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Heat capacity of alkali metal silicates

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It was established that at 298 K the molar heat capacity of alkali metal silicates $K_2O \cdot nSiO_2$, $Rb_2O \cdot nSiO_2$ and $Cs_2O \cdot nSiO_2$ changes linearly when changing n from 1 to 4. Based on the dependencies $C^\circ_{p,298} = f(n)$, the values of the heat capacities K_2O, Rb_2O and Cs_2O have been specified.

Keywords: heat capacity, oxides and silicates of alkali metals.

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1. Introduction

Alkali metal silicates are widely used in the production of glass and ceramics [1], photoceram glasses [2], as a chemically inert material for vials and ampoules containing medicines [3], dishes, etc. Despite the interest in such materials, the question of state diagrams of systems M_2O-SiO_2 (M = Li–Cs) [4–8] remains unsolved. If complete data are obtained for the system Li_2O-SiO_2, then for Cs_2O-SiO_2 there is not enough information. It has been established that in the systems Li_2O-SiO_2 and Na_2O-SiO_2 compounds of compositions 1 : 1 and 1 : 2 are formed, while in systems $K_2O(Rb_2O, Cs_2O)-SiO_2$ — 1 : 1, 1 : 2 and 1 : 4 [4–9].

For thermodynamic modeling of state diagrams of M_2O-SiO_2 systems, reliable information on the thermodynamic properties of all formed compounds is required. The available data are a bit different [9–15]. It is known that on the basis of data on the heat capacity $C_p = f(T)$, the temperature dependences of the thermodynamic properties of inorganic substances are determined [16], therefore, the accuracy of the calculation of enthalpy, entropy and Gibbs energy will depend on the accuracy of the obtained heat capacity values. In turn, the error in determining the heat capacity depends not only on the method of its measurement, but also on the reproducibility of the properties of the material under study [16]. In view of the above, it seemed necessary to clarify the data on the heat capacity of alkali metal oxides M_2O, to establish the influence of the composition of the compounds formed in the systems K_2O-SiO_2, Rb_2O-SiO_2, Cs_2O-SiO_2 on their heat capacity, compare the experimental values of $C^\circ_{p,298}$ of these compounds with the values calculated using different model concepts.

2. Results and discussion

Since Li_2O and Na_2O form 1 : 1 and 1 : 2 compounds with SiO_2, and the other alkali metal oxides 1 : 1, 1 : 2 and 1 : 4, then we represent the latter, following the authors [17,18], as $M_2O \cdot nSiO_2$, where n — is the number of moles of the second component. Like [17], we will not take into account changes in the structure when the composition changes in these systems.

The figure in the coordinates $C^\circ_{p,298} = f(n)$ shows the influence of the content of the second component on the molar heat capacity of the oxide compounds formed in the systems K_2O-SiO_2, Rb_2O-SiO_2 and Cs_2O-SiO_2. The results obtained can be described by the linear equation

$$C^\circ_{p,298} = a + bn, \tag{1}$$

which has the following form for the analyzed systems($J \cdot K^{-1} \cdot mol^{-1}$):

