LOW-TEMPERATURE SYNTHESSES OF KAOLIN MINERALS


ABSTRACT

Two general approaches are used to achieve low-temperature syntheses of kaolin minerals. Since octahedral coordination of aluminum ions to O (or OH) appears to be a necessary prior condition, syntheses have been attempted using (a) various aluminum hydrates and gels in which the six-fold coordination is already satisfied, and (b) systems in which the rate of supply of silica is approximately matched to the rate of conversion of Al from four-fold to six-fold coordination. Both methods have yielded kaolin minerals, but conditions of temperature, pH, cationic and anionic impurities are found to be critical. Platy, lath-like, and rod-like (or tubular) forms have been synthesized and their growth and identification followed by a variety of analytical methods.

INTRODUCTION

Studies on the formation of kaolin minerals fall into two broad groups, geological and soil studies on the one hand (i.e. field studies) and laboratory studies on the other. The latter frequently attempt to reproduce under known conditions, the processes believed to take place in nature. To offset the limitation on the time factor, the temperature, pressure, and/or composition variables are usually enhanced in one respect or another in order to achieve measurable results. By enhancement of temperature and pressure as in hydrothermal studies, the most commonly occurring of the kaolin minerals, kaolinite, is readily synthesized, but dickite and nacrite, generally believed to be higher temperature forms, rather surprisingly have not been reported in hydrothermal syntheses. The synthesis of halloysite also seems uncertain hitherto.

Much interest attaches to the synthesis of kaolin minerals under conditions of temperature and pressure more nearly corresponding to those in soil formation. Field studies suggest that kaolinite may form either by desilication processes in which primary minerals pass, for example, through a sequence such as montmorillonite to kaolinite and finally to
gibbsite, or by a resiliation process in which gibbsite or other hydrate of alumina transforms to kaolinite.

Outstanding among recent investigations are those of Hénin, Caillère, and their collaborators (1961) who for a number of years have performed syntheses at low temperatures using very dilute solutions of silicate and a metal hydroxide which forms a "brucite" layer structure. They succeeded in synthesizing trioctahedral minerals and considered that sheets of silica tetrahedra became attached to the brucite layers forming 2:1 type minerals at high pH with more silica available, and 1:1 type minerals at lower pH with less silica available. The formation of dioctahedral minerals, however, appeared to be exceptionally difficult.

Experiments initiated by Gastuche and DeKimpe (1959), and continued by DeKimpe et al. (1961) focused attention on the conditions necessary to stabilize a six-fold coordination of Al with respect to oxygen in the presence of silica. It was shown that at low pH, \( \sim 4.5-5.0 \), kaolin was formed in small amounts unnoticeable by x-rays but confirmed by electron diffraction data (Brindley and DeKimpe, 1961).

**Experimental**

Experiments of two kinds have been performed. On the hypothesis that the stabilization of Al\(^{VI}\) is a prerequisite for kaolin formation, experiments were carried out in which silica in solution was reacted with alumina already in six-fold coordination in the form of gibbsite, bayerite or boehmite.

To induce crystalline alumina trihydrates to react with silica, it appeared necessary to reach the gibbsite-boehmite transformation, the temperature for which has been given as 120° C. (Roy and Osborn, 1952) but which may be higher in the presence of silica.

About 0.1 g of various forms of alumina (gibbsite, bayerite, gels, etc.) was reacted with 0.2 ml ethyl silicate, together with various acid or basic solutions in sealed Pyrex "security" tubes, which were turned end-over-end in an oven heated to within \( \pm 2^\circ \) C. of a desired temperature.

In a second series of experiments, the influence of pH and ionic content on the pre-organization of mixed Al/Si 1:1 gels was examined, and attempts were made to stabilize the Al\(^{VI}\) coordination at nearly ordinary temperatures and pressures.

Identification procedures included: (i) x-ray diffraction, (ii) x-ray fluorescence particularly to identify Al\(^{IV}\) or Al\(^{VI}\) (cf. Brindley and McKinstry, 1961; DeKimpe et al., 1961). (iii) I-R spectroscopy using KBr pellets and 0.25% of solids. (iv) Specific surface area by the method of Nelsen and Eggertsen (1958). (v) Electron microscopy and single crystal

Syntheses at Slightly Elevated Temperatures and Pressures

pH-dependence of the Al-trihydrate—Al-monohydrate transformation Both gibbsite and bayerite, Al(OH)$_3$, 0.1 g, in the presence of 16 ml N/10 HCl go entirely to boehmite when aged at 170–175° C. for 10 days, but in water under the same conditions a mixture of trihydrate with boehmite is obtained. The acid condition appears to assist boehmite formation.

