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IVTANTHERMO FOR WINDOWS - DATABASE ON THERMODYNAMIC PROPERTIES AND RELATED SOFTWARE

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ABSTRACT: A new version of the software package IVTANTHERMO for Windows intended for thermodynamic modelling of complex chemically reacting systems is described. The package includes an extensive database on thermodynamic properties of individual substances, programs for the database handling and a program, which allows the calculation of equilibrium composition and thermodynamic properties of the system to be examined. The software is intended for scientists, chemical engineers and students.

Introduction

The importance of thermodynamic modelling cannot be overestimated. A number of examples illustrating how thermodynamic calculations may be used as a basic tool in the development and optimisation of materials and processes are presented in the excellent book 'The SGTE Casebook: Thermodynamics at work' (1). Of course, thermodynamic modelling cannot completely substitute for experiments. However, it may help to estimate the area of parameters where the experiment should be carried out. As the computer becomes more of an accepted instrument for a researcher, the applicability of the field and methods of computational thermodynamics is constantly growing. And the requirements for related software are growing too. At present any serious computer program intended for thermodynamic modelling of processes should contain at least three parts: a database on thermodynamic properties of substances, modelling software itself and a special service software for database handling. A software interface should be clear and intelligible. The user should not spend too much time reading manuals before he can accomplish simple calculations. The database of thermodynamic properties should be reasonably extensive and reliable, as incomplete information or wrong data may easily result in errors of modelling and therefore in lost time and effort. All the requirements mentioned were taken in consideration at the development of IVTANTHERMO for Windows.

The whole software package IVTANTHERMO contains a database and six programs:

- THERBASE - tool for database handling;
- EQUICALC - tool for modelling;

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- APPROX - a supplementary tool to input new thermodynamic data;
- DATANAL - a program for statistical analysis of information in the database;
- HB - a program which calculates heat and material balance in the thermodynamic systems;
- REPORTER - supplementary tool for printing the results.

The database and software allow the user to carry out a theoretical study of the

- possibility for deriving optimal parameters of various new high temperature processes;
- optimisation of conditions for the synthesis of chemical compounds including refractory materials and materials for microelectronics;
- stability of refractory materials at high temperature and in aggressive atmospheres;
- processes that occur in power-generating facilities including nuclear ones;
- conditions for the optimisation of chemical-engineering and metallurgical processes;
- optimisation of utilisation of raw materials and the processing of industrial waste products;
- processes resulting in the emission of noxious combustion products and gas-phase industrial waste into the atmosphere;
- methods intended for prevention of environmental pollution etc.

An extensive database on thermodynamic properties of individual substances and modelling abilities make IVTANTHERMO a useful tool for scientists, chemical engineers, who investigate high temperature processes with chemical transformations, and for the senior students of chemical engineering departments. As the software has a relatively simple interface, accomplishing of thermodynamic calculations is possible without the thorough study of documentation. The basic modules of IVTANTHERMO are supplied with a chart analyser so that the user can easily convert most of the data or the results into curves, which can be modified, printed or exported to other programs. Now, let us briefly describe the basic parts of the software.

Database

In Thermocenter of the Russian Academy of Science over many years the theoretical study of thermodynamic properties of individual substances has being carried out. The information has been accumulated in the form of a reference book (2) and a database (3). This information is intended for scientists and engineers who work in various branches of science and engineering so it must be delivered to them in an easy-to-handle form.

The most characteristic feature of IVTANTHERMO is that the stored information is not borrowed from any other database or reference book. This information is obtained by means of the critical analysis and treatment of the original data available in literature. Primary information analysis and all necessary calculations have been performed with the use of the original methods, algorithms and software developed for the 'Thermodynamic Properties of Individual Substances' handbook and updated by its authors for the IVTANTHERMO database. At present, the database contains information about approximately 2500 substances formed by 98 chemical elements.

Much attention was paid to the reliability of the thermodynamic data stored in IVTANTHERMO. The evaluation of the quality of the information published in reference

books and stored in databases is a very complicated task. Still more difficult is the evaluation of results arising from the use of unreliable information when used in a thermodynamic analysis of various processes. The main reason for the complexity of the first task is the absence of complete information about the adopted values, i.e. absence of all primary data and details of their processing. More detailed discussion regarding the questions of accuracy of thermodynamic properties and the influence of erroneous data on the results of chemical equilibrium calculations may be found in references (4, 5).

