

STRUCTURE AND TEXTURE OF ALUMINAS

PROEFSCHRIFT

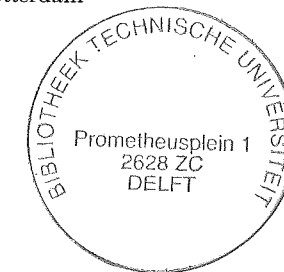
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INTRODUCTION

During the last few decades a growing number of catalytic processes has been used in the petroleum industry, with the aim of improving the quality of certain products, either by elimination of harmful impurities or by modifying the chemical composition. The catalytic cracking of high-boiling fractions into gasoline and kerosine with the aid of such proton-active catalysts as silica-alumina forms an almost classical example of these processes. Of late the so-called "reforming" processes have come to the fore, aiming at quality improvement by isomerisation (formation of branched and of cyclic compounds). Also the necessity of eliminating certain components which may be detrimental to the activity of some catalysts or are undesirable in the final product, has led to the development of new catalytic processes, *e.g.* the desulphurisation of oils by conversion of the sulphur compounds with hydrogen to hydrogen sulphide.

The ever growing demand of new techniques and economic developments led to an increasing interest in practical and fundamental research into the catalytic processes. We can distinguish different trends in this research, according to whether the reaction itself is emphasized or the catalyst accelerating it.

If the reaction itself is to be studied the aim will be to obtain an insight into the factors influencing the rate of reaction and the occurrence of possible side reactions by kinetic measurements *e.g.*, starting with a limited number of catalysts. In many cases diffusion phenomena appear to play a predominant part.

Another way of attacking the investigation of the reaction itself is to start from the simplest form of the reaction and with a catalyst of known structure and texture, which, however, need not have any technical importance. In this way the fundamental principles are investigated. As the investigation progresses the conditions can be adapted to the technical, more complicated method.

Combination of the two methods will finally lead to an understanding of the mechanism and the kinetics of the reaction. It is clear that the method of investigating the catalytic reaction itself is of interest especially to those industries which apply the process themselves. On the other hand, those which are specialized in the commercial manufacture of

catalysts will pay more attention to the catalysts themselves. The final purpose then is to obtain the catalyst most suitable for a given reaction, both technically and economically.

In this respect the activity, the selectivity and the stability of the catalyst are the determining factors. Starting from a given reaction the most suitable method of preparing the catalyst and the optimum reaction conditions have to be found. This, necessarily more or less empirical, research will have to be supported by a more fundamental investigation of the catalyst itself.

A catalytic reaction proceeds at – or in the immediate neighbourhood of – the surface of the catalyst. The initiating reaction will always be the adsorption of a molecule on the surface. Adsorption takes place under the influence of the atomic fields of force in the outer layers of the catalyst. These fields of force will determine the catalytic activity. In the first instance, the stacking arrangement of the atoms in the surface will influence the activity. GWATHMEY *et al.* [1] found, for instance, that the reaction rate between hydrogen and oxygen was twice as high on the (111)-plane as on the (100)-plane of copper single crystals.

Not only the atoms of the outer layer determine the activity, but also the position and the kind of the atoms in the inside layers may have an influence. A well-known example is the decomposition of formic acid on oxidic catalysts, the surface of which is assumed to consist of oxygen atoms only. On MgO, for instance, it principally decomposes into H_2 and CO_2 , whereas on aluminium oxide, however, H_2O and CO are formed preferentially. Other oxides occupy an intermediate position; both reactions can proceed side by side at different ratios [2].

A third factor that may affect the activity of the surface, is the occurrence of distinct lattice defects. As was shown by RHODIN [3], the heat of adsorption of nitrogen on the three main crystal planes of copper single crystals is almost constantly about 2 kcal/mole. On polycrystalline copper, however, the heat of adsorption at low degrees of coverage was many times higher and decreased strongly with increasing coverage. DIENES [4] reported that the activity of silica and of γ -alumina for the ortho-para conversion of hydrogen and for the exchange of hydrogen and deuterium was greatly enhanced by radiation. In the case of gamma- and of beta-radiation, which only produce a change in the energy levels of the electrons, the activity increase is soon lost; radiation with neutrons, which displaces atoms giving interstitials and clusters, produces an increase in activity which remains stable over a very long period.

These examples show the importance of a complete investigation of crystallographic structure and orientation. Besides the crystallographic

factors determining the character of the surface, the magnitude and the accessibility of the surface may have a major influence on catalytic activity.

In the first instance, we may expect activity to be proportional to the surface area. In reality such a proportionality seldom occurs. The extreme division of the solid which is necessary to obtain a large surface area causes the pores between the particles of the solid to become very narrow. In such narrow pores diffusion can easily be hindered. Besides the width of the pores also their shape can be important; in a slit-shaped pore the diffusion will proceed faster than in a cylindrical one having the same wall separation.

Among the catalysts applied and proposed for “reforming” processes there is a great number of compositions consisting of a catalytically active substance on an “inactive” substance such as aluminium oxide as the carrier. It is, however, generally accepted now, that the carrier plays an essential part as regards the activity of the catalyst. From the extensive patent literature it appears clearly that the history of the carrier is a very important factor for the activity and the stability of the catalyst.

Technical aluminium oxide is almost exclusively obtained by heating of the hydroxides. Both the hydroxides and the oxides are described in literature in many forms, comprising all stages from almost completely amorphous to well-crystallized substances. Many conflicting statements on their properties are recorded. The investigations described in this thesis aim at contributing to the understanding of the crystallographic properties and of the shape and size of the pores of the various aluminium hydroxides and oxides. This complex of structure and orientation factors will be denoted by the term “texture”.

The ways along which we have tried to attain our object, are:

- a. optical investigation with light- and electron microscope for observation of the morphology;
- b. X-ray and electron diffraction for the determination of crystal structure and crystal orientation;
- c. adsorption measurements to obtain information on the size and the shape of the pore system.

In the first part of this thesis we shall discuss the preparation methods, the morphological phenomena, the crystal structure and the pseudo-morphous transitions of the hydroxides and the oxides; the second part will describe the evolution and the changes of the pore system during the preparation and the heating of the oxides.

PREPARATION AND MORPHOLOGY OF THE HYDROXIDES

I.1 Introduction

The many forms in which aluminium hydroxides can occur can be represented in the following scheme:

Crystalline modifications		Gelatinous products
trihydroxides $\text{Al}(\text{OH})_3$	oxide-hydroxides AlOOH	$\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$
gibbsite bayerite nordstrandite	diaspore boehmite	<i>e.g.</i> C_α -, C_β -, C_γ -gel of WILLSTÄTTER fibrillar amorphous hydroxide of WISLIGENUS gelatinous boehmite <i>etc.</i>

Other names for the same material occur in literature; thus gibbsite is often called hydrargillite (especially in Germany and in France). Bauxite is the name for the naturally occurring aluminium hydroxide ores. It mostly contains a considerable amount of impurities, such as Fe_2O_3 , SiO_2 , TiO_2 *etc.* According to the origin of the ore, it consists of gibbsite (Surinam, Ural) or of poorly crystallized boehmite (France); the Balkan ores often contain a large quantity of diaspore.

The notation in literature is rather complicated. Often the indication aluminium hydrate is used, though infrared investigations have clearly shown that the water molecules which are expelled on heating are present in the crystalline modifications as OH-groups. Also the use of Greek characters should be rejected, as at least two different notations are used; we therefore prefer the trivial names to distinguish between the different forms.

Gibbsite is the best-known crystalline trihydroxide. BONSDORF [5] described it as early as 1833. Technically, it is the most important hydroxide, because it is used as an intermediate for the production of aluminium metal from bauxite (Bayer process).

Bayerite was discovered in 1928 by FRICKE [6] who studied the formation of the trihydroxides by X-ray diffraction. Its properties are less

known than those of gibbsite, probably owing to the fact that it is very difficult to obtain free from the other hydroxides and that it is mostly poorly crystallized.

Even less is known about the third trihydroxide, which was described for the first time by VAN NORDSTRAND [7] who named it bayerite-II. As far as we know now, it is not obtained in a pure form. As the name of bayerite-II is not very adequate, German and Dutch investigators [8] have suggested to call this modification "*nordstrandite*". This name is more and more generally accepted now.

The two oxide-hydroxides, diaspora and boehmite, are sporadically found in nature in a well-crystallized form. They are always contaminated with iron compounds. Synthetic diaspora is very difficult to prepare since it is stable only at a very high water vapour pressure and high temperatures. Diaspora has not been applied technically, nor has the well-crystallized boehmite which can also be obtained only under hydrothermal conditions.

The systematic investigations of the gelatinous forms date from more than forty years ago. WILLSTÄTTER and KRAUT [9] prepared various gels (or gel-like products) which could be distinguished by their adsorptive properties with respect to enzymes *etc.* The application of X-ray techniques by KRAUT, KOHLSCHÜTTER, WEISER and MILLIGAN (see CHAPTER I.4) showed that at least part of these products was more or less crystalline. The electron microscope gave a picture of the many different forms which can occur in these materials. Many of these gelatinous hydroxides are technically very important, because they make up the base materials for the various types of activated alumina used as adsorbents or as catalysts.

To be suitable for the preparation of reforming catalysts the aluminium hydroxide has to conform to very high purity requirements. Especially the iron and alkali content must be very low. Consequently, the naturally occurring products are almost entirely excluded. Also synthetically prepared gibbsite is not very suitable since it mostly contains a rather considerable amount of sodium which cannot be removed entirely.

Bayerite is sometimes applied as a base for reforming catalysts, mostly in combination with small amounts of gelatinous boehmite and nordstrandite (probably formed occasionally during manufacture). A great part of the patent literature is based on gelatinous aluminium hydroxide as a base material.

We therefore concentrated mainly on the preparation, morphology and texture of bayerite and boehmite, without losing sight of the other compounds.

I.2 The crystalline trihydroxides

I.2.1 Gibbsite

The technical method for producing gibbsite by the Bayer process consists in slowly cooling a concentrated sodium aluminate solution (prepared by treatment of bauxite with a sodium hydroxide solution) with addition of crystal seeds. The gibbsite so obtained mostly consists of fairly large almost spherical crystal conglomerates that can be easily filtered.

A more suitable laboratory method consists of partly neutralizing a sodium aluminate solution with CO_2 . In our research group OOMES [10] investigated this reaction, for which he found the following scheme of transformations:

Sodium aluminate solution + $\text{CO}_2 \rightarrow$ amorphous hydroxide (I) $\rightarrow$ gelatinous boehmite (II) $\rightarrow$ bayerite (III) $\rightarrow$ gibbsite (IV) $\rightarrow$ well-crystallized boehmite (V).

Even at room temperature the formation of (I) is difficult to observe; it is very easily transformed into (II). Also the conversion of (II) into (III) proceeds fast at room temperature, that of (III) to (IV), however, is very slow. Consequently, at room temperature the product obtained mainly consists of bayerite.

At 50 °C bayerite is more easily converted into gibbsite, whereas the first two reactions proceed so fast that they cannot be followed. At a still higher temperature (preferably above 80 °C) gibbsite is slowly converted into well-crystallized boehmite. So starting with gelatinous boehmite and treating this with a strongly alkaline solution, first gibbsite is formed which, later on, is transformed into boehmite again, but then in a well-crystallized form.

The gibbsite obtained from the aluminate solutions with CO_2 sometimes consists of thin six-sided, nearly hexagonal platelets with a diameter of about 0.3 μ , sometimes of rod-shaped crystals with dimensions of about 10 $\times$ 3 μ .

I.2.2 Bayerite

As already stated before bayerite can be obtained as an intermediate during the preparation of gibbsite from aluminate solutions with CO_2 . However, it is very difficult to obtain pure bayerite in this way because it is mostly contaminated with some gelatinous boehmite or with some gibbsite. Moreover this form of bayerite always contains some sodium that is difficult to eliminate. We therefore have not applied this method.

By treating gelatinous aluminium hydroxide with a solution of NH_3

products are obtained consisting for the greater part of bayerite. KRAUT [11], who investigated this conversion in detail, distinguished three types of bayerite (A, B and C) possessing somewhat different X-ray diagrams.

SCHMÄH [12] treated amalgamated aluminium foil with water at room temperature and obtained bayerite with a sharp X-ray diffraction pattern. MILLIGAN [13], however, is of the opinion that pure bayerite cannot be prepared.

The methods of KRAUT and SCHMÄH are very well suited for the preparation of pure aluminium hydroxide, also on a large scale. We have investigated these two methods. For the characterization of the quality of the products obtained we used:

- the loss on ignition of the material previously dried at a temperature of 120 °C, upon heating for about 30 minutes in a platinum crucible at 1100 °C. For pure hydroxides the loss on ignition is equal to the water content W , which we shall express in grammes per 100 grammes of Al_2O_3 ;
- the specific surface area S in $\text{m}^2/\text{g Al}_2\text{O}_3$, measured by adsorption of nitrogen at a temperature of 78 °K (see CHAPTER V). The lower the specific surface area, the greater the particle size of the material;
- the DEBIJE-SCHERRER X-ray pattern. This gives an impression of the perfection of the crystallinity: line broadening points to the presence of small crystallites and/or many lattice imperfections. Moreover, in the latter case, the intensity of the reflections in the region of high diffraction angles (the back-reflection part) will be very low. Sometimes a shift in the diffractions angles of some reflections will occur.

To prepare bayerite by treating gelatinous boehmite with an NH_3 -solution we started with a product obtained by topochemical conversion of alum with an ammoniacal solution of ammonium sulphate (see I.4). The wet cake obtained in this procedure was washed free of sulphate with a 0.5 % NH_3 -solution. Equal parts of it were suspended in the ten-fold quantity by weight of dilute ammonia. We used NH_3 -concentrations of 0.5, 1.0 and 5.0 % both at room temperature and at 45–50 °C. Occasionally a small amount was filtered off, washed with water and dried at 120 °C. Of these preparations the water content W and the specific surface area S were determined. The results are given in TABLE I.1.

In FIG. 1 the specific surface area of the preparations obtained at 20 °C is plotted against the water content W . There exists an almost linear relation between these two quantities. From the slope of the curve

TABLE I.1 Conversion of gelatinous boehmite into trihydroxide

hours	0.5 % NH_3				1.0 % NH_3				5.0 % NH_3			
	20 °C		50 °C		20 °C		50 °C		20 °C		50 °C	
	W	S	W	S	W	S	W	S	W	S	W	S
0	30.9	256	30.9	256	30.9	256	30.9	256	30.9	256	30.9	256
1	25.2	303	29.6	250	29.2	263	31.2	240	30.1	254	33.6	212
4	27.0	274	—	—	34.0	217	—	—	39.0	184	—	—
6	29.2	260	—	—	35.8	202	—	—	42.2	158	—	—
24	—	—	34.2	218	44.2	123	50.1	153	46.8	122	51.0	130
48	31.6	229	40.6	—	46.1	99	51.2	128	50.1	76	51.7	86
96	35.4	191	47.3	97	49.2	67	51.8	74	51.0	57	52.4	53
168	39.8	120	—	—	—	—	—	—	—	—	—	—
672	48.6	42	—	—	—	—	—	—	—	—	—	—
X-ray	bay, gelbo		bay, gelbo		bay, gelbo		bay, nords		bay		bay, nords	

W in g/100 g Al_2O_3

S in $\text{m}^2/\text{g Al}_2\text{O}_3$

bay = bayerite,

nords = nordstrandite,

gelbo = gelatinous boehmite

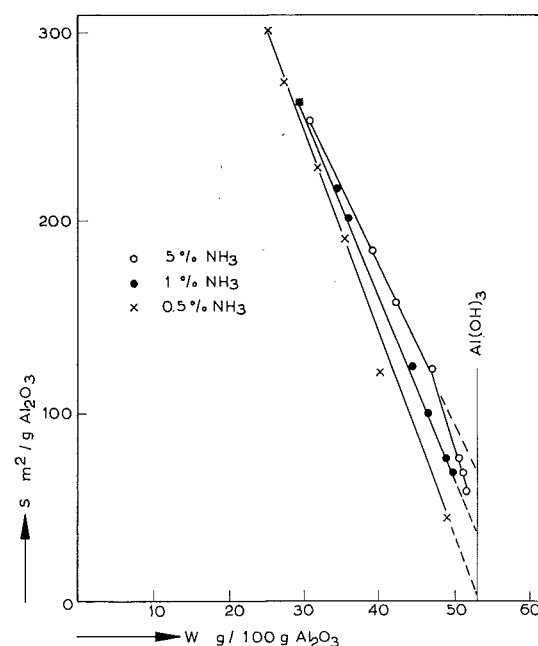


FIG. 1. Conversion of gelatinous boehmite into trihydroxides in dilute ammonia

and the intercept at $W = 53.0$ it follows that the particle size of the bayerite formed is greater according as the ammonia concentration was lower and the conversion proceeded more slowly. Since all X-ray patterns were very weak in the back-reflection part, the degree of crystallinity was low. Also the amount of nordstrandite formed was very low.

None of the preparations showed the theoretical water content of 53.0 g/100 g Al_2O_3 . Probably all of them still contained some gelatinous boehmite which escaped X-ray observation.

It is clear that this method is not very suitable for the preparation of pure bayerite.

For the method given by SCHMÄH we used a very pure aluminium foil (purity 99.99 %, thickness 2 mm). Strips about 10 cm long and 1½ cm wide were degreased with acetone, etched with a 2n NaOH-solution for 10 seconds and then thoroughly rinsed in distilled water. Next they were amalgamated by immersion for 2 seconds in a 1 % HgCl₂-solution and again thoroughly rinsed.

The strips were placed in porcelain disks containing 100 ml water and brought to different pH's by adding NH₃ or by saturating with CO₂. After a week's exposure at room temperature, during which time the pH was kept constant by adding NH₃ (if necessary), all aluminium was dissolved, except the preparation with CO₂. In TABLE I.2 the results are given.

TABLE I.2 Preparation of bayerite with the method of SCHMÄH

pH	W g/100 g Al ₂ O ₃	S m ² /g Al ₂ O ₃	X-ray pattern
12	52.6	48	bayerite, nordstrandite
11	54.4	33	bayerite
9	54.8	28	bayerite
7	54.6	6	bayerite
satd. with CO ₂	31.8	436	gelatinous boehmite

The back-reflection part of the X-ray patterns was invariably very diffuse, except for the preparation at pH = 7.

The best results were thus obtained in water at a pH of 7. It should be mentioned that the presence of electrolytes like ammonium sulphate considerably slowed down the formation of bayerite; in all cases some gelatinous boehmite was formed.

From the magnitude of the specific surface area it appears that the bayerite particles are still small. With the normal light microscope they can hardly be observed. KOHLSCHÜTTER *et al.* [14] succeeded in ascertaining their shape with a magnification of 2000×. They found truncated pyramids or cones, which they called somatoids (particles with equal shape).

Sometimes these somatoids had grown together at their tops, forming hour-glass-shaped particles. WATSON and collaborators [15] and MOSCOU and VAN DER VLIES [16] took electron micrographs of the bayerite somatoids, showing them to consist of a great number of plates approximately perpendicular to the longitudinal direction of the somatoids. Micrographs of our own preparations confirmed this result (PLATE I).

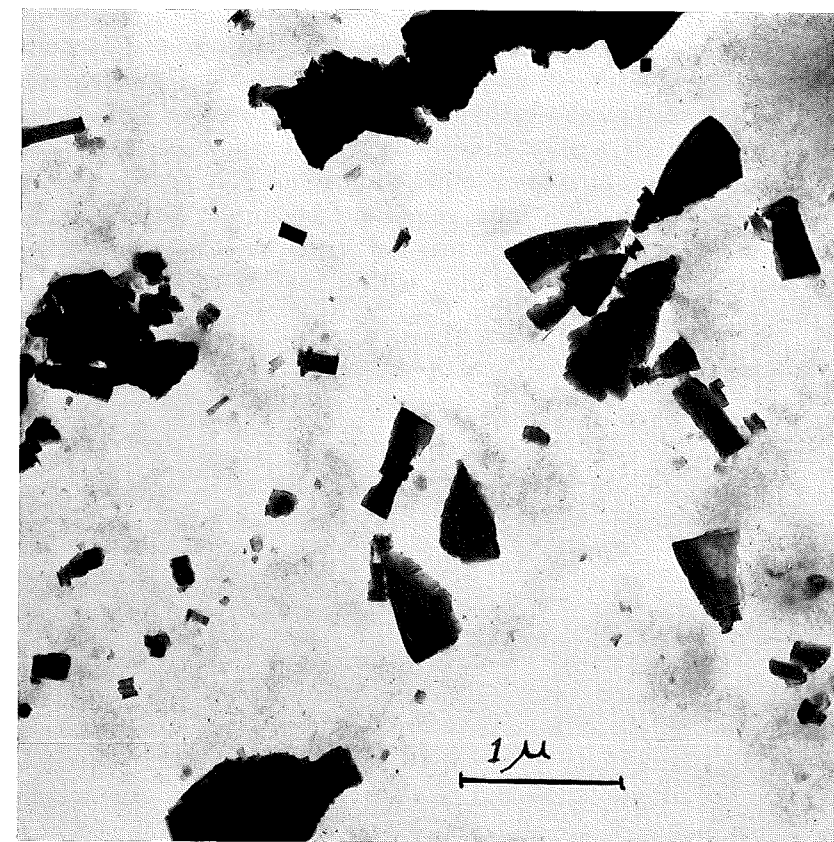


PLATE I. Bayerite (SCHMÄH)

The size of the somatoids can vary considerably. Their width is mostly smaller than 0.5 μ, their length can vary between 3 and 10 times their width.

In the preparations obtained by treating gelatinous boehmite with dilute ammonia we could observe two types of particles with a shape different from the somatoids, *viz.* platelets and rods. These types will be discussed in CHAPTER III.

I.2.3 Nordstrandite

When we started our investigations on the products obtained by treating gelatinous boehmite with ammonia, we often observed in the powder diagrams a number of lines that did not correspond to the reflections of the trihydroxides known at that time. VAN NORDSTRAND

et al. [7] were the first to suggest that this should be a third modification of $\text{Al}(\text{OH})_3$. They proposed the name bayerite-II; European scientists suggested the name nordstrandite. Its structure was stated to be closely related to that of the other trihydroxides. The American authors mentioned regarded it as a spiral-dislocation polymorph of gibbsite.

In the older literature some other indications can be found of the formation of nordstrandite from gelatinous boehmite. A patent taken out by BAKER-SINCLAIR [17] mentions the "trihydrate randomite" which could be recognized by a reflection with a spacing of 4.79 Å between that of gibbsite of 4.85 Å and of bayerite of 4.72 Å. KRAUT *et al.* [11] distinguished bayerite A, B and C, which were supposed to be mixed crystals of gibbsite and bayerite.

We compared their data with our observations, from which it appeared that bayerite A consisted of nearly pure bayerite, bayerite B of a mixture of bayerite and gibbsite, bayerite C of a mixture of bayerite and nordstrandite with possibly some gibbsite. None of these authors succeeded in obtaining nordstrandite in a pure form free from the other trihydroxides. We too made many attempts, which were not very successful however. By treating amalgamated aluminium with a 33 % NH_3 -solution cooled with ice, WALRAVEN [18] obtained a preparation in which bayerite could not be detected with a diffractometer; the nordstrandite lines, however, were rather diffuse, only the strongest being observable.

PAPÉE [19] states to have obtained a preparation of nordstrandite free from the other trihydroxides and he gives a great number of new reflections, which, however, are all weak or very weak. Unfortunately, he did not mention the method of preparation.

Although we had no pure nordstrandite preparation at our disposal, the following chapters will show that we were nevertheless able to obtain further information about the morphology and structure of nordstrandite with the aid of selected-area electron-diffraction techniques and from X-ray observations of mixtures of the trihydroxides.

I.3 The crystalline oxide-hydroxides

I.3.1 Diaspore

Diaspore occurs in nature in a well-crystallized form in some types of clay and bauxite. As was shown by LAUBENGAIJER and WEISS [20], ERVIN and OSBORN [21] and OSBORN and ROY [22], it is the stable phase at temperatures between 275 and 425 °C and a water vapour pressure above 140 atmospheres. In these conditions all hydroxides and

oxides (provided they are not heated before at too high a temperature) will be converted into diaspore. Though diaspore can be a very interesting material for technical application because by heating to 500 °C it is transformed direct into $\alpha\text{-Al}_2\text{O}_3$ (corundum), which is stable to water vapour, it is so difficult to prepare that so far it has not found any application.

I.3.2 Boehmite

Well-crystallized boehmite is sometimes found in nature in some Russian bauxites. It can be prepared synthetically by heating one of the hydroxides or oxides (except diaspore and the oxides heated at a high temperature) with liquid water in an autoclave at a temperature between 150 and 260 °C. The formation of boehmite proceeds faster in alkaline solution; in 2n NaOH gibbsite can be converted into well-crystallized boehmite at a temperature below 100 °C [10].

We studied the conversion of gelatinous into well-crystallized boehmite. Gelatinous boehmite was prepared from alum by topochemical reaction with an ammoniacal ammonium sulphate solution. This material was heated for six hours with ten times its weight of water (or 1n NaOH) in closed glass tubes placed in an autoclave partly filled with water. The heating temperatures were varied between 120 °C and 250 °C. The products obtained were washed free of NaOH (if necessary) and dried at 120 °C. In the same way a gibbsite preparation (PSH) was transformed into boehmite by heating it with water at 250 °C (preparation BoG). The results are given in TABLE I.3.

TABLE I.3 Recrystallization of boehmite

heating temp. °C	in water			in 1n NaOH			
	<i>W</i>	<i>S</i>	<i>V_{sp}</i>	<i>W</i>	<i>S</i>	<i>V_{sp}</i>	Na_2O
original	30.7	490	0.486	30.7	490	0.486	—
120	25.1	300	0.446	—	—	—	—
150	23.9	255	0.433	21.1	158	0.409	0.38
170	22.6	201	0.425	—	—	—	—
200	—	—	—	19.3	100	0.395	0.32
250	19.7	64	0.402	18.9	68	0.393	0.25
BoG	19.3	1.3	0.393				

As could be expected, a high temperature promotes the recrystallization of boehmite, as appears from the decrease in specific surface area

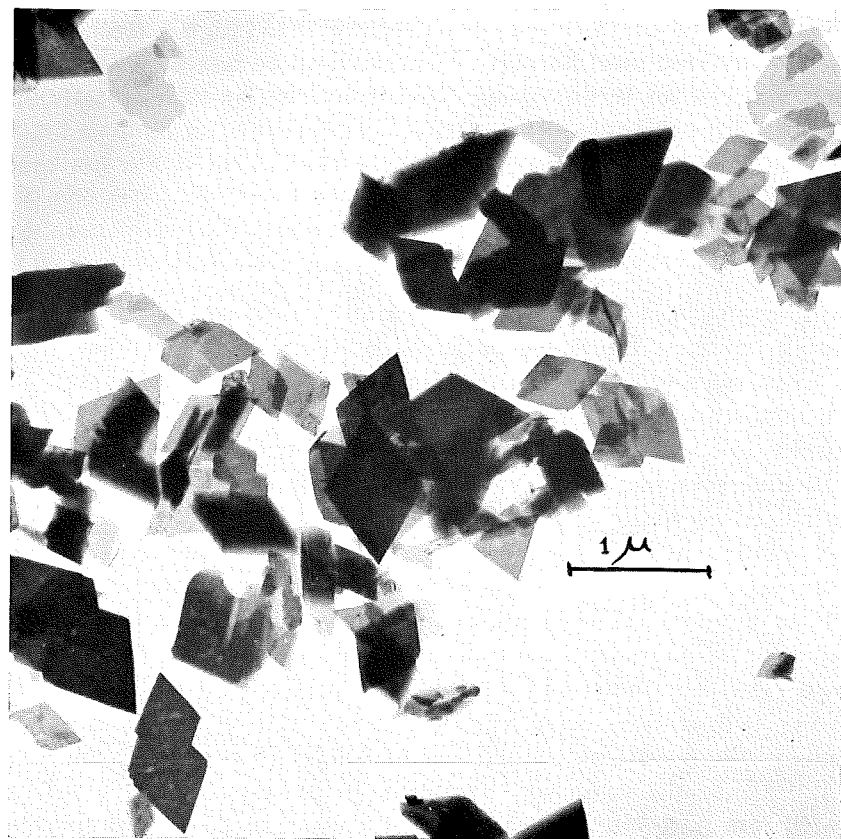


PLATE II. Well-crystallized boehmite (BoG)

and water content. The theoretical water content of 17.7 g/100 g Al_2O_3 has not been reached, however. The specific surface area is still high compared with that of BoG. In the latter case the formation of boehmite can start already inside the gibbsite granules [23, 24]. The complete transformation of the gibbsite into boehmite probably occurs via the liquid phase: gibbsite goes into solution, boehmite crystallizes. The boehmite crystals obtained bear no resemblance ("reminiscence") to the original gibbsite crystals; they consist of rhombic crystals (PLATE II). In the case of gelatinous boehmite, however, extremely small crystal seeds of boehmite have to grow to larger ones at the cost of other crystals. The samples recrystallized from NaOH-solution consist of the same rhombic crystals as BoG, but they are of much smaller dimensions. However, the crystals of the preparations obtained from water have an extended six-sided shape (PLATE III); these crystals are also very small.

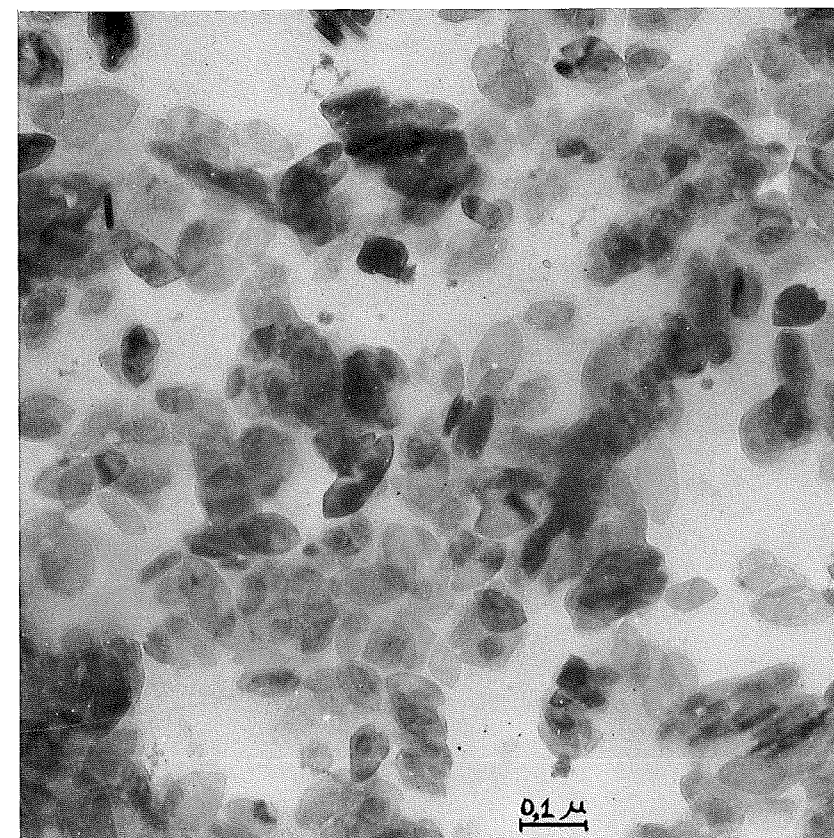


PLATE III. Microcrystalline boehmite (BoW)

I.4 The gelatinous hydroxides

I.4.1 Survey

If solutions of aluminium salts are treated with bases, bulky precipitates are formed containing large amounts of water and anions. The properties of these precipitates are largely determined by the reaction conditions.

WILLSTÄTTER and KRAUT and collaborators [9] extensively investigated the preparation and the adsorptive properties of the gelatinous products obtained from alum or aluminium sulphate solutions by precipitation with ammonia. They distinguished:

- C_α -gel, amorphous to X-rays, easily soluble in 0.1 % HCl;
- C_β -gel, X-ray pattern consisting of broad bands of boehmite, peptises in dilute HCl and dissolves slowly;

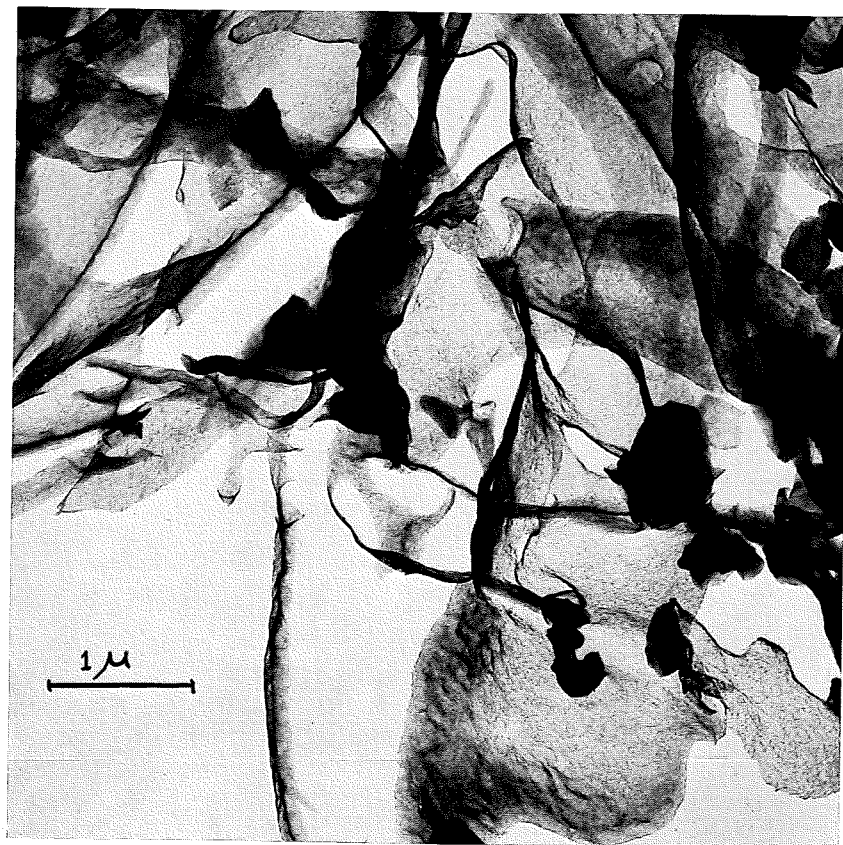


PLATE IV. Sheet-like gelatinous boehmite

- c. C_γ -gel, X-ray pattern shows a mixture of crystalline trihydroxides with small amounts of boehmite, almost insoluble in dilute HCl.

The C_β -gel and the C_γ -gel can be obtained from the C_α -gel by aging in water for a long period or, faster, in dilute ammonia. The morphology of these gels has been studied in detail by SOUZA SANTOS and collaborators [25] and by MOSCOU and VAN DER VLIES [16] with the electron microscope. It appeared from these investigations that the C_α -gel consists of particles of different size, built up from spherules of 50 Å or smaller, very tightly packed.

The C_β -gel consists of very thin wrinkled sheets, probably built up from strongly interlaced fibrils (PLATE IV). The many wrinkles, when observed with electron microscopes of insufficient resolution, create the impression of fibres; the material between these wrinkles is so thin that it could only be observed with microscopes of the highest resolving

power. The C_β -gel often contains some globular material (remnants of the C_α -gel) and sometimes some rods. SOUZA SANTOS *et al.* ascribe a boehmite structure to these rods, MOSCOU and VAN DER VLIES, however, are of opinion that these rods are already trihydroxide particles. The C_γ -gel appeared to be a mixture of the different trihydroxides with their own characteristic crystal shape; mostly some sheets of boehmite can be found (remnants of C_β -gel).

Starting from other salt solutions (nitrate, chloride *etc.*) leads to the same phenomena, as was mentioned by WEISER and MILLIGAN [26].

A curious method of obtaining amorphous aluminium hydroxide is that mentioned by WISLICENUS [27] who reacted amalgamated aluminium with moist air. This method causes bundles of long, very fragile fibres of aluminium hydroxide to grow from the surface of the metal. In this way a very bulky material is obtained not contaminated with acid radicals and almost completely amorphous to X-rays. This material, too, will age very rapidly in water, forming gelatinous products that are morphologically analogous to those obtained from the C_α -gel [16, 28].

A third method to prepare gelatinous aluminium hydroxides is by reacting solid aluminium compounds with ammoniacal solutions of NH_4 -salts. This method, which was first described by KOHLSCHÜTTER [29], yields products of excellent filterability and washability. The reaction proceeds topochemically *i.e.* the external shape of the particles is preserved during the reaction which proceeds within the crystals. MOSCOU and VAN DER VLIES state that in this way the sheet-like gelatinous boehmite is formed direct, without formation of amorphous hydroxide.

We have studied the process of the formation and aging of the gelatinous aluminium hydroxides via the changes in specific surface area. As starting materials we have chosen:

- amorphous aluminium hydroxide prepared by precipitation from dilute alum solutions;
- amorphous fibrillar aluminium hydroxide prepared from amalgamated aluminium according to WISLICENUS' method;
- gels prepared by topochemical conversion of aluminium compounds.

The products mentioned under c. have been studied in more detail.

1.4.2 Amorphous aluminium hydroxide prepared by precipitation

The precipitates obtained from aluminium salt solutions at a sufficiently low pH (below 7.4) are always amorphous to X-rays. These products are impure; they invariably contain a large amount of acid

radicals. Efforts to remove these, *e.g.* by treatment with dilute NH_3 -solutions, lead to crystallization [30, 31].

Some authors state that they succeeded in preparing amorphous gelatinous hydroxides free from anions. TEICHNER [32] dissolved $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in methyl alcohol and introduced twice the theoretical amount of NH_3 -gas. The precipitate obtained was filtered and extracted with absolute methyl alcohol in a Soxhlet apparatus to eliminate the NH_4Cl . The product was then dried in vacuum over P_2O_5 . The dried powder is stated to contain neither chloride ions nor organic material.

Our results with this method were not very successful. The extraction with methyl alcohol took some days before the products were free from NH_4Cl (NH_4 -content lower than 0.1 %). After drying over P_2O_5 or at a temperature of 120 °C the material invariably contained 1 to 3 per cent of chloride and 1 to 2 percent of carbon. In the light of the following observations we doubt if it will be really possible to obtain chloride-free products in this way: 1 g of the amorphous fibrillar hydroxide (of WISLIGENUS), which was completely free from anions, was treated in a shaking device with a solution of 0.5 g of NH_4Cl in 100 ml of methyl alcohol to which a trace of ammonia had been added. After some hours the material was filtered, washed free from NH_4Cl with methyl alcohol and dried at a temperature of 120 °C. The outward appearance of the material had not changed during the treatment; however, it now contained 2.6 % Cl and 1.2 % C (no NH_4 could be detected). These impurities must be adsorbed from the solution and cannot be removed by washing with methyl alcohol.

PAPÉE [19] claims to have obtained an amorphous hydroxide with less than 0.1 % of NO_3^- by precipitating aluminium hydroxide from an aluminium nitrate solution with NH_3 at pH 8, followed by a quick wash. Our attempts with this method were again unsuccessful; the nitrate ions could not be washed out completely before the crystallization to boehmite had started.

The amorphous hydroxides we obtained by precipitation from solutions showed a glassy appearance (like silica) after drying in vacuum over P_2O_5 at room temperature or after slow drying at a temperature of 120 °C. The specific surface area of these materials as determined by low-temperature adsorption of nitrogen, is very low. Such a sample has been prepared as follows: To 30 litres of water at room temperature 1 litre of a 10-percent alum solution and 1 litre of a 1-percent NH_3 -solution is added with vigorous stirring. The rate of dosing the solutions is regulated in such a way that the pH of the liquid is kept between

6.7 and 6.9. After settling of the gelatinous precipitate formed the supernatant solution is siphoned off. The product is stirred up in 30 litres of water, after which NH_3 is added to raise the pH to 7.2. The mixture is stirred for an hour; after settling the clear liquid is again siphoned off. This procedure is repeated until sulphate can no longer be detected in the wash water.

After centrifuging the gel is dried slowly at 120 °C. The product then contains 4 to 4.5 moles of H_2O and 0.3 to 0.4 moles of SO_3 per mole of Al_2O_3 .

TABLE I.4 Aging of an amorphous gelatinous hydroxide

Aging time hours	W g/100 g Al_2O_3	SO_3 g/100 g Al_2O_3	S $\text{m}^2/\text{g Al}_2\text{O}_3$
0	81.3	23.2	< 1
1	40.2	13.1	12
6	33.5	6.3	135
44	27.8	4.0	201
166	26.7	3.5	230

Before drying the gel is quite stable in water at a pH below 7.4. In a dilute NH_3 -solution it ages very rapidly. TABLE I.4 gives the results of aging in a NH_3 -solution the pH of which was kept constant at 9.0.

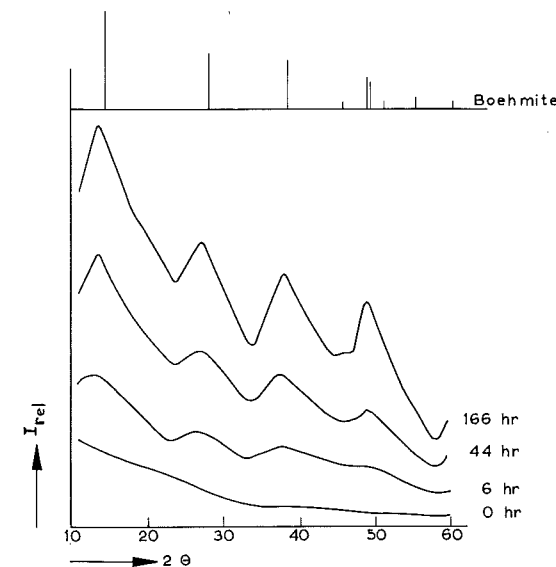


FIG. 2. Aging of gelatinous amorphous aluminium hydroxides to gelatinous boehmite: X-ray diagrams (Cu $K\alpha$ -radiation)

The glassy appearance which the non-aged amorphous gel obtains after drying at 120 °C is not present in the dried samples aged for one hour, these products being opaque. At the same time gelatinous boehmite is formed, as appears from the X-ray diagrams shown in FIG. 2. The formation of boehmite is accompanied by a decrease of the water content W and the SO_3 -content and by an increase in specific surface area.

It is also possible to remove any sulphate present in the amorphous glassy gel after drying. The reaction proceeds very slowly in this case, also with formation of gelatinous boehmite.

I.4.3 Amorphous fibrillar aluminium hydroxide

The method of WISLISCENUS [27] gives an amorphous product free from anions. We obtained the best results by the following procedure: Strips of aluminium foil (99.99 % Al, thickness 2 mm) are degreased by immersion in acetone, etched with a 2n NaOH-solution for some seconds and rinsed very well with distilled water. Amalgamation is attained by 2 seconds' immersion in a 1 % HgCl₂-solution in acetone. After rinsing with acetone the strips are dried between filter paper and placed on some Petri-dishes in a desiccator. On the bottom of the desiccator is a layer of water through which air is blown. The fibrillar aluminium hydroxide which is formed overnight is dried in vacuum over P₂O₅.

The product obtained is completely amorphous to X-rays. It contains 2.5 to 3 moles of water per mole of Al₂O₃. When put in twenty times its amount of water it swells while heat is produced. After an hour the whole mass has transformed into a gel giving the X-ray pattern of gelatinous boehmite. Again a decrease in water content and an increase in specific surface area is observed, as is the case with the glassy material; however, after about a week the reverse process occurs as a result of the formation of bayerite (TABLE I.5).

TABLE I.5 Aging of the amorphous fibrillar hydroxide

Aging time hours	<i>W</i> g/100 g Al ₂ O ₃	<i>S</i> m ² /g Al ₂ O ₃	X-ray diagram
0	46.5	86	amorphous
1	42.6	196	boehmite bands
20	35.2	294	do.
120	30.4	355	do.
190	28.1	414	do.
290	33.7	298	do. and bayerite lines
960	48.6	75	bayerite lines

I.4.4 Topochemical conversion of alum

If finely divided ammonium alum crystals are added in the solid state to an ammonia solution, the conversion to aluminium hydroxide will occur without aluminium ions going into solution [29]. From microscopic observations it appears that the octahedral shape of the alum crystals

is conserved even after complete conversion, while their size does not change much either. According to the reaction conditions the particles remain transparent (low NH₃ and high NH₄-salt concentration, low temperature) or become opaque.

The products can be easily washed free from the mother liquor without any noticeable alteration in the appearance of the particles. During drying an appreciable shrinkage occurs (to about one sixth of the original volume), but the octahedral shape of the particles is retained. Generally the reaction proceeds very fast; within 15 minutes after the addition of the crystal powder to the solution more than 95 % of the sulphate can be removed without loss of aluminium in the wash water.

We investigated various reaction conditions. To obtain a completely topochemical conversion, the presence of a large amount of ammonium sulphate is necessary. Unlike MOSCOU and VAN DER VLIES, we mostly obtained an amorphous product within 15 minutes at a pH lower than 9.4. At longer reaction times aging to gelatinous boehmite occurs; the higher the pH and the temperature, the faster the aging proceeds.

The transformations that occur during aging will be clearly demonstrated by the following example:

1 kg alum was added to a solution consisting of 100 g ammonium sulphate and 400 g of a 25 % ammonia solution in 500 ml water. After some minutes the pH of the suspension had lowered to 9.2; by adding 25 % ammonia this pH was kept constant during further reaction, up to 50 g being required. After certain periods part of the suspension was filtered, washed with water until no sulphate could be detected in the filtrate, and finally dried at 120 °C. Of these samples we determined the water and sulphate contents (*W* and SO₃ respectively) and the specific surface area (*S*), the specific volume in water (*V_w*) and in carbon tetrachloride (*V_c*). The results are given in TABLE I.6.

TABLE I.6 Topochemical conversion of alum at pH 9.2

No.	h	<i>W</i>	SO ₃	<i>S</i>	<i>V_w</i>	<i>V_c</i>	<i>V_{Hg}</i>	<i>V_{pHg}</i>	<i>V_{pN}</i>	<i>V_{rw}</i>	<i>V_c + V_{pN}</i>
1	1/4	27.6	10.9	2	0.486	0.757	0.771	0.285	0.004	0.420	0.761
2	2	26.8	9.6	49	0.478	0.692	0.759	0.281	0.053	0.424	0.745
3	6	26.2	7.6	183	0.461	0.535	0.737	0.276	0.198	0.427	0.733
4	22	25.8	5.2	244	0.449	0.482	0.742	0.293	0.257	0.446	0.739
5	46	26.0	3.6	289	0.442	0.439	0.735	0.293	0.301	0.448	0.740

W and SO₃: g/100 g Al₂O₃; *S*: m²/g Al₂O₃;
other quantities: ml/g Al₂O₃.

To explain the remarkably large difference between V_w and V_e we measured the specific volume in mercury V_{Hg} [33], the pore volume V_{pN} using nitrogen at 78 °K and a relative nitrogen pressure of 0.98 (CHAPTER VI), and the sorption capacity for water V_{pw} . This latter quantity was determined from the increase in weight of the material placed in a desiccator over deliquescent lead nitrate. Under these conditions the relative water pressure is equal to 0.98 (TABLE I.6). It appears that the specific volume in mercury (which may be put equal to the granular volume of the material) is always approximately equal to the sum of the specific volume in carbon tetrachloride V_e and the pore volume measured with nitrogen V_{pN} . V_e will be equal to the sum of the real specific volume of the material and the volume of those pores into which the carbon tetrachloride molecules cannot penetrate (inaccessible pores and/or very narrow pores). From the fact that $V_e + V_{pN}$ is equal to the volume of the granules we may conclude that there are no pores into which nitrogen can penetrate and carbon tetrachloride cannot. This was to be expected, as the mean pore size defined as (CHAPTER VI):

$$\bar{r} = \frac{2V_{pN}}{S}$$

is almost the same for preparations 2 to 5 and equal to about 21 Å, which is large as compared with the diameter of the carbon tetrachloride molecule.

