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(Ph. D. Thesis)

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ABSTRACT

DIFFERENTIAL THERMAL CALORIMETRIC DETERMINATION OF THE THERMODYNAMIC PROPERTIES OF KAOLINITE

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September 1967

ABSTRACT

A differential thermal calorimeter was calibrated by measuring the heat content of SiO_2(quartz) and α-Al_2O_3 between room temperature and 1100°C. The results were compared with accepted literature values and agreement to ±2% observed. Differential thermal calorimetric values of 305, 250 and 280 cals/mole for the $\alpha \rightarrow \beta$ quartz inversion also compared favorably with the accepted 290 cals/mole. Having demonstrated the accuracy of the instrument, thermodynamic property estimations were undertaken on kaolinite.

Four samples of kaolinite were investigated. The 550°C endothermic reaction enthalpy was measured to be 35 to 48 kcals/mole. This range agreed well with the values quoted in the literature. The measured 9 kcals/mole for the 980°C exothermic reaction enthalpy corresponds to the calculated heat of crystallization of silica at this temperature. Such a crystallization was proposed by Schlietz and Soliman based on free-energy considerations. Literature evidence available discounts the crystallization of the other two participating phases, mullite and silicon spinel. An NaOH extraction technique was used to remove the amorphous silica from an 850°C-fired kaolinite and this extraction demonstrated to remove the

980°C exotherm. It was concluded therefore that the majority of the heat release at 980°C on firing kaolinite accompanies the reaction:

$$SiO_2(\text{amorphous}) \rightarrow SiO_2(\beta\text{-quartz}).$$

I. INTRODUCTION

The clay mineral, kaolinite, has been extensively studied during the past 17 years. This mineral is known to undergo an endothermic reaction at about 550°C resulting from the loss of structural water. A sharp exothermic reaction is also known to take place at about 980°C. The exact origin of this reaction however is a subject of considerable controversy. Although the existence of both these reactions has been known for some time, no accurately reproducible values of the enthalpy of either of them has been measured. The following work was undertaken to measure the enthalpy of these reactions and from the information so obtained better describe the reaction involved in the 980°C exotherm.

The mineral kaolinite derives its name from the Chinese kao-lin meaning "high hill", the latter thought to be the location of the first pure clay used in China. Kaolinite is an alumino-silicate with an ideal oxide composition $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. Typical compositions as found in nature are indicated in Table I.[1] Electron micrographs of a well-crystallized kaolinite show well-formed six-sided flakes, frequently with a prominent elongation in one direction. The elongation is parallel to either the (010) or the (110) direction. In poorly crystallized kaolinite, the particles show less distinct six-sided flakes. The maximum dimensions of the flake surfaces vary from 0.3 to about 4μ and the thickness from 0.05 to about 2μ. Structurally kaolinite can be considered to consist of alternate layers of a single silica tetrahedral sheet and a single octahedral gibbsite sheet. These are combined in a unit so that the tips of the silica tetrahedra and one of the layers of the octahedral sheet form a common layer. In the layer common to the octahedral and tetrahedral

Table I. Chemical analyses of kaolinite minerals.

	1	2	3	4	5	Theoretical
SiO_2	46.90%	44.81%	45.20%	46.77%	44.59%	46.54%
Al_2O_3	37.40	37.82	37.02	37.79	36.83	39.50
Fe_2O_3	0.65	0.92	0.27	0.45	1.14	
FeO	--	--	0.06	0.11	--	
MgO	0.27	0.35	0.47	0.24	0.39	
CaO	0.29	0.43	0.52	0.13	1.02	
K_2O	0.84	--	0.49	1.49	0.32	
Na_2O	0.44	--	0.36	0.05	0.13	
TiO_2	0.18	0.37	1.26	--	2.17	
H_2O-	--	1.10	1.55	0.61	--	
H_2O	12.95	14.27	13.27	12.18	13.63	13.96
Total	99.92	100.07	100.47	99.82	100.22	100.00

Origin of sample	Analyses by	Ref.
1. Zettlitz (Czechoslovakia)	C.S. Ross and P.F. Kerr	U.S.Geol. Surf.
2. Mexia Texas	C.S. Ross and P.F. Kerr	Profess Paper 165 E 1931
3. Macon Georgia	P.F. Kerr et al.	Rept. 7 A P 1 project 49(1950).
4. St. Austell(England)	P.F. Kerr et al.	Rept. 7 A P 1 project 49(1950).
5. Anna (Illinois)	R. E. Grim	Econ.Geol. 29 659-670 (1934).

groups, two-thirds of the atoms are shared by the silicon and aluminum and then they become $O^{=}$ instead of $OH^{=}$. This structure is diagrammatically shown in Fig. 1. The flakes of kaolinite consist of sheet units of the type just described, continuous in the a and b directions and stacked one above the other in the c-direction. Brindley[2] has investigated the stacking of the unit layers. He found the mineral to be triclinic with $a = 5.16\text{Å}$, $b = 8.94\text{Å}$, $c = 7.38\text{Å}$, $\alpha = 91.8$, $\beta = 104.5$, $\gamma = 90$, and of space-group P1. Brindley used powder x-ray patterns and some of his results are reproduced in Table II.

The action of heat on kaolinite is of major importance in the field of ceramics. Kaolinite discards its structural water at approximately 550°C and metakaolin is formed i.e., $[Al_2O_3 . 2SiO_2]$. At 925°C a highly ordered spinel-type phase develops with the discarding of silica from the structure. Subsequently the spinel transforms to mullite and at 1100°C cristobalite appears. This reaction series is summarized in the following way by Brindley and Nakahira,[3]

c.550°C	Endothermic reaction	Dehydration of kaolinite and formation of metakolin, Al_2O_3 2 SiO_2
c.925°C	Exothermic reaction	Metakaolin layers condense to form spinel-type phase of approximate composition $2Al_2O_3 . 3SiO_2$ with discard of silica (about 1 in $4SiO_2$); a "sharp" transformation
c.1050°C to 1100°C	Exothermic reaction	Spinel-type structure transforms to a mullite phase, precise composition not certain, with further discard of silica, appearing visibly as cristobalite.

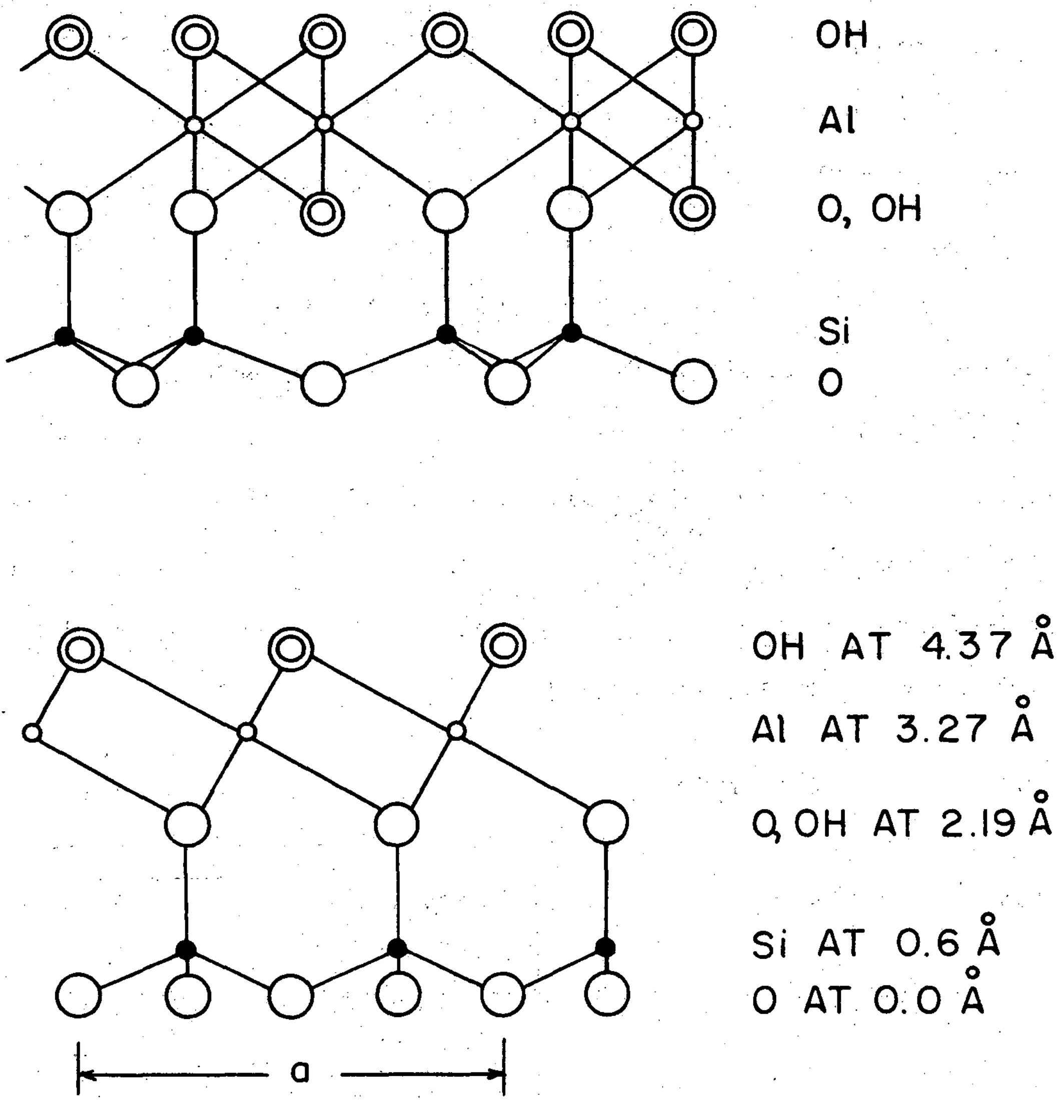


Fig. 1 The ideal kaolin layer seen in projection along a axis (upper diagram) and along b axis (lower diagram) (after Brindley[2]).

Table II. X-ray powder data for kaolinite (Brindley and Robinson[2]).

d(Å)	I	d (calc)	hkl
7.16	10+	7.15	001
4.46	4	4.469	020
4.36	5	4.370	$1\bar{1}0$
		4.332	110
4.18	5	4.172	$1\bar{1}1$
4.13	3	4.125	$1\bar{1}\bar{1}$
3.845	4	3.849	$02\bar{1}$
3.741	2	3.736	021
3.573	10+	3.573	002
		3.423	$1\bar{1}1$
3.372	4	3.370	111
3.144	3	3.148	$11\bar{2}$
3.097	3	3.098	$1\bar{1}\bar{2}$
		2.838	$0\bar{2}2$
2.753	3	2.748	022
2.558	6	2.566	$1\bar{3}0$
		2.563	$20\bar{1}$
		2.548	130
2.526	4	2.530	$13\bar{1}$
		2.520	$1\bar{1}2$
2.491	8	2.500	$1\bar{3}\bar{1}$
		2.490	200
		2.483	112
2.379	6	2.383	003
2.338	9	2.342	$20\bar{2}$
		2.341	$1\bar{3}1$
		2.335	$11\bar{3}$
2.288	8	2.301	$1\bar{3}\bar{1}$
		2.288	131

II. SURVEY OF LITERATURE ON THE HIGH TEMPERATURE KAOLINITE REACTIONS

One of the most powerful tools available for the qualitative investigation of high temperature reactions is differential thermal analysis (D.T.A.). This technique was first used to investigate the effect of heat on clays by Le Chatelier in 1887. D.T.A. traces of typical kaolins are shown in Fig. 2.[1] D.T.A. curves for kaolinite show an intense, sharp endothermic reaction corresponding to the loss of [OH] groups. The reaction begins at about 400°C and for a well crystallized kaolinite the peak maximum is at about 600°C. The exothermic reaction shown by D.T.A. curves between 900 and 1000°C is somewhat less intense but a good deal sharper than the prior endotherm. A further, but much smaller, exotherm is observed at 1250°C with the abrupt appearance of mullite in abundance and cristobalite.

