Simultaneous analysis of the enthalpy increment and heat capacity data measurements for updating the IVTANTHERMO database

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Abstract. An analysis of the enthalpy increment and heat capacity data measurements is required for developing thermodynamic databases such as the IVTANTHERMO database created in the Glushko Thermocenter of JIHT RAS. A new CondensedThermoFit code is developed which provides experts with a comprehensive set of analysis tools for working with data on the specific heat and enthalpy increments for substances in the condensed state. These tools include simultaneous approximation of these two types of data. The enthalpy increment data is treated using the Shomate method while the heat capacity data is fitted with a flexible and manually constructible function. Only polynomial-like fitting functions are implemented so far. The final results are ready for exporting into the database with a fixed form of the fitting function such as the IVTANTHERMO database. The code has a cross-platform design, extensible module structure and graphical user interface.

1. Introduction

Original experimental data on thermodynamic properties of substances in the condensed phase are often presented as tables and need to be approximated with functions that reproduce them with an acceptable accuracy. These functions can be used then for thermodynamic modelling applicable to theoretical studies in such areas as rocket engine engineering, nuclear power, chemical technology, metallurgy, production of semiconductor materials and microelectronics, resource usage, waste recycling, etc [1].

The IVTANTHERMO information system [2, 3] based on the reference book [4] has made a significant contribution to the accumulation of thermodynamic data. It was created in the department of chemical thermodynamics that was founded in 1963 in the Institute of High Temperatures of the Academy of Sciences of the USSR. Nowadays the development is continued in the Department for Thermophysical Data (Glushko Thermocenter) of JIHT RAS [5]. At present the database contains more than 3400 substances, formed by 96 chemical elements.

Creation of the reference book [4] and the IVTANTHERMO information system is inextricably linked to the development of various methods of thermodynamic data processing.
The most common method for obtaining thermodynamic properties of substances in gaseous state is calculation based on molecular constants [6, 7] or using interatomic interaction potentials [8, 9]. Calculating thermodynamic properties of substances in the condensed state is still a challenging task, which requires statistical analysis of direct measurements of enthalpy increments and heat capacity, including estimation of initial data error, robust estimation, examining phase transition areas and approximation of the measured values with appropriate analytical dependencies [10, 11].

By convention, thermodynamic data for substances in the condensed state can be divided into low-temperature ($T < 298.15$ K) and high-temperature ($T \geq 298.15$ K) regions. Following the reference book [4] we mostly focused on the high temperature region, therefore the Shomate method [12] was chosen for fitting the high-temperature data on enthalpy increments. The method has proved itself to be reliable for approximation of smooth curves without $\lambda$-transitions and it was extensively used for preparation of the reference book [4] and the IVTANTHERMO database.

In general, the choice of a fitting function is rather controversial. It is yet being discussed whether analytical view of these functions should reflect the physics of the processes, and different approaches to this question lead to a vast variety of function types. Specific heat of solids at cryogenic temperatures is well described by Debye and Einstein models [13]. In [14] a generalized model is described. It can be extended for high temperature region though it is not physically based in that area. In [15] a thermodynamic modelling strategy of stable solid alloy phases is proposed based on segmented regression approach. The model considers several physical effects and is valid starting from 0 K. The method is a segmented model where the heat capacity of pure elements is described as a combination of functions. The authors claim that model delivers an accurate description down to 0 K for all studied pure elements according to several statistical tests. An overview of some approaches to data analysis in the high temperature area can be found also in [16].

There are several applications and computer codes developed for approximation of experimental data on the heat capacity and enthalpy increments. Some of them are open source, others are distributed as executable files [16].

An application “CpFit” is described in [17]. The program works with heat capacity and enthalpy increments processing the data with a sum of Einstein-Plank functions. It can work with data that includes anomalies such as $\lambda$ and Shottky transitions. It is distributed as a Windows application. Various types of data are processed within one data array.

In [18] the description of another approximation algorithm is provided. It is implemented as a console application “SmoothSTF”. The code does not have a GUI and works with the heat capacity data only.

