13. *The Thermal Decomposition of the Alumina Trihydrate, Gibbsite.*

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It has been found that gibbsite can decompose either to the monohydrate, boehmite, or to χ-alumina, which is virtually anhydrous. When the ignition temperature is raised the decompositions of these two primary products follow independent routes but eventually lead to a common product (α-alumina), at 1000°.

THE thermal decomposition of the hydrates of alumina to corundum (α-Al_2O_3) has recently been shown by *X*-ray diffraction methods to proceed through a number of intermediate stages. Stumpf, Russell, Newsome, and Tucker (*Ind. Eng. Chem.*, 1950, **42**, 1398) have postulated the existence of six intermediate phases that had previously been collectively termed γ-alumina. Thibon, Tertian, and Charrier (*Bull. Soc. chim.*, 1951, 384) have largely confirmed the observations of Stumpf *et al.* but included in their decomposition scheme a seventh intermediate stage. Whilst undertaking an extensive examination of the physical and chemical properties of alumina hydrates and anhydrous aluminas we have obtained similar results. There are, several respects in which our interpretation differs from that of previous workers but fundamentally there is general agreement that the hydrates of alumina, with the exception of diaspore, decompose initially to poorly crystalline substances, the decompositions of which in turn proceed through a series of intermediate stages to well-crystallised corundum.

The thermal decomposition of the trihydrate, gibbsite, is more complex than that of the other three hydrates, bayerite, boehmite, and diaspore. Since our findings agree fully with those of previous workers for the latter hydrates, we shall confine our attention to gibbsite. The nomenclature adopted here is that proposed by Stumpf *et al.*, and we agree with their definitions of the diffraction patterns of the anhydrous modifications, with the possible exception of that of χ-alumina. We do not, however, propose to distinguish in this paper between γ- and η-alumina since the diffraction patterns of the two modifications are very similar and in many specimens any distinction would be quite arbitrary.

EXPERIMENTAL

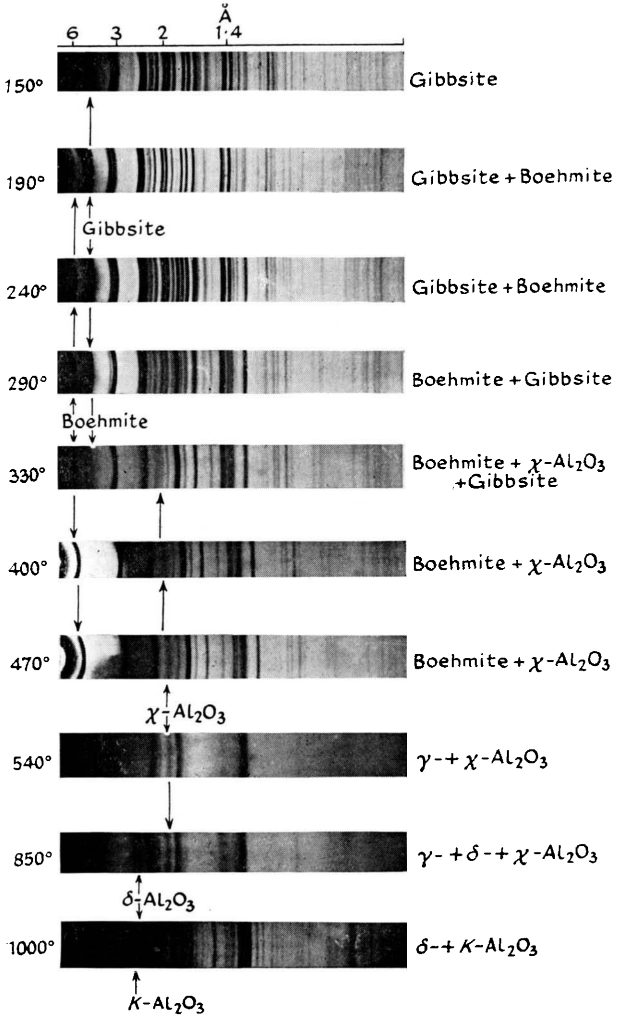
The gibbsite used was prepared by the Bayer process, and contained 0·11% of Na_2O, 0·01% of Fe_2O_3, 0·21% of SO_3, and 34·7% of H_2O. *X*-ray powder diffraction patterns were obtained with Cu-K_α radiation, either 9 or 19 cm. diameter cameras being used. The gibbsite was decomposed thermally in contact with air either by igniting an individual sample to progressively higher temperatures at 40° intervals, retaining each temperature for 1 hour, or by igniting a fresh sample directly to a given temperature which was then maintained for 16 hours.

