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Heat capacity of oxide compounds formed in the $Na_2O-TiO_2(WO_3)$, $K_2O-B_2O_3(WO_3)$ and $Cs_2O-TeO_2(UO_3)$ systems

© L.T. Denisova, N.V. Belousova, V.M. Denisov, N.A. Galiakhmetova

Siberian State University,
Krasnoyarsk, Russia

E-mail: ldenisova@sfu-kras.ru

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The dependence of the standard heat capacity of oxide compounds $M_2O \cdot nTiO_2$ (WO_3, B_2O_3, TeO_2, UO_3), where M = Na, K, Cs, on the concentration of the second component is shown to be linear. Relying on the obtained results, the available information on the heat capacities of complex compounds based on alkali metal oxides was clarified. The standard heat capacities of the analyzed oxide compounds were calculated using empirical equations.

Keywords: complex oxide compounds, standard heat capacity.

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1. Introduction

Thermodynamic modeling of phase equilibria requires reliable data on the thermodynamic properties of the initial components and the resulting compounds. According to [1,2], the revision of thermodynamic information and the accumulation of new information cannot be solved relying only on experimental results. According to the authors of these publications, an alternative source of new information can be the development of calculation methods. For example, the method of regression analysis [3,4] gives good results. To obtain such data, various correlations established by Karapetyants [5,6] are also used. A similar correlation has been established between the standard heat capacity of alkali metal silicates $K_2O \cdot nSiO_2$, $Rb_2O \cdot nSiO_2$, and $Cs_2O \cdot nSiO_2$ and the value of n [4]. It should be noted that the error in measuring heat capacity depends not only on the method of its determination, but also on the reproducibility of the composition and properties of the material being measured [7]. Taking this into account, it seemed necessary to establish the effect of the composition of oxide compounds formed in the Na_2O-TiO_2, Na_2O-WO_3, $K_2O-B_2O_3$, K_2O-WO_3, Cs_2O-TeO_2, Cs_2O-UO_3 systems on their heat capacity, compare their experimental values with those calculated using various model concepts.

2. Results and discussion

As in [4,8,9], we represent the compounds in the form of $M_2O \cdot nTiO_2$ (WO_3, B_2O_3, TeO_2, UO_3), where M = Na, K, Cs. And changes in the structure with changing composition of these systems, similar to [8], will not be taken into account.

Figures 1–3 show the effect of the concentration of the second component on the molar heat capacity of compounds formed in the systems of Na_2O-WO_3 and Na_2O-TiO_2 (Figure 1), $K_2O-B_2O_3$ and K_2O-WO_3 (Figure 2), Cs_2O-TeO_2 and Cs_2O-UO_3 (Figure 3).

It can be seen that in all cases linear dependencies of $C^o_{p,298} = f(n)$ are observed. The obtained data for the systems being analyzed can be described by the following equations ($J\,mol^{-1}K^{-1}$):

$$C^o_{p,298}(Na_2O-TiO_2) = (77.49 \pm 5.92) + (54.31 \pm 1.87) \cdot n_{TiO_2}, \quad (1)$$

$$C^o_{p,298}(Na_2O-WO_3) = (72.10 \pm 0.73) + (70.63 \pm 0.32) \cdot n_{WO_3}, \quad (2)$$

$$C^o_{p,298}(K_2O-B_2O_3) = (75.00 \pm 18.50) + (59.92 \pm 6.87) \cdot n_{B_2O_3}, \quad (3)$$

$$C^o_{p,298}(K_2O-WO_3) = (84.03 \pm 0.74) + (68.08 \pm 0.30) \cdot n_{WO_3}, \quad (4)$$

$$C^o_{p,298}(Cs_2O-TeO_2) = (74.12 \pm 1.93) + (60.66 \pm 0.84) \cdot n_{TeO_2}, \quad (5)$$

$$C^o_{p,298}(Cs_2O-WO_3) = (75.71 \pm 0.64) + (77.61 \pm 0.50) \cdot n_{WO_3}. \quad (6)$$

The correlation coefficients of equations (1)–(6) are, respectively: 0.9982, 0.9999, 0.9871, 0.9999, 0.9999, and 0.9998. The necessary data on the molar heat capacity of complex oxides for plotting the graphs shown in Figures 1–3 were taken from [10], and the data for alkali metal oxides were taken from [4,10,11]. To compare the values of $C^o_{p,298}$ for complex oxides, calculations were carried out using various model representations: the additive Neumann-Kopp method (NK) [10,12], the Kumok incremental

