Influence of Thermodynamic and Thermochemical Data Errors on Calculated Equilibrium Composition

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Influence of thermodynamic data errors upon the results of calculation of equilibrium composition of complex chemically reacting systems is examined. Two possible approaches (sensitivity analysis and statistical approach) are described. The examples showing significance of the error influence are presented.

1. Introduction

Thermodynamic modeling is widely used now for the investigation of metallurgical and other high temperature processes. So the problem of reliability of the results of thermodynamic modeling is very important. Reliability of the results of thermodynamic modeling is determined mostly by the following factors:

1) adequacy of the process model used, i.e., by the correctness of the adopted assumptions and, first of all, by the correctness of the assumption concerning the existence of thermodynamic equilibrium in the system examined;
2) quality of the information on thermodynamic and thermochemical properties of individual substances, i.e., by the errors of the data;
3) completeness of the list of substances taken into account.

In present study an attempt is made to estimate the influence of the errors in thermodynamic and thermochemical data upon the results of thermodynamic calculations. It was found that this factor often being neglected may be very important. Special attention to data errors should be paid when a complicated model with many parameters is used for analysis of the process.

In practice investigators often explain discrepancy between the experimental data and the results of calculations by absence of chemical equilibrium in the system or by wrong parameters of the model used, while the true reason may be the errors of thermodynamic data. As an example showing the actuality of the problem we can mention the work [1], where equilibrium in SiCl$_4$-GeCl$_4$-O$_2$ was examined. The authors of the work discovered that the reason of discrepancy between the results of modeling and the experimental data may be either an error in value of heat of formation of GeO$_2$(l) or the ideal-solution approximation, which they used. Several examples showing the influence of the errors of the data used upon the calculated equilibrium concentrations are presented in [2].

This problem has been examined in the past [3–7]. But the approach used in these works is based on the assumption that the thermodynamic data errors do not influence upon the phase composition of the system investigated. This assumption is not valid in general case.

While investigating the influence of thermodynamic data errors upon the results of modeling one needs an answer to the following questions:

- how will change the results of calculations with variation of standard chemical potential of a substance or group of substances (sensitivity analysis); the sign and magnitude of the change are interesting first of all;
- which will be the scatter of calculated values because of the possible changes of the adopted value of standard chemical potential of a substance (or group of substances) within its uncertainty interval.

The answers to these questions allow on the one hand to detect the upper and lower limits of the calculated results. On the other hand this information may help to define more precisely the uncertainties of properties of individual substances by comparing the experimental data and the results of modeling.

Uncertainties of thermodynamic and thermochemical data used in calculations are caused first by the errors of the experimental determination of heats of formation of substances $\Delta_{f}H^0(T_0)$, atomic and molecular constants (for gases and gas ions), specific heat capacities (for condensed substances). The second reason of uncertainties is methodical errors of calculation of thermodynamic functions.

Some reference books contain estimates of reliability of $\Delta_{f}H^0(T_0)$ made by the authors of experiments or determined by means of thermodynamic consistency procedure [8–10]. The first reference book that presented the systematized errors of thermodynamic functions was [9]. It was this information stored in a database IVTANTHERMO as the accuracy class that was used in present study.
2. Procedure

2.1 Sensitivity Analysis

Uncertainties of the heats of formation of the individual substances and uncertainties of the Gibbs energy values are mutually dependent. But to a first approximation the corresponding errors may be regarded as factors that independently influence upon calculated equilibrium composition and thermodynamic parameters of the system. If the errors are small enough, the linear relation is valid

\[ |\Delta P_i|_{\text{max}} = \sum_j \left| \frac{\partial P_i}{\partial z_j} \right| dz_j, \]

where \( P_i \) designates the \( i \)th equilibrium parameter (volume, entropy, etc.) or equilibrium concentration of a substance, \( z_j \) – the source of error of calculation (heat of formation, Gibbs energy or standard chemical potential). Values of the derivatives \( \partial P_i/\partial z_j \) may be calculated either analytically or using one of the numerical methods. It should be noted here that the error of standard chemical potential includes both the error of heat of formation and the error of Gibbs energy. So using standard chemical potential as \( z_j \) is preferable.

As it was already mentioned above, the influence of thermodynamic data errors upon the results of modeling was studied previously by several authors. It was established for example that the results of calculations for C-H-O-N system at high temperatures may be regarded as reliable ones. However, since only homogeneous systems were investigated in the works mentioned, the more general consideration for the heterogeneous systems is following.

Let us consider an equilibrium thermodynamic system at assigned values of pressure \( p \) and temperature \( T \). The system is closed and the total number of moles of each of \( m \) elements of the system \( b_j \) are given. For the sake of simplicity of description we will assume that there is only one solution – gas mixture and each condensed substance forms a single phase. The system contains \( K \) gas substances and \( L \) condensed substances. For the purposes of the present study we assume that the phase composition of the system is known.