The endothermic reaction at 550°C has been exhaustively investigated. In 1952 Stone[4] studied the effect of varying the partial pressure of water vapor on the decomposition temperature of kaolinite. To do this he utilized the D.T.A. technique and noted the dehydration commencement temperature. Taking as the basic reaction

$$Al_2Si_2O_5\ (OH)_4 \rightleftharpoons Al_2O_3\ 2SiO_2 + 2H_2O$$

then it is easily seen that

$$K' = P^2_{H_2O} \qquad (1)$$

where K' is the equilibrium constant for the reaction and P_{H_2O} the partial pressure of H_2O vapor. Equation (1) can be rewritten as

$$\ln K' = 2\ln P_{H_2O} \qquad (2)$$

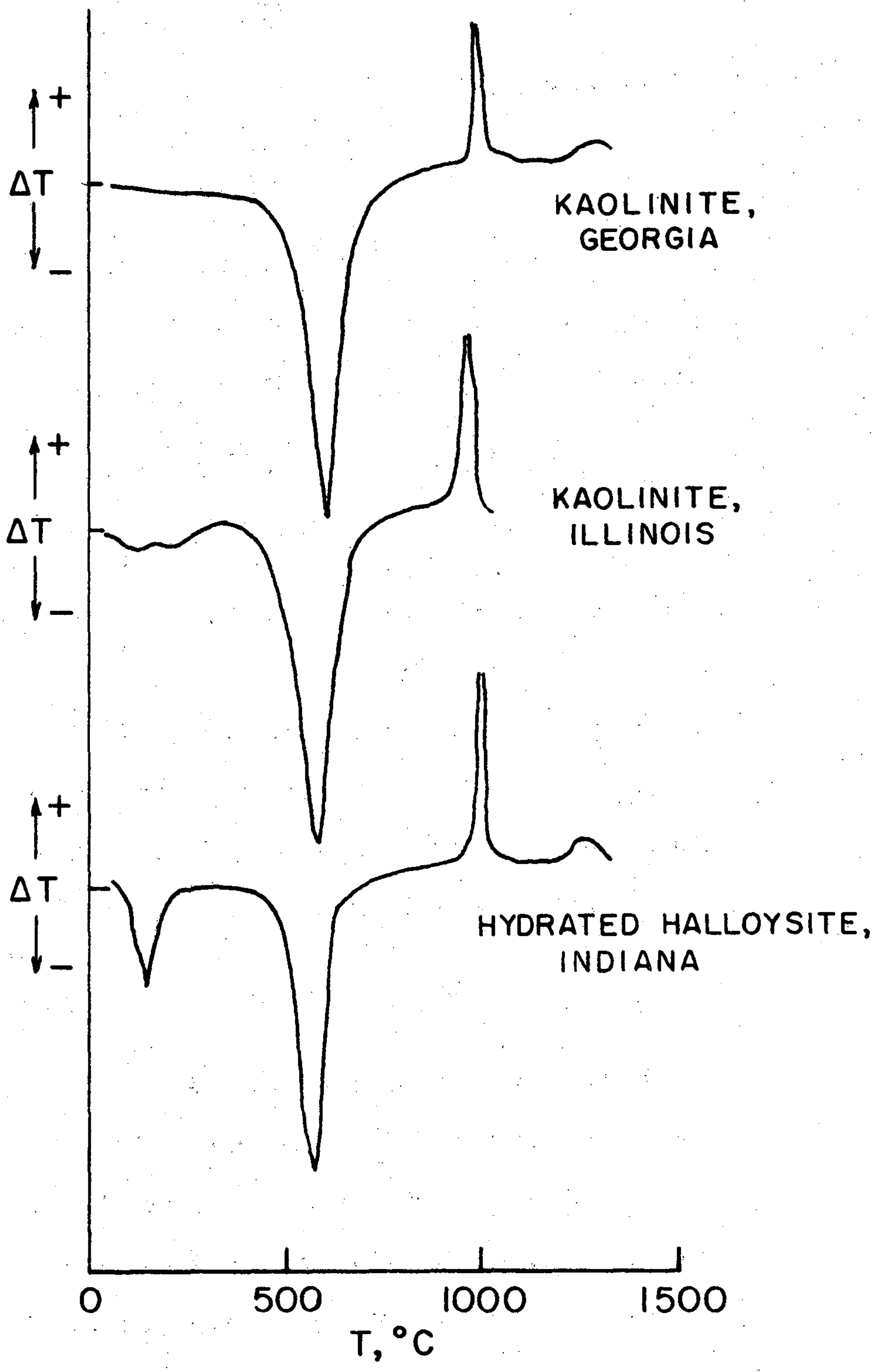


Fig. 2 Typical D. T. A. traces for kaolinites (after Grim[1]).

The Van't Hoff equation is

$$d \ln K' = \frac{\Delta H}{RT^2} dT \qquad (3)$$

and its integrated form is

$$\ln K' = -\frac{\Delta H}{RT} + c \qquad (4)$$

where ΔH = the enthalpy of the reaction, T the absolute temperature, R the gas constant, and c the constant of integration. As Eqs. (2) and (4) are equatable, Stone arrived at the final equation

$$\ln P_{H_2O} = -\frac{\Delta H}{2RT} + c' \qquad (5)$$

By plotting $\ln P_{H_2O}$ vs $1/T$, a straight line of slope $-\frac{\Delta H}{2R}$ results. In this way he obtained an enthalpy value of 37 Kcals/mole for the kaolinite dehydration reaction.

Assuming first order kinetics, Murray and White[5] utilized weight-loss data to obtain an activation energy value for the dehydration reaction. They found that the curve obtained on plotting weight-loss vs time suggested an exponential relationship of the type

$$\frac{dx}{dt} = K(a - x) \qquad (6)$$

where x is the amount of water removed, a, the initial concentration of water in the kaolinite, t, the time, and K the rate constant. They further state that the initial concentration of water is proportional to the final weight loss, (L_∞), of the kaolinite and that the amount reacted, x, is proportional to L, the weight loss at any time t. Hence Eq. (6) can be rewritten as

$$\frac{dL}{dt} = K (L_\infty - L)$$

or

$$\ln \frac{L_\infty - L}{L_\infty} = - kt \qquad (7)$$

By plotting $\log_{10} \frac{L_\infty - L}{L_\infty}$ vs t the value of the rate constant, K, was obtained. The standard free energy relationships of classical thermodynamics were then used to estimate the activation energy of the reaction. From the equation

$$RT \ln K = - E$$

where E is the activation energy for the reaction, a plot of $\log_{10}K$ vs 1/T gave an E value of 45 kcals/mole for the kaolinite dehydration reaction. Following exactly the same procedure, Vaughan[6] obtained a value of 41 kcals/mole for the endothermic activation energy. Vaughan further points out "published values for the heat of dehydration of kaolinite range from about 10,000 to 60,000 cal/g.mol. ($Al_2Si_2O_7 \cdot 2H_2O$), but a value of the order of 30,000 to 40,000 cal/g.mol. is now gaining more general acceptance. For dehydration at 550°C ΔH may be taken as 35,000 cal/g.mol. since the activation energy of an endothermic reaction cannot be less than the heat absorbed in that reaction. It therefore seems likely that ΔH ranges from about 20,000 $\rightarrow$ 45,000 cal/g.mol. for the kaolin minerals".

Disagreeing with the major premise of the Murray-White work, Brindley and Nakahira[7] found that the reaction only approximately followed first order kinetics and that the rate constants obtained from isothermal weight-loss measurements are markedly dependent on factors such as specimen size, shape and compaction. They pressed a series of discs of kaolinite of constant diameter but of differing thickness. The rate constant they observed was inversely proportional to the specimen thickness according to the relation,

$$\frac{1}{K} = a + bx \qquad (8)$$

K being the rate constant, x the specimen thickness and a and b constants. In this way they obtained a K value for an infinitely thin disc by extrapolation. It was their contention that in this way the influence of an accumulation of water vapor within the sample would be negated. They obtained a value of 65 kcals/mole for the activation energy of dehydration of kaolinite. Evans and White[8] found that a loosely-packed specimen more nearly followed first-order kinetics and for such samples obtained endothermic activation energy values of 44 and 45 kcals/mole.

Later in the same year Jacob[9] obtained a value of 38 kcals/mole for the dehydration-reaction heat, utilizing the Freeman-Carroll[10] equation

$$\frac{-H/2\ 3R\ \ \Delta(T^{-1})}{\Delta \log w_r} = -x + \frac{\Delta \log dw/dt}{\Delta \log w_r} \qquad (9)$$

where H is the enthalpy, x the order of the reaction, w the weight loss of the reactant up to time t and $w_r = (w_c - w)$ where w_c is the loss of weight at the completion of the reaction, R is the gas constant and T the absolute temperature. Holt, Cutler and Wadsworth[11] found that if dehydration is carried out in vacuo the result is much closer to the ideal Arrehenius plot. They obtained a value of 44 kcals/mole.

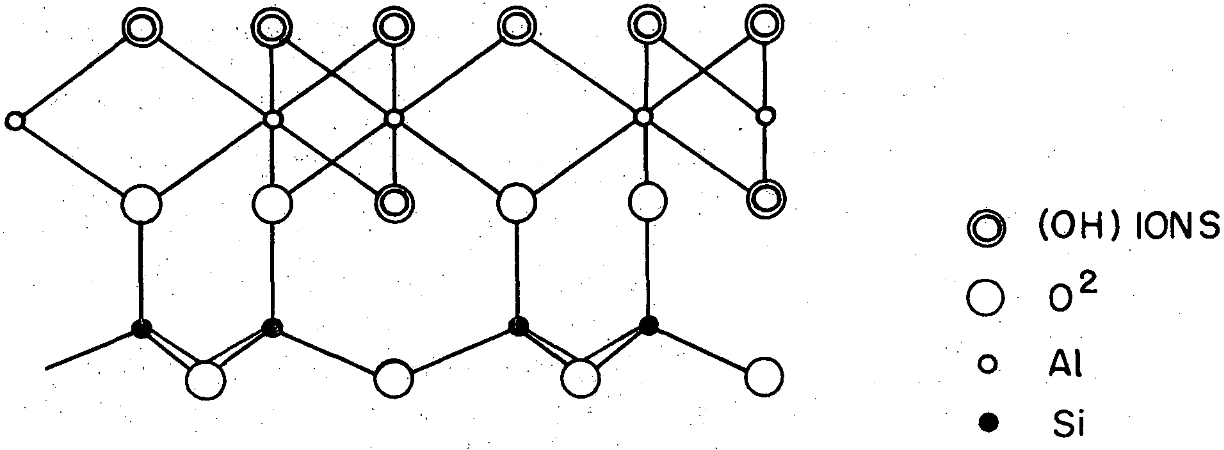
The nature of the product of dehydration of kaolinite has for many years been a matter of controversy. Current thinking is that the product, known as metakaolin,[12] is a single homogeneous phase. The main argument in favor of this hypothesis is based on electron-micrograph and electron-diffraction studies. In 1944 Eitel and Kedesdy[13] demonstrated the persistence of the crystalline form of kaolinite at high temperatures. In 1955 Roy, Roy and Francis[14] and Brindley and Hunter,[15] using the same technique but different materials, also demonstrated the structural nature of metakaolin. Roy, Roy and Francis showed, with the aid of transmission-electron-diffraction, that diffraction patterns obtained throughout a temperature range of 300°C above the dehydration temperature were much the same as those of the original kaolinite. In this work the material investigated was a well-crystallized kaolinite from Langley. Brindley and Hunter on the other hand investigated a sample of nacrite from Hirvivaara, Finland. Nacrite and kaolinite have a similar lamellar morphology and are composed of silicate layers having the same structure and chemical composition; they differ only in stacking arrangement of the layers and in crystallite size. Because kaolinite does not occur in large flakes and nacrite does, the latter is more amenable to investigation. Brindley and Hunter found that the hko reflections persist up to 900°C. This result they interpreted as follows:

> "following the expulsion of the (OH) radicals from the structure, the layers retain a relict structure of hexagonal type having no detectable regularity from one layer to another."

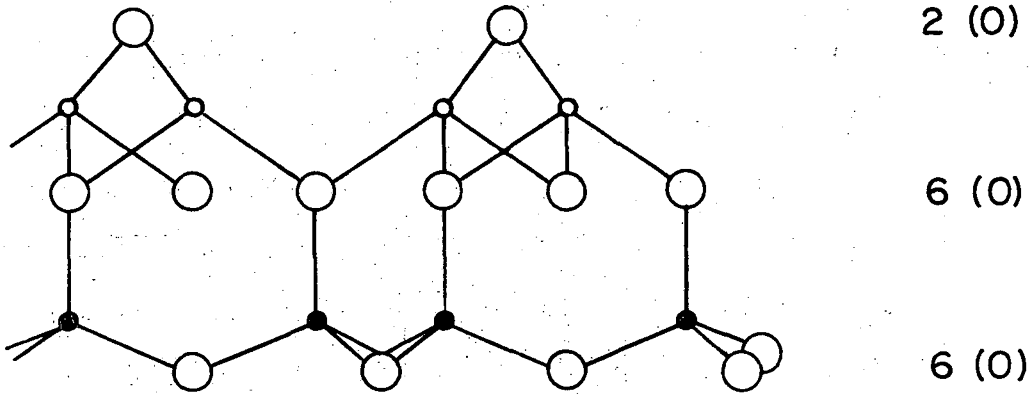
The alternative point of view expressed by many investigators is that when kaolinite loses its water at about 550°C, the product is "amorphous". Colegrave and Rigby[16] obtained evidence that chemical bonds do not exist in metakaolin. All known silicates decomposable by perchloric acid invariably yield a gelatinous precipitate. Hence if the alumina and silica of metakaolin are chemically combined, Colegrave and Rigby state that a gelatinous precipitate would be expected. After such treatment however they found only a powdery residue. They concluded therefore that the kaolinite, after the loss of structural water, is "amorphous". However, as pointed out by Roy, Roy and Francis, experiments demonstrating the relatively greater solubility of the alumina or silica of the dehydroxylated phase in alkalies or acids merely show that the metastable phase is chemically unstable and easily attacked and the experiments themselves immediately destroy the evidence sought.

