[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, CASE SCHOOL OF APPLIED SCIENCE]

A Study of Hydrated Alumina[1]

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In this paper the method originally employed by Foote and Scholes[2] to determine the vapor pressures of hydrates is applied to the study of the hydrous oxides of alumina. That this method is capable of yielding good results with ordinary hydrates, provided certain refinements are introduced, is first shown by redetermining the copper sulfate–water isotherm at 25°.

Literature Résumé

Although the question of the composition of hydrated alumina has attracted many research workers, and although considerable effort has been expended to determine its nature, the problem is still far from settled. The results reported in the literature are not only at variance, but in many instances are diametrically opposed. Thus, one group of workers considers the hydrous aluminum oxides as oxides containing in their interstices and on their surface adsorbed water in no definite stoichiometric ratio; while another is just as insistent that these substances are definite chemical individuals containing water bound chemically in definite stoichiometric proportions. In summarizing the literature up to 1920 and relying mostly on the work of van Bemmelen, Weiser[3] concluded that the hydrous oxide formed by the precipitation of an aluminum salt contains no definite hydrates. However, even before 1920 various hydrates have been reported, as by Tschermak[4] for instance.

This duality of view has continued right through the tremendous literature on the subject that has appeared since 1920. Among the more recent researches adhering to the view that there are no hydrates in the alumina hydrogels may be mentioned Shidei,[5] Hüttig and his co-workers,[6] and Weiser and Milligan,[7] while Guichard,[8] Böhm,[9] and Rooksby[10] reported respectively a tri- and dihydrate, a monohydrate, and a monohydrate plus some other hydrate mixed with it.

From a series of very extensive experiments Willstätter, Kraut and their co-workers[11] concluded that precipitated hydrous alumina contains the following hydrates: $Al_2O_3 \cdot 3H_2O$ (Compound C), $Al_2O_3 \cdot 2H_2O$, $Al_2O_3 \cdot 1.5H_2O$, $Al_2O_3 \cdot H_2O$ (metahydroxide), as well as some complex intermediate hydrates. The trihydrate is supposed to exist in three modifications, α, β, γ. These results have been confirmed by Biltz and his students,[12] who reported that Willstätter and Kraut's metahydroxide is a monohydrate, while the A, B, C_α and C_γ gels are, respectively, $Al_2O_3 \cdot 1.5H_2O$, $Al_2O_3 \cdot 2H_2O$, $Al_2O_3 \cdot 3H_2O$ and $Al_2O_3 \cdot 3H_2O$. These results were obtained both by the ammonia and acetone "extractions."

This brief résumé is very far from being exhaustive but it indicates the uncertain present status of the knowledge of the composition of hydrated alumina. From a thorough study of the literature of the subject the following conclusions may be drawn.

(1) It is quite definitely established that among naturally occurring hydrated aluminas gibbsite (or hydrargillite) and diaspore are, respectively, $Al_2O_3 \cdot 3H_2O$ and $Al_2O_3 \cdot H_2O$. The composition of bauxite is still doubtful.

(2) The crystalline precipitate obtained from solutions of alumina in alkalies is a definite hydrate, $Al_2O_3 \cdot 3H_2O$, either identical with gibbsite or isomeric with it.

(3) The gelatinous precipitate obtained from aluminum salts by precipitation with ammonium hydroxide and aged under water for some time yields a hydrate $Al_2O_3 \cdot 3H_2O$, which is either gibbsite, or an isomer, bayerite.

(4) The nature of the freshly prepared, unaged gelatinous precipitate is still not established. According to Willstätter and Biltz this precipitate contains definite hydrates, among which are

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(1) Presented before the Division of Physical and Inorganic Chemistry at the Cleveland Meeting of the American Chemical Society, September 10–14, 1934.

(2) Foote and Scholes, THIS JOURNAL, **33**, 1309–1326 (1911).

(3) Weiser, *J. Phys. Chem.*, **24**, 505 (1920).

