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METHODS FOR CALCULATING AND MATCHING THERMODYNAMIC PROPERTIES OF SILICATE AND BORATE COMPOUNDS

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New methods for processing the experimental and calculated thermodynamic data have been elaborated and the existing ones have been improved. The developed approaches provide a physically reasonable description of the first-order phase transitions, which makes it possible to compare and correct the values of their thermodynamic properties, as well as to calculate the thermodynamic parameters of unstudied compounds. Regression equations have been proposed for calculating the standard entropy and enthalpy of formation of lithium, sodium, and potassium silicates and borates. The resulting entropy and enthalpy values for 14 alkali metal silicates and 12 alkali metal borates can be used to optimize the technological processes for manufacturing glass, ceramics, and coatings.

Keywords: silicates, borates, standard thermodynamic functions.

Introduction

Systematic comparative analysis of temperature dependences of thermodynamic potentials within a broad range of concentrations and temperatures is used to calculate the excess thermodynamic functions of crystals and glasses required to create the physicochemical model of oxide systems (silicate, borate, germanate, etc.) and to compare the resulting thermodynamic data with the structure of compounds. The enthalpy of formation and standard entropy are the key characteristics of synthesis of new construction materials needed for the high-tech fields of space and nuclear power industries. However, the properties of many silicates, the essential components of these materials, have not been studied to the full extent. The reason is that the thermodynamic properties of sodium, potassium, and lithium silicates given in reference books [1–3] significantly differ due to characteristics of the methods used for processing and estimating the calorimetric data. If no reliable criterion for choosing the proper value is suggested, the accuracy of calculations performed using these data is rather doubtful [4, 5]. Thus, the initial data that can be used to determine the thermodynamic properties of alkali metal silicates in a condensed state for K_2SiO_3 and $K_2Si_2O_5$ are given in [3], while the experimental and calculated thermodynamic data for K_2SiO_3, Li_2SiO_3, $Li_2Si_2O_5$, Na_2SiO_3, and $Na_2Si_2O_5$ are presented in [1]. Hence, currently there is no unified matched database of thermodynamic data suitable for creating an adequate physicochemical model that would include silicate and borate.

Research methods

Inaccuracy of the presented values plays a crucial role in performing critical analysis of the data with respect to their thermodynamic properties, since the measurement accuracy is sometimes overestimated [4]. Hence, in this study we used the data taken from sources [1–3, 6], whose accuracy had been confirmed by large references and the analysis of the experimental work.

The calculation methods are based on empirical correlations between physicochemical values [7]. Therefore, it is reasonable to use the "structure– property" correlations in order to calculate the unknown values. The same correlations are used in additive calculation methods. Regression analysis revealing the correlations between the calculated thermodynamic potential, composition, and certain properties of compounds similar to the ones under study includes a variety of additive methods for calculating thermodynamic properties of individual compounds.

The Neumann-Kopp additive method with its variants has been successfully used previously in the calculation of the thermodynamic properties of silicate minerals [8, 9], phosphates [10], carbonates [11], hydrous sulfates [12], hydrous borates [13, 14] and other compounds. In the outlined papers it has been shown that the error of the calculation may be less than 5 %, which is comparable to the accuracy of the experimental techniques.

The thermodynamic properties of the experimentally unstudied compounds were estimated using regression analysis based on the classical Neumann-Kopp additive rule:

$$F\left(\mathrm{A}_k\mathrm{B}_l\right)=kF\left(\mathrm{A}\right)+lF\left(\mathrm{B}\right), \quad (1)$$

where F is an arbitrary thermodynamic or thermochemical potential; A and B are the structural units (elements, ions, oxides, etc.) into which the compounds under study can be decomposed; k and l are the numbers of structural units.

We refer to the compounds with the known thermodynamic potentials that comprehensively describe the entire system of the stoichiometric units as the fundamental components of the regression matrix for a set of isostructural compounds. For the unstudied compounds, their stoichiometric units need to be known, and the unknown thermodynamic properties can be calculated on this base.