The exothermic reaction of metakaolin at 980°C poses a much more complex problem. The work of Brindley and Nakahira[3,17-19] is now accepted as an explanation of the phase changes that occur at this temperature. They postulated that instead of a number of phases linked together by chemical reactions exclusively, the reaction series can be viewed as having a large degree of structural continuity. They quote the work of Comefero, Fischer and Bradley,[20] and Comer, Koenig and Lyons[21] who demonstrated by electron-microscopy that mullite needles develop in directions related to the original kaolinite flakes. Brindley and Nakahira start by considering the metakaolin problem. They heated individual kaolinite crystals in small platinum dishes to a required temperature and then cooled the furnace slowly with the crystals in situ. They observed little change in clarity between the 490° and 850°C oscillation x-ray patterns. The hexagonal 850°C-pattern was indexed and shown to be essentially the same as that of kaolinite. The pattern indicated that metakaolin maintained a two-dimensional regularity in the a-b plane but an absence of regularity in the c-direction. When heated to 950°C they found that metakaolin transformed into a cubic phase with a spinel structure having a high degree of preferred orientation with respect to the parent material. It appeared that the cubic phase has the [110] direction parallel to the b-direction of the mother kaolinite or metakaolin and that the [111] direction is perpendicular to the cleavage plane.

Figure 3 indicates the relationship between metakaolin and kaolinite as postulated by Brindley and Nakahira. As the (111) close-packed layers of the cubic phase lie parallel to the layer of the kaolinite and the close-packed direction, [110] , is parallel to the close-packed direction of the kaolinite layers, the metakaolin can be regarded as a transition phase in an orderly sequence from kaolinite to the cubic phase. To arrive at their proposed metakaolin structure, Brindley and Nakahira compare the density changes involved and the lattice parameter modifications which occur. When kaolinite goes to metakaolin the theoretical weight loss is 13.95%. If no collapse of the kaolinite structure ensued, the density would also decrease by 13.95%. They made careful measurements on material fired at 800°C and found that the density decreased by only 1.52%. As the a and b parameters remained the same, the layer spacing must have diminished by 12.43%. Hence, they postulate that the structure of metakaolin must permit this collapse. In the light of this stipulation the 6-6-2 oxygen-layer structure, as shown in Fig. 3, was proposed. With only two oxygens in the top layer it is geometrically feasible to insert these partially into the holes in the Si-O network of the layer above them. Brindley and Nakahira hypothesized also that the diminished number of oxygen ions in the network would cause the Al-coordination to be tetrahedral. White, McKinstry and Bates[22] discovered that the K-α emission wavelength of aluminum is affected by the state of coordination of the aluminum ions. Utilizing their technique Brindley and McKinstry[19] showed the aluminum in metakaolin to be tetrahedrally coordinated. This work agrees nicely with the 6-6-2 oxygen-layer configuration and substantially strengthens the Brindley-Nakahira thesis. A strong point in favor of this structure is that a well-orientated cubic-close-packed spinel-type phase results on the interlayer collapse. In-



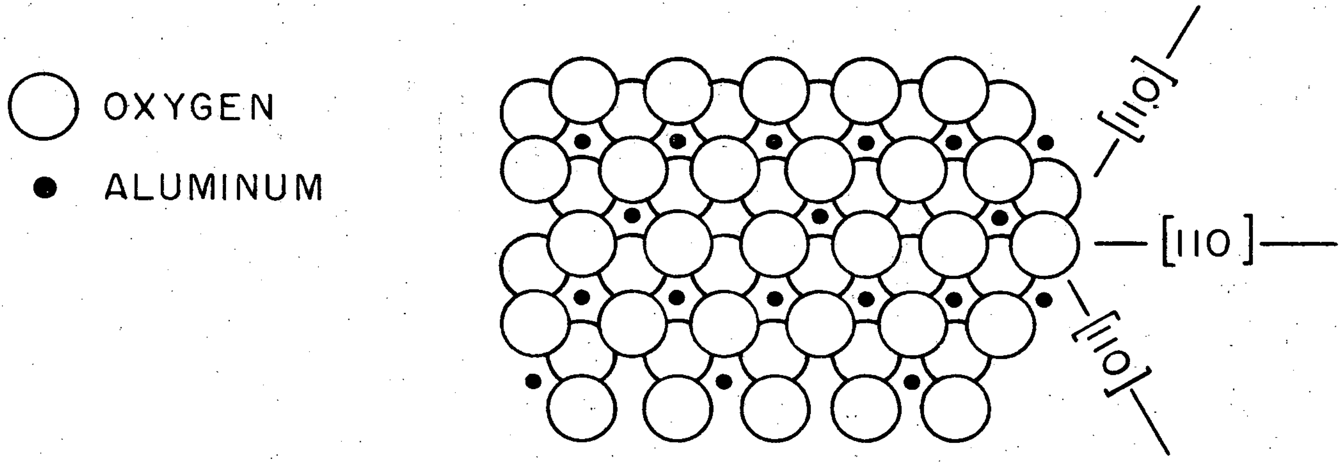
KAOLINITE



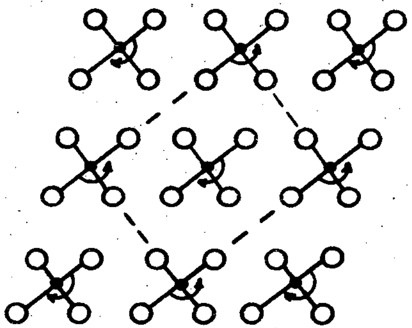
METAKAOLIN
(AFTER BRINDLEY[18])

Fig. 3

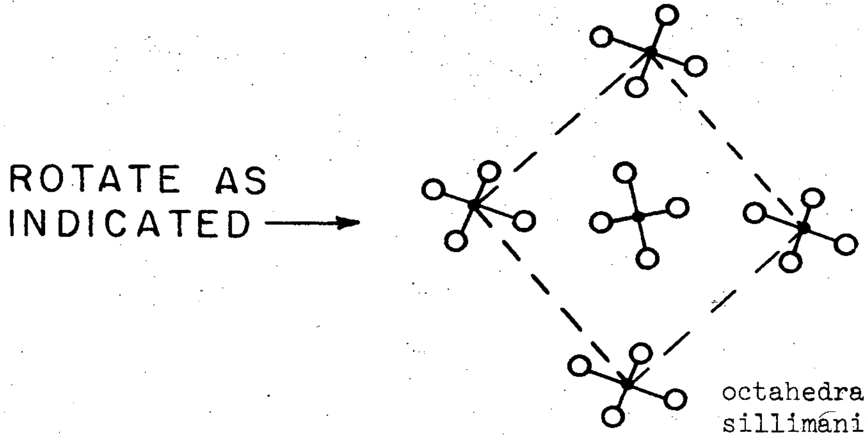
Fig. 4



Projection of the proposed spinel (octahedral layer)



Octahedral chains in the spinel structure as seen along the [110] .



octahedral chains in sillimanite as seen along the c axis.

creasing the temperature above 850°C showed a continued density increase which they considered due to the progressive entry of the top oxygen sheet into the Si-O network above it. In terms of chemical reactions the change is seen thus:

$$\begin{array}{llcll}
\text{Metakaolin layers} & \underrightarrow{O_6Si_4O_6\ Al_4O_2} & \Big| & O_6Si_4O_6\ Al_4O_2 \Big| \rightarrow & \text{etc.} \\
 & & \downarrow & & \\
 & O_8Si_4O_6\ Al_4 & \Big| & O_8Si_4O_6\ Al_4 \Big| \rightarrow & \text{etc.} \\
 & & \downarrow & & \\
\text{Spinel "layers"} & \underrightarrow{O_6Si_3O_6\ Al_4} & \Big| & O_6Si_3O_6\ Al_4 \Big| \rightarrow & \text{etc.} + SiO_2
\end{array}$$

The instability of a system in which alternately six oxygens and eight oxygens are packed in layers can be expected to lead to the expulsion of an SiO_2. It should be noted that for each mole of original kaolinite, a half mole of SiO_2 would be discarded in the formation of the spinel.

The normal spinel structure is cubic with a = 8.0 au. Eight of the cations are tetrahedrally coordinated, sixteen octahedrally coordinated with thirty-two oxygens forming a face-centered-cubic cell. A spinel can also be regarded as a layer structure with respect to the four [111] axes. The cation coordination number in the spinel layers alternates between being purely octahedral in one layer and mixed octahedral and tetrahedral in the next. Hence the layer configuration is,

$$16[O]\ \Big|\, 5\tfrac{1}{3}\ B\_\ \ 8A.\ \Big|\ 16[O]\ \Big|\, 10\tfrac{2}{3}\ B\_\ \Big|\ 16[O]\ \Big| \ \rightarrow$$

where A is a tetrahedrally coordinated ion and B an octahedrally coordinated ion. Based on this configuration, Brindley and Nakahira propose a layer formula for the aluminum-silicon spinel of the form

$$16[O] \mid 5\tfrac{1}{3}\,\square\,\mathrm{Si}_8 \mid 16[O] \mid \mathrm{Al}\ 10\tfrac{2}{3} \mid 16[O] \mid \rightarrow$$

in which the symbol $\square$ indicates a vacant site. They point out that this number of vacancies probably produces an unstable structure and this is consistent with the rather short temperature interval over which the spinel structure persists. They discount an inverse-spinel structure as an alternative for this would require octahedrally-coordinated silicon. The authors continue:

> "from the standpoint of chemical composition, it has been suggested that the aluminum-silicon spinel has an oxide composition of 2 Al_2O_3, 3 SiO_2 and in order that this may transform to mullite, silica must diffuse from the structure. At an intermediate stage in this removal, the composition must pass through the one-to-one ratio."

For mullite of such a composition to be formed, even though highly metastable, another half mole of SiO_2/mole of original kaolinite must be discarded. The advantage of the theory put forward by Brindley and Nakahira is that it explains the topotaxial relationships experimentally observed by Comefero, Fischer and Bradley[20] and Comer, Koenig and Lyons.[21] In summing up their work Brindley and Nakahira observe:

> "In view of the continuity of these reactions, it is conceivable that some mullite may appear at a temperature lower than 1050°C, as a result of the atomic arrangement into a mullite-like arrangement."

Many authors have reported a mullite-type phase below 1050°C and this will be discussed in greater detail later.

The exact phase whose appearence causes the observed exothermic reaction at 980°C is a point of controversy. Some consider the appearance of the mullite phase as the reason and others hold the spinel phase responsible. Authors supporting the spinel explanation are Colgrave and Rigby,[16] Stone,[4] and Brindley and Nakahira,[3,17-19] and most recently Tsuzuki.[23] On the other hand Insley and Ewell[24] showed that on heating co-precipitated alumina and silica to 980°C an exothermic reaction of the same order as that of kaolinite was observed. It is very unlikely that the spinel would develop in such a case. However, mullite might be produced. Glass[25] observes that the formation of a dense hard phase much more easily explains the observed exotherm than does a subcrystalline compound such as a defect spinel. This opinion is also held by Comefero, Fischer and Bradley.[20] Roy, Roy and Francis,[14] in their electron-diffraction work, detected the spinel phase in kaolinite at 850°C and at 650°C in halloysite. In both cases however the exothermic peak was observed at 980°C. Likewise Comer[26] endeavoring to observe the Brindley-spinel with an electron-microscope, identified both spinel and mullite in a kaolinite flake fired to 850°C. In the same experiments he observed the spinel to disappear about 950°C while mullite increased rapidly.