These examples show that the choice of specific codes for working with the data on heat capacity and enthalpy increments is limited. There is a need for an application with a well-developed user interface which allows simultaneous processing of common experimental data types and flexible control of approximation parameters. Processing data with analytical functions mitigates negative effects of data types conversion, for instance, appearance of undesirable oscillations after numerical derivation of enthalpy increments. If the functions have commendable analytical forms, transitions between them are easy.

In this paper we describe the “CondensedThermoFit” code which meets the above mentioned criteria including a possibility to choose from several methods, data visualization and export to a selected database format.

The first section describes approximation methods under consideration; the second section overviews the CondensedThermoFit interface and main features; the third section provides an example of using the application for processing thermodynamic data for UO$_2$. 
2. Description of the algorithms used

2.1. Processing the enthalpy increment data

For approximation of the high temperature data for enthalpy increments only the Shomate method [12] is implemented in CondensedThermoFit so far. Being quite simple, this method proved its reliability during the development of the IVTANTHERMO database. It suits processing arrays of data taken from several experiments. Let us briefly describe the main features.

First the Shomate function and its weights are calculated for each data point:

\[ F_i = \frac{T_i}{(T_i - T_0)^2} \left( [H^0(T_i) - H^0(T_0)] - C_p^0(T_0)(T_i - T_0) \right), \]

\[ \Delta F_i = \frac{T_i}{(T_i - T_0)^2} \left( \Delta [H^0(T_i) - H^0(T_0)] [H^0(T_i) - H^0(T_0)] - \Delta C_p^0(T_0) \right) (T_i - T_0), \]

where \([H^0(T_i) - H^0(T_0)]\) is the measured enthalpy increment related to an initial temperature \(T_0\), \(\Delta [H^0(T_i) - H^0(T_0)]\) is the overall enthalpy increment error reported by experimentalists or estimated, \(C_p^0(T_0)\) and \(\Delta C_p^0(T_0)\) are the heat capacity at the initial temperature and its error, the sign \(\circ\) stands for the standard conditions (\(P = 101325\) Pa).

As seen from Eqs. (1)–(2) the method requires several parameters. The value of the initial temperature is typically taken as \(T_0 = 298.15\) K. The values of \(C_p^0(T_0)\) and \(\Delta C_p^0(T_0)\) can be obtained from an additional analysis of the low temperature data. Assigning weights to the data included in the simultaneous approximation by setting their initial error \(\Delta [H^0(T_i) - H^0(T_0)]\), one can consider the experiments’ reliability which is influenced by measurement errors and purity of used samples.

At the second step the values of \(F_i(T_i)\) are fitted with the Shomate equation using the least square method. In our case we used an extended Shomate equation which leads to the following forms of the fitting functions for the enthalpy increment and heat capacity

\[ H^0 - H^0(T_0) = aT + bT^2 + cT^{-1} + d + eT^3 + fT^4 + gT^5, \]  

\[ C_p^0(T) = a + 2bT - cT^{-2} + 3eT^2 + 4fT^3 + 5gT^4. \]

When using the Shomate method the following boundary conditions are satisfied:

\[ (dH^0/dT)_{T=T_0} = C_p^0(T_0), \quad (H^0(T) - H^0(T_0))_{T=T_0} = 0. \]  

The fixed heat capacity at \(T_0\) provides an exact connection of the fitting curve to this value. Being one of the distinctive properties of the method, this connection should be treated with due caution for at significant distances between the reference point and the interval boundaries it might lead to imprecision. Although with reasonable remoteness from \(T_0\) this connection has shown good results.

The simple forms of the equations (3)–(4) are compatible with the IVTANTHERMO internal fit function format [5] so that the fitted data can be easily exported to this database.