Table 1. Calculated heat capacities $C^o_{p,298}$ of oxide compounds based on alkali metals according to various model representations J mol^{-1}K^{-1}

Compound	[10]	NK	KIM	Kel	GC
Na_2TiO_3	126.77	123.66 (−2.45)	129.20 (1.92)	128.87 (1.63)	127.10 (0.26)
$Na_2Ti_2O_5$	193.13	178.76 (−7.44)	188.11 (−2.60)	187.45 (−2.94)	186.11 (−3.64)
$Na_2Ti_3O_7$	249.66	233.86 (−6.33)	247.02 (−1.07)	246.00 (−1.47)	244.21 (−2.19)
$Na_2Ti_6O_{13}$	397.23	399.16 (0.49)	423.69 (6.66)	421.77 (6.17)	418.56 (5.37)
Na_2WO_4	141.77	141.36 (−0.29)	–	149.39 (5.37)	146.84 (3.57)
$Na_2W_2O_7$	2154.2	214.16 (−0.03)	–	–	224.37 (4.74)
$Na_2W_4O_{13}$	354.45	359.76 (1.50)	–	–	378.86 (6.88)
$K_2B_4O_7$	170.30	210.49 (23.60)	197.30 (15.85)	186.16 (9.31)	195.34 (14.70)
$K_2B_6O_{10}$	265.34	273.47 (3.07)	259.60 (−2.16)	–	252.94 (−4.67)
$K_2B_8O_{13}$	319.06	336.45 (5.45)	321.90 (0.89)	–	315.05 (−1.26)
K_2WO_4	150.81	157.33 (4.32)	–	149.39 (−0.94)	154.99 (2.78)
$K_2W_2O_7$	221.00	230.13 (4.13)	–	–	232.54 (5.22)
$K_2W_2O_{10}$	288.10	302.93 (5.15)	–	–	310.38 (7.73)
$K_2W_4O_{13}$	356.40	375.73 (5.42)	–	–	386.80 (8.53)
Cs_2TeO_3	133.87	139.78 (4.42)	–	135.15 (0.96)	148.48 (10.92)
$Cs_2Te_2O_5$	193.00	203.66 (5.52)	–	199.17 (3.20)	218.78 (13.36)
$Cs_2Te_4O_9$	318.20	331.42 (4.16)	–	327.21 (2.83)	318.45 (0.08)
Cs_2UO_4	152.75	157.09 (2.84)	163.20 (6.84)	153.14 (0.26)	164.31 (7.57)
$Cs_2U_2O_7$	231.23	238.28 (3.05)	247.50 (7.03)	235.17 (1.70)	300.43 (29.93)

Note. In brackets — deviation of the calculated data from the experimental values given in [10], %. Omissions — lack of initial data for calculations.

Table 2. Calculated values of $C^o_{p,298}$ = for $K_2B_2O_4$ and $K_2B_4O_7$

Compound	[19]	NK	KIM	Kel	GC
$K_2B_2O_4$	134.0	147.51 (10.08)	135.0 (0.75)	–	136.69 (2.01)
$K_2B_4O_7$	189.8	210.49 (10.90)	197.3 (3.77)	186.16 (−1.92)	195.34 (2.79)

method (KIM) [13], the Kellogg model (Kel) [14,15], group contributions (GC) [16]. These results are presented in Table 1.

It follows from this table that the largest deviation from the experimental values of the heat capacity for all models

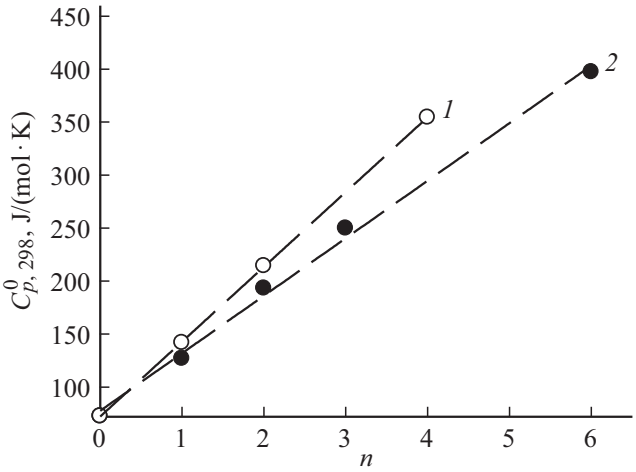

Figure 1. The effect of concentration of the second component on the molar heat capacity of Na_2O-WO_3 (*1*) and Na_2O-TiO_2 compounds (*2*).

