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PHYSICAL METHODS OF INVESTIGATION

Estimation of the Standard Enthalpy of Formation of Crystalline Alkali Metal Borates

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Abstract—A structure–property correlation has been developed, which makes it possible to choose the optimal values of the enthalpy of formation of alkali metal borates, for which, according to the data of various experimental works and reference publications, wide variations are observed. Using this correlation, the enthalpy of formation of unstudied alkali metal borates can be reasonably estimated. It has been found that the contribution of B_2O_3 to the enthalpy of formation is the same not only for alkali metal borates but also for Ba, Ca, and Pb borates, for whose enthalpy of formation a structure–property correlation has also been established. This suggests the suitability of the obtained correlations for estimating the enthalpy of formation in the borate series, where the value is known only for one member of the series, as well as the possibility of estimating the enthalpy of formation of mixed borates of different metals.

Keywords: enthalpy of formation, evaluation of thermodynamic properties, oxide increments

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INTRODUCTION

Due to the unique structure, boron-containing compounds, in particular borates, are widely used in practice. In particular, crystalline borates of alkali and alkaline earth metals are used in the creation of lasers and systems with nonlinear optical properties. Amorphous and crystalline borogermanates are used in telecommunication, laser and LED technologies. Borosilicate glasses are the main type of matrices for radioactive waste disposal, production of membranes, microporous materials, etc.

The practical application of valuable boron-containing substances could be expanded, but the creation of new materials is associated with various technological difficulties, and requires large financial and time costs. Therefore, it is advisable to use theoretical methods and approaches for a preliminary analysis of the structure and properties of compounds of practical interest.

The method of physicochemical simulation has proven itself well in the study of various natural and technological systems in geochemistry, metallurgy, and materials science [1–5]. The authors improved the technology of electrolytic production of aluminum [6], simulated the processes of transformation of dumps of coal-fired thermal power plants [7], and studied the structure of silicate melts [8, 9].

To conduct physicochemical simulation, it is necessary to have a certain set of thermodynamic properties of compounds [10], the formation of which is possible in the systems under study.

The complex of thermodynamic properties required for physicochemical simulation was reported for K, Li, Na metaborates in the crystalline state ($0.5K_2O·0.5B_2O_3$, $0.5Li_2O·0.5B_2O_3$, $0.5Na_2O·0.5B_2O_3$) [11, 12]. In addition to these compounds, a complete set of thermodynamic properties (partially estimated) is given for the following borates [12]: $K_2O·2B_2O_3$, $K_2O·3B_2O_3$, $K_2O·4B_2O_3$, $Li_2O·2B_2O_3$, $Li_2O·3B_2O_3$, $Li_2O·4B_2O_3$, $Na_2O·2B_2O_3$, $Na_2O·3B_2O_3$, $Na_2O·4B_2O_3$.

According to experimental data [13–19], in addition to the above, there are the following K, Li, and Na borates: $K_2O·5B_2O_3$, $2K_2O·B_2O_3$, $Li_2O·B_2O_3$, $Li_2O·5B_2O_3$, $2Li_2O·B_2O_3$, $2Li_2O·5B_2O_3$, $3Li_2O·B_2O_3$, $3Li_2O·2B_2O_3$, $0.5Na_2O·1.5B_2O_3$, $Na_2O·B_2O_3$, $Na_2O·5B_2O_3$, $Na_2O·9B_2O_3$, $2Na_2O·B_2O_3$, $2Na_2O·3B_2O_3$, $2Na_2O·5B_2O_3$, $3Na_2O·B_2O_3$, $3Na_2O·2B_2O_3$, $5Na_2O·2B_2O_3$, thermodynamic characteristics for which have not been reported.

To study borate systems, it is necessary to evaluate the thermodynamic properties of unstudied alkali metal borates. In addition, for the studied substances, the task is to harmonize the thermodynamic properties, which, according to various sources, have significant differences.