2.2. Processing the heat capacity data

There is a long-standing problem of joint approximation of the enthalpy increment and the heat capacity data. Some researchers or experimenters resort to numerical derivation of the enthalpy data when they need to obtain information on the heat capacity, which may lead to a dramatic scatter of the derived values [19]. In this case we suggest preliminary treating the enthalpy data with the Shomate method or any other approximation technique so that the derivative of the enthalpy fit function can be obtained analytically. It helps to avoid accumulation of error and provides a relatively stable form of heat capacity fitting results. Indeed these results still cannot...
be considered as being of the same quality as direct specific heat measurements, but they often show admissible error and may be used as a source of information on the heat capacity even in the absence of direct measurements.

Numerical integration of heat capacity measurements is used less often but in some works this method is used to get extra data on enthalpy, extend existing data sets [20] or compare results.

In CondensedThermoFit the experimental data on the heat capacity can be fitted with a function constructed from an arbitrary set of the terms like $1, T^{1/3}, T^{1/2}, T, T^2, T^3, T^4, T^5, T^6, T^7, T^{-1/2}, T^{-1}, T^{-2}, T^{-3}, \ln T, \ln^2 T$.

The fitting functions, obtained for enthalpy increment data, can be derived and compared to the heat capacity data. Then these functions can be digitized to obtain an array of $C_p(T_i)$ which may be processed simultaneously with the direct heat capacity measurements. In the same way the heat capacity function can be integrated and used along with the original enthalpy increment data.

3. CondensedThermoFit main features and user interface

3.1. General structure

The CondensedThermoFit code has a cross-platform graphical user interface based on the Qt library [21]. It has been tested for Windows, MacOS and Linux operating systems. The application main window is presented in figure 1. It has areas for parameter input/output (left part), a list of loaded input data sets (right bottom box) and the plot area. Visualization of data points and fit functions provides experts with an instrument for fast analysis of the results, tuning approximation parameters, selecting input data points and assigning their weights.

A typical workflow for calculation of the thermodynamical properties of substances in the condensed state used in the Glushko Thermocenter for decades is shown in figure 2. It consists of several steps where output of one step might be used as an input for another. Each step shown in the figure (except the one for low temperature data which is under construction) is presented as a tab in the lower part of the main window.

![Figure 1. CondensedThermoFit main application window with loaded data](image1.png)

![Figure 2. Stages of the thermodynamic data analysis for substances in the condensed state](image2.png)

Enthalpy tab represents an interface for the Shomate method described in section 2.1. The next tab is designed for heat capacity data fitting (section 2.2) and the last one for exporting
the fitted data into the database. This allows processing both discussed types of data within one framework with coordinated calculations and matching systems of units. Calculated reference points, approximation function coefficients and coordinates of data points can be transferred from one tab to another with minimal loss of accuracy.

3.2. Approximation process

Experimental data are loaded into the application as text/XML files or entered manually in a separate editor window (figure 3). After loading input data a new approximation with default initial parameters is created automatically. The loaded data sets can be marked “shown” and “used” for showing on the graph and using in the approximation process respectively.

There is a built-in data editor where one can change data points, add or delete them, and edit information about the set. Relative error of data set or relative/absolute error of a single point can also be adjusted. Each checked data point would be considered in calculation. An empty dialogue can be called for creating a new data set.

After the calculation is triggered the plot and output coefficients appear (figure 1). In the plot area the output can be switched from the enthalpy increment plot \( H(T) \) with incoming data to the heat capacity plot obtained by derivation of the result, to an auxiliary function plot, or to a text report with the full information including approximation errors, etc.

Several approximations with their own parameters including the temperature interval can be created for a data set. It might be convenient for treating phase transitions as the fitting functions for each phase are calculated independently for different temperature intervals. At the same time one can create several approximations for overlapping intervals which can be useful for comparing fitting results with different parameters. Approximations can be switched with the tabs in the left upper part of the window. The output coefficients may be corrected or entered manually. In that case they are highlighted in bold, and a plot is rebuilt. Correcting the output temperature interval may lead to extrapolation of the fitting results.

