

KINETICS OF THE THERMAL DEHYDRATION OF HYDROUS SILICATES

by

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ABSTRACT

Generally, the rate of dehydroxylation of clay minerals may be controlled by reaction at the interface between the decomposed and undecomposed mineral, diffusion through the decomposed phase and/or nucleation of the decomposed phase. Only in rare instances are mineral decomposition reactions homogenous. Some examples are presented to illustrate these principles.

For macrocrystalline muscovite the initial sample weight rather than the external surface area was found to be a parameter of the rate of weight loss. Upon grinding the muscovite to particles smaller than —65 mesh, an internal surface area factor strongly influenced the rate. This surface area was related to dislocations shown to be present in muscovite.

A rate equation is presented that explains the observed weight loss versus logarithm of time dependence based on a model involving a systematic relief of strain during dehydration.

The rate equation for pyrophyllite was exactly the same as that formulated for muscovite. As with muscovite there was a change in free energy of activation throughout the dehydration process. In contradiction to muscovite, the contribution to the free energy of activation was at least partly enthalpy while with muscovite it was an entropy of activation contribution.

The dehydration of kaolinite was carried out in vacuum. At pressures of one micron the reaction was found to be diffusion controlled with hydroxyl ions as the likely diffusing species.

INTRODUCTION

THE clay minerals offer a rich field for investigation from the viewpoint of solid state chemistry and physics. These minerals have largely been excluded from the area of study of the solid state chemist, mainly because of their complex ionic structure.

The clays, being layer type compounds, have been described as possessing poor crystallinity due to stacking disorders. Nevertheless, they have stoichiometric formulae and should have the same type of defects as any other ionic crystal. The decomposition of these minerals, which has both practical and theoretical aspects, should be correlated with their defect structure. Decomposition may be viewed as the reverse reaction to

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crystallization. In many ways it is similar to oxidation of metals and thus depends on structure-sensitive properties in a similar way.

With the above considerations in mind, a kinetic study of the dehydration process of several clay minerals was undertaken. Dehydration or more exactly defined dehydroxylation does not include hydrosopic or interlayer water, but is the removal of water of crystallization which requires the chemical reaction of hydroxyl ions.

THEORY

The thermal decomposition of solids involves the production of a gaseous product and may be represented by



Decomposition commences with solid (*B*) forming on the surface of solid (*A*) at points referred to as nuclei. These nuclei will appear at places on the surface of solid (*A*) where local energy fluctuations are favorable. Potential sites for these nuclei would be some type of lattice imperfection such as dislocations, cleavage steps, impurities, etc. After the nuclei of phase (*B*) have formed, they may grow at a linear rate into phase (*A*). Different shapes will be assumed by the nuclei depending on the anisotropy of the crystal lattice. Nucleation and growth of phase (*B*) will occur at rates determined by their activation energies. The reaction expressed by equation (1) may be categorized into three general cases, depending on the relative values of the activation energies.

Case I. Growth of Phase (B) Rate Controlling

In this case, the activation energy of the nucleation process is much lower than that for growth which allows the instantaneous formation of a layer of phase (*B*) on the surface and the subsequent inward propagation of this interface separating the two phases. The rate controlling step of the growth mechanism may be either (1) reaction at the interface or (2) diffusion through the product layer. When the rate controlling or slow step is the reaction at the interface then the rate is proportional to the interfacial area. Assuming the solid to consist of spheres the rate equation can easily be shown to be.

$$[1 - (1 - X)]^{1/3} = kt \quad (1)$$

where *X* is the fraction reacted, *k* is the rate constant and *t* is time.

Instead of the reaction at the interface, the diffusion of gas (*C*) through an adherent product layer (*B*) may be rate controlling. Applicable rate equations for spherical geometry have been derived by Jander (1937),

Carter (1961), Billy and Valensi (1955) for oxidation and solid-solid reactions, with the following expression from Carter:

$$[1 + (z-1) X]^{2/3} + (z-1) (1-X)^{2/3} = z + 2 (1-z) kt/r_0^2 \quad (2)$$

where z is the ratio of the product volume to the initial volume, and r_0 is the initial radius. Equations similar to (1) and (2) may be derived for other shapes such as cylinders and cubes. Equation (2) is based on the assumption that diffusion through (B) is independent of compositional variations. It is not possible at present to treat cases where diffusion is dependent upon the concentration of the diffusing species.

