

# A KINETIC STUDY OF THE DEHYDROXYLATION OF KAOLINITE<sup>1</sup>

*By*

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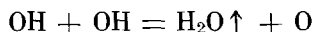
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## ABSTRACT

When dehydroxylation of kaolinite powder is carried out in the usual way, the linear relations anticipated for first-order kinetics and for the Arrhenius plot of  $\log k$  versus  $1/T$  are satisfied only very approximately. Factors relating to the form of the specimen, (shape, size, compaction, container, etc.) are shown to be very important. A method is developed for obtaining data for a specimen in the form of an infinitely thin disc. The first-order kinetic relation and the Arrhenius relation are then linear, and the latter gives an activation energy of 65 K cal./mol. The dehydroxylation process is shown by x-ray analysis to proceed crystal by crystal and this leads to an interpretation of the first-order kinetics. The x-ray method is used to study the distribution of reacted and unreacted material throughout a disc of material. Although isothermal conditions are employed, large differences are found between the interior and exterior of a partially dehydroxylated disc. These effects are attributed to the influence of a water vapor atmosphere within the heated disc.

## (1) INTRODUCTION

The loss of weight when kaolinite is fired to temperatures exceeding about 450°C under normal atmospheric conditions is commonly ascribed to "dehydration" and the water involved in the reaction is designated "structural water." Neither term is correct, as the crystal lattice loses hydroxyl groups. The process is better described as "dehydroxylation" and it can be represented chemically by the equation



The mechanism is most probably one of proton migration so that if two protons momentarily find themselves associated with the same oxygen ion, there is a probability that a water molecule will be formed and will detach itself from the lattice. The present work was undertaken in the hope that a kinetic study of the process accompanied by x-ray examination would provide more detailed information about the process than is currently available.

The crystal structure of kaolinite (Brindley and Robinson, 1946; Brindley and Nakahira, 1956) is so well known that no detailed description is required here. It suffices to recall that the four (OH) groups of the structural unit  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$  are located wholly in the octahedral sheet of the structure, three of them occupying positions on the outside of the layer structure and one within the structure. A previous study of the dehydroxylation of kaolinite

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(Nakahira, 1954) provided evidence that appeared to show that the "exterior" hydroxyls reacted more readily than do the "interior" hydroxyls, but the more extensive work now reported has not confirmed this interpretation, and up to the present there is no evidence distinguishing between the reactivities of the different hydroxyl groups. In what follows, therefore, no distinction will be made between the different kinds of lattice positions occupied by hydroxyl groups.

In the last 25 years a considerable amount of research has been undertaken to elucidate the mechanisms involved in the removal of water from hydrated materials. The work of Bradley, Garner, Tompkins, and of many others in this field is summarized in "Chemistry of the solid state," edited by Garner (1955). Work on kaolinite and other clays has been undertaken by Murray and White (1949, 1949a, 1955, 1955a), Gregg and Stephens (1953), Sewell (1955), Vaughan (1955), Kissinger (1956), and others.

The results for kaolinite tend to show that the reaction proceeds approximately according to first-order kinetics, with an activation energy lying somewhere in the range 30–60 K cal./mol. Why the reaction is approximately first-order and how it proceeds are questions that have not been answered.

At the outset of the present experiments we recognized that kaolinite presents problems that do not arise with such materials as copper sulfate pentahydrate or alum, which can be obtained as single crystals. The fact that kaolinite crystals are of the order of 1 micron in size means that powdered specimens must be used and that macroscopic as well as microscopic factors may be involved in the process.

Prior to considering the present experiments, it will be useful to indicate briefly the various processes which may be involved in the dehydroxylation of kaolinite.

#### (i) *Nucleation*

The interaction of two hydroxyls to form a water molecule creates a vacant lattice position. The subsequent readjustment of adjacent atoms forms a nucleus which grows as further reactions occur in the vicinity. As in other solid state reactions, it is to be expected that the rate of nucleation and the rate of growth of nuclei will be primary factors controlling the dehydroxylation.