Dependence of the gibbsite→kaolinite reaction on pH With 0.1 g gibbsite and 0.2 ml of ethyl silicate, reactions were carried out for 10 days at 170–175° C. in the presence of various acid and alkali solutions. With addition of 16 ml N HCl, an amorphous alumino-silicic gel was obtained. With N/10 HCl, a product was obtained resembling a kaolin mineral. With N/100 HCl, kaolin+gel+boehmite was obtained. When conditions were made less acidic, or more basic, by using respectively N/10$^3$ HCl, N/10$^4$ HCl, water, N/10$^4$ NaOH, N/10$^3$ NaOH, the product was gibbsite, sometimes with traces of boehmite, plus a gel. The experiments gave a product resembling kaolinite only when the pH remained largely constant at about 1.5. If the final pH was in the range 1.5–2.0, gibbsite appeared as well as kaolinite, but if the pH became higher than about 2.2, then gibbsite (possibly with traces of boehmite) plus a gel phase was formed.

The low (but not too low) pH values required for kaolin formation seem rather surprising and several comments may be made. In the first place some “acid activation” of the gibbsite may be required to initiate the reaction. Such acid conditions appear to favor the gibbsite→boehmite transformation. Secondly, impurities from the Pyrex glass containers are likely to be more important at higher pH values and these may disturb the kaolin synthesis.

Influence of primary reactants When the preceding experiments were carried out with Ludox SM silica gel in place of ethyl silicate, no significant differences in the results were observed; the decisive factors for kaolin formation remained the temperature and the pH.

Several forms of alumina, both crystalline and amorphous, were used but kaolin formation was achieved only when the aluminum was already octahedrally coordinated to (OH), as in gibbsite, bayerite, a “pregibbsite” gel, i.e. an alumina gel precipitated at pH 4.5 and subsequently dialyzed, and other alumina gels precipitated at higher pH values and dialyzed (Gastuche and Herbillon, 1962). With AlCl$_3$·6H$_2$O and freshly precipitated alumina gels, mainly x-ray amorphous phases are formed,
though halloysite- and kaolinite-like particles were identified by electron microscope and diffraction methods. Under similar conditions, boehmite does not give rise to kaolinite.

Influence of seed.ing With addition of traces of crystalline muscovite, a little kaolinite is obtained from fresh alumina gel precipitated at pH 6, the final pH being 3. No positive result was observed with gibbsite seeding. Thus an already oriented silica framework seems to induce further layer lattice evolution, which however may give a product nearer to halloysite or allophane.

Role of initial particle size The influence of particle size on the dehydration of gibbsite has been studied by DeBoer et al. (1954) and by Brindley and Choe (1961). Coarse particles were shown to favor boehmite formation and in the present experiments gave rise to lath-like kaolin particles, possibly on account of stresses developing during the gibbsite→boehmite transformation. Fine material, such as a synthetic gibbsite and “gibbositic” gels, was found to yield pseudo-hexagonal platelets.

Time variation of gibbsite→kaolinite reaction The transformation of an “Alcoa” gibbsite, particle size 1–10μ and surface area (B.E.T.) about 3 m²/g, was followed by x-ray diffraction, I-R absorption spectroscopy and electron microscopy. The results are summarized in Table 1, and in Figs. 1–3.

Gastuche and Fripiat (1962) have shown that the destruction of the octahedral layer of kaolinite by dissolution in silica-saturated HCl can be followed quantitatively in I-R spectra by the change in the high-frequency (H.F.) band at about 9.0μ with respect to the low-frequency (L.F.) band at 9.9μ; the H.F. band disappears when the octahedral layer is destroyed. Conversely the development of the octahedral layer of kaolinite is accompanied by increase of the H.F./L.F. ratio. Table 2 shows that good agreement exists between estimates of kaolinite formation based on x-ray data (Fig. 1B) and on the I.R. data (Fig. 2).