METHODS FOR ASSESSING ENTHALPY OF FORMATION

It is advisable to carry out the coordination and calculation of the thermodynamic properties of compounds using parameters that are easily accessible for both investigated and unexplored compounds. The most accessible characteristic is the stoichiometric formula of the compound, therefore, to match experimentally determined thermodynamic properties and calculate unknown quantities, it is convenient to use structure–property correlations.

As structural components, chemical elements, ions, oxides or more complex structural components can be used, reflecting the structural features of compounds.

These correlations are implemented in additive methods for matching and evaluating the thermodynamic properties of complex inorganic substances, for example: anhydrous solutions [20], hydrates [21], minerals [22], binary and ternary oxides [23]. The estimation of the standard thermodynamic potentials of some alkali and alkaline earth metal borates was carried out by the authors [24]; borate ions were used as structural components.

To match and evaluate binary oxides, higher oxides are also used as structural components. Using the decomposition into such oxides, we previously performed the matching and estimation of the standard thermodynamic potentials of silicates [25] and germanates [26] of alkali and alkaline earth metals.

Additive methods assume a linear relationship between a thermodynamic property and the value of the contribution of each structural component to it; therefore, the structure–property correlation can be written as a system of equations:

$$y_i = \sum_{i=1}^{m} b_j x_{ij}, \tag{1}$$

where y_i is the i-th known numerical value of the investigated thermodynamic property of the i-th basic component; b_j are coefficients at structural components; x_{ij} is the amount of the j-th structural component in the i-th basic component; $i = \overline{1,n}$ is the number of basic components; $i = \overline{1,n}$ is the number of structural components.

In matrix form:

$$Y = bX, \tag{2}$$

where $b = (b_1, b_2, ..., b_m)$ is the vector of coefficients to be calculated; Y is the column vector of known thermodynamic properties of basic components; X is the given initial matrix containing the amount of each structural component in each basic component:

$$Y = \begin{bmatrix} y_1 \\ y_2 \\ \cdot \\ y_n \end{bmatrix}; \quad X = \begin{bmatrix} x_{11} & x_{12} & \cdot & x_{1m} \\ x_{21} & x_{22} & \cdot & x_{2m} \\ \cdot & \cdot & \cdot & \cdot \\ x_{n1} & x_{n2} & \cdot & x_{nm} \end{bmatrix}, \tag{3}$$

here, $x_{11}, ..., x_{nm}$ is the number of structural components.

INITIAL DATA ANALYSIS

The disadvantage of many calculation methods is the lack of a critical analysis of the known values of thermodynamic potentials used as basic ones for establishing correlations between the studied properties and the structure of compounds. The use of a single source and ignoring the error of the borrowed values reduce the reliability of the found correlations and can lead to errors in the calculations of the thermodynamic properties of substances [25].

Table 1 shows the enthalpies of formation of K, Li, and Na borates, the thermodynamic properties of which are given in fundamental reference books [11, 12, 18]. In these reference books, the experimental data were processed. Calculations are based on measurements of thermal effects of various reactions; data from [17, 27–31] were used. Table 1 also shows the enthalpies of formation of some borates calculated by the authors of experimental works [17] and [31]. These values were taken into account when choosing the intervals of possible variations in the enthalpies of formation of borates. The enthalpies of formation of K, Li, and Na borates presented in [32–37] were taken into account.

The values of the enthalpy of formation of the same compound in different fundamental editions have significant differences (Table 1). For example, for $0.5K_2O{\cdot}0.5B_2O_3$, the values of the enthalpy of formation recommended [12, 18] differ by 1.3%, and, taking into account the errors, by 3%. The values of errors declared in [12, 18] are significantly lower.

The calculation results and their accuracy are also significantly affected by the enthalpies of formation of oxides from which the compounds under consideration are formed. These quantities are used in calculating the heats of reactions leading to the formation of the compounds in question. Table 2 compares the recommended values of the enthalpy of oxide formation reported [11, 12, 18], as well as the values used in experimental works [17, 27, 31].

Comparison of the data in Tables 1 and 2 shows that the errors in the enthalpy of formation of oxides are much larger than the errors in the enthalpy of formation of borates stated in the reference literature. In addition, as noted [11], the authors of experimental studies often overestimate the accuracy of their measurements, underestimating the effect of systematic errors.