Case II. Nucleation of Phase (B) Rate Controlling

The activation energy of the nucleation may be much larger than for the growth process. This means the rate controlling step is the formation of nuclei and not the rapid growth through the crystal. The rate of formation of nuclei are governed by the normal probability laws expressed as

$$n_t = n_0 \exp(-kt) \quad (3)$$

where n_0 is the total number of nuclei sites, n_t is the number remaining after time t , and k is a constant. If the process of nucleation involves a conversion of a large portion of the crystal for the case of a powdered material of clay size where $n_t/n_0 = x$, (3) becomes

$$\ln x = kt \quad (4)$$

which is equivalent in form to a first order reaction. Other laws of nucleation have been tabulated by Garner (1955).

It has been found (Gandeeva, Zhabrova and Kushnerev, 1959) that experimental data from decomposition reactions may be fit to cover 60 per cent of the total reaction by both equations (1) and (4) which actually represent two directly opposite mechanisms. By careful manipulation of the particle size it may be possible to distinguish the operative mechanism by kinetics. This results from the nucleation rate depending on the inverse of the particle size squared ($1/r_0^2$), while the growth rate is related to the inverse of the radius ($1/r_0$). This further stresses, however, the necessity to compliment kinetic data with information gained from other research methods.

Case III. Rates of Growth and Nucleation are Comparable

When the activation energies for nucleation and growth are about the same, a complex decomposition curve may result which will be a com-

bination of the two individual rates. The form of these fraction reacted versus time curves will generally be sigmoidal and have as their upper and lower limit equations (1) and (4). Garner (1955) has given an extensive summary of decompositions which would fit into this category. A comprehensive treatment of metallurgical reactions by Johnson and Mehl (1939) is also applicable from a kinetic standpoint to many of the decomposition reactions of this type.

The three cases considered above may be referred to as heterogenous solid state reactions since they all require an interface. Notable exceptions to this may be the photochemical reaction in which one of the products is gaseous. Another apparent contradiction is the dehydration of muscovite which will be presented in this paper. Whether other such homogenous solid state reactions exist must be verified.

EXPERIMENTAL

The decomposition of muscovite and pyrophyllite in ambient air was followed by an automatic thermogravimetric apparatus (Hyatt, Cutler and Wadsworth, 1956). For muscovite the temperature range extended from 738° to 817°C, and from 527° to 668°C for pyrophyllite. Both macrocrystalline and microcrystalline muscovite were used while the pyrophyllite was only available as a powder.

Kaolinite was decomposed in a vacuum of one micron Hg to obtain a true kinetic law, i.e., unaffected by water vapor. The kaolinite particles were fractionated by a centrifuge into three size fractions: 1–2 μ in diameter, 4–6 μ , and greater than 10 μ . Runs, using the 1–2 μ fraction, were made at five different temperatures in the range from 360° to 440°C.

RESULTS

I. Macrocrystalline Muscovite

It was determined (Holt, Cutler and Wadsworth, 1958) that the rate of dehydroxylation was independent of the large external face area or the edge area, but was entirely a function of the initial weight of the sample. When Δw (change in weight in milligrams) was plotted versus the logarithm of time, a linear relation was established. It was evident that the slopes were directly related to the initial weight as is shown in Fig. 1. The linear relation between Δw and logarithm of time was observed up to approximately 75 per cent dehydroxylation. The curve fell off rapidly as the remaining 25 per cent of water was removed.

According to the absolute reaction rate theory (Glasstone, Laidler and

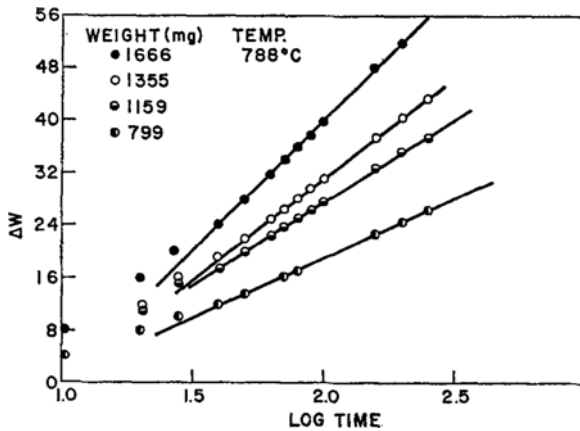


FIGURE 1.—Change in weight versus logarithm of time for muscovite samples of different weight at 788°C.