The multiple regression equation determining the correlation between the thermodynamic (thermochemical) potentials and the composition of compounds is written as follows:

$$y_i=\sum_{i=1}^{m} b_j x_{ij}, \quad (2)$$

where y_i is the i-th dependent value of the known potential (the numerical value of the analyzed thermodynamic property of the i-th fundamental compound); b_j is any multiple regression coefficient; x_{ij} is an independent parameter of the known potential (the amount of the i-th structural unit).

Preparing data for regression analysis involves two main stages:

(1) If variation in the values of the thermodynamic potential under study according to different sources is small (within 5–10 %), the assigned deviations are set from the average value to the upper and lower limits according to the data claimed in the literature.

(2) If the value of the thermodynamic potential under study has significant variations according to different sources, several variants of regression analysis involving the differing values need to be taken into account.

In the present paper, regression analysis has been performed using weights equal to the inverse of the error function for each compound. It should be noted that if the weights taken as the inverse value of the error squares, then the regression quality deteriorates significantly. But the use of such weighting factors gives good results for a set of compounds with error values close to each other.

The adequate matching criteria are evaluated based on an assumption that the contributions of all structural components (the b_i values) to the thermodynamic potential under study must be of the same sign, since every structural component makes a similar contribution to this value. It is only in this case that the calculations for the unstudied compounds with x_{i1} and x_{ij} being different from x_{i1} and x_{ij} of the reference compounds can be performed using the resulting correlations.

The unique solution to the system (equation (2)) cannot be chosen on the basis of mathematical criteria only (such as the correlation coefficient, root-mean-square error, etc.). Additional thermodynamic restrictions caused by properties of the fundamental components must be imposed. It was previously demonstrated [4] that the b_j values of structural components for thermodynamic potentials (e.g., standard entropy) of isostructural compounds clearly depend on the molecular weight of structural units.

The b_j value of thermochemical potentials (e.g. enthalpy of formation) is usually independent of the molecular weight of structural components. Since both metal and nonmetal oxides have been selected as structural units A and B, the b_j value can be written as:

$$b_j=b_j\left(\mathrm{Str}\right)+b_j\left(\mathrm{Ex}\right), \quad (3)$$

where b_j(Str) is the thermodynamic or thermochemical potential of the structural unit x_{ij} as an individual compound in the corresponding phase state; b_j(Ex) is the excess function of the structural component x_{ij} in formation of a compound with the thermodynamic or thermochemical potential y_i.

The studies, which focused on regularities of changes in the enthalpy of formation in series of alkali metal borates and aluminates, as well as alkaline earth metal aluminates, have shown that their excess functions significantly depend on the molecular weight of structural units of the same type. Thus, analysis of equation (3) allows choosing the unambiguous solution to the system (equation (2)) for thermochemical potentials.

Results

Alkali metal silicates

Calculation of the matched thermodynamic properties of alkali metal silicates includes the following steps:

(1) matching the available thermodynamic potentials by finding the “structure-property” correlations using the additive methods;

(2) determining the matched thermodynamic properties of the compounds for which the required amount of the initial data is available;

(3) finding regularities that allow performing interpolation and extrapolation to calculate the unknown thermodynamic properties of compounds having the mM$_2$O-nSiO$_2$ composition (M = Li, Na, K).

The thermodynamic values have been matched using descriptive amount of isostructural compounds; the calculations have been simultaneously performed for potassium, lithium, and sodium silicates. We have used regression equation (2) for matching and calculating the thermodynamic properties of alkali metal silicates:

$$y = b_1 x_{\mathrm{SiO_2}} + b_2 x_{\mathrm{Li_2O}} + b_3 x_{\mathrm{Na_2O}} + b_4 x_{\mathrm{K_2O}}, \tag{4}$$

Let us use the following denotations to write down the general forms of equations in accordance with indices of stoichiometric coefficients in equations (2), (4):

$$x_{\mathrm{SiO_2}} = x_{i1};\, x_{\mathrm{M_2O}} = x_{ij}\,(\mathrm{M} = \mathrm{Li,Na,K}), \tag{5}$$