FORTUIN [34] and STEGGERDA [35] found that the specific volume in water of the crystalline hydroxides and the dehydration products obtained from them can be represented by:

$$V_w = 0.27 + 0.0068 \cdot W.$$

If we apply this equation to the gelatinous preparations of TABLE I.6 we find for V_w values varying from 0.458 to 0.446 ml/g Al_2O_3 . Taking into account the sulphate content, which will give proportionately higher values, we may safely assume that the specific volume in water V_w will not differ much from the real specific volume. It is then possible to calculate the total pore volume from the difference between the specific volume measured in mercury and that measured in water, indicated in TABLE I.6 as V_{pHg} .

It now appears that all five preparations possess a total pore volume of 0.28 to 0.29 ml/g Al_2O_3 . In preparation 1 this volume is freely accessible to water, but not to nitrogen or carbon tetrachloride. It cannot be ascertained whether this pore volume corresponds to very narrow pores, to wider ones with very narrow openings, or to enclosed pores, in which

case water has to diffuse through the walls. We shall describe these pores as "very narrow" ones.

As aging continues the volume of "very narrow" pores decreases. The volume of pores of about 20 Å then increases by the same amount. It is obvious that these pores are formed by the wrinkled sheets or by the particles forming these sheets. The "very narrow" pores will be formed by the openings between the globular particles which constitute the amorphous material.

The sorption capacity for water is about 1½ times as large as the pore volume of the five preparations. It is not likely that the whole quantity of "sorbed" water is present in the pores. In that case the specific volume of the sorbed water would be about 0.67. We must therefore assume that part of the sorbed water is taken up in the solid itself with simultaneous swelling. A measure of this swelling can be found in the difference between the total pore volume and the sorption capacity for water (TABLE I.7). Swelling increases somewhat with de-

TABLE I.7 Swelling of aluminium hydroxide in water

No.	V_{pHg} ml/g Al_2O_3	V_{pw} ml/g Al_2O_3	Swelling ml/g Al_2O_3	SO_3 g/100 g Al_2O_3
1	0.285	0.420	0.135	10.9
2	0.281	0.424	0.143	9.6
3	0.276	0.427	0.151	7.6
4	0.293	0.446	0.153	5.2
5	0.293	0.448	0.155	3.6

creasing sulphate content or with increasing aging. It is a slow process: a small quantity of the amorphous sample 1 was soaked with water for 10 minutes and then dried superficially between filter paper. It was then placed over deliquescent lead nitrate. The total quantity of sorbed water V_{pw} was measured by weighing the product from time to time (TABLE I.8). The initial decrease of V_{pw} is caused by the water between

TABLE I.8

Swelling time (days)	0	1	4	7	14
V_{pw} (ml/g Al_2O_3)	0.368	0.353	0.396	0.402	0.416

the particles, which could not be completely removed by the filter paper. Changes in the composition did not occur: after drying at 120 °C of the last product the water content was 27.9 g/100 g Al_2O_3 , i.e. almost

equal to the original figure, and the X-ray pattern was that of an amorphous product.

We have already mentioned that the fibrillar hydroxide of WISLICENUS also swelled when treated with water; in this case, however, swelling is accompanied by the formation of gelatinous boehmite.

I.4.5 The topochemical conversion of other aluminium compounds

The topochemical formation of aluminium hydroxide is not limited to the reaction of alum with ammonia. A number of other aluminium compounds reacts in the same way. Consequently, aluminium hydroxide preparations can be obtained, having particles of a pre-determined shape. Starting with aluminium sulphate crystallized in platelets, also plate-shaped hydroxide particles are obtained and from the needle-shaped crystals of aluminium chloride also needle-shaped aluminium hydroxide is formed.

Even organic compounds such as aluminium tri-isopropylate (aluminium tri-isopropoxide) can react in a topochemical way.

We compared these three materials with alum and with a nearly saturated solution of aluminium sulphate (27 %). Care was taken that the concentration of the ammonium salts and the pH was the same in all cases. The pH was kept at 9.2, the final solution was saturated with respect to ammonium sulphate. As aging times we have chosen $\frac{1}{4}$ hour, 2 hours and 20 hours. The procedure was the same as that described for alum. For each preparation the volume of the starting material was compared with that of the filter cake.

The volume of the filter cake was determined as follows:

After washing with distilled water until the filtrate was free from sulphate, the cake was sucked dry with a water jet pump. By pressing with a glass stopper the formation of cracks was prevented. Thereupon air was sucked through the cake for five minutes. In this way we succeeded in reproducibly removing by far the greater part of the adhering water. The filter cake was weighed; part of it was used for determination of the specific volume in water, the rest was dried at 120 °C. In the dried material the loss on ignition, the sulphate content and the specific surface area were determined. The results are shown in TABLE I.9.

From TABLE I.9 a. it clearly appears that there exists a narrow relation between the volume of the starting material and the volume of the filter cake. In the preparation from the solids the volume of the filter cake is somewhat greater than that of the starting material and it increases on aging. In the preparation from the solution the volume

TABLE I.9 Topochemical conversion of aluminium compounds

a. wet cake

starting material			% Al ₂ O ₃ in cake			volume cake		
no.	% Al ₂ O ₃	vol.	$\frac{1}{4}$ h	2 h	20 h	$\frac{1}{4}$ h	2 h	20 h
1	8.16	9.43	10.11	10.26	10.33	8.93	8.87	8.83
2	11.21	5.43	15.70	15.41	14.97	5.48	5.62	5.84
3	15.29	4.05	18.05	17.06	16.58	4.64	4.98	5.19
4	21.02	3.20	23.58	20.79	19.27	3.35	3.99	4.35
5	24.96	3.65	22.27	20.20	19.88	3.65	4.12	4.20

b. dried product

W g/100 g Al ₂ O ₃				SO ₃ g/100 g Al ₂ O ₃			S m ² /g Al ₂ O ₃		
no.	$\frac{1}{4}$ h	2 h	20 h	$\frac{1}{4}$ h	2 h	20 h	$\frac{1}{4}$ h	2 h	20 h
1	38.6	29.3	28.5	18.4	10.9	5.6	0	16	285
2	28.3	26.8	26.0	11.9	10.0	4.6	4	33	265
3	30.5	27.2	26.4	12.5	10.5	5.7	3	21	243
4	31.5	28.0	26.3	11.4	10.1	5.1	0	29	250
5	26.3	25.7	25.2	3.7	4.2	4.1	120	235	360

The volumes are given in ml/g Al₂O₃.

1. aluminium sulphate solution
2. solid ammonium alum
3. solid aluminium sulphate
4. solid aluminium chloride
5. solid aluminium tri-isopropoxide

of the filter cake is smaller than that of the starting material and it decreases on aging.

All products having an aging time of $\frac{1}{4}$ hour were amorphous to X-rays. After an aging time of 2 hours boehmite bands were clearly visible. The changes in water content, sulphate content and specific surface area during aging are comparable for the first four preparations. Preparation 5 deviates from the others in that it has a lower sulphate content in the beginning and especially a much higher specific surface area.

It is also observed that the sulphate content of the preparations from aluminium chloride does not deviate from those from the sulphates. Chlorides cannot be detected in it. Apparently a complete ion exchange has taken place.

The mechanism of the topochemical conversion is conceived as follows: Upon addition of salt crystals to the ammoniacal solution a film of

aluminium hydroxide is formed on the surface of the crystals. Diffusion of the ions has to proceed through this film. Coming from the acid side, precipitation of aluminium hydroxide will start at a pH above 4. As in the solution the pH remains above 9 and in the crystal a weak acid reaction will occur, the critical pH will occur at the internal surface of the film. The aluminium hydroxide will be formed within the crystal filling up the whole particle. The remaining ions (ammonium and the anions) can easily pass through the film as appears from the fast exchange of chloride for sulphate and the good washability.

The phenomena during the topochemical conversion of aluminium tri-isopropoxide are somewhat different from those of the salt-like compounds. This has to be ascribed to the non-ionic binding of the (C_3H_7O)-groups to the aluminium atom. Ion exchange is not possible with these groups. Besides, it can be expected that in the hydroxide an appreciable number of these groups will substitute OH-groups. These organic groups prevent the shrinkage that normally occurs. The dried products are soft powders, unlike others, which consist of very hard particles. This influence of organic groups can also be noticed when the precipitated aluminium hydroxides are treated with alcohol (methyl or ethyl) after washing with water. In this case also soft powders are obtained after drying at 120 °C.

The preparations obtained in the presence of alcohols always contain organic substances; their carbon content varies between 1 and 2 %. The specific surface area and especially the pore volume of these products are invariably greater than in the absence of alcohols.

1.5 Summary of Chapter I

A survey is given of the methods of preparation and of the morphology of the aluminium trihydroxides. Special attention was paid to the preparation of pure, well-crystallized bayerite and nordstrandite. SCHMÄH's method appeared to be the best to obtain bayerite; the other methods invariably lead to mixtures of the trihydroxides. Attempts to prepare pure nordstrandite were unsuccessful. One of the oxide-hydroxides, diaspor, had to be left out of consideration, as no feasible preparation method was known. Well-crystallized boehmite was obtained by hydrothermal treatment of gelatinous boehmite and of gibbsite.

The gelatinous hydroxides could be divided into three groups, *viz.* the amorphous hydroxides, the gelatinous boehmites and preparations that were largely recrystallized into a mixture of the trihydroxides. The amorphous hydroxides comprise the fibrillar hydroxide of WISLI-

CENUS and the glassy products. The first type is completely pure, the glassy products always contain rather large amounts of anions. Some statements in literature concerning preparation methods of amorphous products free from anions could not be completely confirmed.

The aging of the amorphous preparations invariably led to the same form of gelatinous boehmite, *viz.* strongly wrinkled extremely thin sheets, built up probably from a felty arrangement of minute fibrils.

The topochemical formation of gelatinous hydroxides was studied in more detail. From the specific volumes in different media and from the adsorption of nitrogen it could be concluded that in the dried gels two kinds of pores may occur, *viz.* "very narrow" pores only accessible to water and pores with a size of about 20 Å. The "very narrow" pores could be described as the openings between the very small, globular particles from which the amorphous products are built up. The larger pores have to be considered as the space between the wrinkled sheets and between the fibrils of the gelatinous boehmite.

On the basis of the phenomena that occurred during the topochemical conversion of various aluminium compounds, a description could be given of the mechanism of this reaction.

X-RAY DIFFRACTION STUDY OF THE HYDROXIDES

II.1 Introduction

As was already stated in the beginning of this thesis, the properties of catalysts are largely determined by their crystallographic structure and texture.

Aluminium oxide as a catalyst base is generally obtained by dehydrating one of the various aluminium hydroxides or mixtures of them. This dehydration nearly always takes place pseudomorphically, which means that not only the external shape is preserved, but also the newly formed crystals are arranged in a distinctly systematic way. Besides the knowledge of the aluminium oxides themselves also that of the hydroxides is important. Exact information on the atom parameters is not necessary for this purpose. Since the original lattice of the hydroxide will be destroyed to a certain extent by dehydration, it will be sufficient to have a good idea of the surroundings of each atom. On the other hand, a certain knowledge of the defect structure may be important, because it is generally assumed that the imperfections of the lattice often affect the reactivity of the solid.

Normally the structure of a material of known composition is determined as follows:

- the dimensions of the unit cell are calculated from the interplanar spacings after indexing;
- the number of atoms of each kind present in the cell is found from the unit-cell dimensions and the density;
- the possible structures are roughly derived from the systematic extinctions and intensity differences;
- the parameters of the atoms are calculated from the exact relative intensities of the reflections.

Powder diagrams, however important they may be for identifying and exactly measuring the interplanar spacings, are not generally suited for structure determinations. In simple cases, *e.g.* for cubic or simple tetragonal and hexagonal lattices, the reflections can be indexed with certainty. Even in these cases it often happens that a number of reflections coincide; as their individual intensities cannot be determined, they can-

not be used for structure determination. In by far the majority of cases single-crystal methods will have to be employed. These single crystals must have a size of at least some tenths of a millimetre, which requirement often cannot be fulfilled.

In this chapter we shall try to describe the most important features of the structure of the trihydroxides and of the oxide-hydroxides. The literature data in this field are very incomplete. We have tried to fill the gaps with the results of our own observations. Because of the lack of single crystals of suitable dimensions, we had to base our conclusions on polycrystalline powder patterns, interpreting them with the aid of the results of electron-diffraction measurements described in the next chapter.

II.2 The unit-cell dimensions of the trihydroxides

II.2.1 Gibbsite

Gibbsite is the best investigated trihydroxide because in this case naturally occurring single crystals of sufficiently large dimensions can be obtained. DANA [36] states that gibbsite is monoclinic (pseudo-hexagonal) with an axis ratio of $a : b : c = 1.709 : 1 : 1.918$ and $\beta = 85^\circ 29'$. MEGAW [37] and SAALFELD [38] determined the structure of the lattice and the exact parameters of the atoms. The unit-cell dimensions of these naturally occurring single crystals given by these authors agree very well, except for a small difference in the a -axis. With the aid of their values we could index the powder diagrams of synthetic gibbsite samples and calculate their cell dimensions. Our results are in very good agreement with those of SAALFELD (TABLE II-1).

TABLE II.1 Unit-cell dimensions of gibbsite

	a	b	c	β
MEGAW	8.641 ± 0.001	5.070 ± 0.001	9.720 ± 0.004	$94^\circ 34' \pm 5'$
SAALFELD	8.676 ± 0.002	5.070 ± 0.002	9.721 ± 0.003	$94^\circ 34' \pm 5'$
Own results (synth.)	8.673 ± 0.005	5.068 ± 0.003	9.716 ± 0.005	$94^\circ 32' \pm 5'$
SAALFELD triclinic	17.338	10.086	9.730	$94^\circ 10' \alpha$ $92^\circ 08' \beta$ $90^\circ 00' \gamma$

(All lattice dimensions are given in Å units)

Besides the monoclinic crystals SAALFELD, in his gibbsite samples from the Ural, also observed triclinic crystals entangled in the monoclinic ones. The structure of these triclinic crystals shows so much similarity to the monoclinic form, that the name gibbsite is still justified. It should be remarked that the *a*- and *b*-axes are doubled, giving a unit cell which is four times as large as that of the monoclinic gibbsite.

II.2.2 Bayerite

Literature data on the unit-cell dimensions of bayerite do not agree. Since single crystals of suitable dimensions are lacking investigators have had to manage with powder patterns. SAALFELD [39] tried to obtain a sample with oriented bayerite crystals by dehydrating gibbsite crystals in high vacuum and rehydrating the oxide obtained with water vapour. Heating under high vacuum yields the almost amorphous alumina described by PAPÉE and TERTIAN [40] and denoted as ρ -Al₂O₃, which on rehydration gives well-crystallized bayerite. SAALFELD found, however, that in these bayerite particles the crystallites are fully disoriented; single-crystal patterns could not be obtained.

The literature data obtained from powder diagrams are given in TABLE II.2.

TABLE II.2 Unit-cell dimensions of bayerite (literature data)

	crystal system	<i>a</i>	<i>b</i>	<i>c</i>	α	<i>a</i> : <i>b</i> : <i>c</i>
MONTORO [41]	hexagonal	8.70	5.02	4.77	—	1.732 : 1 : 0.950
YAMAGUCHI and SAKAMOTO [42]	hexagonal	8.731	5.047	4.730	—	1.732 : 1 : 0.937
UNMACK [43]	monoclinic	8.679	5.060	4.716	90°07'	1.715 : 1 : 0.932

The hexagonal lattices are described here on orthohexagonal axes for reason of comparison with orthorhombic and monoclinic lattices. We chose the axes in such a way that the *a*-axis corresponds to the *a*-axis of gibbsite; for the monoclinic lattice of UNMACK this leads to an unconventional position, with an angle α instead of β ; as this lattice differs only very slightly from orthorhombic, this choice is not objectionable.

In our powder diagrams of various samples of bayerite made according to widely different methods, we always observed a number of reflections that could not be indexed in a hexagonal lattice with an *a*-axis of about 5 Å. YAMAGUCHI and SAKAMOTO also found these lines, but they ascribed

them to an impurity. However, it is highly improbable that so strongly differing preparation methods should always give the same amount of impurities. Moreover, diffractometer diagrams showed, that a number of reflections which should coincide in a hexagonal lattice were clearly separated (reflections for which on orthohexagonal axes $h^2 + 3k^2$ is equal). The separation of the 600- and 330-reflection and the 601- and 331-reflection was practically complete. From these reflections the difference between the ratio of the true orthorhombic *a*- and *b*-axis and that of the *a*_o- and *b*_o-axis of the orthohexagonal coordinates could be calculated. The *c*-axis was known from the easily identifiable basis reflections, which enabled indexing of the whole diffractogram between $2\theta = 18$ and 150° (Co-target) assuming an orthorhombic lattice. We did not find any indication of a monoclinic lattice, as mentioned by UNMACK. As in the back-reflection part of our diffractogram appreciable broadening of the lines occurred, it was not possible to establish with certainty the absence of a doubling of the lines corresponding with UNMACK's lattice.

To calculate the dimensions of the unit cell from the interplanar spacings we used COHEN's method [44]. It is based on the fact that all systematic errors in powder diagrams (except those resulting from the vertical divergence of the beam, which could be neglected in our case) disappear at a diffraction angle of 180° . The extrapolation is most easily done algebraically by putting:

$$Ah^2 + Bk^2 + Cl^2 + Df(\theta) = \sin^2 \theta$$

where $A = \frac{\lambda^2}{4a^2}$, $B = \frac{\lambda^2}{4b^2}$, $C = \frac{\lambda^2}{4c^2}$ and $Df(\theta)$ a correction term for the systematic errors. NELSON and RILEY [46] deduced that for diffraction angles greater than 60° the following equation holds:

$$\Delta d/d = K \cos^2 \theta \cdot (1/\sin \theta + 1/\theta),$$

from which it follows that:

$$\Delta \sin^2 \theta = D \sin^2 2\theta \cdot (1/\sin \theta + 1/\theta) = Df(\theta).$$

The values of $\cos^2 \theta \cdot (1/\sin \theta + 1/\theta)$ are tabulated [46], from which $f(\theta)$ could be calculated. By means of the method of least squares the values of A, B, C and D are calculated using all good quality lines in the region $2\theta > 60^\circ$, and from these values the cell dimensions are derived.

The results were:

$$a = 8.674 \pm 0.002 \text{ Å} \quad b = 5.061 \pm 0.001 \text{ Å} \quad c = 4.713 \pm 0.001 \text{ Å}$$

$$a : b : c = 1.714 : 1 : 0.9312,$$

which is in good agreement with UNMACK's results.

II.2.3 Nordstrandite

By comparing the intensities of reflections in the powder diagrams of samples in which the three trihydroxides are found together with gelatinous boehmite in varying proportions, we were able to attribute a number of reflections to nordstrandite (TABLE II.3). Besides the reflec-

TABLE II.3 Interplanar spacings of nordstrandite

no.	2 θ (CuK α)	d Å	hkl	I_{est}	no.	2 θ (CuK α)	d Å	hkl	I_{est}
1	18.52	4.787	004	vs	13	36.26	2.475	02 $\bar{1}$ /31 $\bar{1}$	m
2	20.5*	4.33	200/110	m	14	36.63	2.451	021/311	w
3	21.11	4.205	201/11 $\bar{1}$	m	15	37.65	2.387	008	s
4	21.36	4.156	111	m	16	39.78	2.264	023	s
5	22.62	3.928	202/11 $\bar{2}$	w	17	44.97	2.014	223	s
6	22.83	3.892	112	m	18	47.46	1.914	00.10	vw
7	24.68	3.604	113	m	19	47.86	1.899	225	m
8	25.0	3.56	203	vw	20	57.90	1.591	00.12	w
9	25.67	3.467	113	w	21	61.36	1.510	135	w
10	27.25	3.270	114	w	22	62.94	1.475	135	w
11	27.7*	3.22	204	w	23	64.78	1.438	600	s
12	28.00*	3.184	006	m					

vs: very strong m: medium w: weak vw: very weak
reflections with * partly coincide with strong bayerite lines.

tions mentioned in this table also other reflections may belong to the nordstrandite diagram. However, these escape observation because they either coincide with lines of the other trihydroxides or are so weak that they disappear in the diffuse background of the gelatinous boehmite. PAPÉE *et al.* [19] give some more reflections which are all very faint. As these authors do not mention the previous history of their samples we have left these out of consideration.

In FIG. 3 we reproduced part of the diagram (2 θ between 18 and 28°). In this region no other lines of bayerite occur than those marked By-*hkl*. Gibbsite is almost absent. Here the most characteristic lines of nordstrandite appear (numbering according to TABLE II.3). The large number of reflections in this region is very remarkable. The nordstrandite lattice must consequently be very complex, having either large unit-cell dimensions or a low symmetry.

Indexing on the basis of this diagram alone is almost useless. Making use of the analogy of the diagram with those of bayerite and gibbsite, and of the results of the electron diffraction (next chapter) we were

able to obtain a justified indexing. The first two reflections of the three trihydroxides nearly coincide, so we may assume that they are corresponding reflections. Line 1 then is a basis reflection, line 2 a prism reflection.

A number of lines are presumably higher-order reflections of the number one line, *viz.*

no.	d	I_{rel}	no.	d	I_{rel}
1	4.787	vs	18	1.914	vw
12	3.184	m	20	1.591	w
15	2.387	s			

From these figures a repetition distance perpendicular to the basic plane of 9.56 Å or a multiple of it can be assumed.

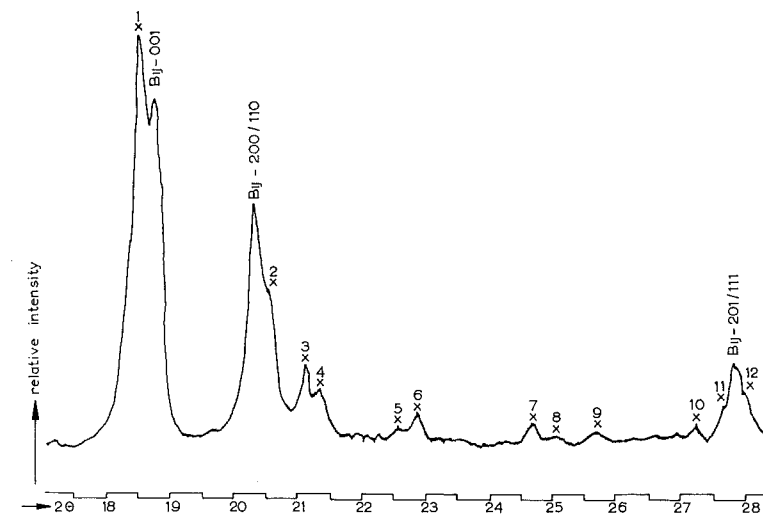


FIG. 3. X-ray diffractogram of a trihydroxide mixture rich in nordstrandite (Cu K α -radiation)
× nordstrandite lines; By-*hkl* bayerite lines

The second line of the bayerite and gibbsite diagrams ($d = 4.3$ Å) is formed by the coinciding 200- and 110-reflections. Of the higher orders the 400-reflection is very weak and the 600-reflection strong, corresponding to the triple oxygen arrangement in the direction of the *a*-axis (see II.3 and FIG. 4). The third order of the second line of the nordstrandite diagram (*viz.* no. 23, $d = 1.438$) is also strong, whereas the second order is missing. So we may assume the same arrangement of the oxygen atoms in the *a*-direction, giving an *a*-axis of about 8.6 Å. With the aid

of electron diffraction we found lath-like crystals having a repetition distance of 9.55 Å in the longitudinal direction and one of 5.0 Å about perpendicular to it. Consequently, we also assumed a third axis of about 5.0 Å. With these data we tried to index the nordstrandite lines in the powder diagrams of the trihydroxide mixtures. It appeared that the *c*-axis had to be doubled and a monoclinic lattice had to be accepted with an angle differing not more than a few degrees from a right angle. In this way we found the indices given in TABLE II.3. The lattice dimensions calculated from these, were:

$$\begin{aligned} a & 8.63 \pm 0.02 \text{ Å} \\ b & 5.01 \pm 0.02 \text{ Å} \\ c & 19.12 \pm 0.03 \text{ Å} \\ \alpha & 92^\circ 00' \pm 10' \end{aligned}$$

II.3 The structures of trihydroxides

II.3.1 Comparison of the lattices of the trihydroxides

TABLE II.4

modification	molec. /cell	<i>a</i>	<i>b</i>	<i>c</i>	α	β	γ	density g/cm ³
bayerite	4	8.674	5.061	4.713	90°	90°	90°	2.50
gibbsite mon.	8	8.673	5.068	9.716	90°	94°32'	90°	2.43
gibbsite tric.	4 × 8	2 × 8.669	2 × 5.043	9.730	94°10'	92°08'	90°	2.44
nordstrandite	16	8.63	5.01	19.12	92°00'	90°	90°	2.50

From TABLE II.4 it appears that the *a*- and *b*-axis of the four modifications are almost equal (apart from the doubling in the case of the triclinic gibbsite), the angle between these axes being 90° in all cases. The differences between the lattices are mainly given by the length of the *c*-axis, which is about proportional to the number of Al(OH)₃ molecules per cell. The differences between the angles in all cases become apparent between the *c*-axis and one or two of the other axes. So we can expect that the four modifications can be obtained by different stacking of a number of units in the direction of the *c*-axis.

Only the structure of the monoclinic gibbsite is well known in literature [37, 38]. The structure of SAALFELD's triclinic gibbsite is closely related to that of the monoclinic form, as follows from the length of the *c*-axis. YAMAGUCHI and SAKAMOTO [42] propose a structure for bayerite,

based on incomplete and partly incorrect data. No data are known for the structure of nordstrandite.

II.3.2 The structure of gibbsite

To describe the structure of gibbsite we can start from a stacking of hypothetical spherical OH'-ions. Assuming a closest stacking in two layers A and B (FIG. 22) we always find the OH'-ions of layer B just above the centre of the triangle formed by the centres of 3 OH'-ions in layer A. Three OH'-ions of the A-layer and three of the B-layer form together an octahedron, of which the projection on the layers gives a hexagon (FIG. 4). In projection on the plane of the layers the simple unit cell of such a stacking has the dimensions of $a_0 = d$ and $b_0 = d\sqrt{3}$, if *d* is equal to the distance between the centres of two adjacent OH'-ions.

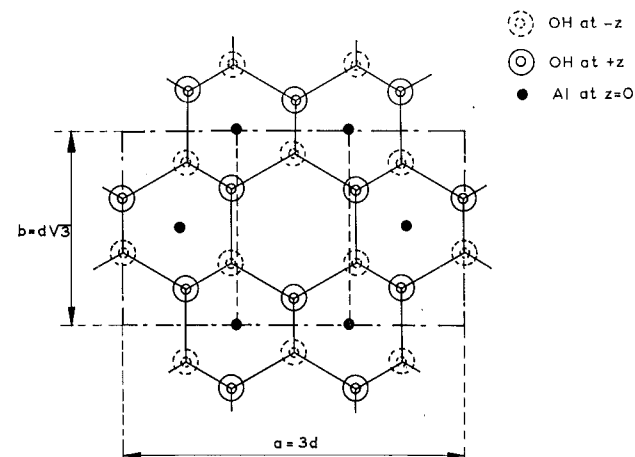


FIG. 4. Schematic representation of the structure of a trihydroxide double layer. Projection on (001)-plane

In such a cell there are 4 OH'-ions and 2 octahedral holes. The positive ions cause the binding in the double layer AB and are distributed over the octahedral holes in such a manner that the whole double layer becomes electrically neutral. The binding between the double layers is formed by hydrogen bonds originating from the OH'-dipoles. As the strength of this dipole binding is very much smaller than that of the ion binding in the double layer itself, all substances of which the lattice is built up in this way will possess a pronounced cleavage parallel to the plane of the double layers.

Brucite (Mg(OH)₂) can be considered the prototype of this kind of

compounds; in its lattice there are just enough positive ions to fill up all octahedral holes in the double layer (*viz.* 2 per 4 OH'-ions). In this case the double layers are stacked in such a manner that the OH'-ions of the third layer (*i.e.* the A-layer of the second double layer AB) are placed above those of the first layer, forming a nearly closest packed arrangement of spheres. Schematically we can represent this by the symbol:



in which the vertical dashes denote the boundaries of the unit cells in the direction perpendicular to the plane of the double layers.

In the case of aluminium trihydroxide only part of the octahedrons can be filled up with the trivalent aluminium ions. As a consequence we now obtain a threefold unit cell the projection of which has the dimensions of $3d$ and $d\sqrt{3}$. In one double layer four aluminium ions have to be placed in six octahedral holes formed by twelve OH'-ions; one third of the holes remains vacant. The four Al-ions are placed in hexagons surrounding the vacant sites, which is the cause of the pseudo-hexagonal character of gibbsite.

As a consequence of the alternation of occupied and vacant octahedrons the lattice is somewhat deformed; according to the rules given by PAULING [47] the empty octahedrons become bigger while those filled with Al-ions become smaller. This leads to a structure of the double layers as schematically given in FIG. 4.

The stacking of the double layers of gibbsite differs from that of brucite. The OH'-ions of the third layer are now placed above those of the second instead of the first layer, as in the case of brucite. The OH'-ions of the fourth layer are above those of the first. The double layers are alternately their mirror image. This stacking can be represented by:



The real structure of gibbsite can now be obtained by deforming the whole stacking in such a way that the layers are displaced over a short distance in the direction of the a -axis (FIG. 5a). This gives the monoclinic lattice.

A second possibility is that the displacement occurs in a direction perpendicular to the (110)-plane. This direction, which makes an angle of 60° with the a -axis, has the same arrangement of the atomic positions as the a -axis (a consequence of the pseudohexagonal character of the double layers). In this way the lattice of the triclinic gibbsite is formed (FIG. 5b).

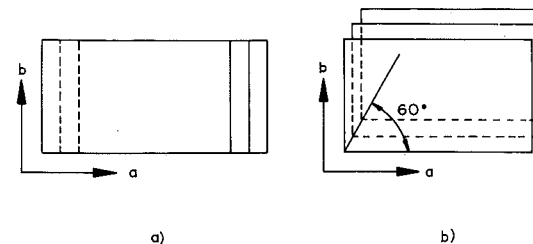


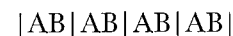
FIG. 5. Double-layer stacking in gibbsite (SAALFELD [38])
a. monoclinic; b. triclinic

From the z -parameters as calculated by MEGAW and by SAALFELD it appears that the distances between the different oxygen layers in gibbsite vary considerably. The mean distance between an A-layer and a B-layer (the thickness of the double layer) is $2.03 \text{ \AA}$, the mean distance between two A-layers or two B-layers (the distance between the double layers) is $2.81 \text{ \AA}$. Considering the double layers as closest-packed oxygen layers we find from the length of the a -axis that the diameter of the oxygen atom has a value of $2.89 \text{ \AA}$.

From this it follows that the b -axis has a value of $5.01 \text{ \AA}$, which is in good agreement with the measured value of 5.07 . However, for the thickness of the double layer we then find $2.36 \text{ \AA}$ as against a measured value of $2.03 \text{ \AA}$. Even if the diameter of the OH'-groups is smaller than $2.89 \text{ \AA}$, assuming that the layers are not closely packed, the low value for the thickness of the double layer cannot be explained, unless the polar OH'-ions are strongly deformed. With the aid of Fourier-synthesis SAALFELD [38] indeed found this to be the case.

II.3.3 The structure of bayerite

From the unit-cell dimensions of bayerite the conclusion can be drawn that the bayerite structure is denser than that of gibbsite. The ratio of the axes of bayerite is $3 : 1.750 : 1.630$, as compared with $3 : 1.723 : 1.632$ for a closest packing of spheres. There are two oxygen layers in the unit cell perpendicular to the c -axis; the atoms of the third layer are consequently placed above those of the first layer, just as in the brucite lattice; the layer sequence therefore is:



Though we had only the disposal of powder diagrams of bayerite so that an exact structure determination was impossible, we were able to obtain from the available data the principal details of the structure.

Systematic extinctions were only $hk0$ -reflections with $h+k$ odd. As all hkl -reflections for $h+k$ odd are very weak we may assume that the lattice does not differ much from a C-face-centered lattice. The intensity ratio of corresponding $2h00$ - and $hh0$ -reflections is about $1 : 2$. As the

multiplicity factors* have the same ratio, the structure factors are nearly equal, showing a pseudohexagonal lattice.

Starting with a closest packing of oxygen ions we find for the structure factor F_O of the oxygen lattice in first approximation:

$$F_O = f_O [1 + \cos \pi (h+k)] \sum \exp 2\pi i(xh+yk+zl)$$

Irrespective of the deformations of the lattice we can put for the coordinates x, y, z of the oxygen atoms:

$$(0, \frac{1}{3}, z); (\frac{1}{3}, \frac{1}{3}, z); (-\frac{1}{3}, \frac{1}{3}, z); (-x, -y, -z)$$

For the [001]-zone and $h+k$ even we get for F_O

$$F_O = 4f_O \cos 2\pi \frac{k}{3} \left[1 + 2 \cos 2\pi \frac{h}{3} \right]$$

With $h = 3n$ we get

$$F_O = 12f_O \cos 2\pi \frac{k}{3}$$

with $h \neq 3n$ F_O equals zero.

Comparison of F_O with the experimental intensities gives:

$hk0$	F_O	I_{exp}
020/310	$-6f_O$	absent
330/600	$+12f_O$	strong
040/620	$-6f_O$	very weak

From this it can be concluded that for $h = 3n$ and for $k \neq 3m$ the structure factor F_A of the aluminium lattice has to be about as large as F_O , but with opposite sign. For the 020/310-reflection the ratio of the scattering factors of aluminium and oxygen is equal to 1.58, from which it follows that F_A is about equal to $3.8f_A$. There are 4 Al-atoms in the unit cell, so for each of the two reflections $xh+yk$ must be approximately equal to an integer. There are six possible combinations for x and y :

no.	1	2	3	4	5	6
x	0	$\frac{1}{3}$	$-\frac{1}{3}$	$\frac{1}{6}$	$\frac{1}{2}$	$-\frac{1}{6}$
y	0	0	0	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$

These parameters correspond to the centres of the octahedral holes in the oxygen lattice.

* For the significance of the factors determining the intensity of the reflections the reader is referred to the textbooks on X-ray methods.

Keeping in mind that all $hk0$ -reflections with $h+k$ odd are extinguished, the possible combinations for the four Al-atoms are: 1-5-2-6, 1-5-3-4 and 2-6-3-4. As these three combinations give identical lattices, we prefer 2-6-3-4, being the most symmetrical one and the same as occurs in gibbsite (Fig. 4).

The z -coordinates of the Al-atoms are still indefinite. In the closest-packed oxygen lattice there are 2×6 octahedral holes, six in the $z = 0$ plane and six in the $z = \frac{1}{2}$ plane. For the intensities of the [001]-zone this makes no difference, consequently we were able to calculate the x - and y -coordinates of the oxygen atoms from the intensities of the $hk0$ -reflections. As we were only interested in the mean values of the atom parameters, we chose the following coordinates for the O-atoms, taking into account the shortening of "shared edges" (edges common to two filled octahedrons) as stated by PAULING [47]:

$$\begin{matrix} x & 0 & \frac{1}{3}-d & -\frac{1}{3}+d \\ y & \frac{1}{3}+2d & \frac{1}{3}-d & \frac{1}{3}-d \end{matrix} \left\{ \left(\frac{1}{2}+x \right) \left(\frac{1}{2}+y \right), \left(\frac{1}{2}-x \right) \left(\frac{1}{2}-y \right), -x-y \right.$$

For the coordinates of the Al-atoms we put:

$$\begin{matrix} x & \frac{1}{6} & \frac{1}{3} & -\frac{1}{3} & -\frac{1}{6} \\ y & \frac{1}{2} & 0 & 0 & \frac{1}{2} \end{matrix}$$

By varying d between zero and 0.05, we estimated by trial and error the value of d giving the best agreement between the ratio of the calculated intensities and that of the experimental ones. The best results were obtained for $d = 0.021$. TABLE II.5 shows the experimental and the calculated intensities for this value. The experimental intensities are expressed as a percentage of the intensity of the 001-reflection; the

TABLE II.5 Observed and calculated intensities of the [001]-zone of bayerite ($d = 0.021$)

hkl	I_{exp}	I_{calc}
110/200	68	68
020/310	<0.4	0.4
220/400	<0.4	0.1
130/420/510	4.6	3.5
330	13.4	13.6
600	7.3	6.8
040	0.0	0.3
620	0.3	0.6

calculated intensities are multiplied by such a factor that the intensity of the 110/200 reflection obtains its experimental value of 68.

From the intensities of the 00*l*-reflections we have to find the distance between the oxygen layers. Putting the mean coordinates of these layers at +*z*₀ and −*z*₀, we find that the structure factor *F*₀ for these reflections is:

$$F_0 = 12f_0 \cos 2\pi z_0 l.$$

The *z*-parameters of the Al-atoms can be put at 0 or $\frac{1}{2}$. There are three possibilities:

- all Al-atoms in the *z* = 0 plane;
- three Al-atoms in *z* = 0 and one in *z* = $\frac{1}{2}$;
- two Al-atoms in *z* = 0 and two in *z* = $\frac{1}{2}$.

The last possibility can be ruled out right away. In this case the structure factor *F*_A is:

$$F_A = 2f_A (1 + \cos \pi l).$$

Consequently for reflections with *l* odd, *F*_A is zero. *F*₀ for the 001-reflection is small, as *z*₀ can be expected to have a value between 0.20 and 0.25. So the 001-reflection would be very weak in this case. In fact this reflection is the strongest in the whole diagram.

Case a. gives:

$$F_A = 4f_A \quad \text{for all reflections } 00l$$

Case b. gives:

$$F_A = 3f_A + f_A \cos \pi l$$

so reflections with *l* even *F*_A = 4*f*_A
l odd *F*_A = 2*f*_A

For both cases we calculated the intensities for *z*₀ between 0.20 and 0.25. Case b. did not show a reasonable agreement with the observed intensities, so we may assume that all Al-atoms are in the *z* = 0 plane. The most acceptable value of *z*₀ was found to be 0.220.

TABLE II.6 shows that for this value there is a good agreement between the experimental and the calculated intensities.

In TABLE II.7 the intensities of some other reflections are given, calculated with *d* = 0.021 and *z*₀ = 0.220.

TABLE II.6 Observed and calculated intensities of the (00*l*)-reflections of bayerite (*z*₀ = 0.220)

<i>hkl</i>	<i>I</i> _{exp}	<i>I</i> _{calc}
001	100	98
002	3.7	3.6
003	0.6	0.1
004	3.3	3.4
005	2.3	5.1

TABLE II.7 Observed and calculated intensities of bayerite

<i>hkl</i>	<i>I</i> _{exp}	<i>I</i> _{calc}	<i>hkl</i>	<i>I</i> _{exp}	<i>I</i> _{calc}
201/111	23	30	601	4.2	3.9
202/112	2.5	2.5	331	6.7	7.7
203/113	1.8	1.4	602	0.2	0.0
204/114	0.2	2.0	332	0.2	0.0
021/311	88	100	603	0.6	1.8
022/312	48	40	333	1.3	3.5
023	2.3	5.1			
313	11.7	10.2			

We may be sure that the structure given covers the principal features of the bayerite lattice. Further refinements based on the data of the normal powder diagrams are hardly possible on account of the many overlapping reflections. There are some points that require a further explanation. For instance the 203/113-reflection is partly resolved in the powder diagram; it appears that the 113-reflection is the weaker one, whereas the calculated intensity of the 113-reflection (as a result of the difference in the multiplicity factor) is twice that of the 203-reflection.

Another fact is the appearance of a number of weak *hkl*-reflections with *l* ≠ 0 and *h*+*k* odd. These reflections appear already at low angles (*e.g.* the 211- and the 301-reflection). They are so distinct then that they can only partly be explained by small changes of the *z*-parameters of the atoms. In connection with the strongly disturbed crystal growth, distinct statistically occurring lattice defects may play an important role; in the absence of single-crystal patterns there is but little chance to solve this problem.

The thickness of the double layer calculated from the *z*-parameters

is 2.07 Å, which is only slightly greater than that of gibbsite (2.03 Å). The distance between the double layers is 2.64 Å. The OH⁻-ions appear to be strongly deformed also in the case of bayerite. The smallest O-O distance between two adjacent double layers is larger in bayerite than in gibbsite (3.13 Å against 2.81 Å). However, we are not allowed to draw conclusions from these figures as regards the stability of the two modifications, since neither the place of the hydrogen atoms nor the strength of the hydrogen binding is known. Literature data on the relative stability of gibbsite and bayerite [6, 48, 49] cannot be taken into consideration in this connection, as these observations were made in strongly alkaline solutions. The results obtained in these ternary systems cannot be transferred to the binary systems.

II.3.4 The structure of nordstrandite

It is of course impossible to obtain a detailed survey of the structure

of nordstrandite on account of the fragmentary data we obtained from the powder diagram of this substance which is invariably mixed with the other trihydroxides. Yet we can form an idea of the frame of the lattice without making too bold assumptions. The lattice must strongly resemble those of the other trihydroxides. The a - and b -axes are practically the same as with the other modifications; the observed reflections all belong to a C-face-centered lattice; the $h00$ - and the $hh0$ -reflections have corresponding intensities. We may therefore assume that the lattice of nordstrandite is based on a stacking of the same neutral double layers of $\text{Al}(\text{OH})_3$ as is the case with the other trihydroxides. The

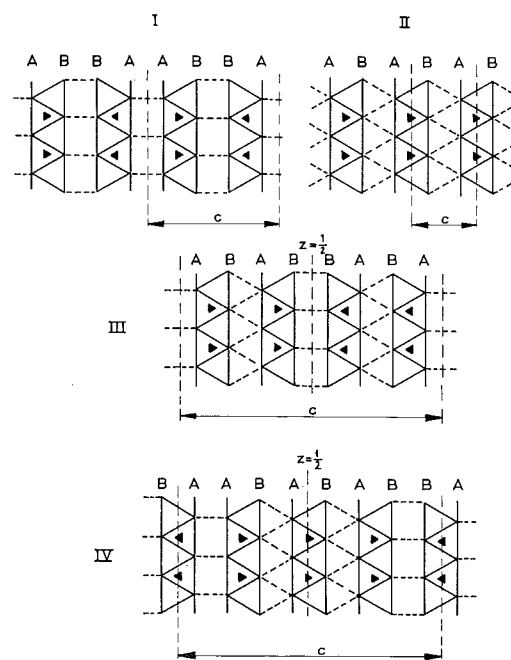


FIG. 6. Layer sequences in the trihydroxides
I. gibbsite sequence; II. bayerite sequence; III. and IV. two possible arrangements in nordstrandite
The full lines represent ionic bonds, the dotted lines hydrogen bonds

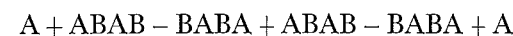
dimension of the *c*-axis shows that there are four double layers in the lattice. The repetition distance perpendicular to the planes of the layers is 19.11 Å, which is exactly equal to the sum of twice the bayerite and once the gibbsite distance:

$$2 \times 4.713 + 1 \times 9.716 \times 0.997 = 19.11 \text{ \AA}.$$

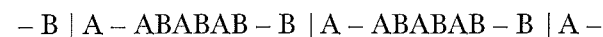
We may think of the nordstrandite lattice as being built up from two double layers with bayerite sequence and two double layers with gibbsite sequence. This can be done in two ways, as is shown in Fig. 6.

Lattice I schematically represents the gibbsite sequence, lattice II the bayerite sequence; lattice III and IV represent the two possible nordstrandite sequences.

Lattice III has the arrangement:



lattice IV:



The succession of four equal layers perpendicular to the c -axis at approximately equal distances in the lattice results in the $00l$ -reflections with $l = 4n$ being strong as compared with those with $l = 4n + 2$. This is actually observed:

00l	004	006	008	00.10	00.12
I_{rel}	vs	m	s	vw	w

The 00*l*-reflections with *l* odd were not observed. Since the difference between the interlayer distance of the bayerite and that of the gibbsite sequences is not very large, it might be that these reflections, which will be very weak, escape observation in the powder diagram. However, electron-diffraction patterns of nordstrandite single crystals showing the [100]-zone, only reveal 00*l*-reflections with *l* even. Extinction of the odd reflections means that the *z*-coordinates of the centre of the four double layers are $\pm z$ and $\frac{1}{2} \pm z$, which is only in agreement with lattice III. This arrangement of the trihydroxide layers can therefore be regarded as the most probable layer sequence in the nordstrandite lattice.

II.4 The structures of the oxide-hydroxides

II.4.1 The unit-cell dimensions

Diaspore occurs in nature in a well-crystallized form; however, it is very difficult to synthesize, and can only be obtained as very small

crystals. The structure determination of diasporite is therefore done exclusively with the aid of the natural single crystals [50, 51].

Crystalline boehmite, on the other hand, is hardly found in nature; synthetic single crystals of sufficient size for X-ray diffraction cannot be obtained. The corresponding iron compounds, goethite and lepidocrocite are isomorphous with diasporite and boehmite respectively. This fact was used by MILLIGAN and McATEE [52] to estimate the structure of boehmite.

TABLE II.6 gives a comparison of the unit-cell dimensions of the oxide-hydroxides.

TABLE II.6*

	<i>a</i>	<i>b</i>	<i>c</i>	
diasporite	2.836	4.409	9.399	ERVIN [51]
boehmite	2.858	3.690	12.238	MILLIGAN and McATEE [52]
boehmite	2.861	3.696	12.233	own observations

II.4.2 The structures of diasporite and of boehmite

The structures of the oxide-hydroxides are very closely related, as is the case with the trihydroxides. Each aluminium atom is again octahedrally surrounded by oxygen atoms.

VAN OOSTERHOUT [53] gave an easy method to describe the structures of the corresponding iron compounds, which we can use as such for the aluminium compounds. In the direction of the *a*-axis there are HO-Al-O chains schematically shown in FIG. 7a and 7b. Two of these chains can be placed in an anti-parallel position to each other in such a way that the O-atoms of the second chain are at the same level as the Al-atoms of the first chain (FIG. 7c). Thus we obtain a kind of polymer double molecule

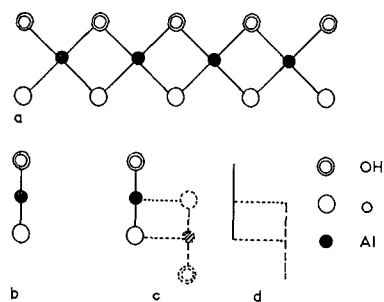
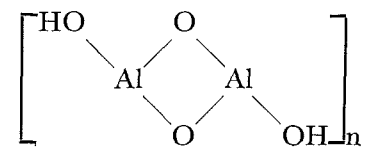


FIG. 7. a. AlOOH-chain; b. Side view of AlOOH-chain; c. Side view of two anti-parallel AlOOH-chains; d. Schematic representation of figure 7c.

* The notation of the axes is rather arbitrary in literature. We annotated the axes in such a way that, just as with the trihydroxides, the *c*-axis is perpendicular to the cleavage plane while the *a*-axis is in the direction of the adjacent oxygen rows. In this way we obtained a greater uniformity in the description of the pore genesis.



schematized in FIG. 7d. The chains give both modifications a repetition distance of 2.85 Å in the direction of the *a*-axis. The difference between the two modifications is due to a different arrangement of the double

molecules. In FIG. 8a and 8b this is shown schematically; in both cases the *a*-axis is perpendicular to the plane of the drawing. The cleavage plane indicated by *s*, is given by the position of the hydrogen bonds, just as in the case of the trihydroxides.