(4) Tschermak, *Monatsh.*, **33**, 1087 (1912).

(5) Shidei, *Chem. Abs.*, **20**, 684 (1926).

(6) Hüttig, *Z. anorg. allgem. Chem.*, **171**, 323 (1928); **187**, 1 (1930).

(7) Weiser and Milligan, *J. Phys. Chem.*, **36**, 3010 (1932).

(8) Guichard, *Bull. soc. chim.*, **37**, 381 (1925).

(9) Böhm and Niclassen, *Z. anorg. allgem. Chem.*, **132**, 1 (1923); Böhm, *ibid.*, **149**, 203 (1925).

(10) Rooksby, *Trans. Ceram. Soc.* (London), **28**, 399 (1929).

(11) Willstätter, Kraut, *et al.*, *Ber.*, 1923–1931; also *Kolloid-Z.*, **49**, 353 (1929).

(12) Biltz and Rahlfs, *Z. anorg. allgem. Chem.*, **172**, 273 (1928); Biltz and Lehrer, *ibid.*, **172**, 292 (1928).

$Al_2O_3 \cdot 3H_2O$, $Al_2O_3 \cdot 2H_2O$, $Al_2O_3 \cdot 1.5H_2O$ and $Al_2O_3 \cdot H_2O$. This is contradicted by Weiser.

The Method

The method of Foote and Scholes, and the one employed here, involve essentially the establishment of an equilibrium at a definite temperature between the hydrated substance studied and an alcohol–water solution. At equilibrium the escaping tendency of the water is the same for both phases, and hence the water vapor pressure of the hydrate must be the same as that of the alcohol–water solution with which it is in contact. If then the concentrations of the alcohol solutions with which various compositions of the hydrated substance are in contact be determined, an isotherm may be constructed; further, if aqueous pressures of the various alcohol solutions are known, the results may be translated into a vapor pressure–composition curve. In short, the alcohol solutions of various concentration may be employed *in lieu* of gaseous vapor phases of various pressures.

In comparison with other methods employed for the study of hydrous alumina this method seems to offer certain advantages.

(1) It allows work at ordinary room temperatures. Results given in the literature indicate that with rise in temperature alumina undergoes an aging process which appears to change its character.

(2) There is intimate contact between liquid and gel.

(3) Approach to equilibrium is rapid, thus eliminating to a very considerable extent the transformations in character which are presumed to take place in hydrated alumina with time.

(4) The solid–gas interphase is removed, eliminating thus, as far as can be told from the experiments to be described subsequently, the effect that Zsigmondy reported of particle size on the vapor pressure.

Before applying the method to alumina, it was deemed advisable to see what accuracy and results may be expected with certain refinements in technique when employing this method with ordinarily well established hydrates. For this reason the copper sulfate–water isotherm at 25° was redetermined.

The Copper Sulfate–Water Isotherm at 25°.—The following is a description of the materials, apparatus and procedure employed.

Materials

$CuSO_4 \cdot 5H_2O$.—Baker and Adamson $CuSO_4 \cdot 5H_2O$, Reagent Grade, was recrystallized twice from distilled water—redistilled from alkaline potassium permanganate using a block tin condenser. It was dried at room temperature protected from dust and then ground with flint pebbles in a ball mill so as to pass a 200-mesh screen. This fine powder was used in the experiments. Analysis of two batches of recrystallized $CuSO_4 \cdot 5H_2O$ showed that the product corresponded to the expected analysis.

Alcohol.—Commercial 95% alcohol was treated with dehydrated lime refluxed for at least twenty-four hours, and then distilled out on a water-bath. It was subsequently treated with potash and again distilled. Repeated tests showed no aldehydes or ketones present. The second distillate was employed in the experiments.

Apparatus

Pycnometers.—As no commercial type of pycnometer was found acceptable, some special ones were made. These were of the Weld type, made of Pyrex glass, and had a capacity of about 50 cc. The capillaries in the plug were made small and hollowed out at the bottom to avoid collection of air bubbles. The plugs and caps were carefully ground to make good seals. These pycnometers proved excellent in service. No loss in weight was ever detected on the balance, and alcohol determinations in two different pycnometers could be checked within 0.01% alcohol.