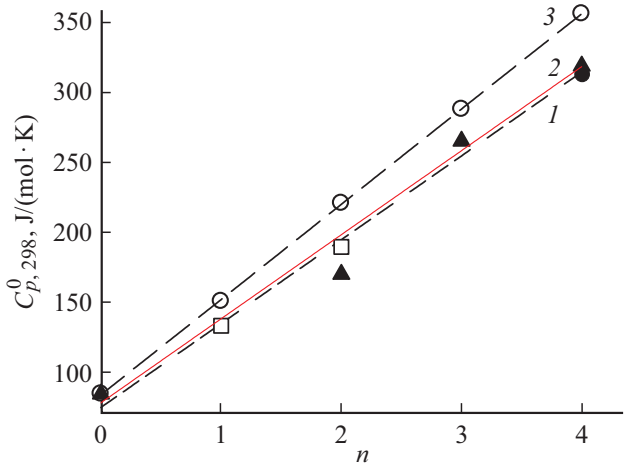

Figure 2. The effect of concentration of the second component on the molar heat capacity of the compounds of the resulting oxide compounds in $K_2O-B_2O_3$ (*1, 2*) and K_2O-WO_3 (*3*) systems, square symbols — data of [19].

is observed for the $K_2B_4O_7$ compound. In addition, for the $K_2O-B_2O_3$ system the correlation coefficient has the smallest value (equation (3)). It can be seen from Figure 2

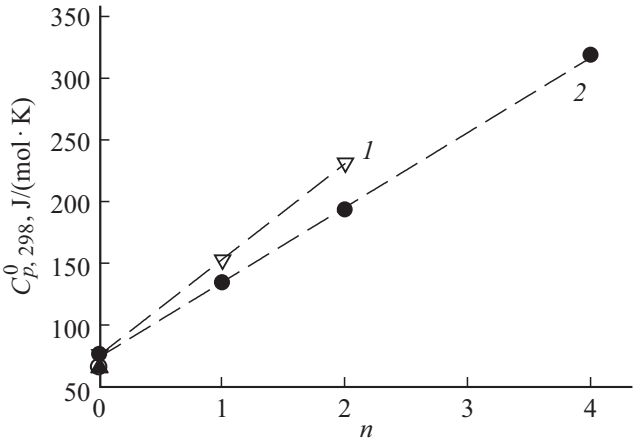

Figure 3. The effect of concentration of the second component on the molar heat capacity of Cs_2O-UO_3 (*1*) and Cs_2O-TeO_2(*2*) compounds.

that precisely for the $K_2B_4O_7$ compound the value of $C^o_{p,298}$ does not fit well on a straight line. It can be assumed that underestimated heat capacity values were obtained for this compound. It is possible that this may be due to the composition of the prepared sample. According to the data of [17,18], properties of B_2O_3 strongly depend on the annealing mode and the degree of dehydration. Therefore, in a number of studies, such borates are calcined for a period from 5 to 13 days [19].

Taking into account the data for heat capacity of $K_2B_2O_4$ and $K_2B_4O_7$ [19] (Figure 2) equation (3) takes the following form:

$$C^o_{p,298}(K_2O-B_2O_3) = (78.32 \pm 6.09) + (60.07 \pm 2.49) \cdot n_{B_2O_3}. \quad (7)$$

The correlation coefficient for equation (7) is 0.9974. Using these results, the heat capacity of these compounds was calculated by the methods described above. The data obtained are shown in Table 2.

It follows from this table that in this case there is better agreement with the available data. Based on this, a conclusion can be made that the established correlation of $C^o_{p,298} = f(n)$ makes it possible to clarify the existing data on the heat capacity of complex oxide compounds.

It is worth to note that similar dependencies of $C^o_{p,298} = f(n)$ were also established for the systems of $SrO-Bi_2O_3$, $V_2O_5-Bi_2O_3$, and $PbO-Fe_2O_3$ [20].

3. Conclusion

It has been established that the values of the standard heat capacity $C^o_{p,298} = f(n)$ for $Na_2O \cdot nTiO_2$, $Na_2O \cdot nWO_3$, $K_2O \cdot B_2O_3$, $K_2O \cdot nWO_3$, $Cs_2O \cdot nTeO_2$, and $Cs_2O \cdot nUO_3$ oxide compounds vary linearly depending on the concentration of the second component. The obtained dependences of $C^o_{p,298} = f(n)$ were used to refine the available data on the heat capacities of complex compounds based on alkali metal oxides. Using empirical equations, standard heat capacities were calculated for the oxide compounds being analyzed.

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Conflict of interest

The authors declare that they have no conflict of interest.

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