Considering which reaction is most favorable thermodynamically, the contribution of Schieltz and Soliman[27] is of great significance. They considered a series of reactions which metakaolin might undergo and from the known enthalpy and entropy values arrived at a free-energy value for each reaction. In this way they concluded that the reaction;

$$\text{Metakaolin} \rightarrow \frac{1}{3}\,\text{mullite} + \frac{4}{3}\,SiO_2\ \text{(crystalline)}$$

is most favorable. Considering the enthalpy change embodied in each of the possible reactions and the energy of crystallization of each phase involved, they solved the thermodynamic equations simultaneously and found the crystallization energy of mullite to be -336 kcals/mole; the spinel -36.5 kcals/mole and quartz -7 kcals/mole. Considering the most favorable reaction they estimated the contribution of the mullite-crystallization to the exotherm as -112 kcals and that of the silica-crystallization -9.6 kcals. They neglected, however, to compare the resultant theoretical enthalpy with any experimentally determined values. De Bruijn and Van der Marel[28] estimated the heats of transformation of forty-two minerals. They utilized the technique of D.T.A. associating the areas of differential temperature peaks obtained with the enthalpy of the reaction taking place. One of the minerals investigated was kaolinite and they estimated the heat released at the 980°C-exotherm between 5 kcals/mole and 8 kcals/mole of kaolinite. In the same year Sabatier,[29] also using D.T.A., measured the reaction heats for 6 minerals including kaolinite and obtained values in the De Bruijn-Van der Marel range. Neither De Bruijn and Van der Marel nor Sabatier utilized their results to postulate what reaction might be the source of the exotherm. D.T.A. results must, however, be suspect as the reaction is very sharp and quantitative D.T.A. inaccurate. It is hoped that the work reported in this dissertation will somewhat clarify the rather confused state of affairs just reviewed.

III. EQUIPMENT AND EXPERIMENTAL TECHNIQUE

A. Apparatus

The technique used in the investigations reported in this thesis was that of differential thermal calorimetry (D.T.C.). The basic principle of D.T.C. is to supply or subtract heat to or from a reacting system so as to maintain the temperature at some point in the system the same as that of a similar point in a physically inert system. A small heater is used to supply the necessary heat and the power supplied to this heater is monitored. In this way the unknowns in the thermodynamic equation,

$$H_T = H_{298} + \int_{298}^{T} C_p \, dT$$

H_T = Heat content at T°K
H_{298} = Heat content at 298°K
C_p = Heat capacity at const pressure

can be evaluated. The technique is not new and was first used by Eyraud[30,31] in 1954 and the following year by Charuel and Traynard[32] and Clareborough, Hargrieves and West.[33] Charuel and Traynard studied a solution reaction by supplying heat to an inert solution and thus keeping its temperature the same as that of an identical reacting solution. Clareborough, Hargrieves and West took two identical pieces of metal and cold-worked one of them. They then heated both samples and estimated the release of energy accompanying the annealing of the worked sample. This they did by supplying a measured amount of heat to the inert sample to keep both sample-temperatures identical. Orani and Murphy[34] utilized the same principle to estimate the heats of formation of solid alloys of the noble metals. The technique was also used by Kleppa[35] to investigate heats of mixing in liquid sodium-posattium nitrates. The first attempt to apply the method to the thermodynamic investigation of ceramic systems was made by Barner.[36] The results Barner obtained for ceramic powders were grossly in error compared with the accepted ones. The cause of the error was deemed to be one of design and the present author[37] redesigned the whole system taking care that heat transfer conditions always be such as to give accurate results.

The present design of the D.T.C. is shown in Fig. 5. A large block of nickel has two parallel holes drilled through it. In the center of each of these holes is placed one of the calorimeter cells. The intervening space between the cell and the cavity-periphery is filled with zirconia powder. The utilization of a large nickel block guarantees that each cell be in an identical isothermal environment. A small 25 ohm Kanthal heater is located in the center of each cell. These heaters are wound on boron nitride formers and the end caps of the cells are also boron nitride. The design of the two heaters is not the same, but both have the same electrical resistance. The heat capacities of both cells are also identical. Cell A contains the sample and the other cell is left empty. The power to the sample cell is maintained constant at all times. The power to the control or empty cell however is varied in such a way as to maintain the outer walls of the two cells at identical temperatures. The power imput to both cells is accurately monitored with watt-meters and their outputs simultaneously traced on a two-pen recorder. In this way any reaction taking place in the sample is directly measured and a power-time curve obtained. The area of the resulting peak gives an estimate of the heat of reaction taking place in the sample. By leaving the control cell empty, the heat content of the sample at any temperature can also be estimated. Thermocouples, D, E, and G enter through the base of the metal block through boron nitride insets. C, D and E are linked differentially

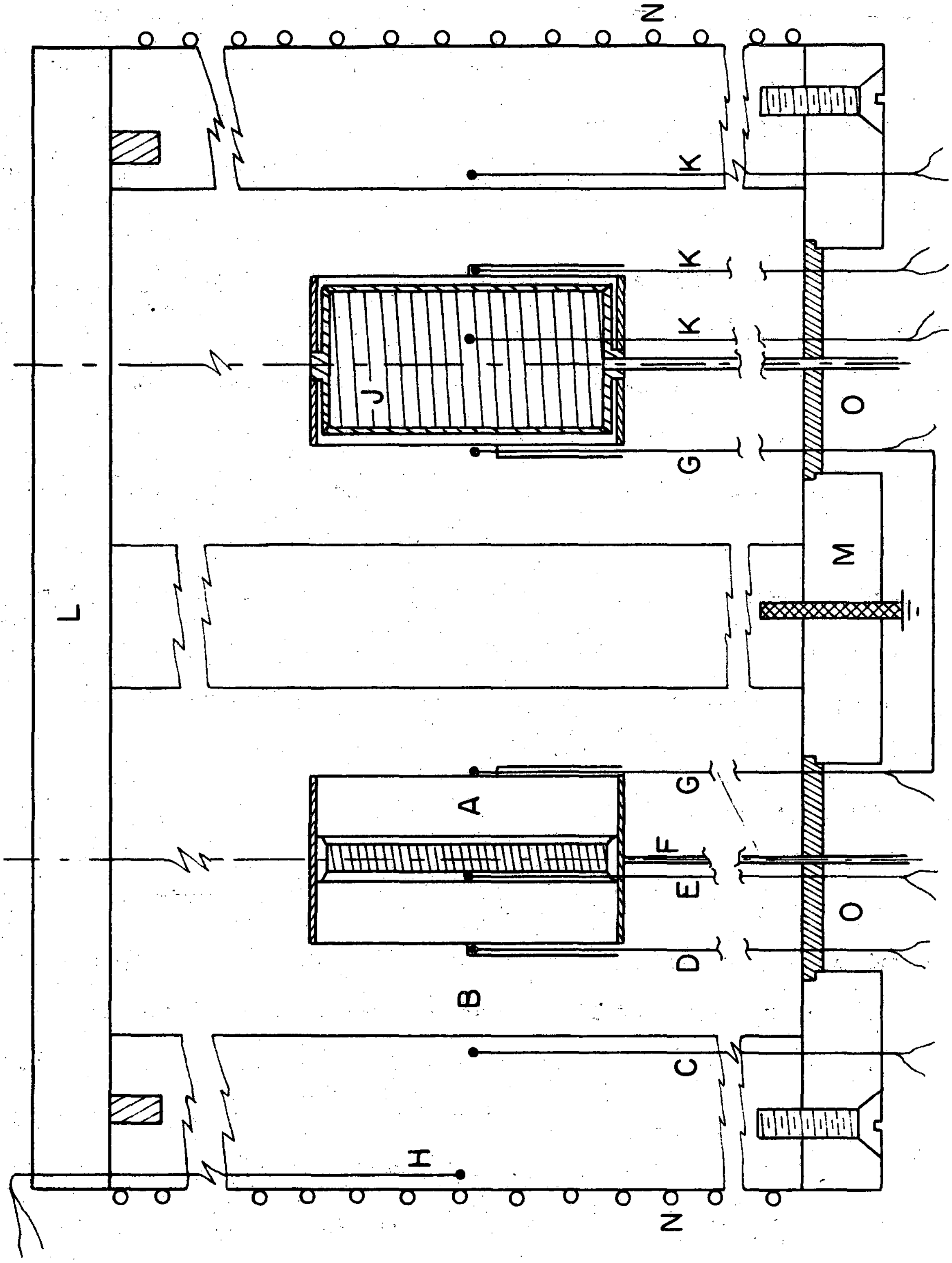


Fig. 5

Key to Differential Thermal Calorimeter Complex

Figure 5

A. Sample in sample-cell.

B. Zirconia powder around each cell.

C. Chromel-alumel thermocouple measuring the nickel block temp.

D. C-A thermocouple differentially linked with C; comparing the temperature of the outer wall of the sample cell with that of the nickel block.

E. C-A thermocouple linked differentially with C; comparing the temperatures of the sample-cell heater wall and that of the nickel block.

F. Sample-cell-heater leads.

G. Platinum-platinum/10% rhodium differential thermocouple used to control the power imput to the control-cell J.

H. C-A thermocouple controlling the main furnace N.

J. Boron nitride control-cell heater.

K. Temperature gradient thermocouples for the control-cell.

L. Nickel top.

M. Nickel bottom.

N. Main-furnace widning.

O. Boron nitride inserts.

in such a way that C records the base temperature and E and D the differential gradients from this temperature. G is the differential couple whose signal controls the power imput to the empty cell. This differential temperature signal is maintained at zero at all times. Thermocouple H monitors the nickel block temperature and controls the power imput to the furnace winding. Heat is supplied to the outer circumference of the nickel block.

Boron nitride is used at various points on the D.T.C. complex to ensure low electrical leakage and low thermal conductivity at high temperatures. The useful range of the instrument is from room temperature to 1100°C. This upper limit is dictated by electrical leakage phenomena interfering with the correct operation of the cell-power control system. For accurate operation of the instrument it was postulated[37] that,

a) There must be complete symmetry within the system.

b) The heater in the center of the cell must supply all the heat required by the cell.

c) For sensitive control, the response of the active or empty cell must be as quick as possible.

d) The gradient across the sample must be as low and as constant as possible.

e) All heat must flow radially from the cell heaters and therefore axial heat flow must be minimized.

f) The cells must be thermally and electrically isolated from one another as far as possible.

Condition (a) was obtained by appropriate design. The zirconia powder between the cells and the nickel block was introduced to meet conditions (b) and (d). Considering the system as it relates to each cell, there are two heat sources in opposition i.e., the main furnace and the cell heater. Located between these is the differential couple which is part of the sensitive cell-power control system. For accurate work no heat from the furnace should reach this couple, i.e., the temperature gradient minimum should always be outside the cell. Differential couples C,D and E monitor this condition constantly. The intervening zirconia powder acts both as an insulator for radiation and convection heat transfer and a heat sink. Zirconia is ideal for this purpose as it has a low and constant thermal conductivity. Zirconia powder is also stable with respect to sintering up to 1100°C, thus its insulative properties are maintained. To ensure the sensitive control required by condition (c), the control-cell heater is of a different design. It is located as close as possible to the controlling differential thermal couple on the cell outer-wall. The whole system is operated in an inert gas atomosphere which contributes significantly to condition (c) also. Axial heat flow is minimized by making the powder thickness above and below the cell ends four times that between the cell outer walls and the surrounding nickel block. Finally the design is such as to completely isolate the cells from each other thermally and electrically. The whole D.T.C. system is shown schematically in Fig. 6.

B. Calibration of the Differential Thermal Calorimeter

To demonstrate the accuracy of the D.T.C. design just described, heat content and specific heat data were obtained on alpha-quartz and alpha-alumina. In the quartz case the alpha-to-beta inversion enthalpy was also measured. The data so obtained were then compared with accepted literature values.