Thermostat.—The thermostat was a large capacity Freas water thermostat controlled within 25.00 ± 0.02°. The thermometer used had a range of 19–26° and was graduated in 0.01°. It was checked against a Bureau of Standards calibrated platinum resistance thermometer.

Weights.—All weights used were calibrated and checked at intervals to ensure accuracy. All alcohol density weighings were reduced to vacuum. Calculation showed that this was not necessary for the other weighings. The correction was applied in the usual manner assuming a mean air density of 0.0012 g. per cc.

Procedure

Into clean, dry and weighed four-ounce oil sample bottles containing glass beads was introduced $CuSO_4 \cdot 5H_2O$ and the bottles weighed again. The desired starting composition was obtained by heating the bottles with the $CuSO_4 \cdot 5H_2O$ at various temperatures for various periods of time. When the desired composition had been reached the bottles were again weighed, alcohol added, and the whole reweighed.

The starting composition of the alcohol was chosen to yield the desired final concentration. Simultaneously with the filling, samples of alcohol were taken for initial analysis. In these transfers every precaution was taken to avoid loss by evaporation or contamination.

After the final weighing the bottles were stoppered, sealed, and allowed to rotate in the constant temperature bath for ten to twelve days. It was found by experience that the addition of glass beads facilitated and accelerated the approach to equilibrium. The latter could be reached from both sides.

When equilibrium was thought to have been established the bottles were removed, opened, and the contents rapidly transferred to dry, clean, 100-cc. oil centrifuging tubes. These were then rotated in a centrifuge at 2500 r. p. m., during which process the liquid phase separated cleanly from the solid residue. The clear liquid was poured off into dry, stoppered Erlenmeyer flasks, and the alcohol concentration determined.

In the determination of alcohol densities weighings were repeated until checks were obtained. In the majority of cases only two such weighings per sample were required to give checks within less than one milligram in a total weight of 75–80 g.

The pycnometers were calibrated by weighing with fresh doubly-distilled water. All specific gravities were reduced to 25°/4°, *in vacuo*. Alcohol percentages corresponding to these specific gravities were read from the tables given in the "International Critical Tables" of the very accurate data of Osborne, McKelvy and Bearce.[13]

No analysis of the solid residue was necessary.

Calculation.—The composition of the solid phase was calculated from the available data by the equation

$$n = \left[\frac{W_T}{W_C} - \frac{W_S(m - K)}{W_C K} - 1\right]\frac{M_C}{M_{H_2O}} = 8.8604\left[\frac{W_T}{W_C} - \frac{W_S(m - K)}{W_C K} - 1\right] \quad (1)$$

where n = moles of water per mole of $CuSO_4$ in solid phase at equilibrium

W_T = weight of precipitate initially started with

W_S = weight of alcohol solution initially added

W_C = weight of anhydrous $CuSO_4$ in W_T

m = percentage of alcohol in initial solution

K = percentage of alcohol in liquid phase at equilibrium

M_C = molecular weight of $CuSO_4$

M_{H_2O} = molecular weight of H_2O

The method of calculation can best be illustrated by the following example. In a typical determination 10.9260 g. of $CuSO_4 \cdot 5H_2O$ was dehydrated to a weight of 6.9956 g. (W_T), and this precipitate then agitated with 66.9237 g. (W_S) of 98.22% alcohol (m). After equilibrium had been established the alcohol concentration was found to have shifted to 99.38% (K). The weight of anhydrous $CuSO_4$ in 10.9260 g. of $CuSO_4 \cdot 5H_2O$ is 6.9908 g. (W_C). Hence

$$n = 8.8604\left[\frac{6.9956}{6.9908} - \frac{66.9237(98.22 - 99.38)}{6.9908 \times 99.38} - 1\right] = 0.996$$

and the solid phase composition is $CuSO_4 \cdot 1.00\ H_2O$.