Eyring, 1941) the differential expression of the rate of weight loss may be given as the equation:

$$d(\Delta w)/dt = \phi(a w_0 - \Delta w) kT/h \exp(-\Delta F^\ddagger/RT) \quad (5)$$

- where Δw = change in weight
 t = time
 ϕ = constant of conversion
 a = 0.045 (fraction by weight of H₂O in muscovite)
 w_0 = initial weight
 k = Boltzmann constant
 h = Planck constant
 T = absolute temperature
 ΔF^\ddagger = free energy of activation
 R = gas constant

This expression as written is simply a first-order rate-of reaction expression that upon integration should provide a linear relation between the logarithm of Δw versus time. Such a relation is not in accordance with observed data indicating a more complex system than a simple first-order reaction as such. On the other hand, equation (5) may be successfully employed if it is assumed that structural variation in the muscovite occurs during dehydroxylation, providing a systematic change in ΔF . A linear dependence of the free energy of activation on the degree of dehydroxylation has been assumed because of simplicity and also because such a dependence has been observed in other systems (Taylor and Thon, 1952; Milliken, Mills and Oblad, 1950; Cook and Oblad, 1953). Such a dependence

may reasonably be expected if relief of strain has a long-range effect within the lattice.

Since the free energy of activation is composed of enthalpy of activation and entropy of activation, $f(\Delta w)$ might contribute to either of these components as expressed by the equation

$$\Delta F^\ddagger + f(\Delta w) = \Delta H_o^\ddagger + b \Delta w / w_o - T \Delta S_o^\ddagger = \Delta F_o^\ddagger + b \Delta w / w_o \quad (6)$$

or the equation

$$\Delta F_o^\ddagger + f(\Delta w) = \Delta H_o^\ddagger - T (\Delta S_o^\ddagger - b \Delta w / w_o) = \Delta F_o^\ddagger + \frac{b T \Delta w}{w_o} \quad (7)$$

where ΔH_o is equal to the enthalpy of activation and ΔS_o is equal to the entropy of activation. Equation (5) now becomes

$$d \Delta w / dt = \phi (a w_o - \Delta w) k T / h \exp (-\Delta H_o / RT + \Delta S_o / R - b' \Delta w / w_o RT) \quad (8)$$

where $b' = b$ if equation (6) is valid or $b' = bT$ if the $f(\Delta w)$ contribution is to the entropy as in equation (7). Integration of equation (8) offers no simple solution but degenerates into an infinite series. A more direct solution may be obtained graphically by measuring slopes of the Δw versus t curve. It was found that the relation was valid over the entire dehydroxylation range.

A simplified approximation of equation (8) that may be integrated to represent the results up to 75 per cent dehydroxylation as illustrated in Fig. 1 is

$$d \Delta w / dt = \phi w_o k T / h \exp (-\Delta F^\ddagger / RT - b' \Delta w / w_o RT) \quad (9)$$

Setting $A = \phi k T / h \exp (-\Delta H_o^\ddagger / RT + \Delta S_o^\ddagger / R)$,

then equation (9) is integrated with the following obtained:

$$\exp (b' \Delta w / w_o RT) = \frac{A b' t}{RT} + 1 \quad (10)$$

Agreement of equation (10) with the data on dehydroxylation is shown in

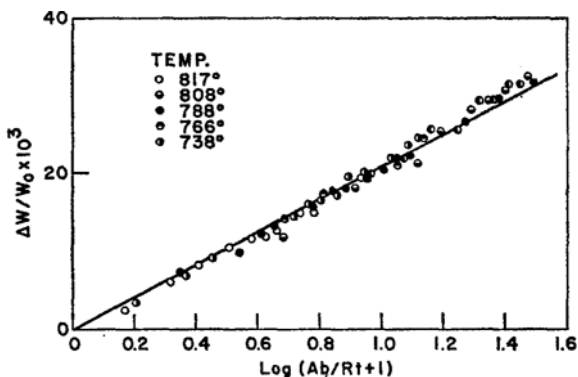


FIGURE 2.—Correlation of data for the various runs at five temperatures.

Fig. 2, where experiments at five different temperatures are correlated. The enthalpy of activation was found to be 90 kcal/mol. The value of the constant b' indicated that $f(\Delta w)$ contributed to the entropy of activation.

