SIMULTANEOUS ASSESSMENT OF THERMODYNAMIC FUNCTIONS OF CALCIUM ALUMINATES

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ABSTRACT

The Gibbs energies of calcium aluminates, $Ca_3Al_2O_6$, $CaAl_2O_4$, $CaAl_4O_7$, and $CaAl_{12}O_{19}$ have been determined from all the available literature experimental values: the enthalpies of formation, the 3rd law entropies derived from low-temperature heat capacities, and the Gibbs energies of reactions obtained from emf measurements. A set of the Gibbs energies recommended in the present work describes experimental results rather accurately even though a difference between experimental values and the recommended solution is greater than reproducibility error. The latter is explained in terms of systematic errors. A modern approach of mathematical statistics, that is the estimation of variance components, has been utilized in order to treat systematic errors. Visualization of the quality of the fit is discussed.

INTRODUCTION

Calcium aluminates, $Ca_3Al_2O_6$, $CaAl_2O_4$, $CaAl_4O_7$, and $CaAl_{12}O_{19}$ are of great importance in ceramics and cement industries [1]. The very alumina-reach phases may be formed as very high-temperature condensates from the primitive solar nebula, and thus they are of special interest to cosmochemistry. Yet, there is a controversy in thermodynamic properties of calcium aluminates that leads to ambiguous results in thermodynamic modeling of the above processes [1].

In the present work thermodynamic functions of calcium aluminates are assessed from all the available literature experimental values. Two new features distinguish our work from the traditional approach in the area of the compilation of thermodynamic properties. First, thermodynamic functions of four calcium aluminates are assessed simultaneously as opposed to the traditional "species-by-species" approach. Second, in order to deal with the systematic errors encountered in original experimental measurements a special modern statistical method [2] has been employed.

In the case of calcium aluminates, there are experimental values for the multiple chemical Reactions (1) to (7)

$$CaO + 6Al_2O_3 = CaAl_{12}O_{19} \qquad (1)$$
$$2CaO + CaAl_{12}O_{19} = 3CaAl_4O_7 \qquad (2)$$
$$CaO + CaAl_4O_7 = 2CaAl_2O_4 \qquad (3)$$
$$2CaO + CaAl_2O_4 = Ca_3Al_2O_6 \qquad (4)$$
$$CaAl_4O_7 + 4Al_2O_3 = CaAl_{12}O_{19} \qquad (5)$$
$$4CaAl_2O_4 + CaAl_{12}O_{19} = 5CaAl_4O_7 \qquad (6)$$
$$Ca_3Al_2O_6 + 2CaAl_4O_7 = 5CaAl_2O_4 \qquad (7)$$
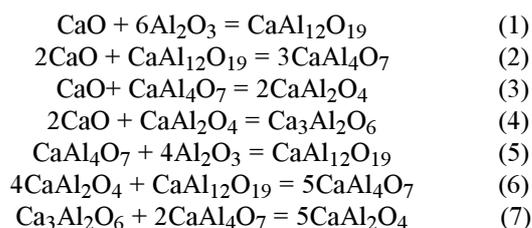
when several aluminates take place in a single reaction. Each experimental Gibbs energy of a reaction is related to several unknown thermodynamic properties, and as a result, there is a system of equations that cannot be separated into several smaller parts which one can solve independently. Hence, the traditional approach "one reaction -- one thermodynamics

property" could not be applied. Combined processing of reaction enthalpies has been reported earlier by Goldshtein et al [3] but nobody seems to have extended such a procedure to the Gibbs energies yet.

Experimental values employed in the present compilation are measured by different authors and by different methods. As one could expect, a difference between results of different experiments is greater than a data scatter within a single experiment. This is explained in terms of experimental systematic errors, and during the simultaneous assessment a new method is necessary in order to cope with this. To this end, the linear error model [2] comprising reproducibility and systematic errors has been utilized.

Whatever a statistical method has been used, the quality of the final solution, in our view, can be inferred by means of the comparison of the solution with primary experimental values only. Special types of graphs that may ease such a comparison significantly in the case of great number of primary experimental points are discussed.

THERMODYNAMIC MODEL

The standard molar Gibbs energy of a stoichiometric compound above the room temperature as related to the "Standard Element Reference (SER)" can be expressed as follows

$$G^o(T) = \Delta_f H^o_{298} - T\,S^o_{298} +$$

$$\int_{298}^{T} C^o_P(T)\,dT - T \int_{298}^{T} [C^o_P(T)/T]\,dT \qquad (8)$$

where S^o_{298} is the absolute entropy of the compound at 298.15 K, C^o_P is its heat capacity, and $\Delta_f H^o_{298}$ is the enthalpy of formation at 298.15 K. The conception of the SER is discussed elsewhere, for example in Ref. [4]. This approach allows us to

separate properties of the pure compound (S^o_{298} and C^o_p) and properties of the reference state ($\Delta_f H^o_{298}$) between each other.

For the sake of simplicity, in the present work the enthalpy of formation, $\Delta_f H^o_{298}$ will correspond to the process of a compound formation from the pure oxides, CaO and Al_2O_3. In order to convert it to the ordinary enthalpy of formation, one has to add the enthalpies of formation of the pure oxides, $\Delta_f H^o_{298}$ (CaO) = -635.09±0.90 kJ·mol^{-1} and $\Delta_f H^o_{298}$ (Al_2O_3) = -1675.7±1.3 kJ·mol^{-1}. These and other thermodynamic properties of the pure oxides, CaO and Al_2O_3 have been taken from Gurvich's reference book [5].