In the state of thermodynamic equilibrium Gibbs energy of the system is minimal with respect to all variations in chemical composition of the system subject to the constraints of element abundance and non-negativity of concentrations provides pressure and temperature are fixed. With this formulation the set of equations for the determination of equilibrium composition for this system can be obtained by Lagrange multipliers method. The set looks as follows [7, p. 47]:

\[ \mu_i + \sum_{j=1}^{\text{m}} a_{ij} \hat{\lambda}_j = 0, \quad (n_i > 0), \quad i = 1, \ldots, K + L; \]

\[ \sum_{i=1}^{K+L} a_{ij} n_i - b_j = 0, \quad j = 1, \ldots, \text{m}, \]

where \( \mu_i \) – chemical potential, \( a_{ij} \) – number of atoms of the element \( j \) in \( i \)th substance, \( \hat{\lambda}_j \) – Lagrange multipliers, \( n_i \) – equilibrium mole number of the \( i \)th substance. For the gas substances

\[ \mu_i = \mu_i^0 + \ln \left( \frac{p}{p_0} \right) + \ln \left( \frac{n_i}{n^*} \right), \quad i = 1, \ldots, K, \]

where \( p_0 \) – reference pressure (usually 1 bar or 1 atm, \( p \) should be expressed in the same units), \( n^* \) – total number of moles of the gas phase:

\[ n^* - \sum_{i=1}^{K} n_i = 0. \]

For condensed substances \( \mu_i = \mu_i^0 \).

Standard value of chemical potential \( \mu_i^0 \) can be computed as

\[ \mu_i^0 = [H_i^0(T) - TS_i^0(T)] \left( R_0 T \right)^{-1}, \]

where \( H_i^0(T), S_i^0(T) \) – values of enthalpy and entropy of the substance \( i \) at the reference pressure and temperature \( T \) and \( H_i^0(T) \) includes the heat of formation of the substance. \( R_0 \) – universal gas constant, so \( \mu_i^0 \) as defined above is non-dimensional.

The question is: how will influence the variations in standard chemical potential value \( \Delta \mu_i^0 \) of the substance \( x \) upon equilibrium composition of the system. To obtain the set of equations for the determination of the error influence upon the calculated equilibrium mole numbers let us differentiate Eqs. (2)–(3) with respect to \( \mu_i^0 \), where \( x \) stands for the index of the substance examined. Two variants are possible – substance with index \( x \) is in gas state or substance with index \( x \) is in condensed state. For the gas substance the set of equations is as follows:

\[ \sum_{i=1}^{K} \sum_{j=1}^{\text{m}} a_{ij} n_i \hat{\lambda}_j = -n_x, \]

\[ \sum_{i=K+1}^{K+L} a_{ij} n_i + (n^*/n^*) \sum_{i=1}^{m} a_{ij} n_i \]

\[ - \sum_{j=1}^{\text{m}} a_{ij} n_i (\hat{\delta}_i + \sum_{j=1}^{\text{m}} a_{ij} \hat{\lambda}_j) = 0, \quad j = 1, \ldots, \text{m}, \]

where

\[ \hat{\delta}_i = 0 \quad \text{if} \quad i = x \quad \text{else} \quad \hat{\delta}_i = 1. \]

If the influence of standard chemical potential error of the condensed substance is investigated the relations (7), (8) should be written as follows:
The unknowns in the set of Eqs. (6)–(10) are

\[ \hat{\eta}_i = \frac{\partial \eta_i}{\partial \mu_k} \xi_k^0, \quad i = K + 1, \ldots, K + L, \]
\[ \hat{\eta}^* = \frac{\partial \eta^*}{\partial \mu_k} \xi_k^0, \quad \hat{\lambda}_j = \frac{\partial \lambda_j}{\partial \mu_k} \xi_k^0. \]

(More accurate designation for the derivatives should include index \( x \), \( \hat{n}_n \) for example. We do not use it for simplicity.) When the solution is found, influence of variations of standard chemical potential of the substance with index \( x \) upon mole numbers of the gas substances may be determined from the relation.

\[ \hat{n}_i = \left( \hat{\eta}^*/\eta^* - 1 - \sum_{j=1}^{m} a_{ji} \hat{\lambda}_j \right) n_i, \quad i = 1, \ldots, K. \] (11)

Having calculated values of \( \hat{n}_i \) with varied values of standard chemical potential of all substances in the system one can get a matrix of the derivatives. Using the matrix and the Eq. (1) one can determine the upper and lower bounds for the computed equilibrium thermodynamic parameters or mole numbers of substances caused by the errors \( \Delta \mu_k^0 \). This approach is usually applied also for the investigation of the system’s response to a change in the parameters that governs the position of the chemical equilibrium [7, 11].

