THERMODYNAMICS OF THE VARIOUS HIGH TEMPERATURE TRANSFORMATIONS OF KAOLINITE

by

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ABSTRACT

THERMODYNAMIC calculations of ΔG for all possible transformations of metakaolin at the temperature of the first DTA exothermic peak indicates that the most stable transformation is the one that yields mullite rather than γ-alumina.

The energy of crystallization of γ-alumina is quite small—36,513 cal per mol, compared with the energy of crystallization of mullite—336,180 cal per mol. Furthermore, the crystallization of γ-alumina is very slow, and the crystal growth never produces crystallite sizes much larger than the lower end of the colloidal region. Hence, the gradual release of the small amounts of energy liberated during the crystallization of γ-alumina would be extremely difficult to detect by DTA methods.

INTRODUCTION

ALTHOUGH the kaolinite–mullite transformation series has been the subject of extensive investigations, some fundamental problems still remain unsolved. The interpretation of the first exothermic peak that is observed in the DTA of kaolinite at about 980°C is still a matter of speculation.

It is a well-known fact that kaolinite, $Al_2O_32SiO_22H_2O$, undergoes some significant changes in its structure when heated to higher temperatures. It loses its (OH) lattice water between 500°–600°C. This loss of lattice water breaks up the regular periodicity in the kaolinite structure along the c-axis producing a dehydrated phase known as metakaolin. By further heating, metakaolin transforms to a crystalline phase or phases, indicated by the first exothermic peak at about 980°C. This phase or these phases are still a point of dispute among different investigators. Insley and Ewell (1935), Jay (1939), Hyslop (1944) and Richardson and Wild (1952) report γ-alumina as the product phase of fired kaolinite at 980°C. Comeforo, Fisher, and Bradley (1948), Johns (1953) and Brindley and Hunter (1955) report mullite as the product phase of fired kaolinite that was responsible for the first exothermic DTA peak at about 980°C.

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DETAILED STUDY OF KAOLINITE–MULLITE TRANSFORMATION SERIES

In this investigation, experimental laboratory work was combined with a thermodynamic approach in an attempt to explain the first exothermic DTA peak of kaolinite. A detailed study of the kaolinite–mullite transformation series was made over the range 950°–1500°C. The transformations were followed by means of X-ray analysis at temperature intervals as small as 10°C in the neighborhood of the first exothermic peak. The heating time was varied between 5 min and several hours. Studies on different kaolinite minerals* and one halloysite sample showed that γ-alumina was always forming before mullite† and at longer heating times it was found that both γ-alumina and mullite coexisted as product phases of fired kaolinite between 950°–1100°C‡ (Plate 1).

In all X-ray patterns of γ-alumina, the lines were always very broad and diffuse, even after heating for as long as 28 hr and furnace cooling. This indicates that γ-alumina never develops into a well-crystallized phase as compared to mullite. The γ-alumina phase could never be identified on a diffractometer trace. It was also found that γ-alumina lines were shifted compared with the lines of the standard pattern, indicating a spinel-type phase as reported by Brindley and Nakahira (1958).

In spite of the fact that both γ-alumina and mullite coexist as product phases of fired kaolinite, the question concerning the source of the first DTA exothermic peak still remains: Which phase is responsible for the first exothermic peak? Is it γ-alumina or mullite or both?

