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CHEMISTRY

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Abstract

Full Text

CHEMISTRY

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ON THE THERMODYNAMICS OF THE CHANGE OF KAOLINITE UPON HEATING

Despite the undoubted validity of the proposition that, like all chemical processes, the change of kaolinite upon heating ^(1,2) must be governed by thermodynamic and kinetic regularities, up to now the predominant number of works has been devoted to the second of these areas, especially over the entire temperature range.

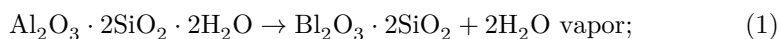
The small number of thermodynamic studies ⁽²⁻⁴⁾ has so far been limited to the conclusion that, in the synthesis of mullite from their oxides, at the ratio $A : S = 1 : 1$, the primary product should be mullite ($\Delta Z_{1200^\circ K} = -66810$ cal/mol), but with increasing temperature the thermodynamic possibility of obtaining sillimanite increases more and more ($\Delta Z_{2000^\circ K}^{A_3S_2} = -52170$ cal/mol, and $\Delta Z_{2000^\circ K}^{AS} = -52300$ cal/mol). For the ratio $A : S = 3 : 2$, over the entire temperature range mullite is most probable ($\Delta Z_{1000^\circ K} = -229490$; $\Delta Z_{1800^\circ K} = -163880$ cal/mol), whereas for sillimanite at these temperatures $\Delta Z_{1000^\circ K} = -118800$ cal/mol, $\Delta Z_{1800^\circ K} = -102860$ cal/mol.

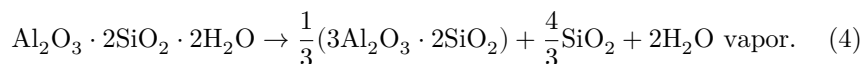
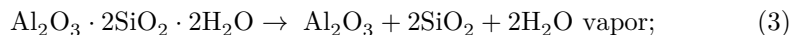
In calculating the reactions of transformation of kaolinite, up to now we have used data for metakaolin ($\Delta H_{298.16^\circ K} = -767500$ cal/mol, $\Delta Z_{298.16^\circ K} = -719410$ cal/mol).

In this case, over the entire temperature range mullite is most probable ($\Delta Z_{1000^\circ K} = -104740$ cal/mol, $\Delta Z_{1600^\circ K} = -96240$ cal/mol). The formation of mullite from metakaolin with the addition of alumina proceeds with a larger change in free energy than without the addition ($\Delta Z_{1800^\circ K} = -203020$ cal/mol), and in this case mullite is again the most preferable ($\Delta Z_{1800^\circ K}^{A_3S_2} = -203020$ cal/mol, whereas in the formation of sillimanite $\Delta Z_{1800^\circ K}^{AS} = -141220$ cal/mol).

The calculation may also be made in another way. In this case, using known and new data ⁽⁵⁻⁷⁾, one can proceed from kaolinite (see Table 1). Its heat capacity was determined by the additivity method from the oxides and water ⁽⁸⁾.

On the basis of the data presented in Table 1 the following reactions were considered:





Calculation for them gives the following equations:

$$\Delta Z = +80814 - 11.72T \cdot \ln T + 10.69 \cdot 10^{-3}T^2 - 2.27 \cdot 10^5T^{-1} - 22.6T; \quad (1)$$

$$\Delta Z = -9605 - 10.33T \cdot \ln T + 7.99 \cdot 10^{-3}T^2 + 3.38 \cdot 10^5T^{-1} - 26.02T; \quad (2)$$

$$\Delta Z = +35964 - 6.74T \cdot \ln T + 5.36 \cdot 10^{-3}T^2 + 2.92 \cdot 10^5T^{-1} - 46.4T; \quad (3)$$

$$\Delta Z = -26712 + 0.09T \cdot \ln T + 6.3 \cdot 10^{-3}T^2 + 1.95 \cdot 10^5T^{-1} - 93.85T. \quad (4)$$

The results of the calculations according to the equations given are presented in Fig. 1.

