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Barium Aluminates and the Study of Their Basic Thermodynamic Data

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Abstract. The article presents the results of studies of thermodynamically stable barium aluminates. A database of thermodynamic data has been created: enthalpies, entropies and coefficients of the heat capacity equation, necessary for the study of multicomponent systems, including barium aluminates. Since the basis of modern materials science is multicomponent systems, on their basis it is possible to create various combinations of phases in structural materials with a set of specified properties. Thus, modern thermodynamics is not a frozen science. It is known that the objects of research are expanding, where thermodynamic methods can be applied to study the area of high and low temperatures, the area of very low and high pressures. And new discoveries give birth to new areas of application of thermodynamics: thermodynamics of thermonuclear reactions, plasma thermodynamics, relativistic thermodynamics, thermodynamics of negative absolute temperatures, etc. And, finally, the methods of thermodynamic research themselves do not remain unchanged: the exergy method, the methods of thermodynamics of irreversible processes, etc. At present, the thermodynamic method of research is widely used in various fields of physics, chemistry, biology, and many other sciences and branches of technology. Being one of the most extensive areas of modern natural science, thermodynamics plays an important role in the system of knowledge necessary for an engineer of any specialty in his practical activities. Chemical thermodynamics, on the other hand, paid the greatest attention to the study of phase transitions and the properties of solutions, and in relation to chemical reactions it was limited mainly to determining their thermal effects. To some extent, this is due to the fact that it was these areas of chemical thermodynamics that were the first to satisfy the needs of production. The practical use of known methods of thermodynamics of chemical reactions for solving major industrial problems for a long time lagged behind its capabilities.

Keywords: thermodynamic data, barium-containing compounds, barium aluminates, standard heats of formation.

INTRODUCTION

Solving the problems of increasing the durability of various materials for the construction of nuclear installations and research reactors, as well as reducing labor costs for their construction and repair, is provided by refractory and heat-resistant cements and concretes based on them, which have high thermomechanical properties.

The study of solid-phase processes occurring in raw mixtures with temperature changes makes it possible to judge the fundamental possibility and the predominant probability of reactions occurring, in addition, they make it possible to substantiate the main technological parameters of the targeted synthesis of materials with desired properties. For purposeful synthesis of barium-containing binders of a new class with desired properties, evaluation of solid-phase reactions occurring in oxide systems, including barium oxide, as well as for theoretical studies in multicomponent systems, it is advisable to carry out thermodynamic analysis.

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RECENT RESEARCH, RESEARCH AND PUBLICATION RESULTS

Due to the fact that there are no thermodynamic data for many barium-containing compounds in the reference literature, the initial thermodynamic constants for barium aluminates were calculated.

The initial thermodynamic constants for a number of binary compounds of barium aluminates have not been found in the literature: $Ba_4Al_2O_7$; $Ba_5Al_2O_8$; $Ba_7Al_2O_{10}$; $Ba_8Al_2O_{11}$; $Ba_{10}Al_2O_{13}$, as well as the equations of dependence of the heat capacity of these substances on temperature $C_p = f(T)$.

MATERIALS AND METHODS OF STUDY

In this regard, the initial thermodynamic quantities were calculated using known methods. The standard heats of formation ΔH^0_{298} of barium aluminates were determined using the methods described in [1, 2]. The calculation results are presented in Table 1.

TABLE 1. Thermodynamic constants of barium aluminates

Chemical compound	$-\Delta H^o_{298}$, kJ/mol	Source	$-\Delta G^o_{298}$, kJ/mol	Source	S^o_{298}, kJ/mol ·K	Source
BaO	558,15	3	528,44	3	70,29	3
α - $BaCO_3$	1218,80	3	1138,89	3	112,13	3
β – $BaCO_3$	-		-		-	
γ - $BaCO_3$	-		-		-	
CO_2	393,51	3	394,38	3	213,94	3
γ - Al_2O_3	1637,20	3	1541,39	3	52,51	3
α - Al_2O_3	1675,61	3	1582,33	3	50,92	3
$BaAl_2O_4$	2334,17	3	2190,25	4	123,43	4
$Ba_3Al_2O_6$	3537,91	3	3309,36	4	267,78	4
$BaAl_{12}O_{19}$	10740,33	4	10151,81	4	376,56	4
$Ba_4Al_2O_7$	4014,49	5	-		329,99	5
$Ba_5Al_2O_8$	4569,03	5	-		427,82	5
$Ba_7Al_2O_{10}$	5682,5	5	-		567,66	5
$Ba_8Al_2O_{11}$	6238,10	5	-		611,68	5
$Ba_{10}Al_2O_{13}$	7350,52	5	-		778,85	5