Electron micrographs (Fig. 3) show that several kinds of kaolin particles are formed. Spherical (globular) particles which might be described as allophane appear in many syntheses in which the yield in kaolinite is poor, mainly those starting from gels or incomplete runs starting with

1 Emphasis must be placed on the expression “under similar conditions,” because in earlier experiments Brindley and Radoslovich (1956) obtained kaolinite in a low-temperature hydrothermal study of acid alteration of albite, in which boehmite was formed as an intermediate product. The ionic environment was different and the crystalline state of the boehmite was not precisely ascertained.
KAOLIN SYNTHESSES

Table 1. Transformation of Gibbsite to Kaolinite at 175° C. in N/10 HCl

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>X-ray data (Fig. 1B)</th>
<th>Infra-red data (Fig. 2)</th>
<th>Electron optical data (Fig. 3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>gibbsite</td>
<td>gibbsite (Kolesova and Ryskin, 1959)</td>
<td>coarse hexagonal particles, 1–10μ</td>
</tr>
<tr>
<td>1 day</td>
<td>gibbsite</td>
<td>gibbsite+ very broad Si-O band at 9.15μ</td>
<td>small particles of silica gel on surface of gibbsite (Fig. 3A)</td>
</tr>
<tr>
<td>2 days</td>
<td>gibbsite slightly decreased. Trace of kaolinite</td>
<td>gibbsite+ narrower Si-O band at 9.30μ. Also Si-O-Al bands at 12–14μ</td>
<td>silica gel appearing to enter cleavage cracks on gibbsite crystals (Fig. 3B)</td>
</tr>
<tr>
<td>4 days</td>
<td>kaolinite prominent. Little or no gibbsite</td>
<td>Si-O band narrower at 9.35μ. δ Al-O-H band at 10.8μ. Si-O-Al bands better developed</td>
<td>thin, lath-like kaolin crystals, swelling with water (Fig. 3C)</td>
</tr>
<tr>
<td>12 days</td>
<td>kaolinite clearly developed</td>
<td>Si-O doublet seen at 9.6, 9.85μ. δ Al-O-H band at 10.8μ. Si-O-Al bands better developed still</td>
<td>lath-like kaolin (Fig. 3D)</td>
</tr>
</tbody>
</table>

Gibbsite. Very clear, pseudo-hexagonal plates (Fig. 3E) are synthesized from small gibbsite crystals, from “pregibbsitic” alumina gels, and also from aluminum chloride. Materials resembling halloysite (Fig. 3F) were obtained from aluminum chloride and in some experiments with Alcoa gibbsite. Lath-like kaolin (Fig. 3C) was obtained from large particle, Alcoa gibbsite.

Table 2. Percentage of Octahedral Layer in Kaolin Evaluated by I-R and by x-Ray Determinations

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>Ratio of I-R absorptions, H.F. band/L.F. band</th>
<th>% Octahedral layer from I-R</th>
<th>Relative (001) x-ray reflection intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>8</td>
<td>not measurable</td>
</tr>
<tr>
<td>2</td>
<td>1.2</td>
<td>18</td>
<td>23</td>
</tr>
<tr>
<td>4</td>
<td>1.6</td>
<td>65</td>
<td>68</td>
</tr>
<tr>
<td>12</td>
<td>1.85</td>
<td>95</td>
<td>100</td>
</tr>
</tbody>
</table>
CONCLUSIONS FROM LOW-TEMPERATURE, LOW-PRESSURE SYNTHESSES

The development of kaolinite from gibbsite and other pre-organized Al-OH layers appears to depend critically on the physical and chemical conditions. The low pH, around 1.5–2.0, is difficult to explain but in the case of gibbsite may be connected with incipient transition to boehmite.

![X-ray diffractometer traces](A) influence of pH on synthesis of kaolin, (B) transformation of gibbsite to kaolinite at 175° C. after (a) 1 day, (b) 2 days, (c) 4 days, (d) 12 days.
Fig. 2. Intra-red absorption spectra of gibbsite transforming to kaolinite at 175° C., after (a) 1 day, (b) 2 days, (c) 4 days, (d) 12 days. For comparison K = Zettlitz kaolinite, G = gibbsite (synthetic, Gastuche and Herbillon, 1962)
Fig. 3. Electron micrographs with length unit showing 1μ.