Thermodynamic Data for Kaolinite and its Products

Vaughan (1955) reported that the values of heats of formation of meta-kaolin, mullite and γ-alumina were given by Avgustinik and Mchedlov-Petrosyan in 1952 as $-767,500$, $-1,804,000$ and $-391,290$ cal per mol. The values reported by Kroger in 1953 (Vaughan, 1955) are: $-803,000$, $-1,804,000$ and $-395,000$ cal per mol respectively, for the same substances. The value for the heat of formation of metakaolin, $-767,500$ cal per mol, is also listed in the Handbook of Chemistry and Physics (1959; 1960. The heat of formation of kaolinite was estimated by Vaughan (1955) as $-964,000$ cal per mol and as $-964,940$ cal per mol by Budnikov and

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* The kaolinite minerals were: (1) E.P.K., produced by the Edgar Plastic Kaolin Company, Edgar, Florida, code no. CT-108-1. (2) Mallinckrodt Kaolinite produced by the Mallinckrodt Chemical Works, St. Louis, Mo., code no. 5643, lot no. KH520. (3) A.P.I. 9b. Kaolinite, Reference Clay Minerals, A.P.I. Research Project 49. (4) Halloysite, Ureka, Utah, A.P.I. Research Project 49.

† The X-ray patterns made at room temperature of kaolinites and halloysite that had been heated at 950°C from 20–40 min showed small crystallites of α-quartz prior to the formation of γ-alumina, which appeared after about 1 hr heating time at 950°C.

‡ The temperature range where both γ-alumina and mullite coexist, i.e. 950°–1100°C, is for E.P.Kaolinite only; for other minerals this temperature range is slightly different, since it depends on the type of mineral used.
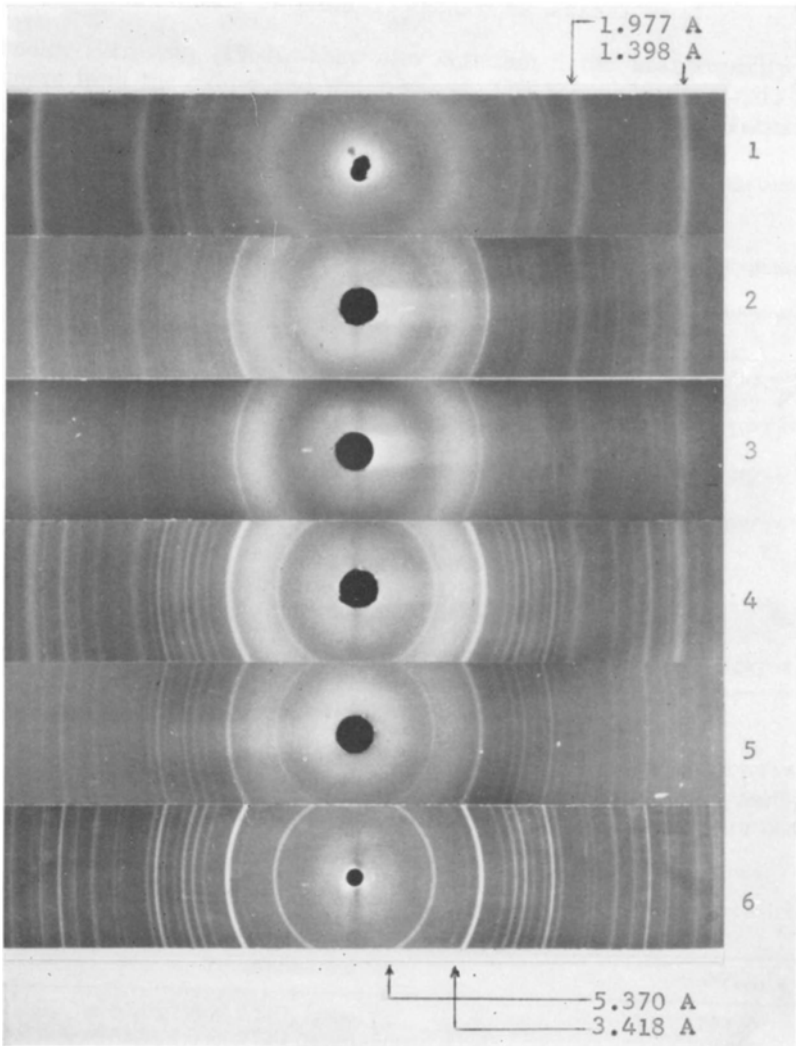
PLATE 1. Coexistence of γ-alumina and mullite at different temperatures.