RESULTS AND DISCUSSION

Let us consider the linear nature of the structure–property dependence using the example of sodium borates, for which data on the enthalpy of formation of two series differing in the Na_2O content are presented in the literature. For sodium borates (Table 1), the dependence of the enthalpy of formation on the content of B_2O_3 can be written as a system of equations that are a special case of Eq. (1):

$$\Delta_f H^\circ_{298.15}\left(Na_2O{\cdot}x_{i1}B_2O_3,\ c\right) = b_1 x_{i1} + b_2; \tag{4}$$

$$\Delta_f H^\circ_{298.15}\left(0.5Na_2O{\cdot}x_{i1}B_2O_3,\ c\right) = b_1 x_{i1} + 0.5b_2, \tag{5}$$

where b_1 is the contribution of B_2O_3 to the enthalpy of formation of a borate; b_2 is the contribution of Na_2O.

Figure 1 shows the result of approximation of the enthalpy of formation in the series of sodium borates by Eqs. (4) and (5).

The intervals of B_2O_3 contributions to the enthalpy of formation of the $Na_2O{\cdot}x_{i1}B_2O_3$ (i = 1, 2, 3, 4) and $0.5Na_2O{\cdot}x_{i1}B_2O_3$ (i = 0.5, 1.5) series obtained by approximating the data in Table 1 are presented in Table 3. The intersection of the intervals shows that within the variation of the data in Table 1 system (4), (5) has solutions, therefore, it can describe the dependence of the enthalpy of formation of sodium borates on the composition.

For potassium borates, the enthalpies of formation are known for the series $K_2O{\cdot}x_{i1}B_2O_3$ (i = 2, 3, 4). The interval of B_2O_3 contributions to the enthalpy of formation of potassium borates obtained by approximating the data in Table 1 with an equation similar to Eq. (4) and presented in Table 3 overlaps with intervals for sodium borates, therefore, it is possible to jointly describe the enthalpy of formation of sodium and potassium borates by a single equation.

In the case of lithium borates, the enthalpies of formation are known for the series $Li_2O{\cdot}x_{i1}B_2O_3$ (i = 2, 3, 4). The interval of B_2O_3 contributions to the enthalpy of formation of lithium borates (Table 1) obtained by approximating this series does not overlap with the intervals for potassium and sodium borates. Eliminating $Li_2O{\cdot}4B_2O_3$ from the approximation gives an interval overlapping with those for potassium and sodium. Hence, we can conclude that the linear structure–property dependence is violated for this compound, since such a phenomenon is not observed for other K, Li, and Na borates. From the data shown in Table 1 it can be seen that for $Li_2O{\cdot}4B_2O_3$ the authors of the handbooks declared extremely low error values, which, apparently, led to the situation described.

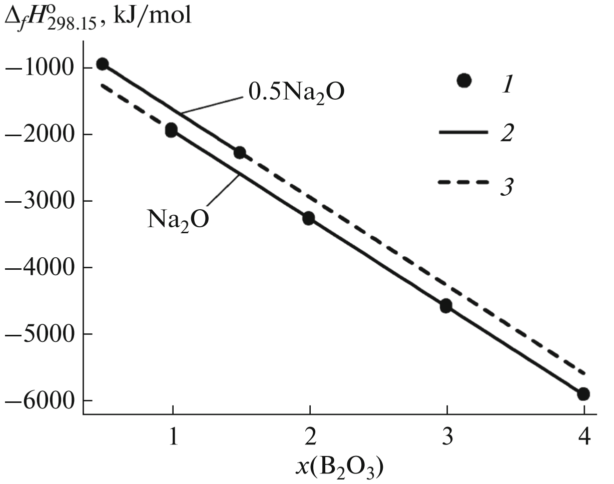

Fig. 1. The result of approximation of the enthalpy of formation in the series of sodium borates by Eqs. (4) and (5): (*1*) intervals of variation of values according to Table 1; (*2*) interpolation between experimental data; (*3*) extrapolation beyond experimental data.