Experimental and Discussion

The summary of experimental data and results from four distinct runs is given in Table I. The first column gives the theoretical value of n, column two the number of determinations in the range of n given in the first column, column three the range of starting alcohol concentrations, column four the final alcohol concentrations with which the solid phase is in equilibrium, while the fifth gives the variation of individual results from the mean where constancy is to be expected. In the sixth column are listed the values of n as calculated by equation (1), and finally in the last column the variations of individual results from the mean value of n in six.

The plot of n against the percentage of alcohol at equilibrium is shown in Fig. 1. It is seen that the shape of the curve is identical with that expected from a plot of vapor pressure against moles of water, n, in the solid phase. These results are in accord with those of various other investigators, namely, that there are only three hydrates of copper sulfate, the mono-, tri-, and pentahydrates. The vapor pressures of the various hydrate mixtures are those which correspond, respectively, to the aqueous tensions of alcohol solutions of the following concentrations:

$CuSO_4$–$CuSO_4 \cdot 1H_2O$–99.87% C_2H_5OH

$CuSO_4 \cdot H_2O$–$CuSO_4 \cdot 3H_2O$–96.48% C_2H_5OH

$CuSO_4 \cdot 3H_2O$–$CuSO_4 \cdot 5H_2O$–93.45% C_2H_5OH

TABLE I

SUMMARY OF RESULTS ON $CuSO_4 \cdot H_2O$ ISOTHERM AT 25°

n in $CuSO_4 \cdot nH_2O$	Detns.	Composition of alcohol Initial %	Final %	Av. devn., %	n in $CuSO_4 \cdot nH_2O$ (obsd.)	Av. devn. of n
0–1	5	99.36–99.93	99.87	±0.02	0.38–0.98	..
1	6	96.77–99.44	97.90–99.38	..	1.01	±0.02
1–3	4	94.70–96.77	96.48	0.03	1.78–2.89	..
3	5	94.73–96.21	93.51–95.99	..	2.96	0.02
3–5	5	92.67–94.74	93.45	0.02	3.13–4.90	..
5	6[a]	65.74–92.78	65.73–92.75	..	4.95	0.01

[a] Three determinations below 88% alcohol corrected for solubility of $CuSO_4 \cdot 5H_2O$.

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(13) Osborue, McKelvy and Bearce, *Bull. Bureau of Stds.*, **9**, 327 (1913).

The values given by Foote and Scholes[2] are in order 99.5, 96.5, 93.6% alcohol. The values for the mono–trihydrate combination agree very well, but the others differ somewhat, especially that for the anhydrous–monohydrate mixture.

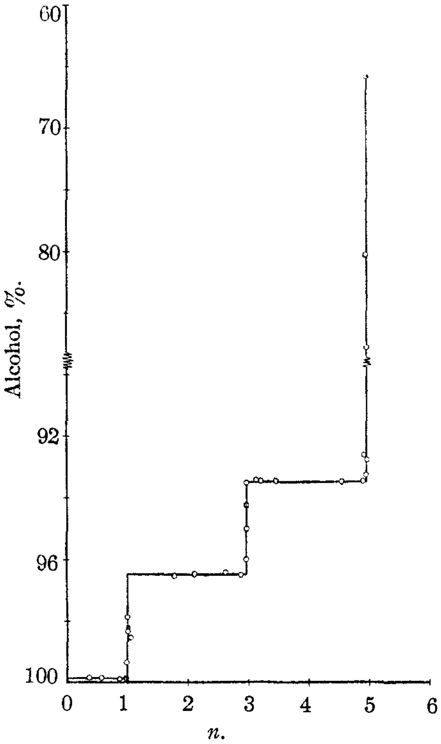

Fig. 1.—Plot of percentage alcohol in equilibrium with copper sulfate hydrates containing n moles H_2O at 25°: ○, single points; ⊡, two points combined.

