

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

**A Hydrothermal Study of Equilibria in the System Alumina-Water<sup>1</sup>**BY A. W. LAUBENGAYER AND R. S. WEISZ<sup>2</sup>

The system alumina-water is one of the most important in the hydrous oxide field. Yet, despite the tremendous amount of accumulated data, there is still great confusion regarding the thermodynamic stability of the various compounds at different temperatures. The purpose of the present investigation is to obtain more precise information on the equilibria involved in this system by means of the hydrothermal method, using X-ray diffraction technique to identify the solid phases.

It has been well established that the following compounds exist as solids<sup>3,4</sup>: two forms of alumina ( $\text{Al}_2\text{O}_3$ ), corundum and gamma alumina; two forms of aluminum hydroxy-oxide ( $\text{AlOOH}$ ), diaspore and böhmite; and two forms of aluminum hydroxide ( $\text{Al}(\text{OH})_3$ ), gibbsite and bayerite. The so-called beta,<sup>5</sup> delta,<sup>6</sup> zeta<sup>7</sup> and trigonal<sup>8</sup> aluminas have been proved to be spurious.

The mineralogical names rather than Greek letters are used in this paper to designate the compounds. This seems desirable because various writers<sup>6,9,10</sup> have proposed at least three different nomenclatures using Greek letters. Contrasted with this confusion, the mineralogical names are unambiguous and are common knowledge to workers in this field. Since the term gamma alumina is the only one which has been suggested for this phase, it is used here.

Most investigations of equilibria in the alumina-water system have been made by dehydration studies. The values reported for a given transition point by this method vary by as much as two hundred degrees.<sup>3,10</sup> It seems probable that equilibrium is not easily established for any hydrous oxide system by means of

the dehydration curve method, because the products obtained are either amorphous or poorly crystallized and very low aqueous pressures are employed. Better results may be expected of the hydrothermal method, which is carried out by holding the substance to be investigated with superheated steam in a bomb. The value of this latter technique has been amply tested.<sup>11,12</sup> The review article of Morey and Ingerson, however, lists only a very few incomplete investigations of the alumina-water system by means of the hydrothermal method.

Briefly, the reliable information on the stability ranges of the alumina-water compounds published prior to this investigation may be summarized as follows. Gamma alumina was shown to be less stable than corundum above *ca.* 900°. <sup>13</sup> It was known that diaspore and böhmite cease to be stable between 400 and 500°, but the relation between the two was obscure.<sup>8</sup> Gibbsite and bayerite were known to decompose between 120 and 200°, and it was certain that below this temperature gibbsite is the stable phase.<sup>3</sup>

**Experimental**

**Identification of the Phases.**—The crystalline substances obtained in this investigation were identified by chemical analysis and by X-ray and microscopical examination. The samples were analyzed by determining the percentage of water lost upon ignition at 1300°. All samples were examined by the powder method of X-ray diffraction, using  $\text{Mo K}\alpha$  radiation in a General Electric type VWC apparatus. The patterns obtained were compared with those given in the literature for the various compounds. The products formed at higher temperature (300–500°) by means of the hydrothermal method were well crystallized and could be identified by their optical properties.

**Materials.**—Gibbsite was precipitated from an aluminate solution at 100° by carbon dioxide, according to the method of Achenbach.<sup>14</sup> The crystals were washed repeatedly with water until the supernatant liquid was neutral to methyl orange, ensuring the removal of alkali. Analysis, after intensive drying over phosphorus pentoxide, gave 35.18 and 35.25% water (theory, 34.59). A negative test for silica was obtained for the sample.

Bayerite was prepared by precipitation from an aluminate solution at room temperature by carbon dioxide, according to the directions of Fricke and Wullhorst.<sup>15</sup> After

(1) Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the Buffalo meeting, September 9, 1942.

(2) Present address: Westinghouse Electric Co., Pittsburgh, Pa.

(3) Fricke and Hüttig, "Hydroxide and Oxyhydrate," *Akad. Verlag. m. b. H., Leipzig*, 1937.

(4) Lehl, *J. Phys. Chem.*, **40**, 41 (1936).