### 2.2 Statistical Approach

Unfortunately, thermodynamic data errors for many substances are too large, and the relations (6)–(11) cannot be applied for the evaluation of the accuracy of calculations. Besides these relations do not take into account possible changes of the phase composition. So carrying out the appropriate investigations using the statistical (or Monte Carlo) approach described in [12, 13] is reasonable. This approach includes the following sequence of actions:

- Obtain the random values of thermodynamic and thermochemical data for all or selected substances within their uncertainty intervals;
- Calculate the equilibrium composition using these random values;
- Memorize the results and repeat the two previous steps;
- Carry out the processing of the calculated results when the number of trials is large enough.

If the goal of investigation is ascertaining of the scatter of results of calculations caused by discrepancies in data one can use any probability distribution function to obtain the random values of thermodynamic data. But the described procedure may be also used for the examination of distribution of results of calculations within their uncertainty interval. In other words, determination of a response function is possible.

The distribution of calculated results depends on the probability distribution function used for the errors. Inasmuch as the data in database IVTANTHERMO are obtained as a result of critical analysis of the experimental data, using the normal distribution function is reasonable. This assumption is valid when the data errors are results of a large number of the independent experimental errors. On the other hand the information about the thermodynamic and thermochemical data errors presented in reference books includes also the methodical errors. So all the points inside the uncertainty interval may have equal degree of reliability, and the uniform probability function may be used.

### 2.3 The Inverse Problem

Using Eqs. (2)–(3) and experimental data (equilibrium concentrations, equilibrium constants, saturated vapor pressure etc.) one can compute the unknown value of standard chemical potential of a substance. This is the inverse problem. An example of such a calculation is presented in [14].

Computation of the uncertainty of the calculated value in this case is a special problem. The described method of statistical trials allows to find out not only the heats of formation of substances but also the errors of their values using the experimental data.

Let us briefly describe the procedure of the inverse problem solution. From the conditions of the experiment on determination of equilibrium concentrations of substances or equilibrium constants the scatter of measured data is established. As a first approximation the upper and lower limits for the heat of formation of the substance examined are assigned. Then a number of calculations of equilibrium composition is accomplished. In each trial thermodynamic properties of a substance or group of substances are varied randomly within their uncertainty interval. Further, from the results of trials only those ones are selected where the investigated value lies within its experimental scatter. And finally for this selected results the statistical treatment is carried out. The treatment allows to find the heat of formation of the investigated substance that fits the experimental data.

The described procedure is comparatively universal as it does not set the additional restrictions upon parameters that define equilibrium state. The procedure may be used for the analysis of reactions at given pressure and temperature as well as for the examination of combustion products at constant pressure or volume.

Of course the procedure does not take into account the factors caused by inadequacy of the model used and in-
completeness of the list of substances taken into consideration.

3. Results

Let us consider first the results of the application of theory described in Sect. 2.1 concerning sensitivity analysis. Table 1 contains values \( n_i \) of the prevailing substances in equilibrium system \((0.2\, O_2+C+0.2\, Fe_2O_3+0.0038S)\) at temperature 1473 K and pressure 1 bar when standard chemical potential of CO(g) was varied. The values in the table show how the equilibrium mole numbers will change when standard chemical potential (non-dimensional) of CO(g) is increased by one (or 12.25 kJ/mole).

To carry out the thermodynamic calculations using the statistical approach, described in Sect. 2.2, a computer program has been developed. Nominal values of thermodynamic data and the values of their errors stored in database IVTANTHERMO were used in calculations. Table 2 displays the marginal values of mole numbers of the prevailing substances in equilibrium system \((As+0.1Sb)\) at temperature 983 K and pressure 1 bar. Calculations were accomplished in assumption that As(c) and Sb(c) form an ideal solution.

Fig. 1 shows the distribution of probabilities for the equilibrium mole numbers of condensed Fe in equilibrium system \((C+0.2Fe_2O_3+0.0038S+0.004CaO+0.5N_7.45O_2)\) at temperature 1473 K and pressure 1 bar. The heats of formation of all substances in the system were varied in calculations. Normal distribution function was used. Number of trials was 100. To compute the probabilities we used the following procedure. The interval of all possible mole numbers of Fe(c) was divided on ten equal parts. For each subinterval the number of hits was computed. The calculated numbers divided by the number of trials is treated as probabilities of appearance of given number of moles of condensed Fe in equilibrium system. As one can see from the figure, the scatter of results is significant. Nominal value of equilibrium mole number of Fe(c) is