However, it should be remembered that these authors could claim no greater accuracy than 0.1% in their alcohol determinations, and that their values represent averages of results which in themselves are in some cases as much as 0.8% apart. The furthest any two of our results are apart is 0.12%, and that for only one pair of values. In fact, the above results are within 0.03–0.06% of the respective means, corresponding to a variation of 0.03–0.05 mm. in vapor pressure.

To determine the actual aqueous pressures exerted by the hydrates, the aqueous tensions of various concentrations of alcohol solutions must be known. A search of the literature has revealed that only two such studies have been made, one by Foote and Scholes,[2] the other by Dobson.[14] The results of these investigators are shown graphically in Fig. 2. It is seen that there is considerable discrepancy between the two, but a greater reliance should be placed on Dobson's data. Unfortunately, however, his study did not extend beyond 90% alcohol, and it is precisely in the range 90–100% that we are interested. As extrapolation here is extremely dangerous, no attempt will be made at present to give the vapor pressures of the hydrates until more reliable data are forthcoming on the partial vapor pressures of alcohol solutions. Preparations are being made to determine this information.

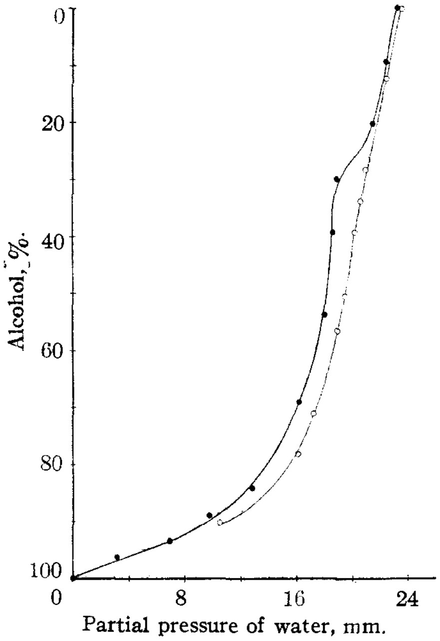

Fig. 2.—Partial aqueous tension of alcohol–water solutions at 25°: ●, data of Foote and Scholes; ○, data of Dobson.

Nevertheless, one observation concerning the vapor pressure of the anhydrous–monohydrate mixture can be made. For this hydrate combination results have been reported at 25°.

TABLE II

THE VAPOR PRESSURES OF $CuSO_4$–$CuSO_4 \cdot H_2O$ AT 25°

	Mm.
Müller-Erzbach[15]	0.5
Foote and Scholes[2]	0.8
Dover and Marden[16]	1.3
Menzies and Hitchcock[17]	0.017

The last value has been calculated by the investigators from the data of Bell and Tabor,[18]

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(14) Dobson, *J. Chem. Soc.*, **127**, 2866 (1925).

(15) Müller-Erzbach in Schottky, *Z. physik. Chem.*, **64**, 415 (1908).

(16) Dover and Marden, THIS JOURNAL, **39**, 1609 (1917).

(17) Menzies and Hitchcock, *J. Phys. Chem.*, **35**, 1660 (1931).

(18) Bell and Tabor, *ibid.*, **12**, 171 (1908).

Crockford and Warrick,[19] and Foote[20] on the concentrations of sulfuric acid solutions in equilibrium with the hydrate pair. They used an average value of 85.77% H_2SO_4. A re-reading of these investigations, however, shows that Foote reported 85.77% H_2SO_4, Bell and Tabor 88.51–90.89%, while Crockford and Warrick do not report data at 25°, but at 0, 20, 40 and 55°. Hence any value obtained from their data for 25° is interpolated.

Since it was found in this study that the anhydrous copper sulfate–monohydrate pair is in equilibrium with a 99.87% solution of alcohol by weight, it should be possible without serious error to apply Raoult's law to such a dilute solution of water in alcohol. The vapor pressure of pure water at 25° is 23.756 mm. Hence the vapor pressure of the salt pair $CuSO_4$–$CuSO_4 \cdot H_2O$ is 0.079 mm. at 25°.