A suitable physical model to fit the kinetic data must be formulated. A strain lattice model appears to meet the requirements. In this model, the normal muscovite lattice is in a strained condition. As hydroxyl ions are removed from the lattice, the strain is relieved proportionally. To overcome the increasing tendency of the ions to remain with the lattice, a corresponding increase in energy must be overcome. This energy is the activation energy mentioned previously.

Credence for the strained lattice model was observed when muscovite samples ranging from 0 to more than 90 per cent dehydroxylation were examined with an infrared spectrophotometer.

In Fig. 3 the wavelength of one of the hydroxyl vibrational modes in microns is plotted versus the percentage of water removed. A systematic shift of the absorption band in the 12μ wavelength region with increasing dehydroxylation is noted. The systematic shift was evident regardless of

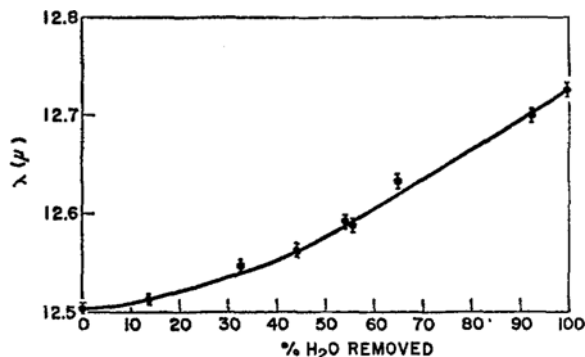


FIGURE 3.—Relation between the percentage of dehydroxylation and the wavelength of the absorption band.

whether the sample sheet was taken from the exterior or interior of the muscovite bundle. This would strongly indicate that dehydroxylation is not taking place in several isolated spots or at an interface, but rather that each hydroxyl ion is equally susceptible to reaction. Thus the dehydroxylation of muscovite cannot be classified into any of the three cases as previously outlined, but has a separate and very different decomposition mechanism.

II. Macrocrystalline Muscovite

When macrocrystalline pieces of muscovite were ground in a rubber-lined ball mill and then decomposed an increase in rate occurred at

approximately 65 mesh (0.23 mm) with the rate becoming even larger with finer particle size. This increase in rate could be due to (1) disruption of the lattice by grinding or (2) a surface area effect.

X-ray diffraction patterns both before and after dehydroxylation indicated that the lattice was not effected by grinding. However, Mackenzie and Milne (1953) found that grinding may cause X-ray powder patterns to become more diffuse and may show new lines belonging to the hydrous micas. This was not observed in our study, perhaps due to a shorter grinding time.

The second possibility of an increased surface area would seem incompatible with the experimental observations on the dehydroxylation of macrocrystalline muscovite. However, it is suggested that muscovite may be composed of crystallites of approximate dimensions indicated above. The decomposition mechanism may then be controlled or influenced by dislocations. By etching with phosphoric acid it was possible to determine the etch pit density which was shown to represent the dislocation density by examining etched pieces which were mirror images of each other. The distance between dislocations was in the order of 0.3 μ m.

The next step would be to establish a relationship between dislocations and dehydroxylation. A high temperature microscope was set up for this purpose, but there was no conclusive visual evidence. Amelinckx and Dalavignette (1962) found that micas exposed to electron radiation form gas bubbles preferentially on dislocations. The thermal decomposition may be very similar to this process. The water vapor may be coming out both the large surface area through dislocations or at least controlled by them, and also out the edges. Cleaving the macrocrystalline muscovite would not influence the rate. The edge area would not become noticeably important until the particle size was within the distance between dislocations. At the present time, however, correlation between dislocations and the dehydroxylation process remains unproven, but provides an interesting field for future endeavor.

III. Pyrophyllite

Pyrophyllite was included in this study because of its structural similarity to muscovite. Sensitivity of the kinetics of dehydroxylation to slight structural changes may be assessed in this manner. As with muscovite, when Δw (change in weight in milligrams) was plotted versus logarithm of time a linear relationship was obtained.

With muscovite it was found that the $f(\Delta w)$ contribution to the free energy of activation was entirely one of enthalpy as determined by the value of b' (refer to equation (8)). The value of b' in turn was calculated from the Δw versus t curves at various temperatures. The same calculation was made with pyrophyllite; the $f(\Delta w)$ factor is almost entirely one of enthalpy from 575°C to 668°C. From 527°C to 575°C this $f(\Delta w)$ contribu-

tion to the free energy of activation is one mainly of entropy. The data certainly indicate a definite change occurring in the state of the activated complex at about 575°C. That this change occurs in anticipation of a phase change is offered as an explanation without experimental proof. It is not necessary to conclude that this change takes place only in pyrophyllite. Such a conclusion could only be made after the experimental investigation of a greater temperature range in muscovite.