(5) Ridgway, Klein and O'Leary, *Trans. Electrochem. Soc.*, **70**, 71 (1936).

(6) Edwards and Tosterud, *J. Phys. Chem.*, **37**, 433 (1933).

(7) Beljankin, *Centr. Mineral. Geol. (A)*, 300 (1933).

(8) Parravano and Onorato, *Atti acad. Lincei*, **10**, 475 (1929).

(9) Haber, *Naturwissenschaften*, **13**, 1007 (1925).

(10) Weiser, "Inorganic Colloid Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1935.

(11) Morey and Ingerson, *Econ. Geol.*, **32**, 607 (1937).

(12) Laubengayer and Engle, *THIS JOURNAL*, **61**, 1210 (1939).

(13) Rooksby, *Trans. Ceram. Soc.*, **23**, 399 (1929).

(14) Achenbach, *Chem. Erde*, **6**, 307 (1931).

(15) Fricke and Wullhorst, *Z. anorg. allgem. Chem.*, **205**, 127 (1932).

washing and drying, analysis for water showed 35.7 and 36.2% (theory, 34.59). No silica was found to be present.

Böhmite was made from gibbsite by holding it in a hydrothermal bomb at 350° for several days. Analysis for water showed 16.4% (theory, 15.0).

Gamma alumina was prepared by heating gibbsite in the air at 750° for twelve hours.

Corundum was obtained as well-formed crystals by heating gibbsite to 450° for a short time in the hydrothermal bomb.

Since diasporé had never been prepared in the laboratory, some of the purest naturally occurring diasporé, from Chester, Mass., was purchased. Analysis showed that it contained 1.6% ferric oxide, 0.6% phosphorus pentoxide, but no significant amounts of other impurities. Its water content was found to be 15.2 and 15.2% (theory, 15.0).

The X-ray diffraction patterns of all these compounds checked those given in the literature. Only samples showing a sharp X-ray diffraction pattern were used.

**Hydrothermal Experiments.**—Hydrothermal experiments were conducted by holding one or more solid phases in contact with water or an aqueous solution in a bomb at a given temperature for a time believed, on the basis of preliminary work with the system, to be long enough to allow equilibrium to be established. This was followed by quenching to room temperature and examination of the products. The procedure in this investigation was essentially that reported by Laubengayer and Engle.<sup>12</sup> The temperature was held constant in a given experiment to  $\pm 2^\circ$  at 100–200° and  $\pm 5^\circ$  at 400–500°. The degree of filling of the hydrothermal bomb was about 0.7, giving an aqueous pressure of roughly 400 atmospheres at 400°. This value is calculated from the data of van Niewenburg and Blumendal,<sup>16</sup> with the assumption that alumina is so slightly soluble in water even at this temperature that it changes the vapor pressure but slightly. Below the critical temperature the aqueous pressure in the bomb was presumably the saturation aqueous pressure for the given temperature, as sufficient water was added to ensure a liquid phase up to the critical point. It has been shown that there is in general no discontinuity in a solubility curve at the critical temperature.<sup>11</sup>

Table I summarizes the hydrothermal experiments. Of the experiments performed, only those which fix the transition temperatures are listed. In certain experiments, seed crystals of a second phase expected to be stable at that temperature were introduced. It was then possible, by means of microscopic examination, to see whether the seed crystals grew in size or dissolved during the experiment. In this way information about reactions proceeding very slowly was obtained without making excessively long runs. Furthermore, it was found that in its stable range diasporé could be formed only if the starting material were seeded with a small amount of natural diasporé.

Experiments 25, 26 and 36 fix the lower limit for the stability of corundum at 450  $\pm$  5°. From Expts. 30 to 36 we can conclude that  $\gamma$ -alumina is not stable throughout the range covered in this investigation. Below 450° and for a considerable range of temperature, diasporé is the stable phase, as shown by Expts. 17, 19, 23, 26 and 35.

(16) van Niewenburg and Blumendal, *Rec. trav. chim.*, **51**, 708 (1932).