#### (ii) *Development of Nuclei*

Nuclei frequently, but not always, occur at crystal boundaries and spread inwards. The fact that kaolinite has a layer structure may well predispose the nuclei to develop in a layer-wise manner. It is a relevant question whether the dehydroxylation proceeds in a two-dimensional or a three-dimensional manner through a crystal.

#### (iii) *Reverse Reaction (Rehydration)*

The possibility of reverse reaction taking place can be considered from two

standpoints. When a water molecule has been formed it has first to diffuse out of the individual crystal, and subsequently out of the powder mass. De Boer, Fortuin, and Steggerda (1954) have demonstrated the importance of "intergranular hydrothermal" conditions in determining the course of dehydration of the trihydrates of alumina, gibbsite and bayerite. Although these effects become less important for small crystals approaching 1 micron in size, they can not be dismissed as unimportant for kaolinite owing to the sintering that occurs when a kaolinite powder is heated. The marked effect of water vapor atmospheres on the differential thermal analyses of kaolinite has been shown by Stone (1951, 1952, 1954) and by Stone and Rowland (1955), and in the light of their results the development of a low water-vapor pressure of little more than 1 atm. between the particles of a kaolinite powder may have an appreciable effect on the rate of the forward reaction.

#### (iv) *Macroscopic Factors*

Under this heading may be considered the effects arising from the shape, size, and degree of compaction of the powder specimen, the degree of orientation of the platy particles, and the nature of the container.

## (2) EXPERIMENTAL DETAILS

Dehydroxylation has been followed by weighing directly a specimen of about 0.2 to 0.5 g suspended from one arm of a balance and located in a uniform temperature zone of a tubular electric furnace with the temperature controlled to within 1°C. A well-crystallized kaolinite was obtained which by x-ray diffraction showed absence of detectable impurities. By repeated sedimentation a fraction was selected between 0.5 and 1 micron equivalent spherical diameter.

Preliminary work was directed towards checking the alleged first-order kinetics and determining the activation energy on the assumption of an Arrhenius relation for the reaction constant. Since the weight,  $w$ , of the reacting material is a function of both time and temperature for a given set of experimental conditions, it was considered desirable to keep one variable, the temperature, constant and to explore the variation of  $w$  with respect to the other variable, the time  $t$ . The experiments have therefore been carried out under *isothermal* conditions at a series of different temperatures.

Specimen preparation was as follows: A quantity of 0.5 to 1 micron material sufficient for a range of experiments was prepared, brought to constant weight in an oven at 110°C, and then stored in a desiccator until required. All subsequent operations to prepare specimens for use, such as weighing, were carried out so far as possible under dry air conditions.

The exact time when an isothermal experiment commences is difficult to define. The uncertainty was minimized by first bringing the furnace temperature to the desired value; the specimen was then placed in position, and the

furnace raised to a predetermined level so that the specimen was correctly located. Because a sequence of measurements usually occupied several hours at least, sometimes several days, an uncertainty in the starting time of about 10 minutes, which was about the time required for the specimen to reach the furnace temperature, was considered unimportant. In any case, extrapolation of the  $\log (w/w_0)$ —time curve back to the initial weight indicated the magnitude of the initial time uncertainty (see Fig. 1 for examples).

Some experiments were made with dry air circulating through the furnace, but the results were not changed. In general, the experiments were carried out under ordinary atmospheric conditions.

### (3) THE EXPERIMENTAL PROGRAM

#### (i) *Kinetic Studies*

Preliminary work was directed towards checking the alleged first-order kinetics and determining the activation energy from rate constants obtained at different temperatures.