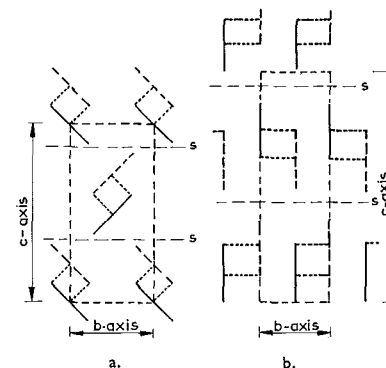


FIG. 8. Schematic representation of the crystal structures of a. diasporite and b. boehmite

II.4.3 Gelatinous boehmite

The DEBIJE-SCHERRER diagram of gelatinous boehmite is characterized by a number of bands or of strongly broadened lines, the tops of which almost coincide with the strongest lines of well-crystallized boehmite. Besides

the strong line broadening there are some other differences with well-crystallized boehmite:

- The water content is variable and always higher than the theoretical value of 17.65 g/100 g Al_2O_3 ; it can even be higher than 30 g/100 g Al_2O_3 .
- The tops of some bands do not exactly coincide with the corresponding lines of well-crystallized boehmite; they have moved to smaller diffraction angles. This shifting depends on the preparation.

The cause of line broadening may be the small size of the crystallites and/or certain lattice defects.

SCHERRER [54] derived for the relation between line broadening β and crystallite dimension *D* the following equation:

$$\beta = \frac{K\lambda}{D \cos \theta}$$

where *K* is a constant varying with the definition of β and *D*. If we

define $\beta_{1/2}$ as the angular width of the intensity peak at half maximum intensity, expressed in radians, and D as the mean dimension in Å of the crystallite, measured perpendicularly to the reflecting plane hkl (D_{hkl}), K is equal to about 0.9; hence

$$\beta_{1/2} = \frac{0.9\lambda}{D_{hkl} \cos \theta} \quad \dots \dots \dots (II.1)$$

For lattice defects giving a variation of $\pm \Delta d$ in the mean spacing d , we find from $d = \lambda/2 \sin \theta$:

$$\Delta \theta = -\tan \theta \cdot \frac{\Delta d}{d}$$

We may put $\beta_{1/2}$ equal to $4|\Delta \theta|$, so we get

$$\beta_{1/2} = 4 \tan \theta \frac{\Delta d}{d} \quad \dots \dots \dots (II.2)$$

Though the wavelength λ does not occur in equation (II.2) (as it does in equation (II.1), WILLIAMSON and HALL [55] showed that it is not yet possible to separate both effects by comparison of records made at different wavelengths, as d , θ and λ are not independently variable. However, it is possible to differentiate between the two effects from their dependency on the diffraction angle. The line broadening for the different orders of the reflection considered due to the small crystallite dimensions is proportional to $1/\cos \theta$, whereas that caused by lattice defects is proportional to $\tan \theta$.

PAPÉE *et al.* [19] were of opinion that on this ground lattice defects could not be the cause of the line broadening of gelatinous boehmite (named pseudoboehmite by them). They found that very often the bands were narrower at large diffraction angles than at smaller angles. However, they did not compare the different orders of the same reflection, so that their conclusion is not justified. Let us assume as an extreme example that the only cause of line broadening is the occurrence of lattice distortions in the direction of the c -axis.

For an $00l$ -reflection we then get:

$$d_{00l} = \frac{c}{l} \quad \left(\frac{\Delta d}{d}\right)_{00l} = \frac{\Delta c}{c} \quad \beta_{1/2} = 4 \tan \theta \frac{\Delta c}{c}$$

resulting in a very strong broadening of the bands at higher angles.

For any reflection hkl we get:

$$\frac{1}{d_{hkl}} = \sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}$$

$$\left(\frac{\Delta d}{d}\right)_{hkl} = \frac{\frac{l^2}{c^2}}{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}} \cdot \frac{\Delta c}{c} = \cos^2 \varphi \cdot \frac{\Delta c}{c}$$

where φ is the angle between the normal to the plane hkl and the c -axis. By substitution in equation (II.2) we now obtain:

$$\beta_{1/2} = 4 \tan \theta \cos^2 \varphi \cdot \frac{\Delta c}{c}$$

From this equation it follows that planes forming an angle φ with the basic plane, which is not too small, give rise to line broadenings appreciably smaller than those of the $00l$ -reflections. It now appears that the narrower bands at large angles indeed correspond to reflections with small l , *e.g.* the bands at 72° , 86° and 113° (2θ , $\text{CuK}\alpha$). In these bands a number of reflections invariably overlap. In TABLE II.7 we compared the product $\tan \theta \cos^2 \varphi$ of these reflections with that of the 002 -reflection.

TABLE II.7

band 2θ	hkl	$\cos \varphi$	$\tan \theta \cos^2 \varphi$	relative line broadening
14°	002	1.000	0.12	1
72°	125	0.535	0.21	1.9
	212	0.213	0.030	0.27
86°	220	0.000	0.00	0.00
	131	0.092	0.092	0.84
113°	20.10	0.760	0.88	8.8
	303	0.227	0.080	0.72
	040	0.000	0.00	0.00
	232	0.151	0.034	0.31
	311	0.075	0.005	0.04

These figures clearly show that in the region of large diffraction angles the influence of lattice defects in the direction of the c -axis on line

broadening is small for reflections with small l , whereas for reflections with large l it is so large that these reflections (*e.g.* the 20.10-reflection) disappear almost completely in the background.

The narrowing of the bands at higher diffraction angles is consequently not an indication of the absence of an influence of lattice defects on line broadening, but rather one of the presence of line-broadening lattice distortions in a distinct direction.

Our observations with the recrystallization of boehmite (CHAPTER I.3.2) can provide further information on the nature of the differences between gelatinous and well-crystallized boehmite. By treating gelatinous boehmite with water at various temperatures we obtained products which after drying at 120 °C showed a decreasing water content with increasing recrystallization temperature (TABLE II.8).

TABLE II.8

No.	Treatment	W g/100 Al_2O_3	spacing 1st band	spacing corr.	c -axis Å	moles H_2O per mole Al_2O_3	S m ² /g Al_2O_3
1	Fresh	30.7	6.70	6.51	13.02	1.74	490
2	24 h 20 °C	28.2	6.58	6.43	12.86	1.60	440
3	6 h 50 °C	26.4	6.51	6.41	12.82	1.50	395
4	6 h 120 °C	25.1	6.36	6.32	12.64	1.42	300
5	6 h 150 °C	23.9	6.31	6.29	12.58	1.36	255
6	6 h 170 °C	22.6	6.28	6.26	12.52	1.28	201
7	6 h 250 °C	19.7	6.15	6.15	12.30	1.12	64

It is seen from this table that the top of the first band, which corresponds to the 002-reflection of boehmite, is shifted to higher spacings according as the water content of the product is higher. For a minor part this is caused by the strong increase of the continuous factors in this region with decreasing diffraction angle (for the definition and the nature of the continuous factors the reader is referred to the text books on X-ray diffraction). For sharp lines this shift can be neglected; for the broad bands of the gelatinous boehmite, which have a width at half maximum intensity of up to 4°, it results in shifting the place of maximum intensity to lower diffraction angles. We corrected it by dividing the intensity for each point of the profile of the band by the product of the continuous factors. These values were plotted against 2θ , and from the place of the top of this peak the corrected spacing was calculated, and further the mean length of the c -axis.

In FIG. 9 we plotted the increase of the c -axis against the excess water content of the preparations (in moles H_2O /mole Al_2O_3). This gives a straight line, from the slope of which we calculated that for each mole of H_2O in excess, *i.e.* for 2 molecules of extra H_2O per unit cell, the mean c -axis increases by 1.17 Å.

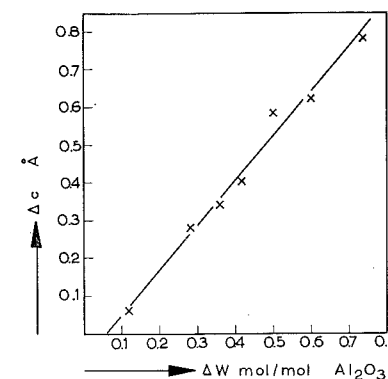


FIG. 9. Increase of the c -axis of gelatinous boehmite (Δc) as a function of the excess water content (ΔW)

The increase of the c -axis must exert its influence on the other bands of the Debye-Scherrer diagram. Indeed we observed a corresponding shift for the second and the third band (see FIG. 2), consisting of the 012- and the 103-reflection respectively. In the case of the other reflections always a number of reflections coincide or overlap, a shifting of the individual reflections cannot be observed then.

Various water-containing silicates, as vermiculite and a number of clay minerals, also show such a relation between the length of one of the axes and the water content. In these cases the water is enclosed between the silicate layers forming the lattice. This water can be expelled by heating, giving a simultaneous decrease of the axis perpendicular to the layers. There exists, however, considerable difference between the behaviour of these minerals and that of gelatinous boehmite. In the case of the silicates the whole process is reversible; by rehydration of the heated products water is again taken up and the original length of axis restored. The changes of the c -axis of gelatinous boehmite, on the contrary, are the results of a recrystallization process, so they are irreversible.

Between preparations 1, 2, 3 and preparations 4, 5, 6, 7 of TABLE II.8 there is another remarkable difference, which does not appear from the table. Electron-microscope observations show that the first three preparations have the sheet-like appearance of gelatinous boehmite as described in CHAPTER I. Electron-diffraction patterns consist of broadened rings with a continuous blackening (PLATE V). The other products, however, consist of separated particles with dimensions increasing from about 50 Å to a few hundred Å with increasing recrystallization temperature. Electron-diffraction patterns of these products show rings consisting of discrete points, proving that they consist of separate crystals (PLATE VI). This difference is also apparent from the width of the lines

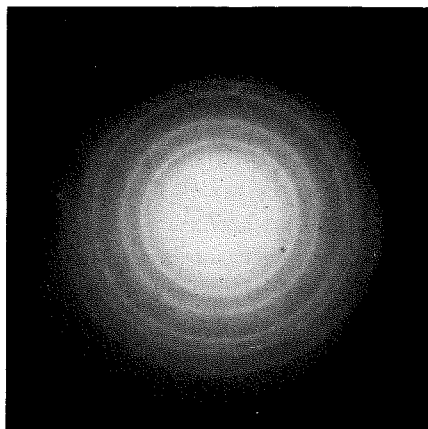


PLATE V. Diffraction pattern of gelatinous boehmite

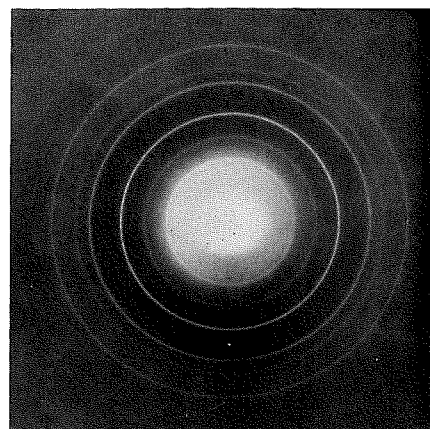
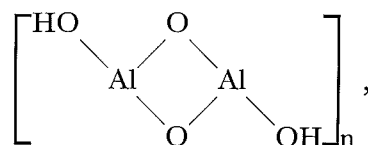


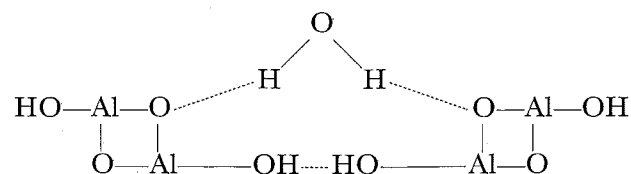
PLATE VI. Diffraction pattern of microcrystalline boehmite

in the Debye-Scherrer diagrams; the line broadening is far less for the preparations 4, 5, 6 and 7 than for the other three.

Starting from the concept of polymeric double molecules of



as described in II.4.1, we are inclined to describe the structure of the sheet-like gelatinous boehmite as an arrangement of probably branched double molecules. This arrangement will approach, at least in small regions (20 to 40 Å), that in boehmite, while in the direction of the *c*-axis extra water molecules are built in. From the infrared investigations of IMELIK [56] and of GLEMSER [57] it appeared that this water is not present in the form of freely mobile molecules, so we may assume that these water molecules act as double hydrogen bridges, *e.g.*:



in which case they are very strongly bound.

At temperatures above 100 °C the sheets of the gelatinous boehmite apparently disintegrate in liquid water to form very small boehmite crystals, the structure of which is still disturbed by built-in water molecules. Especially at higher temperatures a recrystallization via the water phase occurs with formation of larger crystals. Though these products have the appearance of gelatinous products, we have to call them microcrystalline (gelatinous) boehmite.

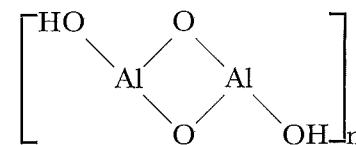
II.5 Summary of Chapter II

From a study of the X-ray powder patterns of the trihydroxides the following results were obtained:

- The unit-cell dimensions of synthetically prepared gibbsite are equal to those of the naturally occurring gibbsite, as determined by MEGAW and by SAALFELD.
- For bayerite we found an orthorhombic lattice agreeing well with the monoclinic (almost orthorhombic) lattice mentioned by UNMACK. The structure of bayerite could be given in broad lines.
- The unit-cell dimensions of nordstrandite could be established; the arrangement of the trihydroxide double layers in the lattice could be indicated.

The literature data on the structure of boehmite could be confirmed. From the relation between the water content and the *c*-axis of gelatinous boehmite it could be proved that there exists a continuous transition between gelatinous boehmite and well-crystallized boehmite.

The gelatinous boehmite could be described as an arrangement of possibly branched chain-like molecules



with hydrogen bonds partly between the OH-groups of the chains and partly between the oxygen atoms via a water molecule.

SELECTED-AREA ELECTRON DIFFRACTION

III.1 Introduction

To be able to study the texture of materials obtained by pseudomorphous transformation of crystalline substances, we must know not only the structures of starting material and final product, but also the orientation of the unit-cell axes. For, in nearly all cases at least one direction is preserved that is common to the lattices of both compounds. As STEGGERDA [35, 38] showed for aluminium oxide obtained from gibbsite, also the texture of the pore system is closely related to the orientations of the unit-cell axes. The orientation of the lattice axes of single crystals of such a size that they are suited for X-ray investigation is not difficult to determine. LAUE, rotating-crystal or WEISENBERG records combined with microscopical observation immediately give the axes orientation of the crystal.

In the case of very small crystals, as we had to deal with during our investigations, X-ray single-crystal techniques cannot be used, as stated already in the preceding chapter. From the electron-microscope observations of our preparations it appears that the size of the crystalline particles could vary from some microns down to 100 Å (and even smaller).

The development of electron microscopy during the last fifteen years has made it possible to obtain diffraction records of such small objects, which can be correlated with the optical image. The possibilities are still rather limited (manipulation of the sample is hardly possible), interpretation sometimes gives many difficulties, reliability and accuracy are inferior to those of the X-ray techniques. Nevertheless remarkable results have been obtained with electron diffraction. WEINSTEIN *et al.* [59] at the Moscow Institute of Crystallography developed the theoretical backgrounds of structure determination by electron diffraction for the use of polycrystalline specimens. COWLEY *et al.* [60] explored the use of single-crystal data for the purpose of structure analysis.

In this chapter we shall discuss the method by which these single-crystal electron-diffraction records can be obtained, and the results we obtained with it on the aluminium hydroxides. In the next chapter

these single-crystal records will often be used for the investigation of the pseudomorphous dehydrations.

III.2 Selected-area electron diffraction

III.2.1 Apparatus and techniques

The available electron microscope was the Elmiskop I (SIEMENS and HALSKE). It is a three-step microscope with two projector lenses. With a diaphragm in the image plane of the objective a part of the sample 0.5 to 2 μ in diameter can be selected. The diffraction pattern can be obtained by using the first projector lens to depict the image-focal plane of the objective in the object-focal plane of the second projector lens. In this way an enlarged picture of the diffraction pattern is obtained on the fluorescent screen or on the photographic plate (FIG.10A). By changing the focal distance of the first projector lens it is also possible to obtain a normal picture of the selected area (FIG.10B).

In spite of the small diameter of the selected area it will often contain more than one crystal. To make sure from what part of the sample

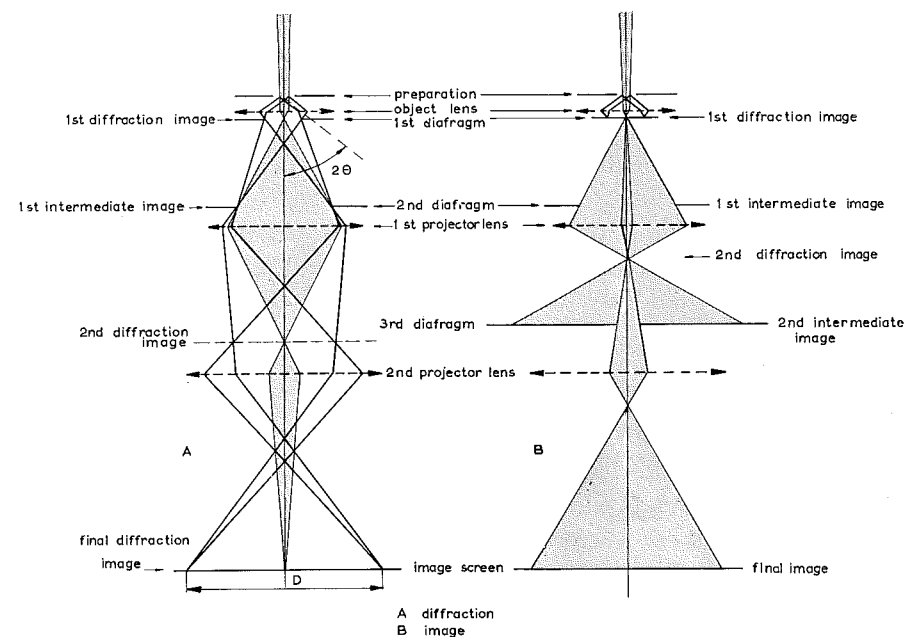


FIG. 10. Schematized beam geometry of selected-area electron-diffraction technique

the beam corresponding to a certain diffraction spot originates, it is possible to intercept all diffracted beams, except the one in question, by a diaphragm. By switching to picture focussing without changing the diaphragm, an image of the part of the sample corresponding to the diffracted beam (seen in the direction of this beam, giving "dark-field illumination") is obtained.

A drawback of the use of an electron microscope for diffraction purposes is that the preparation is placed very close to the central part of the objective. Consequently manipulation of the preparation is very limited. Only lateral motions in two directions perpendicular to the incident beam are possible. Therefore, only those particles of the sample can be used which have the desired orientation with regard to the beam. As a consequence of the preparation technique the sample particles will often possess a certain preferred orientation: platelets will be oriented preferably with their principal plane, needle-shaped particles with their longitudinal axis perpendicular to the beam. Consequently, for a great number of materials only one crystal zone can be observed.

Another difficulty is that the samples are in a high vacuum (10^{-4} mm or lower). Many compounds as *e.g.* hydroxides, will decompose under these conditions, especially under the influence of the electron bombardment, while moreover the temperature may increase considerably. This phenomenon was observed by ROY [61] where it caused dehydration during the investigation of gallium hydroxide. COENEN [62] found a very strong recrystallization of the nickel particles of his nickel catalysts when exposed to radiation in the electron microscope. Initially we also had quite some difficulties resulting from the decomposition of our samples. By decreasing the intensity of the electron beam as far as possible and recording the desired diffraction pattern before looking at the particle itself, we succeeded in obtaining usable diffraction diagrams of our samples. Obviously, the percentage of outfall of the records was very large.

III.2.2 The reciprocal lattice

The reciprocal lattice is an important mathematical aid in the interpretation of diffraction patterns. It is the pole figure of the different lattice planes in relation to a sphere. We shall describe the crystal lattice with the three vectors **a**, **b** and **c**, having the length and the direction of the unit-cell axes and the reciprocal lattice with the vectors **a***, **b*** and **c***. The vectors of the reciprocal lattice are then perpendicular to the planes **b** × **c**, **c** × **a** and **a** × **b** respectively, and therefore also to the coordinate planes of the crystal lattice. The relation between

the reciprocal vectors and the crystal vectors is given by:

$$\begin{aligned} (\mathbf{a} \mathbf{a}^*) &= (\mathbf{b} \mathbf{b}^*) = (\mathbf{c} \mathbf{c}^*) = K \dots \dots \dots \text{(III.1)} \\ (\mathbf{a} \mathbf{b}^*) \text{ etc.} &= 0 \end{aligned}$$

K is a constant with the dimension l^2 , which is often put equal to 1.*

TABLE III.1 Corresponding quantities in the crystal lattice and the reciprocal lattice

crystal lattice	reciprocal lattice
basis vectors a , b , c	basis vectors a* , b* , c*
lattice plane (<i>hkl</i>)	lattice point (<i>hkl</i>)
distance from origin to plane (<i>hkl</i>)	distance from origin to point (<i>hkl</i>)
$d_{hkl} = \frac{1}{ \mathbf{h} }$	$d^*_{hkl} = \mathbf{h}^* $
for an orthorhombic lattice holds:	
$ \mathbf{h} = \sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}$	$ \mathbf{h}^* = \sqrt{h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2}} = K \mathbf{h} $

TABLE III.1 represents the principal corresponding quantities in the crystal lattice and the reciprocal lattice. EWALD [64] showed that with the aid of the concept of the reciprocal lattice the diffraction pattern can be derived in a simple way. If we represent the incident (X-ray or

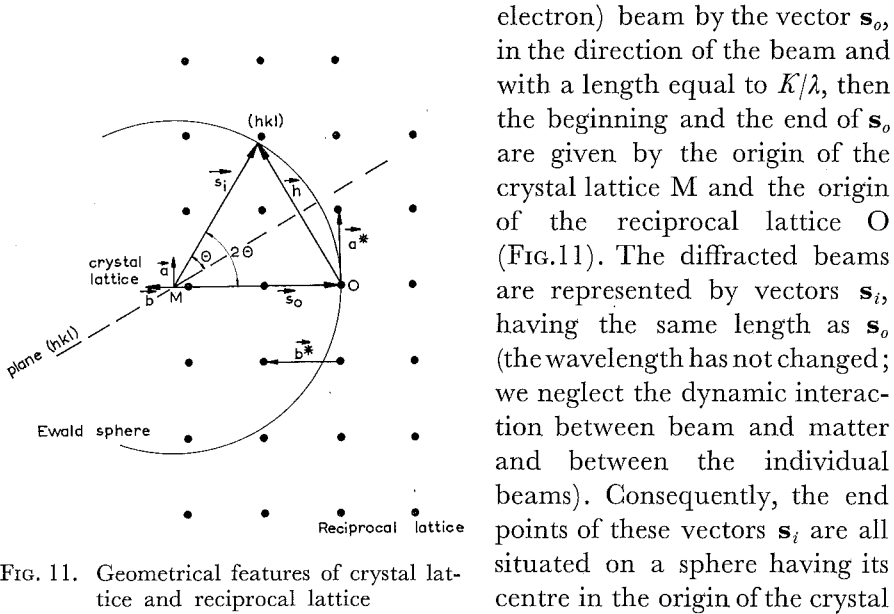


FIG. 11. Geometrical features of crystal lattice and reciprocal lattice

* For the derivation we have to refer the reader to the literature [63].

lattice M and a radius K/λ . This sphere is called the EWALD sphere. From LAUE's diffraction conditions EWALD derived that in the case of an infinitely large crystal a beam diffracted from a plane (hkl) will only exist if the EWALD sphere passes through the point (hkl) of the reciprocal lattice. In general this will not be the case; reflection on a lattice plane will only occur if the orientation of the crystal lattice is such that the Bragg equation

$$2d_{hkl} \sin \theta = \lambda \quad \dots \dots \dots (III.2)$$

is satisfied.

A more extensive significance can be given to the reciprocal lattice by ascribing to each point hkl a "weight" proportional to the structure factor F of the corresponding reflection hkl . From the kinematic theory of the diffraction phenomena for small (or imperfect) crystals it then follows that the reciprocal lattice "points" regarded in this way extend in space. The degree to which they extend in a given direction is in the first instance inversely proportional to the dimension of the crystal in that direction. This gives the EWALD sphere more opportunities to intersect a reciprocal lattice "point". One consequence of this fact is a broadening of the reflections of powder patterns of very small crystals. It is possible to calculate the crystal size from this line broadening.

The wavelength used for electron diffraction is very small, as is also the case with the diffraction angles. The radius of the Ewald sphere is consequently very large, the sphere may be considered to be flat over a limited region of diffraction angles. Moreover, the crystals under consideration have a small dimension in at least one direction, so the reciprocal lattice points extend further in this direction. If now the crystal has a suitable orientation with respect to the beam, diffraction diagrams will be formed consisting of an often complicated pattern of lines and spots.

III.2.3 Calculation and correction

To calculate the interplanar spacings from the diffraction patterns we start from the equation (III.2): $2d \sin \theta = \lambda$. The diffraction angle θ of a diffraction spot at a distance $\frac{1}{2}D$ from the centre is given by:

$$\tan 2\theta = \frac{1}{2} D/R_{\text{eff}} \quad \dots \dots \dots (III.3)$$

where R_{eff} represents the effective diffraction length. This is not equal to the geometrical distance from object to photographic plate, as the diffracted beams pass through three magnetic lenses (see FIG.10).

From (III.2) and (III.3) it follows that

$$d = \frac{\lambda}{2 \sin (\frac{1}{2} \arctan \frac{1}{2} D/R_{\text{eff}})} \quad \dots \dots \dots (III.4)$$

Applying the approximation $\tan 2\theta = \sin 2\theta = 2 \sin \theta = 2\theta$ equation (III.4) passes into:

$$d = R_{\text{eff}} \lambda / \frac{1}{2} D \quad \dots \dots \dots (III.4a)$$

When we measured the diffraction-pattern distances, we arrived at the conclusion that equation (III.4a) could only be applied in a rather limited region; the product $R_{\text{eff}} \lambda$ calculated from patterns with known d 's decreased with increasing D (deviations of more than 1 %).

Passing to reciprocal-lattice units and putting K equal to $R_{\text{eff}} \lambda$, equation (III.4) is transformed into:

$$d^* = 2R_{\text{eff}} \sin (\frac{1}{2} \arctan \frac{1}{2} D/R_{\text{eff}}) \quad \dots \dots \dots (III.5)$$

By series development and neglecting terms of the fifth and higher orders we obtain:

$$d^* = \frac{1}{2} D [1 - 3/8 (\frac{1}{2} D/R_{\text{eff}})^2] \quad \dots \dots \dots (III.5a)$$

However, it appeared that this correction was still insufficient to give an explanation of the deviations. This must be due to the errors of imaging of the electron-microscope lenses. The most important error of this kind is the cushion-shaped misalignment. These errors also give rise to a third-order correction term. As the magnitude of this correction cannot be calculated, the easiest thing to do was to estimate the total correction for a number of calibrating materials with well-known interplanar spacings. We shall write equation (III.5a) as:

$$d^* = \frac{1}{2} D (1 - fD^2) \quad \dots \dots \dots (III.6)$$

The correction constant f was estimated from six diffraction-pattern records, viz. two of finely divided nickel, two of MgO and two of microcrystalline boehmite. The six diffraction patterns consisted of sharp concentric rings. The ring diameters D were measured by means of a Vernier measuring microscope, which could be read to 0.001 mm. The reproducibility of the measurements was only 0.02 mm owing to the breadth of the lines. The measurements were performed in two mutually perpendicular directions. To obtain f (and $R_{\text{eff}} \lambda$) equation (III.6) was transformed as follows:

$$d^* = R_{\text{eff}} \lambda / d = \frac{1}{2} D - \frac{1}{2} f D^3$$

$$D = f D^3 + \frac{2R_{\text{eff}} \lambda}{d} \quad \dots \dots \dots (III.7)$$

The magnitude of $R_{\text{eff}}\lambda$ is not known, but can be approximated by $\frac{1}{2} D \cdot d$ (III.4a). We calculate the mean value of $D \cdot d$, which we represent by P . If we subtract the term P/d from the left- and the right-hand side of equation (III.7) we obtain:

$$D - P/d = fD^3 + \frac{1}{d} (2R_{\text{eff}}\lambda - P) \quad \text{. (III.8)}$$

which represents a linear equation:

$$z = Ax + By \quad \text{. (III.8a)}$$

where

$$\begin{aligned} z &= D - P/d & A &= f \\ x &= D^3 & B &= 2R_{\text{eff}}\lambda - P \\ y &= \frac{1}{d} \end{aligned}$$

The constants A and B in equation (III.8a) can be calculated from the measurements by means of the method of least squares.

For the correction constant f (in mm^{-2}) we found:

$$\left. \begin{array}{ll} \text{Ni} & 1.33 \text{ and } 1.37 \cdot 10^{-6} \\ \text{MgO} & 1.75 \text{ and } 1.51 \cdot 10^{-6} \\ \text{boehmite} & 1.68 \text{ and } 1.36 \cdot 10^{-6} \end{array} \right\} \text{mean value } (1.5 \pm 0.16) \cdot 10^{-6}$$

With this correction constant in equation (III.6) it was possible to obtain an accuracy of about 0.2 % for d^* , provided of course that the diffraction patterns consisted of rather sharp reflections.

To obtain the interplanar spacings from d^* , the product $R_{\text{eff}}\lambda$ must be known accurately. We found strongly divergent values for this product, *viz.* between 19.5 and $24.0 \times 10^7 \text{ \AA}^2$. It apparently varies from record to record.

The wavelength depends on the high tension of the electron generator:

$$\lambda = \sqrt{\frac{149.55}{V(1 - 9.836 \cdot 10^{-7} V)}} \text{ \AA}$$

in which V represents the high tension in Volts.

The effective diffraction length R_{eff} depends on the focal distances of the three lenses; a variation in the strength of the excitation current will cause a corresponding variation in the diffraction length. Although the relative variations in current strength and high tension during the short periods of exposure for the records are very small, they cannot be neglected over a longer period. After an interruption differences of some percent may occur. Consequently, for each record a calibration will be necessary. At first we tried to calibrate by measuring the diffraction pattern of MgO made before and after the record considered;

however, the differences were still too large. Covering the supporting film by a thin layer of gold was not feasible, because the diffraction rings were too diffuse to be measured with a high accuracy. Finally it appeared that a number of samples contained, besides the desired crystal, a sufficient amount of microcrystalline gelatinous boehmite in the selected area to serve as an internal calibration standard. The exact interplanar spacings of this boehmite were derived from X-ray measurements, as the c -axis of this boehmite is variable. Since in this way the correction factor f for each separate record could be calculated at the same time, we were able to obtain an accuracy of 0.2 to 0.3 % for various preparations.

III.3 Results of the selected-area diffraction

III.3.1 Well-crystallized boehmite

The preparation BoG, well-crystallized boehmite obtained by hydro-

thermal conversion of gibbsite PSH, consists of rhombic crystals with an angle of 76° and of triangular particles with a vertical angle of 76° (PLATE II and FIG. 12a and b). The thickness of the crystals is small compared with the other dimensions. The crystals

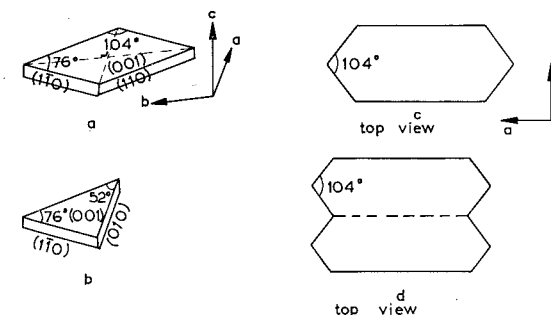


FIG. 12. Crystal shapes of boehmite

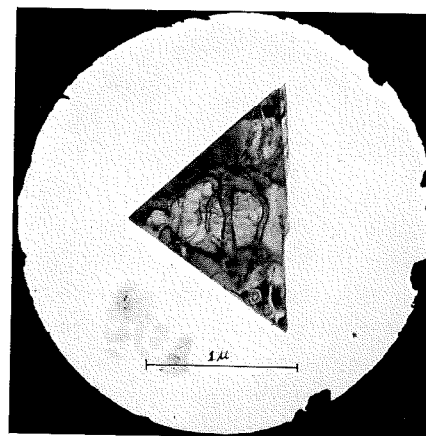


PLATE VII. Single crystal of boehmite

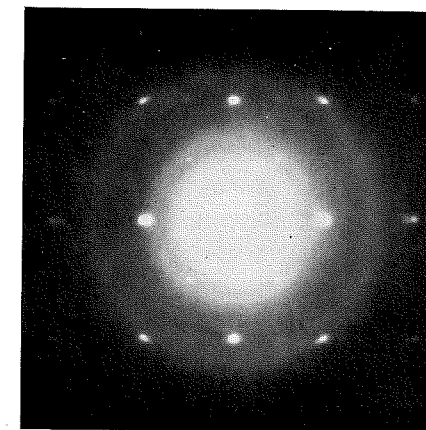
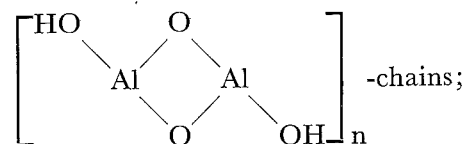


PLATE VIII. Diffraction pattern of VII

that were suited for selected-area diffraction all lay with the plane of the rhombus on the supporting film, *i.e.* perpendicular to the beam. The visible dimensions varied between 0.5 and 1 μ . From the diffraction patterns of these crystals (PLATE VII and VIII) we could calculate a ratio of the axes of 1.292. This ratio agrees very well with that of the *a*- and *b*-axes, as determined from X-ray measurements (1.291). As no calibration standard was present in this case, it could only be ascertained that the lengths of the axes were approximately equal to those found from X-ray measurements. The *a*-axis (2.86 Å) lies in the direction of the short diagonal of the rhombus, the *b*-axis (3.69 Å) is parallel to the long diagonal. Consequently, the *c*-axis (12.24 Å) is parallel to the incident beam. The observed reflections are *hk*0-reflections. The ratio of the lengths of the crystal diagonals is about 1.3 and corresponds with that of the unit-cell axes. The side planes of the rhombus are apparently formed by (110)-planes; basis and top are (001)-planes, *i.e.* parallel to the cleavage plane.

The occurrence of triangular crystals points to a cleavage plane parallel to the *a*-axis. In this direction are the



a cleavage plane can exist between these chains and this will be the (010)-plane.

The preparations obtained by hydrothermal conversion of gelatinous boehmite in water (CHAPTER I) show crystals of a different shape. The crystals were too small to allow good single-crystal diffraction patterns to be made. From the shape, particularly the occurrence of an angle of 104° (PLATE III; FIG.12c), it follows that the longitudinal axis of these crystals is the *a*-axis.

In this preparation some shapes with re-entering angles appear. Probably they are twinned crystals (FIG.12d) in which case the (010)-plane would be the twinning plane. According to the structure given by MILLIGAN and McATEE [52] described in the preceding chapter this plane should be a symmetry plane. As a symmetry plane cannot at the same time be a twinning plane, either the shape of FIG.12d does not belong to a twinned crystal, or the proposed structure is not completely correct.

An explanation can be found in the electron-diffraction pattern of single crystals of boehmite (PLATE VIII). Besides the strong *hk*0-reflections with even *h* and even *k* also a number of weak to very weak reflections

occurs with odd *h* and/or *k*. These reflections are forbidden if the space group corresponding to the proposed structure is correct. In the X-ray diagrams these reflections are completely absent. It is consequently probable that they originate from the protons of the hydroxyl groups. Protons hardly influence the diffraction of X-rays. Electrons, however, are scattered by protons. If it is true that the observed reflections with odd *h* and/or *k* are caused by the scattering of the electrons by the protons of the OH-groups, the symmetry of the lattice is lower if the hydrogen atoms are considered, than if they are not. This means that the OH-dipoles form an oblique angle with the surface of the cleavage plane ((001)-plane). KROON [65] arrived at the same conclusion from his measurements of the nuclear spin resonance of boehmite. If we accept the lower symmetry of the boehmite lattice, the objection that the (010)-plane cannot be a twinning plane, does not hold any more as it is no longer a symmetry plane.

III.3.2 Well-crystallized bayerite

The diffraction pattern of bayerite somatoids prepared according to SCHMÄH's method (CHAPTER I) consists of a row of spots going through the centre and mostly a number of scattered spots (PLATE IX and X). Though calibration material was not present, we could, by comparing this record with those of MgO made directly before and after it, ascertain that the repetition distance in the direction of the central row amounted to 4.7 Å, corresponding to the *c*-axis of bayerite. As the direction of this row of spots coincides approximately with the longitudinal direction of the somatoids we may conclude that the trihydroxide double layers are

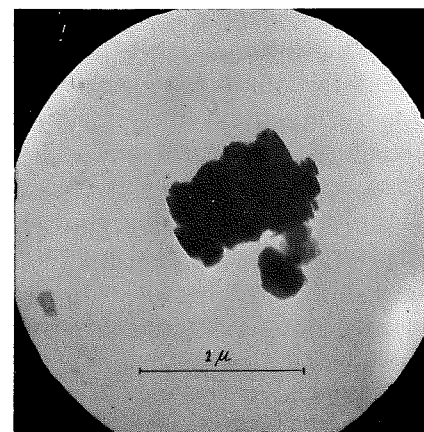


PLATE IX. Bayerite particle



PLATE X. Diffraction pattern of IX

perpendicular to the longitudinal direction of the bayerite particles.

By dark-field illumination we observed that the reflections of the central row originated from the whole crystal; the other spots, on the contrary, only from certain parts of it.

A further peculiarity was that, notwithstanding the fact that both the crystal lattice and the shape of the particles suggested the presence of a pronounced cleavage plane perpendicular to the direction of the c -axis, we seldom observed plate-shaped particles in these preparations.

We presume that these two phenomena are tied up with the way in which these particles have grown. VAN NORDSTRAND [7] supposed that bayerite had to be considered a spiral-dislocation growth of gibbsite, parallel to the c -axis. Another possibility is rotational growth, as described by WILMAN [66] for zinc crystals. In both cases the a - and the b -axis do not possess a fixed position with respect to the c -axis, but rotate. Only the $00l$ -reflections are achieved in a regular way. A third possibility, however, has nothing to do with irregular growth. If the particles always have their a - and b -axis in an unfavourable position with respect to the incident beam, but have their c -axis perpendicular to it, it will be possible to observe only the $00l$ -reflections. Which of these cases occurs cannot be ascertained, because the selected particle cannot be manipulated sufficiently. However we prefer the concept of spiral-dislocation growth, because in this case the hydroxide double layers form spirals through the crystal with their spiral axes parallel to the c -axis. This reduces the cleavability of the crystals.

III.3.3 Trihydroxides obtained by treating gelatinous boehmite with dilute ammonia solutions

By treating gelatinous boehmite with dilute ammonia solutions it is converted to a smaller or greater extent into a mixture of the trihydroxides (CHAPTER I). The amount of gibbsite in this mixture is mostly very small. If the treatment is performed at room temperature the remaining boehmite retains its sheet-like appearance of gelatinous boehmite. After a treatment with water at 120 °C under pressure the gelatinous boehmite is converted into microcrystalline boehmite, as has been described in CHAPTER II.4.3. The crystals of this microcrystalline boehmite are often so small and thin that they can hardly be recognized as such with the electron microscope. Since this kind of boehmite gives an electron-diffraction pattern of rather sharp lines, its presence in the trihydroxide preparations enables us to calculate the lattice dimensions of the trihydroxide particles with a high accuracy.

Besides the sheet-like or the microcrystalline boehmite in the samples

investigated three types of bigger particles are observed, each giving a characteristic single-crystal pattern consisting of fairly sharp spots. These three types are:

- type I (PLATE XI, XII) very thin platelets giving a hexagonal single-crystal pattern with ortho-hexagonal axes of:
 $a = 8.66 \text{ \AA}$, $b = 5.00 \text{ \AA}$ and $a/b = 1.732$
[001]-zone, $hk0$ -reflections with merely $h+k$ even
- type II (PLATE XIII, XIV) rod-shaped particles with poorly developed edges, built up from a number of approximately parallel "packets"; diffraction pattern consisting of a single row through the central spot; the direction of the row of spots approximately corresponding to the longitudinal direction of the particles.
The length of the axis is $4.72 \text{ \AA}$ (c -axis).
Some records show a few more rows of spots parallel to that through the centre with a repetition distance of $2.5 \text{ \AA}$ (b').
- type III (PLATE XV, XVI) rod-shaped crystals with six-sided cross-section. Single-crystal diffraction pattern consisting of a number of parallel rows of spots, showing two mutually perpendicular axes:
 $b = 5.00 \text{ \AA}$, $c' = 9.56 \text{ \AA}$
[100]-zone, $0kl$ -reflections with k odd only with large l .

If we compare these data with those we obtained with X-ray diffraction, some difficulties arise with regard to type I. The absence of $hk0$ -reflections with $h+k$ odd completely excludes the gibbsite lattice, as this, in its X-ray diffraction pattern, shows a number of such reflections with a rather high intensity. The exactly hexagonal character, which follows unmistakably from PLATE XVII, does not agree with the X-ray data of bayerite or of nordstrandite. Differences between the X-ray structure of large crystals and that of very small crystals, as follow from electron diffraction, have been recorded earlier. COWLEY [67] determined the structure of very small boric acid crystals showing very nearly hexagonal symmetry, whereas the normal structure of boric acid is triclinic. In all cases the crystals investigated possess a layer lattice. The differences between electron-diffraction structure and X-ray structure are mostly explained by accepting a high density of stacking faults of the layers. However, this does not explain why the ratios of the axes should differ, as we observed. The anion lattices of these compounds are, according to the X-ray analysis, strongly deformed. Especially OH-groups are apt to modify the closest packing of the anion lattices. The

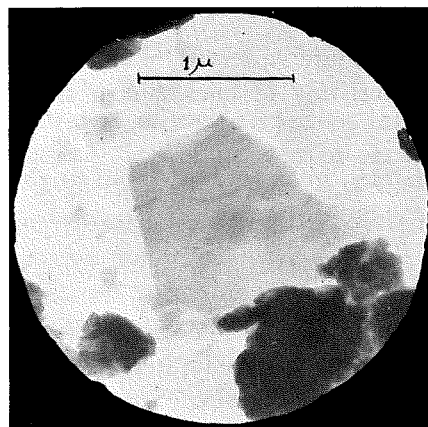


PLATE XI. Type I particle (prototype of trihydroxide)

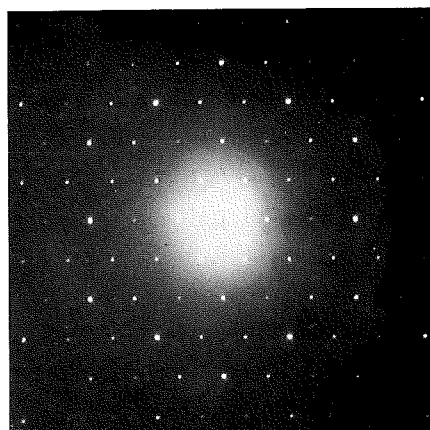


PLATE XII. Diffraction pattern of XI

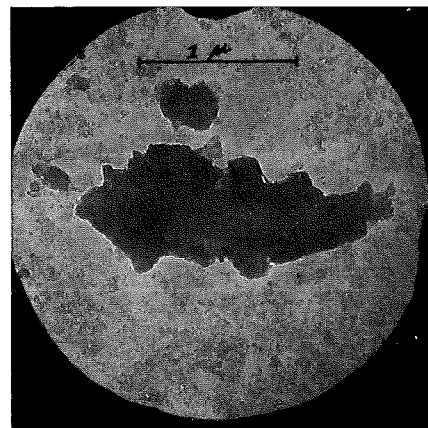


PLATE XIII. Type II particle (bayerite) with microcrystalline boehmite

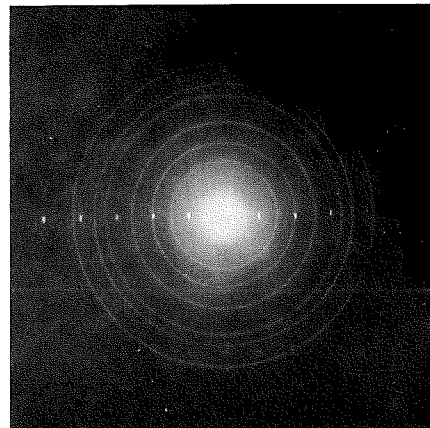


PLATE XIV. Diffraction pattern of XIII

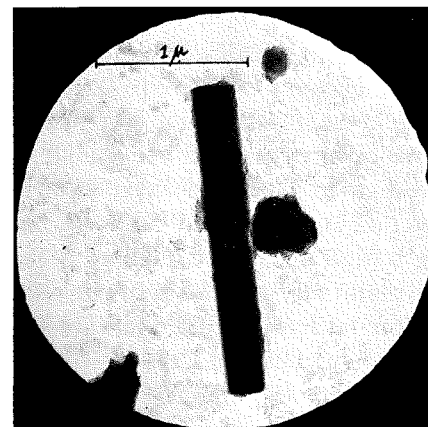


PLATE XV. Type III particle (nord-

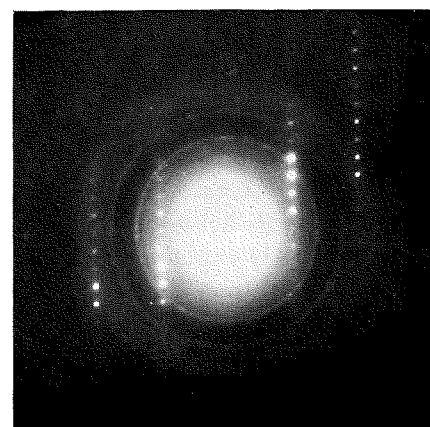


PLATE XVI. Diffraction pattern of XV

very thin crystals with which we are dealing in the case of electron diffraction (thickness often less than 100 Å) contain a number of layers that is probably too small to give the arrangement present in the large crystals. As a consequence of the small number of layers the deformation of the anion lattice will be less than in the large crystals. The structure of the particles of type I will have to be described as a stacking of a limited number of trihydroxide layers, which number is too small to cause the deformation necessary for the less symmetric X-ray structure. The type I particles have thus to be considered a preliminary state ("prototype") before the trihydroxides are formed; a distinct modification should not be ascribed to them.

The type II particles are apparently bayerite particles. Their shape is somewhat less conical than that of the somatoids of the bayerite prepared according to SCHMÄH's method. The frequent occurrence of some rows of $0kl$ -reflections besides the $00l$ -reflections shows that the crystal growth is more regular, and, owing to the less conical shape, the cb -plane will sometimes be approximately perpendicular to the incident beam, *i.e.* the a -axis parallel to the beam.

The type III crystals are nordstrandite crystals as appears from the length of the c -axis. The sequence of the intensities of the $00l$ -reflections is as was to be expected for nordstrandite, *viz.* those with l odd extinguished, those with $l = 4n$ strong and those with $l = 4n + 2$ weak. The c -axis is again parallel to the longitudinal direction of the crystals, the trihydroxide layers are perpendicular to it.