Mchedlov-Petrosyan (1960). They also determined the heat capacity of kaolinite from the oxides and water values. The thermodynamic data for different phases of silica and water were reported by Kelly (1960), Kubaschewski and Evans (1951), Coughlin (1954) and Glassner (1959).

Table 1 lists the most reliable values of the thermodynamic properties of kaolinite and its products.

TABLE 1.—VALUES OF THERMODYNAMIC PROPERTIES S_{298}, ΔH_{298} AND C_p FOR KAOLINITE AND ITS PRODUCTS

Substance	S_{298}	$-\Delta H_{298}$	C_p
Kaolinite	40.50	964,940	$57.47 + 35.30 \times 10^{-3}T - 7.87 \times 10^5 T^{-2}$
Metakaolin	32.78	767,500	$54.85 + 8.80 \times 10^{-3}T - 3.48 \times 10^5 T^{-2}$
Mullite	60.00	1,804,000	$84.22 + 20.00 \times 10^{-3}T - 25.00 \times 10^5 T^{-2}$
γ-Alumina	12.20	395,000	$16.37 + 11.10 \times 10^{-3}T$
α-Quartz	10.06	209,900	$11.22 + 8.20 \times 10^{-3}T - 2.70 \times 10^5 T^{-2}$
β-Quartz	10.06	209,900	$14.41 + 1.94 \times 10^{-3}T$
SiO_2(glass)	10.06	202,000	$13.38 + 3.68 \times 10^{-3}T - 3.45 \times 10^5 T^{-2}$
α-Cristobalite	10.06	209,550	$4.28 + 21.06 \times 10^{-3}T$
β-Cristobalite	10.06	209,550	$14.40 + 2.04 \times 10^{-3}T$
α-Tridymite	10.06	209,400	$3.27 + 24.80 \times 10^{-3}T$
β-Tridymite	10.06	209,400	$13.64 + 2.64 \times 10^{-3}T$
H_2O (water)	16.72	68,320	18.03
H_2O (steam)	45.13	57,800	$7.17 + 2.56 \times 10^{-3}T + 0.08 \times 10^5 T^{-2}$

Possible Transformations of Metakaolin

If one examines the literature, he will find that some investigators observed γ-alumina; others observed mullite; and a few observed both. Consequently, in this investigation, all possible transformations of metakaolin were considered. These transformations are shown in Table 2.

TABLE 2. POSSIBLE TRANSFORMATIONS OF METAKAOLIN AND THE CORRESPONDING VALUES OF ΔG AT 1250°K

Transformation	$-\Delta G_{1250°K}$
1. $Al_2O_3 2SiO_2 \rightleftharpoons Al_2O_3 (\gamma) + 2 SiO_2$ (glass)	24,150
2. $Al_2O_3 2SiO_2 \rightleftharpoons Al_2O_3 (\gamma) + 2 SiO$ (crystalline)	40,919
3. $Al_2O_3 2SiO_2 \rightleftharpoons 1/3 (3Al_2O_3 2SiO_2) + 4/3 SiO_2$ (glass)	93,834
4. $Al_2O_3 2SiO_2 \rightleftharpoons 1/3 (3Al_2O_3 2SiO_2) + 4/3 SiO_2$ (crystalline)	105,022
5. $Al_2O_3 2SiO_2 \rightleftharpoons 1/4 (3Al_2O_3 2SiO_2) + 1/4 Al_2O_3(\gamma) + 3/2 SiO_2$ (glass)	76,309
6. $Al_2O_3 2SiO_2 \rightleftharpoons 1/4 (3Al_2O_3 2SiO_2) + 1/4 Al_2O_3(\gamma) + 3/2 SiO_2$ (cryst)	88,991

Substituting the data of Table 1 into the Gibbs free energy equation* :

$$\Delta G_T = \Delta H_{298} + \int_{298}^{T} \Delta C_p dT - T \Delta S_{298} - T \int_{298}^{T} \Delta C_p dT/T \qquad (1)$$

* Gibbs free energy equation is defined by Kubaschewski and Evans (1951, p. 25).

equations for ΔG as a function of T were obtained for all possible transformations shown in Table 2.