(A) Gel attached to coarse particles of gibbsite.
(B) Cracks appearing on cleavage planes of gibbsite.
(C) Thin sheets and lath-like particle of synthesized kaolinite.
(D) A mass of synthetic lath-like kaolinite.
(E) Kaolinite crystals synthesized from pre-gibbsitic alumina gel.
(F) Halloysite-like tube synthesized from AlCl₃.
for it is only when the conditions approach those necessary to alter gibbsite to boehmite that a kaolin mineral is formed. Poisoning of the reactions seems to occur at high pH and possibly with impurities derived from the Pyrex containers. Cationic impurities strongly affect the silica-gel framework (Fripiat et al., 1963), while anionic impurities disorder the Al-octahedral layers (Gastuche and Herbillon, 1962).

**Experiments at Normal Temperatures and Pressures**

In the following experiments, the temperature was always less than 80° C. and generally less than 65° C., and the pressure atmospheric. Alumina was derived from AlCl₃·6H₂O and silica from ethyl silicate. Experiments of three types were carried out:

(i) The rate of fixation of depolymerized silica by alumina gels and crystalline hydroxides was investigated as a function of the temperature of the solutions for a given silica content.

(ii) Alumino-silicic gels precipitated in the Al/Si = 1 ratio were aged for three months in the mother solution at given pH, NaOH or HCl being used for adjusting pH.

(iii) Aluminic and silicic phases were aged in a dialyzed medium, alumina gels being separated from silica-rich water flowing past a dialysis membrane.

**Factors influencing the rate of silica fixation** A suspension containing 200 mg freshly precipitated alumina gel was introduced into a dialysis bag and the outside solution (150 ml) containing 40 mg SiO₂/liter was renewed every 4 hr. Temperatures were 21–43° and 61° C. and experiments were carried out for 100 hr. Below 43° C., the rate of silica fixation is very dependent on the temperature, but above 43° C. the amount fixed seems to remain constant indicating probably that the rate of formation of the mixed gel is limited by the rate of silica diffusion through the membrane. After 100 hr., 80 mg of SiO₂ were found in the alumina gel at 43° and at
61° C., against 25 mg for the experiment run at 21° C. After about 10 hr. at 61° C., or somewhat longer at 43° C., the inner phase is a translucent sol which does not evolve any further.

Gastuche and Herbillo n (1962) studied the evolution of similar alumina gels treated with distilled water solutions. The gel transforms into a translucent sol (pregibbsitic stage) that evolves later into a milky phase when gibbsite begins to form. The first phase of the evolution is related closely to the rate of Cl− departure, which increases with temperature, $E_A$ being found equal to 5.5 Kcal/mole. This deionization corresponds with the transformation of $\text{Al}^{\text{IV}}$ present in the fresh gel at a ratio of about 75% into $\text{Al}^{\text{IV}}$. It may be thought that kaolin syntheses from ionic solutions or from fresh gels will require very critical conditions if the rate of $\text{Al}^{\text{IV}}$ formation must coincide with the rate of silica fixation since the temperature factor will not favor both processes equally. Attempts at fixing silica on the “pregibbsitic” gel using the same procedure gave deceiving results, for although this gel contains already all the aluminum in six-fold coordination and is very depolymerized, it does not fix more than 1–2% of $\text{SiO}_2$ and it crystallizes in a very strong pseudo-boehmite phase. However, as already described, this type of gel at 175° C. leads to very perfect kaolinite.

As already outlined, gibbsite did not fix silica in these conditions.

Influence of the pH of the mother solution on the structure of alumino-silicic gels Although it was already observed that co-precipitated alumino-silicic gels did not evolve appreciably towards a crystalline phase at ordinary temperature and pressure, the influence of pH and ionic content on their structure needed to be investigated. Knowledge of the behavior of pure aluminic gels was already available and pure silicic gels had been investigated by Iler (1955) and also by Fripiat et al. (1963). The pH values were chosen in order to cover all the characteristic changes observed by Iler in the curve of gelification of silica gel, namely pH 1.5, 3.0, 5.5, 8.0.

Aging was carried out in tubes agitated end over end at ordinary temperatures, and pH was adjusted by HCl or NaOH. The mixed gels prepared with the Al/Si ratio = 1, evolved spontaneously towards pH 3. The aging was carried out during three months at room temperature. All the samples remained x-ray amorphous though important changes in I-R spectra and in exchange capacity were observed related with the ratio of $\text{Al}^{\text{IV}}/\text{Al}^{\text{IV}}$.

