Residual hydroxyl groups in the metakaolin range.[1]

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[Taken as read 29 January 1959.]

Summary. Infra-red absorption spectroscopy has been used to study the retention of hydroxyl groups by kaolinite and halloysite after heat treatment in the range 600° C. to 850° C. Structurally disordered specimens initially lose water more rapidly than do ordered specimens, but retain hydroxyl groups at higher temperatures. Work on the phases obtained above 1100° C. is incomplete, but results for the lower temperatures indicate that the ordered structures tend to retain their atomic arrangement and form metakaolin, whereas disordered structures readily rearrange to yield γ-alumina, to the formation of which water is probably essential.

A NUMBER of investigators have studied the products obtained by the heating of kaolinite and kaolin minerals. In their investigations they have used the samples obtained either by a comparatively quick heating of minerals up to a given temperature followed by air-quenching or by a more prolonged heating at a determined temperature. In the first case data are obtained on phases which may often be intermediate and subject to changes by longer heating, whereas in the second case a picture of more stable phases is brought out. However, to obtain a better insight into the nature of the processes going on in the course of the heating of minerals, the use of both methods is needed in most cases.

In the attempt to explain the nature and the structure of the heating products of kaolinite and kaolin clays, one is faced with two fundamental problems: the problem of the existence of metakaolinite, i.e. the problem of the structure of the products of dehydroxylation in the temperature range from about 600° C. to 850° C., and the problem of the formation of γ-alumina and mullite in the temperature range above 950° C.

Insley and Ewell (1933) dealt with both problems in an extensive form, but the development of new experimental methods has made it possible to obtain a more detailed knowledge of the nature of the phases occurring in the course of heating.

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[1] Extracted from a thesis submitted to the University of Zagreb for a title of Assistant Professor.

Recently Brindley and Hunter (1955), investigating X-ray rotation diagrams of samples of heated nacrite, have given direct experimental evidence of the residual structural regularity maintained by the Si–O hexagonal network in the metakaolinite range.

At the same time, but quite independently, Roy, Roy, and Francis (1955) have succeeded in demonstrating by single-crystal electron diffraction data that in the metakaolin range dehydroxylated kaolinite maintains a two-dimensional (*a–b*) plane structure very similar to that of kaolinite, whereas in halloysite and hydrothermal kaolinite γ-alumina can already be observed at 650° C. after a prolonged heating of primary substances (12 to 200 hours).

In spite of such considerable advances, we thought it worthwhile to supplement these results with a further study of the heating products of kaolin minerals by means of infra-red spectroscopy, on the assumption that this may be a more direct approach to the understanding of the mechanism of dehydroxylation.

Experimental data.

The samples studied were a well-ordered kaolinite (Skočaj, Croatia; different fractions), a poorly crystallized kaolinite showing a random displacement of layers by multiples of $b/3$, and a halloysite (Gradešnica, Macedonia).

The samples of the well-crystallized kaolinite and the halloysite were first purified by sedimentation and then their purity and the degree of crystallinity were determined by X-ray diffraction. The sample of the poorly crystallized kaolinite was prepared hydrothermally, by a method of Saalfeld (1955), from a well-crystallized kaolinite previously heated at 700° C. for an hour. Rehydration was performed in a pressure bomb at 300° C., 100 atm., in 30 hours. The X-ray diagram of the same sample showed fewer reflections than that of a well-crystallized kaolinite; in fact, it was very similar to the X-ray diagram of a fireclay mineral.

To enhance the reliability of the results, parallel experiments were carried out with the purified Zettlitz kaolin and the kaolin from Dry Branch, Georgia, as well as with halloysite from Djebel Debar. The results obtained with these samples were the same as those obtained with the well-crystallized kaolinite from Skočaj and the halloysite from Gradešnica.

It is a well-known fact that on the average the particles of hydrothermal kaolinite and metahalloysite are smaller in size than those of a well-crystallized kaolinite, and in the interpretation of the results the effect of this factor should be taken into account. In view of this, two fractions were separated from the sample of the well-crystallized kaolinite from Skočaj: one with the platelets larger than *c.* 0·6 μ in the direction of the longer axis, and the other with the platelets smaller than *c.* 0·15 μ. The platelets of the hydrothermal kaolinite were smaller than *c.* 0·2 μ, while the size of the primary metahalloysite particles was below *c.* 0·3 μ. The electron micrographs are reproduced in fig. 1.