The quartz used in the calibration was ground crystalline alpha-quartz from Brazil. The alumina used was grade A-14 supplied by the Alcoa Company. This material was milled for two hours before use in order to break up any

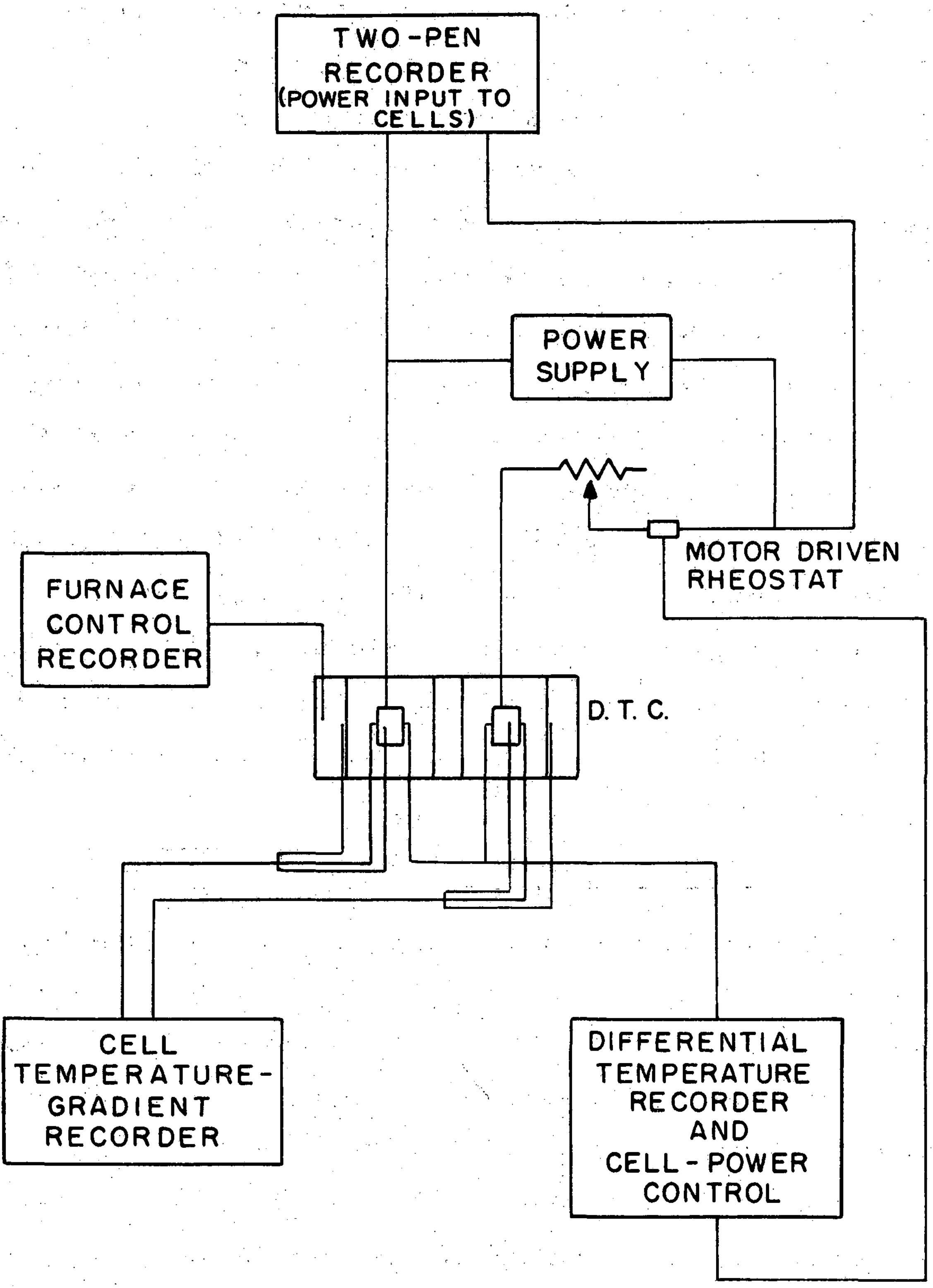


Fig. 6 D.T.C. system.

agglomerates. The quartz powder was sized -100 +200 mesh and was 99.85% SiO_2. Likewise the alumina was sized as -100 +200 mesh with an alpha alumina content of +95%. The D.T.C. results for quartz were compared with those of Kelley,[38] the alumina results compared with those of Furukawa, Douglas, McCoskey and Ginnings.[39] The sample powder was carefully packed into the sample cell and the weight of the powder ascertained by difference. The calorimeter was pumped down to a vacuum of 1μ. Following this the whole system was flushed with argon and the flow or argon finally controlled to 2 cc/sec. Power was introduced into both cells and regulated so that the sample-cell received 5 watts. All differential temperature and power-control circuits were then allowed to equilibrate for one hour. When this step was completed the main furnace was turned on and controlled to give a temperature rise of 1°C per minute. The temperature was increased in steps of 100°C with isothermal periods of one hour between each step. This procedure was continued until the furnace temperature reached 1000°C. Throughout the whole experiment the temperatures across each cell system were continuously monitored. This ensured that the correct temperature sequence was always maintained. Each peak area, corresponding to the retardation of the empty-cell-power due to the sample heat-capacity, was then carefully measured with a planimeter. Accepting the literature values for the material heat-content at room temperature, the measured increase in heat content per 100°C was consecutively added and a heat-content vs temperature curve thus plotted. Three estimations of total heat content were made on the alpha-quartz and two on the alpha-alumina. The results are shown in Figs. 7 and 8. In all cases it can be seen that the D.T.C. values and those of the literature are in close agreement. In view of the comparative brevity of the D.T.C. determination as compared with the protracted procedure normally utilized in the gathering of such data, the

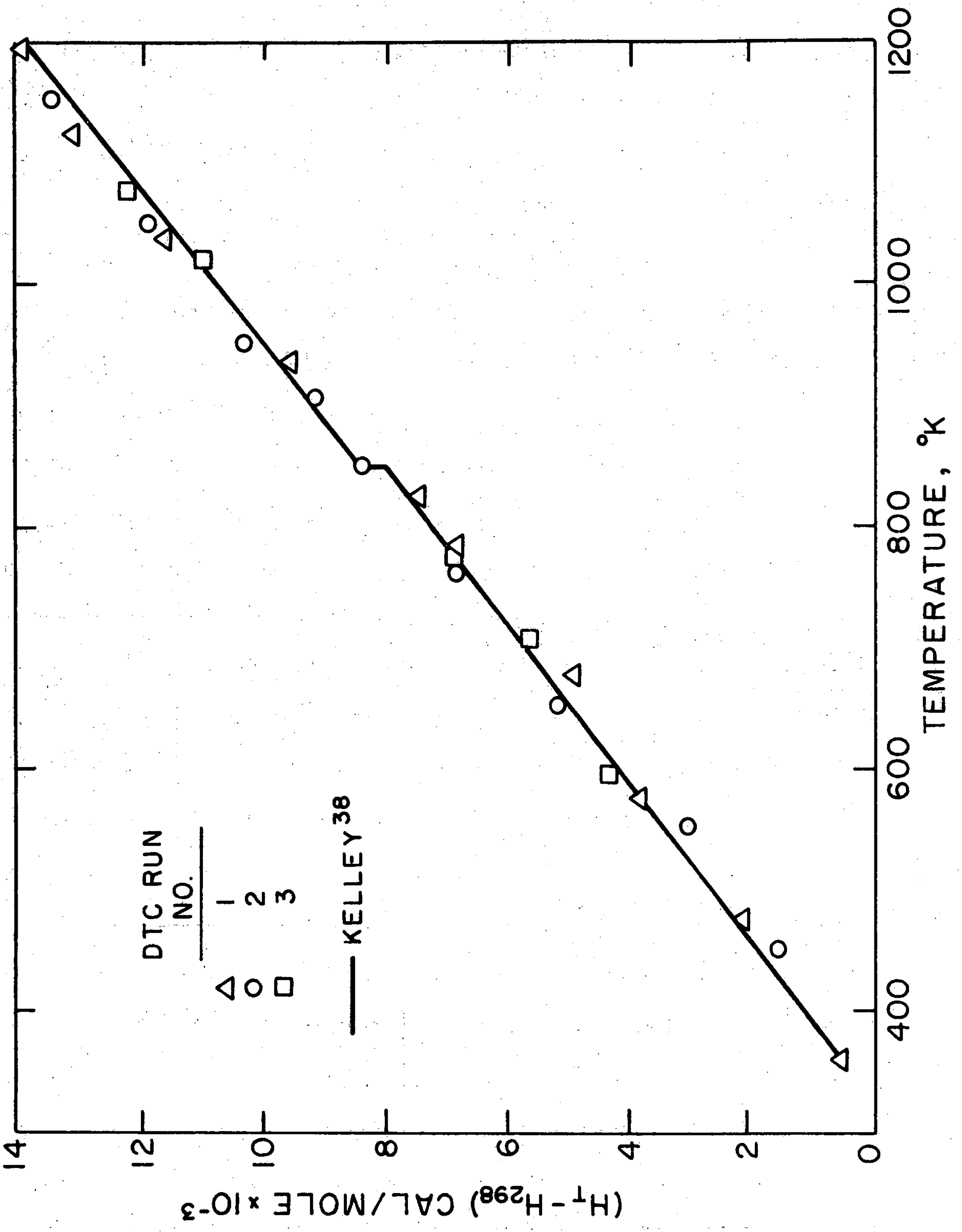


Fig. 7 Total heat content of SiO_2 vs temperature

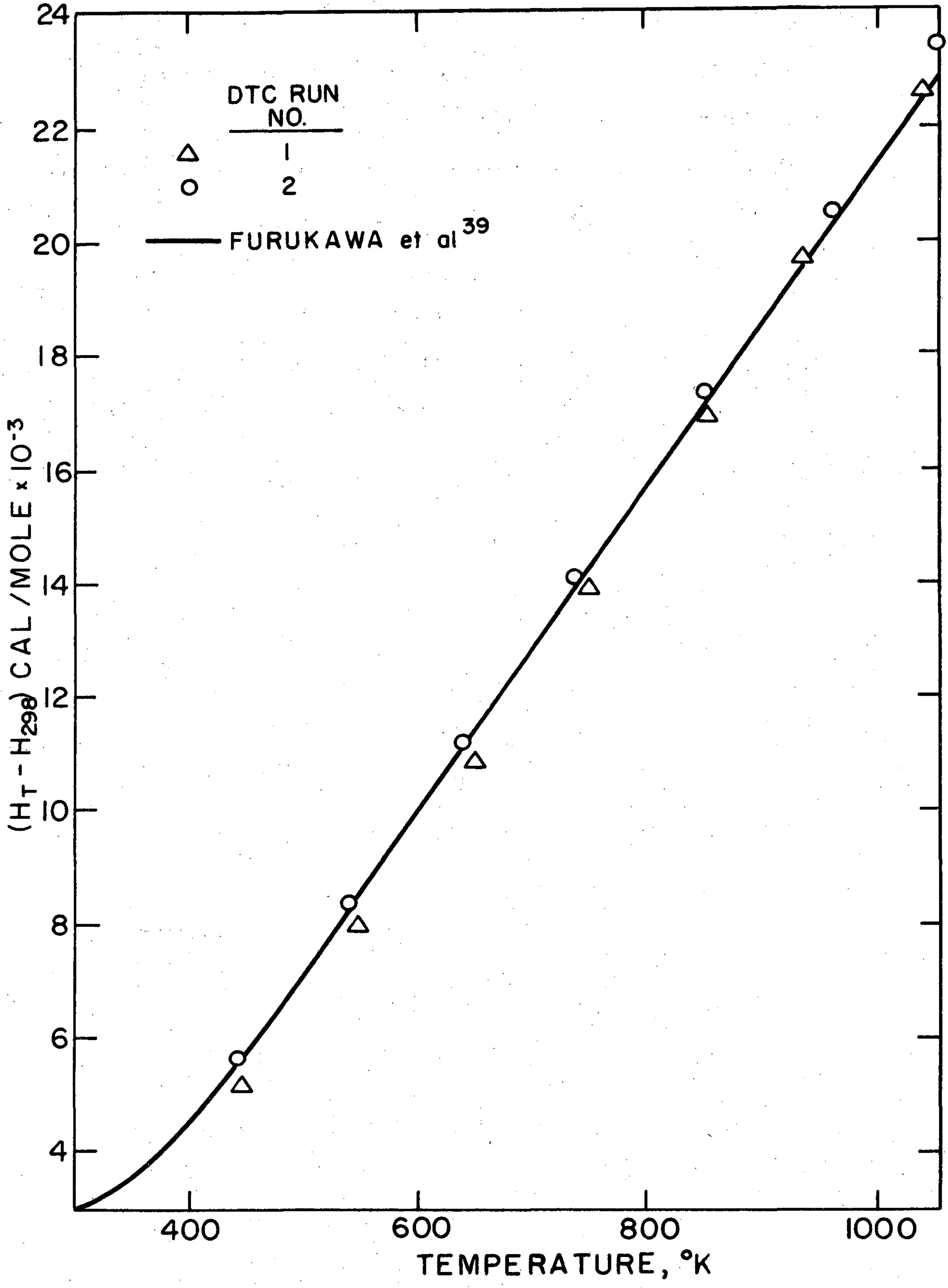


Fig. 8 Total heat content of Al_2O_3 vs temperature.

D.T.C. method has obvious advantages. The data obtained agreed with the literature values within ±2%. Three estimations were made of the alpha/beta quartz inversion enthalpy. The values obtained were 305 cals/mole SiO_2, 250 cals/mole SiO_2 and 280 cals/mole SiO_2. These values compare favorably with the 290 cals/mole SiO_2 of Kelley.

In summary therefore it can be said that the calibration runs undertaken on the D.T.C. demonstrated it to be a reliable and reasonably accurate instrument for the compilation of thermodynamic data.