First-order kinetics implies that the rate of the reaction as measured by the rate of loss of weight,  $-dw/dt$ , is proportional to the quantity of unreacted material  $w$ , that is to say,

$$-dw/dt = kw$$

which on integration gives

$$\log (w/w_0) = -kt,$$

where  $w_0$  is the initial mass of the reacting material. The value of  $w_0$  is the weight of the reacting part of the kaolinite. As the reaction is followed by weight-loss determinations,  $w_0$  is represented ideally by the  $2\text{H}_2\text{O}$  which appears in the oxide formula for kaolinite,  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ . This amounts to 13.95 weight percent of the kaolinite. Experimentally,  $w_0$  is found by the complete dehydroxylation of the material. Values near 14.20 percent were obtained in these experiments, indicating the possibility that a small amount of surface adsorbed water was not removed at  $110^\circ\text{C}$ .

The results obtained broadly confirm first-order kinetics, but systematic deviations are found which will be discussed in section 4.

#### (ii) *Effect Arising from the Type of Powder Specimen*

The deviations from first-order kinetics suggested that specimen shape, size, degree of compaction, and kindred experimental factors might have an important influence on the rate studies. This was confirmed by a variety of tests. These tests finally led to a systematic study of the behavior of a series of thin disc-type specimens prepared by pressing a weighed quantity of powder in a mold of diameter 1.15 cm, with a pressure of 200 lb./in.<sup>2</sup>, maintained for 5 minutes. By using these lightly pressed powder discs, it was possible to elim-

inate the effects of the container which had previously been a thin platinum thimble, 1.43 cm high and 1.27 cm in diameter. The discs were mounted on a frame of thin platinum wire so that dehydroxylation proceeded freely from both sides.

As will be shown, the rate constants vary progressively with the thickness of the discs, in a way which makes possible an extrapolation to the behavior of an infinitely thin disc. In this way, we believe that factors in the dehydroxylation process arising from specimen shape, size, and compaction and from the specimen container, can be eliminated.

(iii) *X-ray Study of Kaolinite as Dehydroxylation Proceeds*

To minimize factors connected with the size, shape, and compaction of the specimen, the powder was spread in a very thin layer on a platinum foil mounted horizontally in the furnace. When dehydroxylation had reached a desired stage, such as 50 percent completion, the powder was removed from the furnace and a standard sample of 4.0 mg was mounted on a glass slide and examined with the diffractometer. In all such work crystal orientation is a serious source of uncertainty; efforts were made to prepare the specimens always in the same manner so that orientation would be similar throughout. The shapes and intensities of the 001 and 002 reflections were given the most