The diffraction patterns, reproduced in the Plate, were obtained by the former method. Gibbsite was undecomposed below *ca.* 190° but between 200° and 300° it slowly decomposed to boehmite until at 300° the two hydrates were present in approximately equal amounts. At 330° the residual gibbsite suddenly decomposed to χ-alumina, giving a mixture of χ-alumina and boehmite. No further change occurred over the temperature range 330—530°, the ratio χ-alumina : boehmite remaining unchanged. At 530° the boehmite suddenly decomposed to γ-alumina; the sample then consisted of a mixture of χ- and γ-alumina. No further change occurred below 800°, the ratio χ-alumina : γ-alumina remaining constant. Between 800° and 1000° the diffraction patterns became more complex and are best accounted for as those of mixtures of κ- and δ-alumina.

Similar results were obtained by using fresh samples ignited to a single temperature, except that at 550—800° the ratio χ-alumina : γ-alumina decreased with increasing ignition temperature.

These results are taken to indicate that gibbsite decomposes by two mechanisms, *i.e.* (i) to χ-alumina and (ii) to boehmite, which subsequently decomposes to γ-alumina. By using a constant sample the ratios χ-alumina : boehmite and subsequently χ-alumina : γ-alumina are

Progressive heating of a sample of gibbsite.



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fixed after the disappearance of gibbsite, but the use of a fresh sample for each ignition allows the relative amounts of χ- and γ-alumina to vary with the ignition conditions.

When gibbsite was ignited rapidly on an electrically heated foil in a vacuum, χ-alumina was never formed but boehmite or γ-alumina was formed depending upon the temperature reached. Further, boehmite prepared by vacuum ignition of gibbsite, on subsequent ignition at 550° in air, decomposed to γ-alumina without the formation of χ-alumina.

In general, on ignition at 1000°, mixtures of γ- and χ-alumina rich in the latter gave predominantly κ-alumina whilst mixtures rich in γ-alumina gave predominantly δ- and subsequently θ-alumina. Both κ-rich and θ-rich mixtures appeared to decompose directly to α-alumina; thus when κ-rich mixtures were heated at 1000° for prolonged periods, α-alumina was slowly formed without any increase in the trace of the θ-form nor did θ-rich mixtures show an increase in the κ-modification present.

FIG. 1.

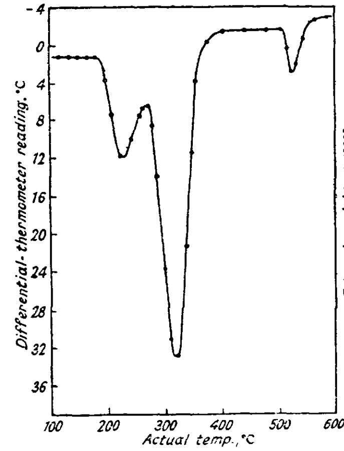
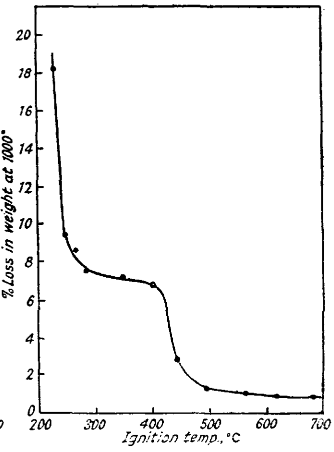


FIG. 2.



The decomposition of gibbsite may thus be represented by the scheme :

$$\begin{tikzcd}
\text{gibbsite} \arrow[r, "300^\circ"] \arrow[d, "200^\circ"] & \chi\text{-} \arrow[r, "800^\circ"] & \kappa\text{-} \arrow[r, "1000^\circ"] & \alpha\text{-alumina} \\
\text{boehmite} \arrow[r, "500^\circ"] & \gamma\text{-} \arrow[r, "800^\circ"] & \delta\text{-} \arrow[r, "900^\circ"] & \theta\text{-} \arrow[u, "1000^\circ"']
\end{tikzcd}$$

The temperatures shown must be considered indicative only since they depend on heating conditions. Thus prolonged heating in air at 200° does not entirely convert gibbsite into boehmite since χ-alumina is still formed after substantial amounts of gibbsite have decomposed. It is not thought that the impurities in the gibbsite control the formation of the χ-modification, since bayerite or boehmite containing similar impurities does not yield it on thermal decomposition.

Differential thermal analysis of gibbsite in an apparatus similar to that described by Voorthüysen and Franzen (*Rec. Trav. chim.*, 1951, **70**, 793) leads to a curve (Fig. 1) exhibiting three peaks below 550°. This curve is further evidence that gibbsite decomposes by two mechanisms. Thus the first peak is due to the change gibbsite ⟶ boehmite, the second to gibbsite ⟶ χ-alumina, and the third to boehmite ⟶ γ-alumina.