It is remarkable that none of the nordstrandite crystals we observed showed other than $0kl$ -reflections. This means that the a -axis always nearly coincides with the incident beam. (The asymmetrical appearance of the diffraction pattern shows that the a -axis will not coincide completely with the incident beam.) So we have to conclude that the crystals in the direction of the a -axis are less developed than in the direction of the other axes. This could be confirmed by shadowing of electron-microscope preparations and by stereoscopic records. The thickness of

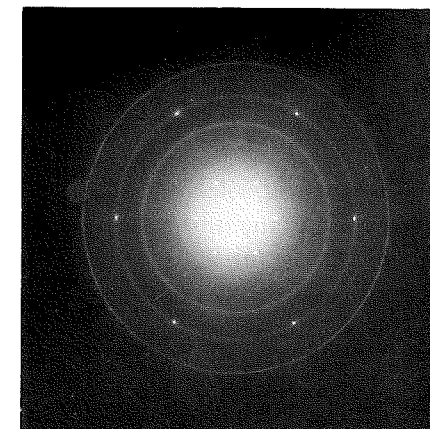


PLATE XVII. Type I particle with microcrystalline boehmite. Diffraction pattern

the crystals appeared to be one half to one sixth of their breadth. Their cross-section was six-sided.

III.4 Summary of Chapter III

By means of selected-area diffraction we were able to ascertain the orientation of the unit-cell axes of the hydroxide crystals. This orientation is very important for the further study of the texture and the surface properties of the aluminas obtained from them.

It could be deduced that the surface of the cleavage plane of boehmite is formed by OH-groups, the dipole of which is *not* perpendicular to the cleavage plane.

The *c*-axis of bayerite appeared to be parallel to the longitudinal direction of the somatoids. As an explanation for some anomalies it was suggested that the shape of the somatoids was determined by systematic lattice faults (probably spiral-dislocation growth); however, other explanations could not be ruled out completely.

In preparations of gelatinous boehmite partially transformed into trihydroxides, three different types of particles occurred that had to be described as trihydroxide particles. The thin plates of type I have to be considered a stacking of a number of trihydroxide layers insufficient to give a distinct trihydroxide modification. Type II particles are bayerite particles, type III are nordstrandite crystals. The *c*-axes of the latter two types are parallel to the longitudinal direction of the particles. Consequently the cleavage plane is perpendicular to this direction.

THE DEHYDRATION PRODUCTS OF THE HYDROXIDES

IV.1 Introduction

In literature a great number of compounds are mentioned which have been given the name of "aluminium oxide", although they often contain a very large amount of other components, such as H_2O and alkali oxides or alkaline earth oxides. To be able to distinguish between all these "aluminium oxides" a great part of the Greek alphabet had to be used, extended with accents and asteriks. Some of these compounds fall outside the scope of this thesis, *e.g.* the alkali or alkaline earth oxide-containing β -aluminium oxides and the compounds obtained as films on aluminium by heating in air or by anodic oxidation. We shall restrict ourselves to those products which can be obtained by dehydration of hydroxides. These compounds will be referred to as "aluminas" in accordance with the term "silica", indicating by this name that these compounds can have a (variable) water content.

We shall make the following classification:

- Low-temperature aluminas: $\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$, in which $0 < n < 0.6$; obtained by dehydrating at temperatures not exceeding 600°C .
- High-temperature aluminas: nearly anhydrous Al_2O_3 ; obtained at temperatures between 900 and 1000°C .

In group a. we shall distinguish the aluminas:

ρ, χ, η, γ

and in group b:

κ, θ, δ .

The stable form of aluminium oxide, $\alpha\text{-Al}_2\text{O}_3$ (corundum), is obtained from all aluminas by prolonged heating at temperatures above 1100°C . The temperatures indicated have only to be regarded as a means of classification and not as existence limits.

Other types of alumina mentioned in literature are sometimes based on a different degree of purity, sometimes on (supposed) differences in the X-ray powder diagrams. For the material of our investigation there was no need to make a further differentiation.

More or less complete surveys of the various aluminas and of their formation are given by STUMPF *et al.* [68], ROOKSBY [69], DAY and HILL [70], RUSSELL *et al.* [71], TERTIAN and PAPÉE [72], whilst other authors restricted themselves to some specific aspects. Much work has been done on the dehydration of gibbsite, which is the starting material for the preparation of aluminium metal. These investigations showed that the transitions to other modifications in most cases occurred in a pseudomorphous * way (THIBON *et al.* [73], STEGGERDA [23, 35], SAALFELD [38]). Also with diaspore ERVIN [51] observed a strict pseudomorphous dehydration. On the possible pseudomorphous dehydration of boehmite and bayerite only one publication [38] is known in literature.

In this chapter the results of our investigations into the crystallographic phenomena occurring during dehydration of bayerite and boehmite are recorded. The dehydration of gibbsite is studied in our research group by OOMES; his results will be published shortly.

IV.2 The dehydration sequences

IV.2.1 Characterisation of the aluminas

The low-temperature aluminas obtained from gibbsite are ρ - and χ -alumina. Besides these, some well-crystallized boehmite can be formed under the influence of intragranular hydrothermal conditions; this boehmite decomposes at a higher temperature with formation of its proper aluminas (see IV.2.2).

ρ -alumina is obtained from gibbsite by heating in a high vacuum. Its X-ray powder pattern shows only a few very diffuse bands, the most pronounced of them having a spacing of about 1.4 Å; it must consequently be regarded as an almost amorphous material.

χ -alumina is obtained from gibbsite by heating in air or nitrogen; its X-ray powder pattern consists of some strongly broadened lines with a diffuse underground. It can be distinguished from the other low-temperature aluminas by a line with a spacing of 2.12 Å.

At a higher temperature ρ -alumina is transformed into η - and θ -alumina, which forms will be discussed further on, whereas χ -alumina gives α -alumina as its high-temperature modification. The latter form gives an X-ray powder pattern clearly distinguishable from the other high-temperature forms. The structure of its unit cell was determined

* By the term "pseudomorphosis" we mean the phenomenon of preserving not only the external shape of the crystals during the transformation of a crystalline compound into another, but also the occurring of a distinct orientation of the axes of the lattice of the newly formed compound with respect to those of the original one.

by SAALFELD [38]; it shows a close relationship to that of the sodium oxide-containing β -Al₂O₃.

During the dehydration of boehmite and bayerite four aluminas are formed, *viz.* γ and η at low temperatures and δ and θ at high temperatures. The γ - and η -type as well as the δ - and θ -type give powder patterns that are very similar. In the literature there exists much confusion in this respect, so it seemed useful to us to indicate the main differences between them. As regards the notation, we have based ourselves on the observations made by TERTIAN and PAPÉE [72], who published, besides a survey of the spacings, the diffractometer records of their samples. Our own observations agree very well with those of these authors; however, especially in the region of small diffraction angles, we found a number of weak reflections, which probably also occurred in their records, but were not mentioned by them.

FIG.13 shows the powder patterns of γ - and η -alumina (diffractometer record, Cu K α -radiation). TABLE IV.1 gives the spacings and the (integrated) intensities. The intensities of the 2.77, 2.40 and 2.28 Å spacings are only approximate, owing to the diffuse character of the pattern in this region. The agreement with published data [72, 74] is very good, except for the 2.77 Å spacing, for which TERTIAN and PAPÉE [72] found 2.80 Å and VAN NORDSTRAND [74] 2.75 Å. In view of the very diffuse character of this line this discrepancy is not surprising. In the last column we give the indices corresponding to a spinel lattice having a (cubic) unit cell with an a -axis of 7.91 Å. From this table it appears

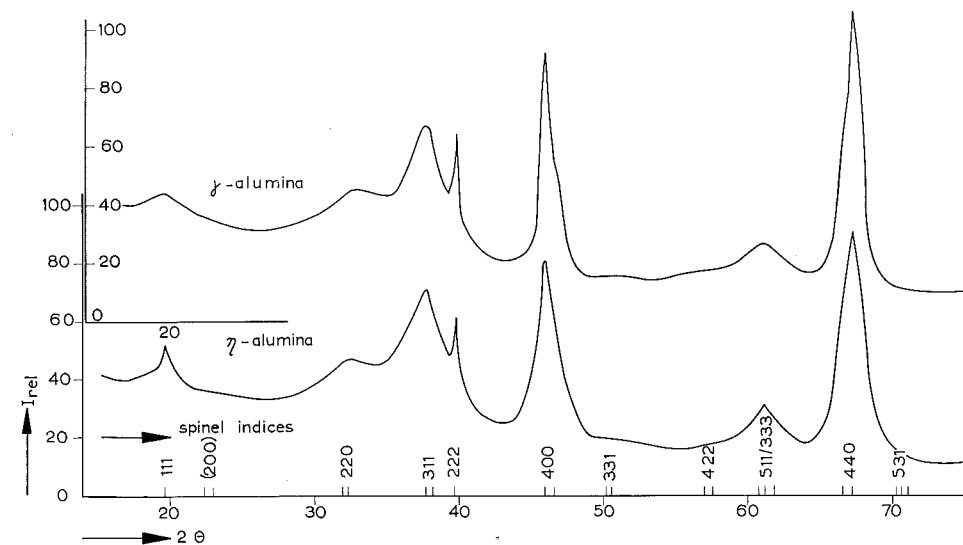


FIG. 13. X-ray powder diagram of η - and γ -alumina (Cu K α -radiation)

TABLE IV.1 X-ray powder-diffraction data of γ - and η -alumina

γ -alumina			η -alumina			
2θ	d	I	2θ	d	I	hkl (spinel)
19.3	4.6	12	19.4	4.57	16	111
32.3	2.77	25	32.4	2.76	33	220
37.49	2.397	60	37.52	2.395	70	311
39.42	2.284	33	39.41	2.284	36	222
45.54	1.990	65	45.80	1.980	70	400
46.38	1.956		—	—	—	—
60.90	1.520	15	60.94	1.519	16	333/511
66.38	1.407	100	66.95	1.396	100	440
67.04	1.395		—	—	—	—

that the two types of alumina are closely related. The principal differences are:

- the 111-reflection of γ -alumina is very diffuse, that of η -alumina is sharp with a broadened base;
- the 400- and the 440-reflection of γ -alumina are clearly doubled, those of η -alumina have only an asymmetrical profile and a broadened base.

The powder diagrams of δ - and θ -alumina consist of a great number of fairly sharp lines; especially δ -alumina gives many weak reflections with large spacings. In TABLE IV.2 the spacings of the two forms are given (later on we shall revert to the indexing of the δ -alumina). The differences between the powder patterns are small, distinction on the basis of intensity differences of some reflections being difficult. A characteristic difference between δ and θ can only be found in the region of spacings of 2.0 Å (in TABLE IV.2 outlined). In FIG. 14 and 15 we have made a comparison of this region as well as of the region of 1.4 Å between η and θ and between γ and δ . The 1.980-spacing of η is split up into two lines with spacings of 2.028 and 1.913 Å for θ , whereas the double line with spacings of 1.990/1.956 Å of γ gives three lines (1.986, 1.953 and 1.914 Å) for δ . It will be clear now that if we are dealing with mixtures of the low- and high-temperature forms or with mixtures of δ and θ , differentiation will be very difficult indeed.

IV.2.2 The dehydration sequence of crystalline boehmite

In the literature no agreement exists concerning the dehydration scheme of crystalline boehmite. It is generally accepted that the first

TABLE IV.2 X-ray powder-diffraction data of δ - and θ -alumina

δ -alumina				θ -alumina		
2θ	d	I	hkl	2θ	d	I
11.6	7.6	2	101	16.20	5.47	5
13.8	6.4	2	102/004	17.50	5.06	3
16.0	5.53	2	111	19.42	4.57	10
17.35	5.10	5	112	22.20	4.00	3
19.40	4.57	8	113	25.48	3.493	5 (α)
21.80	4.07	8	114/105	31.26	2.859	60
24.65	3.61	2	115	32.76	2.731	100
27.60	3.23	2	116	35.06	2.557	10 (α)
29.25	3.05	2	107/214/205	36.46	2.462	80
31.01	2.881	5	117	37.67	2.386	5 (α)
32.80	2.728	20	222	38.88	2.314	40
34.45	2.601	15	302/118	39.78	2.264	30
36.50	2.460	40	312	43.20	2.092	5 (α)
37.40	2.402	10	313	44.64	2.028	80
38.87	2.315	5	314/305	47.50	1.913	40
39.50	2.279	25	226	50.66	1.800	5
41.78	2.160	3	11.10	51.65	1.768	5 (α)
45.64	1.986	50	400	57.04	1.613	5 (α)
46.45	1.953	25	00.12	60.11	1.538	20
47.46	1.914	8	318	62.54	1.484	20
49.87	1.827	3	333	63.88	1.456	20
50.36	1.810	5	319/22.10	65.22	1.429	10
56.47	1.628	5	426/31.11	66.37	1.407	30
57.40	1.604	3	11.14	67.18	1.392	100
60.11	1.538	5	513	68.14	1.375	3 (α)
61.02	1.517	10	339/11.15			
63.88	1.456	5	523/516/20.15			
66.38	1.407	35	440			
66.98	1.396	65	40.12			

The lines indicated by (α) have a varying intensity for different samples; they must be ascribed to small amounts of α - Al_2O_3 . The outlined spacings show the most characteristic differences between the patterns of δ - and θ -alumina.

step will be the formation of γ -alumina,* but for the following steps the opinions diverge rather much. GLEMSER and RIECK [57] state that at about 700 °C γ -alumina is converted into δ , which, at a high temperature, is transformed without an intermediate step into α - Al_2O_3 . GINSBERG *et al.* [75] also observed only the formation of δ -alumina. STUMPF *et al.* [68] are of opinion that δ -alumina will be partly converted into θ -alumina before the transformation to α - Al_2O_3 . TERTIAN

* We shall exclusively use the notation we developed in the preceding section. If necessary the data of other authors are adapted to it.

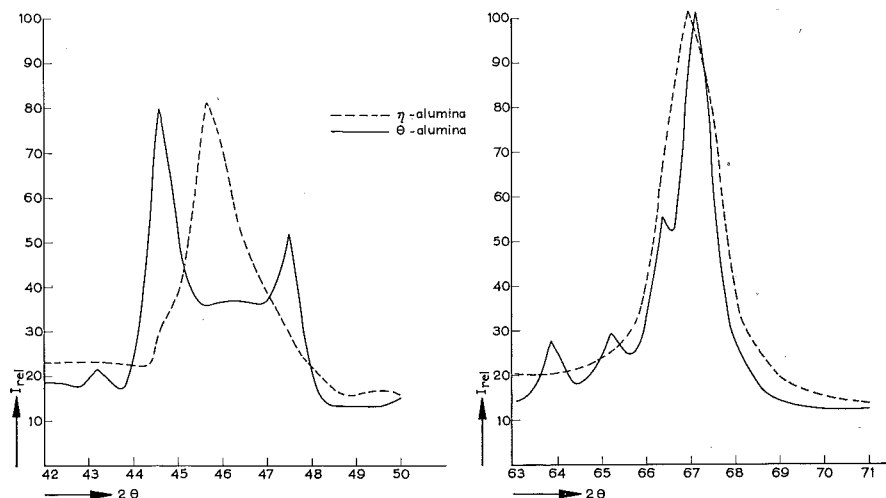


FIG. 14. Detail of the 2.0 and 1.4 Å spacings of η - and θ -alumina

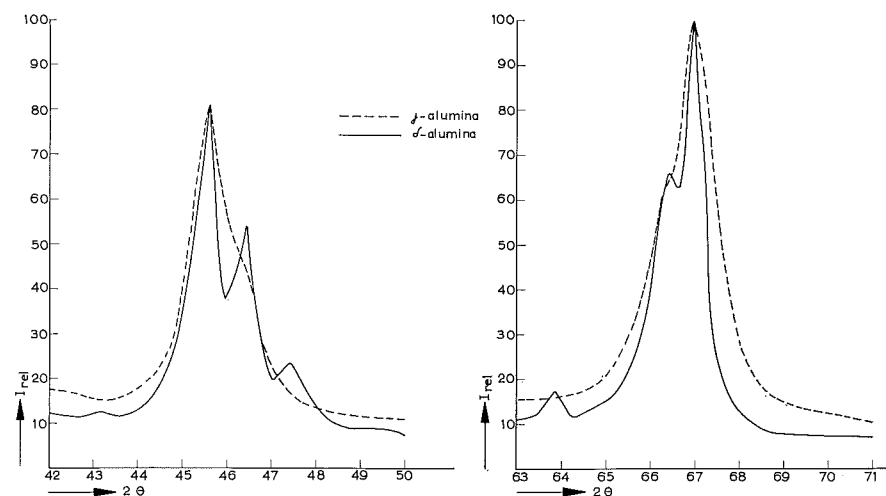


FIG. 15. Detail of the 2.0 and 1.4 Å spacings of γ - and δ -alumina

and PAPÉE [72], on the other hand, mention that θ -alumina will be quantitatively formed from δ -alumina. BIELANSKY [76] is of the same opinion, but he finds that α is formed intermediately between θ and α . Contrary to this, SAALFELD [38] denies the existence of δ -alumina, and states that γ -alumina is changed direct into θ -alumina.

Undoubtedly part of these discrepancies have to be ascribed to an insufficient interpretation of powder diagrams. However, a critical

revision of literature data revealed that at least two possible sequences remained:

1. boehmite $\xrightarrow{450^\circ} \gamma \xrightarrow{750^\circ} \delta \xrightarrow{(900^\circ)} \theta \xrightarrow{1100^\circ} \alpha\text{-Al}_2\text{O}_3$
2. boehmite $\xrightarrow{450^\circ} \gamma \xrightarrow{800^\circ} \theta \xrightarrow{1100^\circ} \alpha\text{-Al}_2\text{O}_3$

Our own observations on various starting materials and heating periods have led to the following results:

- a. The conversion into γ -alumina occurs at a temperature between 350 and 400 °C, depending on the particle size; at 400 °C the decomposition of well-crystallized boehmite still proceeds extremely slowly; after a heating period of six weeks only about 60 % had decomposed. A fast decomposition is obtained at 450 °C: within six hours more than 95 % had decomposed.
- b. By heating γ -alumina obtained from crystalline boehmite, δ -alumina was obtained in all cases and this at a lower temperature according as the boehmite was better crystallized. At a temperature of 650 °C a definite amount of δ could be observed starting from a nicely crystallized boehmite. Complete and fast formation of δ -alumina (within some hours) was obtained only above 800 °C.
- c. Thus obtained δ -alumina remained unchanged during a heating period of six weeks at a temperature of 950 °C, except for an improvement of crystallinity, as appeared from the decrease of the line breadths in the powder diagram.

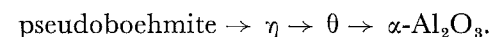
Up to a temperature of 950 °C we could not observe the formation of θ -alumina. We have not tried higher temperatures. Heating over a Meker burner in a platinum crucible to determine the water content of the samples, yielded $\alpha\text{-Al}_2\text{O}_3$. The temperature inside the crucible will have reached about 1150 °C. Of course it is not impossible that between 950 and 1150 °C θ -alumina has formed intermediately.

Though these observations allow us to conclude with certainty that δ -alumina is formed from our samples, it is nevertheless as certain a fact that SAALFELD [38] obtained θ -alumina from his boehmite preparation in the same temperature region. He even succeeded in determining the structure of this θ -alumina. Perhaps there might be an explanation for this discrepancy in the pre-treatment of the different samples. SAALFELD started from large gibbsite single crystals which he heated under hydrothermal conditions. Heating was performed in such a way that the boehmite particles obtained had completely the shape of the original

gibbsite crystals and also showed a strict pseudomorphosis to the gibbsite lattice. Our own préparations, like those of TERTIAN and PAPÉE, were completely recrystallized into their own characteristic crystal shape, having no "reminiscence" of the original gibbsite crystals. It is surely not improbable that in the boehmite crystals of SAALFELD lattice stresses will occur as a consequence of the pseudomorphosis to gibbsite. These stresses will then confer to the γ -alumina obtained from this boehmite a texture deviating from the normal one and somewhat similar to that of the aluminas obtained from the trihydroxides. Differences in texture may have a considerable influence on the limits of existence of the aluminas, as we will also see in the case of gelatinous boehmite.

IV.2.3 The dehydration sequence of gelatinous boehmite

TERTIAN and PAPÉE [72] give for gelatinous boehmite (which they call pseudoboehmite) a dehydration sequence different from that of crystalline boehmite, *viz.*:



The formation of η -alumina and the shift of the 002-reflection of boehmite to lower diffraction angles (CHAPTER II), is for these authors a reason to consider the pseudoboehmite a separate modification. It must be kept in mind, however, that their definition of η - and γ -alumina is based on the doubling of the 400-reflection of γ -alumina. As we have shown, the 400-reflection of η -alumina is also asymmetrical, therefore, the difference between η - and γ -alumina will hardly be visible in the case of appreciable line broadening; erroneous interpretations can easily occur with this criterion.

Our results of the dehydration of gelatinous boehmite can be summarized as follows:

The water content of the sample (previously dried at 120 °C) was determined during a step-wise heating to constant weight at each chosen temperature. It decreases continuously with increasing temperature (FIG. 16) as was already observed by FORTUIN [34] and PAPÉE *et al.* [19]. At about 270 °C the stoichiometric water con-

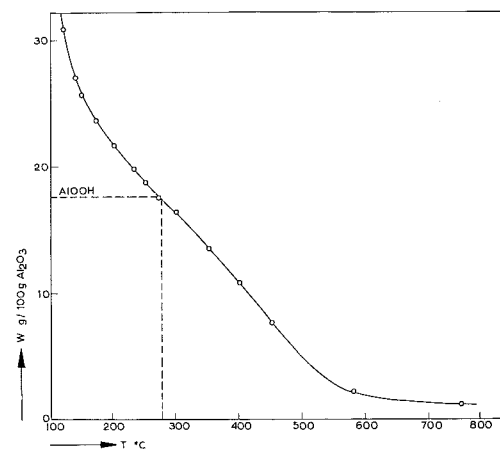


FIG. 16. Dehydration of gelatinous boehmite

tent of 1 mole H_2O per mole Al_2O_3 (17.7 g H_2O /100 g Al_2O_3) is reached. The powder pattern at this temperature is still that of gelatinous boehmite, without a trace of one of the aluminas. At 300 °C, the water content being 16.5 g/100 g Al_2O_3 , bands of γ -alumina were observed besides the bands of gelatinous boehmite. At 400 °C boehmite bands could no longer be detected. The bands of γ -alumina in this sample were so broad that the doubling of the 400- and the 440-reflection could not be observed. However, because in the 111-reflection no sharp peak (characteristic of η) was present we have to regard this form as γ -alumina according to our notation.

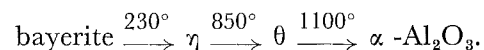
Only after prolonged heating (during a week) at a temperature of 850 °C some lines appeared indicating the formation of δ - or θ -alumina; the diagram was still too diffuse to distinguish between them. After heating for one hour at 980 °C we clearly found δ -alumina. However, after 24 hours at this temperature we got the impression that some θ -alumina had at least partly been formed. Moreover the strongest lines of $\alpha\text{-Al}_2\text{O}_3$ were already present.

For the dehydration of gelatinous boehmite we can therefore conclude that:

- The boehmite lattice remains intact until the stoichiometric water content is approximately reached.
- The dehydration sequence shows the same order as with crystalline boehmite.
- The region of existence of the γ -alumina has widened to higher temperatures, that of δ -alumina has shrunk apparently on both sides. The differences observed with respect to crystalline boehmite will have to be ascribed to differences in texture of the two forms (CHAPTER VII).

IV.2.4 The dehydration sequence of bayerite

The normal dehydration sequence of bayerite as given in the literature [68, 71, 72] can be described as:



Under the influence of intragranular hydrothermal conditions a small part of the bayerite is converted into well-crystallized boehmite [23, 34, 72]. The amount of boehmite formed is far less than in the case of gibbsite samples; for the dehydration scheme it can be neglected.

GLEMSE and RIECK [57] assume the formation of a type of boehmite with a strongly distorted lattice as an intermediate between bayerite and η -alumina. We could not find any indication for this suggestion in

our X-ray records, which, for the rest, confirm the sequence mentioned above.

In high vacuum the first dehydration product is the amorphous ρ -alumina (just as in the case of gibbsite [72]). On heating at a higher temperature this ρ -alumina is converted first into η - and further into θ -alumina. On heating samples by electron bombardment in the high vacuum of the electron microscope we often observed the formation of an amorphous product which is apparently ρ -alumina.

VI.3 The structure of the aluminas

IV.3.1 The structure of γ - and η -alumina

To study the texture of products formed by a pseudomorphous conversion it is necessary to know the structure of the products in question at least to some extent.

The structure of γ -alumina is closely related to that of spinel ($\text{Mg Al}_2\text{O}_4$). The unit cell of spinel is formed by a cubic close stacking of 32 oxygen atoms. The 16 aluminium atoms occupy layerwise half of the octahedral interstices, the 8 magnesium atoms are placed in tetrahedral holes. Consequently, there are 24 cation positions. The spinel can be represented by the formula $\text{Mg}_8 [\text{Al}_{16}] \text{O}_{32}$; the sign [] indicates that the aluminium atoms are placed in octahedral holes.

RINNE [77] showed that γ -alumina and spinel form a series of mixed crystals. According to VERWEY [78] and HÄGG and SÖDERHOLM [79] the unit cell of γ -alumina contains 32 O-atoms and consequently only $21\frac{1}{3}$ Al-atoms. In the cation lattice vacant places must occur. Verwey assumed that these vacant places are distributed over the 24 cation positions with a preference for the octahedral holes.* JAGODZINSKI and SAALFELD [80] found, by Fourier synthesis, that in mixed crystals of spinel and γ -alumina the vacancies occupy exclusively octahedral positions. On the other hand SAALFELD [38] maintains that in γ -alumina obtained from boehmite occupation of tetrahedral holes could hardly occur.

All γ -aluminas contain a varying amount of very strongly bound water. GLEMSEY and RIECK [57] derived from infrared measurements that this water is not present as isolated H_2O -molecules but as OH-groups. According to their measurements at least part of these OH-groups will be present in the lattice; even in some instances a part of the water that is adsorbed in the sample must be built-in in the lattice probably

* The γ' -alumina, obtained by anodic oxidation of aluminium is supposed to have its vacant places distributed at random over all possible cation positions.

as OH-groups. DE BOER and HOUBEN [81, 82] suppose that the composition of the γ -alumina is $5 \text{ Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ or $\text{Al}_8 [\text{H}_4\text{Al}_{12}] \text{O}_{32}$ analogous to the lithium spinel described by KORDES [83] which is represented by $\text{Al}_8 [\text{Li}_4\text{Al}_{12}] \text{O}_{32}$ *. On the other hand FORTUIN [34] and MEIJS [84] determining the relation between the specific surface area and the water content of samples that had been heated and then rehydrated in water vapour could derive that all OH-groups were located at the surface of the γ -alumina.

The doubling of the 400- and the 440-reflection in the powder pattern of γ -alumina clearly indicates that we are dealing with a tetragonally deformed spinel lattice, as was pointed out by VAN NORDSTRAND [74], SAALFELD [85] and BRINDLEY and NAKAHIRA [86]. From our observations we found that the unit-cell constants are:

$$a = b = 7.96 \text{ \AA}, c = 7.82 \text{ \AA}$$

which is in good agreement with the values given by SAALFELD and by BRINDLEY and NAKAHIRA.

η -alumina is often described as a cubic spinel. However the asymmetrical profile of the 400- and the 440-reflections points to a somewhat deformed spinel lattice also for this form.

VAN NORDSTRAND [74] drew the attention to the occurrence of sharp and diffuse lines in the diagrams of γ - and η -alumina. The reflections with indices which after dividing by two still belong to a face-centered lattice, give lines which are sharp. However, he overlooked the 111-reflection of η , which also gives a sharp peak, whereas the tops of the other lines of η are fairly sharp, notwithstanding the appreciable line broadening. VAN NORDSTRAND did not give an explanation for these peculiarities.

Summarizing we can conclude that γ - and η -alumina possess tetragonally deformed spinel lattices. These lattices are strongly disturbed. It may be possible that OH-groups play a roll in the building up of the lattice or the lattice defects.

VI.3.2 The structure of δ -alumina.

The structure of δ -alumina is not described in literature. STUMPF [68] calculated from the powder pattern an orthorhombical lattice with axes of 4.25, 12.75 and 10.21 Å. However, these axes do not show a relation with the certainly existing oxygen arrangement.

The powder diagram of δ -alumina has much resemblance with that

* The lithium spinel of Kordes gives a powder pattern with a number of super-structure lines; so it can not have a simple spinel lattice.

of the lithium spinel of KORDS. For $\gamma\text{-Fe}_2\text{O}_3$, which can also be regarded as a defect spinel, VAN OOSTERHOUT and ROOYMANS [87] found a tetragonal super-structure with the unit-cell dimensions of $a_{\text{tetr}} = a_{\text{cub}}$, and $c_{\text{tetr}} = 3a_{\text{tetr}}$. When we tried to index the powder diagram of δ -alumina assuming the existence of such a super-cell, we obtained a good solution for all reflections, both for our own diagram and for that of TERTIAN and PAPÉE [72]:

own diagram: $a = b = 7.943 \text{ \AA}$, $c = 23.50 \text{ \AA}$, $c/a = 2.958$;

TERTIAN and PAPÉE: $a = b = 7.967 \text{ \AA}$, $c = 23.47 \text{ \AA}$, $c/a = 2.946$.

In TABLE IV.2 the indexing based on this lattice is given. The super-cell contains three spinel cells; consequently an integer number of molecules Al_2O_3 (*viz.* 32). A more or less statistical partition of the vacancies over the available cation positions, as in the case of the spinel lattice of γ - and η -alumina, is not necessary now. VAN OOSTERHOUT and ROOYMANS found for $\gamma\text{-Fe}_2\text{O}_3$ a fourfold screw axis parallel to the c -axis; they assume that the vacancies occupy octahedral positions distributed according to this screw axis. With the aid of selected-area electron diffraction of a sample of δ -alumina prepared by heating well-crystallized boehmite (see IV.4.1) we could confirm the structure given above; moreover, we indeed found a fourfold screw axis parallel to the c -axis. Whether we have to assume that in δ -alumina the vacancies also occupy octahedral positions, could not be ascertained from lack of sufficiently accurate intensity data.

VI.3.3 The structure of θ -alumina

ROY, HILL and OSBORNE [88] observed that θ -alumina and $\beta\text{-Ga}_2\text{O}_3$ are able to form a series of mixed crystals over an extended range of compositions. The powder patterns of the two compounds are very similar, so they are supposed to be isomorphous. KOHN *et al.* [89] described a method to obtain $\beta\text{-Ga}_2\text{O}_3$ in large single crystals. SAALFELD [38] and GELLER [90] used these single crystals to determine the structure of the unit cell of $\beta\text{-Ga}_2\text{O}_3$ with the aid of FOURIER synthesis. With these data SAALFELD could give a satisfactory solution of the structure of θ -alumina.

θ -alumina has a monoclinic lattice with the cell dimensions of:

$a = 11.24 \text{ \AA}$, $b = 5.72 \text{ \AA}$, $c = 11.74 \text{ \AA}$, $\beta = 103^\circ 20'$.

It is built up from the somewhat deformed oxygen lattice of spinel with the aluminium atoms divided over the available octahedral and

tetrahedral positions. In contrast with the spinel lattice, the Al-atoms preferentially occupy tetrahedral positions. θ -alumina has to be considered a transition phase between the spinel lattice with a cubic oxygen arrangement and aluminium atoms in octahedral and tetrahedral positions and the corundum lattice with a hexagonal oxygen arrangement and aluminium atoms exclusively in octahedral positions. Apparently Al-atoms in tetrahedral holes promote the reorientation of the oxygen lattice. In this line of thought the formation of θ -alumina as an intermediate between δ -alumina and corundum, as is assumed by various authors, is quite probable, although we could not observe it with certainty.

IV.4 Pseudomorphosis during dehydration of bayerite and boehmite

IV.4.1 Phenomenology

When trihydroxide particles are heated by electron bombardment in the electron microscope, usually ρ -alumina (amorphous) is obtained as a result of the heat and the high vacuum. Sometimes, however, under obviously favourable (hitherto unknown) conditions we observed the formation of spinel-type alumina, as followed from the changes of the selected-area diffraction records. Almost identical diffraction patterns were observed in samples, which were heated in air, and which consisted of η -alumina. Consequently, we could make use of the results of the heating in the electron microscope for establishing the axes orientations of these samples.

In the case of well-crystallized boehmite it was not possible to heat the samples in the electron microscope to a sufficiently high temperature; no noticeable dehydration occurred. For these samples it was necessary to heat in air. In this case this is less important, however, as for the characteristic rhombus-shaped crystals the establishment of the axes orientations is greatly simplified.

Reorientation of the dehydrating trihydroxide lattice on heating in the electron microscope occurs very rapidly. Within one or two seconds after observation of the first changes of the diffraction pattern (*viz.* a change in the intensity of certain reflections, or the appearance of new ones) the complete lattice appeared to have changed into that of alumina.

PLATE XVIII gives the pattern of a heated type I particle (the prototype of the trihydroxides, see III.2.3). In FIG. 17 we indexed a part of this diagram. The reflections appear to originate from the planes of the [111]-zone of the spinel. Each strong reflection (which has indices

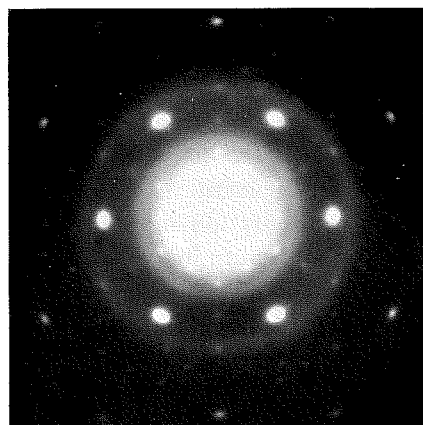


PLATE XVIII. Diffraction pattern of heated type I particle

divisible by 4) is surrounded by 12 weak to very weak ones situated in a hexagon. The reflections at the corners of these hexagons are so-called abnormal reflections, having indices which are not integers. Such reflections are observed more often in electron-diffraction patterns; they originate from certain lattice defects.

If we compare PLATE XVIII with PLATE XII of the non-heated material, it appears that the $[001]$ -zone of the trihydroxide is transformed into the $[111]$ -zone of the spinel. The a -axis of the trihydroxide coincides with the $[01\bar{1}]$ -direction of the spinel, the b -axis of the trihydroxide with the $[\bar{2}11]$ -direction (TABLE IV.3). From the measured values of D (equation III.6) in the $[01\bar{1}]$ - and in the $[\bar{2}11]$ -direction we could calculate the ratio of the c - and the a -axis of the spinel. For the various records of heated type I particles we found values between 0.985 and 0.993. Obviously, therefore, the spinel obtained from this type of hydroxide is tetragonal.

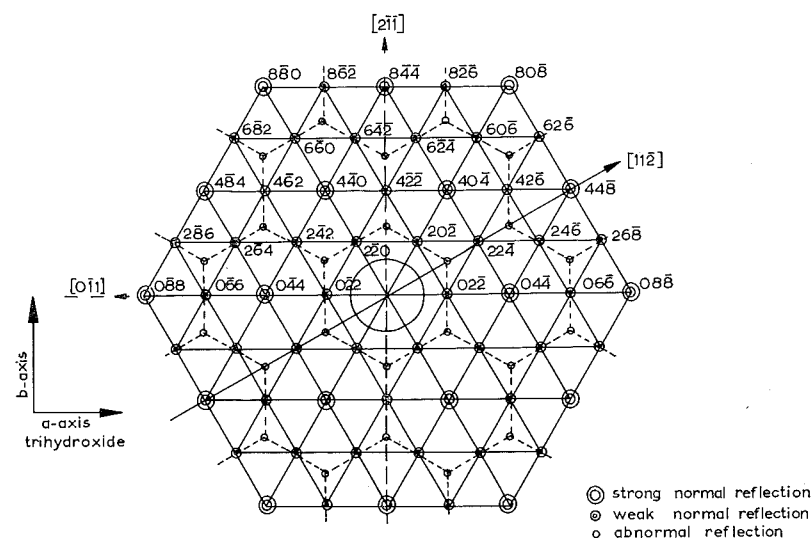


FIG. 17. Indices of diffraction pattern of heated type I particle (PLATE XVIII)

TABLE IV.3 Pseudomorphosis relations of the trihydroxides and η -alumina

trihydroxide			spinel		$\frac{\Delta l}{l}$
axis	type I	type II	axis	d	
a	$8.66 = 3 \times 2.89$	(8.67)	$[01\bar{1}]$	$5.58 = 2 \times 2.79$	-3.3 %
b	$5.00 = 3/2 \times 3.33$	5.00	$[\bar{2}11]$	3.24	-2.9 %
c	—	4.72	$[111]$	4.57	-52 % *

* Calculating the change of the lattice dimension in this direction (perpendicular to the cleavage plane) we have accounted for the loss of OH-groups during the dehydration.

PLATE XIX and XX show the results for a type II particle (bayerite, see III.2.3) before and after heating. The bayerite particle gives, besides the row of spots through the centre corresponding to the $00l$ -reflections, also rows of spots arising from $02l$ - and $06l$ -reflections. Consequently the b - and the c -axis of the bayerite are lying approximately parallel to the supporting film, the a -axis parallel to the incident beam. The reflections are those of the $[100]$ -zone of bayerite.

In FIG.18 we give the indexing of the diagram of the heated particle. The reflections observed belong to the $[01\bar{1}]$ -zone of the spinel. Abnormal reflections were not found. The pseudomorphosis relations for this type of particles appear to be the same as those for type I particles (TABLE IV.3).

SAALFELD [39] dehydrated gibbsite single crystals in vacuum via the

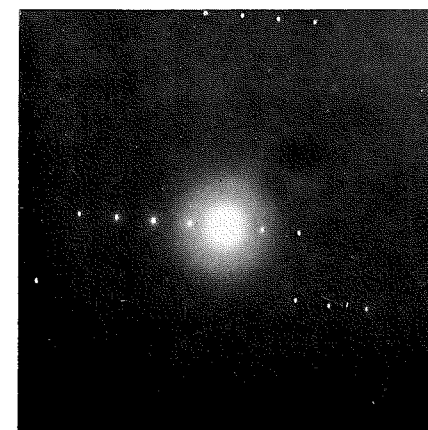


PLATE XIX. Diffraction pattern of type II particle before heating

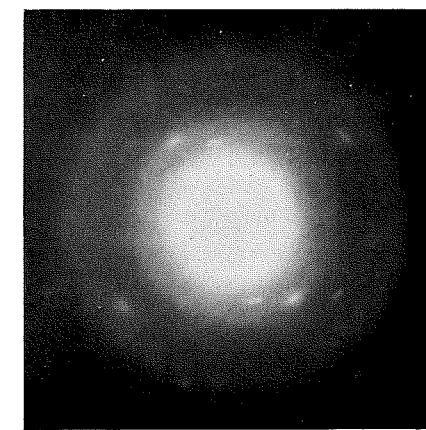


PLATE XX. Diffraction pattern of XIX after heating

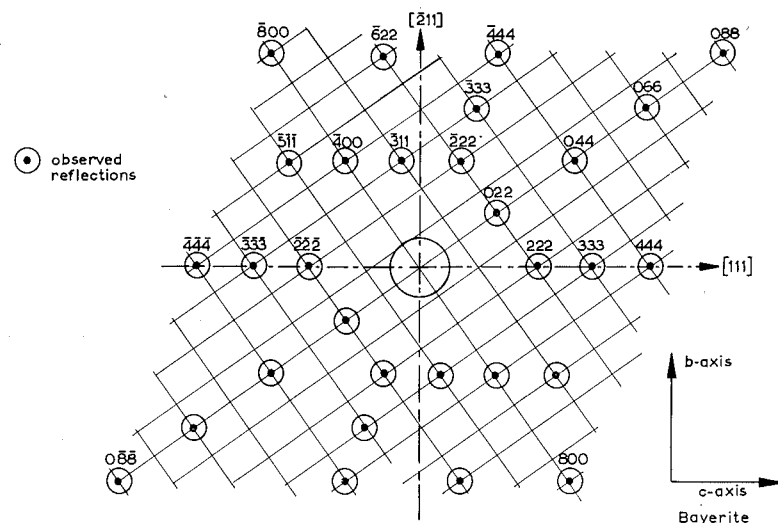


FIG. 18. Indices of diffraction pattern of heated bayerite (PLATE XX)

amorphous ρ -alumina to η -alumina. The pseudomorphosis relations in this case are also the same as we observed for the trihydroxides.

The spinel lattice of heated type II (bayerite) particles is also tetragonal; the ratio of the c - and the a -axis was found to be between 0.985 and 0.990.

PLATE VIII, XXI and XXII give the results of the heating of well-crystallized boehmite. PLATE VIII shows that the a - and the b -axis of the boehmite lattice are lying parallel to the supporting film; the c -axis is then perpendicular to it and parallel to the incident beam (see CHAPTER III). On heating at a temperature of 500 °C the pattern of γ -alumina is obtained (PLATE XXI). It is indexed in FIG.19; the reflections belong to the $[1\bar{1}0]$ -zone of the spinel lattice.

The pseudomorphosis relations are given in TABLE IV.4. These relations are the same as those observed by SAALFELD [38] on boehmite crystals obtained by pseudomorphous hydrothermal conversion from gibbsite single crystals and analogous to those stated by VAN OOSTERHOUT [53] for the transformation of lepidocrocite (γ -FeOOH) into γ -Fe₂O₃.

The γ -alumina again possesses a tetragonal lattice with $c/a = 0.983$ to 0.987.

On heating of the boehmite sample at a temperature of 950 °C, when δ -alumina is formed, a diffraction pattern is obtained as shown in PLATE XXII. The strong recrystallization clearly appears from the sharpening

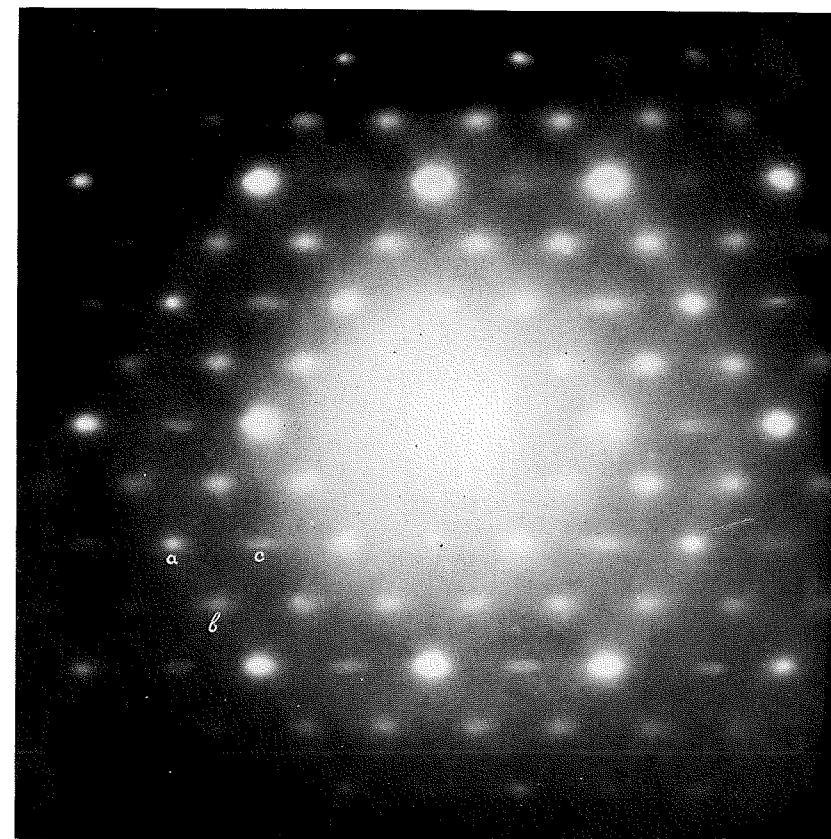


PLATE XXI. Diffraction pattern of γ -alumina from a boehmite single crystal

TABLE IV.4 Pseudomorphosis relations of boehmite and γ -alumina

boehmite		spinel		$\frac{\Delta l}{l}$
axis	d	axis	d	
a	2.85	$[110]$	$5.63 = 2 \times 2.81$	-1.2 %
b	3.69	$[001]$	$7.82 = 2 \times 3.91$	+6.0 %
c	12.24	$[1\bar{1}0]$	5.63	-31 % *

* Calculating the change of the lattice dimension in this direction (perpendicular to the cleavage plane) we have accounted for the loss of OH-groups during the dehydration.

of the diffraction spots. FIG. 20 gives the indexed diagram. The long c -axis (three times the c -axis of the spinel) finds expression in the numerous hhl -reflections with odd h . The fourfold screw axis follows from the

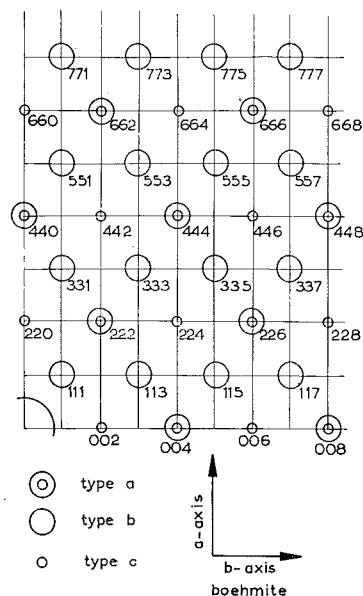


FIG. 19. Indices of diffraction pattern of γ -alumina from well-crystallized boehmite (PLATE XXI)

absence of $00l$ -reflections with $l \neq 4n$. The weak continuous lines in the pattern (indicated in FIG. 20 by thicker lines) show that a perfect ordering of the lattice is not yet completely achieved. The orientation of the axes has not changed with regard to those of the γ -alumina spinel.

The question now arises whether for gelatinous boehmite the same pseudomorphosis relations will hold as given above. The sheet-like structure of the gelatinous boehmite is maintained up to high temperatures. Recrystallization of the γ -alumina formed from gelatinous boehmite on heating will only occur at a much higher temperature than that obtained from well-crystallized boehmite. The sheet-like structure is not suited for texture investigations with electron diffraction; only equally blackened rings are observed. In low- and high-angle X-ray scattering studies FRICKE and EBERSPÄCHER [91] found that the γ -alumina crystallites probably have a certain orientation with regard to each other. As their starting materials are not properly defined, no further conclusions can be drawn. From lack of other data and as long as the reverse has not been proved we shall assume that a similar pseudomorphosis will occur as in the case of well-crystallized boehmite.