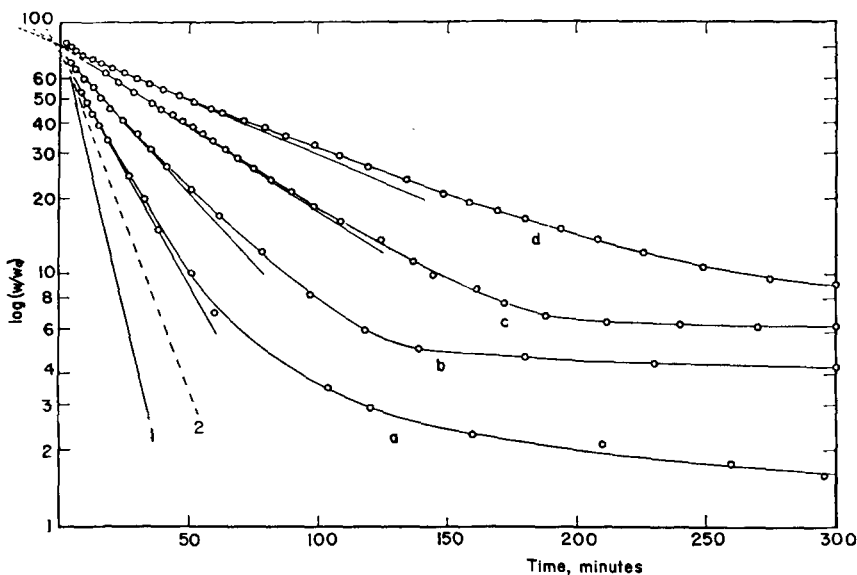


FIGURE 1. — Variation of  $\log(w/w_0)$  with time for kaolinite heated at  $497^\circ\text{C}$ : ( $w/w_0$ ) is expressed as a percentage of total weight loss by dehydroxylation. Curves a, b, c, d correspond to compressed discs of thickness 0.38, 0.83, 1.55, 2.68 mm respectively. Curve 1 is the extrapolated curve for an infinitely thin disc. Curve 2 corresponds to a thin layer of uncompacted powder.

attention, as any changes in the layer structure would be expected to show up mainly in the behavior of these reflections.

*(iv) Dehydroxylation as a Function of Depth in Discs of Powder*

The results obtained from (iii) were extended to a study of the reaction of the powder at different depths within a partially dehydroxylated disc. This was ground down in layers parallel to the disc surface and 4-mg samples were examined by x-rays in the same manner as described in section (iii) above.

These are the four main problems that have been studied, for which the results will be given in section 4 under corresponding subheadings.

#### (4) RESULTS

*(ia) Kinetic Measurements*

In section 3(i) it is shown that in a first-order reaction there is a linear relation between  $\log(w/w_0)$  and the time  $t$ , with a negative slope of gradient  $k$ .

Initial results with powders contained in a platinum thimble or spread thinly on platinum foils confirmed the observations of Murray and White (1949, 1949a, 1955, 1955a) and others that over a considerable part of the dehydroxylation process the relation is linear within the accuracy of the observations. In Figure 1, curves are given for  $\log(w/w_0)$  versus time for several lightly compressed discs of powder held at 497°C; the curves are linear down to about  $w/w_0 = 50$  percent. The departure from linearity sets in so gradually that it is not possible to say where it first commences; in fact, mathematically the departure from linearity may well be present from the commencement of the reaction. However, beyond about 50 percent, it is clear that the linear relation no longer holds, and the question arises whether at any particular temperature of the order of 450° to 600°C the reaction eventually will go to completion or to some final stationary value. This question is not easily answered, because however long the experiment is continued at one fixed temperature, there remains some uncertainty whether a prolongation of the experiment for a further week, month, year, . . . , might bring about full dehydroxylation.

Within the limits of the present experiments, however, it is considered that at temperatures of the order of 450° to 600°C complete dehydroxylation does not occur within reasonable time limits. Figure 2 illustrates the results of an experiment lasting several weeks in which the specimen was deemed to have attained a stationary weight if on two consecutive days the same weight was recorded. The process was continued at a higher temperature until a new stationary weight was obtained. With each elevation of temperature, an immediate further weight loss was recorded.

The interpretation of these results is still not fully ascertained, but the most probable explanation is that they represent a balance between a forward and a backward reaction which is displaced increasingly towards complete dehydroxylation as the temperature is raised.

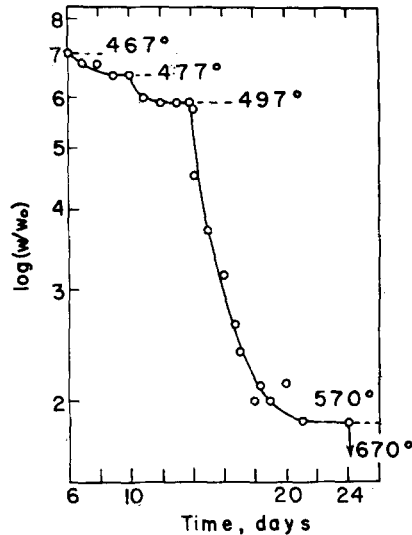


FIGURE 2. — Variation of  $\log (w/w_0)$  for a specimen of kaolinite heated to constant weight at different temperatures. ( $w/w_0$ ) is expressed as a percentage of total weight loss by dehydroxylation. Six days were required to reduce ( $w/w_0$ ) to 7 percent at  $467^\circ\text{C}$ .