The software allows a user to work with two databases: MAIN and OWN. The MAIN database contains IVTANTHERMO data on thermodynamic properties of individual substances. The OWN database may be used to work with some limited sets of data or for experimental purposes. For example, it may be used for the storage the user's data about substances. Both databases use the same format for keeping information. The information can be copied from the MAIN database into the OWN database.

THERBASE

This program provides access to all information about substances stored in the database: a chemical formula, substance name, class of accuracy, molecular mass, reaction of dissociation (sublimation) and the enthalpy of this reaction $\Delta_r H°$ as well as the following thermochemical information

$\Delta_f H°$ (0) - the enthalpy of formation at $T = 0$ K,
$\Delta_f H°$ (298) - the enthalpy of formation at $T = 298.15$ K,
$Cp°$ (298) - the isobaric heat capacity,
$S°$ (298) - entropy,
$H°$ (298)-$H°$ (0) - change of enthalpy between 298.15 K and 0 K,
S(nucl) - the nuclear spin component,
coefficients of polynomials approximating the Gibbs energy as a function of temperature.

THERBASE allows the user to review database contents, extract information about substances, modify this information, add new information, examine thermodynamic properties of chemical reactions, carry out a quick search for a given substance or group of substances for a set of elements and phase state etc. THERBASE can display information in TPIS format and JANAF format tables for a given temperature interval with an assigned step, save it in a text file and visualise it as charts.

A table in TPIS format contains values of Cp - heat capacity, F - Gibbs energy function related to T=0 K, S - entropy, H - enthalpy change and $\log_{10}(Kp)$ - decimal logarithm of the equilibrium constant of the reaction of dissociation (sublimation).

A table in JANAF format contains values of Cp - heat capacity, S - entropy, $-(G-H(T_r))/T$ - Gibbs energy function related to 298.15 K, H - $H(T_r)$ - change of enthalpy, $\Delta_f H$ - the enthalpy of formation, $\Delta_f G$ - Gibbs energy of formation and $\log_{10}(K_f)$ - decimal logarithm of the equilibrium constant of the reaction of formation of the given substance from the elements in their standard states, T_r - standard temperature (always 298.15 K).

A table for the reaction analysis contains the values: ΔH_r, ΔG_r, ΔS_r, ΔCp_r and $\log_{10}(Kp)$ of the reaction as functions of the temperature.

The tables can be generated for any temperature range from 298.15 K to T_{max} with a defined step.

EQUICALC

This is the central program in the software package. It allows the calculation of chemical compositions and equilibrium parameters of complex chemically reacting systems. At present, there are two versions of the program - for Windows 3/x and for Windows95/98/NT. Windows 3/x version of the program can handle simultaneously up to 350 substances and up to 40 phases including one or two condensed solutions. The Windows 95/98/NT version can handle simultaneously up to 700 substances and up to 60 phases. These limits were set from practical considerations and may be easily extended if necessary. Specially for the Windows version a new algorithm for the calculation of equilibrium composition has been developed. Possible combinations of parameters specifying the equilibrium are

(T, p) : temperature and pressure; *(T, V)* : temperature and volume; *(T, S)* : temperature and entropy; *(p, V)* : pressure and volume; *(p, H)* : combustion at constant pressure; *(p, S)* : adiabatic expansion down to a given pressure; *(V, U)* : combustion at constant volume; *(V, H)* : volume and enthalpy; *(V, S)* : adiabatic expansion up to a given volume.

The equilibrium compositions may be presented in moles, mole fractions or mass fractions. Various calculated thermodynamic parameters are listed below:

p - pressure, ***T*** - temperature, ***V*** - volume, ***S*** - entropy, ***H***-enthalpy , ***U*** - internal energy, ***M(g)*** - number of moles of gas substances, ***Mcond*** - mass fraction of all condensed substances, ***Cp***, ***Cv*** - specific heat at constant pressure and volume respectively (frozen), ***a*** - sound velocity, ***γ = Cp/Cv***, ***Cp"***, ***Cv"*** - heat capacity at constant pressure and volume (equilibrium), ***a"*** - sound velocity (equilibrium), ***γ " = Cp"/Cv"***, ***m*** - total mass of the substances, etc.