To solve this problem, the possible intervals of the contribution of B_2O_3 to the enthalpy of formation of Pb, Ca, and Ba borates, the values of which are given [12, 18, 38], were studied. From the intervals presented in Table 3, it can be seen that for all the considered borates, the generalized interval of the B_2O_3 contribution can fall in the range of –1319.1...–1317.4 kJ/mol.

Taking into account a series of approximations of the enthalpy of formation in the series of borates listed in Table 3, it was found that the optimal value of the B_2O_3 contribution, which makes it possible to describe the structure–property dependences without deviations from the error interval, is –1318.8 kJ/mol. In the same series of approximations, the optimal values of contributions to the enthalpy of formation of metal oxides constituting the considered borates are determined.

The single value of the contribution of B_2O_3 to the enthalpy of formation of borates, which include metal oxides from different groups and periods, makes it possible to estimate the enthalpy of formation in the series of borates, in which the value for only one member of the series is known.

In [11], the estimated values of the enthalpy of formation of cesium and rubidium metaborates are given:

$$\Delta_f H^\circ_{298.15}\left(0.5Cs_2O{\cdot}0.5B_2O_3,\ c\right) = -962 \pm 20\ \text{kJ/mol};$$

$$\Delta_f H^\circ_{298.15}\left(0.5Rb_2O{\cdot}0.5B_2O_3,\ c\right) = -975 \pm 20\ \text{kJ/mol}.$$

Table 1. Enthalpy of formation of K, Li, and Na basic borates

Compound	Ref.	$\Delta_f H^\circ_{298.15}$, kJ/mol	Procedure	Variation interval	Calculation according to Eq. (6)
$0.5K_2O\cdot 0.5B_2O_3$	[11]	−983 ± 5 (±0.51%)	*a*	−973.62	−994.5
	[18]	−981.985 ± 8.37 (±0.85%)	*a*	−1002.96	
	[12]	−994.955 ± 8 (±0.8%)	*b*		
$K_2O\cdot 2B_2O_3$	[18]	−3340.924 ± 6.3 (±0.19%)	*a*	−3307.56	−3307.7
	[12]	−3334.23*	c**	−3347.22	
$K_2O\cdot 3B_2O_3$	[18]	−4653.863 ± 6.3 (±0.135%)	*a*	−4623.13	−4615.5
	[12]	−4633.529 ± 10.4 (±0.22%)	*b*	−4660.16	
$K_2O\cdot 4B_2O_3$	[18]	−5976.426 ± 6.3 (±0.11%)	*a*	−5939.23	−5945.3
	[12]	−5945.129 ± 5.9 (±0.1%)	*b*	−5982.73	
$0,5Li_2O\cdot 0.5B_2O_3$	[11]	−1022.9 ± 2.5 (±0.24%)	*a*	−1018.40	−1018.6
	[18]	−1022.151 ± 3.347 (±0.33%)	*d*	−1025.50	
	[12]	−1019.2 ± 0.8 (±0.08%)	*b*		
$Li_2O\cdot 2B_2O_3$	[18]	−3376.906 ± 7.113 (±0.21%)	*d*	−3355.96	−3356.0
	[12]	−3362.262 ± 6.3 (±0.19%)	*b*	−3384.02	
$Li_2O\cdot 3B_2O_3$	[18]	−4675.202 ± 7.531 (±0.16%)	*d*	−4654.29	−4674.8
	[12]	−4659.888 ± 5.6 (±0.12%)	*b*	−4682.73	
$Li_2O\cdot 4B_2O_3$	[18]	−5948.811 ± 8.368 (±0.14%)	*d*	−5907.58	−5993.6
	[12]	−5914.377 ± 6.8 (±0.11%)	*b*	−5957.18	
$0.5Na_2O\cdot 0.5B_2O_3$	[11]	−976.5 ± 2.5 (±0.26%)	*d*	−973.61	−979.0
	[18]	−976.127 ± 3.35 (±0.34%)	*g*	−979.00	
	[12]	−975.709 ± 2.1 (±0.215%)	*h*		
	[17]	−975.709 ± 2.51 (±0.257%)	*i*		
$0.5Na_2O\cdot 1.5B_2O_3$	[17]	−2300.782 ± 3.347 (±0.145%)	*i*	−2297.44	−2297.8
				−2304.13	
$Na_2O\cdot B_2O_3$	[31]	−1974.011 ± 11.715 (±0.6%)	*i*	−1943.69	−1958.0
		−1959.368*	*j*	−1985.73	
$Na_2O\cdot 2B_2O_3$	[18]	−3289.04 ± 5 (±0.15%)	*k*	−3268.74	−3276.8
	[12]	−3276.741 ± 8 (±0.24%)	*b*	−3294.48	
	[17]	−3290.298 ± 4.184 (±0.13%)	*i*		
$Na_2O\cdot 3B_2O_3$	[18]	−4603.655 ± 6.3 (±0.14%)	*k*	−4571.28	−4595. 6
	[12]	−4580.476 ± 9.2 (±0.2%)	*b*	−4609.96	
$Na_2O\cdot 4B_2O_3$	[18]	−5911.574 ± 7.95 (±0.13%)	*k*	−5901.53	−5914.4
	[17]	−5909.9 ± 8.368 (±0.14%)	*i*	−5919.52	