The enthalpy of activation was computed from an Arrhenius plot gives a value of 14.4 kcal/mol. This low value indicates the thermal instability of pyrophyllite as compared to muscovite.

IV. Kaolinite

The thermal dehydroxylation has been studied in numerous investigations (Holt, Cutler and Wadsworth, 1962). Murray and White (1949, 1955) conducted extensive research on the thermal decomposition of clay minerals. Their results indicate that the dehydroxylation process follows first order kinetics and agrees with the Arrhenius relation. Brindley and Nakahira (1957) recognized that the dehydroxylation mechanism is very sensitive to water vapor pressure and attempted to answer this difficulty by considering kaolinite pellets of different thicknesses and extrapolating their results to zero thickness. The present study was undertaken in vacuum so the kinetics would be unaffected by water vapor.

It was found that the kinetics of dehydroxylation in a vacuum fit the parabolic rate expression very well. This means that the rate is inversely proportional to the thickness of the dehydroxylated layer for constant area. Since the fraction reacted, R , is proportional to the product layer thickness, the rate equation describing diffusion may be expressed as

$$R^2 = k_p t \quad (11)$$

Figure 4 shows a plot of R^2 versus time at 400°C for the three size fractions. The linear relation holds to 50 per cent dehydroxylation after which it drops off. The non-linearity may be attributed to a decrease in surface area brought about by the fact that the smaller particles are completely dehydroxylated before the large particles. This situation could be corrected only by all particles being exactly the same size and would require extremely precise fractionation techniques.

Data from all three size fractions may be plotted on the same line by using the following procedure. If R is arbitrarily taken to be 0.30, it will correspond to a time $\tau_{0.30}$ for each of the three sizes. By putting these values into equation (11) an expression for k_p may be obtained. This value of k_p is then substituted back into equation (11) and the following equation is produced:

$$R^2 = R_{0.30}^2 t / \tau_{0.30} \quad (12)$$

If R^2 is plotted versus $t/\tau_{0.30}$, a straight line should result with a slope of 0.09. Fig. 5 is this plot; its slope of 0.098 provides good correlation.

Dependence of the rate on surface area coupled with the distinct difference between the undecomposed phase and the almost amorphous metakaolinite phase, requires the movement of an interface. The reaction should then fit into Case I as outlined in the section on theory. The geometrical aspect may be examined by consideration of a single kaolinite crystal.

For convenience one may assume that the kaolinite crystal is a flat cylindrical plate with the interface moving inward from the two flat surfaces. Assuming that all lattice water can diffuse, the number of diffusing species in the crystal is

$$n = \pi r_o^2 h / \lambda^3 \quad (13)$$

where n = number of diffusion species

r_o = radius of crystal

h = thickness of undehydrated portion at time t

λ = crystal equivalent diameter of diffusion species.

Differentiating equation (13) and combining with Fick's first law, one obtains the following expression:

$$\frac{dh}{dt} = - \frac{4\lambda^2 k'}{(h_o - h)} \quad (14)$$

where h_o is the initial thickness of the crystal. The fraction reacted may be expressed as

$$R = \frac{\pi r_o^2 h_o - \pi r_o^2 h}{\pi r_o^2 h_o} = 1 - \frac{h}{h_o} \quad (15)$$

Equation (15) is now differentiated and combined with equations (14) and (15) to give the expression

$$\frac{dR}{dt} = \frac{4\lambda^2 k'}{h_o^2 R} \quad (16)$$

Equation (16) is integrated to obtain the final expression

$$R^2 = \frac{8\lambda^2 k^1}{h_o^2} t \quad (17)$$

Equation (17) agrees with the data of Fig. 4 with the exception of the intercept, which may be attributed to an induction period. This would indicate that the interface is moving inward from the flat surfaces of the kaolinite crystal.