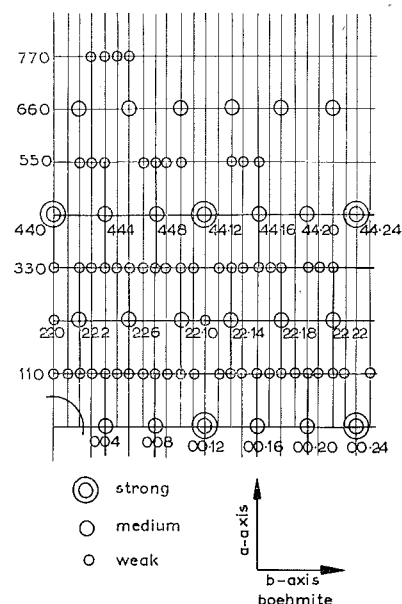


FIG. 20. Indices of diffraction pattern of δ -alumina from well-crystallized boehmite (PLATE XXII)

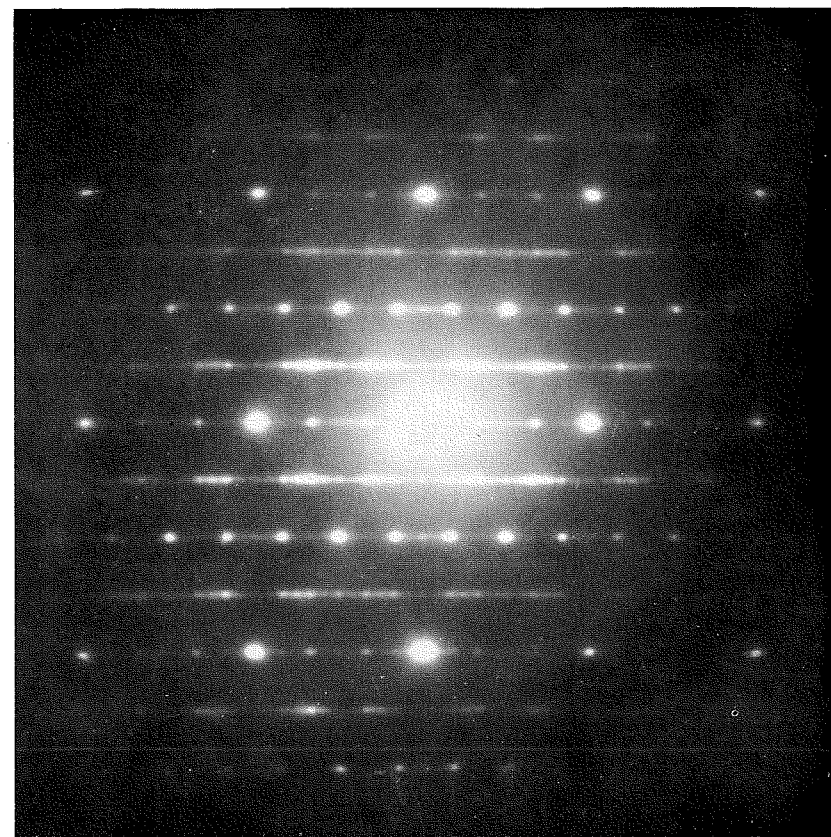


PLATE XXII. Diffraction pattern of δ -alumina from a boehmite single crystal

IV.4.2 The crystallographic texture of η -alumina

In the diffraction patterns of heated type I particles we noticed a number of reflections which could only be indexed with fractional numbers instead of integers, e.g. $\frac{4}{3} \frac{4}{3} \frac{-8}{3}$. For the rest these reflections can be distinguished from the others neither in appearance, nor in intensity. In the powder diagrams they do not occur; only a more pronounced diffuse underground can be observed. These reflections can be explained by assuming a suitable extension of the reciprocal lattice "points". FIG. 21 gives the cross-section through the reciprocal lattice of the spinel perpendicular to the $[1\bar{1}0]$ -direction. The $[111]$ -axis is placed parallel to the incident beam, as it was during the recording. It now appears that the abnormal reflections are lying on the connecting line between two neighbouring points as $11\bar{3}$ and $22\bar{2}$ for the $\frac{4}{3} \frac{4}{3} \frac{-8}{3}$ -reflection.

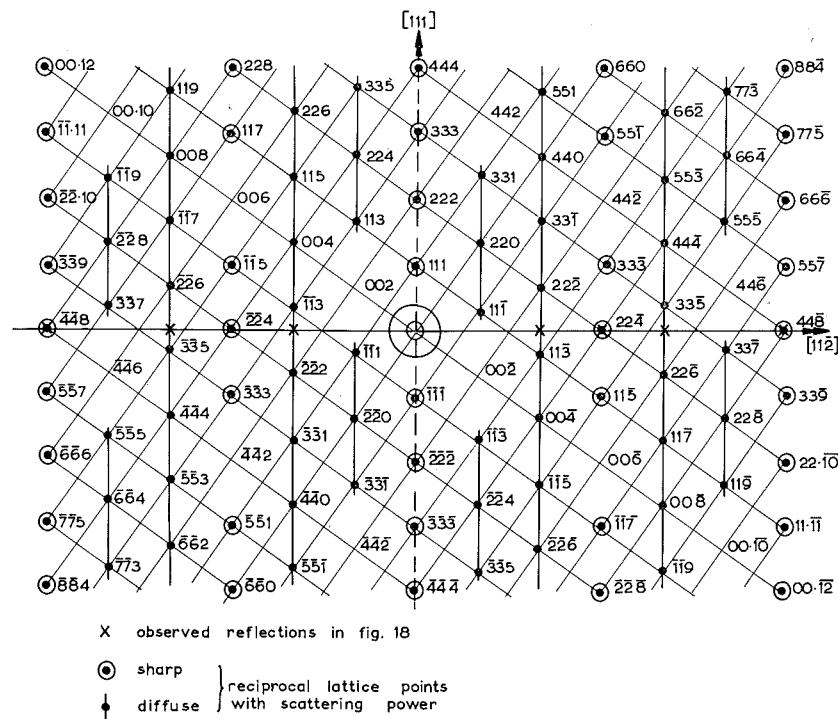


FIG. 21. Cross-section through the reciprocal lattice of η -alumina perpendicular to $[1\bar{1}0]$

The abnormal reflections are caused by certain lattice defects. The trihydroxide lattice itself is fairly regular, the reflections are sharp and abnormal reflections do not occur. During the transformation into η -alumina nearly half of the total number of oxygen atoms will have to disappear as H_2O -molecules. This implies an almost complete breaking down and rebuilding of the oxygen lattice. These transformations will occur via the cleavage plane (001)-plane of the trihydroxide, which then becomes the (111) -plane of the spinel. The originally hexagonal oxygen arrangement (layer sequence ABABABAB) is converted into the cubic arrangement ABCABCABC. The energy difference between the hexagonal and the cubic arrangement, which for the trihydroxides is large owing to the hydrogen bridges, will become small when the greater part of the hydrogen bridges have disappeared. Now deviations from the regular arrangement can occur as ABCACABABCBC. JAGODZINSKI and LAVES [92], COWLEY and REES [93] and others have shown that in these cases the scattering power in the reciprocal lattice cannot be represented any more by points. If we describe the oxygen lattice on the hexagonal axes a and b (FIG. 22) putting the c -axis perpendicular to

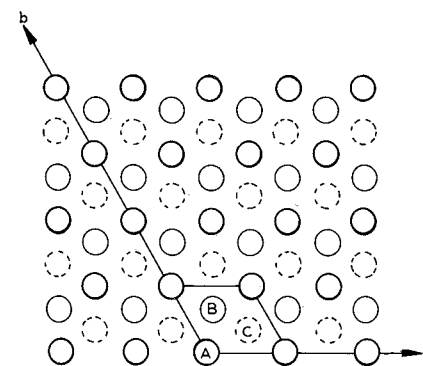


FIG. 22. Possible stacking arrangements of planes of close-packed atoms

the plane of the drawing, the lengths of the a - and the b -axis are equal to the O-O distance. The possible arrangements are indicated by A, B and C. If the stacking is completely at random, it can be derived that only for those reflections for which $h-k = 3n$ there will be a sharp maximum of scattering power. For $h-k \neq 3n$ the rows of spots parallel to the (reciprocal) c^* -axis having the same h - and k -indices are replaced by continuous lines of scattering power. If the degree of randomness is smaller these continuous lines also occur, but with a correspondingly different distribution of scattering power along their lengths. If we transform the condition for sharp reflections $h-k = 3n$ from the hexagonal lattice to the cubic lattice we obtain: $h-2k+l = 3n$. For the oxygen lattice of the spinel, which is twofold in all three directions, this becomes $h-2k+l = 6n$.

Besides the oxygen lattice also the aluminium lattice must be taken into consideration. HOUBEN [82] showed that there are two types of cation partitions present in the spinel lattice parallel to the (111) -plane (FIG. 23), an A- and a B-layer. The B-layer contains for each 32 O-atoms 24 cation positions, all in octahedral interstices; the A-layer also contains 24 cation positions, but 8 in octahedral and 16 in tetrahedral interstices. If we compare this with the structure of the trihydroxide layers, we need for each layer of 32 O-atoms of the spinel 64 O-atoms in two trihydroxide layers (half of the oxygen atoms disappears as water). These 64 O-atoms correspond to $21\frac{1}{3}$ Al-atoms, which have to be divided over the 24 cation positions in each spinel layer (in the concept of HOUBEN's hydrogen spinel for each layer 20 Al-atoms are needed, the remaining 4 cation positions will be occupied by H-atoms). It is to be expected that the Al-atoms will follow the faults in the stacking of the oxygen lattice, giving rise to similar phenomena. As, however, the Al-arrangement proceeds over two different layers the condition for sharp reflections will then be $h-2k+l = 3n$.

The occurrence of continuous lines was demonstrated by COWLEY [94]. This author obtained polycrystalline material from the oxidation of aluminium foil. In an oriented specimen of this material (indicated as γ -alumina) electron-diffraction records with the incident beam parallel

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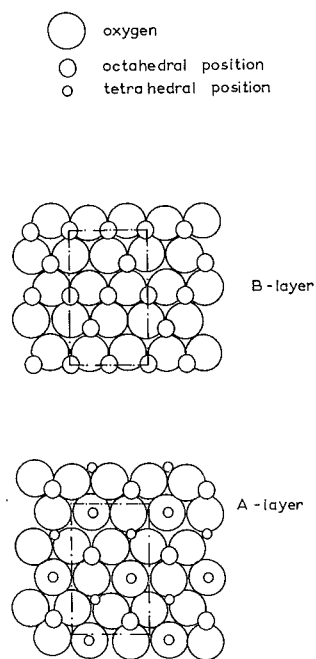


FIG. 23. Cation positions in the spinel lattice; oxygen layers parallel to (111)-planes

be a small variation in the orientation of the axes with respect to the incident beam. This will probably be caused by a strong mosaic character in the layers of the oxygen- and aluminium-arrangement.

IV.3.4 The crystallographic texture of γ -alumina

The appearance of the electron-diffraction patterns of γ -alumina obtained from well-crystallized boehmite differs considerably from those of η -alumina from the trihydroxides. PLATE XXI gives the $[1\bar{1}0]$ -zone, in which we can distinguish three types of reflections, viz.:

- type a: with sharp maximum and broadened base; these are reflections of which the indices, after division by two, still belong to a face-centered lattice.
- type b: reflections without sharp maximum, length about twice the breadth*; they are all reflections with odd indices.

to $[1\bar{1}0]$ show some reciprocal-lattice lines parallel to the $[111]$ -directions.

FIG. 21 represents some continuous lines in the reciprocal lattice, which can sufficiently explain the abnormal reflections. Some reciprocal-lattice points have no scattering power as can be calculated from the structure factor (*e.g.* the 002- and the 006-reflection). In the neighbourhood of such points the continuous lines will also have only a very low scattering power. Abnormal reflections corresponding to parts of the continuous lines with very low scattering power (*e.g.* $\frac{2}{3} \frac{2}{3} -\frac{4}{3}$) are apparently so weak that they escape observation.

PLATE XX shows no reciprocal lattice lines. We are dealing here with the $[01\bar{1}]$ -zone of the spinel. Parallel to the $[111]$ -direction reciprocal-lattice lines should be present (FIG. 18), but probably owing to the very weak and diffuse character of this pattern these lines cannot be observed.

The shape of the spots in PLATE XVIII and in PLATE XX indicates that there must

type c: reflections without sharp maximum, length more than three times the breadth; these reflections have even indices which, upon division by two, do not belong any more to a face-centered lattice.

The type a reflections originate from the oxygen lattice and from the cation lattice together, the type b reflections from the total cation lattice, the contribution from the oxygen lattice being negligible. Finally, the type c reflections originate only from the cations in tetrahedral positions, the contributions from the oxygen lattice and the cations in octahedral positions being negligible.

If we consider the possible mechanism of the dehydration of boehmite we notice that only half of the oxygen layers are included in the dehydration (unlike the dehydration of the trihydroxides, where all oxygen layers contribute). Only the layers formed by the OH-groups are broken down, the oxygen layers remaining two and two intact. These latter layers form the skeleton on which the spinel lattice will be rebuilt.

In the orientation which the spinel lattice takes in by pseudomorphosis we find, just as with the η -alumina from the trihydroxides, two oxygen layers with a different cation occupation (C and D, FIG. 24). The stacking of these layers on each other is, apart from the cation arrangement, only possible in one way, viz. CDCD *etc.* Consequently, the oxygen lattice of γ -alumina from boehmite will have a much better ordering than that of η -alumina from the trihydroxides. In agreement with this all reflections in which the oxygen lattice plays an important role are of type a.

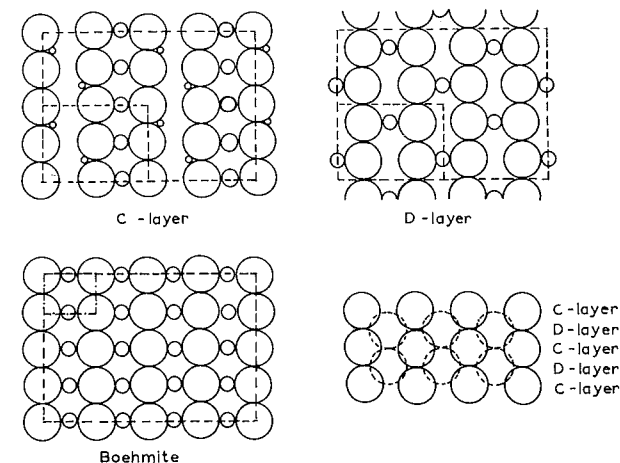


FIG. 24. Cation positions in the spinel lattice; oxygen layers parallel to (110)-planes

* length and breadth here indicate the size at half maximum intensity.

Let us compare the aluminium lattice of boehmite with that of the spinel. FIG. 24 shows the situation of the Al-atoms in an oxygen layer of boehmite. Of all rows of aluminium atoms in the boehmite layer (all in octahedral position) only $\frac{1}{4}$ is taken over by the spinel lattice. The other $\frac{3}{4}$ of the Al-atoms will have to be distributed over the octahedral and tetrahedral positions that are left. Which of the Al-rows of the boehmite remains, depends on chance. Displacements of Al-atoms in the [110]-direction will be easier than in the [001]-direction, as in this latter case coherent oxygen chains will have to be passed. Consequently a greater irregularity in the succession of the aluminium lattice is to be expected in the [001]-direction than in the [110]-direction. In the reciprocal lattice this will result in the scattering power being more extended in the reciprocal [001]-direction than in the [110]-direction. This is confirmed in the diffraction pattern.

The vacant cation sites (or the H-atoms in the hydrogen-spinel concept) will occur in the disturbed rows. Whether these vacant sites will occur in octahedral or in tetrahedral positions, the greatest disorder is to be expected for the atoms in tetrahedral position. Those reflections which mainly originate from the tetrahedral lattice will possess the strongest diffuse character. They all (the 220-, 660-, 224-, 664-reflection *e.g.*) belong to type c. The disorder of the tetrahedral lattice makes it also probable that its fourfold screw axis can disappear. This will explain why such reflections as 002 and 006 may occur, which are forbidden in the spinel pattern and which also belong to type c.

IV.4.4 Comparison of the results of X-ray and electron diffraction

The results of the electron diffraction of the aluminas entirely agree with those of X-ray diffraction (FIG. 13). A broadening of a reciprocal-lattice point corresponds to a line broadening in the powder diagram, with a decrease of the intensity maximum. Line broadening, especially at the base, is a common phenomenon in the X-ray diagrams of the aluminas.

For γ -alumina the reflections to whose intensity the oxygen lattice contributes to a large degree, are sharp (compare type a) all other reflections are broad. Especially the 220-reflection is very diffuse (type c).

The reflections of η -alumina often have a fairly sharp top and always a strongly broadened base. Only part of the coinciding reflections satisfies the condition for sharp reflections $h-2k+l=3n$. This is clear especially in the case of the 111-reflection, which is characteristic of η -alumina. The intensity of the sharp portion of this line is about one fourth of the total intensity, which is in agreement with the coincidence

of the four 111-reflections of which only one is sharp. It must be noticed that also in this case the 220-reflection is more diffuse than the other reflections; apparently the tetrahedral positions of η -alumina are also very irregularly occupied.

The tetragonal character of η -alumina is weaker than that of γ -alumina. If we compare the changes of the lengths of the axes of the hydroxides during the transformation to the aluminas ($\frac{\Delta l}{l}$, TABLE IV.3 and IV.4) we observe a great difference between the two types of alumina. In the two main directions parallel to the cleavage plane the lattice shrinkage during the conversion of bayerite into η -alumina is almost equal and about 3 %. During the dehydration of boehmite to γ -alumina the changes of the axes in the directions parallel to the cleavage plane can be strongly different. In the direction of the *a*-axis of boehmite there is a small shrinkage of about 1 %; however, perpendicular to it in the direction of the *b*-axis the lattice will have to expand. This strong anisotropy of the shrinkage will apparently be the cause of the more pronounced tetragonal character of the γ -alumina lattice.

IV.5 Summary of chapter IV

The dehydration sequences of bayerite and boehmite were investigated again by means of a detailed X-ray characterisation of the aluminas. The literature data about the bayerite sequence were confirmed. For boehmite it was found that the temperature region of the existence of γ - and δ -alumina strongly depends on the crystallinity and the texture of the starting materials.

The pseudomorphosis relations between bayerite or well-crystallized boehmite and their dehydration products could be established by means of selected-area electron diffraction. It could be demonstrated that both η - and γ -alumina possess a somewhat deformed and strongly disordered spinel lattice. From details in the selected-area electron-diffraction patterns the nature of the disturbances could be established. During the dehydration of bayerite the oxygen lattice is entirely broken down; during re-building faults in the cubic stacking sequence of the oxygen layers are formed in one direction, *viz.* the [111]-direction of the spinel (corresponding with the [001]-direction of the trihydroxide).

In the case of γ -alumina half of the oxygen lattice of the boehmite remains intact. From the pseudomorphosis relations it appears that the oxygen lattice can have only a low degree of disorder. Here, the lattice faults are caused mainly by reorientation of the aluminium lattice which

is difficult especially in the [001]-direction, owing to the presence of coherent oxygen chains perpendicular to it.

The most important features of the structure of δ -alumina could be derived. It is probably isomorphous to γ - Fe_2O_3 . The unit cell contains a fourfold screw axis in the long direction. This screw axis originates from the ordering of the necessary vacant cation positions.

EVOLUTION OF THE SURFACE AREA DURING DEHYDRATION OF THE ALUMINIUM HYDROXIDES

V.1 Introduction

In the general introduction it was stated that besides the crystallographic structure and texture also the porous texture comprising the magnitude of the surface area and its accessibility determines the practical suitability of a catalyst. In this chapter we shall deal especially with the magnitude of the surface area; the accessibility will be the subject of the next chapter.

The *crystalline* hydroxides have only a small specific surface area (defined as the total accessible inner and outer surface area per unit weight of material); that they are nevertheless of importance as a starting material for the preparation of catalysts is due to the fact that their specific surface areas increase considerably upon heating. This is because dehydration, while giving rise to pseudomorphosis, does not change the volume of the particles very much. As water is expelled, space will be created *in* the particle, which so becomes porous. If the internal surface area corresponding with the internal space is accessible to molecules from the outside, the total specific surface area of the particle increases. This internal surface area is only meta-stable; on heating the material is reoriented in such a way that the surface area decreases again.

The *gelatinous* hydroxides often have a very large specific surface area, which also changes on dehydration by heating.

For the determination of the specific surface area various methods have been described in literature. Most of these are based on the adsorption of certain substances on the surface, the specific surface area being calculated either direct from the amount of substance adsorbed, or indirect from the heat of adsorption liberated. As the measurement of the heat of adsorption gives results which are often difficult to correlate with the specific surface area, we have limited ourselves to measuring the amount of substance adsorbed.

The method generally applied at present is the adsorption of inert gases, such as nitrogen, argon or krypton at low temperatures (*e.g.* the boiling point of nitrogen or oxygen). To calculate the specific surface area from the amount of gas adsorbed the method developed by BRU-

NAUER, EMMETT and TELLER [95] is generally used. We applied this method for our surface-area determinations. As an adsorbate (the substance being adsorbed) we used gaseous nitrogen which gives the most reliable results of all gases. On the other hand we also used the adsorption of lauric acid from pentane solutions. This method was developed by HOUBEN [82] for aluminium oxide; FORTUIN [34] obtained some remarkable results with it.

V.2 Surface-area determination by means of nitrogen adsorption

V.2.1 The adsorption apparatus

The nitrogen adsorption can be evaluated by measuring either the weight or the volume of the nitrogen adsorbed. Since the weighing method requires a rather expensive vacuum balance, whereas the volume method can be performed in a glass apparatus without any special requirements, we preferred the latter. A great number of techniques has been described in literature, a comprehensive survey being given by JOY [96].

For the choice of our apparatus we were guided by the following considerations:

- An important factor influencing the rate at which equilibrium is reached, is the removal of the heat of adsorption or the supply of the heat of desorption.
- The establishment of the equilibrium must be clearly indicated.
- In order to be able to check for leakages, the total amount of nitrogen adsorbed must be recovered quantitatively on desorption.
- The changes in the temperature of the liquid nitrogen must be measured continuously.
- To avoid supervision overnight it must be possible to interrupt the measurements at certain points.

As the apparatus should also be suited for determining complete adsorption/desorption isotherms, the adsorption and desorption will have to be performed slowly and in small steps, in order to prevent the appearance of "scanning" of the hysteresis loop in the irreversible part of the isotherm (see CHAPTER VI).

None of the apparatuses described in literature fulfils all these requirements. We therefore designed a new one which is schematized in FIG. 25.

The gas burette A has a volume of 100 ml and is divided in tenths of a millilitre. It was calibrated by weighing with mercury; an accuracy of 0.01 ml was obtained. The mercury pump B, which is operated by

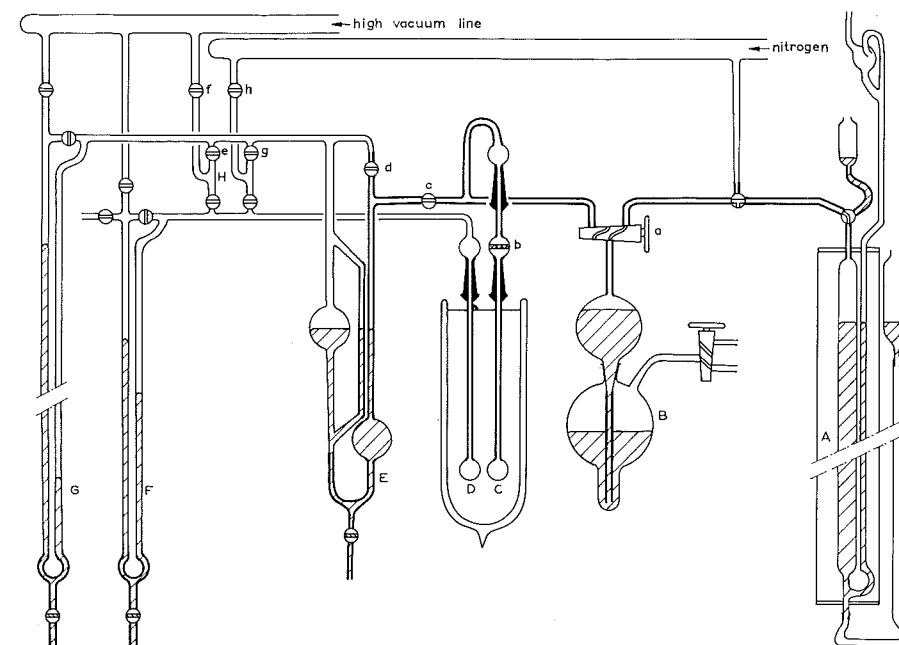


FIG. 25. Schematic representation of the apparatus for measuring nitrogen adsorption isotherms

means of the pressure in the lower bulb, quantitatively transports the gas at the desired rate from burette A to the adsorption tube C (and vice versa); a very accurate construction of the cock a is essential to prevent leakage. The adsorption tube C (volume of the sample bulb ca. 1 ml) is provided with a sintered glass plate b which prevents finely divided samples from being blown through the whole apparatus by a wrong manipulation. To keep the dead space as small as possible the part of C not immersed in the liquid-nitrogen bath is made from capillary tubes with a diameter of 3 mm. The capillary differential manometer E serves to keep the volume of the dead space as constant as possible; both legs should be made from the same precision capillary tube. With the aid of the pressure and vacuum locks H the pressure in the left-hand part of the manometer E is made equal to that in the adsorption tube C; the manometer G shows the pressure left of E.

Any temperature changes of the liquid-nitrogen bath are observed with the manometer F, connected with tube D in which some purified nitrogen is condensed. High vacuum is obtained with an oil pump and a mercury-diffusion pump; the pressure is measured with a McLEOD gauge.

Nitrogen gas, which is used as the adsorbate, should be of high purity; traces of oxygen are removed by passing it over a de-oxidizing catalyst (B.T.S.-catalyst of B.A.S.F.). Non-condensable gases such as hydrogen are removed by condensation and boiling. After distillation very pure nitrogen is obtained which is used for filling the gas burette and tube D. Using this purified nitrogen in the pressure lock between E and G is not essential; it is done for manipulative reasons.

V.2.2 Procedure

To calibrate the dead space of C cocks c, d, e and f are opened, which establishes a connection between C and the high vacuum line. When the pressure is below 10^{-4} mm mercury and the apparatus is checked for leakages, cocks d, e and f are closed. The dewar flask is filled with liquid nitrogen and placed under C.

Gas burette A is filled in the mean time with purified nitrogen. With the aid of mercury pump B a certain volume of nitrogen is transported from A to C. As the pressure in C increases the mercury level in the right-hand part of E is lowered. Via cocks g and h the pressure at the other side of E is increased till the levels in the two legs of E are about equal (there would be little sense in making the pressures over both legs exactly equal; the time required for manipulation would not balance the few additional calculations to be made).

If the pressure read on G is equal to p_G mm mercury and the difference between the mercury levels of E is equal to p_E mm (positive if the level is higher on the right-hand side than on the left-hand side), the pressure in C is equal to:

$$p = p_G - p_E \quad \dots \dots \dots (V.1)$$

We define the dead space V_a as the volume of nitrogen (in ml STP), which, under measuring conditions (room temperature 20°C , temperature of the liquid nitrogen 78°K , level of the liquid nitrogen in the dewar flask at a fixed mark on tube D) and at an indicated reference level of the mercury in the right-hand leg of E, would give a pressure of 1000 mm mercury in the empty sample tube C (as a reference level we chose the reading at which the mercury in both legs has the same level).

If the volume of nitrogen added to C from the gas burette is equal to V (ml STP), we get:

$$V = 0.001 p (V_a - K p_E) \quad \dots \dots \dots (V.2)$$

in which K is a constant given by the diameter of the capillary.

From a sufficient number of measuring points at various values of p and p_E , the constants V_a and K can be calculated*. In the case of the isotherm measurements the dead space V_a of the empty tube C must be lowered by the sample volume. The volume V_s (in ml STP) of the gas that is displaced by the sample at a pressure of 1000 mm mercury under measuring conditions, is equal to:

$$V_s = \frac{1000}{760} \times \frac{273}{78} \times V_{sp} \times G = 4.72 \times V_{sp} \times G \quad \dots \dots (V.3)$$

where V_{sp} represents the specific volume of the sample and G its weight.

The isotherm itself is measured in the same manner as the calibration of the dead space. As all our samples were very sensitive to heating we had to choose as a standard pretreatment de-gassing at room temperature until the pressure in the whole system was lower than 10^{-4} mm mercury; the time necessary to obtain this pressure varied from 1 to 6 hours.

As a criterion that equilibrium was reached we took the point where the pressure in C did not alter more than 0.1 mm in one minute. In the reversible part of the isotherm equilibrium was reached within some minutes; in the region of capillary condensation this took much more time, especially on desorption.

From the volume of nitrogen V present in C, the pressure p_G , the pressure difference p_E and the weight of the sample G the adsorbed volume V_a in ml STP per gram of material is found:

$$V_a = \frac{1}{G} \left[V - \frac{p_G - p_E}{1000} \times (V_a - V_s - K p_E) \right] \quad \dots \dots \dots (V.4)$$

To obtain the isotherms, the values of V_a are plotted against the relative pressure $x = p/p_0$, in which p represents the equilibrium pressure $p_G - p_E$, and p_0 the saturation pressure. The saturation pressure is found during the measurements of the isotherm as the maximum equilibrium pressure in C. The variations in p_0 during the measurements as a result of the variations in temperature of the liquid-nitrogen bath are given by the pressure changes in tube D, in which purified nitrogen is condensed, and which are observed with the manometer F.

* We presume that the ideal gas laws obtain under the given conditions. Though this is not admissible theoretically, it appears in practice that there exists a linear relation between V and $V_a - K p_E$; even in the neighbourhood of the saturation pressure the deviations are still negligibly small compared with the accuracies that can be obtained in this region.

V.2.3 Calculation of the specific surface area from the reversible part of the isotherms

The method generally used to calculate the specific surface area from the reversible part of the isotherms is that given by BRUNAUER, EMMETT and TELLER [95]. This method is based on the theory of multimolecular adsorption of gases on the surface. This theory supposes that in the case of normal adsorption by VAN DER WAALS forces, before the surface is completely covered by a closed layer of molecules of the adsorbate, the formation of a second (third, fourth *etc.*) layer on the first one can start. BRUNAUER, EMMETT and TELLER added to this three assumptions, which enabled them to put the theory in a mathematical, usable form. Though their assumptions are open to doubt, it has been surely established in the course of years that surface areas calculated with this method are often in striking agreement with those found by other independent methods [97].

The most direct check is to compare the specific surface area of non-porous solids, calculated according to the method of BRUNAUER, EMMETT and TELLER (mostly abbreviated to B.E.T.-method), with that calculated from the geometrical dimensions of the particles obtained from electron micrographs. ZWIETERING [98] made this comparison for a sample of aerosil. He found a specific surface area of 165 m²/g by the adsorption method and of 175 m²/g from the geometrical dimensions. We, too, obtained a striking agreement between these two methods (see TABLE V.3), for some samples of microcrystalline boehmite.

The assumptions from which BRUNAUER, EMMETT and TELLER started for the derivation of their equation, may follow here in the formulation of DE BOER [99]:

- the time during which an adsorbed molecule remains on the surface of the solid (the first layer in the case of multimolecular adsorption), can be represented by a mean adsorption time τ , which is independent of the degree of occupation of the surface.
- the adsorption time of a molecule on a layer of molecules of its own kind (second and following layers of the multimolecular adsorption), can be represented by a mean adsorption time τ_1 , which is independent of the thickness of the adsorbed layer and of the degree of occupation.

(The third assumption of BRUNAUER *et al.* according to which the heat of adsorption for the second and following layers is equal to the heat of condensation, is superfluous according to DE BOER).

The equation that can be derived from these assumptions, is:

$$\sigma = \frac{k\sigma_0\kappa}{1-\kappa} \times \frac{1-(n+1)\kappa^n + n\kappa^{n+1}}{1-\kappa+k\kappa(1-\kappa^n)} \dots \dots \dots (V.5)$$

where

σ the total number of molecules adsorbed on 1 cm²
 σ_0 the number of molecules that is sufficient to form a unimolecular layer on 1 cm²

$k = \tau/\tau_1$ the ratio between the adsorption time of the molecules in the first layer and the adsorption time of the molecules in the second (and following) layers

n the total number of layers, which, partly or fully filled, can be adsorbed

$\kappa = p/q$ the ratio between the equilibrium pressure p and the (real or imaginary) pressure q , at which the degree of occupation $\theta = \sigma/\sigma_0$ becomes infinite.

Now q is inversely proportional to τ_1 ; if τ_1 is of the magnitude of the time during which a molecule remains in the surface of its liquid at evaporation equilibrium, then q is approximately equal to the saturation pressure p_0 of the liquid. In this case κ is approximately equal to the relative pressure $x = p/p_0$.

If further the number n of the adsorbed layers is large, then for low pressures (V.5) becomes:

$$\sigma = \frac{k\sigma_0x}{(1-x)(1-x+kx)} \dots \dots \dots (V.6)$$

Passing from molecular quantities to volume quantities we obtain:

$$V_a = \frac{V_m C x}{(1-x)(1-x+Cx)} \dots \dots \dots (V.6a)$$

where

V_a volume of gas adsorbed in ml STP/g of adsorbent
 V_m volume of gas in ml STP/g of adsorbent that should be able to cover the whole surface with a unimolecular layer ("monolayer capacity")
 C constant, numerically equal to k .

Equation (V.6a) is usually the starting point for calculating the specific surface area of porous materials and is called the B.E.T.-equation.

The derivation from the generally valuable equation (V.5) shows that even in the case that the B.E.T.-assumptions would hold exactly, equation (V.6a) may only be applied at low relative pressures. From the shape of the adsorption isotherms it appears that in most cases the deviation of q from p_0 has very little influence on the isotherm at lower pressures (see e.g. FIG. 6 of lit. [99]). In this region the number of molecules in the higher layers is small compared with that in the second layer, so that the assumption of a constant adsorption time τ_1 for the second and following layers is not objectionable (assumption b).

The region of very low relative pressures is not suited for the application of the B.E.T.-equation as a consequence of the approximation applied in assumption a. For, the heat of adsorption for the first layer is often strongly dependent on the degree of occupation, as is shown *a.o.* by RHODIN [3] and by VLEESKENS [33]. Especially at a very low degree of occupation the heat of adsorption can obtain very high values (adsorption on "active" sites, such as lattice distortions, crystal boundaries *etc.*). In general it is only possible to use an average value of the heat of adsorption if these active sites are occupied. In practice this means that the application of the B.E.T.-equation is restricted to the region of relative pressures between 0.05 and 0.25.

To calculate the quantity V_m from the measured values of V_a and x equation (V.6a) is mostly written in the form:

$$\frac{x}{V_a(1-x)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} x \quad \dots \dots \dots (V.7)$$

By plotting the function $y = \frac{x}{V_a(1-x)}$ against x , we obtain the so-called B.E.T.-plot, which is represented by a straight line

$$y = B + Ax$$

if the B.E.T.-equation is valid. In this case:

$$A = \frac{C-1}{V_m C} \quad \text{and} \quad B = \frac{1}{V_m C}$$

The values of A and B can be found graphically or algebraically, whilst V_m follows from:

$$V_m = \frac{1}{A+B}$$

Deriving equation (V.6a) we have assumed that the multimolecular adsorption could take place undisturbed. This is not allowed for materials

having a great portion of their surface in narrow pores inside the particles; the pore walls put a limitation to the number of adsorbed layers. JOYNER, WEINBERGER and MONTGOMERY [100] rearranged equation (V.5) to a manageable form. Just as was done in the case of equation (V.6a) they used volume quantities and introduced the approximation $x = p/p_0$. Equation (V.5) then becomes:

$$V_a = \frac{V_m C x}{1-x} \times \frac{1-(n+1)x^n + nx^{n+1}}{1-x+Cx(1-x^n)} \dots \dots \dots (V.8)$$

This equation can be transformed to:

$$\frac{\Phi(n, x)}{V_a} = \frac{1}{V_m C} + \frac{\Theta(n, x)}{V_m} \dots \dots \dots (V.9)$$

in which

$$\Phi(n, x) = \frac{x[(1-x^n) - nx^n(1-x)]}{(1-x)^2}$$

$$\Theta(n, x) = \frac{x(1-x^n)}{1-x}$$

After choosing a certain value for n we plot the quantity $\frac{\Phi(n, x)}{V_a}$

as a function of $\Theta(n, x)$. If we chose the right value for n , we obtain a straight line with a slope having the reciprocal value of V_m . As the width of the pores generally will not be a whole multiple of the thickness of the unimolecular layer, it will be necessary also to accept fractional values of n .

For a number of samples of activated charcoal, for which the B.E.T.-plot did not show a straight line, JOYNER *et al.* obtained acceptable values of V_m with this method. OKKERSE [101] applied the n -method of JOYNER *et al.* for submicroporous silica, for which the equation (V.6a) could not be used, and also obtained usable results. Our own results with this n -method, when applied to η -alumina with narrow pores, were on the contrary far less favourable, as will be discussed in V.3.1.

To obtain the specific surface area from the calculated value of V_m it is necessary to know the part of the surface, that is taken in by one molecule of the adsorbate in a closed layer. EMMETT and BRUNAUER [102] assume that the density of a physically adsorbed layer is equal to that of the liquid at the same temperature. If we consider the liquid as a

closest packing of spheres with a diameter d , the specific surface s of one molecule is given by

$$s = \frac{1}{2}d^2\sqrt{3}$$

and the volume by

$$v = \frac{1}{2}d^3\sqrt{2} = \frac{MV_{sp}}{6.022 \times 10^{23}} \times 10^{24} \text{ \AA}^3$$

from which follows

$$s = \frac{1}{2}\sqrt{3} \times \sqrt[3]{2v^2} = 1.530 \sqrt[3]{M^2 V_{sp}^2} \text{ \AA}^2 \dots \dots \dots (V.10)$$

where M the molecular weight of the adsorbate

V_{sp} the specific volume in ml/g of the adsorbate in the liquid state.

For nitrogen we obtain from (V.10) with $M = 28.016$ and $V_{sp} = 1.238$ ml/g a specific surface s of the nitrogen molecule of $16.27 \text{ \AA}^2/\text{molec.}$ With this value we find for the B.E.T.-surface area:

$$S_{BET} = 6.022 \times 10^{23} \times 16.27 \times 10^{-20} \times \frac{V_m}{22414} \text{ m}^2/\text{g} = 4.371 \cdot V_m \text{ m}^2/\text{g} \dots \dots \dots (V.11)$$

DE BOER *et al.* [103] pointed out, however, that this concept is not generally justified. In the case of very strong adsorption it will be possible that the bar-bell-shaped nitrogen molecule loses one of its rotational degrees of freedom, so that the specific surface s of the nitrogen molecule changes. From the comparative investigations of HARKINS and JURA [104] and of LIVINGSTON [105] it appeared indeed that s could obtain values between 14 and $17 \text{ \AA}^2$. By comparing the adsorption of nitrogen and of lauric acid on aluminium oxide MEIJES [84] made it plausible that the best value for s in this case is about $16.3 \text{ \AA}^2$. Therefore we accepted the value of $16.27 \text{ \AA}^2$, calculated from the density of the liquid, for all our products.

V.3 Dehydration of bayerite

V.3.1 The development of the surface area

The dehydration curve of bayerite is somewhat dependent on the crystallinity of the material. Poorly crystallized bayerite, as is obtained in a rather impure form by treatment of gelatinous boehmite with

dilute ammonia (see CHAPTER I), loses a noticeable amount of combined water already at a temperature of 100°C . Well-crystallized bayerite, as obtained by SCHMÄH's method (see CHAPTER I), is stable up to a temperature of about 150°C . At this temperature the weight starts to decrease slowly; a fast decomposition does not occur, however, until above 200°C .

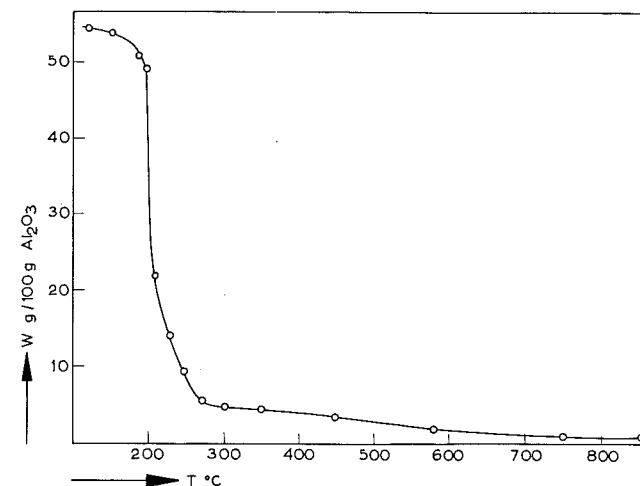


FIG. 26. Dehydration of bayerite (By)

FIG. 26 shows the dehydration curve of a bayerite sample obtained by SCHMÄH's method, which will further be referred to as sample By. The dehydration curve is obtained by a step-wise heating at the temperature indicated until constant weight is obtained (except at temperatures of 190 and 200°C , where constant weight was not yet attained after 72 hours). At temperatures above 450°C a heating time of 4 hours was already sufficient to obtain constant weight, in the other cases up to 24 hours was necessary. During heating from 150 to 190°C a small amount of boehmite was formed. The formation of η -alumina could not be observed in the powder diagrams at a temperature of 200°C ; at 210°C practically all the bayerite had decomposed into η -alumina. The well-crystallized boehmite formed at lower temperatures decomposed at 450°C ; after heating for four hours boehmite could no longer be detected. At a temperature of 750°C θ -alumina could not yet be indicated.

For a number of samples the nitrogen adsorption isotherms were determined, and from these we calculated the specific surface areas by means of the B.E.T.-equation. In FIG. 27 the specific surface areas are

plotted as a function of heating temperature (see also TABLE V.1). We have not tried to draw a smooth curve through the points observed.

Comparison of FIG. 27 with FIG. 26 shows clearly that on dehydration the specific surface area increases considerably, but that sintering (decrease of the specific surface area on heating) starts at about the same time.

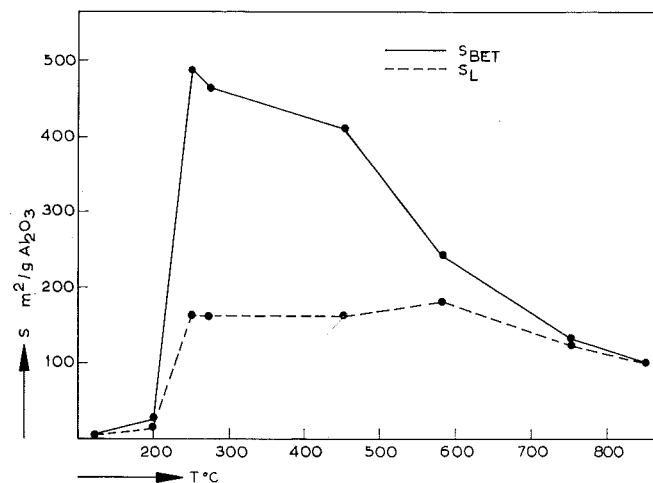


FIG. 27. Specific surface area of heated bayerite (By)

We shall now compare the surface area with the volume taken in by the expelled water in the original material. According to FORTUIN [34] and STEGGERDA [35] the specific volume of the dehydration products of gibbsite can be represented by

$$V_{sp} = 0.27 + 0.0067 \cdot W.$$

If we assume that this equation is approximately valid for the dehydration products of bayerite and further that the bayerite particles will not shrink on dehydration, we can calculate the pore volume (V_p). For sample By 250*, for instance, 43.4 g H₂O/100 g Al₂O₃ is expelled. The calculated pore volume is then $0.67 \times 0.434 = 0.29$ ml/g Al₂O₃ (this value is too high, as a certain shrinkage of the particles can be expected). If from this value we calculate the mean pore width by means of the equation $\bar{d} = \frac{2V_p}{S}$, we obtain a value of about 12 Å, which is a maximum

* The heated samples were distinguished by adding a suffix indicating the heating temperature.

(in the next chapter it appears that the pores are even appreciably narrower). This dimension of the pores is so small that we have to wonder, whether it should not be necessary to apply the n-method of JOYNER *et al.* for calculating the specific surface area.

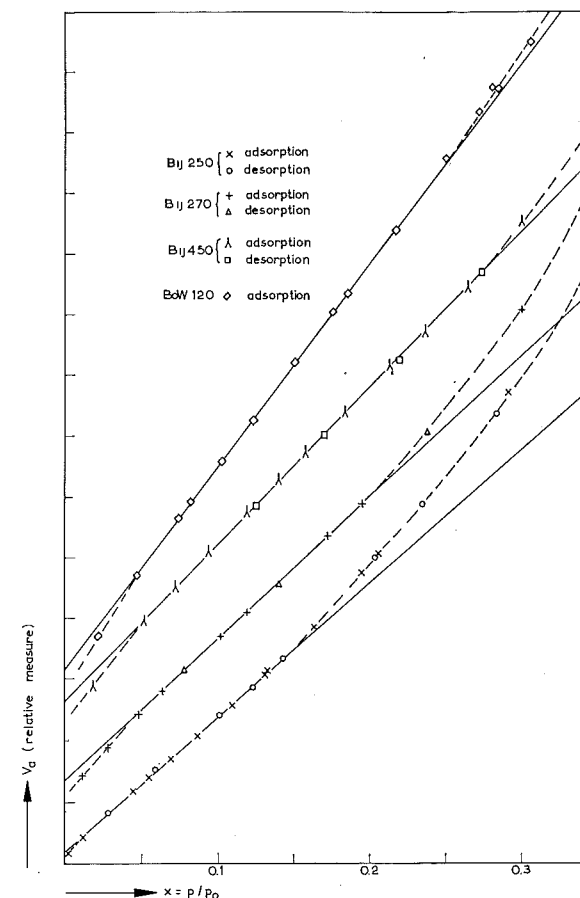


FIG. 28. B.E.T.-plots of By' preparations with narrow pores (the origins are on different levels)

In FIG. 28 we compared the B.E.T.-plots of samples By 250, By 270 and By 450 with that of sample BoW 120, using a varying origin for the y-axis, in order to prevent the lines falling together. The latter material is a crystalline boehmite prepared by treating gelatinous boehmite with water at 250 °C. It consists of plate-shaped, six-sided crystals; hindrance of the multimolecular adsorption in narrow pores is not to be expected in this case. It appears that for the three By samples a sufficient number of points is present to enable a straight line to be

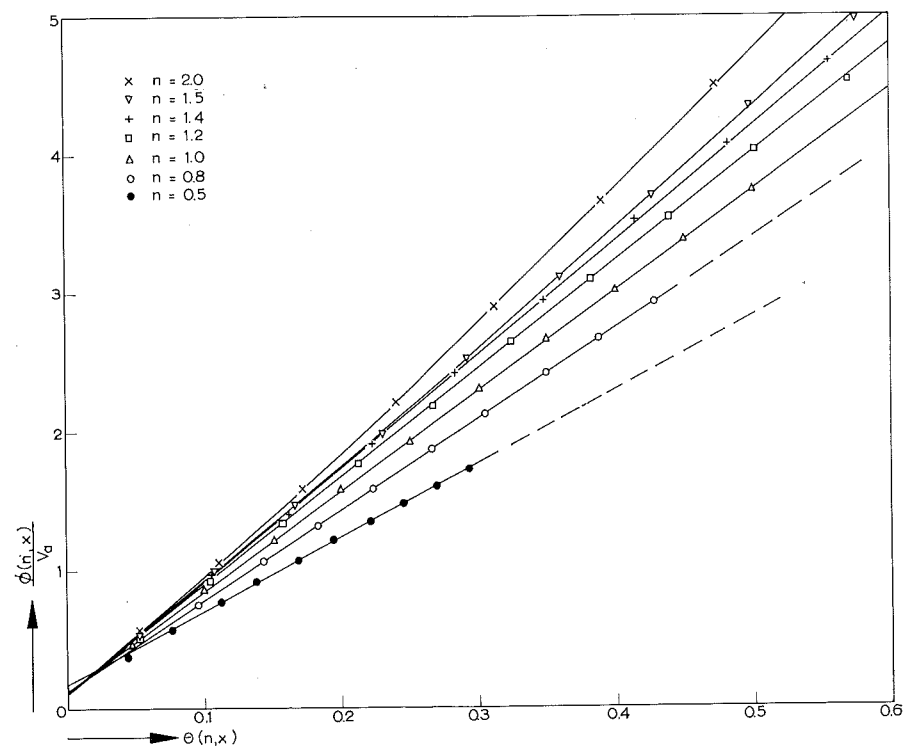


FIG. 29. Function: $\frac{\Phi(n, x)}{V_a} = \frac{1}{V_m C} + \frac{\Theta(n, x)}{V_m}$ for By 250

drawn through the B.E.T.-plot. For sample By 250 (and to a lesser extent also for By 270) the pressure range of usable observations is rather limited compared with that of BoW 120.