For compounds $Ca_3Al_2O_6$, $CaAl_2O_4$, and $CaAl_2O_4$, the high temperature heat capacities, C^o_p as functions of temperature have been measured by high temperature drop calorimetry [6]. They have been employed in the present work without changes. The high temperature heat capacity of $CaAl_{12}O_{19}$ has been assumed to obey the additivity rule. As can be seen from Fig. 1, the high temperature heat capacities of calcium aluminates comply with the additivity rule with rather good accuracy of 2-4%.

As a result, the model accepted in the present work contains eight unknowns to be determined for four aluminates from the simultaneous assessment, that are four standard enthalpies of formation, $\Delta_f H^o_{298}$ and four absolute entropies, S^o_{298} at 298.15 K.

LITERATURE EXPERIMENTAL VALUES: THE SYSTEM OF EQUATIONS

Primary experimental thermodynamic results employed in the present work in order to estimate thermodynamic functions of calcium aluminates, $Ca_3Al_2O_6$, $CaAl_2O_4$, $CaAl_4O_7$, and $CaAl_{12}O_{19}$ were emf values [7-10], low temperature heat capacities [11], and the enthalpies of formation [1, 12-15]. There are experimental results on activity measurements in CaO-Al_2O_3 [8, 16, 17] and CaF_2-CaO-Al_2O_3 [18] melts (see also references therein), and in principle, they can also be used to estimate thermodynamic properties of calcium aluminates by using additional information on heterogeneous equilibria. However, this would require including the Gibbs energies of binary and ternary melts as additional unknowns under consideration. The latter would greatly complicate calculations, and in the present work input values were limited to results of subsolidus experiments only.

Emf values of Reactions (1) to (7) in the temperature range from 1000 to 1500 K have been reported in four papers [7-10]. This gives us a main part of the system of equations

$$E_{ij} = -\{\textstyle\sum_k \nu_{ik} G^o_k (T_{ij})\}/(n_i F) + \varepsilon_{ij} \qquad (9)$$

where the index i enumerates the experiments (see Table 1), the index j does the experimental points in the i-th experi-

ment, the index k lists all the substances in Reactions (1) to (7). E_{ij} is the experimental value of the electromotive force measured at the temperature T_{ij}, F is the Faraday constant, n_i is the number of electrons associated with the electrode reaction, ν_{ik} is the stoichiometric number, G^o_k is the Gibbs energy of the k-th compound given by Eq. (8), and ε_{ij} is the measurement error.

It should be stressed that the index i is the ordinal number of an individual emf experiment {$i = 1, ..., 13$}, and the total number of emf experiments is more than the number of reactions. Thus, in order to know which a reaction is associated with the i-th experiment one has to consult with Table 1. The total number of substances taking place in Reactions (1) to (7) is 6 {$k = 1, ..., 6$}. Two of them are pure oxides in which Gibbs energies are known functions of temperature [5], and others are calcium aluminates in which Gibbs energies given by Eq. (8) contain eight unknowns, as was mentioned above.

It is the system (9) that does not allow us to use the traditional approach, "one reaction - one property" during the assessment of thermodynamic properties of calcium aluminates. Each reaction but Reaction (1) contains two or three calcium aluminates (several unknown Gibbs energies), and each calcium aluminate also takes part in more than a single reaction. The system of equations (9) can not be simplified, *i.e.,* reducing it to several systems with a lower number of unknowns is impossible without some kind of approximation.

Heat capacity has been measured for $Ca_3Al_2O_6$, $CaAl_2O_4$, and $CaAl_4O_7$ in the temperature range from 50 to 300 K [11]. After the measured values have been extrapolated to zero temperature in accordance with the Debye law, the standard entropies at 298.15 K have been estimated by taking an appropriate integral. This gives us additional equations

$$S^o_{298,ij}/(m + n) = S^o_{298,k}/(m + n) + \varepsilon_{ij} \qquad (10)$$

where $S^o_{298,ij}$ is the experimental 3rd law entropy, $S^o_{298,k}$ is the entropy of the k-th substance, $A_m B_n$ to be found, and ε_{ij} is the experimental error. The index i continues enumerating individual experiments {$i = 14, ..., 16$} (see Table 1), and hence the indices i and k do not match each other. The molar entropy in Eq. (10) is divided by the sum of $m + n$ that is the total mole number of oxides, and thus Eq. (10) is written in terms of the entropy in respect to one mole of oxides. The reason is that in this case the variances of experimental errors can be considered as homogeneous for all the calcium aluminates, and this simplifies the data processing that follows.

Finally, there is a series of papers on solution calorimetry [1, 12-15] when the enthalpy of formation of a calcium aluminate is measured at some temperature (see Table 1)

$$\Delta_f H^o_{T,ij}/(m + n) = \{ \Delta_f H^o_{298,k} +$$
$$\int_{298}^{T} \Delta_f C^o_{p,k}(T)\,dT \}/(m + n) + \varepsilon_{ij} \qquad (11)$$

Eq. (11) is quite similar to Eq. (10), and the difference between the indices i and k is the same. The term with the heat capacities is necessary in order to recalculate the experimental enthalpy of formation to 298.15 K. It contains no unknowns because, as was mentioned above, all the high-temperature heat capacities were taken from literature without changes.

SIMULTANEOUS ASSESSMENT

Formally speaking, a task of the simultaneous assessment is to solve the system of equations (9), (10), and (11) over the unknown enthalpies of formation and entropies of calcium aluminates. In other words, the task is to find such unknown enthalpies of formation and entropies that will give us some best description of the primary experimental values.