(*a*) processing of measurements [27, 28]; (*b*) processing of measurements [27]; (*c*) estimation based on the data reported [27]; (*d*) processing of measurements [27, 28, 30]; (*e*) processing of measurements [17, 28]; (*g*) processing of measurements [17, 28, 31]; (*h*) borrowing from [17]; (*i*) calorimetry of reactions; (*j*) calculation based on the data [27]; (*k*) processing of measurements [17], [27–29].

* When assigning an interval for the calculation, an error of ±0.8% was accepted by analogy with that stated [12] for $0.5K_2O\cdot 0.5B_2O_3$.

** In [12], an error was noted that was made [27] when calculating the molecular weight of a sample close in composition to $K_2O\cdot 2B_2O_3$; a fix has been made; error estimate was not made.

Table 2. Comparison of the enthalpy of formation of oxides, kJ/mol

Oxide	Ref.					
	[18]	[11]	[12]	[17]	[27]	[31]
B_2O_3	−1272.9 ± 1.2	−1273.5 ± 1.4	−1271.9 ± 2.1	−1272.4 ± 1.7	−1263.6	−1277.4
K_2O	–	−361.7 ± 4.0	−363.17 ± 2.1	–	−361.5	–
Li_2O	−597.94 ± 0.33	−597.88 ± 0.3	−598.73 ± 2.1	–	−595.8	–
Na_2O	−414.84 ± 0.25	−414.57 ± 0.3	−417.98 ± 4.2	−411.1 ± 0.33	−415.9	−415.9

Table 3. B_2O_3 contributions to the enthalpy of formation of borates

Borates	B_2O_3 contribution, kJ/mol	
	min.	max.
$K_2O{\cdot}2B_2O_3$, $K_2O{\cdot}3B_2O_3$, $K_2O{\cdot}4B_2O_3$	−1337.6	−1296.0
$Li_2O{\cdot}2B_2O_3$, $Li_2O{\cdot}3B_2O_3$, $Li_2O{\cdot}4B_2O_3$	−1300.6	−1261.8
$Li_2O{\cdot}2B_2O_3$, $Li_2O{\cdot}3B_2O_3$	−1326.8	−1270.3
$0.5Na_2O{\cdot}0.5B_2O_3$, $0.5Li_2O{\cdot}1.5B_2O_3$	−1330.5	−1317.4
$Na_2O{\cdot}2B_2O_3$, $Na_2O{\cdot}3B_2O_3$, $Na_2O{\cdot}4B_2O_3$	−1319.1	−1305.3
$BaO{\cdot}B_2O_3$, $BaO{\cdot}2B_2O_3$	−1414.2	−1303.4
$CaO{\cdot}B_2O_3$, $CaO{\cdot}2B_2O_3$	−1329.4	−1317.2
$PbO{\cdot}B_2O_3$, $PbO{\cdot}2B_2O_3$, $PbO{\cdot}3B_2O_3$	−1328.5	−1313.5

Based on these data, using equations similar to Eq. (5) and taking into account the obtained contribution of B_2O_3, the contributions of cesium and rubidium oxides to the enthalpy of formation of borates were calculated.