Since SiO_2 is a possible product, all phase transitions of silica from α-quartz to fused silica had to be considered in obtaining the ΔG equations for transformations 2, 4, and 6. The SiO_2 phases and their transition data are given in Table 3. ΔG equations for the phase transition of silica are listed in Table 4.

TABLE 3.—TEMPERATURES AND HEATS OF TRANSITIONS OF DIFFERENT PHASES OF SILICA

Phase	Temperature range	ΔH_t cal/mol
α-Quartz	298°– 848°K	
		290
β-Quartz	848°–1140°K	
		180
β-Tridymite	1140°–1743°K	
		30
β-Cristobalite	1743°–1953°K	
		2150
Glass	1953°–2100°K	

TABLE 4.— ΔG EQUATIONS FOR THE VARIOUS PHASE TRANSITIONS OF SILICA

SiO_2 (α-quartz) $\rightleftharpoons$ SiO_2 (β-quartz)
$\Delta G = 154.076 + 18.861\,T - 3.190\,T\ln T + 3.13 \times 10^{-3}T^2 - 1.35 \times 10^5 T^{-1}$
SiO_2 (β-quartz) $\rightleftharpoons$ SiO_2 (β-tridymite)
$\Delta G = 602.940 - 5.549\,T + 0.770\,T\ln T - 0.35 \times 10^{-3}T^2$
SiO_2 (β-tridymite) $\rightleftharpoons$ SiO_2 (β-cristobalite)
$\Delta G = -383.265 + 5.369\,T - 0.760\,T\ln T + 0.30 \times 10^{-3}T^2$
SiO_2 (β-cristobalite) $\rightleftharpoons$ SiO_2 (glass)
$\Delta G = 837.760 - 6.602\,T + 1.020\,T\ln T - 0.82 \times 10^{-3}T^2 + 1.725 \times 10^5 T^{-1}$

The ΔG equations for all possible transformations are listed in Table 5 for the different temperature ranges between 298°–2100°K (m.p. of mullite). Table 6 gives the ΔH_T equations for the different transformations. Table 7 gives the ΔH_T equations of the phase transitions of silica up to β-tridymite.

The Most Stable Transformation

The calculated values of ΔG of the different transformations have been plotted against temperature as shown in Fig. 1. Since the reaction that has the maximum $-\Delta G$ is the most stable, we find that transformation 4, being the one with the highest $-\Delta G$, is the most stable. Transformation 4:

$$Al_2O_3 2SiO_2 \rightleftharpoons 1/3(3Al_2O_3 2SiO_2) + 4/3SiO_2 \text{ (crystalline)}$$