Table 1

No.	Compound	S_{298}	ΔH	ΔZ	$c_p = f(T)$
1	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	100.5	-964.94	-883.0	$c_p = 57.47 + 35.3 \cdot 10^{-3} \cdot T - 7.87 \cdot 10^5 \cdot T^{-2}$
2	$\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ (sill.)	27.0	-648.9	-615.0	$c_p = 42.24 + 6.0 \cdot 10^{-3} \cdot T - 12.1 \cdot 10^5 \cdot T^{-2}$

No.	Compound	S_{298}	ΔH	ΔZ	$c_p = f(T)$
3	$3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	60.0	-1804.0	-1712.5	$c_p = 84.22 + 20.0 \cdot 10^{-3} \cdot T - 25.0 \cdot 10^5 \cdot T^{-2}$
4	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	32.78	-767.5	-719.41	$c_p = 54.85 + 8.8 \cdot 10^{-3} \cdot T - 3.48 \cdot 10^5 \cdot T^{-2}$
5	$\gamma\text{-Al}_2\text{O}_3$	12.186	-384.84	-	$c_p = 16.37 + 11.1 \cdot 10^{-3} \cdot T$
6	$\alpha\text{-Al}_2\text{O}_3$	12.186	-399.09	-376.77	$c_p = 27.43 + 3.06 \cdot 10^{-3} \cdot T - 8.47 \cdot 10^5 \cdot T^{-2}$
7	$\text{SiO}_2\text{-}\beta$ quartz	10.0	-205.4	-192.4	$c_p = 11.22 + 8.2 \cdot 10^{-3} \cdot T - 2.7 \cdot 10^5 \cdot T^{-2}$
8	$\text{SiO}_2\text{-}\alpha$ quartz	-	-205.62	-192.33	$c_p = 14.41 + 1.94 \cdot 10^{-3} \cdot T$
9	$\text{SiO}_2\text{-}\alpha$ tridymite	10.36	-204.80	-191.9	$c_p = 13.64 + 2.64 \cdot 10^{-3} \cdot T$
10	$\text{SiO}_2\text{-}\alpha$ cristo- balite	10.29	-205.0	-192.1	$c_p = 14.40 + 2.04 \cdot 10^{-3} \cdot T$

No.	Compound	S_{298}	ΔH	ΔZ	$c_p = f(T)$
11	H ₂ O, liquid	16.72	-68.32	-56.69	$c_p = 7.93 + 16.95 \cdot 10^{-3} \cdot T + 2.67 \cdot 10^5 \cdot T^{-2}$
12	H ₂ O, vapor	45.13	-57.80	-54.64	$c_p = 7.17 + 2.56 \cdot 10^{-3} \cdot T + 0.08 \cdot 10^5 \cdot T^{-2}$

It should be stipulated that the accuracy of the calculations performed is determined by the degree of accuracy of the currently available initial data.

Fig. 1

The data obtained are of interest above all because, for the first time, they provide a thermodynamic substantiation for the formation of metakaolin at a temperature of about 900° K (600° C). Thus it becomes clear that no duration of heating below this temperature boundary makes it possible to obtain metakaolin.

Secondly, it is very interesting that the straight lines for reactions 2 and 4 are very close, i.e., sillimanite and mullite may form with almost the same degree of thermodynamic probability. Apparently, the formation of one or the other compound must be determined by kinetic factors and, in particular, by the degree of crystallinity of the initial kaolinite.

This view is fully consistent also with the new, recent views^(9,10) on the process of change of kaolinite upon heating, which, incidentally, coincide to a considerable extent with our earlier considerations on this question⁽¹⁾ and our interpretation of the first exothermic effect^(1,2).

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Note: Figure translations are in progress. See original paper for figures.

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