Based on the data on the enthalpy of formation of crystalline francium hydroxide [18] using the method used [11], we estimated the enthalpy of formation of francium metaborate:

$$\Delta_f H^\circ_{298.15}(0.5Fr_2O{\cdot}0.5B_2O_3,\ c) = -937.5 \pm 20\ \text{kJ/mol},$$

on the basis of which the contribution of francium oxide to the enthalpy of formation of borates was calculated.

The dependence of the enthalpy of formation of alkali metal borates on the composition is obtained:

$$\begin{aligned}\Delta_f H^\circ_{298.15}(x_{ij}Me_2O{\cdot}x_{i1}B_2O_3,\ c) &= -1318.8x_{B_2O_3} - 718.4x_{Li_2O} - 639.2x_{Na_2O} \\ &- 670.1x_{K_2O} - 631.2x_{Rb_2O} \\ &- 605.2x_{Cs_2O} - 556.2x_{Fr_2O}\ \text{kJ/mol}.\end{aligned} \quad (6)$$

In the geometric interpretation, dependence (6) is a hyperplane located in eight-dimensional space. The projection of this hyperplane into three-dimensional space is a plane describing the dependence of the enthalpy of formation on the composition for borates, including oxides of one alkali metal; projection into four-dimensional space is for mixed borates formed by oxides of two alkali metals, etc. An example of projection (6) into three-dimensional space for sodium borates is shown in Fig. 2.

The enthalpies of formation of the studied borates calculated in accordance with Eq. (6) are within the

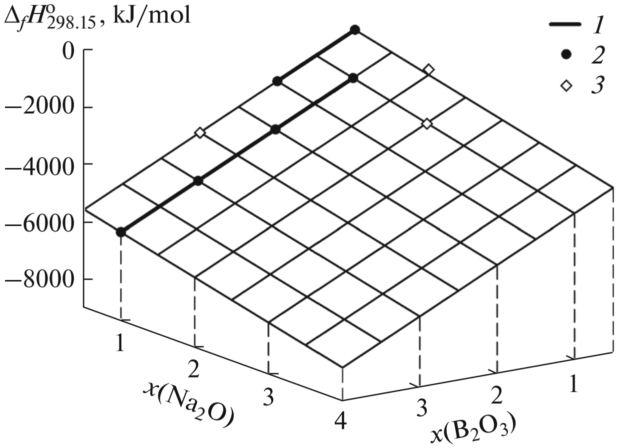

Fig. 2. Example of the projection of Eq. (6) into three-dimensional space for sodium borates: (*1*) interpolation between experimental data; (*2*) values [12]; (*3*) estimated values [24].

Table 4. Comparison of literature data and estimated values of the enthalpy of formation of some borates

Compounds	Ref.	$\Delta_f H^\circ_{298.15}$, kJ/mol	Calculation according to Eqs. (6), (7)	Deviation, %
$K_2O{\cdot}B_2O_3$	[32]	−1963.133	−1988.9	1.31
$Li_2O{\cdot}B_2O_3$	[34]	−2038.394	2037.2	0.06
$2PbO{\cdot}5B_2O_3$	[39]	−6997.15	−7059.2	0.89*
$2CaO{\cdot}B_2O_3$	[18]	−2734.58 ± 2.1 (±0.08%)	−2737.8	0.04
$2CaO{\cdot}3B_2O_3$		−5392.79 ± 7.1 (±0.13%)	−5378.4	0.14
$3CaO{\cdot}B_2O_3$		−3429.25 ± 2.9 (±0.08%)	−3447.3	0.44
$0.5Na_2O{\cdot}CaO{\cdot}0.5B_2O_3$	[40]	−1664.5 ± 0.9 (±0.05%)	−1688.5	1.4
$2Li_2O{\cdot}CaO{\cdot}B_2O_3$		−3391.7 ± 1.9 (±0.06%)	−3465.1	2.2

* The calculations [39] used the enthalpy of formation of B_2O_3 equal to −1270.4 kJ/mol. Information about the used value of the enthalpy of formation of PbO is not given. When using the value of the enthalpy of formation of B_2O_3 recommended by CODATA, which is −1273.5 ± 1.4 kJ/mol [41], the deviation of the value obtained in accordance with Eq. (7) from the data [39] is 0.56%.

ranges of variations presented in Table 1. Deviation from the range of 0.6% is present only for $Li_2O{\cdot}4B_2O_3$.