(ib) *The Activation Energy for Dehydroxylation*

The Arrhenius relation for the reaction constant  $k$  is

$$k = Ae^{-E/RT}$$

where  $A$  is a constant,  $E$  the activation energy,  $R$  the gas constant, and  $T$  the absolute temperature.

$$\log k = \log A - E/RT$$

Therefore  $\log k$  plotted against  $1/T$  gives a straight line of gradient  $(-E/R)$ .

Murray and White (1949, 1949a, 1955, 1955a) especially have considered this relation. Their results, when considered strictly, do not conform with a linear relation (see curve "a" in Fig. 3). A straight line can be drawn approximately through their experimental data, but the value obtained for the energy  $E$  is very ill-defined; the precision which some recent investigators have claimed for similar results is, in our opinion, quite illusory.

Early data obtained in the present experiments using powders in platinum thimbles are shown by curve "b" in Figure 3. The general trend of the present results is in line with those of Murray and White (curve "a") and confirms the curvature of the  $\log k$  versus  $1/T$  curve.

The deviations from linearity of the curves for  $\log(w/w_0)$  versus time, and  $\log k$  versus  $1/T$  called for more careful scrutiny and eventually led to the series of experiments using dislike specimens of various thicknesses,  $x$ . As will be shown in the following section (ii), these experiments enable the  $\log(w/w_0)$  versus time relation to be extrapolated to the case where  $x = 0$ , i.e.,

the infinitely thin disc. It is then found that  $\log(w/w_0)$  varies linearly with time over a considerably longer range of  $(w/w_0)$ , and when the experiments are made at different temperatures  $T$ , the resulting relation for  $\log k$  versus  $1/T$  is also linear, at least over the temperature range investigated so far.

The  $\log k$  versus  $1/T$  relation for infinitely thin powder discs is shown by curve "c" in Figure 3. From the gradient of this line, the activation energy is obtained, namely,

$$E = 65 \text{ K cal./mol.}$$

As the gradient of curve "c" corresponds with the maximum gradient of curve "a", the activation energy now obtained corresponds with the highest estimate obtainable from the data of Murray and White and from our own preliminary observations.

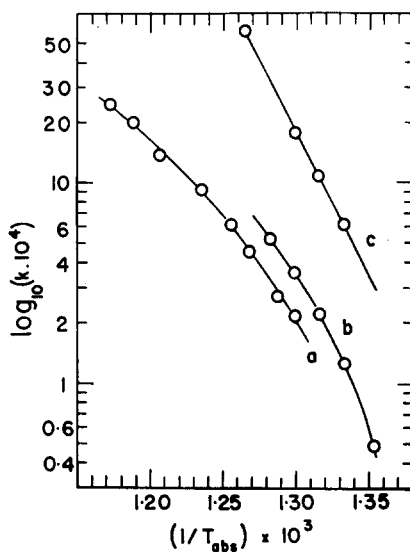


FIGURE 3. — Arrhenius plot of  $\log k$  versus  $1/T$  (absolute). Curve a, data by Murray and White. Curve b, present data for specimens in platinum thimble. Curve c, data for infinitely thin disc specimens.

### (ii) Results for Different Types of Powder Specimens

Preliminary experiments showed that when a powder is placed in a platinum thimble, the slope of the  $\log(w/w_0)$  versus time curve is very dependent on the precise nature of the powder specimen. Thus when the thimble was filled to different levels with powders having the same degree of compaction, or to the same level with different degrees of compaction, the dehydroxylation curves at a particular temperature were changed considerably. The disc specimens already described, prepared at constant load for a constant time, have



one major variable, namely the thickness  $x$ . Figure 1 shows the variation of  $\log (w/w_0)$  versus time for a series of these discs with the thickness  $x$  ranging from 0.38 mm to 2.68 mm. When the reciprocal gradient,  $1/k$ , for various values of  $(w/w_0)$  is plotted against  $x$ , as in Figure 4, we see that the resultant curves extrapolate to a single value of  $1/k$  when  $x = 0$ . Thus for the infinitely thin disc there is a single value of  $k$  for all values of  $(w/w_0)$ . This means that when we extrapolate to the case  $x = 0$ , the logarithmic dehydroxylation curve is linear. This extrapolated curve is shown in Figure 1.