TABLE 5.— ΔG EQUATIONS FOR THE POSSIBLE TRANSFORMATIONS OF METAKAOLIN AT DIFFERENT TEMPERATURES

Temp. range °K		ΔG_T
1. 298 to T	$-$	$29,684 - 73.22T + 11.72T\ln T - 4.83 \times 10^{-3}T^2 + 1.71 \times 10^5 T^{-1}$
2. 298 848	$-$	$44,095 - 100.31T + 16.04T\ln T - 9.35 \times 10^{-3}T^2 + 0.96 \times 10^5 T^{-1}$
848 1140	$-$	$43,787 - 62.59T + 9.66T\ln T - 3.09 \times 10^{-3}T^2 - 1.74 \times 10^5 T^{-1}$
1140 1743	$-$	$42,581 - 73.69T + 11.20T\ln T - 3.79 \times 10^{-3}T^2 - 1.74 \times 10^5 T^{-1}$
1743 1953	$-$	$43,348 - 62.95T + 9.68T\ln T - 3.19 \times 10^{-3}T^2 - 1.74 \times 10^5 T^{-1}$
1953 T	$-$	$41,672 - 76.16T + 11.72T\ln T - 4.83 \times 10^{-3}T^2 + 1.72 \times 10^5 T^{-1}$
3. 298 T	$-$	$103,798 - 54.33T + 8.94T\ln T - 1.39 \times 10^{-3}T^2 + 4.73 \times 10^5 T^{-1}$
4. 298 848	$-$	$113,406 - 72.40T + 11.82T\ln T - 4.40 \times 10^{-3}T^2 + 4.23 \times 10^5 T^{-1}$
848 1140	$-$	$113,201 - 47.25T + 7.56T\ln T - 0.23 \times 10^{-3}T^2 + 2.43 \times 10^5 T^{-1}$
1140 1743	$-$	$112,397 - 54.65T + 8.59T\ln T - 0.69 \times 10^{-3}T^2 + 2.43 \times 10^5 T^{-1}$
1743 1953	$-$	$112,908 - 47.49T + 7.58T\ln T - 0.29 \times 10^{-3}T^2 + 2.43 \times 10^5 T^{-1}$
1953 T	$-$	$111,791 - 56.29T + 8.94T\ln T - 1.39 \times 10^{-3}T^2 + 4.73 \times 10^5 T^{-1}$
5. 298 T	$-$	$85,270 - 58.98T + 9.64T\ln T - 2.25 \times 10^{-3}T^2 + 3.97 \times 10^5 T^{-1}$
6. 298 848	$-$	$96,078 - 79.37T + 12.87T\ln T - 5.64 \times 10^{-3}T^2 + 3.41 \times 10^5 T^{-1}$
848 1140	$-$	$95,847 - 51.08T + 8.09T\ln T - 0.94 \times 10^{-3}T^2 + 1.39 \times 10^5 T^{-1}$
1140 1743	$-$	$94,944 - 59.40T + 9.24T\ln T - 1.47 \times 10^{-3}T^2 + 1.39 \times 10^5 T^{-1}$
1743 1953	$-$	$95,519 - 51.35T + 8.10T\ln T - 1.02 \times 10^{-3}T^2 + 1.39 \times 10^5 T^{-1}$
1953 T	$-$	$94,262 - 61.25T + 9.63T\ln T - 2.25 \times 10^{-3}T^2 + 3.98 \times 10^5 T^{-1}$

TABLE 6.— ΔH_T EQUATIONS FOR THE POSSIBLE TRANSFORMATIONS

Transformation	ΔH_T
1	$- 29,684 - 11.72\,T + 4.83 \times 10^{-3}T^2 + 3.42 \times 10^5 T^{-1}$
2	$- 44,095 - 16.04\,T + 9.35 \times 10^{-3}T^2 + 1.92 \times 10^5 T^{-1}$
3	$-103,798 - 8.94\,T + 1.39 \times 10^{-3}T^2 + 9.45 \times 10^5 T^{-1}$
4	$-113,406 - 11.82\,T + 4.40 \times 10^{-3}T^2 + 8.45 \times 10^5 T^{-1}$
5	$- 85,270 - 9.64\,T + 2.25 \times 10^{-3}T^2 + 7.95 \times 10^5 T^{-1}$
6	$- 96,078 - 12.87\,T + 5.64 \times 10^{-3}T^2 + 6.82 \times 10^5 T^{-1}$