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Influence of error of chemical potential of CO(g) upon equilibrium composition of the system ((0.2O_2+C+0.2Fe_2O_3+0.0038S)) at (T=1473) K, (p=1) bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>(Fe(c))</td>
</tr>
<tr>
<td>(n_i), mole</td>
<td>(-1.20\cdot10^{-2})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Nominal and marginal values of concentrations of the prevailing substances (mole) in equilibrium system ((As+0.1Sb)) at (T=983) K and (p=1) bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>(As(c))</td>
</tr>
<tr>
<td>Nom. value</td>
<td>(7.21\cdot10^{-2})</td>
</tr>
<tr>
<td>Min. value</td>
<td>(1.16\cdot10^{-2})</td>
</tr>
<tr>
<td>Max. value</td>
<td>0.907</td>
</tr>
</tbody>
</table>

Fig. 1 Distribution of probabilities of equilibrium concentration of Fe(c), mole, in a system \((C+0.2Fe_2O_3+0.0038S+0.004CaO+0.5N_7.45O_2)\) at temperature 1473 K and pressure 1 bar

Fig. 2 Distribution of probabilities of combustion temperature in a system \(Mg_5C_6Cl_6\), pressure 6 MPa, enthalpy \((-322)\) kJ/kg
where \( \text{As}(c) \) and \( \text{Sb}(c) \) form an ideal solution. Nominal value of \((\text{As}+\text{Ar}+0.1\text{Sb})\) at temperature 925 K and pressure 1 bar pointed out and draw a conclusion.

fluence of the heat of formation of the substance examined and will be demonstrated later. In this example only heat of formation of \( \text{As}_4(g) \) was varied.

adiabatic combustion temperature of \( \text{Mg}_5\text{C}_6\text{Cl}_6 \) at pressure 6 MPa, enthalpy of the system is \(-322 \text{ kJ/kg}\). In this example normal distribution function was used too, number of trials was 100. As one can see from the figure, the scatter of combustion temperature is more than 300 K. Nominal value of the temperature is 2396 K. The asymmetry of the scatter should be marked too.

The statistical method may be also used for the detailed examination of dependence of equilibrium composition of thermodynamic system on the value of standard chemical potential of a substance. Fig. 3 displays the calculated dependence of equilibrium mole number of \( \text{As}_4(g) \) on the value of its heat of formation in the system \((\text{As}+\text{Ar}+0.1\text{Sb})\) at temperature 925 K and pressure 1 bar where \( \text{As}(c) \) and \( \text{Sb}(c) \) form an ideal solution. Nominal value of \( \Delta_r^0H^\circ(298\text{K}) \) for \( \text{As}_4(g) \) is \(156.189\pm40 \text{ kJ/mol}\). In this example only heat of formation of \( \text{As}_4(g) \) was varied. Looking at the figure the investigator can evaluate the influence of the heat of formation of the substance examined and draw a conclusion.

4. Discussion

The relations (6)–(11) are only valid if the variations of \( \mu_i^0 \) do not cause the change of the phase composition of the system examined. It should be noted that appearance or disappearance of the phase may occur even with small variation of standard chemical potential. Besides, these relations do not allow to take into account the mutual dependence of the uncertainties of thermodynamic data of various substances. Nonetheless, Eqs. (6)–(11) help to establish tendencies of changes of equilibrium mole numbers of substances with variation of their standard chemical potentials.

In many cases the influence of the data errors upon the results of modeling is insignificant and it only slightly distorts the real picture. However, when a complicated model with many parameters is used, the influence of thermodynamic data errors may be considerable and may result in an unsuccessful scheme of a technological process and its parameters.

The procedure of evaluation of the thermodynamic data errors used in [9] takes into account both the experimental errors of all published data and the discrepancy of results from various data sources. So the errors of thermodynamic properties stored in database IVTANTHERMO for some substances are too large. That is why the computed deviations from nominal value in the examples above may be exaggerated.

5. Concluding Remarks

The use of incorrect thermodynamic properties of individual substances for thermodynamic modeling may result in significant errors of calculation of the phase and chemical composition of the system and its characteristics. Without the quantification of these errors the investigator cannot trust the results of calculations. The method of statistical trials best fits that purpose.

The examples presented above show that information about thermodynamic data errors stored in a database allows to evaluate reliability of the results of modeling. This information also simplifies the procedure of the choice of an adequate process model and its parameters.

Results of calculation of equilibrium composition of chemically reacting system may be changed by variation of the heat of formation of a substance (or group of substances) within its uncertainty interval. So, the values of the heats of formation of substances may be treated as additional parameters of thermodynamic model. However the variation of these parameters is reasonable only when there are sufficient grounds to do that.

Values of thermodynamic data errors of substances obtained as a result of critical analysis of published data are often too large and special work should be accomplished to make them as small as possible. Of course, this is a very complicated task but we would like to draw attention to the problem.

References


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