TABLE I

HYDROTHERMAL EXPERIMENTS				
Expt.	Starting material	Temp., °C.	Time, hours	Product
1	Gibbsite	140	150	Gibbsite
2	Gibbsite	152	130	Gibbsite
3	Gibbsite	154	50	Gibbsite + böhmite
4 <sup>a</sup>	Gibbsite	160	85	Böhmite (seed persisted)
5	Gibbsite	164	105	Böhmite
6	Gibbsite	200	40	Böhmite
7	Bayerite	139	80	Bayerite
8	Bayerite	152	130	Bayerite
9	Bayerite	154	50	Bayerite + böhmite
10	Bayerite	160	85	Böhmite
11	Bayerite	164	105	Böhmite
12 <sup>b</sup>	Böhmite	120	110	Böhmite (seed persisted)
13	Böhmite	125	300	Böhmite
14 <sup>a</sup>	Böhmite	202	110	Böhmite (seed persisted)
15 <sup>a</sup>	Böhmite	248	150	Böhmite (seed persisted)
16 <sup>a</sup>	Böhmite	278	150	Böhmite + diasporé (?)
17 <sup>a</sup>	Böhmite	305	105	Böhmite + diasporé
18	Böhmite	340	65	Böhmite
19 <sup>a</sup>	Böhmite	375	50	Diasporé
20	Böhmite	410	55	Böhmite
21	Böhmite	420	95	Böhmite + corundum
22	Böhmite	442	85	Corundum
23 <sup>a</sup>	Böhmite	442	155	Diasporé
24	Diasporé	125	300	Diasporé
25	Diasporé	442	85	Diasporé
26	Diasporé	450	48	Diasporé + corundum
27	Diasporé	480	35	Corundum
28 <sup>a</sup>	Corundum	400	205	Corundum + diasporé
29	Corundum	420	75	Corundum
30 <sup>a</sup>	$\gamma$ -Alumina	202	110	Böhmite (seed persisted)
31	$\gamma$ -Alumina	278	150	Böhmite
32	$\gamma$ -Alumina	400	65	Böhmite
33 <sup>a</sup>	$\gamma$ -Alumina	400	205	Diasporé
34	$\gamma$ -Alumina	408	70	Corundum
35 <sup>a</sup>	$\gamma$ -Alumina	430	40	Diasporé
36	$\gamma$ -Alumina	455	50	Corundum

<sup>a</sup> Seeded with about 2% diasporé. <sup>b</sup> Seeded with about 2% gibbsite.

The lower limit for the existence of diasporé seems to be about 280° (Expts. 15, 16 and 31); however, since these reactions are very sluggish below 300°, the transition point böhmite–diasporé–water may actually be much lower. (Note that in Expts. 4, 12, 14, 15 and 30 seed crystals remained after the experiment was concluded, although the rest of the material also was unchanged.) In fact, it is possible that böhmite is never a stable phase in the alumina–water system, though this seems unlikely. Experiments 3, 4, 14 and 15 seem to indicate that the upper limit for the existence of gibbsite is 155  $\pm$  5°, and that between this temperature and 280°, böhmite is the stable phase (see also Expts. 16 and 30).

Two metastable transition points have been found. In the absence of diasporé the metastable transition point böhmite–corundum–water is 415  $\pm$  10° at a pressure of about 500 atmospheres, as shown by Expts. 20, 21, 32 and 34. Experiments 8, 9 and 10 indicate that the metastable transition point bayerite–böhmite–water is very close to the transition point gibbsite–böhmite–water, but theoretically must be somewhat lower.

**Further Hydrothermal Studies.**—To obtain qualitative information about the effects of pressure and solvents other than pure water on the alumina–water system, several additional hydrothermal experiments not listed in Table I were performed.

Two experiments were carried out with the bomb filled

with water to 0.2 of its volume. When held at 430° for 40 hours, diaspore remained unchanged, while gamma alumina, seeded with diaspore, was completely transformed to diaspore. The calculated pressure in these experiments was 240 atmospheres, whereas the calculated pressure at 450° and a degree of filling of 0.7 (Expt. 26) was 700 atmospheres (extrapolated from the data of van Niewenburg and Blumendal<sup>16</sup>). Hence, we can conclude that lowering the aqueous pressure from around 700 atmospheres to 240 atmospheres lowers the transition point diaspore–corundum–water less than 20°. Therefore the phase relationships shown to exist at the high aqueous pressures in the bomb probably hold at the much lower aqueous pressures at which the alumina–water system is ordinarily handled, although the transition temperatures then may be expected to be correspondingly lower.

