. Turkdogan, Physical Chemistry of High Temperature Technology, Academic Press New York, 1980

### 3.2.7 File care

This menu is a separate part of the program. It enables a check of the files used or produced by the program such as data files, files of data tables or plot data files. Most files are saved as text files and the user can check and manipulate them by any text program, e.g. Wordpad. Thus, the data can easily be transferred to own documents by a user who is accustomed to do this. Such actions are, of course, within your own responsibility and saving backups before manipulating is recommended.

The program uses the following file types:

- 1) DataBasis.txt  
Checked data which should be protected against incorrect manipulations. Therefore, the file is not included in the file filter \_\_\_\_Data.txt and saved write protected. If the user has an own basic data file he can rename it to DataBasis.txt and replace the present one.
- 2) Other data files (\_\_\_\_Data.txt)  
Two files, TempData.txt and PrivData.txt, are already prepared and others can be added by the user.
- 3) Plot data files (\_\_\_\_Plot.txt)  
This list of data points of plots can be used or prepared for input into more advanced plot programs.
- 4) Bitmap files (\_\_\_\_.bmp)  
Bitmaps of data plots
- 5) Text files (\_\_\_\_.txt)  
They can be used for documentation of data tables.
- 6) Backup files (\_\_\_\_.bak)
- 7) Help files (\_\_\_\_.H.txt)

The consequent use of file names and extensions is not controlled by the program, but some routines use these name styles as flag. Therefore, correct names may avoid confusion.

**Submenu Files:** In the list box on the left side you see an incomplete copy of the data file selected from the load menu and can check whether or not it is present. With the buttons on the right side some manipulations can be made.

- |    |                 |  |
|----|-----------------|--|
| 1) | Rename file     | -Renames the file.                     |
| 2) | Delete + backup | -The file is renamed to (____.bak).    |
| 3) | Clear file      | -Removes all lines, the file is empty. |
| 4) | New file        | -Makes a new file with a new name.     |
| 5) | Save file as    | -Makes a file copy with a new name.    |

**Submenu Data set:**

This submenu reads the system names from a data file \_\_\_\_Data.txt and shows them in a separate list box. When you click a system name the data are shown in a data sheet. If data for more than one reaction exist the Next button shows them all. The Delete button on the right corner removes the data set shown in the sheet from the file. If you wish to lose no information you can get a print copy by pushing the Print button.

If you wish to replace a data set in a file the following procedure is recommended, because then the control routines of the program remain active: First add the new data set using the Data input menu of the main program and then Delete the old data set by this menu.

To *move* a data set from one file to another one you can use the menu calculate. One has to set the factor 1/1 and to write the reaction equation and references into the edit windows shown. With the Store button you can add the new data set to another file.

### 3.3 Data on the solubility of H, C, N, and O in metals

#### 3.3.1 Some basic definitions

At first a few basic remarks on reaction G values, molal compound g values and chemical potentials  $\mu$ . For details one should consult a textbook on thermochemistry.

The *molal g value* of  $\text{Al}_2\text{O}_3$  ( not the  $\Delta G$  value for formation !)

$$g(\text{Al}_2\text{O}_3) = 2/5 \mu(\text{Al in Al}_2\text{O}_3) + 3/5 \mu(\text{O in Al}_2\text{O}_3)$$

is constant, and for phases with more extended concentration range it can be set constant for estimations within the error limits. Thus, the G value of  $\text{Al}_2\text{O}_3 = 5g(\text{Al}_2\text{O}_3)$  is constant, too, and can be defined as  $G_0$  and  $a(\text{Al}_2\text{O}_3)$  as 1. However, the two  $\mu$  terms in the sum of g can change drastically with concentration.

*Phase equilibrium* is defined by the condition that the chemical potentials of all elements in all phases have the same value. This has the consequence that  $\mu(\text{Al})$  and  $\mu(\text{O})$  depend on the type of equilibrium considered. If  $\text{Al}_2\text{O}_3$  is in equilibrium with the gas phase, then  $a(\text{O in Al}_2\text{O}_3) = a(\text{O in O}_2 \text{ gas})$  holds and  $a(\text{Al in Al}_2\text{O}_3)$  is very small. However, if  $\text{Al}_2\text{O}_3$  is in equilibrium with Al metal, e.g. in a closed receiver, then  $a(\text{Al in Al}_2\text{O}_3) = 1$  holds and  $a(\text{O in Al}_2\text{O}_3)$  is extremely small as well as the  $\text{O}_2$  pressure. These changes of the  $\mu$  values depend on the defect structure of compounds. This is normally not well known and of little interest for usual thermochemical calculations.