TABLE 7.— ΔH_T EQUATIONS OF THE PHASE TRANSITIONS OF SILICA UP TO β-TRYDIMITE

SiO_2 (α-quartz) $\rightleftharpoons$ SiO_2 (β-quartz)
$$\Delta H_T = 154.08 + 3.19\,T - 3.13 \times 10^{-3}T^2 - 2.7 \times 10^5 T^{-1}$$
SiO_2 (β-quartz) $\rightleftharpoons$ SiO_2 (β-tridymite)
$$\Delta H_T = 602.94 - 0.77\,T + 0.35 \times 10^{-3}T^2$$

This does not mean that the other transformations do not occur; it does mean that transformation 4 is the ultimate one, and it also means that less stable transformations may occur before the ultimate one. In other words, by heating, metakaolin may transform to alumina and silica, then to alumina,

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TABLE 8.— ΔH_{1250} FOR THE POSSIBLE TRANSFORMATIONS

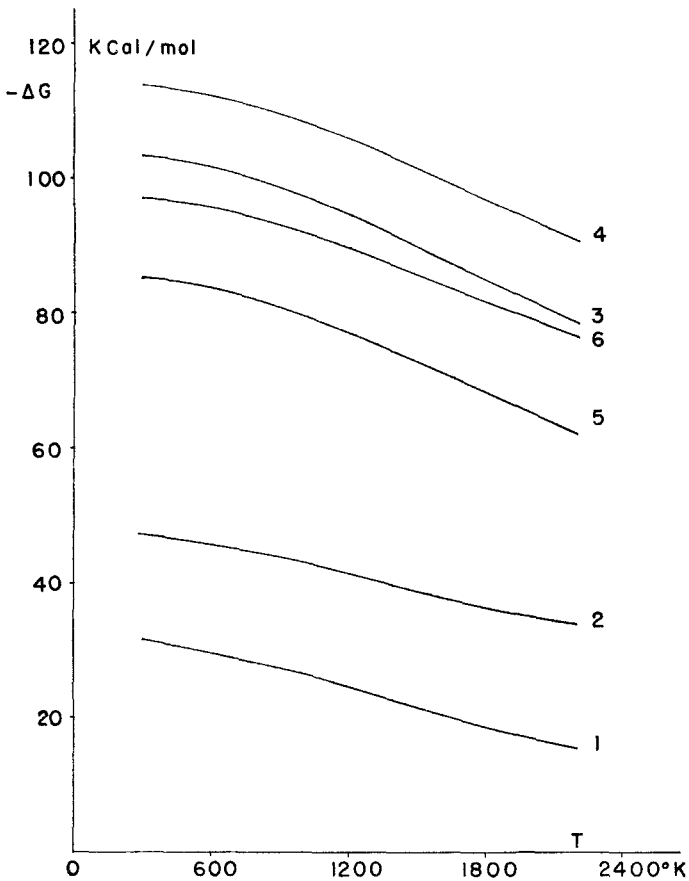| Transformation	ΔH_{1250} cal/mol
1	— 36,513
2	— 50,936
3	— 112,045
4	— 121,669
5	— 93,168
6	— 103,973

FIG. 1. Change of free energy with temperature for all possible transformations.

silica, and mullite; and, at the end of its transformation series, it yields mullite and silica that is in excess of the silica required for mullite.

Evaluation of Energy of Crystallization

Any exothermic peak observed on the DTA curve of kaolinite is due to a thermoelectromotive force in the thermocouple circuit, which, in turn, is due to a temperature difference between the sample and the inert material in the DTA unit. The rise in the temperature of the sample occurs as a result of a certain amount of heat being evolved during an exothermic reaction. Accordingly, the energy that produces the peak is the enthalpy, ΔH, rather than the free energy, ΔG.

The exothermic peak also indicates a crystallization process so that it is possible to calculate the energy of crystallization of the products of reactions or transformations.

In order to calculate the energy of crystallization of alumina, silica, and mullite at the temperature of the first exothermic peak, the values of ΔH at 1250°K should be calculated for all possible transformations.

Equations of ΔH_T as a function of T for all possible transformations were obtained from the calculations made to obtain ΔG_T as functions of T.