With current computer power at hand, the main problem is not the solving the system by itself but rather formulating what we mean by the "best" description.

Let us start with the traditional weight least squares (WLS) approach. Here the "best" solution is such that brings the weight sum of squares

$$SS = \sum_{ij} \varepsilon_{ij}^2 \, / \, W_{ij} \qquad (12)$$

to the minimum. Without doubt, the final solution depends on the numerical values of the weights that express our expert opinion in the quantitative form. Thus, inside the WLS method the task of the simultaneous assessment becomes

TABLE 1.
Primary experimental values chosen for the simultaneous assessment

Code	Quantities	Comment	N_i	Ref.
A1	$\{E_{ij}, T_{ij}\}$	Reaction 1, 945-1225 K	14	[8]
K1	-"-	Reaction 1, 1100 - 1500 K	9	[9]
C1a	-"-	Reaction 1, 1256 - 1376 K	18	[7]
C1b	-"-	Reaction 1, 1282 - 1364 K	20	[7]
A2	-"-	Reaction 2, 933 - 1222 K	14	[8]
K2	-"-	Reaction 2, 1040 -1495 K	9	[9]
A3	-"-	Reaction 3, 928 - 1212 K	7	[8]
K3	-"-	Reaction 3, 1050 - 1475 K	9	[9]
K4	-"-	Reaction 4, 1045 - 1315 K	9	[9]
R4	-"-	Reaction 4, 1000 - 1200 K	-	[10]
R5	-"-	Reaction 5, 1000 - 1200 K	-	[10]
R6	-"-	Reaction 6, 1000 - 1200 K	-	[10]
R7	-"-	Reaction 7, 1000 - 1200 K	-	[10]
Sa	$S_{298,ij}^o$	$Ca_3Al_2O_6$	1	[11]
Sb	-"-	$CaAl_2O_4$	1	[11]
Sc	-"-	$CaAl_4O_7$	1	[11]
Ha	$\Delta_f H_{T,ij}^o$	$Ca_3Al_2O_6$, 298.15 K	1	[13]
Hb1	-"-	$CaAl_2O_4$, 298.15 K	1	[13]
Hb2	-"-	$CaAl_2O_4$, 950 K	1	[14]
Hc	-"-	$CaAl_4O_7$, 1063 K	1	[15]
Hd	-"-	$CaAl_{12}O_{19}$, 1063 K	1	[15]

mainly of that of the weight assignment. Mathematical statistics tells us that the weight matrix should be equal to inverse of the dispersion matrix up to the constant

$$\mathbf{W} = k \; \mathbf{D}(\varepsilon)^{-1} \qquad (13)$$

in order to obtain the reliable estimates. In statistical terms, Eq. (12) means that 1) the diagonal form is implied for the dispersion matrix (all the error ε_{ij} are postulated to be non-correlated), and 2) the ratios between variances for all the errors are known. Unfortunately, the both last statements are not held in the case of calcium aluminates as well as in many other real applications.

In our case, there are results obtained by different authors in different laboratories and by different methods. This means that we should expect systematic errors to appear (as shown below, systematic errors are detected indeed - the between-errors are greater than within-errors). Ratios between variances of the emf, calorimetry and 3rd law entropies values are also not known.

The statistical model of systematic errors has been discussed previously [2]. It allows us to employ more realistic error models such as the linear error model

$$\varepsilon_{ij} = \varepsilon_{r,ij} + \varepsilon_{a,i} + \varepsilon_{b,i} \, (T_{ij} - T_i) \qquad (14)$$

where ε_{ij} is the total experimental error, $\varepsilon_{r,ij}$ is the reproducibility error, $\varepsilon_{a,i}$ is the systematic calibration error (shift error), and $\varepsilon_{b,i}$ is the systematic tilt error. The latter is not applicable to the third law entropies and enthalpies of formation (Eqs. 11 and 12) and it is assumed to be equal to zero there.

The linear error model brings forth the block-diagonal dispersion matrix. The values of ε_{ij} are non-correlated for different series (when the index i is different), but because of the systematic errors they are correlated within a single experiment. As a result, the number of variances in the dispersion matrix increases -- in addition to the reproducibility variance, $\sigma_{r,i}^2$, there are the variances of the two systematic errors, $\sigma_{a,i}^2$ and $\sigma_{b,i}^2$. Certainly, the ratio between them is not know a $priori$, and the whole task is to determine both unknown parameters and variances simultaneously. To this end, the maximum likelihood method can be applied, that is maximizing of the function

$$L = - \ln \{ \det [\, \mathbf{D}(\varepsilon) \,] \} - \varepsilon' \, \mathbf{D}(\varepsilon)^{-1} \varepsilon \qquad (15)$$

Note that the weight least squares is a special case of the maximum likelihood method when zero values are assigned to the variances $\sigma_{a,i}^2$ and $\sigma_{b,i}^2$ a $priori$, and the ratios between reproducibility variances are known. Then the maximization of (15) is reduced to the minimization of (12).

The first step in the present work has had no differences with the traditional approach -- all the papers have been carefully read. At this stage some of them has been marked as "wrong" and removed from the further analysis:

1) Skolis' emf values for reactions (2) and (5) from Ref. [7] that are in strong disagreement (about 100 mV) with all other emf experiments [8-10],

2) Koehler's enthalpy of formation of $CaAl_2O_4$ [12] because it is based on the enthalpy of formation of gibbsite that by itself is not very reliable (see also discussion in Ref. [19, 20]),

3) Ayed's enthalpies of formation of calcium aluminates [15], they are in disagreement with the previous works [1, 13, 14].