We now tried to calculate the specific surface area of By 250 by means of the n -method of JOYNER *et al.* (equation V.9). FIG. 29 shows the plots for values of n between 0.5 and 2.0 and for x between 0.05 and 0.50. For all values of n between 0.5 and 1.4 we obtained beautifully straight lines. The specific surface areas calculated from the slopes of these lines are plotted in FIG. 30 as a function of n . This figure clearly demonstrates the minute value of the n -method for our samples. The only conclusion to be drawn from this is that the amount of nitrogen that can be adsorbed on the surface is not much more than corresponds to a unimolecular layer.

Consequently we have used the B.E.T.-method for all our surface-area measurements, also in the presence of narrow pores. It was always possible to obtain a sufficient number of observations at relative pressures

in the neighbourhood of 0.1, with which in an unmistakable way a quantity S_{BET} could be calculated. Although this quantity S_{BET} does not represent the absolute surface area, it is a reproducible and usable value for comparative measurements.

V.3.2 The adsorption of lauric acid

HOUBEN [82] and FORTUIN [34] applied the adsorption of lauric acid from pentane solutions for determining the specific surface area of aluminium oxide. The reasons for choosing lauric acid and pentane are sufficiently explained by these authors; we may therefore restrict ourselves to the revelation of some particularities.

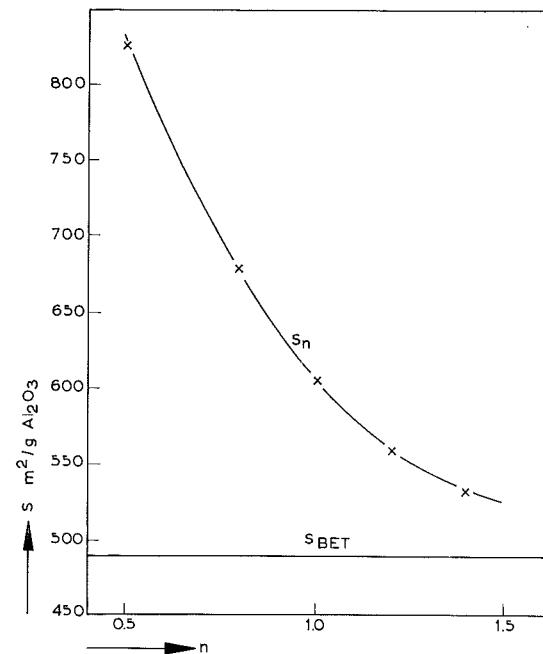


Fig. 30. Specific surface area S_n calculated with the n -method of JOYNER *et al.* as a function of n

(ca. 18 Å). MEIJS [84] found that only for pore widths (expressed as $\frac{2V_p}{S}$) greater than 60 Å the adsorption of lauric acid on the aluminium oxide surface could be regarded as unhindered. On the other hand an adsorption of lauric acid considerably lower than corresponds to the specific surface area measured with nitrogen will be a strong indication for the occurrence of narrow pores.

On crystallographic grounds HOUBEN [82] could derive that a lauric

acid molecule adsorbed on an aluminium oxide surface formed by a closest packing of oxygen atoms, will occupy a surface area of 26.9 Å², if the adsorption is unhindered.

TABLE V.1 summarizes the results we obtained with some of the By samples. In FIG. 27 the values of S_L are compared with the specific

TABLE V.1 Lauric acid adsorption on heated bayerite

sample	W g/100 g Al ₂ O ₃	S_{BET} m ² /g Al ₂ O ₃	ads. L.A. mmole/g Al ₂ O ₃	S_L m ² /g Al ₂ O ₃
By 120	54.6	6.0	0.025	4.1
By 200	49.6	26.5	0.082	13.3
By 250	9.6	489	0.998	162
By 270	5.03	462	0.994	161
By 450	3.90	412	1.003	163
By 580	1.45	245	1.126	182
By 750	0.65	134	0.768	125
By 850	0.60	103	0.635	103

ads. L.A.: adsorbed amount of lauric acid.
 S_L : apparent specific surface area calculated from lauric acid adsorption with the molecular surface-area figure given by HOUBEN.

surface areas S_{BET} . A very great difference is found between S_{BET} and S_L for those samples which are heated not too far above the decomposition temperature. STEGGERDA [35] and FORTUIN [34] found an analogous phenomenon with the dehydration of gibbsite. Only at temperatures above 750 °C the values are comparable to some extent. STEGGERDA tried to explain this phenomenon by supposing that on dehydration at low temperatures besides a certain amount of wide pores also a number of narrow pores is formed, which are accessible to nitrogen but not to lauric acid. These narrow pores are supposed to disappear again at temperatures above 500 °C by a sintering mechanism. In the next chapter we shall see that, broadly speaking, this conception is justified.

V.4 Dehydration of boehmite

V.4.1 Well-crystallized boehmite

By heating gibbsite in liquid water at a temperature of 250 °C and a pressure of about 40 atm. we obtained a product consisting of well-crystallized boehmite (see CHAPTER I), which we shall indicate as BoG. As we used a fairly large amount of water the material obtained was composed entirely of the characteristic diamond-shaped crystals of boehmite with edges of about 1 μ and a thickness of about 300 Å. (By

using less water boehmite crystals can be obtained which are pseudomorphous to the original gibbsite, see CHAPTER IV). The Na₂O-content of our sample was lower than 0.02 %; the loss on ignition after drying at 120 °C was 19.7 g/100 g Al₂O₃.

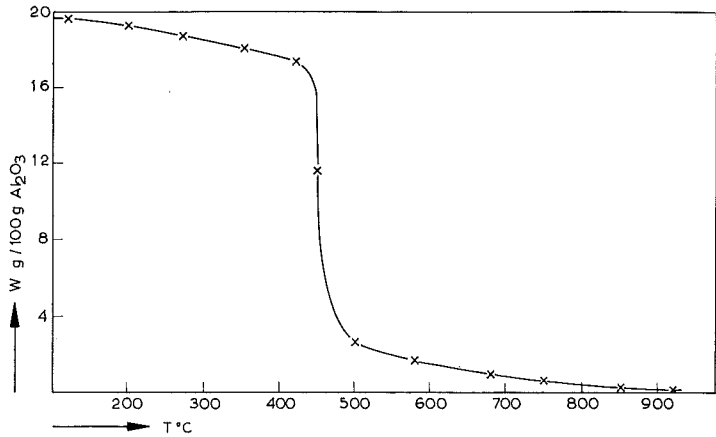


FIG. 31. Dehydration of well-crystallized boehmite (BoG)

Dehydration was achieved by stepwise heating to the indicated temperatures during 6 hours. FIG. 31 shows the changes of the water content during heating. The theoretical water content of 17.7 g/100 g Al₂O₃ is reached at about 400 °C. X-ray powder patterns then only show the lines of boehmite. At a temperature of 450 °C the product is a mixture of boehmite and γ-alumina; at 500 °C the boehmite lines have disappeared.

For a number of samples (distinguished by adding to the indication

TABLE V.2 Specific surface area and lauric acid adsorption on heated BoG

heating temp. °C	W g/100 g Al ₂ O ₃	S_{BET} m ² /g Al ₂ O ₃	ads. L.A. mmole/g Al ₂ O ₃	S_L m ² /g Al ₂ O ₃
200	19.3	1.3	0.005	0.8
350	18.1	3.5	0.011	1.8
450	11.6	17.1	0.055	8.9
500	2.7	65.3	0.211	34.2
580	1.65	65.7	0.219	35.6
750	0.65	19.1	0.116	18.8
850	0.38	16.8	0.106	17.2

a suffix denoting the heating temperature) S_{BET} and the lauric acid adsorption were estimated (TABLE V.2 and FIG. 32). Just as in the case of bayerite, the greatest evolution of the surface area occurs during the decomposition of the hydroxide. The specific surface area, however, is

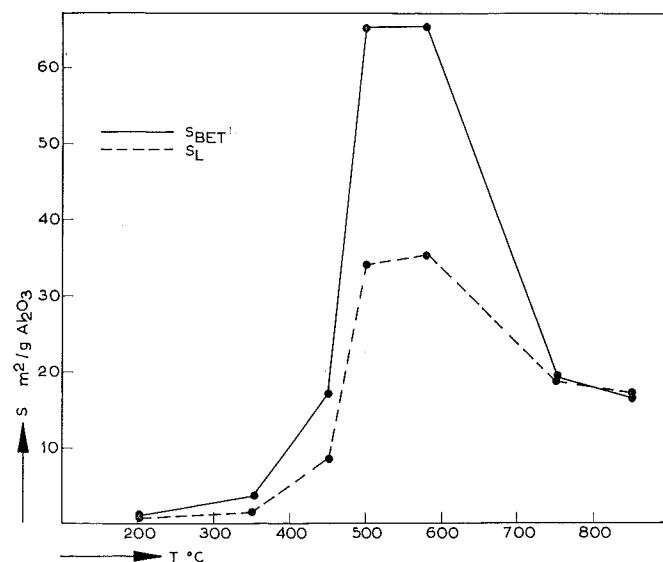


FIG. 32. Specific surface area of heated BoG

by an order of magnitude smaller than that of bayerite. Here, too, the lauric acid adsorption is smaller than would agree with S_{BET} accepting a value of $26.9 \text{ \AA}^2$ for the specific surface of the lauric acid molecule. Only at temperatures of 750°C and higher, S_{L} equals S_{BET} .

V.4.2 Microcrystalline boehmite

By recrystallization of gelatinous boehmite at temperatures above 100°C we obtained a number of samples consisting of microcrystalline boehmite (see I.3.2, TABLE I.3). Of the samples dried at 120°C we compared S_{BET} with the lauric acid adsorption (TABLE V.3). If we compare the amount of lauric acid adsorbed with S_{BET} , it appears that there exists a constant ratio between these two values. For f , i.e. the number of mmols of lauric acid adsorbed on 100 m^2 B.E.T.-surface area, we find an average value of 0.43 ± 0.01 instead of 0.617 , which follows from the specific surface of a lauric acid molecule on the aluminas (calculated from the value of $26.9 \text{ \AA}^2$ given by HOUBEN). It is not very probable that this lower value is caused by steric hindrance in these products. The separate small crystals forming these samples are not

TABLE V.3 Specific surface area and lauric acid adsorption on microcrystalline boehmite

recrystallization		dried at 120°C					heated 6 h at 450°C	
$^\circ\text{C}$	medium	W	S_{BET}	ads. L.A.	f	S_{geom}	W	S_{BET}
150	H_2O	23.9	255	1.122	0.441	—	4.6	226
170	H_2O	22.6	201	0.870	0.434	—	—	—
250	H_2O	19.7	64	0.272	0.426	68	2.7	92
150	1n NaOH	21.1	158	0.659	0.418	—	—	—
200	1n NaOH	19.3	100	0.420	0.420	98	3.0	100
250	1n NaOH	18.9	68	0.296	0.436	75	2.8	98

W g/100 g Al_2O_3 ; S_{BET} and S_{geom} $\text{m}^2/\text{g Al}_2\text{O}_3$; L.A. mmole/g Al_2O_3 ; f mmole/100 m^2 .

porous, as we could affirm by estimating the geometrical surface area.

To this end a number of electron micrographs was made for some samples. With the aid of a counting machine ("Teilchengrösse Analysator" TGZ 3 of Carl Zeiss) one dimension of a great number of particles (400 for each product) and its frequency were estimated. As the ratio of the dimensions varied only between narrow limits, we were able to calculate approximately the geometrical surface area (S_{geom}) from the size distribution obtained and the specific volume. The fair agreement between S_{BET} and S_{geom} is in support of the theory of BRUNAUER, EMMETT and TELLER and indicates that the particles do not have an internal surface area, so that they are not porous.

The same low value for f of about 0.43 was found by MEIJS [84] for other aluminium hydroxide samples as well as for some non-heated cracking catalysts consisting of silica coated with much aluminium hydroxide. It thus appears that the packing of lauric acid adsorbed is less dense on a hydroxide surface than on an oxide surface. MEIJS found that on rehydration of the aluminas the lauric acid adsorption is only very little lower than on the dehydrated surface. So possibly no OH-groups are formed during the rehydration process, but the adsorbed water molecules behave in nearly the same way as oxygen atoms in the surface.

The magnitude of the internal surface area formed by dehydration on heating strongly depends on the particle size of the material. The smaller the crystals, the smaller the increase of the surface area (see TABLE V.3). For sample 150 H_2O we even observe a decrease. This is because the decrease of the external surface area as a result of the particle shrinkage during the expelling of the water is greater than the formation of internal surface area by new pores.

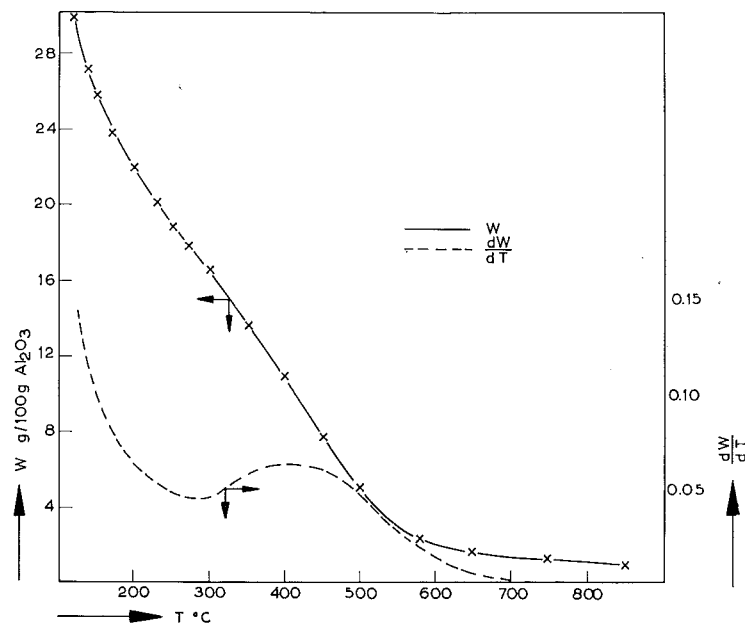


FIG. 33. Dehydration of gelatinous, sheet-like boehmite (A)

V.4.3 Gelatinous boehmite

The dehydration curve of gelatinous (sheet-like) boehmite has quite another appearance than that of well-crystallized boehmite (FIG. 33, solid curve). The vertical part in FIG. 31 at the temperature at which the greater part of the dehydration of BoG takes place is missing in FIG. 33. The dehydration proceeds much more gradually. In CHAPTER II we concluded already from the changes in the powder patterns during heating that the dehydration nevertheless occurs in two distinct steps. Up to a temperature of 270 °C only the water in excess over the theoretical quantity of 17.7 g/100 g Al_2O_3 is expelled; dehydration to γ -alumina does not start until this temperature is reached.

By plotting the change of the water content per degree C as a function of the temperature it also appears clearly that the dehydration proceeds in two steps (FIG. 33, dotted curve). It is remarkable that the same conclusion can be drawn from the observations of FORTUIN [34, page 29] and of STEGGERDA [35, page 38, Fig. 8].

Gelatinous boehmite has a large specific surface area already before dehydration. On heating only a decrease of it is observed (TABLE V.4, FIG. 34).

The adsorption of lauric acid from the usual pentane solution on the

TABLE V.4 Specific surface area and lauric acid adsorption on heated gelatinous boehmite

heating temp. °C	W g/100 g Al_2O_3	S_{BET} $\text{m}^2/\text{g Al}_2\text{O}_3$	ads. L.A. mmole/g Al_2O_3	S_L $\text{m}^2/\text{g Al}_2\text{O}_3$	f mmole L.A./ 100 m^2
120	30.9	609	2.57–3.20	—	0.42–0.53
170	23.8	593	—	—	—
200	21.8	580	—	—	—
230	20.0	—	2.56–2.97	—	ca. 0.47–0.54
270	17.8	516	—	—	—
300	16.5	492	—	—	—
350	13.7	458	—	—	—
450	7.7	417	2.28	371	0.55
580	2.3	355	2.02	328	0.57
635	1.75	—	1.91	310	—
750	1.35	280	1.64	266	0.59
850	1.00	236	1.45	235	0.614

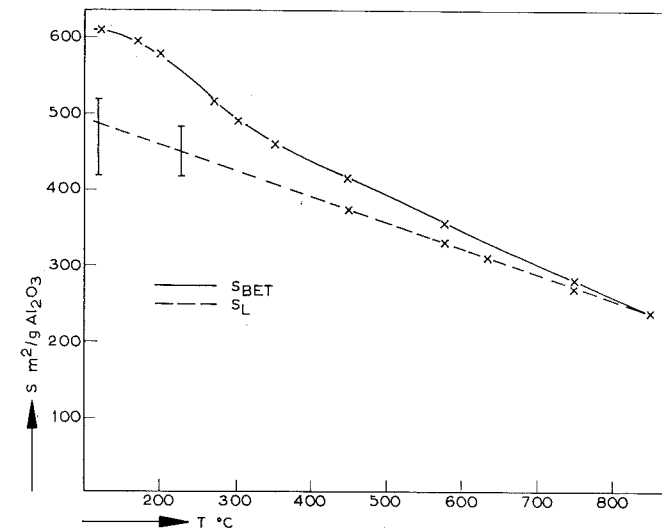


FIG. 34. Specific surface area of heated gelatinous boehmite (A) as a function of the heating temperature

samples heated below 300 °C could hardly be determined; within a short time the whole mass gelatinized. Duplicate runs, obtained after centrifuging, gave scattering results. As with other samples discussed before, only for those heated above 750 °C a good agreement between the lauric acid adsorption and the B.E.T.-surface area was found.

In FIG. 35 we plotted S_{BET} against the water content of the samples.

In this curve three regions can be distinguished, *viz.* a. the region above 16 g H₂O per 100 g Al₂O₃, b. a practically straight part between 16 and 2 g H₂O per 100 g Al₂O₃, and c. a strongly decreasing part at lower water content.

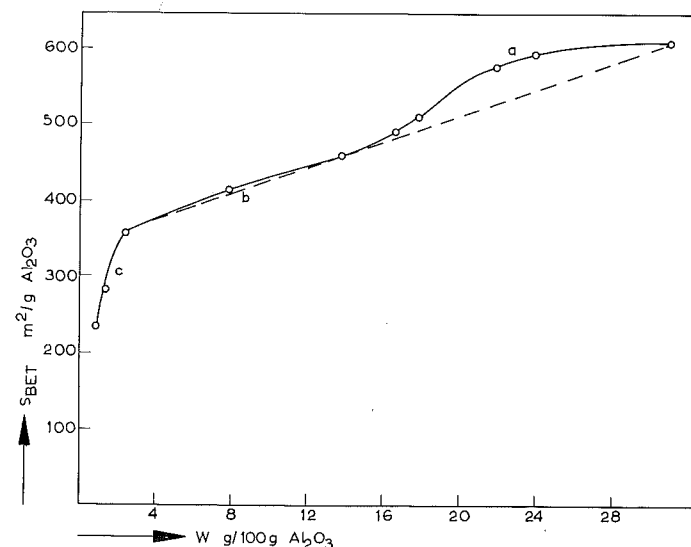


FIG. 35. Specific surface area of heated gelatinous boehmite (A) as a function of the water content

The straight line of the second part b. can be described by:

$$S = 340 + 8.50 W \text{ m}^2/\text{g Al}_2\text{O}_3 \quad (\text{V.12})$$

We may put:

$$S = S_{ab} + S_c + S_i \quad (\text{V.13})$$

where

S_{ab} surface area perpendicular to the c -axis of the crystallites

S_c surface area parallel to the c -axis

S_i internal surface area

As will be shown in the next chapter, S_i can be neglected in this sample. The continuous increase of the f -value, as shown in TABLE V.4 indicates that there is a continuous change from a hydroxide surface to an oxide surface (see V.4.2).

If we assume that the pseudomorphosis phenomena for gelatinous boehmite are the same as those observed with well-crystallized boehmite, the decrease of the surface area is caused almost entirely by the shrinkage

of the particles in the direction of the c -axis of the boehmite (the changes in the direction of the other axes are small compared with that of the c -axis). In CHAPTER IV we showed that the c -axis of the boehmite forms the [110]-direction of the γ -alumina. The eight oxygen layers perpendicular to the c -axis in the unit cell of boehmite correspond to six oxygen layers perpendicular to the [110]-axis of the γ -alumina. As the unit cell of the γ -alumina contains eight oxygen layers perpendicular to the [110]-axis, the c -axis of boehmite corresponds to $\frac{3}{8} \cdot d_{[110]}$ of the γ -alumina. If now we assume that the decrease of the length of the particle parallel to the c -axis of the boehmite crystallites is proportional to the decrease of the water content, we get:

$$\frac{S_c}{S_{co}} = 1 + \frac{c_{\text{boehmite}} - \frac{3}{8}d_{[110]}}{\frac{3}{8}d_{[110]}} \cdot \frac{W}{17.7} = 1 + 0.0256 W \quad (\text{V.14})$$

in which S_{co} represents the surface area parallel to the c -axis, in the fully dehydrated state, if sintering phenomena or modification changes would not occur.

From equations (V.13) and (V.14) it follows, if S_i is neglected:

$$S = S_{ab} + S_{co}(1 + 0.0256 W) \quad (\text{V.15})$$

When we compare (V.12) and (V.15) we find:

$$S_{ab} + S_{co}(1 + 0.0256 W) = 340 + 8.50 W \quad (\text{V.16})$$

which holds for all values of W between 2 and 16 g/100 g Al₂O₃. From (V.16) we calculate for S_{co} a value of 333 m²/g Al₂O₃ and for S_{ab} 7 m²/g Al₂O₃.

Though, of course, this calculation will not give exact values, we take it as an indication that the surface of γ -alumina obtained from gelatinous boehmite is mainly formed by the surface parallel to the c -axis of the original boehmite crystallites, whereas the surface area perpendicular to the c -axis is small. This, then, is in striking contrast with the phenomena observed with well-crystallized and microcrystalline boehmite, for which the external surface of the γ -alumina is mainly formed by the planes perpendicular to the c -axis of the original boehmite crystals (compare III.3.1).

In the region of water contents above 16 g/100 g Al₂O₃ the c -axis does not change much, *viz.* from 13.0 Å for samples heated to 120 °C, to 12.4 Å for those heated at a temperature of 270 °C. Correspondingly, we observe in the beginning only a small decrease of the specific surface area. The strong decrease between 200 and 270 °C is not easy to explain, however. A decrease of the surface area by sintering is not probable

at this temperature, in view of the high stability at higher temperatures. A possible explanation could be, that during the disappearance of the last amounts of "extra" water and the beginning of the decomposition of the boehmite in this temperature region, the surface activity is so great that some crystallites having their *c*-axes almost parallel, stick together forming a new crystallite with a smaller surface.

Real sintering occurs in the region *c* with a water content below 2 g/100 g Al₂O₃, *i.e.* at temperatures at which the oxides formed from the well-crystallized hydroxides recrystallize to the high-temperature forms of the aluminas (see CHAPTER IV).

V.5 Summary of chapter V

The dehydration of well-crystallized bayerite largely occurs at a temperature slightly above 200 °C. During dehydration a very large surface area is formed, which, however, disappears again to a considerable extent by sintering upon heating at higher temperatures.

During dehydration of well-crystallized boehmite the surface area also increases, but appreciably less so than in the case of bayerite. Here again, the greater part of the surface area disappears on heating at higher temperatures.

The increase of the surface area during the dehydration of boehmite is smaller as the crystallites are smaller. In the case of gelatinous boehmite the formation of γ -alumina does not produce a noticeable internal surface area; the shrinkage of the particles in the direction of the *c*-axis of the boehmite crystallites during the transition causes the surface area to decrease. From the magnitude of this decrease it could be derived that the surface of gelatinous boehmite and of the γ -alumina formed from this is largely composed of the surfaces of the planes parallel to the *c*-axis of the boehmite, whereas in the case of well-crystallized boehmite the [001]-plane is the principal plane.

The lauric acid adsorption on bayerite samples heated to temperatures between 200 and 500 °C is appreciably lower than corresponds with the B.E.T.-surface area, so that a considerable amount of narrow pores must be present. Calculation of the specific surface area of these samples by the n-method of JOYNER *et al.* did not give unequivocal results, contrary to the B.E.T.-method.

Comparison of the lauric acid adsorption on microcrystalline boehmite with the B.E.T.-surface area shows that the surface coverage of lauric acid is less dense on these non-heated materials than on the aluminas heated to temperatures above 750 °C.

SHAPE AND WIDTH OF THE PORES

VI.1 Introduction

The specific surface area alone is not sufficient to qualify a porous material; it is also necessary to have a measure for the size of the pores. For technical purposes the mean pore radius is often used to this end. The mean pore radius $\bar{r}$ can be defined as:

$$\bar{r} = \frac{2V_p}{S} \quad \dots \dots \dots (VI.1)$$

V_p represents the pore volume, *i.e.* the total volume of the pores. In deriving equation (VI.1) the pores are assumed to be cylindrically shaped, to have all the same size and not to intersect. These idealized conditions will not occur in practice, so $\bar{r}$ may not be considered a real quantity. For comparison of a number of closely related products equation (VI.1) is a quite suitable measure, however.

Attempts to obtain a better description of the pore sizes by introducing a shape factor and an intersection factor (WHEELER [106], STEGGERDA [35]), failed. Better results are obtained by the theory of capillary condensation in the pores at pressures below saturation pressure.

According to the KELVIN equation the vapour pressure over a liquid with a curved surface is given by

$$\ln x = \ln p/p_0 = - \frac{2\sigma V \cos \psi}{RT \cdot r_k} \quad \dots \dots \dots (VI.2)$$

where

- $x = p/p_0$ relative vapour pressure over the liquid
- σ surface tension of the liquid
- ψ contact angle between the liquid surface and the solid
- V molecular volume of the liquid
- r_k KELVIN radius

For a non-spherical surface the KELVIN radius r_k is given by the two main radii of curvature:

$$\frac{1}{r_k} = \frac{1}{2} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \dots \dots \dots \text{(VI.3)}$$

Decreasing the pressure will cause evaporation of the liquid in completely filled pores as soon as the relative pressure is lower than corresponds to equation (VI.2). The amount of liquid evaporating is equal to the volume of the pores after correcting for the amount adsorbed on the surface.

In order to be able to ascertain the magnitude of the corrections and to calculate the dimensions of the pores from the KELVIN equation it is necessary to form a picture of the shape of the pores. In some cases it has been possible to establish the shape of the pores by optical measurements. DE BOER, STEGGERDA and ZWIETERING [58] concluded from conoscopic observation that largely dehydrated gibbsite contains plan-parallel, slit-shaped pores. Sometimes it is possible to obtain indications about the shape of the pores with the aid of the electron microscope [108]; in most cases the pore shape is so complicated, that we have to restrict ourselves to a schematized description.

Applying the KELVIN equation to pores of different shapes, it appears that in empty pores the liquid will sometimes condense at a higher relative pressure than it evaporates from the fully filled pores. This phenomenon called hysteresis, can give an indication about the shape of the pores. BARRER, MCKENZIE and REAY [107], DE BOER [108] and others have tried to draw conclusions about the shape of the pores from the shapes of hysteresis loops.

In the present part of this thesis we shall use these methods to gain an insight into the shape and the dimensions of the pores in the hydroxides and the aluminas, and into the transformations taking place during heating. Moreover, we shall try to obtain additional data from the shape of the adsorption branch of the isotherm.

VI.2 The pore volume

Technically, the pore volume of a porous material is an important quantity in that it determines a number of technological properties of catalysts, such as bed volume, product retention *etc.* As a means of characterizing the texture it is of little value, as was explained in the introduction to this chapter.

The determination of the pore volume gives no special difficulties in

the case of coarse-grained materials. It can be done in a direct way by measuring the amount of liquid that can be taken up in the pores, or indirectly, as the difference between the specific volume in mercury and that in water (or another suitable inhibition medium). We applied both principles in CHAPTER I.

The samples which come up for discussion in this chapter all consist of very finely divided material, the largest particles having a size of some μ 's. There is no sense in measuring the specific volume in mercury since it cannot penetrate into the space between the particles. Filling the pores by adding a liquid, as is sometimes done with dye-stuffs, was impossible for most samples from lack of a liquid not reacting with the material and being able to penetrate into even the narrowest pores.

Capillary condensation of nitrogen at a pressure somewhat below saturation pressure was feasible indeed, but the adsorption isotherms always assumed a very steep course in this region; it was therefore not possible to obtain a differentiation between the pore volume proper and the intergranular space.

That is why we abandoned the pore volume as a means of describing the texture. As far as we needed the pore volume for the calculation of the pore-size distribution, we took the point on the desorption branch of the nitrogen adsorption isotherm at a relative pressure of 0.999. As this pressure corresponds to a KELVIN radius of ca. 1 μ , a large part of the intergranular space is included in this figure.

VI.3 The shape of the hysteresis loop

VI.3.1 The main types of the hysteresis loops

DE BOER [108] investigated what conclusions could be drawn regarding the shape of the pores from the shape of the hysteresis loops. He distinguished five types, characterized by at least one vertical (or at least very steep) branch. The adsorption isotherms of our samples (FIG. 36, 37, 38 and 39) have hysteresis loops corresponding to three of these main types (or combinations of them): *viz.* the types A, B and E of DE BOER's classification.

Type A (FIG. 40a) has two very steep branches and can be related in its simplest form to cylindrically shaped pores open at both ends. If r represents the radius of the cylinder then the pore will be filled up completely at a relative pressure x_a given by the KELVIN equation:

$$\ln x_a = \frac{-2\sigma V \cos \psi}{2RT(r-t_a)}$$

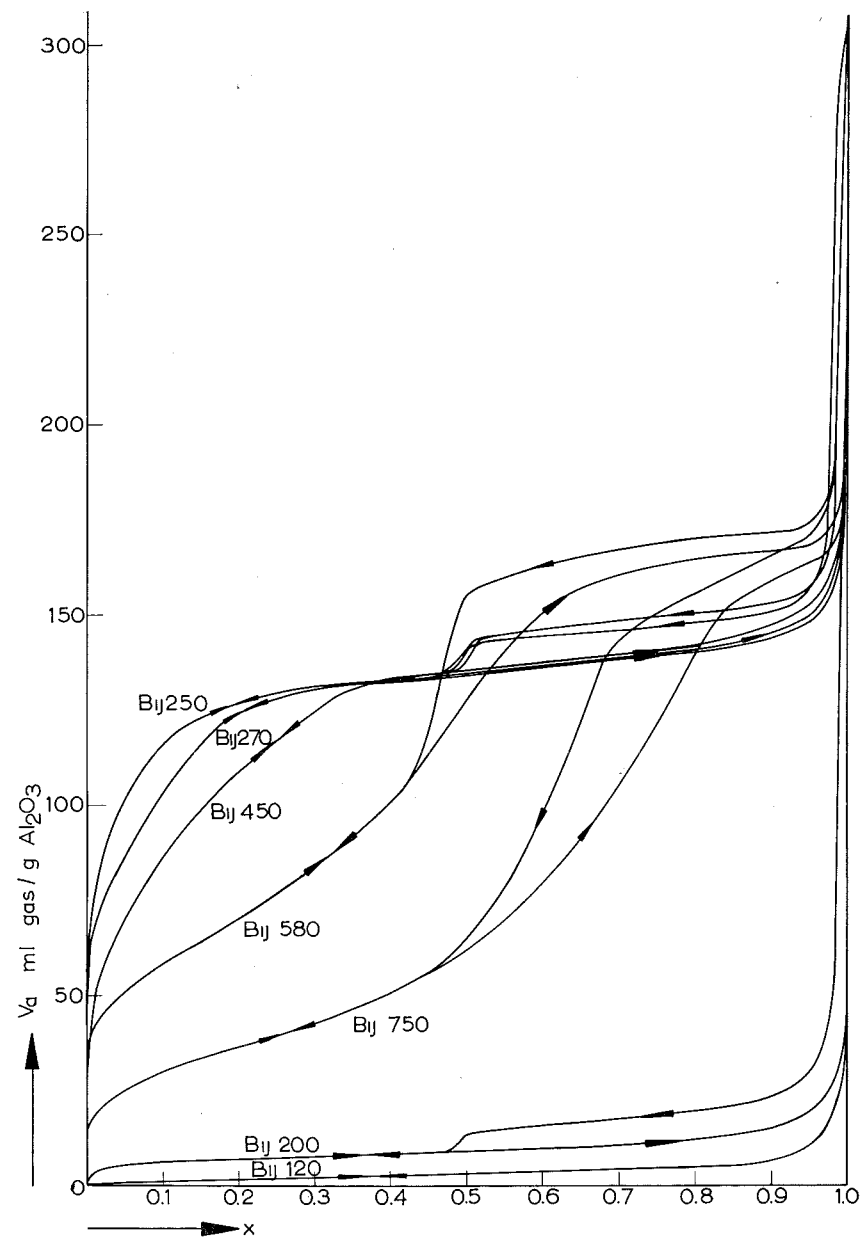


FIG. 36. Nitrogen adsorption isotherms of heated By-preparations

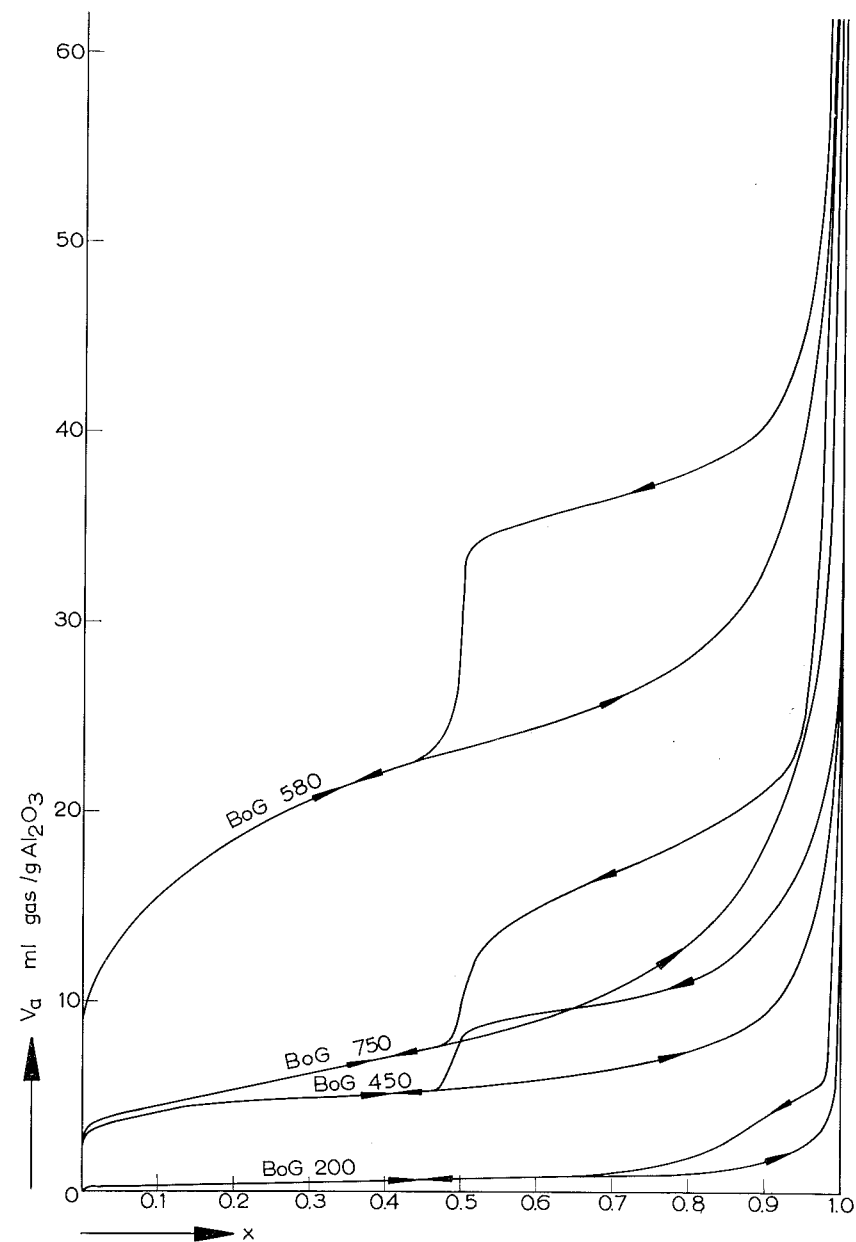


FIG. 36. Nitrogen adsorption isotherms of heated BoG-preparations

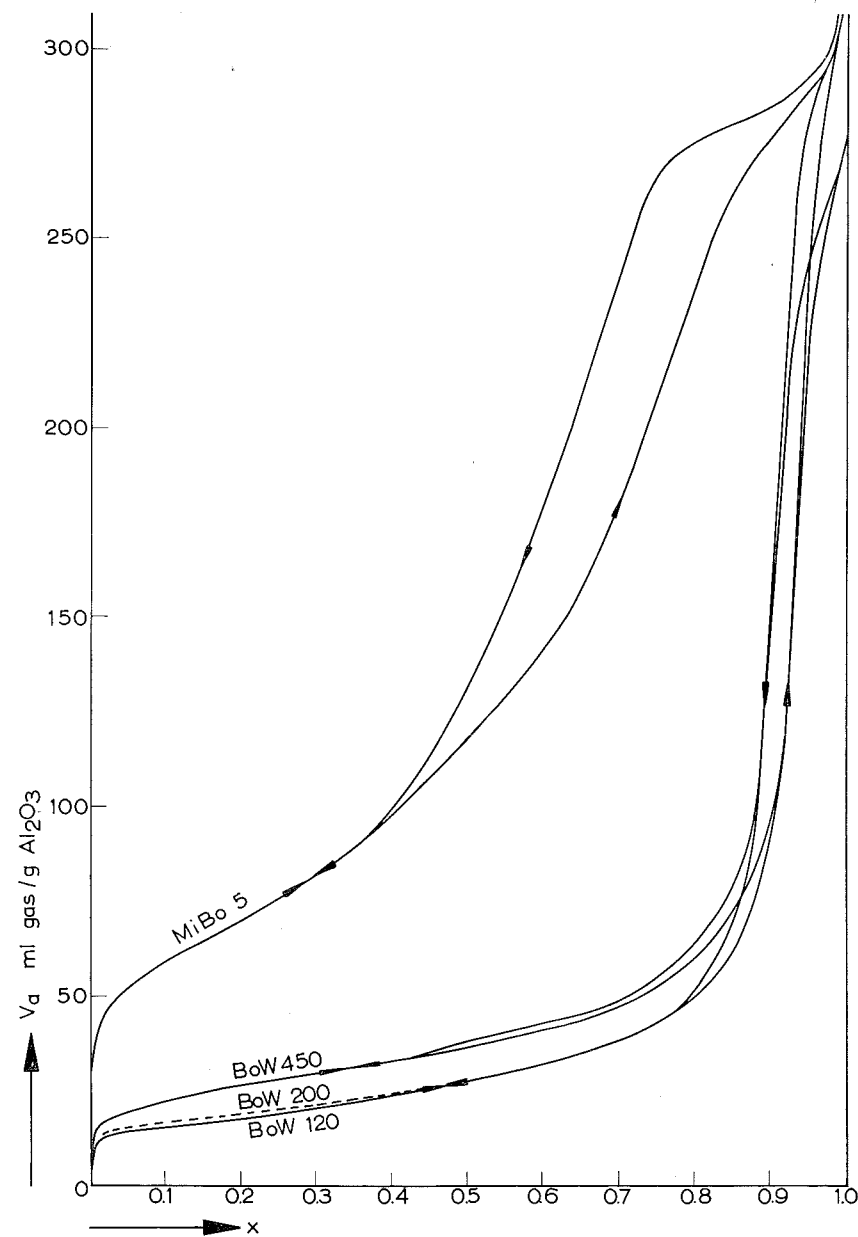


FIG. 38. Nitrogen adsorption isotherms of microcrystalline boehmite

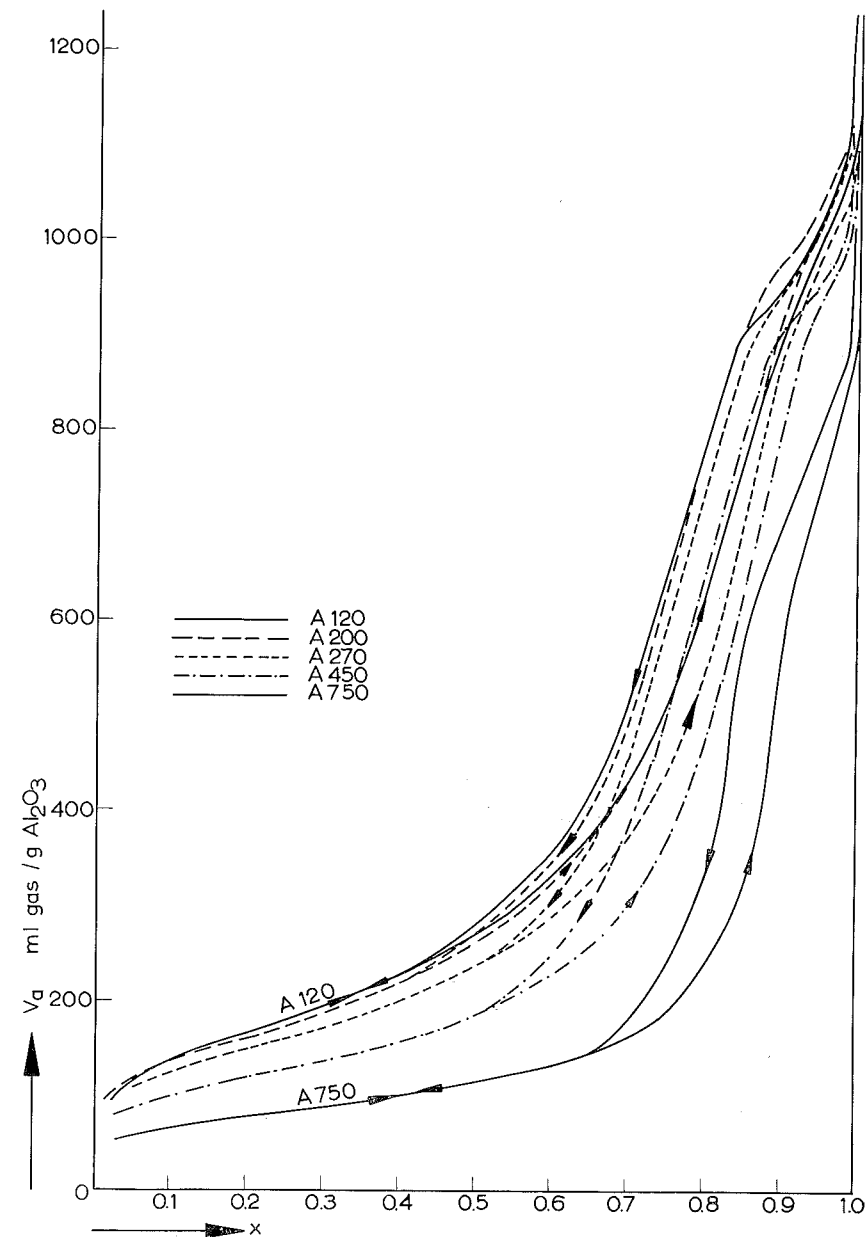


FIG. 39. Nitrogen adsorption isotherms of heated A-preparations

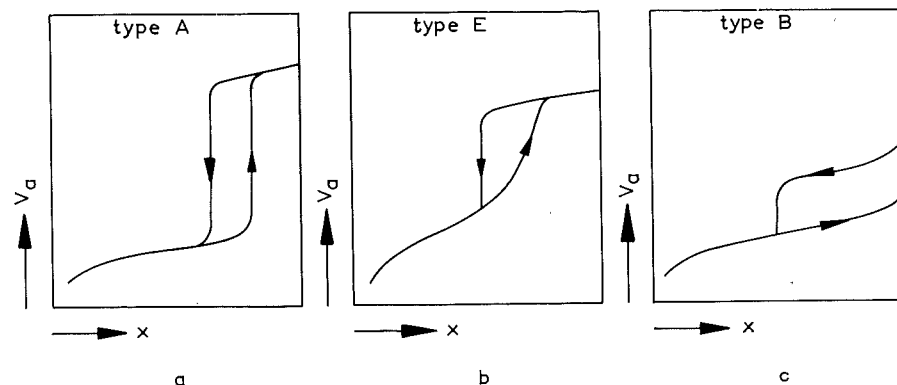


FIG. 40. Three types of hysteresis-loops (according to DE BOER [108])

(t_a and t_d are corrections to the pore radius for the thickness of the adsorbed layer).

Emptying takes place if

$$\ln x_a = \frac{-2\sigma V \cos \psi}{RT(r-t_a)}$$

Consequently the following relation exists between the relative pressures at filling and emptying:

$$\log x_a = 2 \left(1 + \frac{t_d - t_a}{r - t_d} \right) \cdot \log x_a \dots \dots \dots \text{(VI.4)}$$

For high relative pressures $t_d - t_a$ is small compared with $r - t_d$, so in this case (VI.4) can be approximated by:

$$x_a = x_a^2 \dots \dots \dots \text{(VI.4a)}$$

DE BOER showed that for all tubular pores in which an inscribed cylinder can be formed, a hysteresis loop of type A is formed. In these cases the equation (VI.4) is valid if r is put equal to the radius of the inscribed cylinder. Also tubular capillaries with slightly widened parts belong to type A and satisfy equation (VI.4) as long as the radius of the widened part does not exceed twice that of the narrower parts. In a number of cases, mentioned by DE BOER, equation (VI.4) does not hold, *e.g.* in the case of tubular pores with a cross-section in which no inscribed circle can be drawn, as *e.g.* rectangular cross-sections. If we have to do with varying pore widths, the branches of the loop are no longer vertical. The more the widths vary, the branches are less steep.

Type E (Fig. 40b), with a steep desorption branch and a sloping adsorption branch, has much resemblance to type A. This type can be attributed to pores with openings of the same radius r_n and with widened, somewhat spherically shaped, parts with varying radii, while $r_w > 2r_n$. If there is a variation in the radius r_n also the desorption branch will have a sloping character, but the broadening of the loop upwards still exists.

As DE BOER pointed out, porous materials consisting of more or less spherically shaped particles or of particles with irregular polyhedral shape often show hysteresis loops of type A and E, mostly combined.

Type B (Fig. 40c) is a hysteresis loop with a vertical adsorption branch at a relative pressure very closely to 1 and a desorption branch at some medium pressure. The KELVIN radius for adsorption is very large, so the radii of curvature of the liquid surface too. On desorption it appears, however, that the pores must yet have a small dimension. DE BOER gives two cases in which a loop of type B can be formed. Very wide capillaries (widths more than 500 Å) having narrow short openings are filled up only at very high relative pressures. Desorption can only occur, however, when the relative pressure corresponds to the widths of the narrow openings. The second kind of pores, for which a loop of type B can exist, is formed by parallel plates at some distance from each other. The pores can be filled up only at a relative pressure of 1, or at a pressure for which the adsorbed layer is so thick that it fills up the pores completely. If the pores are completely filled up, a meniscus can be formed which will have the shape of a half cylinder; desorption will take place at a lower relative pressure. In VI.5 we shall discuss how we can distinguish between the two cases of type B loops.