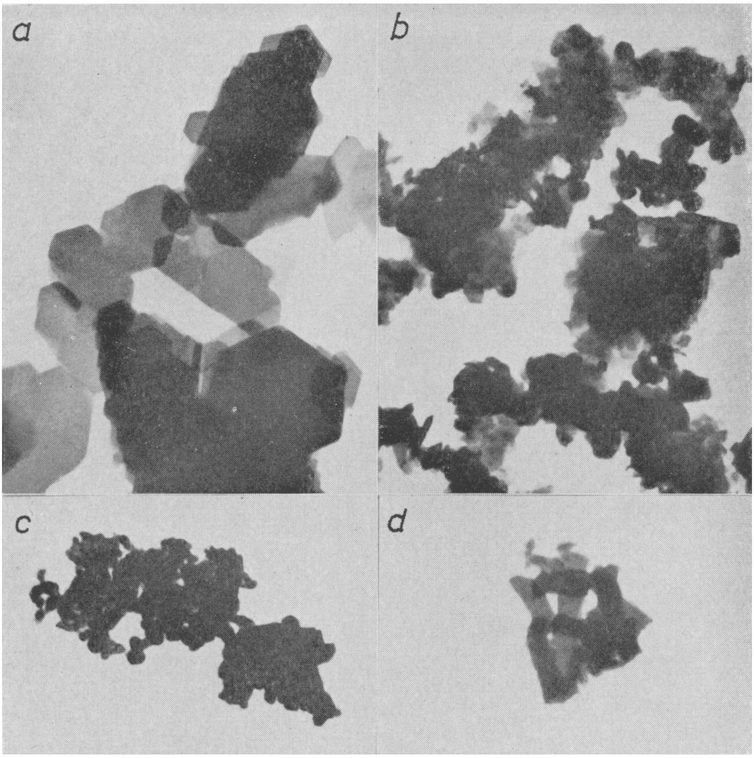

FIG. 1. Electron micrographs: (*a*) a well-crystallized kaolinite, particles larger than 0·6 μ; (*b*) a well-crystallized kaolinite, particles smaller than 0·15 μ; (*c*) a hydrothermal kaolinite; (*d*) a halloysite. All the samples heated at 650° C.

The characteristic temperature ranges of thermal reactions in the minerals examined were determined by differential thermal analysis in a very sensitive apparatus described by Preining and Schedling (1953) (fig. 2).

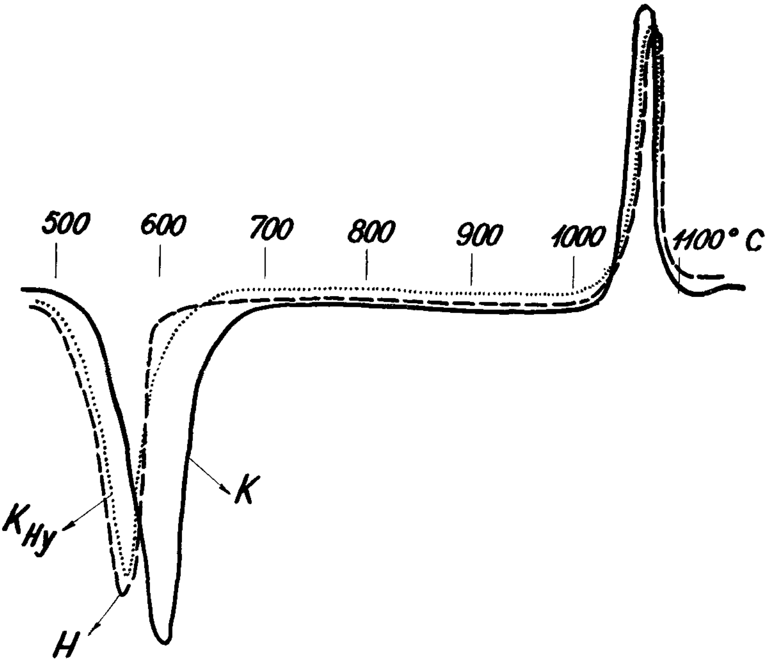

Fig. 2. Differential thermal curves: (K) a well-crystallized kaolinite; (K_{hy}) a hydrothermal kaolinite; (H) a halloysite. Rate of heating 10°/min. Ni-CrNi.

For the preparation of infra-red spectra the samples were for the most part heated in a differential thermal apparatus, air quenched, and mulled after weighing in high-boiling paraffin ('Nujol') or hexachlorbutadiene. Infra-red spectra were obtained on a Perkin-Elmer Model 21 spectrometer.