The Alumina–Water Isotherm at 25°

The method employed with hydrous alumina was essentially the same as that employed with copper sulfate hydrates. The slight modifications in procedure will be pointed out below.

Materials

Alumina.—The alumina precipitate was prepared by dissolving about 200 g. of c. p. $Al_2Cl_6 \cdot 12H_2O$ in approximately three to four liters of doubly distilled water, and then adding rapidly with vigorous stirring enough concentrated ammonia (sp. gr. 0.90) to give a slight excess.

The precipitates, after settling overnight, were filtered next morning through three 76 cm. Büchner funnels, using filter press cloth as filters. The cakes of alumina were washed under moderate suction with 4–5 liters of distilled chloride-free water to which were added a few drops of ammonia to prevent peptization of the precipitate. The last liter or so of water, however, was ammonia free. At the end of about eight hours only an extremely faint chloride test could be observed with silver nitrate.

To cut down the water content of the precipitates, the latter were well mixed in a porcelain mortar, fed into a centrifuging basket, and allowed to revolve at 2000–2500 r. p. m. for about fifteen minutes. Through this treatment the alumina content was increased considerably, a factor very essential for accuracy. The precipitate was transferred then from the centrifuge into another porcelain mortar and worked with a porcelain spatula to form a more plastic and uniform mixture; it was then ready for filling the bottles.

Alcohol and apparatus were the same as for copper sulfate.

Procedure

Unlike the case of the copper sulfate, the alcohol was added first and the alumina second. To facilitate filling and expedite the addition of alumina, a glass syringe, similar to a hypodermic, was employed to introduce the alumina into the bottles. After the final weighing and sealing the bottles were allowed to rotate in the thermostat kept at 25.00 ± 0.02°, for forty to forty-five hours. This period of time was chosen for convenience over a week-end. Trials extending anywhere from thirty to sixty-five hours have yielded the same results, indicating that equilibrium is established in most cases within thirty hours or less.

The procedure from this point on was similar to that for copper sulfate except for the following differences. If difficulty was experienced due to peptization during the final centrifuging, addition of a trace of concentrated ammonia was sufficient to clear the alcohol solution. And again, the Al_2O_3 content of the precipitate had to be determined. To do this, each precipitate with its centrifuging tube was dried overnight in an oven at 150°, and the dry precipitate then transferred to crucibles. Any adhering alumina was removed from the bottles with hot hydrochloric acid, reprecipitated with ammonia, filtered, washed, and then added to the main bulk of the precipitate. Ignition to constant weight was carried out in an electric furnace at 1000°.

The precautions as to weighings, specific gravity determinations, vacuum reductions, etc., observed with copper sulfate were adhered to here.

Results and Discussion

The data and results obtained in the above described manner are given in Table III. The values of n were calculated by equation (1) except that the factor 5.658 was used.

TABLE III

SUMMARY OF RESULTS OBTAINED WITH HYDRATED ALUMINA AT 25°

n in $Al_2O_3 \cdot nH_2O$	Detns.	Composition of alcohol		Av. devn., %	n in $Al_2O_3 \cdot nH_2O$ (obsd.)	Av. devn. of n
		Initial %	Final %			
3.0	20	92.90–99.22	76.75–85.78	..	3.00	±0.03
2.5–3.0	9	95.35–99.93	87.52	±0.17	2.47–2.82	..
2.5	9	91.53–99.93	87.80–92.87	..	2.50	0.04
2.0–2.5	6	98.27–99.96	93.60	0.14	1.93–2.36	..
2.0	1	99.30	95.20	..	1.97	..
1.5(?)–2.0	6	99.22–99.30	96.28	0.12	1.36–1.93	..
1.5(?)	2	99.29–99.30	96.74–97.60	..	1.47	0.03

Table IV gives some results obtained on a sample as follows. The alumina was prepared

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(19) Crockford and Warrick, *J. Phys. Chem.*, **34**, 1064 (1930).