VI.3.2 Hysteresis loops of the samples investigated

The isotherms of sheet-like gelatinous boehmite (A) and of the products obtained from it by heating (Fig. 39) all have a hysteresis loop of type A combined with a little of type E (two steep branches, broadening upwards). The higher the heating temperature the less pronounced the broadening upwards. The type E character consequently disappears on heating. The pore spectrum of all samples is very broad, as can be concluded from the broad region of relative pressures over which the hysteresis loop extends. The picture of this gelatinous boehmite we built up in the preceding chapter is in accordance with this. The composition of sheets formed by fibrillar particles makes a broad pore spectrum to be expected as well as the presence of tubular, though short, pores with widened parts. The disappearance of the type E character (especially

perceptible for the product heated at 750 °C) can be ascribed to the smoothening of the pore walls by sintering.

The changes occurring during hydrothermal conversion of sheet-like into microcrystalline gelatinous boehmite (compare CHAPTER I), can be followed by comparing FIG. 38 and 39. In FIG. 38 we can see that sample MiBo 5, which is obtained from sheet-like gelatinous boehmite A 120 by hydrothermal treatment at 150 °C, gives a loop with a pronounced type E character; product BoW, obtained from the same gelatinous boehmite at 250 °C, has lost the type E character completely. The sheets of gelatinous boehmite forming the wider pores are broken up. The type E character of MiBo 5 is in line with the building up from very small, irregularly shaped particles. Sample BoW 120 consists of small, six-sided platelets. A packing of these platelets will give rise to formation of pores; with approximately rectangular cross-section; this kind of pores will give a narrow hysteresis loop of type A, which is indeed observed.

When heated the well-crystallized boehmite BoG samples give adsorption isotherms which are characterized by a hysteresis loop of type B (FIG. 37). Whether we are dealing with very wide pores with narrow openings or with slit-shaped pores, will have to be decided by further analysis of the isotherm (see VI.4 and VI.5). We also observe a number of very wide pores, which can be attributed to the space between the particles.

FIG. 36 shows the isotherms of heated bayerite. At a temperature below 450 °C a small hysteresis loop of type B is formed. After heating at a higher temperature the hysteresis loop is a combination of type E and type B. The shape of the pores therefore appears to have changed considerably in this case. This transformation of the pore shape will also be discussed in more detail in sections 4 and 5 of this chapter.

VI.4 The pore-size distribution calculated from the desorption branch of the isotherms

VI.4.1 The method of calculating the pore-size distribution

From the shape of the isotherms of the samples investigated we already concluded that many of them possessed a broad or an irregular pore-size distribution. To obtain more quantitative data, we calculated the complete pore-size distribution. The calculation method is based on the KELVIN equation and depends to some extent on the shape of the pores. BARRETT, JOYNER and HALENDA [109] and CRANSTON and INKLEY [110]

gave a method for cylindrically shaped pores, STEGGERDA [35] and INNES [111] for slit-shaped pores.

Starting from the desorption branch of the isotherm the KELVIN radius is calculated for various relative pressures. The dimensions of the pores are then given by:

$$\begin{aligned} r &= r_k + t \text{ (cylindrical pores)} \quad \text{ (VI.5)} \\ d &= r_k + 2t \text{ (slit-shaped pores)} \end{aligned}$$

where:

- r radius of cylindrically shaped pores
- d wall separation of slit-shaped pores
- t thickness of the adsorbed layer

As long as t is small compared to r_k , as it is the case at high relative pressures, the differences between the two calculation methods are not very large. At lower pressures t is of the same magnitude as r_k ; the two methods then give different results. However, at these low pressures the pores are so narrow that r_k loses its significance as radius of curvature of the liquid surface. Since the method for slit-shaped pores requires less ciphering and since from the crystallographic properties we expected slit-shaped pores to be present in a number of our samples, we gave preference to this method.

Let us assume that at a relative pressure $x = 1$ all pores (including a part of the intergranular space) are filled with liquid nitrogen. If we divide the desorption branch into pieces corresponding to equal steps in relative pressure of $2\Delta x$, at the beginning of the i -th step the relative pressure is $x_i + \Delta x$, the volume adsorbed (expressed in ml liquid nitrogen) $X_{x_i + \Delta x}$, the surface area of the pores (or parts of pores) not filled with liquid nitrogen $S_{x_i + \Delta x}$ and the thickness of the layer of nitrogen adsorbed on this surface $t_{x_i + \Delta x}$.

If we lower the pressure to $x_i - \Delta x$, the pores are having a KELVIN radius (VI.3) between $r_{k_{x_i + \Delta x}}$ and $r_{k_{x_i - \Delta x}}$ are emptied. If we choose Δx sufficiently small we may assign to this group of pores a mean KELVIN radius $r_{k_{x_i}}$, corresponding with the relative pressure x_i . The thickness of the adsorbed layer at this pressure is t_{x_i} , so that the mean pore width d_{x_i} of this group of pores is:

$$d_{x_i} = r_{k_{x_i}} + 2t_{x_i} \quad \text{ (VI.6)}$$

Representing the surface area of this group of pores by ΔS_{x_i} the volume ΔV_{x_i} is:

$$\Delta V_{x_i} = \frac{d_{x_i}}{2} \cdot \Delta S_{x_i} = \frac{1}{2} (r_{k_{x_i}} + 2t_{x_i}) \cdot \Delta S_{x_i} \quad \text{ (VI.7)}$$

At the end of the i -th step the pressure is $x_i - \Delta x$, the adsorbed volume of nitrogen $X_{x_i - \Delta x}$, the surface area of the pores which are not completely filled with liquid nitrogen $S_{x_i - \Delta x}$ and the thickness of the adsorbed layer $t_{x_i - \Delta x}$. During the i -th step the desorbed volume is given by:

$$\Delta X_{x_i} = X_{x_i + \Delta x} - X_{x_i - \Delta x} \quad \dots \quad (VI.8)$$

This desorbed volume is formed by:

- the volume originating from the capillary evaporation from the i -th group of pores at the pressure x_i and which is equal to $\frac{1}{2}r_{k_{x_i}} \cdot \Delta S_{x_i}$;
- the decrease of the thickness of the adsorbed layer of this group of pores by lowering the relative pressure from x_i to $x_i - \Delta x$, which is equal to $(t_{x_i} - t_{x_i - \Delta x}) \cdot \Delta S_{x_i}$;
- the decrease of the thickness of the adsorbed layer in the pores, which were already emptied at the relative pressure $x_i + \Delta x$, during the lowering of the pressure to $x_i - \Delta x$, equal to $(t_{x_i + \Delta x} - t_{x_i - \Delta x}) \cdot S_{x_i + \Delta x}$.

Now $S_{x_i + \Delta x}$ is obtained by summing up all contributions ΔS_x of the groups of pores having a width greater than $d_{x_i + \Delta x} \equiv d_{x_{i-1} - \Delta x}$, consequently is $S_{x_i + \Delta x} = \Sigma \Delta S_{x_{i-1}}$. Equation (VI.8) is then transformed into:

$$\Delta X_{x_i} = \frac{1}{2}r_{k_{x_i}} \cdot \Delta S_{x_i} + (t_{x_i} - t_{x_i - \Delta x}) \cdot \Delta S_{x_i} + (t_{x_i + \Delta x} - t_{x_i - \Delta x}) \cdot \Sigma \Delta S_{x_{i-1}} \quad (VI.9)$$

Combination of (VI.9) and (VI.7) gives after reduction:

$$\Delta V_{x_i} = \frac{1}{2}d_{x_i} \cdot \Delta S_{x_i} = R_{x_i} \cdot \Delta X_{x_i} - R_{x_i} \cdot \Delta t_{x_i} \cdot \Sigma \Delta S_{x_{i-1}} \quad \dots \quad (VI.10)$$

in which:

$$R_{x_i} = \frac{d_{x_i}}{r_{k_{x_i}} + 2(t_{x_i} - t_{x_i - \Delta x})}$$

$$\Delta t_{x_i} = t_{x_i + \Delta x} - t_{x_i - \Delta x}$$

With equation (VI.10) it is possible to calculate the pore-size distribution, if the thickness of the adsorbed layer as a function of x is known. In general it is sufficient to give Δx the value of 0.01; only for high x it is better to take the steps smaller and to put $\Delta x = 0.0025$.

VI.4.2 The thickness of the adsorbed layer

SCHÜLL [112] showed that for a number of non-porous solids, the nitrogen adsorption isotherms of which gave no indications of capillary

condensation, the ratio between the adsorbed volume V_a and the volume of the unimolecular layer V_m , if plotted as a function of x could be represented approximately by a single curve. With the aid of this function the thickness of the adsorbed layer as a function of x could be calculated, if for one point of the curve this thickness is known. SCHÜLL supposed that the thickness of a unimolecular layer is equal to the diameter of the nitrogen molecule. Assuming a closest packing of spheres he calculated from the specific volume that this diameter has a value of 4.3 Å. BARRETT, JOYNER and HALENDA [108] adopted SCHÜLL's t -curve to establish the values of t for their method of calculating the pore-size distribution. However, if for the point where V_a equals V_m we put the thickness of the adsorbed layer $t = 4.3$ Å, for a point where $V_a = nV_m$, t equals $4.3n$ Å; the nitrogen molecules are lying above each other. The density of such a layer of adsorbed nitrogen will be lower than that of liquid nitrogen, for which we have assumed a closest packing of spheres. Of course it is impossible to indicate the real density of an adsorbed layer with a thickness of only a few molecules. For the calculation method of BARRETT *et al.*, however, it is indeed essential to assign the same density to the adsorbed layer as to the capillary condensed liquid, which is taken to have the density of normal liquid nitrogen. Therefore it is necessary to use in this case a statistical thickness, which we shall define as:

$$t = \frac{X}{S} \cdot 10^4 \text{ Å} = \frac{M \cdot V_{sp}}{22414} \cdot \frac{V_a}{S} \cdot 10^4 \text{ Å} \quad \dots \quad (VI.11)$$

where:

- t the statistical thickness of the adsorbed layer
- X the adsorbed volume in ml of liquid adsorbate
- S the specific surface area in m²/g of adsorbent
- M the molecular weight of the adsorbate
- V_{sp} the specific volume of the adsorbate in ml/g
- V_a the adsorbed volume of the adsorbate in ml gas STP/g of adsorbent

For nitrogen (VI.11) passes into

$$t = 15.47 \cdot \frac{V_a}{S} \text{ Å} \quad \dots \quad (VI.11a)$$

If we further replace the real surface area S by the surface area calculated by the B.E.T.-method (S_{BET}), we get with (V.11) $S_{BET} = 4.371 \cdot V_m$:

$$t = 3.538 \cdot \frac{V_a}{V_m} \text{ Å} \quad \dots \quad (VI.11b)$$

Consequently, for a unimolecular layer, when $V_a = V_m$, we find $t = 3.54 \text{ \AA}$ instead of $4.3 \text{ \AA}$ as given by SCHÜLL. It will be necessary, therefore, to correct the values given by BARRETT *et al.* [113] by multiplying them by $\frac{3.54}{4.3}$. These corrected values are plotted in FIG. 41 against x (curve denoted as B.J.H.).

CRANSTON and INKLEY [110] also calculated a t -curve from a number of isotherms of other samples. This curve differs considerably from that of BARRETT *et al.*, as appears from FIG. 41 (curve denoted as C.I.): From the adsorption branches of the isotherms of a number of our own samples we calculated the quantity $15.47 \cdot V_a/S_{\text{BET}}$, which is equal to t as long as capillary condensation does not occur. In FIG. 41 we also plotted this quantity as a function of x . Especially at relative pressures higher than 0.6 we observe a large divergence of the values, because capillary condensation gives rise to too high values. As most of our values lie between those of BARRETT *et al.* and those of CRANSTON and INKLEY we preferred to use the lower curve, *i. e.* the B.J.H.-curve for calculating the pore size distribution.

It should be borne in mind that introducing one single t -curve for a number of samples implies that the constant C in equation (V.6a), which varies for the different samples, is replaced by an average constant, independent of the adsorbent.

VI.4.3 The pore-size distributions

FIG. 36, 37, 38 and 39 show the adsorption isotherms of a number of samples. From their desorption branches we calculated the pore-size distributions. Notwithstanding the objections that can be raised against the application of this method at low relative pressures, we continued the calculation down to a relative pressure of 0.08. This pressure mathematically corresponds to a KELVIN radius of about $4 \text{ \AA}$ and a width of about $10 \text{ \AA}$ (assuming slit-shaped pores). Though it is impossible to ascribe the physical significance of capillary condensation to the part of the isotherm below a relative pressure of about 0.3 we can indeed draw qualitative conclusions from this part. TABLE VI.1 records the principal quantities calculated from the pore-size distribution. In FIG. 42a to 45a the volume of the pores with a width smaller than d_x , ($V_p - \Sigma \Delta V_x = V_p - V_{\text{cum}}$), is plotted as a function of d_x ; FIG. 42b to 45b show the surface areas of the pores with a width greater than d_x , ($\Sigma \Delta S_x = S_{\text{cum}}$).

If we compare the pore volume V_p and the B.E.T.-surface area with the corresponding cumulative quantities, we observe that in a number

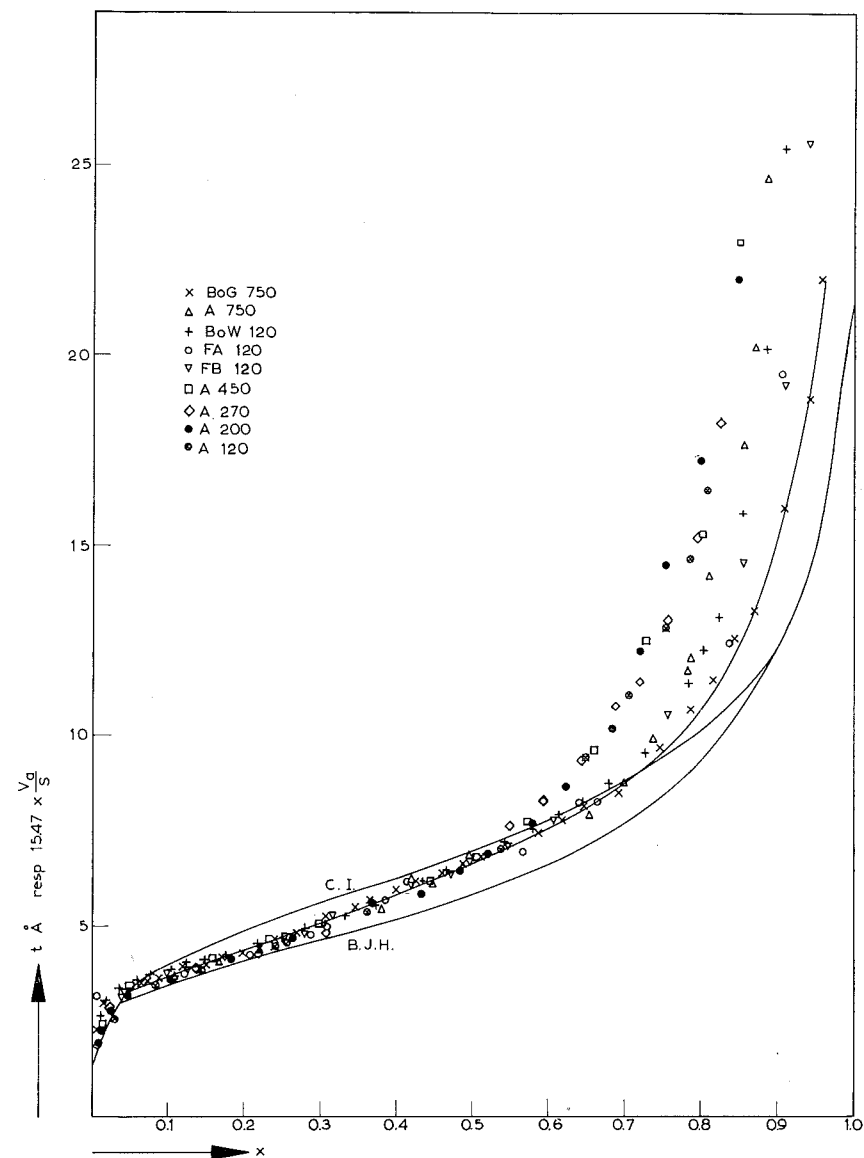


FIG. 41. Comparison of calculated t -values with literature data as a function of the relative pressure x

TABLE VI.1

sample	V_p	S_{BET}	$V_{cum\ 0.3}$	$S_{cum\ 0.3}$	$V_{cum\ 0.08}$	$S_{cum\ 0.08}$	$\frac{S_{cum\ 0.3}}{S_{BET}}$	$\frac{V_{cum\ 0.3}}{V_p}$
gelatinous boehmite								
A 120	1.982	609	2.018	727	2.022	733	1.19	1.02
A 450	2.042	414	2.150	594	2.105	594	1.43	1.03
A 750	1.547	280	1.603	371	1.603	371	1.32	1.04
microcrystalline boehmite								
MiBo 5	0.520	255	0.517	279	0.525	291	1.09	0.99
BoW 120	0.435	64	0.430	73	0.430	73	1.14	0.99
BoW 450	0.494	92	0.480	82	0.487	93	0.89	0.97
well-crystallized boehmite								
BoG 200	0.034	1.5	0.035	2.4	—	—	—	—
BoG 450	0.056	17.1	0.054	12.1	0.056	16.2	0.71	0.96
BoG 580	0.222	65.7	0.185	34.9	0.197	53.3	0.53	0.83
BoG 750	0.139	19.1	0.140	22.4	0.140	22.6	1.17	1.01
bayerite								
By 120	0.068	5.0	0.052	2.6	—	—	—	—
By 200	0.454	26.5	0.450	23.6	0.450	24.2	0.89	0.99
By 250	0.500	489	0.310	34.2	0.363	211	0.07	0.62
By 270	0.495	462	0.310	40.1	0.412	203	0.09	0.63
By 450	0.495	412	0.329	59.5	0.461	260	0.14	0.67
By 580	0.534	245	0.490	194	0.525	243	0.79	0.92
By 750	0.526	134	0.534	162	0.538	168	1.21	1.02

V : ml/g Al_2O_3

S : m^2/g Al_2O_3

of cases the ratio $S_{cum\ 0.3}/S_{BET}$ is greater than 1, whereas $V_{cum\ 0.3}$ is almost equal to V_p .

DE BOER [108] mentioned a number of reasons why S_{cum} may be greater than S_{BET} . Cylindrical pores having a hysteresis loop of type A and satisfying equation (VI.4) may intersect. The volume of the intersections is not bounded by the surface of the solid; however, if we calculate S_{cum} this volume is included, leading to too high values for S_{cum} . Pores with widened parts (type A or type E hysteresis loops) also give too high values for S_{cum} . In that case the volume of the widened part is attributed to pores with a width of the narrower parts. In all these cases it can be expected that S_{cum} lies between once and twice S_{BET} .

Also with pores giving a hysteresis loop of type B, too high values

* $S_{cum\ 0.3}$ gives the cumulative surface area calculated down to a relative pressure of 0.3; the same definition holds for $V_{cum\ 0.3}$ etc.

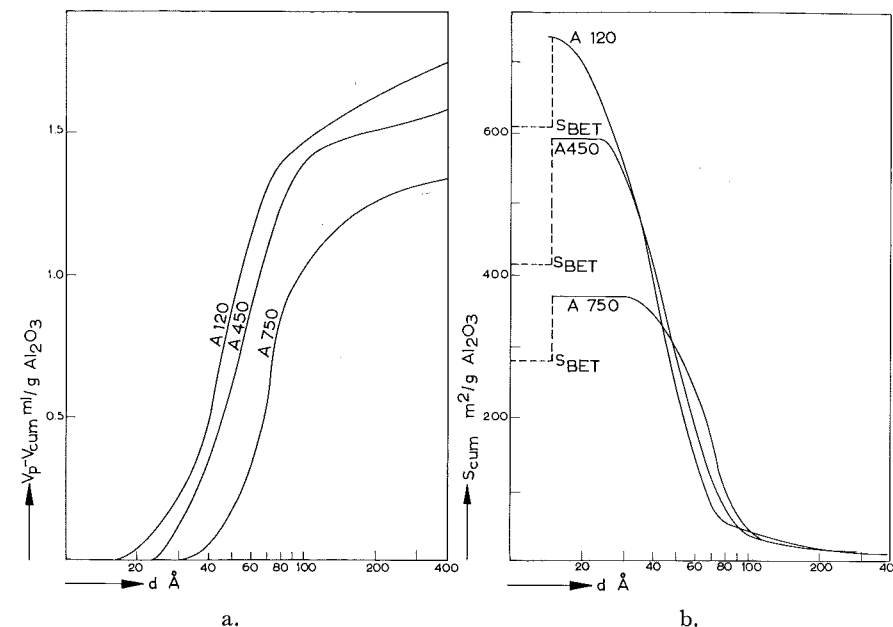


FIG. 42. a. Cumulative pore volume V_{cum} and b. cumulative surface area S_{cum} of heated gelatinous boehmite (A) as a function of pore width d

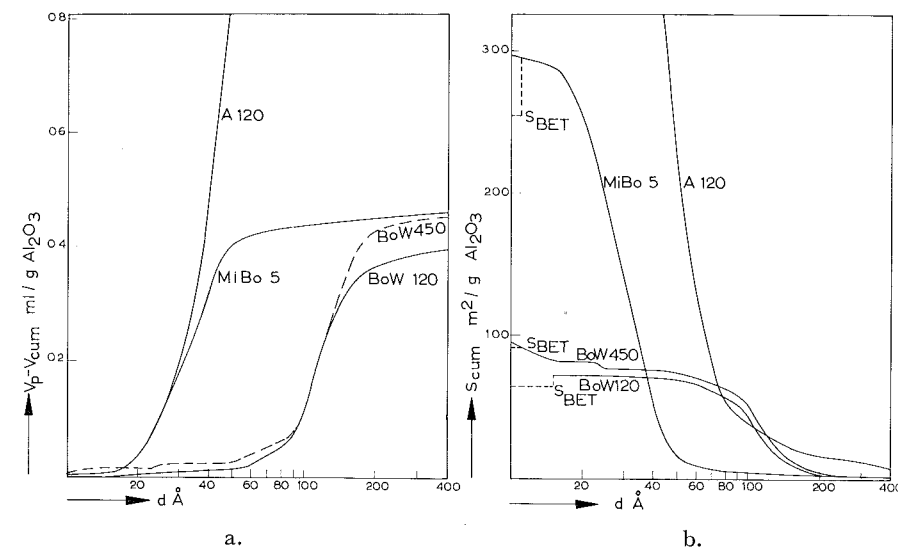


FIG. 43. a. Cumulative pore volume V_{cum} and b. cumulative surface area S_{cum} of microcrystalline boehmite

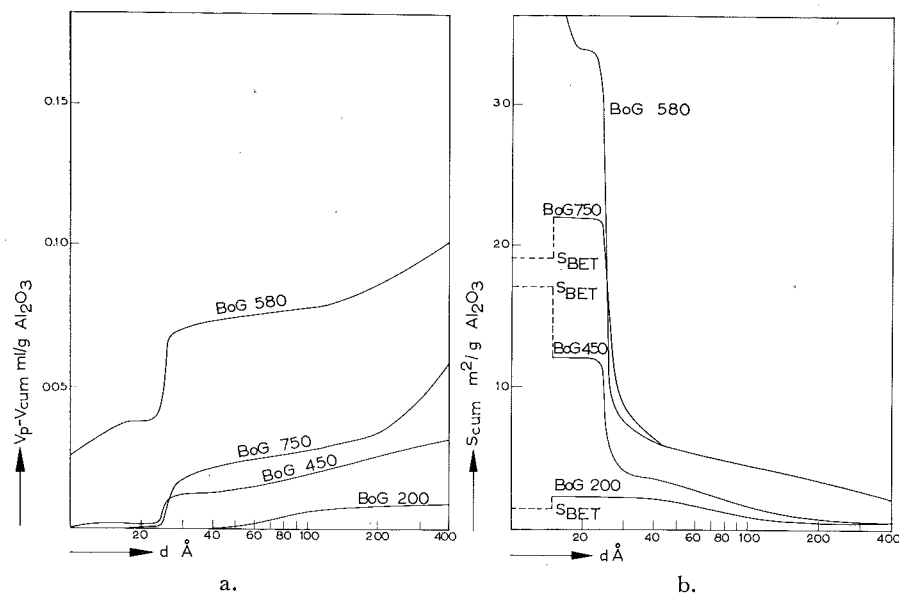


FIG. 44. a. Cumulative pore volume V_{cum} and b. cumulative surface area S_{cum} of heated well-crystallized boehmite BoG

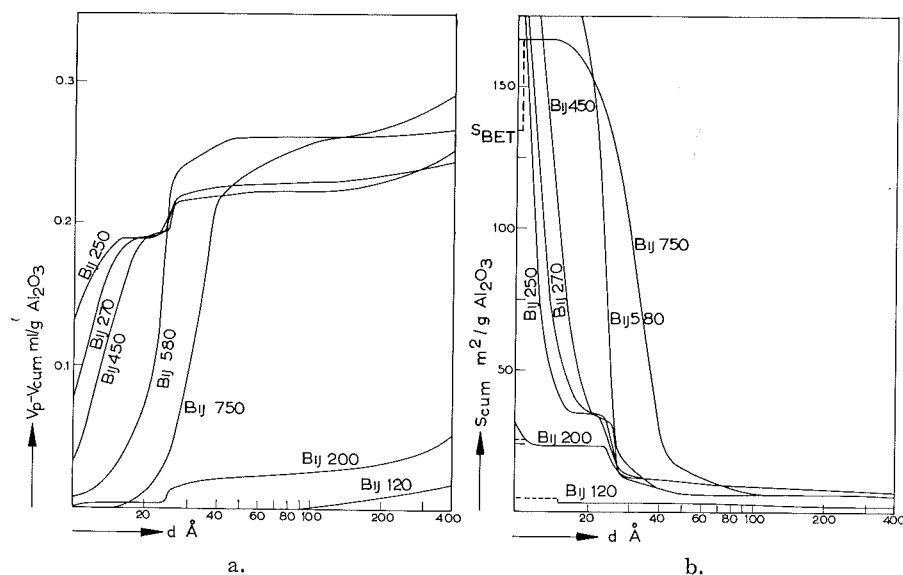


FIG. 45. a. Cumulative pore volume V_{cum} and b. cumulative surface area S_{cum} of heated bayerite Bij

for S_{cum} can be obtained, viz. in the case of large pores with narrow openings. A typical example of the latter phenomenon is mentioned by DE BOER *et al.* [58] for a gibbsite sample heated at 200 °C. While the B.E.T.-surface area amounted to 1.3 m^2/g , a value of about 40 m^2/g was calculated for S_{cum} from the desorption branch.

For our samples it appears that in nearly all cases in which the ratio $S_{cum\ 0.3}/S_{BET}$ is greater than 1, the hysteresis loop is of type A or type E. Only sample BoG 750 belongs to type B. Moreover, in all these cases the cumulative quantities calculated down to a relative pressure of 0.3 are almost equal to those calculated down to 0.08. Pores narrower than ca. 17 Å therefore do not occur.

For the other samples $S_{cum\ 0.3}$ is smaller than S_{BET} , sometimes even very much smaller. Even $S_{cum\ 0.08}$ is often smaller than S_{BET} . The same holds for the volumes. These samples apparently contain a number of narrow pores, the size distribution of which may certainly not be calculated on the basis of the KELVIN equation. This kind of pores appears to originate mainly during the dehydration of the crystalline compounds. Qualitatively it can be stated that these pores grow wider as the heating temperature is higher.

STEGGERDA [35] tried to calculate the mean width of the narrow pores ($\bar{d}_n$) in his samples obtained by the heating of gibbsite. To this end he used the difference between the measured pore volume and B.E.T.-surface area on the one hand and the corresponding cumulative quantities calculated up to a relative pressure of 0.3 on the other hand with the equation:

$$\bar{d}_n = 2 \cdot \frac{V_p - V_{cum\ 0.3}}{S_{BET} - S_{cum\ 0.3}} \quad \dots \dots \dots (VI.12)$$

This method is more real than one assuming in such narrow pores a liquid meniscus with a radius smaller than twice the diameter of the adsorbate molecules. It should be noted, however, that all systematic differences between the cumulative quantities and their real values are included when equation (VI.12) is applied. In the next paragraph we shall try to obtain an idea of the volume and the width of these narrow pores by a method independent of the cumulative quantities.

VI.5 The pore width calculated from the adsorption branch of the isotherms

VI.5.1 Adsorption in slit-shaped pores

From the KELVIN equation it follows that in slit-shaped pores (with

plan-parallel walls) capillary condensation cannot occur, because the two main radii of curvature of a liquid on a flat surface (assuming complete wetting) are infinitely large. If, however, the pores are completely filled a curved liquid surface can be formed, which has the shape of a half-cylinder mantle. If the wall separation is equal to d , the KELVIN radius of the liquid surface is also equal to d . Desorption will occur only at a relative pressure given by $\ln x = \frac{-2\sigma V \cos \psi}{RT \cdot d}$. The hysteresis loop

has the shape of that of type B, *i.e.* two almost parallel horizontal branches, a vertical adsorption branch at a relative pressure $x = 1$ and a vertical desorption branch at a lower relative pressure.

Reasoning like this we have not accounted for the multimolecular adsorption on the surface of the pores. For the cylindrical pores of type A or type E the adsorption on their surface has relatively little influence on the shape of the hysteresis loop (see VI.3.1). For slit-shaped pores this influence is much more pronounced. As long as the multimolecular adsorption in the pore is unhindered, the adsorption branch will have the shape of the normal t -curve (FIG. 41). If the pressure increases, the free space in the pore becomes smaller owing to the growth of the adsorbed layer. At a certain moment the pore is completely filled by the adsorbed layer on both parallel walls. Further adsorption in the pore is then impossible. We shall assume that this point is reached when the statistical thickness t of the adsorbed layer is equal to half the width d of the pore. When the pore is completely filled up, at a high relative pressure, a liquid meniscus has formed. If now the pressure is decreased, desorption will occur only at a lower relative pressure, because one of the radii of curvature has obtained a finite value.

FIG. 46 shows the shape of a hysteresis loop of this type (type B') for slit-shaped pores with a width of about 25 Å. This shape resembles very much that of type E. The difference between these two types is that on the adsorption branch of type E capillary condensation occurs, whereas on that of type B' it does not. It is therefore important to know if and when capillary condensation occurs on the adsorption branch.

VI.5.2 The t -curve of nitrogen adsorbed on aluminium hydroxide and oxide

In FIG. 41 we have drawn a curve through the values of the quantities $15.47 \cdot V_a/S_{\text{BET}}$ of our samples, which can be considered their t -curve. To verify this curve we compared it with those of BARRETT *et al.* and CRANSTON and INKLEY by plotting the t -values against each other at the same relative pressure (FIG. 47). It now appears that up to a relative pressure of ca. 0.86 there is an almost rectilinear relation between the

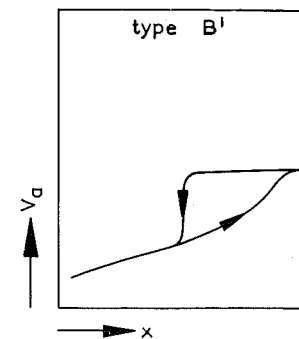


FIG. 46. Type B' hysteresis loop

t -values found for our samples and those of BARRETT *et al.* This strengthens our opinion that the experimental t -curve of our samples indeed gives only the thickness of the absorbed layer and is not disturbed by capillary condensation or blocked pores. Moreover, it is clear that the values of CRANSTON and INKLEY, which are mean values of measurements on substances of very divergent nature, are not suitable for our samples. Our experimental values for the thickness of the adsorbed layer on aluminium hydroxide and oxide [at the various relative pressures up to 0.86 are represented in TABLE VI.2.

TABLE VI.2 Experimental thickness t of the multimolecular layer adsorbed on aluminium hydroxides and oxides

p/p_0	t Å	p/p_0	t Å	p/p_0	t Å	p/p_0	t Å	p/p_0	t Å
0.08	3.51	0.24	4.62	0.40	5.71	0.56	6.99	0.72	8.91
0.10	3.68	0.26	4.75	0.42	5.86	0.58	7.17	0.74	9.27
0.12	3.83	0.28	4.88	0.44	6.02	0.60	7.36	0.76	9.65
0.14	3.97	0.30	5.01	0.46	6.18	0.62	7.56	0.78	10.07
0.16	4.10	0.32	5.14	0.48	6.34	0.64	7.77	0.80	10.57
0.18	4.23	0.34	5.27	0.50	6.50	0.66	8.00	0.82	11.17
0.20	4.36	0.36	5.41	0.52	6.66	0.68	8.26	0.84	11.89
0.22	4.49	0.38	5.56	0.54	6.82	0.70	8.57	0.86	12.75

VI.5.3 Analysis of the adsorption branch with the aid of the t -curve

According to the preceding three cases can occur during adsorption on a porous material, which determine the shape of the adsorption branch of the isotherm, *viz.*:

- the surface is freely accessible up to high relative pressures; the multimolecular layer can form unhindered on all parts of the surface; the adsorption branch has entirely the shape of the t -curve;
- at a certain pressure capillary condensation will occur in pores of certain shapes and dimensions; the material takes up more adsorbate than corresponds to the volume of the multimolecular layer; the adsorption branch lies above the t -curve;
- slit-shaped pores (or other pores in which no capillary condensation will take place) get filled at a certain pressure by the multimolecular

layer; the pores are closed and the surface is no longer accessible; above this relative pressure the adsorption branch drops below the t -curve.

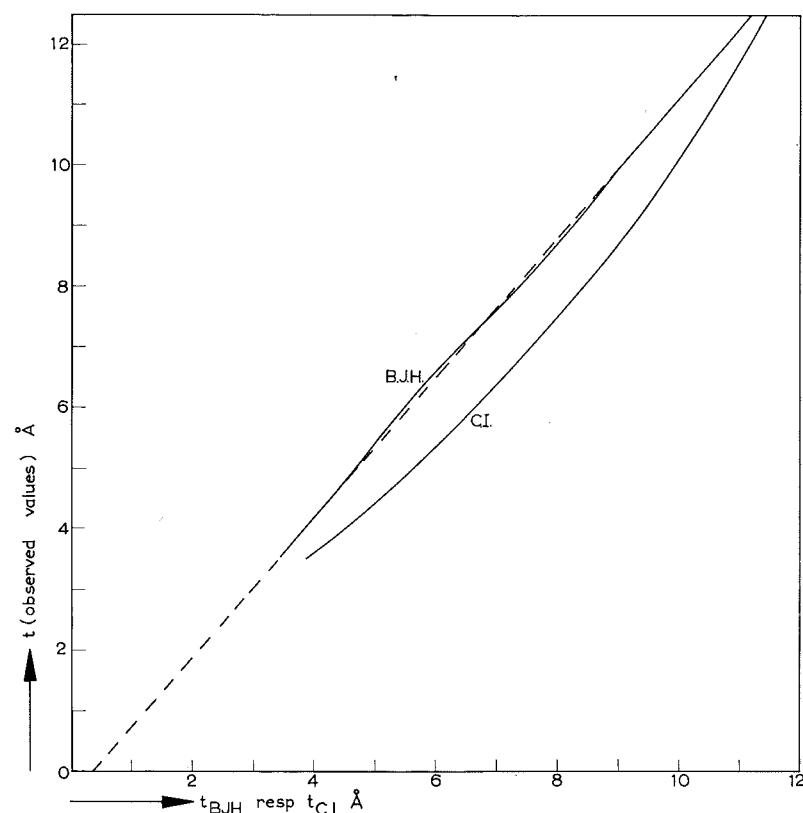


FIG. 47. Mutual comparison of t -values observed on aluminium hydroxide and oxide with literature data (B.J.H. according to BARRETT *et al.* [113]) C.I. according to CRANSTON and INKLEY [110])

By plotting the adsorbed volume V_a as a function of t with the aid of TABLE VI.2, these three cases can be clearly demonstrated. As long as no disturbances occur in the formation of the adsorbed multimolecular layer, a straight line is obtained according to equation (VI.11a). This straight line will go through the origin and its slope is a measure of the surface area:

$$S = 15.47 \cdot V_a / t.$$

The surface area calculated in this way will not be exactly equal to

S_{BET} , while, as was already stated in VI.4.2, instead of the various C -values in the B.E.T.-equation (depending on the sample) an averaged value is used by introducing the t -curve. We shall indicate the surface area calculated with equation (VI.11a) by S_t .

A further consequence of averaging the C -values is that at lower relative pressures, where the influence of the C -value on the shape of the isotherm is largest, noticeable deviations from the straight line through the origin may sometimes occur. We have therefore applied the t -curve only to the measuring points at relative pressures above 0.08; for those few cases in which the beginning of the V_a - t -curve was not completely a straight line, we drew the tangent from the origin to the curve and calculated S_t from the slope of the tangent (see *e.g.* curve By 450 in FIG. 50).

FIG. 48, 49 and 50 show the measured values of V_a for a number of our samples as functions of t . The three cases a, b and c clearly stand out. All samples consisting of sheet-like gelatinous boehmite (A 120, *etc.*, FIG. 48 and TABLE VI.3) show capillary condensation at a relative pressure lower than that corresponding to the beginning of the hysteresis loop (see FIG. 39). DE BOER [108] pointed out already that this reversible

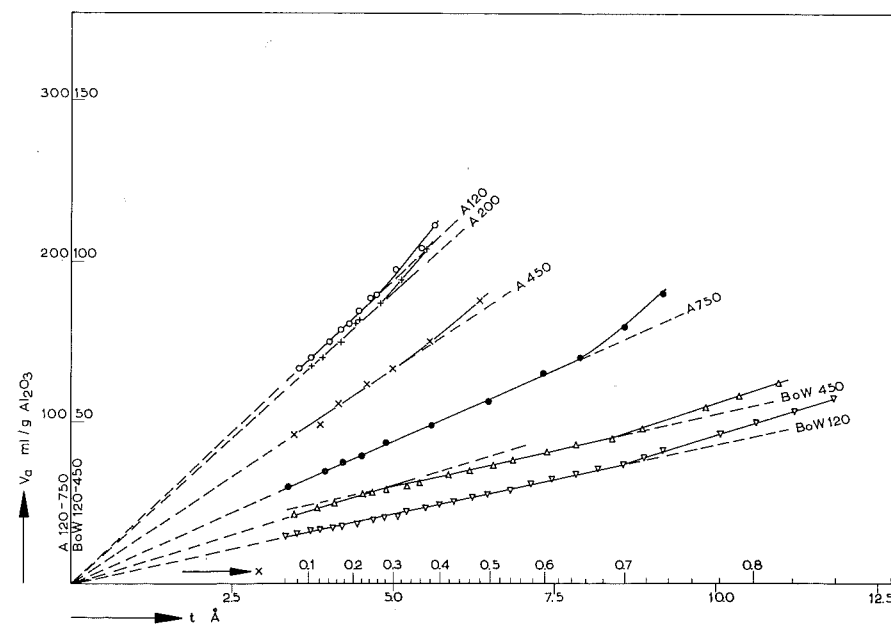


FIG. 48. V_a - t -plot of A- and BoW-preparations

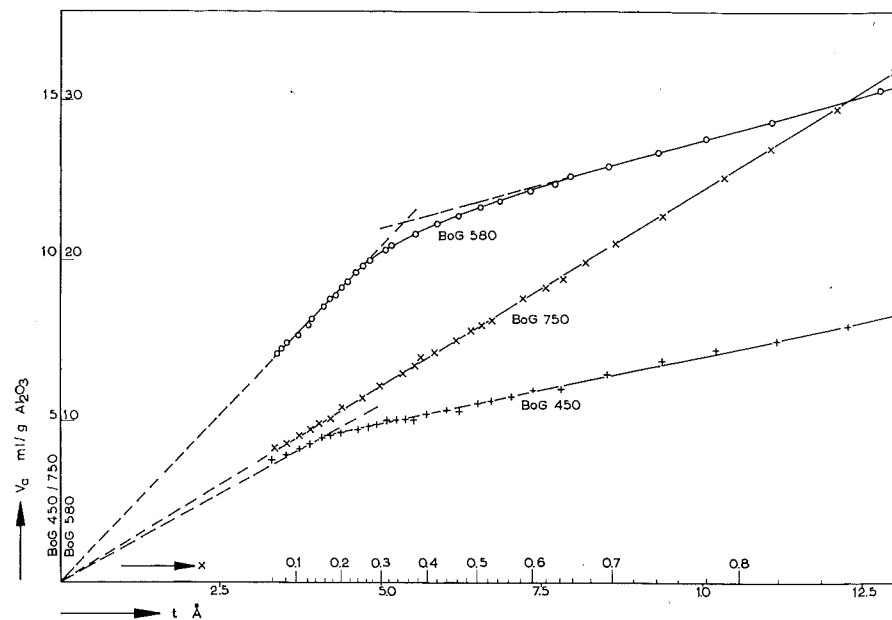


FIG. 49. V_a - t -plot of BoG-preparations

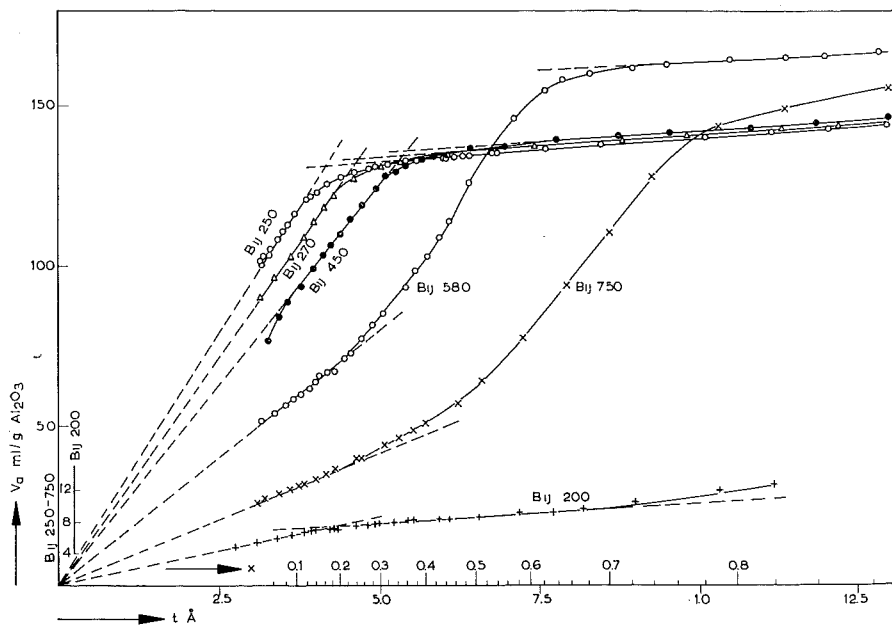


FIG. 50. V_a - t -plot of By-preparations

capillary condensation can take place in the cones and wedges formed *e.g.* by the planes of crystals touching each other. For sample A 750 the beginning of the capillary condensation almost coincides with that of the hysteresis loop; at a temperature of 750 °C a noticeable sintering has already occurred, as was concluded from the decrease of the surface area in FIG. 35 (see CHAPTER V); the sharp edges are apparently rounded by this sintering. The same conclusion has already been drawn from the changes of the shape of the desorption isotherms (see VI.3.2).

TABLE VI.3

sample	S_{BET}	S_t	S_w'	p/p_0 at the beginning of cap. cond.	p/p_0 at the beginning of hysteresis
A 120	609	586	—	0.26	0.40
A 200	580	568	—	0.26	0.40
A 450	414	409	—	0.34	0.51
A 750	280	275	—	0.63	0.63
BoW 120	64.0	65.6	—	0.70	0.76
BoW 450	92.1	93.5	68.0	0.70	0.40

Sample BoW 120, consisting of small crystals, shows a straight line up to a relative pressure of about 0.70; the surface is completely formed by the outer surface of the crystals, as was proved in CHAPTER V. Heating this sample at 450 °C gives sample BoW 450. The V_a - t -curve of the latter shows two breaks, one at a relative pressure of about 0.26, the other at 0.70. The first break must apparently be explained by pores being closed by the adsorbed layer. Assuming that this will occur when the thickness of the adsorbed layer is equal to half the width d of the narrow pores, we find from TABLE VI.2 for this width a value of $2 \cdot 4.75 = 9.5$ Å. From the slope of the second part of the V_a - t -curve we can calculate that the surface area of the wide pores, S_w' amounts to 68.0 m²/g Al₂O₃.

Capillary condensation in this sample BoW 450 occurs only at a relative pressure of 0.7, whereas the hysteresis loop closes at a relative pressure of 0.4. This points to the presence of pores of type B or type B' (large pores with openings of about 25 Å or slit-shaped pores with a width of about 25 Å), where "capillary retention" is observed. The course of the curve BoW 450 in FIG. 43b, at 25 Å, indicates that from the pore-size distribution a surface area of about 5 m²/g can be calculated for these pores. For the outer surface of the crystals of this sample we then find a value of 63 m²/g, which is somewhat lower than that of the non-heated sample BoW 120 (TABLE VI.3). For BoW 450 capillary con-

densation starts at the same relative pressure as for BoW 120 (FIG. 38); the two curves have the same slope above this relative pressure. Therefore, apparently nothing has changed in the outer shape of the particles.

During the heating of the well-crystallized hydroxides (BoG and By) also narrow pores are formed, as follows from the V_a - t -curves, which disappear again on heating at still higher temperatures (FIG. 49 and 50, TABLE VI.4). For samples having a hysteresis loop of type B or B'

TABLE VI.4

sample	SBET	S_t	S_w'	p/p_0 at the beginning of cap. cond. hysteresis	
BoG 450	17.1	17.2	5.1	0.86	0.46
BoG 580	65.7	65.0	17.2	0.86	0.44
BoG 750	19.1	19.1	19.1	0.86	0.48
By 200	26.5	26.6	8.7	0.7	0.47
By 250	489	483	20.1	0.86	0.46
By 270	462	440	20.6	0.86	0.47
By 450	412	386	21.5	0.86	0.48
By 580	245	243	(243)	0.24	0.42
By 750	134	127	(127)	0.24	0.46

capillary condensation starts again at a relative pressure much higher than that at which the hysteresis loop is closed. The cumulative surface area calculated from the desorption branch of the isotherm is always greater than the surface area S_w' of the wide pores calculated from the second part of the V_a - t -curve. So we may conclude that in these cases we are dealing with wide pores with narrow openings (of about 25 Å). The complete absence of capillary condensation at relative pressures up to 0.86 on the adsorption branch indicates, that either the volume of the "openings" of the wide pores is negligibly small, or the openings are formed by slit-shaped pores. In view of the crystallographic properties of these materials the last supposition is the most probable one.

Samples By 580 and By 750 apparently have a completely different pore structure. The wide pores are still present but other pores have a shape in which capillary condensation on adsorption is possible. Consequently severe sintering must have occurred, by which the slit-shaped character of the pores has largely disappeared.