In one series of experiments, potassium hydroxide solutions (20% potassium hydroxide per weight of sample) were used in an attempt to hasten the attainment of equilibrium. Although unmistakable evidence of increased solution was found, no appreciable increase in the rate of attainment of equilibrium was noted. The transition point of diaspore to corundum was found to be about 10° lower in the presence of 20% potassium hydroxide than in the presence of pure water, due undoubtedly to the lower vapor pressure of the solution.

Bruhns<sup>17</sup> reported that at 300° “ignited alumina,” as well as alumina gel, when held for ten hours in a dilute aqueous solution of ammonium fluoride, gave corundum. When the authors repeated these experiments, they obtained böhmite; no explanation of Bruhns’ statement is available.

Two experiments were performed using a 10% solution of hydrofluoric acid as the solvent at 400°. Both  $\gamma$ -alumina and corundum gave fluorine-containing compounds. These probably were oxy-fluorides, since they gave X-ray diffraction patterns very similar to that of an oxy-fluoride reported by Schober and Thilo.<sup>18</sup>

**Synthetic Diaspore.**—It is noteworthy that in this investigation diaspore was obtained in the laboratory for the first time. The optical properties of this synthetic diaspore check those for the mineral very closely. The crystals are similar to those found in nature, being acicular in habit and showing a combination of orthorhombic prism and dome. Figure 1 is a photomicrograph of diaspore growing on a seed crystal. The X-ray diffraction pattern of the synthetic material matched that of the mineral, although the synthetic diaspore is undoubtedly purer.

Before 1907 several articles appeared claiming the preparation of diaspore in the laboratory.<sup>19,20,21</sup> Later, the evidence on which these identifications were made was pointed out to be very questionable.<sup>3,11</sup> However, it seemed to the present authors worth while to repeat the experiments, basing the identification of the products on the X-ray diffraction method, which was, of course, unknown at the time of these earlier experiments.

Friedel<sup>19</sup> claimed that at 400° diaspore could be obtained

(17) Bruhns, *Neues Jahrb. Mineral. Geol., Beilage Bd.*, 62 (1889).

(18) Schober and Thilo, *Ber.*, **73B**, 1219 (1940).

(19) Friedel, *Bull. soc. franc. mineral.*, **14**, 7 (1891).

(20) Thugutt, *Neues Jahrb. Mineral Geol., Beilage Bd.*, **9**, 554 (1894–5).

(21) Doelter, *Mineralog. petrog. Mitt.*, **25**, 108 (1906).



Fig. 1.—Diaspore growing from seed (100 X).

by heating alumina for eighteen hours with sodium hydroxide. A repetition of this experiment, without seeding with diaspore, gave böhmite, and it is probable that Friedel was dealing with böhmite, which was unknown at that time.

Thugutt<sup>20</sup> said that a solution of sodium aluminate, sodium hydroxide, and sodium carbonate at 184–190° gave mostly amorphous alumina but also some dawsonite ( $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2\text{CO}_2\cdot 2\text{H}_2\text{O}$ ) and diaspore. We found that such an experiment gave only poorly crystallized böhmite.

Doelter<sup>21</sup> reported that a mixture of soda, alumina, and silica kept at 190° for 200 hours gave diaspore. We were unable to prepare diaspore by such a method.

### Discussion

The most important question which must be answered in connection with these experimental results is whether the transition points found are the true equilibrium values. A practical criterion in such a case is the attainment of equilibrium from either side of the transition point. With the system diaspore–corundum–water this was realized. The important transition points gibbsite–böhmite–water, and böhmite–diaspore–water could not be approached from the low temperature side. Nevertheless, we believe that the reported values are more accurate than any of those obtained from dehydration curves, chiefly because of the higher aqueous pressures used in the hydrothermal method.