The equations for the dependence of heat capacity on temperature CP = f(T) of the substances under consideration were determined using the method of N.A. Landia [6]. This method is based on the relationship between the heat capacities of solids and entropies. In accordance with this method, the equations for the dependence of heat capacity on temperature CP = f(T) of the substances under consideration were determined.

RESEARCH RESULTS

The heat capacities of barium silicates were calculated as for complex oxygen compounds consisting of solid oxides without polymorphic transformations.

For barium aluminates, the equation for the dependence of heat capacity on temperature CP = f(T) has the form [7 – 9]:

for $Ba_4Al_2O_7$ $Cp = 275,85 + 0,56894T - 2332814,3T^{-2}$ (298 – 1673 K);
for $Ba_5Al_2O_8$ $Cp = 298,73 + 0.1239T$ (298 – 1213 K);
for $Ba_7Al_2O_{10}$ $Cp = 374,18 + 0.1649T$ (298 – 1323 K)
for $Ba_8Al_2O_{11}$ $Cp = 441,99 + 0.096232T$ (298 – 1673 K);
for $Ba_{10}Al_2O_{13}$ $Cp = 441,99 + 0.096232T$ (298 – 1403 K).

The results of calculations of the constants of the heat capacity equations for barium aluminates are given in Table 2.

TABLE 2. Heat capacity equation constants for barium aluminates

Chemical compound	$C_p = a + в \cdot T + c \cdot T^{-2}$, J/mol ·K			Source	Temperature range, K	Source
	a	в ·10^{3}	- с 10^{-5}			
BaO	53,30	4,35	8,3	3	298-1270	3
α - $BaCO_3$	86,96	48,99	11,97	3	До 1079	3
β – $BaCO_3$	154,91	-	-	3	1079-1241	3
γ - $BaCO_3$	163,29	-	-	3	выше 1241	3
CO_2	44,14	9,04	8,54	3	298-2500	3
γ -Al_2O_3	68,49	46,44	-	3	-	
α - Al_2O_3	114,77	12,08	35,44	3	298-1800	3
$BaAl_2O_4$	148,32	35,44	29,25	13	298-2103	13
$Ba_3Al_2O_6$	247,86	48,53	17,41	13	298-2023	13
$BaAl_{12}O_{19}$	738,22	70,5	221,75	13	298-2171	13
$Ba_4Al_2O_7$	275,85	56,89	23,33	5	298-1673	5
$Ba_5Al_2O_8$	298,73	123,87	15,51	5	298-1213	5
$Ba_7Al_2O_{10}$	374,18	164,90	14,03	5	298-1323	5
$Ba_8Al_2O_{11}$	441,99	96,23	25,31	5	298-1673	5
$Ba_{10}Al_2O_{13}$	487,25	226,40	12,24	5	298-1403	5

A graphical interpretation of the dependence of heat capacity on temperature is shown in FIGURE 1. As can be seen from the presented results, the greatest bending of the curves for barium aluminates is observed in the temperature range of 200–600 K. At temperatures above 600 K, the dependence Cp = f(T) is practically linear.

Thus, as a result of the calculations performed, the initial thermodynamic data for barium aluminates were obtained, which are not available in the reference literature. However, all thermodynamic constants obtained in this work by calculation are taken as a first approximation. To obtain more accurate values of thermodynamic constants, it is necessary to carry out calorimetric measurements.