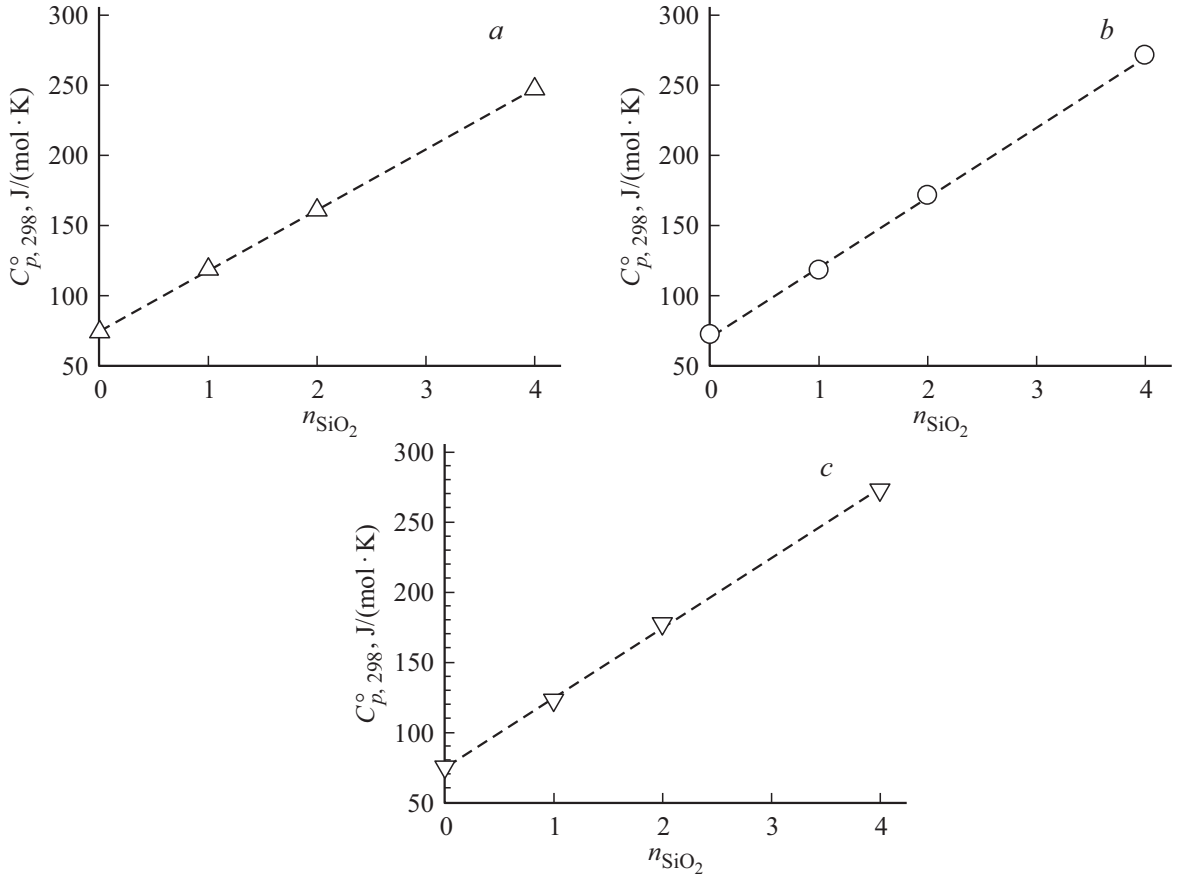
$$C^\circ_{p,298}(K_2O-SiO_2) = (74.63 \pm 0.60) + (43.13 \pm 0.26)n_{SiO_2}, \tag{2}$$

$$C^\circ_{p,298}(Rb_2O-SiO_2) = (69.98 \pm 1.76) + (50.10 \pm 0.77)n_{SiO_2}, \tag{3}$$

$$C^\circ_{p,298}(Cs_2O-SiO_2) = (74.66 \pm 1.91) + (49.74 \pm 0.83)n_{SiO_2}, \tag{4}$$

The correlation factors for equations (2–4) are 0.9999, 0.9998 and 0.9997, respectively. When constructing the graphs shown in the figure, the values of the heat capacity of alkali metal silicates taken from the review paper [10] were used. It follows from the equations (2–4) that at $n = 0$ the molar heat capacity values should correspond to alkali metal oxides. In our case they are equal for K_2O, Rb_2O and Cs_2O, respectively, 74.63 ± 0.60, 69.98 ± 1.76 and 74.66 ± 1.91 $J \cdot K^{-1} \cdot mol^{-1}$.

Comparing these values with the data of other authors presented in Table 1 shows that for K_2O the best agreement is observed with the results of works [12,20], for Rb_2O — [13], and for Cs_2O — [10,12]. It can be assumed that the accuracy of determining the heat capacity of alkali metal oxides by this method will be determined by the data for the corresponding alkali metal silicates.



Influence of SiO_2 content on the molar heat capacity of oxide compounds formed in K_2O-SiO_2 (*a*) systems, Rb_2O-SiO_2 (*b*) and Cs_2O-SiO_2 (*c*).

Table 1. Heat capacity of alkali metal oxides ($J \cdot K^{-1} \cdot mol^{-1}$) according to different authors

Li_2O	Na_2O	K_2O	Rb_2O	Cs_2O
57.17 [9]	72.42 [9]	84.64 [9]	78.70 [10]	75.90 [10]
54.25 [10]	68.56 [10]	84.53 [10]	74.0 [12]	76.0 [12]
54.1 [11]	72.95 [11]	83.7 [11]	71.72 [13]	
54.1 [12]	69.1 [12]	74.0 [12]	74.0 [20]	
54.26 [13]	72.43 [13]	72 [20]		
54.13 [14]	71.69 [14]			
54.25 [19]	69.1 [19]			
54.1 [20]	72.2 [19]			
	69.1 [20]			

Calculation of heat capacity of alkali metal silicates Li_2O (Na_2O, K_2O, Rb_2O, Cs_2O) $\cdot n SiO_2$ at 298 K was carried out according to various model representations: by the additive method of Neumann–Kopp (NK) [10,16], Kumok incremental method (KIM) [21], method of group contributions (GC) [22] and regression analysis method (RA) [15]. The results obtained are given in Table 2 (data on the heat capacity of the initial oxides for calculation by the NDT method are taken from [10]). It follows from it that the best agreement with the experimental data [10] is in the $C^{\circ}_{p,298}$ values calculated by the regression analysis method. Unfortunately, this method failed to determine the heat capacities of rubidium and cesium silicates, because the original values for Rb_2O and Cs_2O are not given in the work [15].