The infra-red spectrum of the well-ordered kaolinite (fig. 3 A) shows an absorption band at 2·72 μ, which belongs to the hydroxyl groups in the structure; absorption bands between 8 and 10 μ are likely to belong to the Si–O linkage, while the octahedral alumina sheet gives the absorption band between 10 and 11 μ (Adler *et al.*, 1950; Hunt, Wisherd, and Bonham, 1950; Keller and Pickett, 1950). The absorption bands at 3·4, 6·8, and 7·2 μ belong to 'Nujol'. The infra-red spectrum of halloysite (fig. 3 B) differs from that of kaolinite in that it shows an additional absorption band at 2·9 μ suggesting the presence of interlayer water molecules. Other minor differences in the spectra of kaolinite and halloysite in the range of 8 to 14 μ are not very clear.

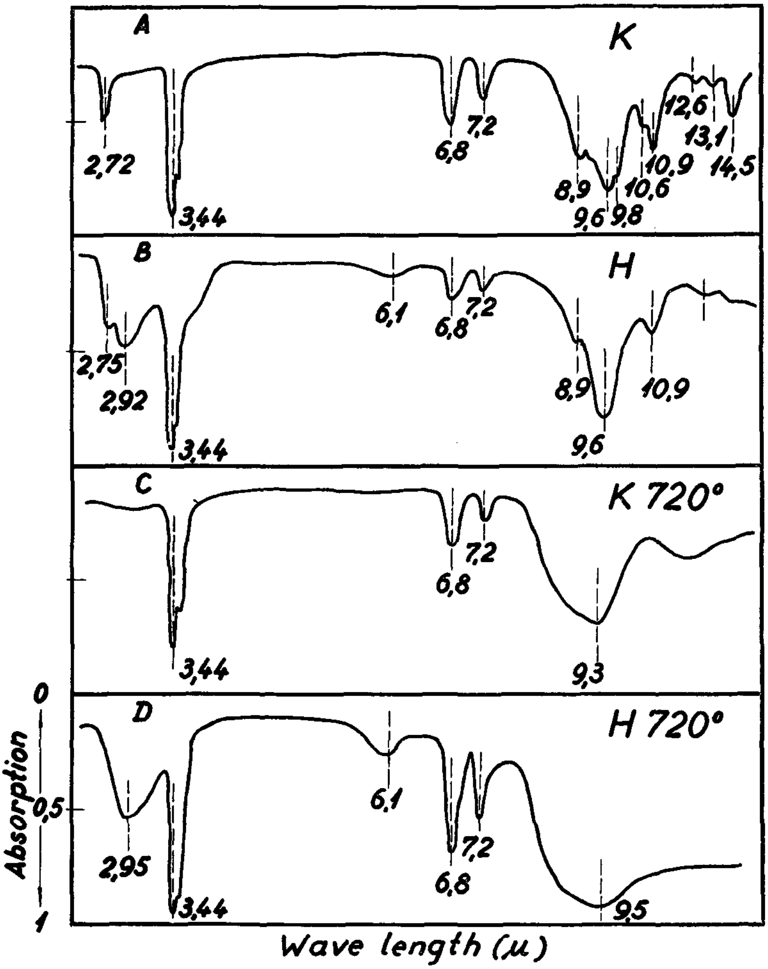

FIG. 3. Infra-red spectra in 'Nujol': (A) a well-crystallized kaolinite; (B) a halloysite; (C) a well-crystallized kaolinite heated up to 720° C.; (D) a halloysite heated up to 720° C.

Heating at 720° C. results in several important changes in the absorption spectra of the well-crystallized kaolinite and halloysite over the spectral range of hydroxyl groups from 2·3 to 4 μ, as well as in the range above 11 μ (fig. 3 C and D). The samples of the well-crystallized kaolinite no longer show the absorption band at 2·72 μ, indicating the