(20) Foote, THIS JOURNAL, **37**, 288 (1915).

TABLE IV

RESULTS OBTAINED WITH PREDRIED HYDRATED ALUMINA AT 25°

1 Sample	2 Alcohol, g.	3 Hydrated alumina, g.	4 Al_2O_3 in g.	5 Alcohol, % Initial	6 Final	7 n in $Al_2O_3 \cdot nH_2O$
XXVI	69.7231	3.4434	2.3460	91.03	90.99	2.56
A	72.8200	3.4857	2.3748	93.53	93.43	2.47
F	68.7931	3.1492	2.1455	93.70	93.57	2.39
XXX	73.3706	3.0617	2.0859	87.55	87.53	2.59
XI	67.4657	2.9624	2.0183	87.55	87.53	2.60

as above and then dried at 55° in an electric oven to a composition of 68.13% Al_2O_3, or $Al_2O_3 \cdot 2.65H_2O$. The precipitate was used then to make a run.

In Fig. 3 is given the graphic representation of the data. The percentage alcohol is that in equilibrium with the precipitate of composition *n*. The open circles represent single points, the solid circles two combined points at approximately the same alcohol concentration, while the triangles represent the points given in Table IV.

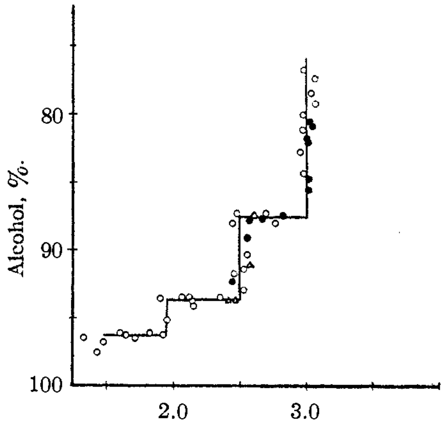

Fig. 3.—Plot of % alcohol in equilibrium with Al_2O_3 containing *n* moles of H_2O at 25°: ○, single points; ●, two points combined; △, pre-dried alumina.

Before proceeding with a discussion of the significance of the results, a word about the accuracy is in order. The method employed here is extremely sensitive to small errors in the determination of the percentage alcohol if the Al_2O_3 content of the original precipitate is low. In the alcohol range 90–60% and a precipitate of 8% Al_2O_3 an error of 0.01% alcohol corresponds to a change of 0.1 mole of water in the final results. However, since alcohol determinations were made with an accuracy of 0.01% or better, the final result is estimated in this range to be *within* 0.1 mole of water. The accuracy above 90% and below 60% alcohol is less.

The method can be made more exact if some means were found to increase the Al_2O_3 contents without leaving doubts as to the identical nature of the precipitate. The results to be discussed now point to such a way.

Figure 3 exhibits at least three discontinuities. From analogy with similar vapor pressure composition curves these point to the existence of the hydrates $Al_2O_3 \cdot 3H_2O$, $Al_2O_3 \cdot 2.5H_2O$, and $Al_2O_3 \cdot 2H_2O$. Whether the last three points indicate a break and hence an $Al_2O_3.1.5H_2O$ is problematical. There is some indication of a break but it is not sharp enough to allow conclusions before further work is done in the range 0–1.5H_2O.

One point is worth emphasizing. These results were obtained not with one sample of hydrous alumina, but with *nine* different precipitates prepared during the course of a year and a half. Yet they all fell along the same curves, in spite of a rather large scale of plotting along the abscissa. From the nature of these results and from their similarity to those for copper sulfate hydrates, the only plausible explanation which the authors can offer is that these curves represent the ranges of existence and coexistence of definite chemical hydrates.

Again, a very interesting and important point is the fact that the results on predried alumina fall in line with those on undried precipitate, as may be seen from the plot. The suspicion has been entertained by the authors for some time that the various forms of alumina are similar if not identical in nature if suitable methods of studying them are available. These results, although far from conclusive, indicate that this may be the case. If so, it ought to be possible to study the lower portions of the isotherm on predried samples and thus ensure a higher order of accuracy. Such experiments are contemplated.