IV. ESTIMATION OF THERMODYNAMIC PROPERTIES OF KAOLINITE

A. Introduction

The experiments described in the previous section were repeated on samples of kaolinite. Four samples from different geographical areas of the United States were studied. These kaolins were chosen by virtue of their comparative freedom from impurities. Three of the samples were A.P.I.[40] standard kaolins and the fourth a Georgia kaolin. Hereafter the four samples will be referred to as API 4, API 9, API 17 and DRG kaolin. The API 4 sample came from Macon, Georgia and is known locally as "crude O'Neal" kaolin. The O'Neal kaolin is hard, white and contains no grit. The only reported impurity is mica. The API 9 sample occurs as flat lenticular bodies of kaolinite in the horizontal sedimentary rocks in-and-about Mesa Alta, New Mexico. The third API sample came from Lewistown, Montana. The final kaolin investigated, i.e., the DRG sample, also comes from Georgia. Chemical analyses of each clay are given in Table III. D.T.A. curves for each kaolinite are shown in Fig. 9.

B. Experimental

Each clay sample was ground, ball-milled and sieved through a 200 mesh sieve. Half of each sample was then fired at 1050°C and the other half dried at 110°C. Calorimeter samples were obtained by carefully remixing a 50/50 combination of the 110°C and 1050°C treated samples. This procedure was necessary owing to the magnitude of the heats to be measured. The calorimeter cell was carefully packed with about 16 grams of sample. Two estimations of the 550°C endotherm and the 980°C exotherm were made on each of the API clays. Three endothermic and five exothermic estimations were made on the DRG sample. Typical endo- and exothermic D.T.C. peaks are shown in Fig. 10.

Table III. Chemical analyses of kaolinite samples.

	API 4*	API 9*	API 17*	DRG.**
SiO_2	44.82%	46.07%	45.72%	47.24%
Al_2O_3	37.20	38.07	39.82	35.72
Fe_2O_3	0.41	0.33	0.10	0.27
FeO	0.07	---	---	0.06
MgO	0.25	0.01	trace	0.47
CaO	0.58	0.38	trace	0.52
Na_2O	0.40	0.27	0.16	0.36
K_2O	0.43	0.43	0.36	0.49
H_2O	14.68	13.90	14.22	14.82
TiO_2	1.26	0.50	0.42	0.26
Total	100.10	99.96	100.80	100.21

* American Petroleum Institute.

** Chemical analysis given by supplier.

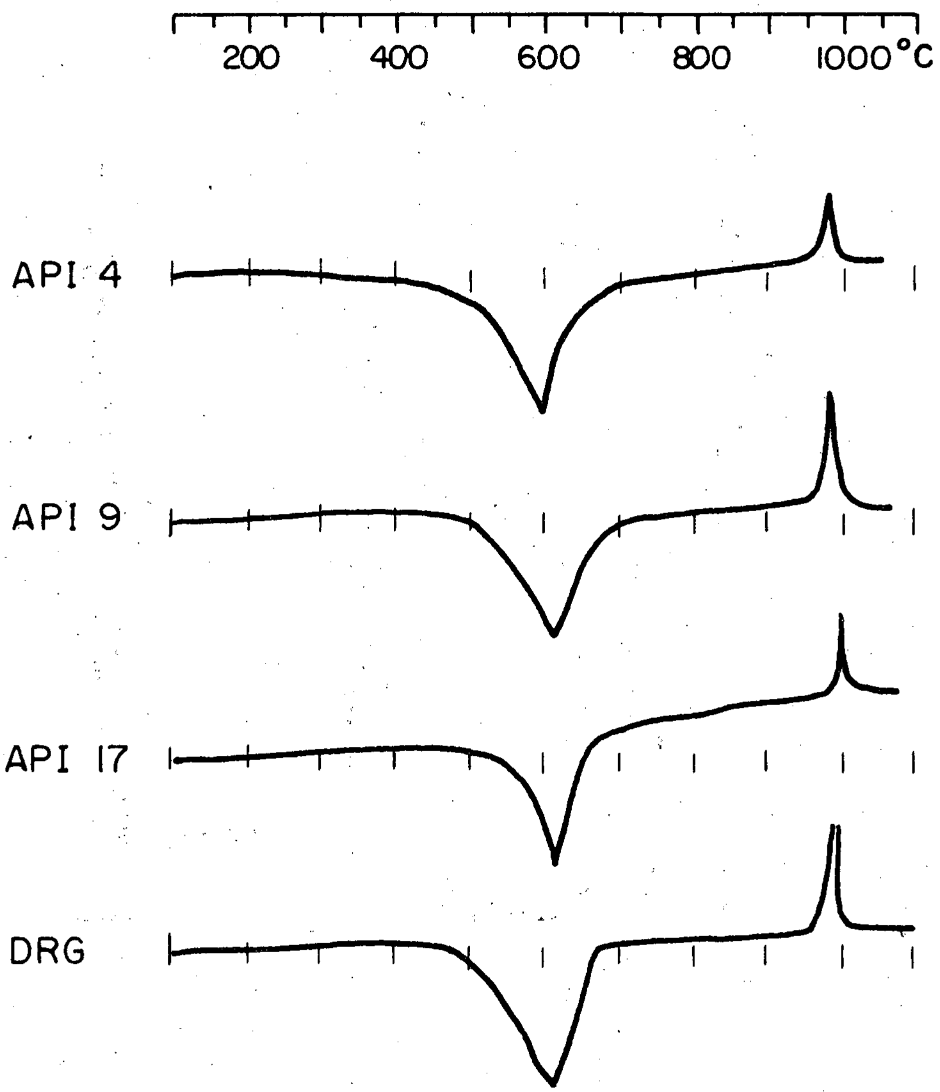


Fig. 9 D.T.A. curves for kaolinite samples:

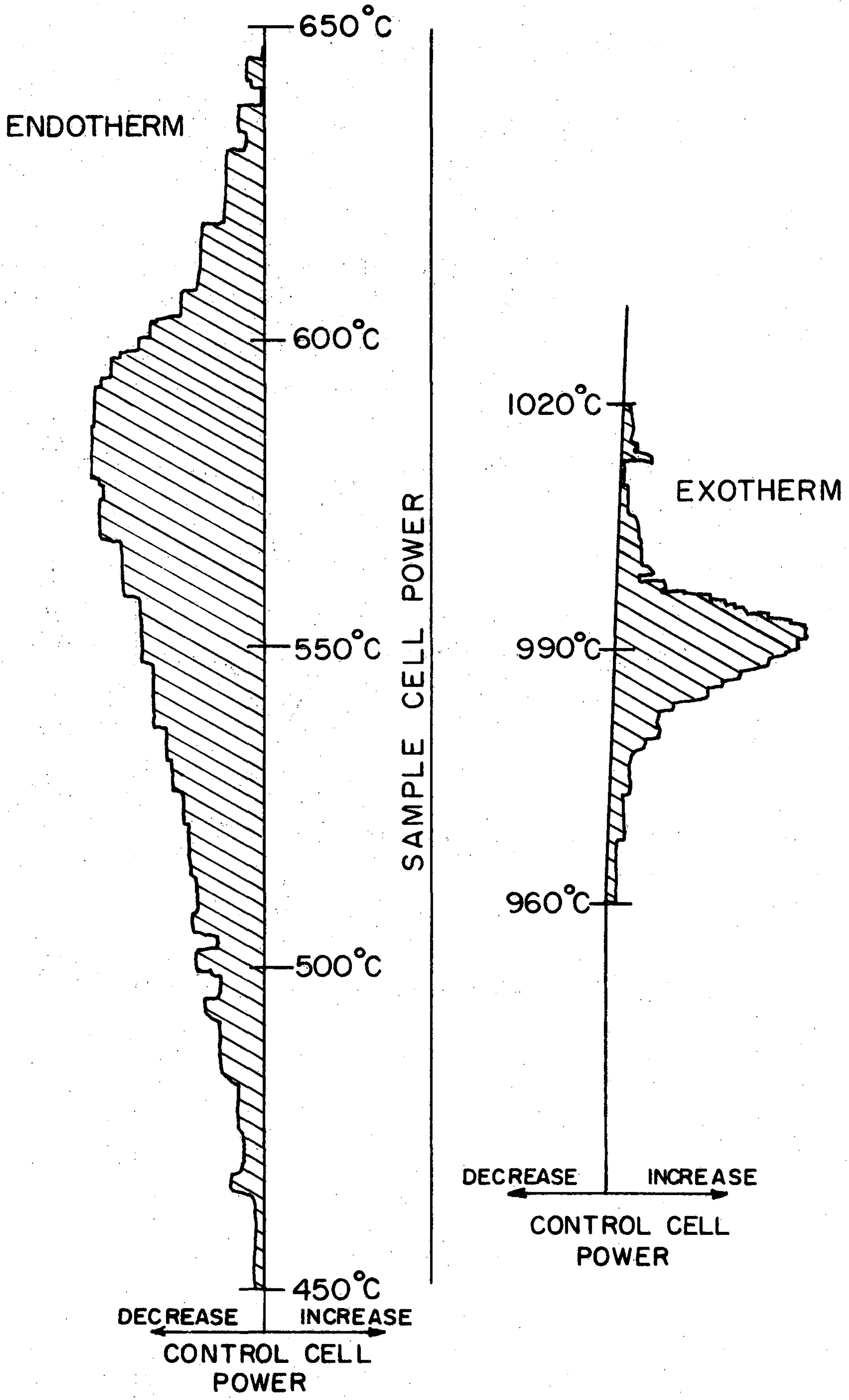


Fig. 10 D.T.C. curves for kaolinite.

A total heat content vs temperature run was made on DRG-metakaolin and the curve obtained is shown in Fig. 11. The results obtained for the 550°C-endotherm and the 980°C-exotherm are summarized in Table IV. All these results are based on one molecular weight or original kaolinite.

C. Discussion

The D.T.C. 550°C-endotherm heats agree well with all but one of the literature values previously discussed. To demonstrate this agreement concisely, the literature and D.T.C. values are shown in Table V.

The results obtained for the 980°C-exotherm are extremely interesting because their magnitude allows a new interpretation of this controversial reaction. Schlietz and Soliman[27] calculated the heat of crystallization of mullite to be -336 kcals/mole, of the alumina-silica spinel -36.5 kcals/mole, and of silica -7 kcals/mole. They obtained these values by simultaneously solving the enthalpy-equations for the six possible metakaolin reactions. The only crystallization enthalpy in approximate agreement with the D.T.C. results is that of silica. This author, utilizing the Schlietz-Soliman summary of reliable values of thermodynamic properties of kaolinite and its products, estimated the enthalpy of crystallization of one mole of amorphous silica at 1000°C as follows;

$$\Delta H_{298} \text{ for } \beta\text{-quartz} = -209,900 \text{ cals/mole}$$

$$C_p = 14.41 + 1.94 \times 10^{-3} T$$

$$\Delta H_{298} \text{ for } SiO_2 \text{ glass} = -202,000 \text{ cals/mole}$$

$$C_p = 13.38 + 3.68 \times 10^{-3} T - 3.45 \times 10^{-5} T^{-2}$$

From

$$\Delta H_{1280^\circ K} = \Delta H_{298} + \int_{298}^{1280} \Delta C_p \, dT$$