The experiments that remain are listed in Table 1, and all of them are assumed to be of the same quality. This is the second expert conclusion in the present work that leads to the statement that the analogous variances are the same for the experiments separated by the solid lines in Table 1. This means that there are three unknown variances for 13 emf experiments, two unknown variances for three experiments on 3rd law entropies, and two unknown variances for the five calorimetry experiments (see Table 2). As was mentioned before, the last two types of experiments have the shift calibration error only and the tilt systematic error is not applicable. In the case of the 3rd law entropies and the enthalpy of formations, the mean values only were available in the original works. As a result, the reproducibility variances for these experiments were set equal to those that were found in the original papers and have not been changed during maximization of (15) (the total is five unknown variance components).

Our qualitative expert conclusion was enough to form the sensible statistical task and to obtain the results. The likelihood functions (15) has been maximized in respect to eight unknown parameters (four enthalpies and four entropies) and five unknown variance components. The effective algorithm for maximizing (15) under the linear error model (14) has been described elsewhere [2]. The values of the variance components obtained are given in Table 2 and those of the enthalpies and entropies are in Table 3.

DISCUSSION

The new statistical method [2] allowed us to obtain the results in one step based on the qualitative expert information. Thus, there are two major differences with the traditional thermodynamic assessment: 1) the system of equations (9), (10), (11) has been solved simultaneously, 2) the expert did not have to assign numerical values of the weights. The role of the

TABLE 2.
Estimates of the variance components

group	$\sigma_{r,i}$	$\sigma_{a,i} / \sigma_{r,i}$	$\sigma_{b,i} / \sigma_{r,i}$
E_{ij}, mV	3.8	1.8	0
$S_{298,ij}^{o}$, $J\,K^{-1}mol^{-1}$	0.4*	2.0	n/a
$\Delta_f H_{T,ij}^{o}$, $kJ\,mol^{-1}$	1.0*	2.1	n/a

* value has been fixed in accordance with the original work and has not been changed during the maximization of (15). The standard deviations are given for the entropies and enthalpies in respect to one mole of oxides.
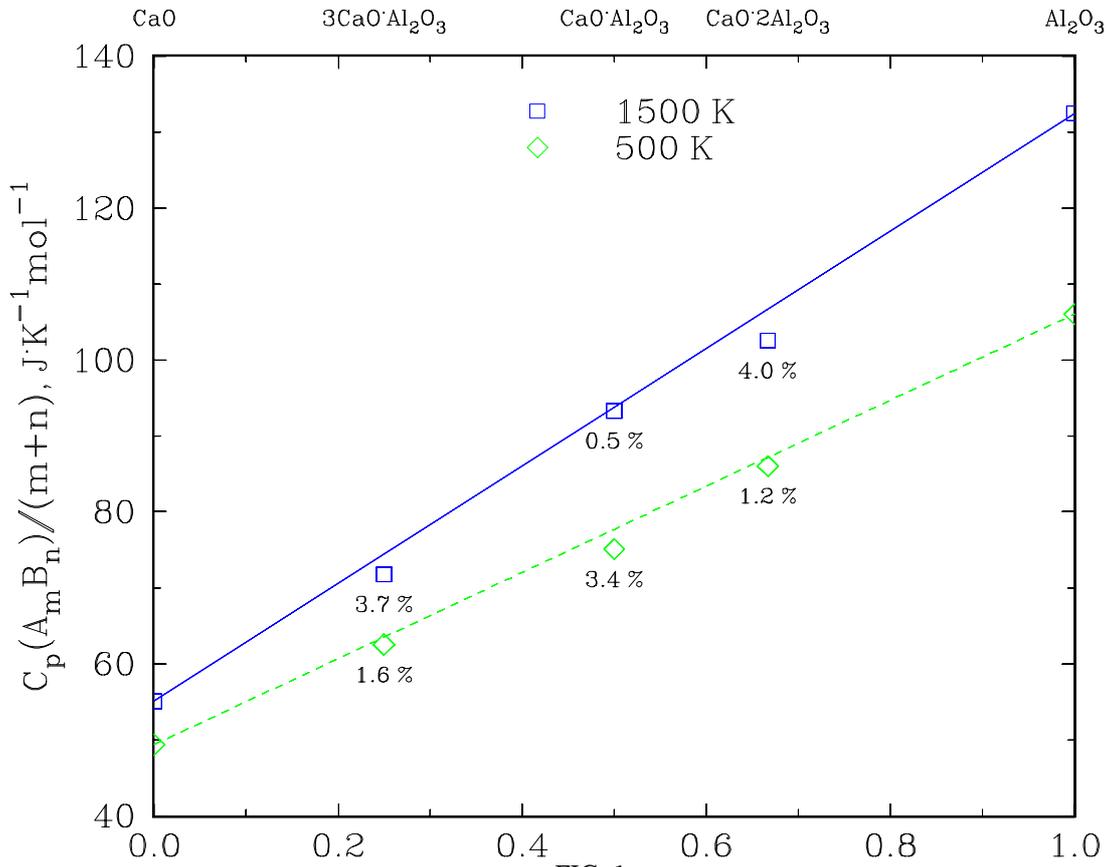
FIG. 1.