Tran-Huu-The and Prettre (*Compt. rend.*, 1952, **234**, 1366) carried out a similar analysis on gibbsite. They did not resolve the low-temperature peaks into two components nor did they record the peak at 550°, resulting from the decomposition of boehmite. They attached considerable importance to the fact that the zero point after the gibbsite deflections was different from the initial zero point, but their view that the change in zero point is due to the exothermic decomposition of boehmite is untenable because of the subsequent peak at 550°. The relatively small variation in zero points could be accounted for by the change in physical properties accompanying the decomposition of gibbsite to χ-alumina + boehmite.

The water content–ignition temperature curve for gibbsite is shown in Fig. 2. This curve was obtained by igniting fresh samples of gibbsite to various temperatures and determining the subsequent loss in weight on ignition to 1000° for 4 hours. It is seen there is no break corresponding to the formation of boehmite (15% of H_2O), but there is a break at *ca.* 6% of H_2O; this break corresponds to the fixed ratio of boehmite to χ-alumina in the range 300—400° to which we have previously referred.

The significance of the *ca.* 1% of water that remains on ignition to 500—700° is discussed by De Boer and Houben (Gothenburg Conference on Chemistry of Solids, 1952). They suggest that the water is constitutional and that γ-alumina has a pseudo-spinel structure, HAl_5O_8.

The interplanar spacings of the intermediate anhydrous modifications are tabulated below.

κ	χ	θ	δ	γ	η
6·0 w					
		5·4 w			
5·02 wvv			5·0 mw		
4·45 w	4·5 wb	4·5 mw	4·5 wb	4·5 wb	4·5 wb
4·15 vw			4·05 vw		
3·80 vvw					
		3·54 w	3·54 w		
3·33 vvw		3·32 vw	3·32 vvw		
3·06 m		3·04 vvw			
		2·86 s	2·86 mw		
2·81 ms					
				2·77 vwb	2·77 vwb
2·73 vw		2·73 s	2·73 ms		
			2·59 mw		
2·57 s		2·57 w			
		2·44 s	2·44 ms		
2·43 m				2·41 mb	2·40 mb
2·33 m		2·32 ms			
			2·28 ms	2·28 m	2·29 wb
2·26 vvw		2·26 ms			
2·18 vvw		2·17 ?	2·19 vvw	2·20 vvw	
2·12 s	2·13 mvb	2·11 vvw		2·09 ?	
2·06 mw					
		2·02 ms			
1·99 m		1·99 vvw	1·99 s	1·98 msb	1·98 msb
1·95 w		1·95 w	1·94 m	1·95 m	
		1·91 mw			
1·87 m	1·87 vvw				
1·83 mw					
		1·80 w	1·80 w		
		1·78 w			
1·75 w					
		1·74 ww			
1·71 vw	1·71 vvw	1·71 ?			
1·64 m					
1·61 vvw		1·62 w	1·61 vw		
		1·57 vw			
1·545 vvw		1·54 m.	1·54 mw	1·53 mwb	1·53 vwb
		1·51 vw	1·51 mw		
1·490 mw		1·49 mw			
1·450 mw		1·45 m			
1·435 s		1·43 vw			
	1·40 sb	1·40 m	1·40 m	1·40 m	1·40 msb
1·392 vs		1·39 s	1·39 s	1·39 s	

s = strong. m = moderate. w = weak. v = very. b = broad.

DISCUSSION

There are three independent indications that the trihydrate gibbsite decomposes by two routes, either to the monohydrate boehmite, or directly to the virtually anhydrous χ-alumina. First, the *X*-ray diffraction patterns show that the formation of χ-alumina is coincident with the disappearance of gibbsite and subsequently the amount of the χ-modification does not increase. If boehmite decomposed to χ-alumina it would be expected that the ratio χ-alumina : boehmite would increase with increasing temperature in the range 300—400°. Secondly, differential thermal analysis indicates a thermal arrest in the region 200—300° which may be resolved into two components, neither of which is the decomposition of boehmite to γ-alumina, which occurs at *ca.* 550°. Although only two hydrates are known to exist in the ignition sequence, three deflections are observed; therefore, one of the hydrates must be decomposing by a dual mechanism. Thirdly, the water content–ignition temperature curve exhibits an arrest in the region 300—400° corresponding very approximately to a hemihydrate. Since there are no independent indication of the existence of an alumina hemihydrate it is reasonable to associate this arrest with a constant ratio of the monohydrate to the virtually anhydrous χ-alumina.