The authors have been unable to find a satisfactory explanation for the remarkable facts that diaspore can be obtained only by seeding and that without seeding böhmite is formed in preference to diaspore, even though the latter should be stable in the given experiment. A careful study of the crystal structures of gibbsite, böhmite, and diaspore might shed some light on this. One fact is worth noting. Diaspore has a higher specific gravity than böhmite (3.33 vs. 3.06).

Hence, the latter should be more easily formed by dehydrating gibbsite (specific gravity of 2.43), since dehydration would certainly lead to an open structure.

On the basis of this investigation it is possible to construct a tentative solubility curve for the system alumina-water. Figure 2 shows the solubility in water of the stable phases of the alumina-water system as a function of temperature. Quantitative data for the solubilities have not been obtained but we know qualitatively that

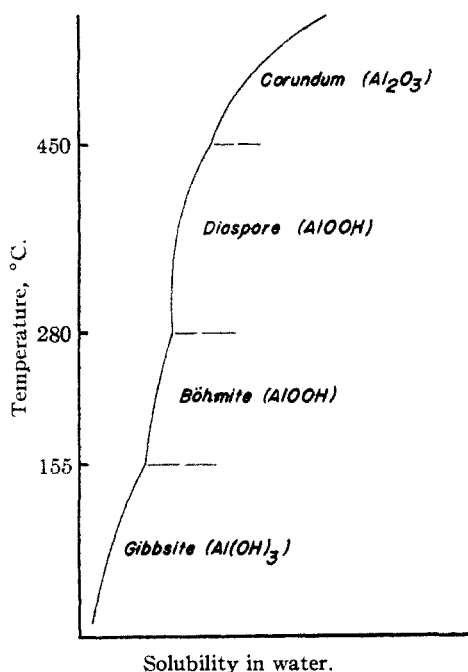


Fig. 2.—Solubility curves for the system alumina-water.

the solubility curves should show discontinuities at the various transition points and should indicate greater solubility at higher temperatures, and that the stable phases should be less soluble than the metastable phases.

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### Summary

1. The system alumina-water has been studied by the hydrothermal method in the temperature range 100–500°. The phases involved were identified by X-ray and microscopic methods.

2. Corundum is the stable phase above 450 ± 5°.

3.  $\gamma$ -Alumina is metastable throughout the range investigated.

4. Diaspore is stable below 450 ± 5°, and the lower limit for its stability seems to be around 280°.

5. Böhmite apparently is stable between 155 and 280°.

6. Gibbsite is unstable above 155°.

7. Bayerite is unstable above 155°, while the indications are that it is less stable than gibbsite below this temperature.

8. Diaspore has been prepared in the laboratory for the first time.

9. The value of seeding in phase rule studies has again been demonstrated.

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## Studies in the Chromamines. II. Preparation of Luteo Salts<sup>1,2</sup>

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In the course of investigations concerning the chemistry of the chromamines, a convenient method for preparing salts of the tridiamine series was required. None of the available syn-

thetic methods was found to be entirely satisfactory.

The reaction of an aqueous diamine with trichloro-tripyridine-chromium has been used for the synthesis of luteo<sup>5</sup> salts of the ethylene-

(1) For the first paper in this series, see Baithis and Bailar, *This Journal*, **58**, 1474 (1936).

(2) Presented at the 99th meeting of the American Chemical Society, Cincinnati, Ohio, April 9, 1940.

(3) Abstracted from a portion of a thesis submitted in partial fulfillment of the requirement for the degree of Doctor of Philosophy in Chemistry at the University of Illinois, 1939.

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(5) In 1852 Fremy proposed a system of nomenclature for the cobalt ammonia compounds, utilizing the colors of the salts as the means of distinguishing between them. According to this system the salt now known as hexammine cobaltic chloride was given the name "luteo cobaltic chloride" (latin *luteus* = yellow). The meaning of the term was gradually extended to include the compounds of all trivalent metals coordinated with six ammonia or amine groups, regardless of color. Used in this way to describe a whole class of compounds, the term is still useful and convenient.