The dependence of the standard entropy of lithium, sodium, and potassium silicates on composition has been found using regression analysis:

$$\begin{gathered} S°\left(x_{ij}\mathrm{M_2O}\cdot x_{i1}\mathrm{SiO_2};\ \mathrm{cr};\ 298.15\ \mathrm{K}\right) = 43.153\cdot x\left(\mathrm{SiO_2}\right) + 38.366\cdot x\left(\mathrm{Li_2O}\right) + \\ +73.796\cdot x\left(\mathrm{Na_2O}\right) + 103.426\cdot x\left(\mathrm{K_2O}\right)\ \mathrm{J\cdot K^{-1}\cdot mole^{-1}}. \end{gathered} \tag{6}$$

Equation (6) mathematically substantiates the correlation between the contributions of alkali metal oxides to standard entropy of silicates and their molecular weight. Deviation of the calculated standard entropy values from the literature data (Table 1) for some silicates is explained by overestimation of the measurement accuracy and results of their processing by the authors of experimental studies.

The standard enthalpy of formation of lithium, sodium, and potassium silicates is a function of composition:

$$\begin{gathered} \Delta_f H°\left(x_{ij}\mathrm{M_2O}\cdot x_{i1}\mathrm{SiO_2};\ \mathrm{cr};\ 298.15\ \mathrm{K}\right) = -919.788\cdot x\left(\mathrm{SiO_2}\right) - 720.705\cdot x\left(\mathrm{Li_2O}\right) - \\ -625.385\cdot x\left(\mathrm{Na_2O}\right) - 650.962\cdot x\left(\mathrm{K_2O}\right)\ \mathrm{kJ\cdot mole^{-1}}. \end{gathered} \tag{7}$$

The excess functions of contributions of alkali metal oxides to equation (7) are as follows (in kJ·mole^{-1}): $b_{\mathrm{Li_2O}}(\mathrm{Ex}) = -122.825$; $b_{\mathrm{Na_2O}}(\mathrm{Ex}) = -210.815$; $b_{\mathrm{K_2O}}(\mathrm{Ex}) = -289.262$. The strict dependence of the value of excess functions on the molecular weight of structural components is also confirmed by the fact that the calculated standard enthalpy values do not deviate from the literature data (Table 1). The possibility to use this correlation in order to calculate the enthalpy of formation of unstudied silicates is confirmed by the values of the coefficients in equation (7), which provide comparable contributions.

Therefore, the results of estimating the standard enthalpy of formation of alkali metal silicates using equation (7) are reliable.

Table 1

Standard entropy and enthalpy of formation of K, Li, Na silicates in the crystalline state