Experimental heat capacities of calcium aluminates as compared with the additivity rule.
The numbers display the difference in percent.
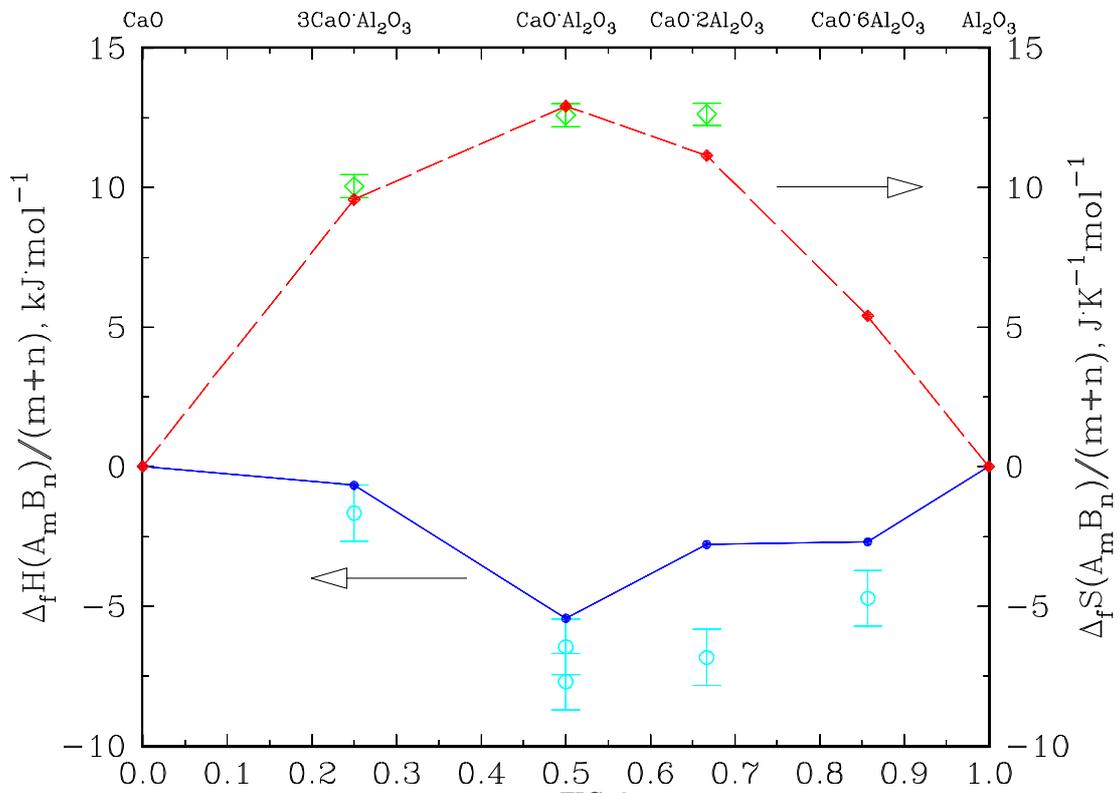
FIG. 2.

Enthalpies and entropies of formation from oxides of calcium aluminates.
The points represent the experimental values, the lines connect the recommended values.

TABLE 3.
Recommended values of the enthalpies and entropies in respect to one mole of oxides
(standard deviations are given as the errors)

	$\Delta_f H^o_{298,k}/(m+n)$		$S^o_{298,k}/(m+n)$	
	recommended	exp.*	recommended	exp.
$Ca_3Al_2O_6$	-0.66±0.82	-1.66±1.0 [13]	50.9±0.63	51.4±0.40 [11]
$CaAl_2O_4$	-5.43±0.47	-6.45±1.0 [13] -7.70±1.0 [14]	57.4±0.35	57.1±0.40 [11]
$CaAl_4O_7$	-2.79±0.37	-6.84±1.0 [15]	57.8±0.27	59.3±0.40 [11]
$CaAl_{12}O_{19}$	-2.69±0.23	-4.71±1.0 [15]	54.5±0.17	n/a

* - recalculated to 298.15 K

expert was to formulate in which experiments were of the same quality and then the values of the variance components, *i.e.* weights, have been found concurrently with the values of the unknown parameters.

In order to discuss the solution obtained let us have a look at the agreement with the primary experimental values (see Fig. 2 and 3). In our view, this is the only criterion that can be employed to explore the quality of the solution. Having compared experimental and recommended values in Fig. 2 and 3, one may say that the overall agreement is not bad. The biggest disagreement is with the enthalpy and entropy of $CaAl_4O_7$ and with the enthalpy of formation of $CaAl_{12}O_{19}$ (see Fig. 2).

Fig. 2 clearly shows that the difference between experimental and predicted enthalpies and entropies is bigger than the reproducibility error. Actually, the same, between-errors are greater than within-errors, can be said about the emf experimental values even though it is difficult to observe it in Fig. 3 because of the low scale.

In order to enhance the scale of Fig. 3, the emf deviates (differences between experimental and predicted values) are plotted in Fig. 4 (compare with Fig. 3). Here one can perfectly see that the differences between different experiments (between-errors are about 10 mV) are greater indeed than the reproducibility error (within-errors are about 3 mV). Hence, it can be said that the agreement between the experimental and recommended values is about the same in Fig. 2 and 3. This can also be seen from Table 2 with the variance components obtained. The estimated ratio of the shift systematic variance to the reproducibility variance, $\sigma^2_{a,i}/\sigma^2_{r,i}$ is about the same for all three groups of the experiments that means that the solution found is a fair compromise.