In order to calculate correct equilibrium constants one has not to care about these details if the following points are obeyed:

The equilibrium constant of our example

$$2\text{Al} + 3/2 \text{O}_2 \rightarrow \text{Al}_2\text{O}_3 \quad \text{is}$$

$$\lg K_p(T) = \lg [a(\text{Al}_2\text{O}_3) / (a(\text{Al})^2 p(\text{O}_2)^{3/2})] = - \Delta G_0 / (R \cdot T \cdot \ln 10),$$

where in the numerator we have the terms for the activities of components formed and in the denominator for components consumed.

$$\Delta G_0 = G_0(\text{Al}_2\text{O}_3) - 2G_0(\text{Al}) - 3/2 G_0(\text{O}_2).$$

As mentioned above,  $a(\text{compound})$  and  $a(\text{element})$  are 1 by definition and  $a(\text{H}_2)$ ,  $a(\text{N}_2)$ , and  $a(\text{O}_2)$  are  $p[\text{atm}]^{1/2}$ .

Fortunately, during correct addition or subtraction of  $\Delta G_0$  values of reaction equations the equilibrium conditions are automatically described correctly by the equilibrium constant

obtained if

- 1) the definition of activities is the same in all equations and if
- 2) the direction of the reaction is correctly defined by the sign of the  $\Delta G_o$  value (formation, not decomposition of  $Al_2O_3$ ).

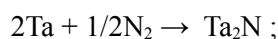
Before new data are calculated one has to check these points. Then one has to combine the initial reactions in such a way that only the phases being in equilibrium show up in the new equilibrium constant and in the reaction equation and all others are eliminated.

### 3.3.2 Data available

The file DataBasis.txt is a compilation of:

**1) The solution reaction** of  $H_2$ ,  $N_2$ , and  $O_2$  in metals. This is a phase transition reaction of atoms, e.g.  $1/2 N_2 \rightarrow N(\text{in Ta})$ . The equilibrium or Sieverts constant  $\lg K_p(T) = x[\text{mol fraction}] / p[\text{atm}]^{1/2}$  describes the concentration of gas atoms dissolved in the metal as a function of gas pressure and temperature. However, it does not tell us the terminal solubility in equilibrium with a compound.

**2) The compounds** (carbides, hydrides, nitrides, and oxides) forming equilibria with the solution phases **1)**. Such a reaction can be written as



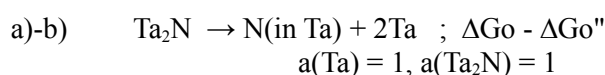
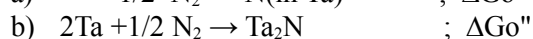
$$\lg K_p(T) = \lg (a(Ta_2N) / (a(Ta)^2 \cdot p(N_2)^{1/2}) \text{ or with } a(Ta) = a(Ta_2N) = 1$$

$$\lg p(N_2) = 2 \cdot \Delta G_o / RT \cdot \ln 10.$$

The activity of the metal in the solution phase deviates only little from one. The  $N_2$  pressure defined by the equilibrium constant is the decomposition pressure of the nitride. At pressures below this value no  $Ta_2N$  is formed.

#### 3) Calculation of the terminal solubility of N in Ta.

We can write



$$\lg K_p(T) = \lg x[\text{mol fraction}] = -(\Delta G_o - \Delta G_o'') / RT \cdot \ln 10$$

This equation gives the terminal solubility of N in Ta. If we increase the pressure at constant temperature  $Ta_2N$  is formed and the N concentration remains constant.

The data for the solubility **1)**, the decomposition pressure **2)** and the terminal solubility **3)** are no independent data. If two are known the third one can be calculated or controlled. This has been done with most data in the file DataBasis.txt. To get the phase boundary line of the  $Ta_2N$  phase on the low N concentration end one should have an equation for the dependence of  $a(N \text{ in } Ta_2N)$  as a function of  $x(N)$ . This is normally not available and a complex problem not suited to be discussed here.

**4) Carbon solubility:** If the terminal solubility of C in a metal is known and the  $\Delta G_o$  value for formation of the equilibrium carbide one can determine the C activity in the metal with the routine shown above. This enables the calculation of  $CO/CO_2$  equilibria.

Other metal/gas interactions are  $H_2/H_2O$ ,  $H_2/CH_4$  or  $H_2/NH_3$  reactions. The  $O_2$  equilibrium

pressure in a two phase range between two oxides can be calculated by forming, for example, a reaction equation  $\text{CuO}_2 \rightarrow \text{CuO} + 1/2\text{O}_2$  from the standard equations of formation for the two oxides.

More detailed treatises on the subject are found in Refs.1,4,6 given in section *Data input*.

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