The thermodynamics of solid-phase reactions in the $BaO - Al_2O_3$ system was studied in [7, 8], which presented a thermodynamic estimate of the formation of only three barium aluminates: $BaAl_2O_4$, $Ba_3Al_2O_6$, $BaAl_{12}O_{19}$. Barium aluminates discovered by R. Appendino [10-12] were not considered. In this regard, thermodynamic calculations of solid-phase reactions in this system were performed by calculating the change in the Gibbs free energy with temperature.

The study of solid-phase processes occurring in raw mixtures with a change in temperature makes it possible to judge the direction of the reactions and the preference for the formation of certain phases. Using the thermodynamic method of analysis, studies of solid-phase reactions in the $BaO - Al_2O_3$ system were carried out by calculating the change in the Gibbs free energy from temperature $\Delta G = f(T)$, in accordance with the formulas given in [3]:

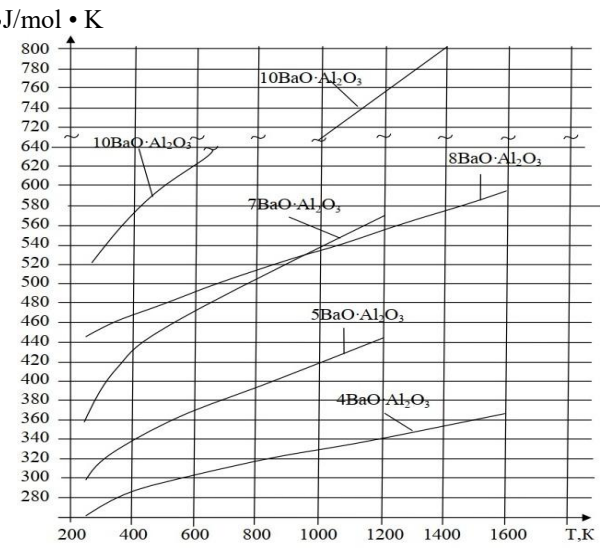

FIGURE 1. Plot of heat capacity of barium aluminates versus temperature.

$$\Delta G(T) = \Delta H^0 - \Delta a \cdot T \cdot lnT - 1/2 \cdot \Delta b \cdot T^2 - 1/2 \cdot c \cdot T^{-1} + y \cdot T, \quad (1)$$

where

$$\Delta H^0 = \Delta H^0 298 - \Delta a \cdot 298 - 1/2 \cdot \Delta b \cdot 298^2 + \Delta c\ (298)^{-1} \quad (2)$$

and y is determined from the formula:

$$\Delta G^0 298 = \Delta H^0 - \Delta a \cdot 298 \cdot ln298 - 1/2 \cdot \Delta b \cdot 298^2 - 1/2 \Delta c (298)^{-1}. \quad (3)$$

The initial data for calculating the Gibbs energy of the following reactions of the formation of barium aluminates are given in Table. 1 and Table. 2.

The coefficients of the equations for the dependence of the change in Gibbs free energy on temperature were calculated for the following reactions:

1. $4BaCO_3 + Al_2O_3 = Ba_4Al_2O_7 + 4CO_2$
2. $5BaCO_3 + Al_2O_3 = Ba_5Al_2O_8 + 5CO_2$
3. $7BaCO_3 + Al_2O_3 = Ba_7Al_2O_{10} + 7CO_2$
4. $8BaCO_3 + Al_2O_3 = Ba_8Al_2O_{11} + 8CO_2$
5. $10BaCO_3 + Al_2O_3 = Ba_{10}Al_2O_{13} + 10CO_2$

The calculations were made taking into account the Al_2O_3 polymorphism at a temperature close to 1500 K and $BaCO_3$ at 1079 and 1241 K.

As a result of the calculations, the equations for the dependence of the Gibbs free energy on temperature Δ G=f(T) were obtained and their graphical dependence presented in FIGURE 2 and FIGURE 3.