For the first transformation,

$$\Delta H_T = -29{,}684 - 11.72T + 4.83 \times 10^{-3}T^2 + 3.42 \times 10^5 T^{-1}$$

For the second, fourth, and sixth transformations, where the product silica is crystallized, the transitions of silica at different temperatures up to the temperature of the first exothermic peak must be considered.

For the second transformation,

$$\begin{aligned}\Delta H_T = &-44{,}095 - 16.04\,T + 9.35 \times 10^{-3}T^2 + 1.92 \times 10^5 T^{-1}\\ &+ 2(154.08 + 3.19\,T - 3.13 \times 10^{-3}T^2 - 2.7 \times 10^5 T^{-1})\\ &+ 2(602.94 - 0.77\,T + 0.35 \times 10^{-3}T^2)\\ = &-42{,}581 - 11.20\,T + 3.79 \times 10^{-3}T^2 - 3.48 \times 10^5 T^{-1}\end{aligned}$$

For the third transformation:

$$\Delta H_T = -103{,}798 - 8.94\,T + 1.39 \times 10^{-3}T^2 + 9.45 \times 10^5 T^{-1}$$

For the fourth transformation:

$$\begin{aligned}\Delta H_T = &-113{,}406 - 11.82\,T + 4.4 \times 10^{-3}T^2 + 8.45 \times 10^5 T^{-1}\\ &+ 4/3\,(154.08 + 3.19\,T - 3.13 \times 10^{-3}T^2 - 2.7 \times 10^5 T^{-1})\\ &+ 4/3\,(602.94 - 0.77\,T - 0.35 \times 10^{-3}T^2)\\ = &-112{,}397 - 8.59\,T + 0.69 \times 10^{-3}T^2 + 4.85 \times 10^5 T^{-1}\end{aligned}$$

For the fifth transformation,

$$\Delta H_T = -85{,}270 - 9.64\,T + 2.25 \times 10^{-3}T^2 + 7.95 \times 10^5 T^{-1}$$

For the sixth transformation,

$$\begin{aligned}\Delta H_T = &-96{,}078 - 12.87\,T + 5.64 \times 10^{-3}T^2 + 6.82 \times 10^5 T^{-1}\\ &+ 3/2\,(154.08 + 3.19\,T - 3.13 \times 10^{-3}T^2 - 2.7 \times 10^5 T^{-1})\\ &+ 3/2\,(602.94 - 0.77\,T + 0.35 \times 10^{-3}T^2)\\ = &-94{,}942 - 9.24\,T + 1.47 \times 10^{-3}T^2 + 2.77 \times 10^5 T^{-1}\end{aligned}$$

Substituting 1250° for T, the temperature of the first exothermic peak in degrees Kelvin in the ΔH_T equations of all transformations, we obtain the values of ΔH_{1250} for all transformations as shown in Table 8.

Using the calculated values of ΔH_{1250} one can form the six following simultaneous equations:

$$
\begin{array}{llll}
E_a & & & = - \ \ 36{,}513 \text{ cal per mol} \\
E_a & + \ \ 2\,E_s & & = - \ \ 50{,}936 \text{ cal per mol} \\
& & + 1/3\,E_m & = - \ 112{,}045 \text{ cal per mol} \\
& 4/3\,E_s & + 1/3\,E_m & = - \ 121{,}669 \text{ cal per mol} \\
1/4\,E_a & & + 1/4\,E_m & = - \ \ 93{,}168 \text{ cal per mol} \\
1/4\,E_a & + 3/2\,E_s & + 1/4\,E_m & = - \ 103{,}973 \text{ cal per mol}
\end{array}
$$

or

$$
\begin{array}{llll}
E_a & & & = - \ \ 36{,}513 \text{ cal per mol} \\
E_a & + \ \ 2\,E_s & & = - \ \ 50{,}936 \text{ cal per mol} \\
& & E_m & = - \ 336{,}135 \text{ cal per mol} \\
& 4\,E_s & + \ \ E_m & = - \ 365{,}007 \text{ cal per mol} \\
E_a & & + \ \ E_m & = - \ 372{,}672 \text{ cal per mol} \\
E_a & + \ \ 6\,E_s & + \ \ E_m & = - \ 415{,}892 \text{ cal per mol}
\end{array}
$$

where E_a, E_s, and E_m are the energies of crystallization of γ-alumina, crystalline silica and mullite respectively.