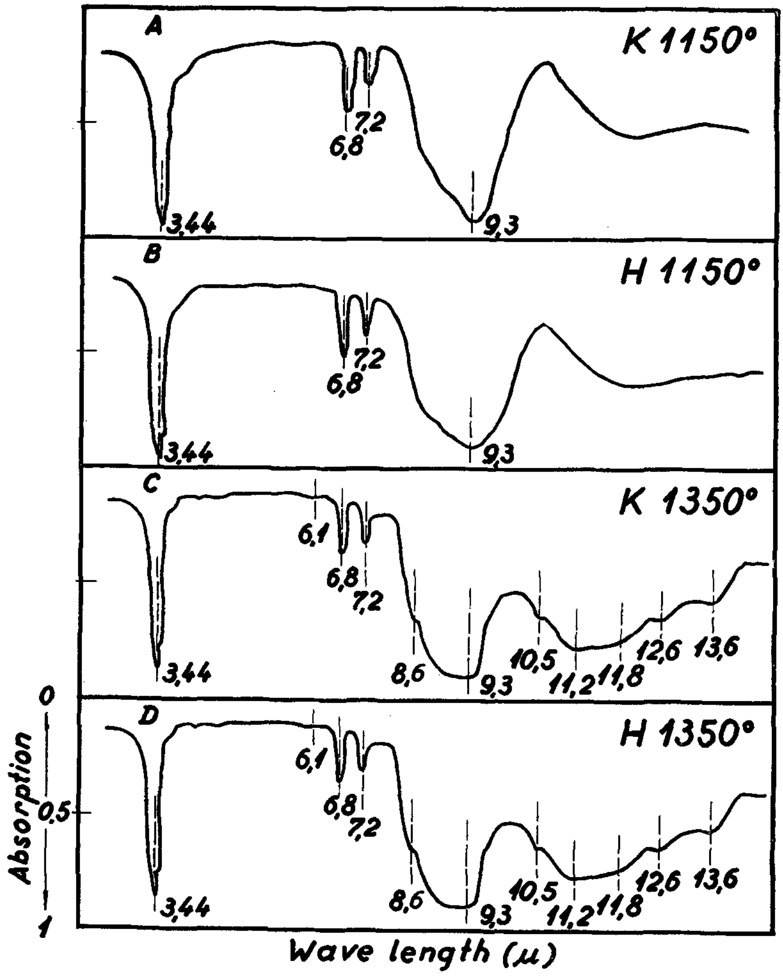

FIG. 4. Infra-red spectra in 'Nujol': (A) a well-crystallized kaolinite heated up to 1150° C.; (B) a halloysite heated up to 1150° C.; (C) a well-crystallized kaolinite heated at 1350° C. for 3 hours; (D) a halloysite heated at 1350° C. for 3 hours.

absence of hydroxyl groups; absorption bands between 8 and 10 μ are replaced by a wider band with a maximum at 9·3 μ, while the absorption band at 10·9 μ has completely disappeared, suggesting a dislocation of the octahedral sheet. By more quantitative work with spectra corrected for background absorption it can be shown that the absorption band with a maximum at 9·3 μ is of lower intensity and narrower than that produced by a coprecipitated alumina–silica gel of the same composition heated at the same temperature. This suggests a greater order in the Si–O linkage in metakaolinite.

Halloysite heated at 720° C. shows a wide absorption band in the absorption range of hydroxyl groups with a maximum at 2·95 μ, as well as an absorption band at 6·1 μ corresponding to adsorbed molecules of water. The absorption spectrum reveals also a very strong absorption in the range above 11 μ. It might be assumed that this absorption is due to some aggregation of particles brought about by heating. However, if the samples are reground and fractionated after heating, and the secondary particles smaller than 2 μ are photographed, a high absorption in this spectral range is observed again. The samples of kaolinite and halloysite heated at 1150° C. give absorption maxima only at 9·3 μ (fig. 4 A and B). However, if heated at 1350° C. for 3 hours, they show a more complicated spectrum with maxima at 8·6, 9·3, 10·5, 11·2, 11·8, 12·6, and 13·65 μ (fig. 4 C and D).

Further study was concentrated on the explanation of the occurrence of an absorption band between 2·5 and 3·5 μ in the samples of halloysite heated in the temperature range 680°–800° C., and on the investigation of the products obtained by heating in the temperature range above 1150° C.

Fig. 5 shows a wide absorption band in the absorption range of hydroxyl groups of the halloysite samples heated above the endothermic maximum. The intensity of this band depends on the relative humidity of the air. The samples heated at temperatures between 800 and 1000° C. do not show this band any longer.

These preliminary results have shown that the properties of the heating products of a well-crystallized kaolinite and halloysite in the temperature range 650° C.–800° C. are different. This led us to the assumption that the mechanism of dehydration of these minerals might be different as well. Since the primary structures of metahalloysite and kaolinite are similar with regard to the structure of layers, the differences obtained by heating may be understood either as a result of the different degree of crystallinity or as an effect of the particle size of the primary substances.