The Gibbs energy versus temperature equations for these reactions are:

for reaction: $4BaCO_3 + Al_2O_3 = Ba_4Al_2O_7 + 4CO_2$

in the temperature range 400 – 1079 K

$$\Delta G(T) = 926100{,}85 - 29{,}93T \cdot lnT + 0{,}073T^2 - 689312/T - 532{,}67T$$

in the temperature range 1079 – 1241 K

$$\Delta G(T) = 1045160{,}75 + 241{,}69T \cdot lnT - 0{,}025T^2 + 1703936{,}00/T - 2499615T$$

in the temperature range 1241 – 1500 K

$$\Delta G(T) = 1074984631 + 275{,}16T \cdot lnT - 0{,}025T^2 - 1703936/T - 2770{,}27T$$

in the temperature range of 1500 K and above

$$\Delta G(T) = 1137584{,}68 + 321{,}44T \cdot lnT - 0{,}042T^2 - 68064/T - 3096{,}73T$$

ΔG, kJ/mol

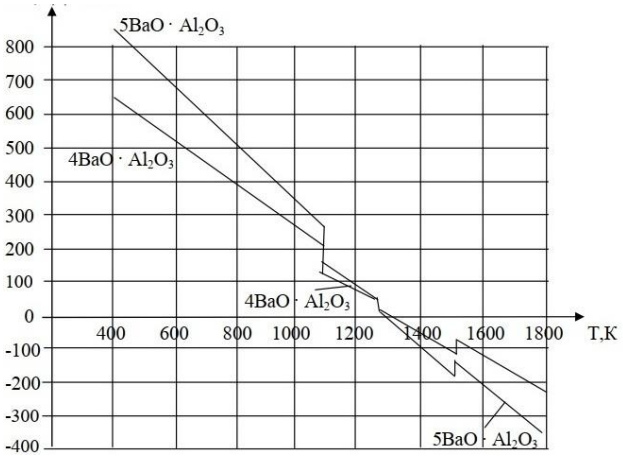

FIGURE 2. Graphical dependence ΔG (T) for barium aluminates

for reaction: $5BaCO_3 + Al_2O_3 = Ba_5Al_2O_8 + 5CO_2$

in the temperature range 400 – 1079 K

$$\Delta G(T) = 1195775{,}61-16{,}46T\cdot\ln T+0{,}061T^2-86140/T-816{,}93T$$

in the temperature range 1079 – 1241 K

$$\Delta G(T) = 1344600{,}49+323{,}07T\cdot\ln T-0{,}061T^2+2905420/T-3275{,}03T$$

in the temperature range 1241 – 1500 K

$$\Delta G(T) = 1381879{,}93+364{,}9T\cdot\ln T-0{,}061T^2\ 2905420/T-3613{,}93T$$

in the temperature range 1500 K and above

$$\Delta G(T) = 1444480{,}31+411{,}19T\cdot\ln T-0{,}078T^2+1133420/T-3940{,}39T$$

for reaction: $7BaCO_3 + Al_2O_3 = Ba_7Al_2O_{10} + 7CO_2$

in the temperature range 400 – 1079 K

$$\Delta G(T) = 1740440{,}29-6{,}4T\cdot\ln T+0{,}08T^2-504796/T-1247{,}71T$$

in the temperature range 1079 – 1241 K

$$\Delta G(T) = 1948795{,}13+468{,}95T\cdot\ln T-0{,}091T^2+3683388/T-4689{,}05T$$

in the temperature range 1241 – 1500 K

$$\Delta G(T) = 2000986{,}34+527{,}52T\cdot\ln T-0{,}091T^2+3683388/T-5163{,}52T$$

in the temperature range 1500 K and above

$$\Delta G(T) = 2063586{,}72+573{,}8T\cdot\ln T-0{,}108T^2+1911388/T-5489{,}98T$$

for reaction: $7BaCO_3 + Al_2O_3 = Ba_7Al_2O_{10} + 7CO_2$

in the temperature range 400 – 1079 K

$$\Delta G(T) = 1740440{,}29-6{,}4T\cdot\ln T+0{,}08T^2-504796/T-1247{,}71T$$

in the temperature range 1079 – 1241 K

$$\Delta G(T) = 1948795{,}13+468{,}95T\cdot\ln T-0{,}091T^2+3683388/T-4689{,}05T$$

in the temperature range 1241 – 1500 K

$$\Delta G(T) = 2000986{,}34+527{,}52T\cdot \ln T-0{,}091T^{2}+3683388/T-5163{,}52T$$