Silicate	Average value S°, $\mathrm{J \cdot K^{-1} \cdot mole^{-1}}$	References	Average value $\Delta_f H^\circ$, $\mathrm{kJ \cdot mole^{-1}}$	References
Li_2SiO_3	81.76±2.22 (±2.7 %)	[1, 2, 6]	–1630±24 (±1.5 %)	[1, 2, 6, 15]
	81.52	This work	–1640.49	This work
$Li_2Si_2O_5$	123.85±2.1 (±1.7 %)	[1, 2, 6, 15]	–2520.86^{a}	[6]
	124.67	This work	–2561±4 (±0.2 %)	[1, 2, 15]
			–2560.28	This work
Na_2SiO_3	113.85±1.3 (±1.1 %)	[1]	–1544.5±23.5 (±1.5 %)	[1, 2, 16, 17]
	116.95	This work	–1545.17	This work
$Na_2Si_2O_5$	161.88^{a}	[15]	–2439.5±39.5(±1.6 %)	[1, 2, 16, 17]
	164.82±2.5 (±1.5 %)	[16]	–2464.96	This work
	160.10	This work		
K_2SiO_3	138.07^{a}	[6]	–1568±50 (±3.2 %)	[1–3, 6]
	146.15±0.8 (±0.6 %)	[1]	–1570.75	This work
	146.58	This work		
$K_2Si_2O_5$	182.00^{a}	[6]	–2496±18 (±0.7 %)	[1–3, 6]
	190.58±0.42 (±0.2 %)	[3]	–2490.54	This work
	189.73	This work		
Na_4SiO_4	195.78±2.5 (±1.3 %)	[17]	–2180±100 (±4.6 %)^{b}	[2, 6, 17]
	190.74	This work	–2170.56	This work
$K_2Si_4O_9$	198.93±3.98 (±2 %)	[18]	–3402.4±5^{a}	[2]
	232.1±10.4 (±4.5 %)	[19]	–4325±11 (±0.2 %)	[6, 18]
	256.8±0.6 (±0.2 %)	[20]	–4330.11	This work
	265.68	[6]		
	276.04	This work		
$Na_6Si_2O_7$	348.05^{a}	[17]	**–3582.16^{c}**	[17]
	309.62±12.55 (±4 %)	[2]	**–3715.73**	This work
	307.69	This work		
$Na_2Si_3O_7$	**215.89**	[6]	–3385±2.6 (±0.1 %)^{b}	[2, 6]
	203.26	This work	–3384.75	This work
Li_4SiO_4	**125.52**	[6]	**–2311.66**	[6]
	119.88	This work	**–2361.20**	This work
$Li_4Si_3O_8$	**206.19**	This work	**–4159.31^{c}**	[2]
			–4200.77	This work
$Na_2Si_4O_9$	**246.41**	This work	**–4295.71^{c}**	[2]
			–4304.54	This work
$Na_4Si_3O_8$	**277.05**	This work	**–4035.47^{c}**	[2]
			–4010.13	This work

[a] the unit value is significantly different from those of other sources;

[b] the error is not specified, so the minimum and maximum values calculated on the basis of the mean have been used;

[c] individual data from the literature sources without data errors;

The bold-face type is used for values that are not included in the regression matrix.

Alkali metal borates

The thermodynamic properties of the compounds used to create the regression matrix for determining the unknown thermodynamic properties of potassium, lithium, and sodium borates with arbitrary stoichiometry were given in [1]. The number of reliable experimental values of thermodynamic potentials is smaller compared to the regression analysis performed for potassium, lithium, and sodium silicates. Furthermore, approximately 50 % of the values of thermodynamic potentials of borates [1] have been estimated, which also reduces the reliability of correlations obtained by the regression analysis.

In order to perform physicochemical modeling of the systems containing potassium, lithium, and sodium borates, one needs to create a matched system that would describe the thermodynamic properties of these compounds. The algorithm for creating a matched system of thermodynamic properties of alkali metal borates involves the following steps:

(1) Matching the known thermodynamic potentials by finding the "structure-property" correlations using the additive methods. Diboron trioxide (B_2O_3) and alkali metal oxides (K_2O, Li_2O, Na_2O) are the optimal stoichiometric units describing the structure of potassium, lithium, and sodium borates. Then the structure of the compounds under study can be written as mM_2O-nB_2O_3 (where M = K, Li, Na; m, n are positive values) and matching ought to be performed using the "contribution of oxides – property" correlation.

(2) Records for the matched thermodynamic properties are created for the compounds for which the required amount of the initial data is available.

(3) Based on these records, the correlations that allow performing interpolation and extrapolation are found, which are required to estimate the unknown thermodynamic properties of compounds with mM_2O-nB_2O_3 structure.

The regression equation for matching and calculating the thermodynamic properties of potassium, lithium, and sodium borates based on contributions of oxides is written as follows:

$$y = b_1 x_{B_2O_3} + b_2 x_{Li_2O} + b_3 x_{Na_2O} + b_4 x_{K_2O}. \tag{8}$$

Let us use the following denotations in accordance with the indices of stoichiometric coefficients for the general forms of equations:

$$x_{B_2O_3} = x_{i1}; x_{M_2O} = x_{ij} \, (\mathrm{M} = \mathrm{Li,Na,K}). \tag{9}$$