Further investigations have, therefore, been carried out with the samples whose electron micrographs are shown in fig. 1. Care was taken that the heated samples should be protected from humidity as much as possible. The samples were heated in Pyrex tubes in a very thin

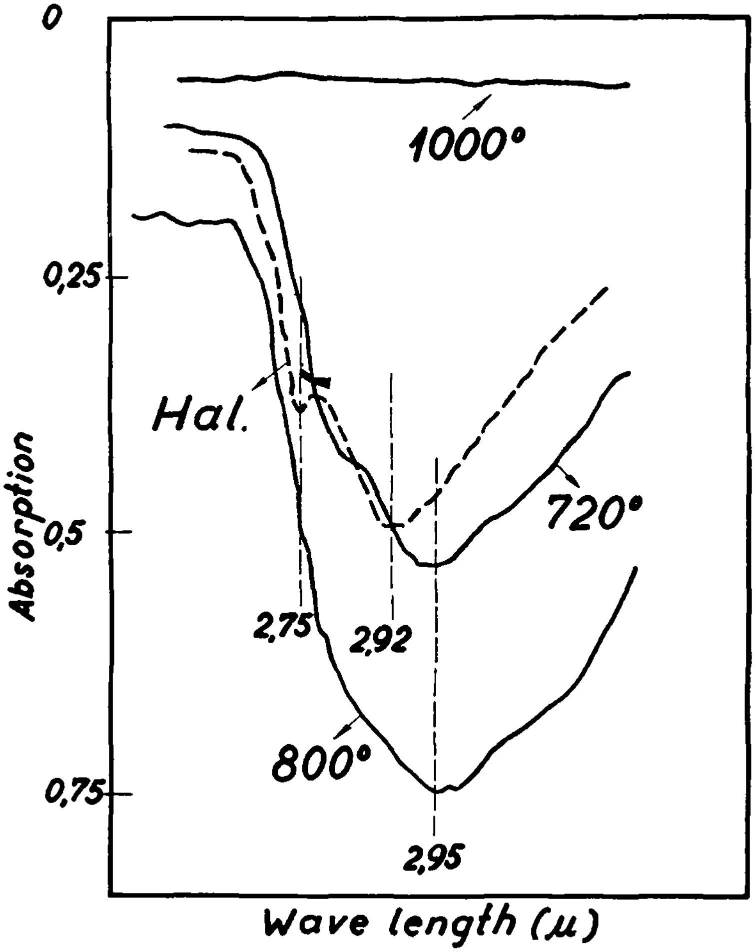

FIG. 5. Absorption of the samples of halloysite heated up to 720°, 800°, and 1000° C. in the range of hydroxyl groups. Rate of heating 10°/min. 'Nujol.'

uncompacted layer. The tubes were sealed as soon as the proper temperature was obtained. After cooling, the tubes were broken and the samples immediately mixed with 'Nujol' or hexachlorbutadiene. In another case, the heated samples were cooled and dried in a vacuum. The best resolution of the absorption bands was obtained when the first procedure was applied.