$\text{Al}^{\text{VI}}$ was stabilized at low pH values, but above pH 5 entered increasingly the silica framework, taking fourfold coordination (Table 3). Chloride which disturbed the development of $\text{Al}^{\text{IV}}$ coordination for pure Al gels prepared at pH 4.5 seems to play a lesser role here. Also, a very clear relationship is found between $\text{Al}^{\text{VI}}$ content determined by x-ray fluores-
ence and an increase in the base exchange capacity of the gel (Fig. 4).

Infrared spectra show that the increase in Al<sup>IV</sup> induces a shift in the SiO vibration from 9.9-9.2<sub>μ</sub> to 9.8<sub>μ</sub> (Fig. 5). This has been connected already with the presence of tetrahedral aluminum by Stubican and Roy (1961), while Lyon and Tuddenham (1960) applied it to measure the amount of isomorphous substitution in mica and chlorite tetrahedral layers. This shift, which is observable in fresh gels, emphasizes the importance of pre-organization for further crystal evolution.

Gels prepared at pH 3 and 5.5 present a very broad Si-O band with a tendency to shift into several components indicating perhaps a beginning of octahedral layer stabilization, but short ranged and very disordered.

**Separate aging of aluminic and silicic phases; attempts at stabilizing alumina or silica layer lattices** The co-precipitation of Al-Si mixtures gave mixed gels with very disordered structures. Besides the pH influence, already outlined, the presence of anions seems to affect mainly the Al coordination, and the presence of cations distorts the Si-O bond length (see x-ray Fourier analysis studies by Fripiat et al. 1963). In the present experiments, aging was carried out at 43° and 61° C., the fresh alumina

### Table 3. Percentage of Al<sup>VI</sup> Coordination Found in Mixed 1:1 Al-Si Gels as Function of pH and Aging Period

<table>
<thead>
<tr>
<th>pH</th>
<th>Percentage Al&lt;sup&gt;VI&lt;/sup&gt; after various aging periods</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 week</td>
</tr>
<tr>
<td>1.5</td>
<td>94</td>
</tr>
<tr>
<td>2</td>
<td>72</td>
</tr>
<tr>
<td>4</td>
<td>64</td>
</tr>
<tr>
<td>5.5</td>
<td>36</td>
</tr>
<tr>
<td>6</td>
<td>36</td>
</tr>
<tr>
<td>8</td>
<td>13</td>
</tr>
</tbody>
</table>

### Table 4. Results from Separate Aging of Silica and Alumina Phases

<table>
<thead>
<tr>
<th>Alumina source</th>
<th>Silica dialyzing solution</th>
<th>T in °C.</th>
<th>I-R data</th>
<th>x-ray data</th>
<th>Electron optical data</th>
</tr>
</thead>
<tbody>
<tr>
<td>fresh Al gel prepared from AlCl&lt;sub&gt;3&lt;/sub&gt;·6H&lt;sub&gt;2&lt;/sub&gt;O, precipitated with NaOH and purified by dialysis</td>
<td>40 mg/L</td>
<td>61</td>
<td>gel</td>
<td>gel</td>
<td>halloysite, bayerite</td>
</tr>
<tr>
<td></td>
<td>120 mg/L</td>
<td>61</td>
<td>20% octahedral layer</td>
<td>gel</td>
<td>traces of bayerite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>43</td>
<td>gel</td>
<td>gel</td>
<td>(b=8.93 Å)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>—</td>
</tr>
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</tr>
</tbody>
</table>
The experiments prove again how critical are the alumina and silica layer building rates. Only partial success was obtained with the more dilute silica solution and the slowest flow rate. I-R spectra showed that the amount of octahedral layer could be estimated at about 20%. Morphologically, this kaolin resembles halloysite (Fig. 6). Seeds of gibbsite,
kaolinite and muscovite did not provide any definite increase in crystallization.

Another attempt at stabilizing the silica layer lattice was carried out starting from a white mica residue coming from an acid attack of Gjerstad biotite (Gastuche, 1963). This presents under the optical microscope a kind of layer lattice organization, though completely x-ray and I-R amorphous. Experiments were carried out in dialysis bags with Al gels co-precipitated at acid pH. After the same time of aging, the results were mainly negative, the main evolution being towards a gel-like phase.