Fig. 4 also tells us that the linear error model is quite appropriate, emf values of an experiments are shifted and tilted from the recommended solution as described by Eq. (14). This allow us to suggest the third type of a graph when the tilt is plotted *vs.* the shift and thus a whole experiment is shown as a single point (see Fig. 5, some more information on such type of a graph is elsewhere [2]). In Fig. 5, the shift and tilt are normalized by the standard deviation of reproducibility (square root from $\sigma^2_{r,i}$). This allow us to plot all the experiments (emf, 3rd law entropies and enthalpies) altogether and to see what the overall agreement looks like at a single graph.

Note that all the points for the 3rd law entropies and enthalpies of formation lie on the X-axis. This is explained by the fact that the tilt systematic error is not applicable for these experimental values and it was set equal to zero *a priori* (see above).

The values of coordinates in Fig. 5 measure the shift and tilt error of a particular experiment in terms of the standard deviation of reproducibility of this experiment. It means that if the coordinate of a point is about unit value or less than the shift (or tilt) error is comparable with the reproducibility error (the difference between experiments is statistically insignificant). If the coordinate of a point is more than two, then it can be said than the between-errors are greater than within-errors (the systematic errors are more than the reproducibility noise). From this point of view, tilt errors of the emf values for the recommended solution (see Fig. 5 on the left) is statistically insignificant but shift systematic errors do exist (see also Fig. 4 and Table 2).

Fig. 5 (on the left) confirms that the recommended solution if a fair compromise between different types of experiments but a question remains whether it is possible to describe the entropies and enthalpies of formation (see Fig. 2) more accurately. To this end, three other solutions have been found (an analysis of the type "what if"). The recommended solution will be referenced as **Solution I**.

Solution II. The value of the entropy of $CaAl_4O_7$, has been fixed during the maximization of (15) at the value $S^o_{298}/3 = 58.9$ J K^{-1}mol^{-1} (experimental value minus one standard deviation of reproducibility). The result is shown in Fig. 5 on the right.

Solution III. The value of the enthalpy of formation of $CaAl_4O_7$, has been fixed at the value $\Delta_f H^o_{298}/3 = -5.84$ kJ mol^{-1} (experimental value plus one standard deviation of reproducibility). The result is shown in Fig. 6, above.

Solution IV. Two values from the solutions above have been fixed simultaneously. The result is shown in Fig. 6, below.

The analysis of the results obtained (see Fig. 5 and 6) gives us that one can easily describe the entropies accurately. The description of the emf values changes insignificantly from the recommended solution to the solution II (see Fig. 5). The problem here is that the description of the enthalpy of formation of $CaAl_4O_7$ gets much worse. The accurate description of
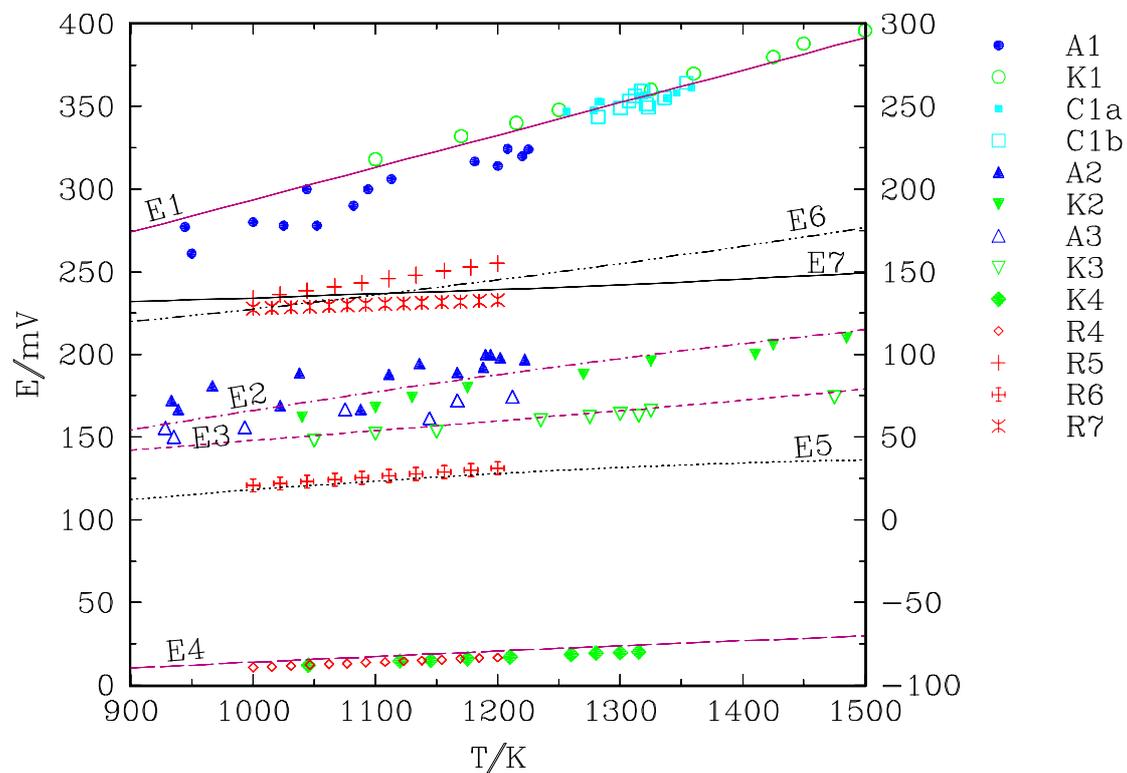
FIG. 3.