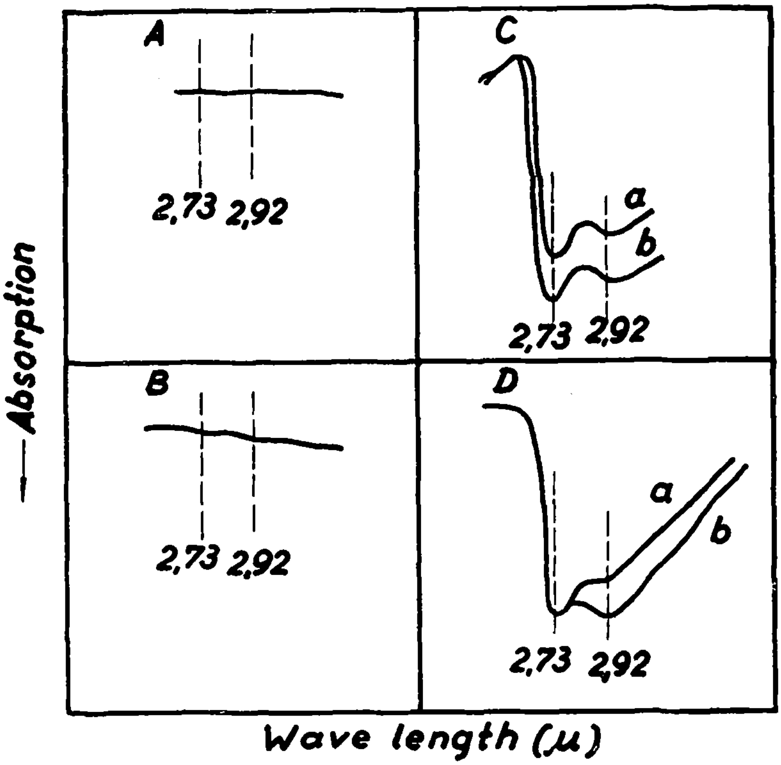

FIG. 6. Absorption in the range of hydroxyl groups: (A) a well-crystallized kaolinite heated up to 680° C., particles larger than 0·6 μ, 'Nujol'; (B) a well-crystallized kaolinite heated up to 680° C., particles smaller than c. 0·15 μ, 'Nujol'; (C) a hydrothermal kaolinite heated up to 680° C. (*b*) and 720° C. (*a*), 'Nujol'; (D) a halloysite heated up to 680° C. (*b*) and 720° C. (*a*), hexachlorbutadiene. Rate of heating 10°/min.

The samples of the well-crystallized kaolinite heated at the temperature immediately above the endothermic peak no longer show absorption in the range of hydroxyl groups, the dehydroxylation being complete regardless of the size of platelets (above 0·6 μ or below 0·5 μ) (fig. 6 A and B). But the samples of hydrothermal kaolinite and halloysite heated in the same temperature range and protected from humidity show in the range of hydroxyl groups two absorption bands with maxima at 2·73 μ and 2·92 μ (fig. 6 B and C), one hardly noticeable band at 6·1 μ, and one pronounced absorption band in the range above 11 μ.

It is interesting to note that the presence of hydroxyl groups is observed in samples of hydrothermal kaolinite heated at 650° C. for an even longer time (3 or 8 hours), while dehydroxylation is complete if heating is performed at 750° C. (heating velocity 10° per minute). With halloysite, dehydroxylation is complete after about a 10-minute heating at 750° C. (fig. 7).

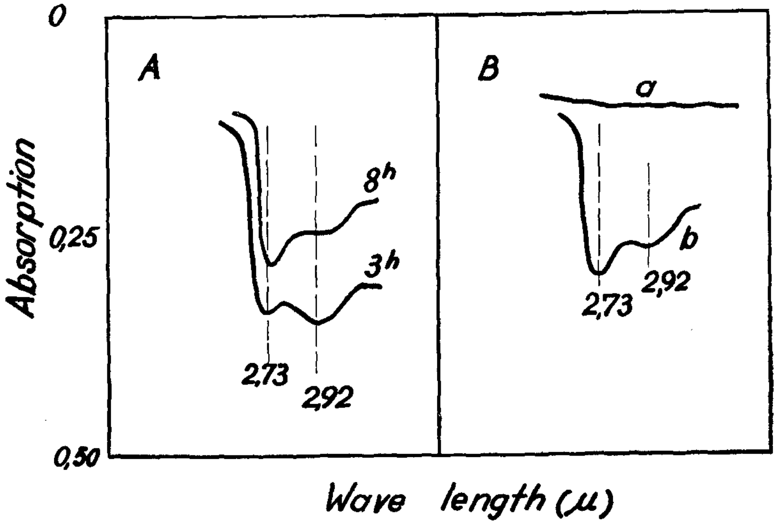

Fig. 7. Absorption in the range of hydroxyl groups: (A) a hydrothermal kaolinite heated at 650° C. for 3 and 8 hours respectively; (B) a hydrothermal kaolinite (*a*) and a halloysite (*b*) heated up to 750° C. Rate of heating 10°/min. 'Nujol.'

No doubt the band at 2·73 μ belongs to free hydroxyl groups most probably present in the structure of the phases occurring in the course of heating. The absorption band at 2·92 μ may be partly but not entirely assigned to adsorbed water. The difficulties in interpreting these bands have already been pointed out by Roy, Roy, and Francis (1957). According to Glemser (1957), in the heating products of hydroxides (aluminium, iron, &c.) the same band can be split into two bands: one supposed to correspond to the free and the other to the bound hydroxyl groups. It is very likely that this band is of a very complex nature.

The further problem relates to the nature of the absorption maxima in the samples heated up to 1350° C. Since in this temperature range a part of the silica remains free, heated samples were treated with 40 % HF for 4 hours at 0° C. (Konopicky, Hopmann, and Kampa, 1956). Infrared spectra of these samples show maxima at 8·55 μ and 8·66 μ respectively, and at 8·96, 9·25, 10·5, 11·2, and 13·6 μ (fig. 8).