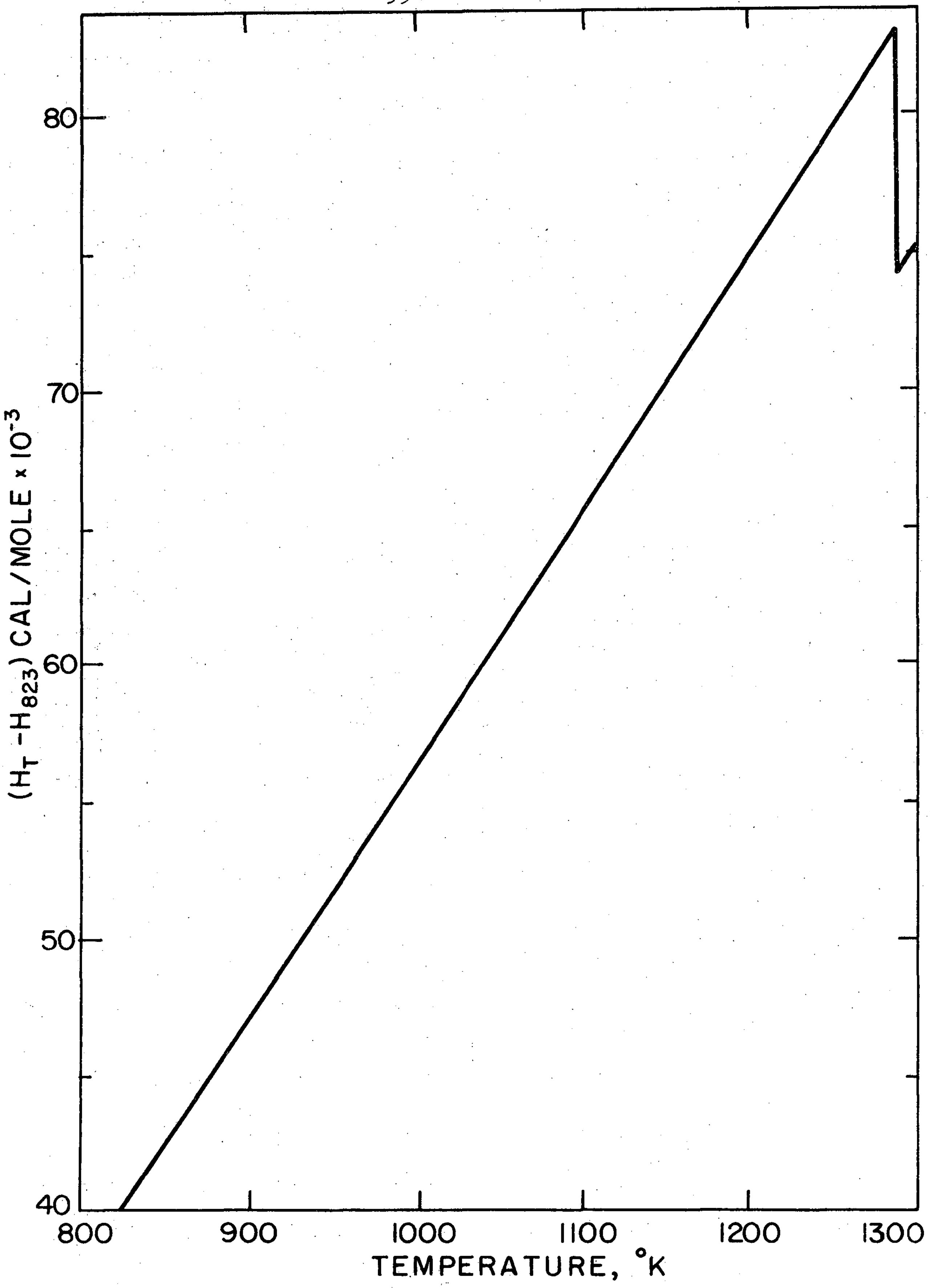


Fig. 11 Total heat content of metakaolin vs temperature °K.

Table IV.

D.T.C. values for the endothermic and exothermic reactions of kaolinite.

Material	Reaction	ΔH (kcals/mole)
API 4	550°C endotherm	35
		44
API 9	550°C endotherm	39
		41
API 17	550°C endotherm	39
		39
API 4	980°C exotherm	9.1
		8.5
API 9	980°C exotherm	8.4
		8.3
API 17	980°C exotherm	8.3
		8.7
DRG	550°C endotherm	48
		47
		45
DRG	980°C exotherm	8.7
		9.2
		8.8
		8.7
		8.7

Table V.

Comparison of ΔH values for the 550°C endotherm of kaolinite.

Reference	Method	ΔH (kcals/mole)
5	DTA and kinetics	37
6	Weight-loss	45*
7	Weight-loss	41*
8	Weight-loss from a specimen of zero thickness	65*
9	Loosely-packed sample and weight-loss	44*
10	Freeman-Carroll equation	38
12	Weight-loss in vacuo	44
This paper	D.T.C.	35 44 39 41 39 39 48 47 45

* Activation energies.

$$\Delta H_{1280^\circ K}\ [SiO_2 \text{ glass} \rightarrow \beta\text{-quartz}] = 9.1 \text{ kcals/mole}$$

This result is even closer to the measured value.

Three phases are known to be present at the 980°C exotherm, i.e., mullite, silicon spinel and silica. Brindley and Nakahira[3] consider the exotherm to be the result of the condensation of the metakaolin layers to form the spinel-type phase. However, as reported earlier, Roy, Roy and Francis[14] observed the cubic spinel phase at 850°C in the case of kaolinite and at 650°C in the case of halloysite. On heating both samples to 980°C the exotherm was observed. This evidence alone would discount spinel formation as being the reason for the heat release. It has been pointed out[3] that the reaction series is a continuous process rather than an intermittent one. Hence there is no reason why the spinel phase which has been continuously appearing should give rise to a sudden sharp exothermic reaction such as observed at 980°C. The same argument will also apply to the mullite phase. Comer[26] observed mullite at 850°C. Brindley and Hunter[15], on the other hand, feel that:

> "it is still necessary to explain the apparent absence of mullite after the exothermic effect."

The only phase remaining is the amorphous silica. This silica has been continuously discarded during the spinel and mullite crystallizations and it could be that the concentration of silica at 980°C is such as to favor a sudden crystallization. Hence, although it is not possible to completely discount any heat contribution due to the mullite and spinel crystallization, it is the contention of this thesis that the exothermic heat release is due mainly to the crystallization of the discarded amorphous silica.

The measured heat corresponds to the crystallization of one mole of silica/mole of original kaolinite. This amount of silica corresponds to a mullite composition of $Al_2O_3:SiO_2$. Although no such phase has ever been experimentally observed on heating kaolinite, its existence was tentatively suggested in this connection by Brindley and Nakahira.[3] To form the conventional 3:2 mullite it is necessary to discard 4/3 mole of silica/mole of original kaolinite. Were such an amount of amorphous discarded silica present at 980°C the calculated heat release on its crystallization would be approximately 12 kcals/mole of silica. However, as pointed out by Brindley and Nakahira:[3]

> "It appears that the mullites at lower temperatures are not strictly the same as the 3:2 type and that at the lower temperatures some of the excess silicon ions may still be distributed among the interstitial sites of the mullite lattice."

This, it is postulated, would account for the crystallization of only one mole of the silica.

How does this quartz crystallization explanation of the exotherm concur with the rest of the literature evidence available? In 1951 Grim and Bradley[41] observed a quartz phase to develop suddenly in montmorillonite at a temperature of 1000°C. Ross and Hendricks[42] noted that if a montmorillonite specimen has no Al^{3+} substitution for Si^{4+}, then quartz is obtained on firing. If, however, some Al^{3} is tetrahedrally substituted in the silica layers then a spinel phase also appears. Montmorillonite and kaolinite are both clay minerals; however, montmorillonite possesses two silica sheets sandwiching an octahedral gibbsite layer. Kaolinite has only one silica sheet. A marked characteristic of kaolinite is the lack of tetrahedral site substitution that occurs in the mineral. Were the two minerals to behave in a similar manner on heating therefore, the Ross-Hendricks criteria would predict the formation of β-quartz. It should be emphasized here that the similarity of high temperature behavior of montmorillonite and kaolinite is merely hypothesized; β-quartz has yet to be experimentally proven as present after the 980°C kaolinite exotherm. Reporting at the 5th National Congress on Clays and Clay Minerals, Kulbicki[43] observed on the heating of montmorillonite:

> "The first crystalline product to appear is β-quartz at temperatures ranging from 910°C to 1200°C."

Figure 12 shows one of the diagrams included in this paper indicating the variation of x-ray intensity of different mineral phases as a function of the firing temperature. Similar observations were made in 1961 by Grim and Kulbicki[44] and later by Wahl and Grim.[45] Owing to the proximity of the Si-O layers in montmorillonite the x-ray appearence of β-quartz is easily understood. In kaolinite the Si-O layers are separated by an Al-O octahedral layer and consequently any β-quartz crystallites will be much smaller and hence are not detectable by x-ray techniques. However, the precedent for the formation of β-quartz can be considered well established.

One of the striking points about the exotherm is the consistency of the temperature at which it occurs for diverse alumino-silicates.[14] The exact temperature at which the peak occurs depends on such factors as particle-size and heating rate. Figure 13 shows some of the data obtained by Speil[46] on the effect of particle size on the exothermic D.T.A. peak of kaolinite. It will be noticed that the peak occurs over a range from approximately 980°C down to 950°C for a particle size ratio of 200:1!

On the effect of the heating rate, Smothers and Chang[47] state that:

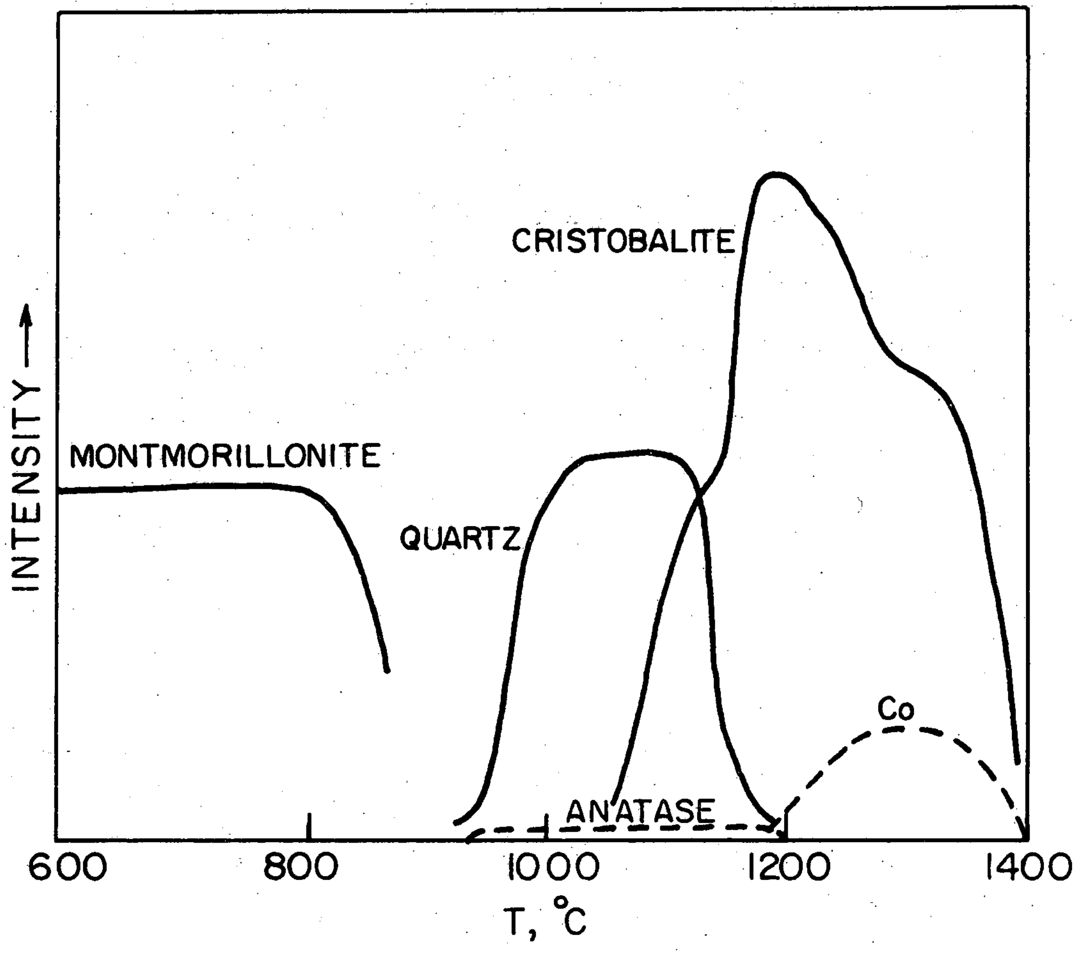


Fig. 12 Intensities of diffraction lines of high temperature phases in cheto montmorillonite (Kulbicki[43]).