The contributions of Pb, Ca, and Ba oxides to the enthalpy of formation of borates were estimated preliminary, since a detailed analysis of the initial data, similar to that presented in Table 1, was not carried out. For these borates

$$\begin{aligned}&\Delta_f H^\circ_{298.15}\left(x_{ij}\mathrm{MeO}{\cdot}x_{i1}\mathrm{B_2O_3},\ \mathrm{c}\right)\\&= -1318.8x_{\mathrm{B_2O_3}} - 232.6x_{\mathrm{PbO}}\\&- 709.5x_{\mathrm{CaO}} - 668.3x_{\mathrm{BaO}}\ \mathrm{kJ/mol}.\end{aligned} \tag{7}$$

Equation (7) describes the enthalpy of formation of the rows of borates presented in Table 3 without deviating from the variation intervals stated [12, 18, 38].

Table 4 compares the results of calculating the enthalpy of formation of some borates not used in obtaining correlations (6) and (7) with the data reported [18, 32, 34, 39, 40].

In [32, 39], the sources, methods of obtaining and errors of the enthalpy of formation of $K_2O{\cdot}B_2O_3$ and $2PbO{\cdot}5B_2O_3$ are not given; therefore, errors (6) and (7) presented in Table 4 can be considered admissible.

Since the errors reported [18] are probably significantly underestimated, the presented result for calcium borates can also be considered acceptable.

The deviations of the enthalpy of formation of mixed borates from the experimental data [40] are quite large, but they are within the limits acceptable for evaluation methods. This shows the possibility of using the correlations presented above to estimate the enthalpy of formation of mixed borates.

CONCLUSIONS

A feature of the presented method for assessing the thermodynamic properties of substances is a critical analysis of experimentally determined and reference values, which makes it possible to establish a physically and mathematically substantiated structure–property relationship.

Since the enthalpy of formation of substances is additive in nature (thermal effects of various reactions are summed up), the linear form of the structure–property dependence for this parameter is pronounced. The deviation from the linear form may be due to large errors in measurements and processing of experimental data. Thus, it is possible to identify parameters with insufficient reliability or underestimated errors. This is shown above using the enthalpy of formation of $Li_2O{\cdot}4B_2O_3$ as an example.

Equation (6) reproduces the data in Table 1 without deviations from the range of variations; therefore, the error in calculating the enthalpy of formation of K, Li, and Na borates is assumed to be sufficiently small for the evaluation method (no more than ±1%). Since for Cs, Rb, and Fr, the estimated values of the enthalpy of formation of metaborates of these metals were used as base values, we estimate the error (6) for Cs, Rb, and Fr borates to be ±2.5%.

Equation (7) within the error interval without deviations describes the enthalpies of formation of Pb, Ca and Ba borates; therefore, the error (7) is also estimated to be no more than ±1%.

It should be noted that in periodicals and reference literature for borates, in addition to those listed in Tables 1 and 3, there are no experimental data on the enthalpy of formation for series suitable for establishing correlations. At best, the values for single borates are known. This data is partially estimated or obtained by indirect methods, for example, from the analysis of state diagrams. In this case, a single value of the contribution of B_2O_3 makes it possible to estimate the enthalpy of formation of borates of any metals with acceptable reliability.

The results of calculating the enthalpy of formation of two mixed alkali metal and calcium borates and their comparison with experimental data show the possibility of estimating the enthalpy of formation of triple oxides using Eqs. (6) and (7) with acceptable reliability. There is reason to believe that more complex borates can be evaluated if they are found experimentally.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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