in the temperature range 1500 K and above

$$\Delta G(T) = 2063586{,}72+573{,}8T\cdot \ln T-0{,}108T^{2}+1911388/T-5489{,}98T$$

for reaction: $8BaCO_3 + Al_2O_3 = Ba_8Al_2O_{11} + 8CO_2$

in the temperature range 400 – 1079 K

$$\Delta G(T) = 2015105{,}85-25{,}1T\cdot \ln T+0{,}133T^{2}-1378624/T-1298{,}57T$$

in the temperature range 1079 – 1241 K

$$\Delta G(T) = 2253225{,}39+518{,}15T\cdot \ln T-0{,}063T^{2}+3407872/T-5231{,}53T$$

in the temperature range 1241 – 1500 K

$$\Delta G(T) = 2312872{,}49+585{,}10T\cdot \ln T-0{,}063T^{2}+3407872/T-5773{,}78T$$

in the temperature range 1500 K and above

$$\Delta G(T) = 2375472{,}87+631{,}38T\cdot \ln T-0{,}08T^{2}+1635872/T-6100{,}23T$$

for reaction: $10BaCO_3 + Al_2O_3 = Ba_{10}Al_2O_{13} + 10CO_2$

in the temperature range 400 – 1079 K

$$\Delta G(T) = 2559511{,}31+8{,}80T\cdot \ln T+0{,}11T^{2}-1111280/T-1895{,}8T$$

in the temperature range 1079 – 1241 K

$$\Delta G(T) = 2857161{,}07+687{,}87T\cdot \ln T-0{,}135T^{2}+4871840/T-6812{,}0T$$

in the temperature range 1241 – 1500 K

$$\Delta G(T) = 2931719{,}95+771{,}55T\cdot \ln T-0{,}135T^{2}+4871840/T-7489{,}8T$$

in the temperature range 1500 K and above

$$\Delta G(T) = 2994320{,}32+817{,}83T\cdot \ln T-0{,}152T^{2}+3099840/T-7816{,}26T.$$

ΔG, kJ/mol

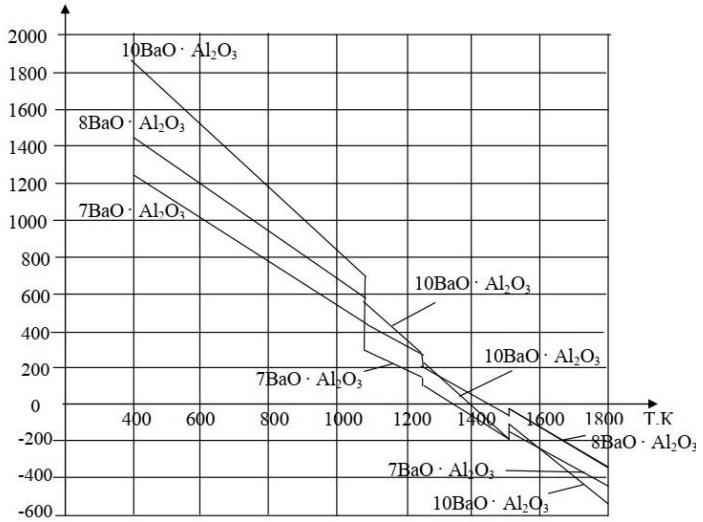

FIGURE 3. Graphical dependence ΔG (T) for barium aluminates

CONCLUSIONS

As a result of the thermodynamic analysis, it was found that among the barium aluminates considered by us, the formation of compounds is most preferable and thermodynamically probable $Ba_4Al_2O_7$ и $Ba_5Al_2O_8$, their synthesis is theoretically possible at a temperature of about 1300 K. The synthesis of the $Ba_7Al_2O_{10}$, $Ba_8Al_2O_{11}$ and $Ba_{10}Al_2O_{13}$, phases, as calculations show, is possible at temperatures of 1350–1450 K.

Thus, the calculations performed made it possible to determine the initial thermodynamic constants for barium aluminates, which are not available in the reference literature.

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