This is a very laborious way of eliminating factors arising from specimen size, shape, compaction, etc. A test carried out on a thin uncompacted layer of powder, about 1 mm thick, showed that it approximated fairly closely (see Fig. 1) to the infinitely thin layer, and for many purposes it may suffice to use such a thin layer of material as a good working approximation to an infinitely thin specimen.

(iii) X-ray Study of Kaolinite during Dehydroxylation

As described in the section on the experimental program, 4-mg samples of kaolinite, taken from powder discs at various stages of dehydroxylation, were examined by x-rays.

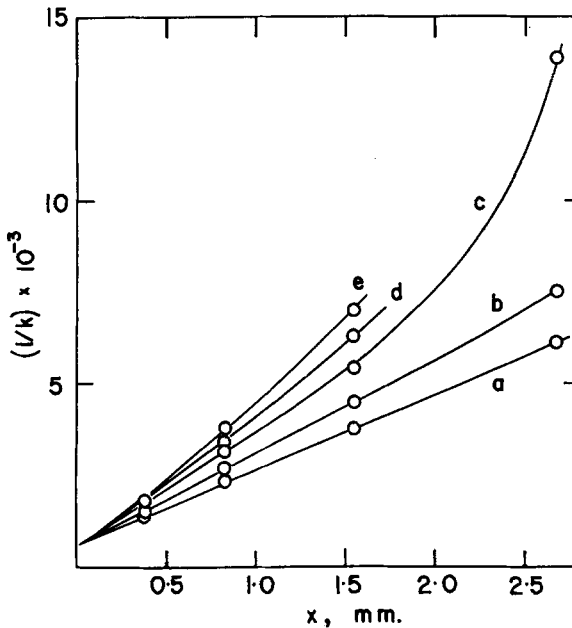


FIGURE 4. — Reciprocal of  $k$  plotted against  $x$ , disc thickness, for various values of  $(w/w_0)$  as follows: (a) 100 percent–50 percent, (b) 20 percent, (c) 10 percent, (d) 9 percent, (e) 8 percent.

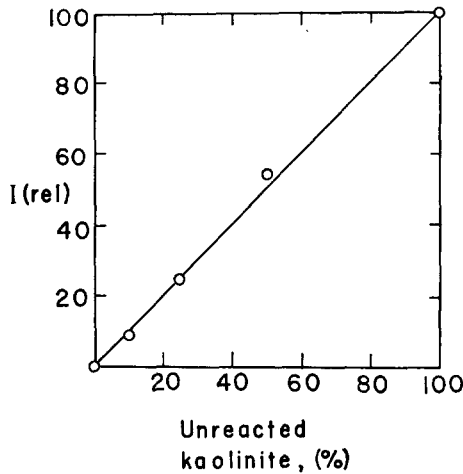


FIGURE 5.—X-ray intensity of 001 reflection from material partly dehydroxylated at 497°C expressed as percentage of the intensity reflected from the initial material. The percentage of unreacted kaolinite is obtained from weight-loss data.

Two results were clearly established. In the first place, the 001 and 002 reflections showed no broadening even up to 90 percent of complete dehydroxylation. If the crystals broke down in a layer by layer manner as the hydroxyl groups reacted, then a broadening of these reflections would be expected, either because of a reduction in thickness of the platy crystals, or because of an interstratification of unreacted and reacted layers.