**Conclusions from Experiments at Normal Temperatures**

The structure of mixed alumino-silicic gels is related closely to pH and ionic content of the solutions. The stabilization of six-fold coordinated aluminum in the presence of silica occurs only at low pH but the preparation of mixed gels in the mother solution under these conditions leads to
structures poisoned at the very beginning and which evolve very little. As observed in the experiments at higher temperatures, the alumina gel structure needs to be in a dynamic stage, potentially able to transform into gibbsite, in order to induce a 1:1 silica layer lattice. The optimum pH for this transformation seems to be 4.5–5.5 but the rate of silica fixation is very critical and depends closely on the rate of deionization.

**Discussion**

It is of interest to consider the formation of kaolinite from alumina-silica mixtures of various kinds from the standpoint of absolute reaction rate theory as developed by Glasstone, et al. (1941), also Laidler (1950), even though no more than a qualitative discussion can be attempted. According to this formulation, the specific reaction rate \( k_1 \) for the formation of an activated state denoted by \( \dagger \) from an initial state denoted by 'O' is given by

\[
k_1 = \frac{kT}{h} \cdot \exp \left( \frac{\Delta S^*}{R} \right) \cdot \exp \left( - \frac{\Delta H^\dagger}{RT} \right)
\]

(Laidler, 1950, pp. 74–5) where

\[
\Delta S^* \cong \Delta S^\dagger = S^\dagger - S^0
\]

and

\[
\Delta H^\dagger = H^\dagger - H^0
\]

\( T \) is absolute temperature, \( k, h, \) and \( R \) are basic constants, \( \alpha \) is a transmission coefficient often equal to unity, \( S \) denotes entropy and \( H \) enthalpy.

From this expression, it is evident that the initial state must be favorable with respect to the activated state in order that the reactants may attain the activated state in appreciable amount. With starting materials which are unfavorable for low-temperature syntheses, it is likely that \( \Delta H^\dagger \) is large and positive, so that high temperatures are essential. Thus, for example, from data given by Rayner (1962) for hydrothermal syntheses of kaolinite from alumino-silicic gels, a value of \( \Delta H \) around 280 kcal/mol can be estimated, which implies an immeasurably slow rate below 100° C. for these starting materials.

For other starting materials and conditions, such as those which have yielded low temperature syntheses, one cannot make any firm statement regarding the enthalpy factor, though it seems possible that it may be of the same high order as indicated in the previous paragraph. If this is the case, then one must look to the entropy term as being the reason for the results obtained. A statement of potentially considerable importance by Glasstone *et al.* (1941, p. 22) is that
"When reaction occurs between complex molecules and there is a considerable rearrangement of energy among the degrees of freedom, there is a decrease of entropy in the formation of the activated complex. . . ."

In the present work, it has been seen that an essential condition for low-temperature synthesis of kaolinite is that the initial state should contain Al in six-fold coordination, and the probable reason for this is that it makes the decrease $\Delta S^\ddagger$ less than in situations where a coordination change is required. Consequently, it will tend to make the free energy barrier $\Delta F^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$ to be surmounted smaller.

However, a six-fold coordination of Al in the starting materials is not alone sufficient. Experiment proved that the gibbsite lattice is too stable to be attacked by depolymerized silica solution, unless the alumina phase itself is in a "dynamic" stage where the lattice is on the point of reorganization into boehmite, though boehmite itself also is unsuitable. But positive results are obtained from gibbsite under suitable acid conditions favoring breakdown to boehmite, and from alumino-silicic gels in which the Al is in six-fold coordination. The present studies have shown that successful low-temperature synthesis of kaolin minerals involves many factors which in various ways will influence the terms $\Delta S^\ddagger$ and $\Delta H^\ddagger$ which jointly determine the free energy barrier to be scaled in order to reach the activated complex (or complexes) prior to the final crystallization.

ACKNOWLEDGMENTS

These investigations have been carried out partly at The Pennsylvania State University, College of Mineral Industries, where they were supported by a grant from the American Petroleum Institute (Project A.P.I. 55) and partly by an IRSIA grant at the Institut Agronomique, University of Louvain. It is a particular pleasure to record the interest and helpful advice of Professor J. J. Fripiat at all stages of the work.

REFERENCES


Manuscript received, June 14, 1963; accepted for publication, October 25, 1963.