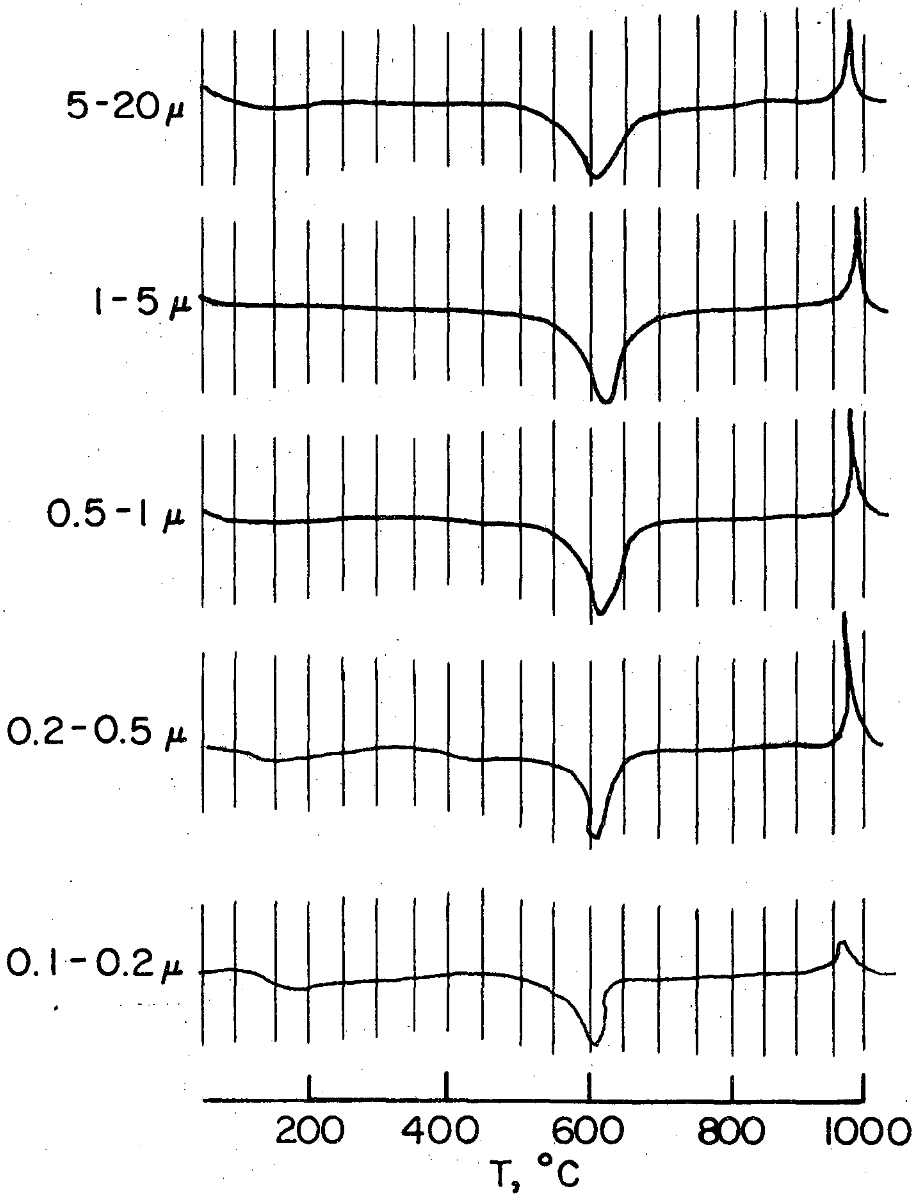


Fig. 13 Variation of differential thermal curves of kaolinite with particle size. (Speil et al.[47]).

> "for rapid transitions and those which are not accompanied by a loss of weight the initial transition temperature is not greatly affected by changes in the rate of heating."

Barshad,[48] using small amounts of compounds having relatively sharp transitions, found that the rate of heating had no effect on the temperature defining the initial thermal breaks. Arens[49] working with kaolinite observed that a three-fold increase in the heating rate produced a peak-temperature difference of 65°C. Comer observed mullite at 850°C and this would require a peak shift of 130°C. The remarkable agreement between the experimental and theoretical enthalpies is perhaps the strongest evidence however in favor of the quartz crystallization hypothesis. The quartz will be finely dispersed and therefore not detectable by x-rays. However Schleitz and Soliman note that:

> "The x-ray patterns made at room temperature of kaolinite and halloysite that had been heated at 950°C from 20 to 40 minutes showed small crystallites of alpha-quartz."

This however is the only observation recorded in the literature.

If the crystallization of quartz does in fact cause the exotherm, then removal of the discarded amorphous silica should eliminate the exotherm. Comer[26] found in his electron microscopic work on kaolinite that:

> "Replicas failed to show conclusively the presence of the spinel-type phase on any specimens, even at temperatures between 850°C and 1000°C. It was believed that this was due to excess scattering by the amorphous silica: An etching technique was therefore applied to the fired clays to remove free silica and thus make

> visible by both electron diffraction and electron microscopy the spinel-type and the mullite phases. Specimens were heated for 20 hours at temperatures of 850°C and 950°C. Upon removal from the furnace, the foils were placed in a 10% sodium hydroxide solution for one week. They were then washed in distilled water, rinsed in ethyl alcohol and allowed to dry."

Following this treatment, both the spinel-type phase and mullite could clearly be seen. Following Comer's procedure to the letter, four D.T.C. runs were made on an NaOH-treated D.R.G. kaolin. A further run was made on a D.R.G. sample which had been subjected to the same treatment except for the NaOH extraction. This sample served as a check on the correct functioning of the D.T.C. apparatus. The NaOH-treated samples showed no exothermic peak whereas the untreated sample showed the usual peak. To further demonstrate the absence of the exotherm, a multisample D.T.A. run was made. The three samples investigated were as follows:

a) raw D.R.G. dried at 110°C.

b) 850°C-fired D.R.G. untreated with NaOH.

c) 850°C-fired D.R.G. treated with NaOH.

The resultant trace is shown in Fig. 14 and this indicates the absence of the exotherm in the case of the NaOH-treated D.R.G. kaolinite sample. It is possible that the NaOH treatment also removes a good deal of the metakaolin. This would also remove the exotherm. Comer however observed mullite, spinel and the metakaolin matrix in his electron-micrographs after the NaOH treatment.

Hence, it can be concluded that removal of the amorphous silica as per Comer, in fact, eliminates the 980°C exotherm, thereby supporting the quartz crystallization hypothesis.

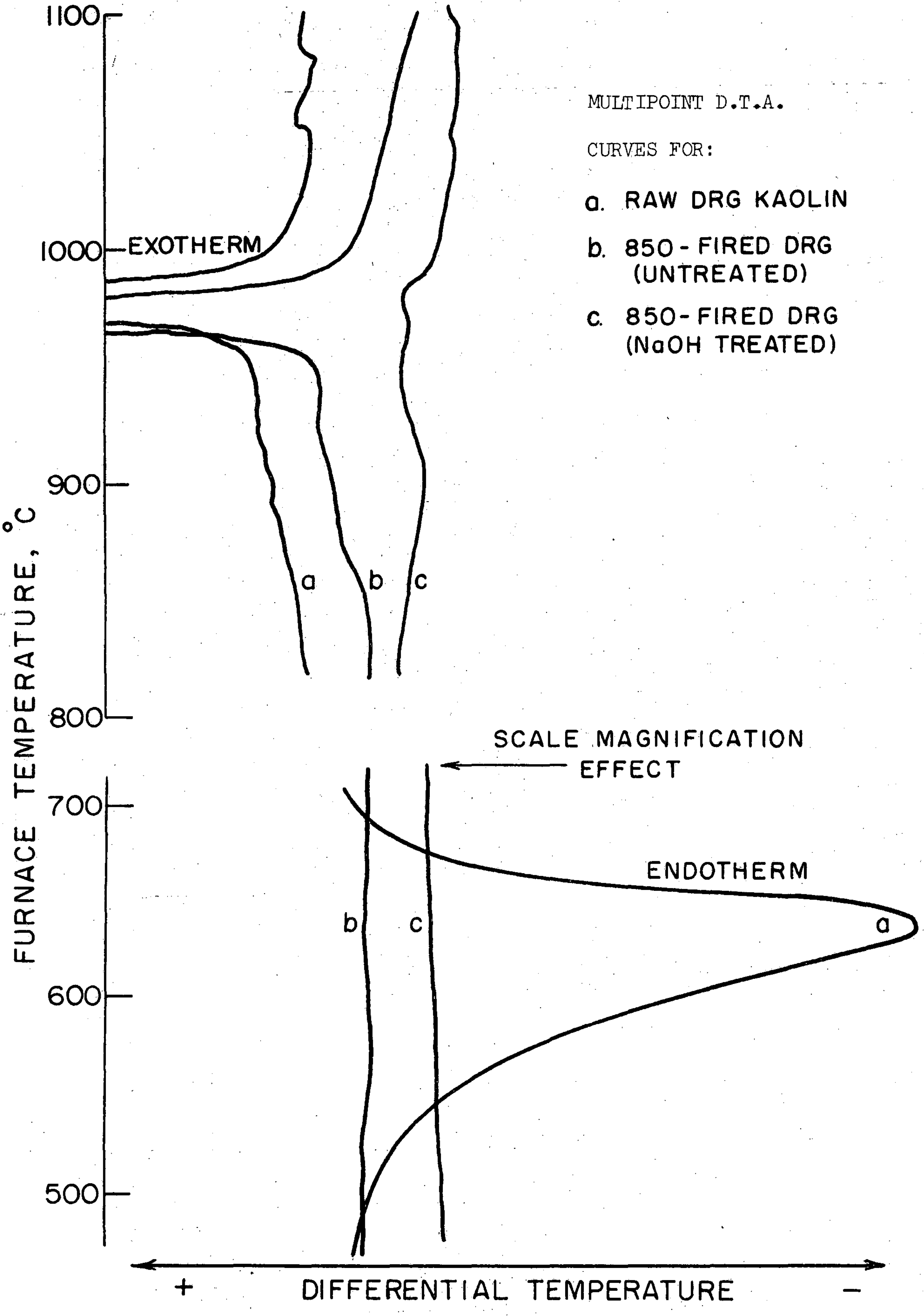

MULTIPOINT D.T.A.
CURVES FOR:
a. RAW DRG KAOLIN
b. 850-FIRED DRG (UNTREATED)
c. 850-FIRED DRG (NaOH TREATED)
1100
1000
900
800
700
600
500
FURNACE TEMPERATURE, °C
EXOTHERM
a
b
c
SCALE MAGNIFICATION EFFECT
ENDOTHERM
b
c
a
+
DIFFERENTIAL TEMPERATURE
−

Fig. 14

V. SUMMARY AND CONCLUSIONS

Following the modification of the original D.T.C. design,[36] the apparatus was carefully calibrated. The total heat contents of α Al_2O_3 and SiO_2 between room temperature and 1100°C were measured. The quartz $\alpha \rightarrow \beta$ inversion enthalpy was also measured. All the specific heat results were compared with accepted literature values and an agreement within ±2% observed. Having thus demonstrated the reliability of the apparatus, measurements were made of the 550°C-endothermic and the 980°C-exothermic heats of reaction of kaolinite. To eliminate any question of singularity, four specimens of kaolinite from different locations were investigated. The values obtained for the 550°C endothermic enthalpy varied from 35 to 48 kcals/mole. These values agree well with all literature values except the one obtained by Brindley and Nakahira.[7] The reason why the Brindley-Nakahira result is so much larger than the other literature and D.T.C. values is not clear.

The measured 9 kcals/mole for the 980°C exotherm facilitated a new appraisal of this reaction. Schlietz and Soliman[27] estimated the enthalpy values associated with the crystallization of the major phases known to be present at this temperature but failed to draw any conclusions as to the nature of the reaction. Van der Marel et al.[28] and Sabatier[29] measured the enthalpy by D.T.A. but again drew no conclusions as to the crystallization producing the exotherm. The Van der Marel-Sabatier results cannot be considered accurate. The work reported in this thesis is, as far as the author is aware, the first accurate measure of the 980°C exothermic enthalpy and also the first attempt to interpret the reaction on the basis of this enthalpy together with all known literature evidence.

Of the possible crystallizations that could give rise to such an exotherm that of silica is the most reasonable. Both mullite and silicon-spinel have been observed at temperatures below that of the exothermic reaction reported range. Also if the appearance of these two phases is to be considered a continuous process, then there is no reason to expect a sharp crystallization at 980°C. The hypothesis of this dissertation is therefore that the majority of the exothermic enthalpy accompanies the reaction:

$$SiO_2(\text{amorphous}) \rightarrow SiO_2(\beta\text{-quartz})$$

The calculated heat of this reaction is 9.1 kcals/mole. This value agrees very closely with that observed in the D.T.C. measurements. It must be emphasized however that it is not possible to completely discount any contribution of the mullite-spinel crystallizations to this enthalpy. Such contributions can however be reasonably considered as minor. The crystallization of silica hypothesis agrees with the work of Schlietz and Soliman.[27*] Such a crystallization would also indicate a possible similarity in the high-temperature behavior of kaolinite and montmorillonite.

Utilization of the Comer-NaOH extraction technique to remove the amorphous silica from an 850°C-fired kaolinite also removed the 980°C exotherm. This is further evidence in favor of the SiO_2 crystallization.

Finally this explanation of the origin of the exothermic enthalpy satisfactorily correlates thermodynamic and crystallographic thought on this reaction and in no way is achieved by any other explanation.

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[*] The crystallization of one mole of silica as suggested by the measured enthalpy would further confirm the reaction series envisaged by Brindley and Nakahira.

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