The correlation for calculating the $\Delta_f H°(\mathrm{cr}; T_C)$ value of potassium, lithium, and sodium borates obtained by regression analysis is written as:

$$\begin{gathered} \Delta_f H°\left(x_{ij} M_2O \cdot x_{i1} B_2O_3;\ \mathrm{cr};\ 298.15\ \mathrm{K}\right) = -1305.296 \cdot x\left(B_2O_3\right) - 738.059 \cdot x\left(Li_2O\right) - \\ -678.501 \cdot x\left(Na_2O\right) - 723.862 \cdot x\left(K_2O\right)\ \mathrm{kJ \cdot mole^{-1}}. \end{gathered} \tag{10}$$

The results of matching $\Delta_f H°(\mathrm{cr}; T_C)$ of the fundamental components are listed in Table 2. For most components, the deviation from the literature data is insignificant, thus indicating that $\Delta_f H°(\mathrm{cr}; T_C)$ strictly depends on contributions of structural components. This very fact explains the high quality of the regression analysis. The excess functions of contributions of alkali metal oxides to equation (10) are as follows (kJ·mole^{-1}): $b_{Li_2O}(\mathrm{Ex}) = -140.179$; $b_{Na_2O}(\mathrm{Ex}) = -263.931$; $b_{K_2O}(\mathrm{Ex}) = -371.162$.

Table 2

Standard entropy and enthalpy of formation of K, Li, Na borates in the crystalline state

Borate	Average value $S°$, J·K^{-1}·mole^{-1}	References	Average value $\Delta_f H°$, kJ·mole^{-1}	References
$LiBO_2$	51.73±0.2 (±0.4 %)	[1]	–1019.2±0.8 (±0.1 %)	[1]
	51.25±0.63 (±1.2 %)	[2]	–1022.15±3.35 (±0.3 %)	[2]
	52	This work	–1021.68	This work
$Li_2B_4O_7$	155.6±4.2 (±2.7 %)	[1]	–3362±6.3 (±0.2 %)	[1]
	157.5±2.5 (±1.6 %)	[2]	–3377±7.1 (±0.2 %)	[2]
	147.3	This work	–3348.65	This work
$Li_2B_6O_{10}$	188.3±4 (±2.1 %)	[1]	–4660±5.6 (±0.1 %)	[1]
	197±8.4 (±4.3 %)	[2]	–4675±7.5 (±0.2 %)	[2]
	190.61	This work	–4653.95	This work
$Li_2B_8O_{13}$	265±4 (±1.5 %)	[1]	–5914±6.8 (±0.1 %)	[1]
	251±16.7 (±6.6 %)	[2]	–5949±8.4 (±0.1 %)	[2]
	233.92	This work	–5959.24	This work
$NaBO_2$	73.54±0.08 (±0.1 %)	[1]	–975.7±2.1 (±0.2 %)	[1]
	73.51±0.21 (±0.3 %)	[2]	–976.1±3.35 (±0.3 %)	[2]
	73.14	This work	–991.90	This work
$Na_2B_4O_7$	189.49	[1]	–3277±8 (±0.2 %)	[1]
	189.60	This work	–3289±5 (±0.2 %)	[2]
			–3289.09	This work

Table 2 (end)

Borate	Average value $S°$, J·K^{-1}·mole^{-1}	References	Average value $\Delta_f H°$, kJ·mole^{-1}	References
$Na_2B_6O_{10}$	232.2±6.3 (±2.7 %)	[1]	–4580±9.2 (±0.2 %)	[1]
	232.91	This work	–4604±6.3 (±0.1 %)	[2]
			–4594.39	This work
$Na_2B_8O_{13}$	276±16.7 (±6.1 %)	[2]	–5912±7.95 (±0.1 %)	[2]
	276.22	This work	–5899.68	This work
K_2BO_2	79.98±0.12 (±0.2 %)	[1]	–995±8 (±0.8 %)	[1]
	80±0.25 (±0.3 %)	[2]	–982±8.4 (±0.9 %)	[2]
	80.18	This work	–1014.58	This work
$K_2B_4O_7$	208.4±6.3 (±3 %)	[1]	–3334.2	[1]
	203.68	This work	–3341±6.3 (±0.2 %)	[2]
			–3334.45	This work
$K_2B_6O_{10}$	251±13 (±5.2 %)	[2]	–4634±10.4 (±0.2 %)	[1]
	247	This work	–4654±6.3 (±0.1 %)	[2]
			–4639.75	This work
$K_2B_8O_{13}$	294±16.7 (±5.7 %)	[1]	–5945.1±5.9 (±0.1 %)	[1]
	290.30	This work	–5976.4±6.3 (±0.1 %)	[2]
			–5945.04	This work