We do not fully understand the factors controlling the degree to which gibbsite decomposes to χ-alumina or to boehmite. Therefore we shall only record that the following ignition conditions increase the degree to which gibbsite yields boehmite or boehmite-decomposition products: (*a*) autoclaving it with water at *ca.* 200°; (*b*) ignition in a vacuum, (*c*) direct ignition in air to about 750° rather than to about 500°.

We have not been able to prepare pure χ-alumina since the decomposition of gibbsite yields χ-alumina + boehmite followed by χ- + γ-alumina. The unique *X*-ray diffraction spacings of the χ-modification must therefore be deduced by subtraction of boehmite or of γ-alumina spacings from the diffraction patterns of the appropriate mixtures. Thus we believe that the diffraction pattern of the χ-form is substantially 2·13 m, 1·87 vvw, 1·40 s.

When gibbsite has completely decomposed to χ-alumina + boehmite, the two components of the mixture follow their own decomposition routes and we have found no evidence of cross linking of the two routes. We have been unable to observe any of the transitions, boehmite $\rightleftharpoons$ χ-, χ- $\rightleftharpoons$ γ-, δ- $\rightleftharpoons$ κ-, θ- $\rightleftharpoons$ κ-alumina.

It follows from the dual decomposition of gibbsite that κ-alumina as defined above and by Stumpf *et al.* and Thibon *et al.* may contain δ- or θ-alumina. A close examination of several preparations of κ-alumina shows small variations of intensity in certain diffraction spacings which are more especially associated with δ- and θ-alumina. There can be no doubt, however, of the existence of two well-crystallised modifications, κ- and θ-, which represent the final states of the two decomposition routes before the formation of the common end product, α-alumina.

Our scheme for the decomposition of gibbsite thus differs from that proposed by Stumpf *et al.* It is not necessary to postulate (cf. Stumpf *et al.*) that boehmite may decompose to either χ- or γ-alumina or that formation of the γ-form may precede the formation of either δ- or κ-alumina. The scheme proposed by Stumpf *et al.* does not account for (i) the constant ratio of χ-alumina to boehmite and of χ- to γ-alumina obtained on ignition of an individual sample, or for (ii) the differential thermal analysis curve.

Thibon *et al.* (*loc. cit.*) proposed a more complex scheme in which the ignition of an individual sample produces κ^1-alumina (which passes through κ- to α-alumina), whilst ignition of a fresh sample produces χ- followed by η-, and thence through θ- to α-alumina. We believe that κ^1-alumina is a mixture of χ- and η-(or γ-)alumina for two reasons. Firstly, the proposed diffraction pattern of κ^1-alumina does not account for the fact that all of the diffuse reflections obtained in the region 500—750° (so-called κ^1-form) are not apparent in the region 300—400° (so-called κ^1-form + boehmite). Secondly, the conclusion that fresh samples alone give χ- + η-(or γ-)alumina appears to be an arbitrary interpretation that is required by the fact that the ratio χ- to γ-alumina varies in the 500—700° region only when a fresh sample is used for each ignition.

The decomposition routes of the four hydrates of alumina may be summarised as follows:

$$\begin{tikzcd}
\text{gibbsite} \arrow[r] \arrow[d] & \chi\text{-} \arrow[r] & \kappa\text{-} \arrow[r] & \alpha\text{-alumina} & \text{diaspore} \arrow[l] & & \\
\begin{array}{c}\text{boehmite}\\ \text{(well}\\ \text{crystallised)}\end{array} \arrow[r] & \gamma\text{-} \arrow[r] & \delta\text{-} \arrow[r] & \theta\text{-} \arrow[u] & \eta\text{-} \arrow[l] & \begin{array}{c}\text{boehmite}\\ \text{(poorly}\\ \text{crystallised)}\end{array} \arrow[l] & \text{bayerite} \arrow[l]
\end{tikzcd}$$

Boehmite decomposes to γ- or to η-alumina, depending on the crystallinity of the monohydrate and the η-form may be regarded as an extremely poorly crystalline γ-alumina.

The precise physical significance of the six modifications of alumina that precede the formation of corundum is at present obscure. It is, however, doubtful whether η-, γ-, or δ-modifications should be considered to be well-defined phases. No sharp changes can be observed in the powder patterns of the η-, γ-, δ-, or θ-forms which suggests that the transitions are continuous and represent a gradual ordering of the structure by diffusion of Al^{3+} and possibly O^{2-}. θ-Alumina represents the final, completely ordered member of this sequence and is a definite crystallographic structure, as yet undetermined. Similarly χ-alumina may be considered as the precursor of the well-defined κ-alumina.

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