For the substances with \( \lambda \)-transitions one can manually divide temperature interval while processing heat capacity data and construct two functions: for the regular part of the heat capacity curve and for the transition area.
Data sources for “Cp/high temp” tab are files with arrays of the heat capacity data or manually added data sets. Also one can see the enthalpy increment data transferred to this tab provided that an according calculation has already been performed. In the parameter section one can pick polynomial terms to construct a fitting function. The formula appears above the check marks. Calculation results are shown either as a plot or as a text report, similar to the previous tab. Simultaneous approximation of experimental heat capacity sets with the data exported from enthalpy increment approximation stage is shown in figure 4.

The last tab of the main window is dedicated to the export functions. In this tab the coefficients of enthalpy and/or heat capacity fit functions are recalculated to obtain the functions in the form suitable for exporting into the database. At present only the IVTANTHERMO database is supported although the support for other database formats is to be done.

4. Study of thermodynamic properties of UO$_2$

As an example of using the CondensedThermoFit code we report on evaluating the thermodynamic functions of UO$_2$. The data published in the reference book [4] needed to be revised due to appearance of new experimental results in a wide temperature range up to 8000 K.

The U–O binary system and, in particular, UO$_2$ have been studied for decades (see e.g. [22–25]), however, the reason of anomalous heat capacity growth of the crystalline UO$_2$ at high temperatures is still controversial (figures 5, 6). There are experimental and theoretical evidences of an oxygen sublattice disordering which can be attributed to the so called superionic phase transition near $T = 2700$ K [22, 26–28]. Nevertheless an analysis of the experimental data for the enthalpy increments and heat capacity shows a monotonous increase of the heat capacity in this region without a typical $\lambda$ peak [23, 25].

![Figure 5](image1.png)

**Figure 5.** Crosses are approved experimental data for UO$_2$ taken into approximation, diamonds are expelled experimental points [11] not included in the final curve

![Figure 6](image2.png)

**Figure 6.** Solid line is heat capacity of UO$_2$ considered in [11]; crosses and asterisks are the heat capacity measurements [29, 30] not included in approximation curve [11]

The latest review on this issue was made in [11]. Within this work new equations for the heat capacity of UO$_2$ were determined for the solid state in the range of 298.15 K < $T$ < 3130 K:

$$C_p^0(T) = 70.396 + 34.134 \cdot 10^{-3}T - 13.020 \cdot 10^5T^{-2} - 29.227 \cdot 10^{-6}T^2 + 10.258 \cdot 10^{-9}T^3 \quad (\text{J/mol/K})$$

(6)
and for the liquid state in the range of 3130 K < T < 8000 K:

\[
C_p^L(T) = -891.887 + 324.653 \cdot 10^{-3}T + 32523.060 \cdot 10^{5}T^{-2} + 40.147 \cdot 10^{-6}T^{-2} + 1.833 \cdot 10^{-9}T^{-3} \quad (J/mol/K).
\] (7)

The equations were obtained with the help of CondensedThermoFit as a result of combined approximation of the data on enthalpy increments, published in nine works and the data on heat capacity, measured in five works. Due to the fact that obtaining a single equation for each state was a priority, the CondensedThermoFit visualisation instruments helped to accelerate the process of picking data. Some data sets were excluded from the approximation procedure due to high systematic deviation from other experiments. For the remaining data sets different uncertainties were assigned to the experiments leading to different weight factors in the Shomate function. Finally the statistical analysis helped to find an optimal polynomial degree.

5. Conclusion
The CondensedThermoFit cross-platform GUI application is developed for evaluation and approximation of experimental data on the enthalpy increments and heat capacity for pure substances in the condensed state. It provides a convenient workspace for experts and allows obtaining satisfactory results along with making technical data processing less time-consuming. The Shomate method is implemented for the enthalpy data which allows analytical differentiation of the obtained fit functions and using them for evaluation of the heat capacity depending on temperature along with direct heat capacity measurements. As an example the evaluation of the thermodynamical properties of solid and liquid UO\textsubscript{2} is considered.

The description and license information for the CondensedThermoFit code will be available soon at the JIHT RAS Thermocenter web site [31].

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