Taking into account the complexity of obtaining samples of alkali metal oxides for measuring the heat capacity, we calculated $C^{\circ}_{p,298}$ for them using the KIM, GC, Kellogg (Kel) [14,23] methods using melting point values T_m [13] according to the relation [19]:

$$C^{\circ}_{p,298} = Km/T_m^{1/4}, \tag{5}$$

where m — is the number of atoms in a molecule of a crystalline substance, $K = 138$. In addition, the calculation was also performed by the method of L.I. Ivanova [24] using the semi-empirical formula

$$C^{\circ}_{p,298} = m(22.14 + 8.32T/T_m). \tag{6}$$

The results obtained are shown in Table 3. It can be noted that the best agreement with the available data (Table 1) is given by the Kumok incremental method, group contributions, as well as the calculation using equation (5).

Table 2. Calculated values of heat capacity $C^{\circ}_{p,298}$ of alkali metal silicates according to different model representations ($J \cdot K^{-1} \cdot mol^{-1}$)

Compound	[10]	NK	KIM	GC	MRA
Li_2SiO_3	100.00	98.67 (−1.33)	103.60 (3.6)	102.52 (2.52)	98.02 (−1.98)
$Li_2Si_2O_5$	138.77	143.09 (3.11)	149.10 (3.11)	146.33 (5.45)	141.58 (2.03)
Na_2SiO_3	111.81	112.98 (0.98)	115.80 (3.57)	116.34 (4.06)	112.02 (0.19)
$Na_2Si_2O_5$	156.50	157.40 (0.58)	161.30 3.39)	158.25 (1.12)	155.58 (−0.59)
K_2SiO_3	118.70	128.95 (8.61)	118.20 (−0.42)	122.25 (2.99)	120.07 (1.15)
$K_2Si_2O_5$	160.95	173.37 (7.72)	163.70 (1.87)	167.14 (3.85)	163.63 (1.66)
$K_2Si_4O_9$	247.20	262.21 (6.07)	254.70 (3.03)	254.68 (3.03)	250.76 (1.44)
Rb_2SiO_3	117.45	123.12 (4.83)	123.80 (5.41)	122.56 (4.35)	–
$Rb_2Si_2O_5$	170.72	167.54 (−1.86)	169.30 (−0.83)	167.49 (−1.89)	–
$Rb_2Si_4O_9$	270.89	256.38 (−5.36)	260.89 (−3.69)	255.30 (−5.55)	–
Cs_2SiO_3	122.23	120.30 (−1.58)	124.40 (1.77)	121.85 (−0.31)	–
$Cs_2Si_2O_5$	176.73	164.74 (−6.98)	169.90 (−3.86)	166.56 (−5.75)	–
$Cs_2Si_4O_9$	272.86	253.58 (−7.06)	260.90 (−4.38)	254.81 (−6, 61)	–

Note. In parentheses — deviation of the calculated data from the experimental data obtained in the work [10], %.

Table 3. Calculation of $C^{\circ}_{p,298}$ for alkali metal oxides using various model representations ($J \cdot K^{-1} \cdot mol^{-1}$)

Oxide	KIM	GC	Kel	Equation (5)	Equation (6)
Li_2O	58.1	57.90	57.73	61.90	70.14
Na_2O	70.3	69.68	70.29	70.44	72.65
K_2O	72.7	78.10	70.29	73.99	74.01
Rb_2O	78.3	78.64	71.13	75.59	74.68
Cs_2O	78.9	7830	71.13	78.72	76.19

3. Conclusion

It has been established that the values of $C^{\circ}_{p,298}$ of alkali metal silicates $K(Rb,Cs)_2O \cdot nSiO_2$ vary linearly depending on the content of the second component. Based on the dependences $C^{\circ}_{p,298} = f(n)$, the heat capacities of alkali metal oxides $K(Rb, Cs)_2O$ have been specified. As per various model concepts, the heat capacities of silicates and oxides of alkali metals at 298 K are calculated.

Conflict of interest

The authors declare that they have no conflict of interest.

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