The possibility of using the resulting dependence to calculate the $\Delta_f H°(\text{cr};\ T_C)$ value of unstudied borates is confirmed by the coefficients in equation (10): alkali metal oxides and diboron trioxide make comparable contributions to the value being calculated.

The $S°(\text{cr};\ T_C)$ values for the four components of the fundamental regression matrix in [1] are characterized by high reliability, since they have been obtained on the basis of the low-temperature calorimetry data. The compounds $K_2B_4O_7$ and $Li_2B_4O_7$ are the only exceptions: their standard entropy has been determined using the comparative methods. Borates, for which the estimated standard entropy values are available, have also been added to the regression matrix.

The relationship for matching and calculating the $S°(\text{cr};\ T_C)$ values of potassium, lithium, and sodium borates has been obtained according to the principles used to calculate $\Delta_f H°(\text{cr};\ T_C)$:

$$\begin{aligned} S°\left(x_{ij}\mathrm{Me_2O}\cdot x_{i1}\mathrm{B_2O_3};\ \text{cr};\ 298.15\ \text{K}\right) &= 43.311\cdot x\left(\mathrm{B_2O_3}\right)+60.682\cdot x\left(\mathrm{Li_2O}\right)+ \\ &+102.978\cdot x\left(\mathrm{Na_2O}\right)+117.058\cdot x\left(\mathrm{K_2O}\right)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mole}^{-1}. \end{aligned} \qquad (11)$$

The results of matching the $S°(\text{cr};\ T_C)$ values for the main and additional fundamental components are shown in Table 2.

Conclusions

The results of the research have allowed supplementing the thermodynamic database required for investigation of silicate and borate systems. The resulting entropy and enthalpy values can be used to optimize the technological processes of manufacturing glass, ceramics, and coatings. The proposed method for calculating thermodynamic properties of the experimentally unstudied compounds is performed using the regression analysis based on the classical Neumann–Kopp additive rule and allows creating an adequate physicochemical model that takes silicate and borate into account.

The following algorithm has been proposed for creating a matched system of thermodynamic properties of alkali metal borates and silicates. The first step involves matching of the known thermodynamic potentials by finding the "structure – property" correlations using the additive methods. Next, the matched thermodynamic data are determined for the compounds for which a required amount of the initial data is available. The results are used to find the correlations that allow performing interpolation and extrapolation needed for estimating the unknown thermodynamic properties of compounds. The regression equations have been obtained in order to calculate the standard entropy and standard enthalpy of formation of lithium, sodium, and potassium silicates and borates in crystalline form. The findings have been tested for the physicochemical model of the alkali silicate system in a broad temperature range [21] and have shown good results in comparing the calculated and the experimental data.

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МЕТОДЫ РАСЧЕТА И СОПОСТАВЛЕНИЯ ТЕРМОДИНАМИЧЕСКИХ СВОЙСТВ СОЕДИНЕНИЙ СИЛИКАТОВ И БОРАТОВ

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Разработаны новые методы обработки экспериментальных и расчетных термодинамических данных и улучшены уже существующие. Предлагаемые подходы позволяют разумно описать фазовые переходы, что позволяет сравнивать и корректировать термодинамические свойства, а также помогут рассчитать термодинамические параметры неизученных соединений. Предложены уравнения регрессии для расчета стандартной энтропии и энтальпии образования силикатов и боратов лития, натрия и калия. Полученные значения энтропии и энтальпии 14 силикатов щелочных металлов и 12 боратов щелочных металлов могут быть использованы для оптимизации технологических процессов изготовления стекла, керамики и покрытий.

Ключевые слова: силикаты, бораты, стандартные термодинамические функции.

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