Having six equations and three unknowns, a 3-by-6 matrix can be formed to solve for E_a, E_s, and E_m.

$$
\begin{pmatrix}
1 & 0 & 0 \\
1 & 2 & 0 \\
0 & 0 & 1 \\
0 & 4 & 1 \\
1 & 0 & 1 \\
1 & 6 & 1
\end{pmatrix}
\begin{pmatrix}
E_a \\
E_s \\
E_m
\end{pmatrix}
=
\begin{pmatrix}
- \ 36{,}513 \\
- \ 50{,}936 \\
- \ 336{,}135 \\
- \ 365{,}007 \\
- \ 372{,}672 \\
- \ 415{,}892
\end{pmatrix}
$$

This 3-by-6 matrix can be reduced to the following 3-by-3 matrix:

$$
\begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
E_a \\
E_s \\
E_m
\end{pmatrix}
=
\begin{pmatrix}
- \ \ 36{,}513 \\
- \ \ \ \ 7{,}199 \\
- \ 336{,}180
\end{pmatrix}
$$

Therefore, the average values of the energies of crystallization are:

$$
\begin{aligned}
E_a &= - \ 36{,}513 \text{ cal per mol} \\
E_s &= - \ \ \ 7{,}199 \text{ cal per mol} \\
E_m &= -336{,}180 \text{ cal per mol}
\end{aligned}
$$

Comparing the energy of crystallization of mullite to that of alumina, mullite has an energy of crystallization at the first exothermic peak that is nine times that of γ-alumina.

Contributions of the Product Phases to the Exothermic Energy at $1250°K$.— From the values of the energies of crystallization of mullite and crystalline silica at $1250°K$ and the mol fractions involved in the most stable transformation, it is possible to calculate the contributions of mullite and crystalline silica to the exothermic energy at $1250°K$.

Contribution of mullite $= 1/3 \times -336,180 = -112,060$ cal
Contribution of silica $= 4/3 \times -7,199 = -9,600$ cal
Exothermic energy at $1250°K = -112,060 - 9,600$
$$= -121,660 \text{ cal}$$
Percentage contribution of mullite
$$= (112,060/121,660) \times 100 = 92 \text{ per cent}$$
Percentage contribution of silica
$$= (9,600/121,660) \times 100 = 8 \text{ per cent}$$

CONCLUSION

The interpretations of all previous investigators concerning the first exothermic DTA peak were based on experimental observations. However, the experimental observations were different and caused disagreement among different investigators. Since the differential thermal analysis technique is based on energy changes that accompany any thermal reaction, the interpretation should be based on the thermodynamic considerations.

The calculated free-energy changes of the possible transformations of metakaolin indicate that:

1. The most stable transformation at any high temperature is the one that yields mullite rather than γ-alumina or both mullite and γ-alumina.

2. The energy of crystallization of mullite at 980°C ($-336,180$ cal per mol) is about nine times as much as that of γ-alumina at the same temperature ($-36,513$ cal per mol).

Adding to these results the fact that the crystallization of γ-alumina is very slow, as observed experimentally, it is unlikely that the crystallization of γ-alumina, under such conditions, can liberate energy rapidly enough to produce such a sharp exothermic peak as the one observed at 980°C. On the contrary, mullite, with its much higher crystallization energy and rapid growing rate, is very probably the phase that is responsible for that peak.

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