With the aid of the electron microscope this sintering can be clearly observed on samples of bayerite heated at higher temperatures. Though the original cleavage plane of the material heated to 750 °C can yet clearly be observed (PLATE XXIII), recrystallization to small rod-shaped

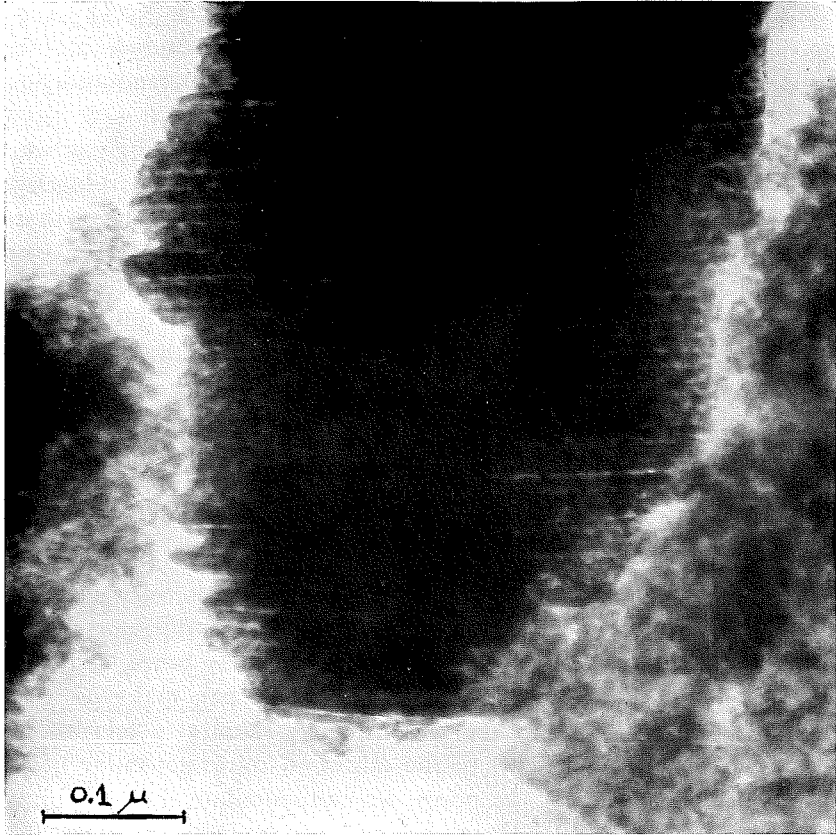


PLATE XXIII. Pore system in η -alumina from bayerite heated to 750 °C

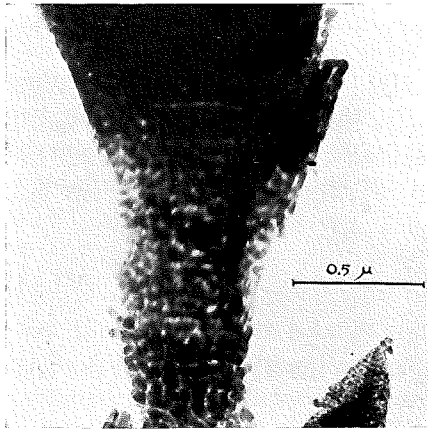


PLATE XXIV. Pore system in θ -alumina from bayerite heated to 980 °C

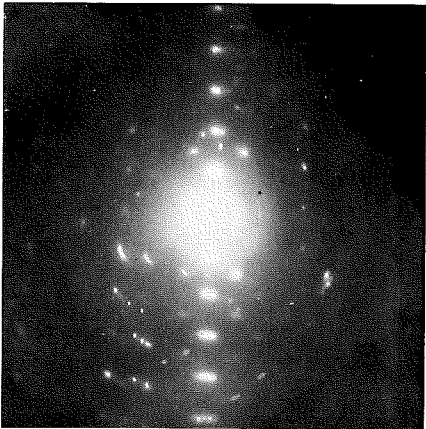


PLATE XXV. Diffraction pattern of XXIV

crystals has occurred at a temperature of 980 ° (PLATE XXIV). From their diffraction pattern (PLATE XXV) it can be concluded that these rod-shaped crystals are still somewhat orientated, but pseudomorphism is no longer complete.

In this connection the work of DE BOER, STEGGERDA and ZWIETERING [58] should be mentioned. From measurements of the optical birefringence of heated gibbsite crystals they arrived at the conclusion that at lower temperatures slit-shaped pores are formed, which are separated by plate-like particles parallel to each other and perpendicular to the *c*-axis of the original gibbsite. At higher temperatures, however, rod-like particles are formed which are perpendicular to the *c*-axis of the original gibbsite and parallel to each other. They also observed a marked change in the shape of the adsorption isotherms of their samples. These optical observations give a picture analogous to that we developed for the dehydration products of bayerite.

VI.5.4 The volume of the narrow pores

Although the surface area of the narrow pores is very large (for By 250 almost 96 % of the total surface area!) its significance is rather limited. Much more important is the volume of these pores, as it determines the maximum amount of adsorbate which can make use of the surface. Assuming slit-shaped pores completely filled at a relative pressure for which the thickness *t* of the adsorbed multimolecular layer is equal to the half width of the pores, we can calculate their volume *V_n* from the surface area *S_n* of these narrow pores and the thickness of the adsorbed layer:

$$V_n = S_n \cdot t \dots \dots \dots (VI.13)$$

It appears from FIG. 49 and 50 that also in these cases we are dealing with a distribution of pore dimensions; the break between the two straight parts of the *V_a*-*t*-curve does not occur abruptly but via a curved line. For each point of this line the surface area that is still available is given by:

$$S = 15.47 \cdot \frac{dV_a}{dt} \dots \dots \dots (VI.14)$$

In (VI.14) $\frac{dV_a}{dt}$ is the slope of the tangent to the *V_a*-*t*-curve in the considered point.

To calculate the total volume of the narrow pores we divide the *V_a*-*t*-curve into *j* steps, each corresponding to an increase of 2Δ*t* in the

thickness of the multimolecular layer. At the beginning and the end of such a step we draw the tangent to the curve, determine its slope and calculate the corresponding surface area with the aid of equation (VI.14). The difference between the surface area at the beginning and that at the end of the *j*-th step, Δ*S_j*, represents the surface area of the group of pores having a width between 2(*t_j* - Δ*t*) and 2(*t_j* + Δ*t*). If we assume that the mean width of the pores of this group is equal to 2*t_j*, the volume of these pores is given by:

$$V_j = t_j \cdot \Delta S_j$$

The total volume *V_n* of the narrow pores then is:

$$V_n = \Sigma \Delta V_j = \Sigma t_j \cdot \Delta S_j \dots \dots \dots (VI.15)$$

For the samples containing narrow pores we calculated these volumes *V_n* and compared them with those calculated from the desorption branch of the isotherms (TABLE VI.5). For the latter volumes we took the

TABLE VI.5

sample	<i>S_t</i>	<i>S_n</i>	<i>V_n</i>	<i>V_p</i> - ΣΔ <i>V_{loop}</i>	<i>d_n</i>
BoG 450	17.2	12.1	0.0051	0.0020	8.4
BoG 580	65.0	47.8	0.0260	0.0380	10.9
BoW 450	93.5	25.5	0.0121	0.0146	9.5
By 200	26.6	17.9	0.0075	0.0004	8.4
By 250	483	463	0.1965	0.1907	8.5
By 270	440	419	0.1972	0.1914	9.4
By 450	386	386	0.1982	0.1930	10.9

difference between the total pore volume and the cumulative pore volume calculated up to the relative pressure at which the hysteresis loop closes (*V_p* - ΣΔ*V_{loop}*). Moreover, we calculated the mean width *d_n* of the narrow pores with:

$$\bar{d}_n = \frac{2V_n}{S_n}$$

For the samples with a large volume of narrow pores (By 250, By 270 and By 450) there is a good agreement between the volume *V_p* - ΣΔ*V_{loop}* calculated from the desorption branch and the volume calculated from the adsorption branch with the aid of equation (VI.15). For the other samples there is much less agreement; the systematic errors in the calculation from the desorption branch make themselves felt especially

for these small differences. According to the expectation the pore widths appear to increase on heating.

Finally we shall make some more remarks on sample BoG 750. The V_a - t -curve is completely straight, up to a relative pressure of 0.86. Partly this is trivial: the adsorption branch of this sample largely determined the shape of our t -curve. However, the fact that for a number of other samples also at high relative pressures a straight line is found in the V_a - t -curve, as well as our conclusions in VI.5.2, make it acceptable, that in this sample the multimolecular layer can indeed form unhindered up to this high relative pressure. This means that the pores are at least 25 Å wide. Now it follows from the pore-size distribution (FIG. 44), calculated from the desorption branch, that there exist pores with a width of 25 Å. Moreover, the ratio $S_{cum\ 0.3}/S_{BET}$ is but little greater than 1. The other BoG samples all contain a number of wide pores with openings of 25 Å, so that it is probable that such pores also exist in BoG 750. We can assume two extremes:

- the pore openings of 25 Å have a negligibly small surface area; in that case the wide pores must have widths not much greater than those of the openings, whilst moreover capillary condensation on adsorption may not occur at a relative pressure of 0.86 (r_k = ca. 63 Å);
- the wide pores are so great that their surface area hardly counts; in this case the greater part of the surface area is in the pores with a width of 25 Å.

In both cases we arrive at the conclusion that sample BoG 750 must contain a considerable amount of slit-shaped pores with a width of 25 Å or a little greater.

VI.5.5 The adsorption of lauric acid in samples with narrow pores

In CHAPTER V (TABLE V.1 and V.2) we concluded that in a number of samples the specific adsorption of lauric acid f (in mmole per 100 m² surface area) is considerably lower than calculated. According to the conception of STEGGERDA [35] such samples must contain narrow pores in which lauric acid cannot penetrate. Since, in the preceding, we could determine quantitatively the presence of narrow pores, we are able to obtain more data about the adsorption of lauric acid in these pores.

We shall assume that in the wide pores 0.617 mmole lauric acid can be adsorbed per 100 m² of B.E.T.-surface area (this value corresponds to the value of 26.9 Å² derived by HOUBEN [82] for the specific surface of the lauric acid molecule adsorbed on alumina). We can then calculate the amount of lauric acid adsorbed on the surface of the wide pores.

The excess amount of lauric acid is adsorbed in the narrow pores. TABLE VI.6 gives the results.

TABLE VI.6

sample	S_{BET}	S_t	S_w'	S_n	V_n	lauric acid adsorption		
						L.A. _{tot}	L.A. _w	L.A. _n
By 200	26.5	26.6	8.7	17.9	0.0075	0.082	0.054	0.028
By 250	498	483	20.1	463	0.1965	0.998	0.124	0.874
By 270	462	440	20.6	419	0.1972	0.994	0.127	0.867
By 450	412	386	21.5	364	0.1982	0.003	0.132	0.871
BoG 450	17.1	17.2	5.1	12.1	0.0051	0.055	0.032	0.023
BoG 580	65.7	65.0	17.2	47.8	0.0260	0.219	0.106	0.113
	m ² /g Al ₂ O ₃				ml/g Al ₂ O ₃	mmole/g Al ₂ O ₃		

To describe the texture use has been made of the characterization of the hysteresis loops according to DE BOER and of the pore-size distributions calculated from the desorption branches of the isotherms with the aid of the KELVIN equation.

The sheet-like gelatinous boehmite (A) shows a hysteresis loop that can be described as intermediate between the types A and E. This is in agreement with the picture, developed in the preceding chapters, *viz.* that it is built up from sheets with a porous, felty structure. The change on heating of the hysteresis loop to type A could be explained by the smoothening of the surface as a result of the disappearance of sharp angles and edges. The pore-size distribution curves confirm that during the formation of microcrystalline gelatinous boehmite from sheet-like gelatinous boehmite, the sheets of the latter are broken down, whereas the boehmite crystallites recrystallize.

On heating of the crystalline hydroxides it appears that besides pores giving a hysteresis loop of type B, also a number of narrow pores is formed in which capillary condensation cannot occur.

The shape of the hysteresis loop of slit-shaped pores in which also multimolecular adsorption exists was derived. This gave a new type of hysteresis loops, type B', which is intermediate between type E and type B. The desorption branches of these three types have the same shape, the adsorption branches are different.

To distinguish between these types in the experimental isotherms we have made a closer investigation of the adsorption branch of the isotherms by means of the experimental *t*-curve. In this way we succeeded in estimating the surface area and the volume of the narrow pores, in which capillary condensation cannot occur (and for which the calculation of the pore-size distribution by the KELVIN equation would give incorrect results).

By comparing the surface area of the wider pores calculated from the adsorption branch with that from the desorption branch, it could be ascertained that, for products made by heating well-crystallized boehmite, only for sample BoG 750 these wider pores will be slit-shaped. For the other samples with a type B loop they are wide cavities with (probably slit-shaped) openings of about 25 Å.

By a systematic comparison of the adsorption and desorption branches of the isotherms of heated bayerite it appeared that the formation of the pores in this case takes place in about the same way as found by STEGGERDA for gibbsite with optical measurements. At a lower temperature at first slit-shaped pores are formed between plan-parallel plates; at a higher temperature (for bayerite between 450 and 580 °C)

a sintering phenomenon starts giving finally rise to formation of short rod-shaped particles.

Contrary to the view of STEGGERDA lauric acid can also be adsorbed in narrow pores. In that case the hydrocarbon chains are no longer in upright position, but they lie almost flat on the surface. So much lauric acid can be adsorbed in these narrow pores that their total volume is filled up.

TEXTURE OF η - AND γ -ALUMINAVII.1 The skeleton of the solid material of η - and γ -aluminaVII.1.1 The skeleton of η -alumina from bayerite, formed at temperatures below 500 °C

In the preceding chapter we have shown that in η -alumina obtained at temperatures below about 500 °C a group of wide pores is formed with a specific surface area of about 20 m²/g Al₂O₃ and with openings of about 25 Å width, and a group of narrow pores with a volume up to about 0.2 ml/g Al₂O₃ and a width of 8.5 to 11 Å. The volume of the former group cannot be given exactly; according to the boundary that will be chosen between the pores and the intergranular space it varies from 0.07 to 0.3 ml/g Al₂O₃. Likewise the specific surface area of the narrow pores cannot be determined with certainty (it depends on the dimensions of the "measuring device", in this case the nitrogen molecule), but it is certainly greater than 350 to 400 m²/g Al₂O₃. The absence of capillary condensation on the adsorption branch of the isotherm up to high relative pressures has been taken as an indication of the slit-like nature of the wide pores, while for crystallographic reasons we also described the narrow pores as being slit-shaped.

We shall now try to obtain an impression of the skeleton of the solid material. To this end we shall have to know the volume of the granules (V_k). In general it can be assumed that the granular volume V_k is equal to the sum of the specific volume of the solid itself (V_{sp}) and the volume of the intragranular space (V_i). The pore volume V_p , as we have defined in the preceding chapter (the total volume of nitrogen adsorbed at a relative pressure of 0.999 on the desorption branch) includes an important part of the intergranular space, too.

To be able to calculate V_i we have arbitrarily assumed that the cumulative pore volume, calculated from the desorption branch at a relative pressure greater than 0.9, only corresponds to the intergranular space and below this pressure only to the intragranular volume. We then obtain:

$$V_i = V_p - V_{0.9}$$

In the same way we find the surface area of the intragranular space

$$S_i = S - S_{0.9}$$

in which $V_{0.9}$ and $S_{0.9}$ is given by the cumulative pore volume and surface area for relative pressures above 0.9.

The mean width ($\bar{d}_b$) of the group of wide pores (having opening widths d_m of about 25 Å) can then be calculated from:

$$\bar{d}_b = 2 \frac{V_b}{S_b} = 2 \frac{V_i - V_n}{S_i - S_n} \quad \dots \dots \dots \text{(VII.1)}$$

in which S_n and V_n represent the specific surface area and the volume of the narrow pores respectively (see CHAPTER VI), and S_b and V_b those of the wide pores. (The quantity S_w' , applied in the preceding chapter, is equal to $S_b + S_{0.9}$).

The mean distance between the wide pores ($\bar{D}_b$) is calculated from:

$$\bar{D}_b = \frac{V_k}{V_b} \cdot \bar{d}_b = 2 \frac{V_{sp} + V_i}{S_b} \quad \dots \dots \dots \text{(VII.2)}$$

The mean width of the narrow pores has been calculated in CHAPTER VI ($\bar{d}_n$); their mean distance ($\bar{D}_n$) is given by:

$$\bar{D}_n = \frac{V_k - V_b}{V_n} \cdot \bar{d}_n = 2 \frac{V_k - V_b}{S_n} = 2 \frac{V_{sp} + V_n}{S_n} \quad \dots \dots \dots \text{(VII.3)}$$

If we apply equations (VII.1) and (VII.2) to sample By 200 we find $\bar{d}_b = 117$ Å and $\bar{D}_b = 3900$ Å. From the dimensions of the bayerite particles (length 1 to 10 μ , breadth some tenths of a μ) it follows, that a granule can contain only few of these pores. As the mean width of these pores is more than four times the width of the openings (25 Å), it follows that these pores have to be considered as "holes" in the particles. OOMES [115] ascertained that for gibbsite the formation of such holes (which are still much wider with gibbsite than with bayerite, as was found by STEGGERDA [35, 58]) corresponds with the formation of well-crystallized boehmite under intragranular hydrothermal conditions. Probably this will be the case also for bayerite.

If we now calculate $\bar{d}_b$ for sample By 250, we find 50 Å, so much lower than for By 200. It seems very improbable that the wide holes formed at 200 °C will have narrowed to such an extent at 250 °C. The decrease must have been caused by the formation of a number of new and narrower pores. Therefore we shall divide the group of wide pores with openings of 25 Å into two sub-groups, the first consisting of pores

formed during the formation of boehmite, which we have described as holes; the other being pores with openings of 25 Å formed besides the narrow pores during the dehydration.

Distinguishing the quantities of this sub-division with the indices h (holes) and w (wide) we arrive at:

$$\bar{d}_h = \frac{2V_h}{S_h} \quad \bar{D}_h = \frac{2V_k}{S_h} = 2 \frac{V_{sp} + V_i}{S_h} \dots \dots \dots \text{(VII.4a)}$$

$$\bar{d}_w = \frac{2V_w}{S_w} = 2 \frac{V_b - V_h}{S_b - S_h} \quad \bar{D}_w = 2 \frac{V_k - V_h}{S_w} = 2 \frac{V_{sp} + V_n + V_w}{S_w} \dots \text{(VII.4b)}$$

$$\bar{d}_n = \frac{2V_n}{S_n} \quad \bar{D}_n = 2 \frac{V_k - V_b}{S_n} = 2 \frac{V_{sp} + V_n}{S_n} \dots \dots \text{(VII.4c)}$$

If we assume that the shape and size of the holes formed at 200 °C (the end of the formation of boehmite) does not change on heating at a higher temperature, we find for all samples:

$$\begin{aligned} V_h &= 0.0188 \text{ ml/g Al}_2\text{O}_3 & \bar{d}_h &= 117 \text{ Å} \\ S_h &= 3.2 \text{ m}^2/\text{g Al}_2\text{O}_3 & \bar{D}_h &= 3900 \text{ Å} \end{aligned}$$

With equations (VII.4) we have calculated the values of the different texture quantities (TABLE VII.1) for samples By 250, 270 and 450. It is remarkable in all three cases approximately the same value is found for $\bar{d}_w$. The mean value for the three samples is 22 Å. The pore openings have a width of 25 Å; consequently these pores appear to be slit-shaped! The number of these pores is small, however (maximum 12 pores per μ). The number of narrow pores is very large: about 400 per μ .

TABLE VII.1 Texture quantities of η -alumina from bayerite below 500 °C

sample	V_i	V_{sp}	V_k	V_b	V_w	V_n	S_b^{**}	S_w	S_n	$\bar{d}_w$	$\bar{d}_n$	$\bar{D}_w$	$\bar{D}_n$
By 200*	0.0263	0.598	0.624	0.0188	—	0.0075	3.2	—	17.9	—	8.4	—	676
By 250	0.2230	0.336	0.559	0.0265	0.0077	0.1965	10.6	7.4	463	20.8	8.5	1460	23.0
By 270	0.2293	0.312	0.541	0.0321	0.0133	0.1972	14.3	11.1	419	24.0	9.4	940	24.3
By 450	0.2299	0.302	0.531	0.0317	0.0129	0.1982	15.2	12.0	364	21.5	10.9	855	27.5
	ml/g Al ₂ O ₃			ml/g Al ₂ O ₃			m ² /g Al ₂ O ₃			Å			

* $\bar{d}_h = 117 \text{ Å}$ $\bar{D}_h = 3900 \text{ Å}$
 ** $S_b = S_w' - S_{0,9}$

In CHAPTER IV we derived that the c -axis of bayerite is parallel to the [111]-direction of the spinel and that on complete dehydration the solid material shrinks by more than 50 % (in the direction of the other axes the shrinkage can be neglected). However, the decrease of the granular volume V_k is only 16 % (TABLE VII.1). Therefore we are right in assuming that the pores (and also the lamellae of the solid material) are lying approximately perpendicular to the c -axis of the original bayerite lattice. In FIG. 52a we have given a schematical representation

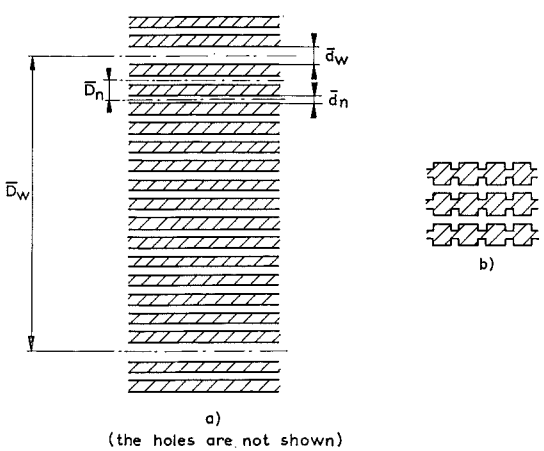


FIG. 52. Schematic representation of the skeleton of η -alumina
 a. dehydrated below 500 °C
 b. dehydrated above 500 °C

of the skeleton of the solid material of η -alumina (below 500 °C); the dimensions of $\bar{d}_n$ and $\bar{D}_n$ are exaggerated.

If we subtract the width of the pores from their mean distance we obtain the thickness of the solid lamellae. For the three samples we find 14.5 Å, 14.9 Å and 16.6 Å respectively. The length of the unit cell of the spinel in this direction (perpendicular to the (111)-plane) is $7.9 \sqrt{3} = 13.7 \text{ Å}$. The

lamellae are consequently on the average only a little thicker than one unit cell!

The alternation of pores and lamellae will, provided the distribution of their dimensions is not too broad, give rise to a new periodicity determined by the distance between the narrow pores. This distance is of the order of magnitude of 25 Å; it must be possible to find such a periodicity by means of small-angle X-ray diffraction. Small-angle scattering data on heated bayerite are not published. From lack of the necessary apparatus we were not able to study these phenomena. BRINDLEY and NAKAHIRA [86] observed small-angle scattering effects on aluminas obtained by heating *gibbsite*. In the region of spacings greater than 20 Å they observed a rather broad peak, the spacings of which depended on the heating temperature. At 325 °C they found a peak at 32 Å with a width at half maximum intensity of about 8 Å. On heating at higher temperatures this spacing increased; at 500 °C it was about

65 Å. Pore dimensions or adsorption isotherms were not measured by them.

STEGGERDA [35, 58] published some isotherms of heated gibbsite samples. One of these was heated at 344 °C (PSH 344) so that it was to some degree comparable to that of BRINDLEY and NAKAHIRA heated at 325 °C. By means of the method we developed in this chapter and the preceding we have calculated the mean distance of the narrow pores. The results are:

$$S_w' = 33 \text{ m}^2/\text{g}, S_n = 244 \text{ m}^2/\text{g}, V_n = 0.124 \text{ ml/g}, \bar{d}_n = 10.2 \text{ Å}, \bar{D}_n = 40 \text{ Å}.$$

This value of $\bar{D}_n$ from the observations of STEGGERDA corresponds very well with the small-angle spacing of 32 Å observed by BRINDLEY *et al.*

More systematic investigations will be necessary to settle whether the small-angle diffraction peaks found by these authors correspond to the periodicity formed by the pore system.

VII.1.2 The skeleton of η -alumina formed from bayerite above 500 °C

In CHAPTER VI we concluded from the changes of the shape of the isotherms that the skeleton of the solid material of samples obtained from bayerite alters considerably on heating above 500 °C. At a sufficiently high temperature the lamellae described in the preceding section are transformed into rod-shaped particles which still have a preferred orientation. However, a pronounced pseudomorphosis relation with the original bayerite lattice no longer exists.

In analogy with STEGGERDA's observations on gibbsite we may assume that this change of the shape starts already at lower temperature. Initially the rods are situated in the plane of the lamellae and parallel to each other. They are so closely arranged, that (reversible) capillary condensation can occur at relative pressures substantially lower than that at which the hysteresis loop begins. We then obtain a picture of which the cross-section is schematized in FIG. 52b. We shall represent it by rods having a square cross-section with an edge length of a . From the specific surface area and the specific volume we obtain for a a value of about 50 Å for sample By 580 and of about 100 Å for By 750. Compared with the thickness of the lamellae an appreciable material transport must have taken place.

Finally it must be remarked that the rod-like character is formed at the decomposition temperature of the well-crystallized boehmite formed under hydrothermal conditions inside the granules at the beginning of the dehydration of the bayerite.

VII.1.3 The skeleton of γ -alumina from well-crystallized boehmite

In the same way as we did for η -alumina we have calculated the skeleton of the solid material of γ -alumina from boehmite BoG (TABLE VII.2). It must be noticed that in this case, too, large holes ($\bar{d}_h = 115 \text{ Å}$)

TABLE VII.2 Texture quantities of γ -alumina from boehmite BoG

sample	V_i	V_{sp}	V_k	V_b	V_w	V_n	S_b	S_w	S_n	d_w	$\bar{d}_n$	$\bar{D}_w$	$\bar{D}_n$
BoG 450*	0.0206	0.361	0.382	0.0155	—	0.0051	2.7	—	12.1	—	8.4	—	610
BoG 580	0.0778	0.302	0.380	0.0518	0.0263	0.0260	13.4	10.7	47.8	49	10.9	660	137
BoG 750	0.0286	0.310	0.339	0.0286	0.0131	—	14.4	11.7	—	22	—	550	—
	ml/g Al_2O_3			ml/g Al_2O_3			$\text{m}^2/\text{g} \text{Al}_2\text{O}_3$			Å			

* $\bar{d}_h = 115 \text{ Å}$ $\bar{D}_h = 2800 \text{ Å}$

with openings of 25 Å have been formed. Their large mean distance $\bar{D}_h$ indicates that these holes can occur only in a few particles (probably crystal agglomerates).

We have ascribed the formation of these holes in bayerite and in gibbsite to the intragranular hydrothermal conditions during the formation of boehmite. Apparently we shall have to assume such conditions also in this case. The water necessary for these conditions could originate from a slight decomposition of the boehmite, or from the water present in excess over the stoichiometric ratio.

The wide pores, too, can occur only in a few particles because most of these are only a few hundred Å thick.

The lamellae between the narrow pores are many times thicker than for bayerite. The number of narrow pores in a particle therefore is low. The skeleton of the solid material of γ -alumina from well-crystallized boehmite gives a much more massive impression than that of η -alumina.

At a temperature of 750 °C the narrow pores have disappeared. As follows from the strong decrease of the granular volume V_k (TABLE VII.2) these pores are flapped together for the greater part. As, however, the specific volume is higher than at 580 °C, holes are apparently formed which are no longer accessible to water or nitrogen. This phenomenon was already observed by STEGGERDA [35].

VII.1.4 The skeleton of γ -alumina from gelatinous boehmite

In CHAPTER V and VI we found that the skeleton of γ -alumina from gelatinous boehmite can be described as a sheet-like felty net-work of particles whose surface is formed almost completely by planes parallel

to the c -axis of the original boehmite crystallites. On heating no new pores are formed.

If we neglect the surface that is not parallel to the c -axis, we get an idea of the dimensions of the particles in the direction of the a - and b -axes of the boehmite crystallites. If we put these equal to a and b , we obtain:

$$\frac{V_{sp}}{S} = \frac{ab}{2(a+b)}.$$

If we put $a = b$ (fibrillar particles with square cross-section) we find for the region between 270 and 600 °C a value of 30 to 33 Å. Of course it is quite probable that one of the dimensions is more developed than the other (*e.g.* the a -direction parallel to the aluminium oxide-hydroxide chains). In the extreme case of $a \rightarrow \infty$ we obtain a value of about 16 Å for b .

During recrystallization of gelatinous boehmite in water at 120 °C particles are formed with dimensions of 40 to 60 Å. The existing oxide-hydroxide chains will probably not be broken down by such a treatment. We may therefore assume that a will be smaller than 60 Å; consequently, b will be greater than about 22 Å. We can conclude that the fibrillar (or lath-shaped) particles of gelatinous boehmite, and consequently those of γ -alumina obtained from it, will have a cross-section with dimensions between 30×30 Å and 60×20 Å.

VII.2 Thermal stability of η - and γ -alumina

In CHAPTER IV we stated already that the transformation (recrystallization) of the low-temperature forms of the aluminas γ and η into the high-temperature form (δ and θ) can occur at strongly different temperatures according to the nature of the starting material. Moreover, it is a remarkable fact that γ - and η -alumina, which undoubtedly can be described both by an almost identical spinel lattice, are transformed on heating into two distinctly different modifications.

The easiest recrystallization occurs in the case of γ -alumina from well-crystallized boehmite; even at 600 °C δ -alumina is formed on prolonged heating. The γ -alumina from gelatinous boehmite needs a much higher temperature to obtain a noticeable recrystallization. These differences can be explained by the facts discussed in the preceding sections. The unit cell of δ -alumina consists of a threefold spinel cell with a c -axis of about 23.5 Å and eight vacant cation positions arranged along a fourfold screw axis parallel to the long axis. The oxygen lattice of the

γ -alumina obtained from well-crystallized boehmite, is already fairly well-formed and is the same as that of δ -alumina. Only a number of Al-atoms will have to take in a more ordered position. As the thickness of the lamellae is sufficiently great, the diffusion of the Al-atoms can occur without being hindered by the surface layer.

In the case of γ -alumina formed from gelatinous boehmite this diffusion will proceed with much more difficulty. The direction of the long c -axis of δ -alumina according to the pseudomorphosis relations, is that of the b -axis of the gelatinous boehmite. The crystallites of the gelatinous boehmite, however, are very poorly developed in this direction (see preceding section). Before a noticeable amount of δ -alumina can be formed a strong sintering of the fibrils or laths will have to occur; apparently this requires a temperature of more than 800 °C.

Also in the case of η -alumina from bayerite recrystallization is more difficult than in the case of γ from well-crystallized boehmite. The lamellar skeleton of η -alumina hinders the diffusion of the Al-atoms in the direction perpendicular to the lamellae. Only at a higher temperature than that at which the sintering to rod-shaped particles starts, recrystallization to the high-temperature form (now θ) will be possible.

The question arises now why η -alumina is transformed into θ and γ -alumina into δ . Obviously this is connected with the differences in the texture of the low-temperature forms. In this respect the formation of θ -alumina from the γ -alumina of SAALFELD [38] (obtained from boehmite which was pseudomorphous to gibbsite) may be important. However, as long as little is known about the factors influencing the stability of a lattice this question will stay unanswered.

VII.3 The "hydrogen spinel" and surface acidity

In CHAPTER IV.3.1 we have already mentioned the hydrogen spinel hypothesis of HOUBEN [82]. The alumina spinel was assumed to have the composition $\text{Al}_8[\text{H}_4\text{Al}_{12}]\text{O}_{32}$. Whereas GLEMSEY and RIECK [57] derived from infrared measurements, that at least part of the hydrogen atoms belong to the lattice in the form of OH-groups, FORTUIN [34] and MEIJS [84] found that all OH-groups are present in the surface.

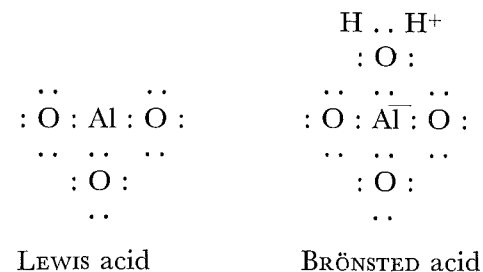
This contradiction in views is only apparent. We have already stated that the Al-atoms are irregularly distributed, especially over the tetrahedral positions (CHAPTER IV.4.2); in particular this will be the case in the surface layers. So we may expect that locally at the surface the concentration of Al-atoms will be either too low or too high. If an OH-group is located on the surface at a site with too low a concentration

of Al-atoms, it can be expected that the OH-dipole will not direct its proton to the outside, as is usually assumed, but to the inside of the material. This proton is then present in the lattice of the solid, whereas the OH-group is situated at the surface. It may even be possible that a water molecule adsorbed on the surface will give up one of its protons to a site with too low a concentration of Al-atoms. This explains why GLEMSEY and RIECK found that part of the adsorbed water molecules must have been taken up in the lattice. In this way bonds and groupings could be formed corresponding to the "hydrogen-spinel" concept of HOUBEN.

Surface sites with too high a concentration of Al-atoms will also have a particular influence on the properties of the surface. So far we have always considered the spinel lattice to be built up from ions (though we mostly spoke of atoms in accord with common practice). In this lattice the positive Al-ions are always surrounded by four or six oxygen ions (in tetrahedral or in octahedral interstices of the oxygen lattice). However, we have to expect that on the surface of largely dehydrated samples a shortage of oxygen ions will exist; the decrease of the water content on heating is not nearly compensated by a corresponding decrease of the specific surface area. Part of the Al-atoms will consequently be present at the outside of the surface with an incomplete coordination (three- instead of four- or six-fold). The Al-concentration in the surface at these sites will then be too high compared with the number of oxygen atoms.

DE BOER and VERWEY [116] investigated the differences in surface properties of compounds with ionic lattices such as NaCl, of which the molecules also have ionic bonds in the gaseous state, and compounds such as BeO and CaO, which possess an ionic lattice in the solid state, but the vapour of which consists of molecules with a covalent binding. They arrived at the conclusion that on the surface of NaCl ionic bonds will certainly occur, but that in the case of oxides the binding in the surface will have a more pronounced covalent nature. We are therefore allowed to assume that on the surface of the alumina spinel certainly covalent bonds will occur locally, particularly between incompletely coordinated Al-atoms and the surrounding oxygen atoms.

TAMELE [117] associated such Al-atoms with acid sites on the surface. They can behave as "electron pair acceptors" (LEWIS acids) and will strongly bind a water molecule with formation of protonic acids (BRÖNSTED acids):



In such a BRÖNSTED acid a negatively charged, tetravalent Al-atom appears the charge of which is compensated by a free proton.

The presence of LEWIS and BRÖNSTED acids in the aluminas has been proved by various investigators [118, 119, 120, 121]. Notably TRAMBOUZE [119] could not observe acid sites in well-crystallized boehmite and its dehydration products. If we compare the water contents and the specific surface areas of our BoG samples it appears that the former always amply suffice to assume that the whole surface is covered by a complete layer of OH-groups. Consequently Al-atoms with incomplete coordination will not occur at the surface, and therefore no acid sites either. From the experiments of PINES and HAAG [121] it follows that in γ -alumina from gelatinous boehmite (indicated by them as η) the maximum number of acid sites occurs in those samples of which the degree of occupation of the surface by OH-groups is a minimum.

It is obvious that the number and the strength of the acid sites depends on the structure of the surface, which follows from the pseudomorphosis relations. The surface of η -alumina from bayerite is formed mainly by the (111)-plane of the spinel. The surface of γ -alumina from well-crystallized boehmite is formed by the (110)-plane of the spinel. About the surface of γ -alumina from gelatinous boehmite we only know that it is formed by planes parallel to the c -axis of the boehmite crystallites. In view of the tendency of the aluminium oxide-hydroxide to form chains lying in the direction of the a -axis of boehmite it is probable that the (100)-plane of spinel forms a considerable part of the surface. Indeed PINES and HAAG found from their experiments that the starting material has a marked influence on a number of isomerization reactions attributed to acidic properties of the aluminas. They concluded that η -alumina from bayerite contains a larger number of acid sites per unity of surface area than γ -alumina from gelatinous boehmite, however, of lower acid strength. How far the porous texture of their samples has influenced their results cannot be judged, the indications concerning the history of their samples being rather vague.

VII.4 Summary of chapter VII

From the specific volume, the pore volume and the specific surface area of our samples we have developed a picture of the skeleton of their solid material. The samples obtained from bayerite by dehydration at temperatures below 500 °C appear to consist of very thin lamellae with a thickness of hardly more than the dimension of one unit cell of the spinel lattice. If the bayerite samples are heated above 500 °C a sintering phenomenon occurs, giving rise to formation of rod-shaped particles.

The lamellae of samples obtained from well-crystallized boehmite are much thicker. At a higher temperature a number of these lamellae flap together, sometimes under formation of holes which are not accessible from the surroundings.

The fibrillar or lath-shaped particles of the samples from gelatinous boehmite have small dimensions in two directions. The differences in thermal stability of the low-temperature forms of the aluminas have been connected to the dimensions of their lamellae or fibrils.

Finally it has been shown that the irregular distribution of the Al-atoms over the surface layer points to the presence of acid sites on the surface.

SUMMARY

The activity and the selectivity of catalysts consisting of a catalytically active substance on an "inactive" carrier are determined for an important part by the structure and the texture of this carrier.

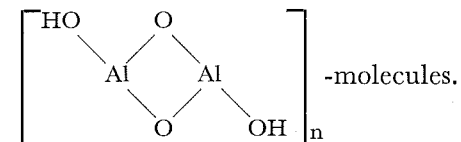
A carrier often applied technically is aluminium oxide obtained by heating one of the aluminium hydroxides. This thesis aims at obtaining a closer insight in the factors determining the structure and texture of these aluminium oxides (aluminas).

CHAPTER I gives a survey of the preparation and morphology of the various hydroxides. Special attention was paid to the phenomena occurring during the aging of gelatinous products to crystalline hydroxides.

The topochemical formation of gelatinous hydroxides from crystalline aluminium compounds was studied in more detail. A description of the mechanism of this reaction, which is governed by ion exchange, is given.

The crystallographic phenomena during the formation of the aluminas from the hydroxides are discussed in CHAPTERS II, III and IV.

The structures of the various hydroxides are discussed in CHAPTER II. From X-ray powder diagrams further data were obtained concerning the structure of the trihydroxides bayerite and nordstrandite. From the relation between the water content and the length of the *c*-axis it was derived that a continuous transition exists from gelatinous to well-crystallized boehmite. The water present above the stoichiometric ratio of one mole H₂O to one mole Al₂O₃ apparently forms special hydrogen bridges between the oxygen atoms of the chain-like



The selected-area electron-diffraction technique as a means for structure investigation of very small crystals is described in CHAPTER III.

With this technique the identity and the axes orientation of the various crystalline forms could be ascertained.

The dehydration sequences of bayerite and boehmite were investigated again with the aid of an accurate characterization of the aluminas (CHAPTER IV). The literature data concerning the bayerite sequence could be confirmed. The discrepancies in literature concerning the boehmite sequence were ascribed to differences in texture and crystallinity of the starting material. The pseudomorphosis relations between the hydroxides and their dehydration products were determined. By comparison of the X-ray powder diagrams with electron-diffraction patterns further data could be obtained concerning the structures and the lattice imperfections of the aluminas.

The porous texture of the aluminas is described in the CHAPTERS V, VI and VII.

During the dehydration of the hydroxides the specific surface area sometimes changes considerably (CHAPTER V). The formation of the aluminas from the crystalline hydroxides occurs over a limited temperature range. During the transformation a great number of narrow pores are formed with a large surface area and also a few wide pores. This internal surface area decreases rapidly on heating at a higher temperature.

No internal surface area is formed during the dehydration of gelatinous boehmite. From the decrease of the surface area on heating it was derived that the planes attributing mainly to the magnitude of the surface area must be parallel to the c -axis of the boehmite.

From the shape of the nitrogen adsorption isotherms a picture could be formed regarding the shape and the dimensions of the pores (CHAPTER VI). It was confirmed that gelatinous boehmite is built up from sheets having a porous, felty structure. These sheets are broken down during the formation of microcrystalline boehmite (under hydrothermal conditions), whilst the boehmite crystallites recrystallize.

From the adsorption branch of the isotherms the surface area and the volume of the narrow pores in the aluminas from the crystalline hydroxides were determined. In these pores having a wall separation of 8 to 11 Å, capillary condensation cannot occur; they are completely filled by the layer adsorbed on the surface. Lauric acid will indeed be adsorbed in these narrow pores; the hydrocarbon chains, however, lie almost flat on the surface now.

The formation of the pores in bayerite occurs in about the same way as STEGGERDA found in gibbsite: at temperatures below 500 °C slit-shaped pores between plan-parallel plates are formed, whereas at higher temperatures a sintering occurs giving rise to the formation of rod-shaped particles.

In CHAPTER VII we took a closer observation of the solid material. The aluminas from bayerite consist of very thin lamellae which are hardly one unit cell thick. On heating well-crystallized boehmite also lamellae are formed; these, however, are much thicker. The fibrillar or lath-shaped particles forming the sheets of gelatinous boehmite have small dimensions in two directions.

The differences between the thermal stability of the various aluminas could be connected to the differences between the dimensions of the particles of the solid material.

It was shown that the presence of acid sites follows from the unequal distribution of the Al-atoms in the surface layer.

SAMENVATTING

De activiteit en de selectiviteit van katalysatoren bestaande uit een katalytisch actieve stof op een „inactieve” drager worden voor een belangrijk deel bepaald door de structuur en de textuur van deze drager.

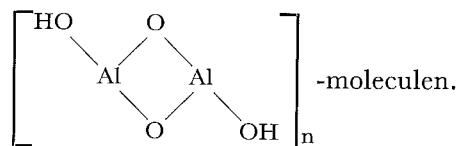
Een technisch veel toegepaste drager is aluminiumoxyde, verkregen door verhitting van één der aluminiumhydroxyden. Dit proefschrift beoogt een nader inzicht te verkrijgen in de factoren, die de structuur en de textuur van deze aluminiumoxyden (alumina's) bepalen.

HOOFDSTUK I geeft een overzicht van de bereiding en de morfologie van de verschillende hydroxyden. Bijzondere aandacht werd besteed aan de verschijnselen, die optreden bij de veroudering van de gelatineuze produkten tot kristallijne hydroxyden.

De topochemische vorming van de gelatineuze hydroxyden uit kristallijne aluminiumverbindingen werd meer in detail bestudeerd. Een beschrijving van het mechanisme van deze door ionenwisseling beheerste reactie kon worden gegeven.

De kristallografische verschijnselen bij de vorming van de alumina's uit de hydroxyden worden besproken in de HOOFDSTUKKEN II, III en IV.

De structuur van de hydroxyden is besproken in HOOFDSTUK II. Uit poederopnamen konden nadere gegevens worden verkregen omtrent de structuur van de trihydroxyden bayeriet en nordstrandiet. Uit het verband tussen het watergehalte en de lengte van de *c*-as kon worden afgeleid, dat er een continue overgang bestaat van gelatineus tot goed gekristalliseerd boehmiet. Het boven de stoichiometrische verhouding van één mol H₂O per mol Al₂O₃ aanwezige water vormt klaarblijkelijk extra waterstofbruggen tussen de zuurstofatomen van de ketenvormige



De klein-veld elektronendiffractietechniek als hulpmiddel voor het structuuronderzoek van zeer kleine kristallen is beschreven in HOOFD-

STUK III. Met behulp hiervan kon van de verschillende kristallijne vormen de identiteit en de assenoriëntatie worden vastgesteld.

De dehydratatiereeksen van bayeriet en boehmiet werden aan de hand van een nauwkeurige karakterisering van de alumina's opnieuw onderzocht (HOOFDSTUK IV). De literatuurgegevens betreffende de bayeriet-reeks werden bevestigd. De discrepanties in de literatuur over de boehmiet-reeks konden worden toegeschreven aan een verschil in textuur en kristalliniteit van het uitgangsmateriaal. De pseudomorfie-relaties tussen de hydroxyden en hun dehydratatieprodukten werden vastgesteld. Door vergelijking van röntgendiagrammen met elektronendiffractiepatronen konden nadere gegevens worden verkregen omtrent de structuur en de roosterstoringen van de alumina's.

De poreuze textuur van de alumina's is beschreven in de HOOFDSTUKKEN V, VI en VII.

Tijdens de dehydratatie van de hydroxyden verandert het oppervlak soms belangrijk (HOOFDSTUK V). De vorming van de alumina's uit de kristallijne hydroxyden voltrekt zich in een beperkt temperatuurgebied. Tijdens de transformatie ontstaat een aantal nauwe poriën met groot oppervlak naast enkele wijde poriën. Dit inwendige oppervlak daalt bij verhitting op hogere temperatuur snel.

Bij de dehydratatie van gelatineus boehmiet ontstaat geen inwendig oppervlak. Uit de daling van het oppervlak bij verhitting kon worden afgeleid, dat het grotendeels gevormd wordt door vlakken evenwijdig aan de *c*-as van het boehmiet.

Uit de vorm van de stikstof-adsorptie-isothermen kon een beeld worden gevormd van de vorm en de afmetingen van de poriën (HOOFDSTUK VI). De opbouw van het gelatineuze boehmiet uit vliezen met een poreuze, vezelachtige structuur kon worden bevestigd. Deze vliezen worden bij de vorming van microkristallijn boehmiet (onder hydrothermale omstandigheden) afgebroken, terwijl de boehmietkristallieten rekristalliseren.

Uit de adsorptietak van de isothermen kon het oppervlak en het volume van de nauwe poriën in de alumina's uit de kristallijne hydroxyden worden bepaald. In deze poriën, die een wandafstand hebben van 8 à 11 Å, kan geen capillaire condensatie optreden; zij worden geheel gevuld door de aan het oppervlak geadsorbeerde laag. Laurinezuur kan in deze poriën wel worden geadsorbeerd; de koolwaterstofketens liggen dan echter vrijwel plat op het oppervlak.

De porievorming in bayeriet geschiedt op dezelfde wijze als STEGGERDA vond bij gibbsiet: bij een temperatuur beneden 500 °C ontstaan spleetvormige poriën tussen planparallele platen, bij hogere temperatuur treedt een sintering op, waardoor staafvormige deeltjes ontstaan.

In HOOFDSTUK VII hebben we de vaste stof aan een nadere beschouwing onderworpen. De alumina's uit bayeriet blijken uit zeer dunne lamellen te bestaan, die nauwelijks één eenheidscel dik zijn. Ook bij verhitting van goed gekristalliseerd boehmiet ontstaan lamellen, die echter veel dikker zijn. De fibrillaire of latvormige deeltjes waaruit de vliezen van gelatineus boehmiet zijn opgebouwd, hebben kleine afmetingen in twee richtingen.

De verschillen in de thermische stabiliteit van de alumina's kon in verband worden gebracht met de verschillen in afmetingen van de deeltjes van de vaste stof.

Aangetoond werd, dat uit de onregelmatige verdeling van de Al-atomen in de oppervlaktelaag de aanwezigheid van zure plaatsen in het oppervlak volgt.

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LEVENSBERICHT

BERNARDUS CORNELIS LIPPENS werd op 2 december 1918 te Rotterdam geboren. Na de Rijksleerschool te Nijmegen doorlopen te hebben, volgde hij het onderwijs aan de Gemeentelijke Mulo aldaar, waar hij de diploma's Mulo A en B behaalde. In maart 1935 werd hij volontair aan het laboratorium van de Gasfabriek en Waterleiding der Gemeente Nijmegen, waar hij werd opgeleid voor analyst. Het eerste gedeelte van het analystexamen behaalde hij in 1936. Van 1936 tot 1938 werkte hij als analyst bij de Algemene Kunstzijde Unie te Arnhem, van 1938 tot 1946 bij de Hollandsche Metallurgische Bedrijven te Arnhem. Het tweede gedeelte van het analystexamen (diploma A) behaalde hij in 1938. In 1942 legde hij met goed gevolg het Staatsexamen H.B.S.-B af. Na de oorlog liet hij zich inschrijven aan de Technische Hogeschool te Delft, waarvan hij in juni 1950 het diploma van scheikundig ingenieur met lof behaalde. Hierna trad hij in dienst van de Belgischimie S.A. te Gent (België). Sinds april 1953 is hij in dienst van de Koninklijke Zwavelzuurfabrieken v/h. KETJEN N.V. te Amsterdam. Vanaf januari 1956 is hij gedetacheerd bij de researchgroep Katalyse te Delft, waar hij onder leiding van Prof. Dr. J. H. DE BOER het materiaal voor dit proefschrift kon bewerken.