The procedure for the calculation of equilibrium values of specific heat and sound velocity, which are different from frozen ones, takes into account possible changes of composition as function of temperature. At high temperatures, where concentrations of substances may change quickly with temperature the difference between frozen and equilibrium values of the specific heat can be very significant. Table 1 illustrates the difference between the values of *Cp* and *Cp"* in the reacting mixture $AsCl_3(g)+2H_2(g)$.

TABLE 1

Cp and *Cp"* in the Reacting Mixture $AsCl_3(g)+2H_2(g)$

T/ K	*600*	*650*	*700*	*750*	*800*
Cp/ kJ $(kg \cdot K)^{-1}$	0.704	0.708	0.710	0.703	0.685
Cp"/ kJ $(kg \cdot K)^{-1}$	0.714	0.794	1.223	3.136	0.689

Details of the algorithm of EQUICALC are to be described in a future article. We use a Gibbs energy minimisation approach to find the unknown equilibrium concentrations of substances. The main advantage of the algorithm is its ability to find reliably the phase composition of the system even when the number of possible phases is large. It allows the

determination of the equilibrium concentrations even if the gas phase is negligibly small or it is virtually absent.

In some cases EQUICALC provides a possibility to calculate an approximate value of saturated vapour pressure p(sat). It is possible, for example, that a specified pressure p is more than saturated vapour pressure. In this situation finding an equilibrium composition which fits the defined pressure and temperature values is impossible, because p(sat) is function only of one parameter according to the Gibbs phase rule, but nevertheless p(sat) value may be estimated. The file of results in this case will contain p(sat) values and partial pressure values for all gas components, mole numbers of gas substances are assumed to have a zero value. Table 2 shows experimental (6) and calculated decomposition pressure values, MPa, in the system Si-O_2 at T=1890 K, the total pressure (calculated) is $2.49 \cdot 10^{-7}$ MPa. Figure 1 displays the calculated dependence of the partial pressures (MPa) of the gases over the condensed Al_2O_3.

TABLE 2
Experimental (6) and Calculated Decomposition Pressure Values, MPa, over SiO_2

Substance	*SiO_2*	*SiO*	*O_2*	*O*
Experiment	$9.99 \cdot 10^{-9}$	$1.94 \cdot 10^{-7}$	$9.38 \cdot 10^{-8}$	$3.47 \cdot 10^{-8}$
Calculation	$9.52 \cdot 10^{-9}$	$1.44 \cdot 10^{-7}$	$7.19 \cdot 10^{-8}$	$2.31 \cdot 10^{-8}$

Calculations are also possible with partially frozen compositions, if the concentrations of some substances are known. Available activity coefficients of mixture components can be taken into account too.

Thermodynamic analysis of metallurgical processes often requires knowledge of activity coefficients of single condensed compounds. Values of these coefficients serve as a measure of the stability of the phase or the possibility of its appearance when the parameters specifying equilibrium or reactants' composition are changed.

If a series of calculations has been completed, the concentrations of the selected substances or the values of the selected parameters can be extracted into a table or presented. as charts on the display screen. This useful feature makes it easier to understand the specific details of the process examined. In the simplest case, to accomplish the calculation of the equilibrium compositions and related thermodynamic properties of a system, it is necessary to assign only the values of two thermodynamic parameters and specify the reactants and their quantities.

An example of the results of calculations is shown of Figure 2, only the dominating gas substances are listed for brevity.