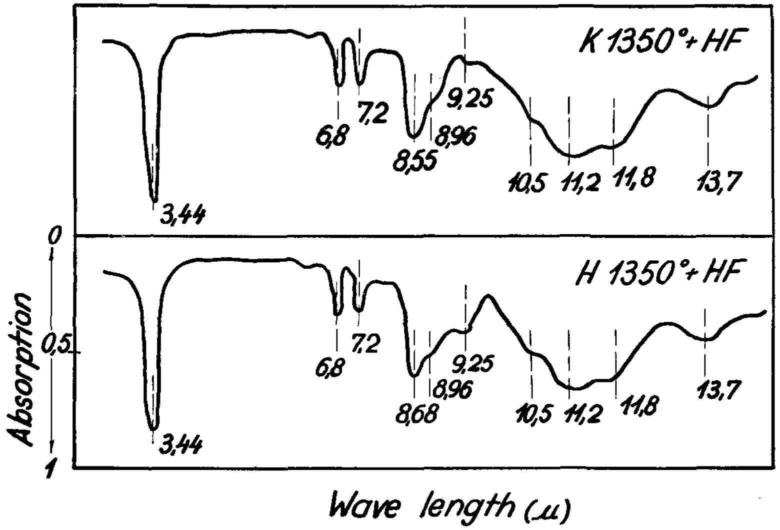

FIG. 8. Absorption spectra of samples of kaolinite and halloysite heated at 1350° C. for 3 hours and treated with hydrofluoric acid. 'Nujol.'

Discussion.

At first sight the results of these experiments may seem incompatible with the fact that structurally disordered kaolin minerals decompose by heating more quickly than well-crystallized kaolinite. This relates to the velocity of dehydroxylation. Kinetic investigations carried out by Murray and White (1955) have given evidence that in some clays of the kaolin type and in halloysite dehydroxylation follows only approximately the first order kinetics, and that there is a certain retardation in the velocity of dehydroxylation after *c.* 90 % of the water produced by the reaction of hydroxyl groups has left the structural network. The same problem has recently been treated by Brindley and Nakahira (1957) when observing isothermally the velocity of dehydroxylation on compact specimens of different thicknesses. The reaction rate constants at various temperatures depend on the size, shape, and compactness of the specimen. If the extrapolation is performed to an infinitely thin disk, the reactions strictly follow the first order kinetics. According to these authors, the retention of water vapour within the specimen and the retardation of the process of dehydroxylation are considerably influenced by geometrical factors.

The results obtained in the study of infra-red spectra show distinct differences in the mechanism of dehydroxylation of kaolin minerals, which are determined by the crystal order of the primary minerals. The same differences may be observed in the samples heated in a very thin layer of uncompacted powder. A well-crystallized kaolinite heated immediately above the endothermal peak no longer shows the presence of hydroxyl groups, while structurally disordered kaolin minerals show two absorption bands in the range of hydroxyl groups ($2{\cdot}72\,\mu$ and $2{\cdot}92\,\mu$).[1] Pronounced differences can also be observed in the properties of the phases obtained above the endothermal peak. The question arises: what brings about these differences, and how do they relate to the nature of the dehydroxylated products?

Johns (1953) discussed the problem of the occurrence of new phases in the process of heating kaolin minerals in relation to structural disorders. A well-crystallized kaolin heated at 1000° C. shows mullite and γ-alumina interferences, while at that temperature with structurally disordered kaolin only γ-alumina can be observed. However, this only relates to the samples heated at the temperature mentioned for a short time. According to Glass (1954), the crystal order of the primary material and the impurities determine the quantitative relations of the phases near the exothermic maximum. Thus, for instance, the amount of mullite near the exothermic peak decreases as the structure becomes more random, and with halloysite smaller dimensions of layers bring about a poor development of mullite nuclei, so that the X-ray diagrams of the samples heated near the exothermic maximum show γ-alumina as the only crystallized phase. Experimental methods used by these authors were not appropriate to give more decisive evidence with regard to the properties of the phases occurring immediately after the endothermal peak.

The present-day knowledge of the phases in the metakaolinite range has considerably advanced, offering strong evidence that a well-crystallized kaolinite heated in the temperature range 650° to 850° C. retains a certain crystal order, while in halloysite a more pronounced decomposition of the network is observed, as well as the formation of γ-alumina by longer heating (Roy, Roy, and Francis, 1955).