Experimental emf values as compared with the calculated ones based on the recommended set of the Gibbs energies (Table 3). E1 to E7 correspond to Reactions from 1 to 7 respectfully. The values of E1 to E4 should be read on the left Y-axes and those of E5 to E7 are on the right.
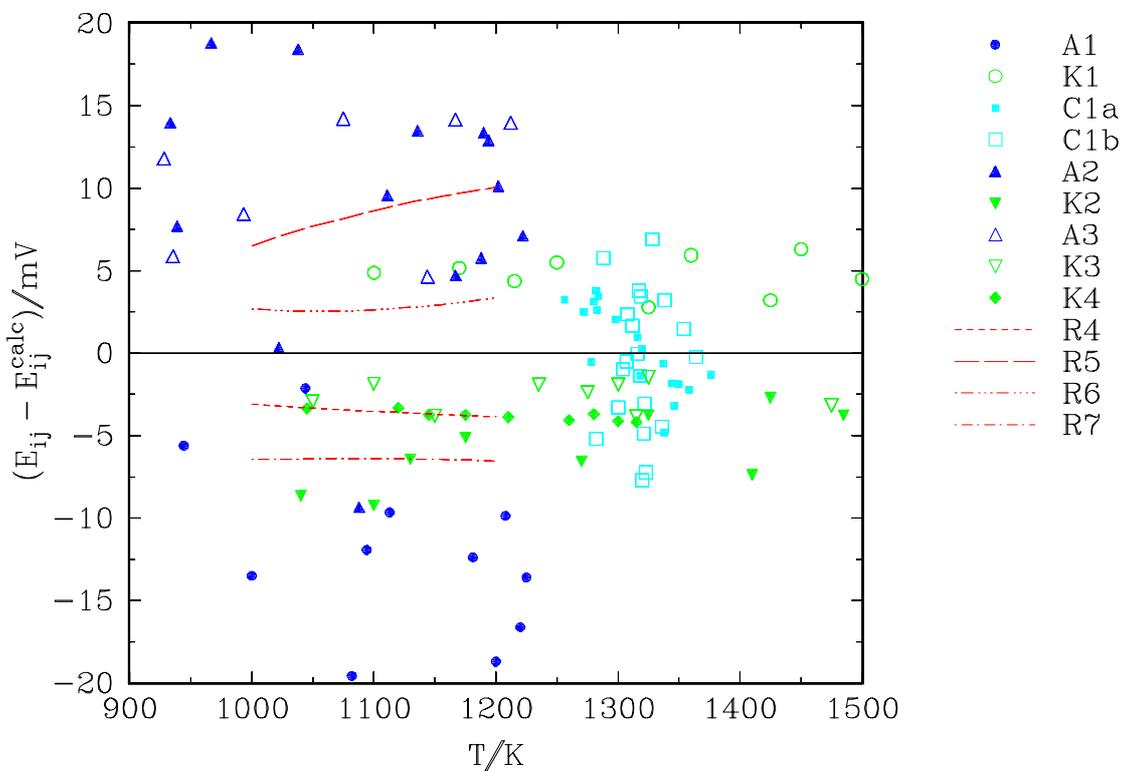
FIG. 4.

The differences between experimental and calculated emf values (compare with Fig. 3).
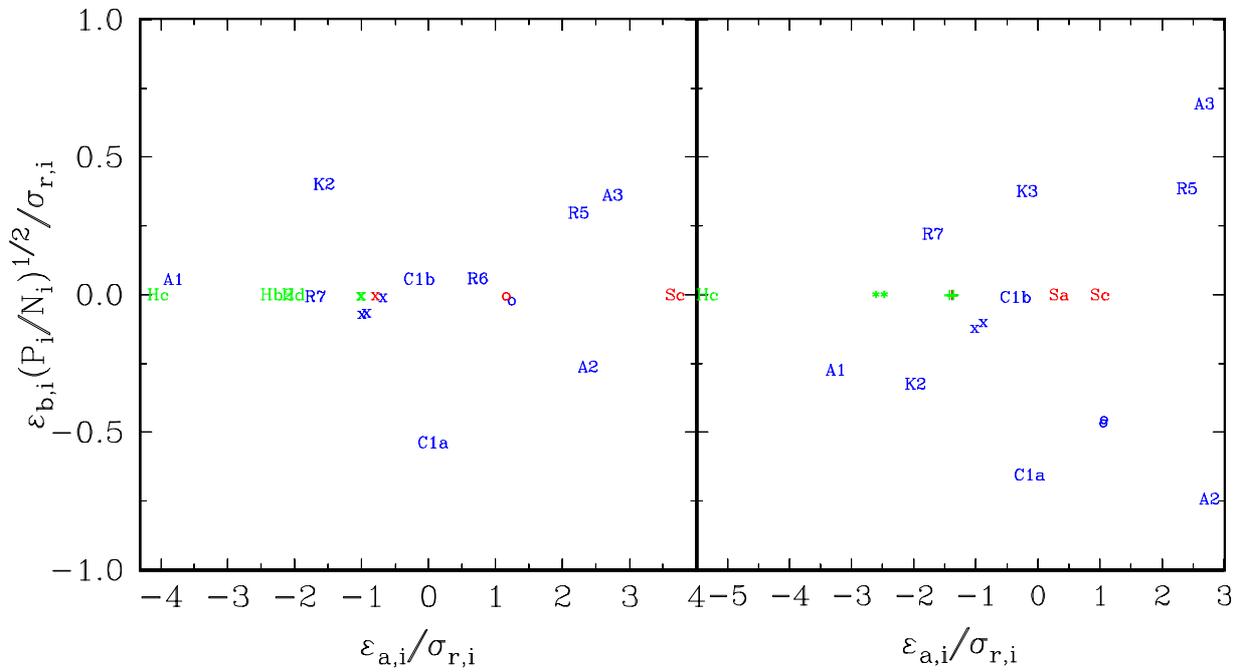
FIG. 5.