If the interface does progress inward from the two flat surfaces, the (001) and (002) X-ray diffraction peaks should be broadened. Brindley and

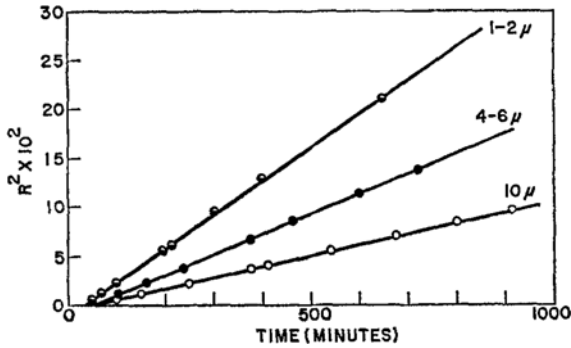


FIGURE 4.—Parabolic plots for three size fractions of kaolinite at 400°C.

Nakahira (1957) observed no broadening with these two peaks in their investigation of kaolinite. Additional X-ray diffraction studies at this laboratory confirmed their conclusions.

Equation (17) could still be valid if the interface moved in a direction parallel to either the *a* or *b* axis. (These directions are not equivalent since kaolinite belongs to the monoclinic system.) Confirmation or rejection of movement in these directions should come on examination of the (020), (060), or (200) peaks. The kaolinite, however, would have to be dehydrated more than 90 per cent before the range of line broadening would be reached. It would then be difficult to observe the presence or absence of broadening.

With the foregoing evidence it may be concluded that the interface separating kaolinite from metakaolinite does not progress inward from the flat crystal faces; it may move in either the *a* or *b* direction, but not in both directions at once.

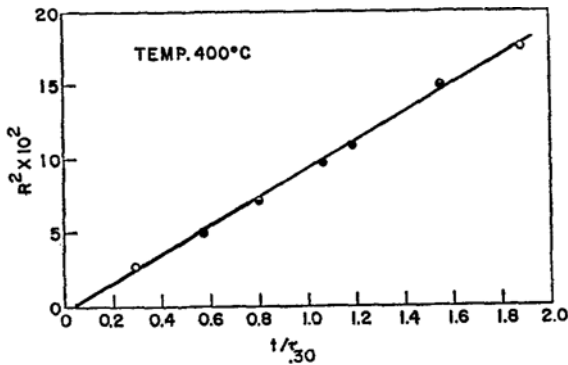


FIGURE 5.—Plot of R^2 versus $t/\tau_{0.30}$ at 400°C using three size fractions.

The experimental data may also be plotted according to the following equation:

$$(1-R) \ln (1-R) + R = \frac{4\lambda^2 k^1}{r_0^2} t \quad (18)$$

This equation is for radial flow through a cylindrical shell with the thickness of the shell increasing. The derivation follows the same procedure as in the foregoing except that the flux equation is modified for diffusion through a cylindrical surface.

On the basis of present experimental data it would be impossible to select unambiguously the correct model. However, that the process is diffusion-controlled seems to be fairly well established.

The activation energy was found to be 43.5 kcal/mol, suggesting that the diffusing species may be hydroxyl ions rather than water molecules. Toussaint *et al.* (1963) in their recent work described the rate-limiting process to be the diffusion of water molecules to the surface of the crystal. The activation energy for this process was 25 kcal/mol. However, their work was conducted in air and thus may account for the difference in values of the activation energy as well as interpretation.

SUMMARY

The dehydroxylation of macrocrystalline muscovite appears to be a homogeneous solid state reaction entirely independent of surface area. A derived equation explains the linear relation between weight loss and logarithm of time. The derivation requires a continual change in the free energy of activation during the process of dehydroxylation. The physical picture presented by the strain lattice model appears to express very well the experimental data.

The rate of decomposition of microcrystalline muscovite increases with a decrease of particle size below about 65 mesh. This may reflect the influence of dislocations on the thermal dehydroxylation. So far, there is no direct proof of such a relationship.

The rate equation of the dehydroxylation of pyrophyllite is based on the same logarithmic time-dependence as muscovite. One difference between the dehydroxylation of the two minerals is that the change in the free energy of activation was found to occur in both the enthalpy and entropy terms depending on the temperature range. The structural difference between pyrophyllite and muscovite has no influence on the formal kinetics, although there is a large difference in heat of activation.

The kinetics of dehydroxylation of kaolinite in vacuum belongs to the class of heterogeneous solid state reactions. It is based on a model of diffusion probably of hydroxyl ions through the metakaolinite layer. The activa-

tion energy is relatively high and in between the activation energies for muscovite and phyllosilite.

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