Secondly, a strictly linear relation is observed between reflected intensity and amount of unreacted material. The results are shown graphically in Figure 5.

It is deduced from these results that dehydroxylation proceeds essentially crystal by crystal. It must, of course, take a finite time for a nucleus, once formed, to envelop an entire crystal. However, it appears that the time scale of the experiment is large compared with the time for a crystal, once nucleated, to react completely. Therefore, for the most part, we observe with x-rays either unreacted or fully reacted crystals. This result is in accord with the first-order character of the reaction, which can now be interpreted as follows: At any stage of the reaction, the probability of further dehydroxylation is proportional to the number of unreacted crystals, which is proportional to the weight of unreacted material.

#### *(iv) Dehydroxylation as a Function of Depth in Discs of Powder*

The relation shown in Figure 5 between x-ray intensity and proportion of unreacted material enables us to study rather easily the distribution of unreacted material within a disc of powder reacted to a certain over-all dehydroxylation.

Figure 6 gives representative results. A disc of kaolinite 1.15 cm diameter, 2.94 mm thick, was heated at 517°C until the over-all dehydroxylation amounted to 50 percent of completion. Figure 6 shows that the surface layers are almost fully dehydroxylated, whereas the interior of the disc still has as much as 65 percent unreacted material.

This shows a striking difference between the surface and the center of the disc. It is especially striking when it is realized that the disc was relatively thin, 2.94 mm, and was maintained at *isothermal* conditions. The effects can not be attributed to temperature variation through the specimen. In the first place, the temperature would have to be considerably *lower* in the center to account for the much reduced reaction. The only way by which the interior temperature could be lowered would be by a vigorous endothermic reaction. Such an explanation seems contrary to the facts, since the internal reaction is much less, not greater, than that at the surface.

It seems most probable that the retardation must be attributed to the development of a water-vapor atmosphere in the specimens, and although this can not be visualized as exceeding to any appreciable extent 1 atm. pressure, nevertheless even this low pressure of water vapor must significantly retard the dehydroxylation. This is in line with the results established by Stone (1951) and Stone and Rowland (1955) using D.T.A. equipment in controlled atmospheres, which show that the *peak* position for the endothermic reaction of

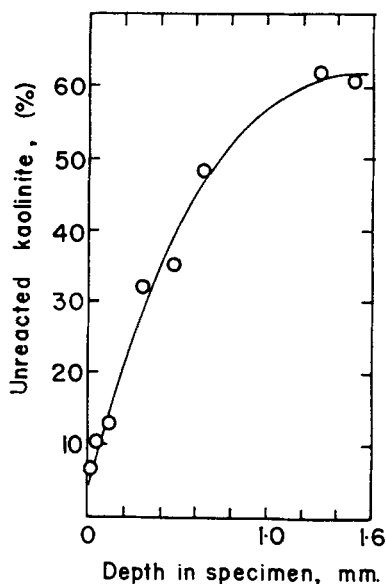


FIGURE 6. — Percentage of unreacted kaolinite in a disc specimen heated at 517°C to 50 percent dehydroxylation, plotted against depth in specimen. Disc thickness = 2.94 mm. Measurements extend from the surface to the center of the disc.

kaolinite is raised by 10° to 20°C per atm. of water-vapor pressure, while the starting temperature is raised even more.

### CONCLUSIONS

The process of dehydroxylation of kaolinite is shown to follow first-order kinetics when factors relating to the form of the specimen (its shape, size, compaction, container, etc.) are eliminated. The Arrhenius relation is then obeyed and the activation energy for dehydroxylation is found to be 65 K cal./mol. The reaction proceeds on a crystal by crystal basis, as shown by x-ray analysis, and this provides an interpretation of the first-order kinetics. It is concluded that a water-vapor atmosphere within a partly dehydroxylated sample leads to a marked difference in the proportions of reacted and unreacted material at different depths within the sample.

### ACKNOWLEDGMENTS

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