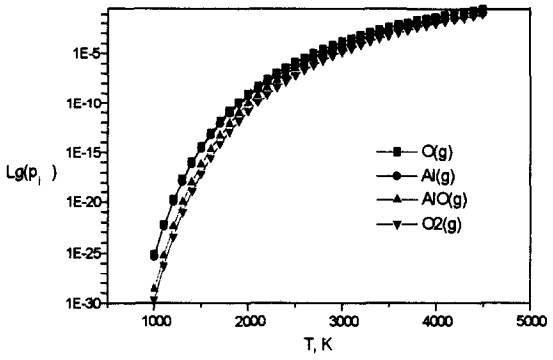

FIG.1

Partial pressures of gases over condensed Al_2O_3

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Assigned values of equilibrium parameters :
          p =     0.10000 MPa              T =  1000.00000 K
          Elements in system, mole
[Fe]=   1.000   [ C]=   1.000   [ S]=   1.000   [ O]=   2.000
                Equilibrium parameters :
        p =     0.10000 MPa               S =     3.13660 kJ/(kg*K)
        T =  1000.00000 K                 H = -3136.52270 kJ/kg
        V =     0.63127 cub.m/kg          U = -3199.64968 kJ/kg
     M(g) =     1.0016  mole           V(g) =  0.63127 cub.m/kg
     R(g) =     0.00833 kJ/mole       Mcond =  0.666
       Cp =     0.86501 kJ/(kg*K)        Cv =  0.80189 kJ/(kg*K)
       Cp"=     0.91427 kJ/(kg*K)        Cv"=  0.84900 kJ/(kg*K)
        a =   260.95312 m/s            GAMMA =  1.07872
        a"=   260.72912 m/s            GAMMA"=  1.07687
        m =  0.13192 kg
        v =     0.08328 cub.m          s =     0.41379 kJ/K
        h =  -413.77886 kJ             u =  -422.10675 kJ
                    Concentrations of species, mole:
Phases
 1)                    S(c) 0.00000E+00  (activity: 4.435E-03)
 2)          C(c;graphite) 0.00000E+00  (activity: 1.699E-05)
 3)                   Fe(c) 0.00000E+00  (activity: 8.160E-04)
 4)                  FeO(c) 0.00000E+00  (activity: 1.979E-01)
 5)                 Fe2O3(c) 0.00000E+00  (activity: 1.448E-01)
 6)                 Fe3O4(c) 6.98957E-04  (activity: 1.000E+00)
 7)                  FeS(c) 9.97903E-01  (activity: 1.000E+00)
 8)                 FeS2(c) 0.00000E+00  (activity: 1.486E-02)
 9)       Gas. Moles of phase:  1.00162E+00
                  CO2(g) 9.94177E-01                  CO(g) 5.45562E-03
                  SO2(g) 1.51214E-03                 COS(g) 3.67016E-04
                   S2(g) 1.06211E-04                 S2O(g) 2.29074E-06
                   SO(g) 2.70629E-07                  S3(g) 1.37674E-07
                  CS2(g) 1.44980E-08
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FIG. 2

An example of the output of results of the calculations

DATANAL

This program is intended for statistical analysis of the information stored in the database. Though the database IVTANTHERMO is extensive enough, experience shows that some data for modelling may be missing. Sometimes approximate values of unknown data can be obtained using methods of comparative calculations. The theoretical background to these methods is the chemical similarity of substances with related compositions and structure.

DATANAL can help to find correlation between some properties using the information from the database and obtain an approximate value for an unknown parameter. To carry out statistical analysis we use traditional least squares techniques for a polynomial.

APPROX

This program is intended for the calculation of the coefficients of a polynomial for representing the specific heat *Cp*. Calculations can be carried out providing values of specific heat for some temperature range are known. Values of basic thermodynamic parameters for the reference state and values of heats of the phase transitions should be known too. The results of calculations may be saved either into a text (ASCII) file or into IVTANTHERMO database.

It is possible to "design" a polynomial, different from that used in IVTANTHERMO, and to calculate its coefficients. In other words, APPROX makes it possible to import or export thermodynamic information from one database into another.

The input of *Cp* values can be done by two routes. If one knows the data for some temperature range, these can be typed into the table of APPROX. After this, the polynomial's coefficients will be computed. Sometimes the values of the coefficients of an approximating polynomial are known and it is necessary to convert this information into IVTANTHERMO format. For this purpose, APPROX has a built-in calculator, which can use the formula to calculate *Cp* values in an assigned temperature range with a given step. Calculated data may then be used for further computation of the coefficients of the new polynomial.

Conclusion

Finally, we would like to return to the modelling software and the database already discussed. At present there are many algorithms and computer programs intended for calculation of equilibrium parameters of chemically reacting systems, see (7, 8) for example. The main reason for the appearance of all these programs is that none of them is universal (if there were any it would be used everywhere). This fact, in its turn, can be explained by the variety of existing thermodynamic systems and by the specific nature of computer mathematics with its limited accuracy of calculations. However, one can discuss the relative universality of an algorithm, which implies that it may be used for thermodynamic analysis of various kinds of thermodynamic systems without significant modifications. The algorithm of EQUICALC, we believe, meets this requirement.

As it was already mentioned, for many years Thermocenter has been involved in an activity concerned with thermodynamic data assessment. In addition to the verified data stored in IVTANTHERMO database, we have a large array of information about

thermodynamic properties of individual substances which we cannot formally recommend but which may be used in calculations if there is no other information.

Acknowledgments

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