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[1] G. Kulbicki and R. E. Grim (this issue, p. 53) have also adduced direct evidence of the retention of water in metakaolin.

The question may now be raised, in what relation these results stand to the properties of the heating products of kaolin minerals heated in the metakaolinite range under non-equilibrium conditions for a short time. Particularly interesting is the retention of hydroxyl groups above the endothermic peak, not being dependent on the size of particles but only on the structural order of primary minerals.

No doubt there is a considerable effect of water vapour pressure on the velocity of dehydroxylation. According to Karšulin (1956), this pressure may be high owing to the presence of water vapour produced in the process of dehydroxylation (hydrothermal conditions). The same author assumes that the mechanisms of dehydroxylation in kaolinite and halloysite are identical, since amorphous silica and a compound of the $5Al_2O_3.H_2O$ type are obtained in the process of dehydroxylation. According to Karšulin, the difference in the behaviour of inner and outer hydroxyls plays an important part in the mechanism of dehydroxylation.

In fact, Houben and de Boer (1952) have shown that the presence of a certain amount of water is probably essential to the existence of γ-alumina. According to this idea, in the spinel structure the aluminium ions should be found in octahedral and tetrahedral configuration, the hydrogen ions only in octahedral configuration. Consequently, the optimum structure of such γ-alumina would correspond to the formula HAl_5O_8. Besides the hydroxyl groups in its structure, such γ-alumina may also, under certain conditions (the effect of water vapour pressure, heating time), contain hydroxyl groups on the surface, and adsorb water molecules.

This interpretation of the phases produced by the thermal decomposition of aluminium hydroxide is supported by the infra-red absorption spectra, i.e. by a wide absorption band in the range of hydroxyl groups and the absence of the absorption band at 6·1 (Glemser and Rieck, 1956). Moreover, the small nuclei of aluminium oxide show an intense absorption in the range above 11 μ. This absorption also seems to be characteristic of very thin aluminium oxide films (250 Å.) obtained by anodizing aluminium foil (Harris, 1955).

It would be difficult to explain the results of our experiments if the properties of the phases occurring in the process of dehydroxylation of kaolin minerals were not taken into account. As has already been said, structurally disordered kaolin minerals obtained in the temperature range 650°–800° C. by even a short heating show some characteristics of mixed phases, i.e. the characteristics of amorphous silica and small crystal nuclei of active γ-alumina.

In a well-crystallized kaolinite dehydroxylation is complete after the endothermic peak, the residual structure of the primary material no longer containing hydroxyl groups. The Al–O groups remain in the monolayer, while the Si–O hexagonal network prevents the nucleation of γ-alumina. So far it has not been possible to determine either the structure of the dehydrated gibbsite sheets or the relation between these sheets and the Si–O hexagonal network, but a strong charge deficiency of the metakaolinite phase has been proved by the adsorption of colloidal gold on the (001) faces of dehydroxylated platelets (Stubičan and Wrischer, 1958).

It seems very likely that in disordered kaolinite minerals the process of dehydroxylation is connected with the more complete destruction of the crystal lattice by even a short heating. The gibbsite sheet produces small nuclei of active γ-alumina, which contain a certain number of hydroxyl groups and can adsorb water molecules on their surface. The properties of these nuclei depend on the duration of heating, on temperature, and on the presence of water vapour. A greater movability of the Si–O complex from the hexagonal network in the structurally disordered kaolin minerals is most probably connected with a weaker bond between successive layers.

Our experiments have offered no evidence in favour of the assumption that the so-called inner and outer hydroxyl groups behave differently in the process of dehydroxylation.

As regards the identification of the heating products above the endothermic peak by their infra-red absorption spectra, the problem is far more complex, and requires further investigation. The heating products of kaolinite and halloysite obtained by short heating in the temperature range 1100°–1350° C. only show a maximum absorption at 9·3 μ, which does not appear to contradict the assumption that mullite is formed in this range. However, the absorption maxima observed in the products obtained by longer heating at 1350° C. (fig. 4) led us to the idea of making spectra of the same samples treated with hydrofluoric acid. The absorption spectra of these samples were not typical of mullite, neither did they show all the maxima of sillimanite (Roy and Francis, 1953).

Acknowledgements. The author thanks Prof. Dr. D. Hadži for his help in the preparation of spectra and for many stimulating discussions. Thanks are also due to Miss M. Wrischer, of the Institute 'Rudjer Bošković', for her work on electron micrographs.

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