Normalized tilt systematic error vs. shift systematic error. Experiment's code is used as a mark if it is not stated otherwise. On the left is the solution I (recommended); o is for K1, Sa; x is for K3, K4, R4, Sb, Ha, Hb1 series. On the right is the solution II when the entropy of $CaAl_4O_7$ is fixed in accordance with the experimental value (see text); o is for K1, R6; x is for K4, R4, + is for Sb, Ha, Hb1; ∗ is for Hb2, Hd series.
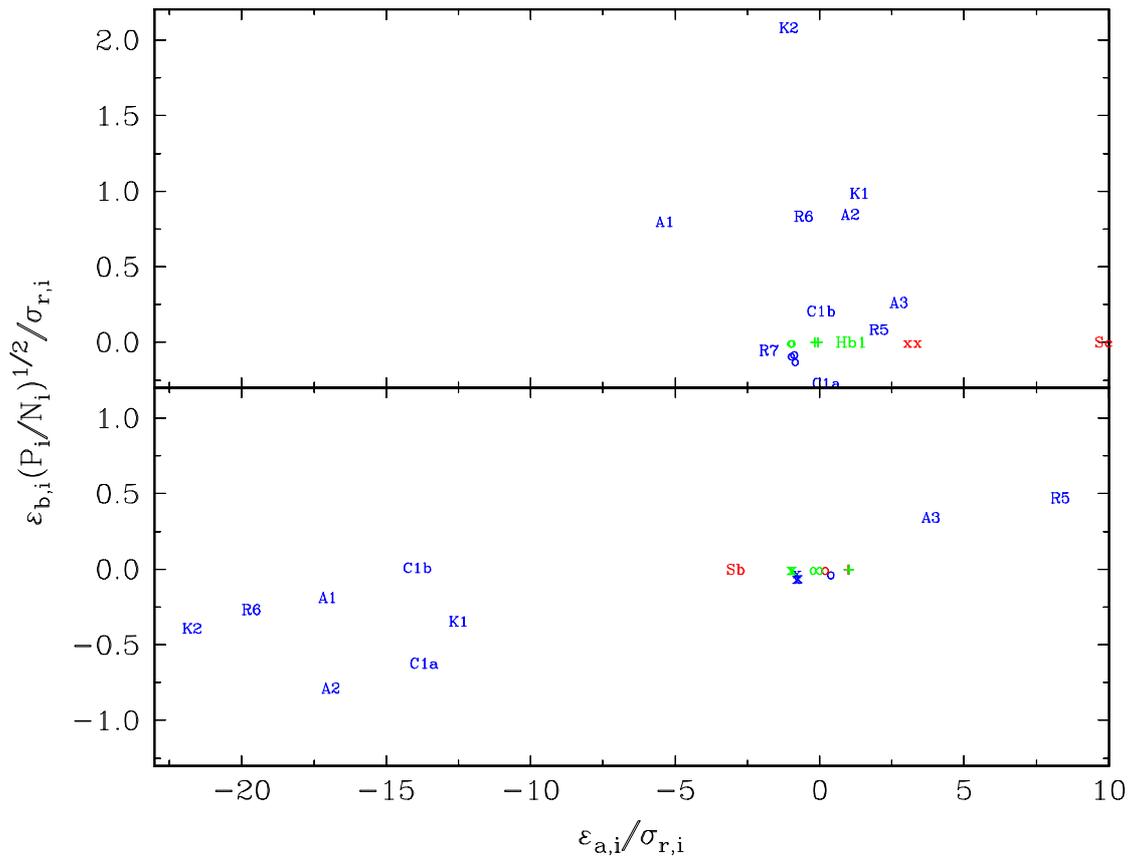
FIG. 6.

Normalized tilt systematic error vs. shift systematic error. Experiment's code is used as a mark if it is not stated otherwise. Above is the solution III when the enthalpy of $CaAl_4O_7$ is fixed in accordance with the experimental value; o is for K3, R4, Hc, Hd; x is for Sa, Sb; + is for Ha, Hb2 series. Below is the solution IV when both the enthalpy and the entropy of $CaAl_4O_7$ are fixed in accordance with the experimental value (see text); o is for K3, Sc, Ha, Hb2; x is for K4, R4, R7, Hc, Hd; + is for Sc, Hb1 series.

the enthalpies of formation (solution III) is more difficult task (compare Fig. 6 above with Fig. 5 on the left. Note the difference in the scale). The description of the emf values here is rather bad but the description of the entropy of $CaAl_4O_7$ is even worse. Finally, we can obtain the good fit for the enthalpy and entropy of $CaAl_4O_7$ (solution IV) but the cost is that the description of the emf values becomes unacceptable (shift errors are about twenty times more than reproducibility errors).

As a result, our expert conclusion is that the solution I (see Table 2 and 3) is better than the others and it is recommended in the present work. Still, we think that the questions on thermodynamics of calcium aluminates remain. New experiments are probably needed to obtain unambiguous results.

Finally, the peculiarity of the recommended solution is to be mentioned. Two calcium aluminates, $Ca_3Al_2O_6$ and $CaAl_4O_7$ become thermodynamically unstable at room temperature (all four aluminates are stable at higher temperatures). The question whether this is an artifact of unsatisfactory primary experimental values, or the "truth" is left unanswered.

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