It should be mentioned, however, that several attempts made to rehydrate dehydrated alumina to a definite point have not been very successful. The reason may be either that insufficient time was allowed to approach equilibrium, or that the process is not completely reversible.

Although not reported in detail, studies were also made with alcohol solutions below 75% alcohol. These yield results between $3H_2O$ and $3.5H_2O$, the composition in no case dropping below $3H_2O$ or going above $3.5H_2O$. These results, it seems to us, do not indicate a higher hydrate, but rather that with certain particle sizes adsorption of water on the trihydrate takes place above certain vapor pressures. The limiting vapor pressure is not fixed but fluctuates with the particle size of the precipitate. There is some indication that for any one particle size there may exist a definite adsorption isotherm, but there are not enough data available to make this statement with certainty.

These results seem to lead to the conclusion that precipitated gelatinous alumina is composed of $Al_2O_3 \cdot 3H_2O$ containing water adsorbed on its surface and entrained in its interstices. The latter is lost first to an atmosphere of lower vapor pressure and then the adsorbed water. No adsorption could be detected above 77% alcohol (16 mm. aqueous tension). If the vapor pressure is low enough, water is lost by the trihydrate to yield successively lower hydrates.

If, as the authors believe, the results do indicate hydrates, and as practically nothing is as yet known about the vapor pressures of such hydrates, it may not be amiss to overlook the objections raised in conjunction with copper sulfate, and translate Fig. 3 to a vapor pressure–composition curve. To do this, Dobson's results were plotted on a large scale and the vapor pressure corresponding to various alcohol solutions read off. The plot of these vapor pressures against *n* is shown in Fig. 4. This curve is identical in shape with Fig. 3 except that the vertical portions and the discontinuities are more accentuated. Further, this curve seems to show better evidence for an $Al_2O_3 \cdot 1.5H_2O$.

From this plot we obtain the following as the vapor pressures of the various hydrate pairs at 25°.

$Al_2O_3 \cdot 3H_2O$–$Al_2O_3 \cdot 2.5H_2O$	12.1 mm.
$Al_2O_3 \cdot 2.5H_2O$–$Al_2O_3 \cdot 2H_2O$	8.3 mm.
$Al_2O_3 \cdot 2H_2O$–$Al_2O_3 \cdot 1.5H_2O$ (?)	5.6 mm.

Thiessen and Thater[21] reported a vapor pressure of 5 and 7 mm. (in two determinations) for the trihydrate at 17°. Hüttig, on the other hand, obtained by calculation 5 × 10^{-6} mm. at 20°. Our results seem to be more in accord with Thiessen and Thater's.

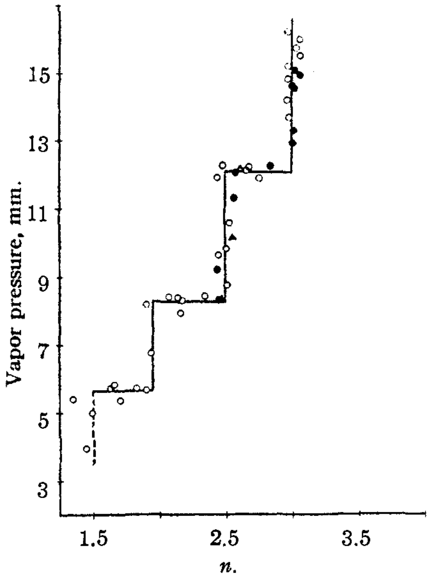

Fig. 4.—Vapor pressure–composition diagram of alumina hydrates at 25°: ○, single points, ●, two points combined, △, pre-dried alumina.

Summary

1. The method of Foote and Scholes for the study of hydrates has been shown to be capable of yielding good results, if certain refinements in technique are employed, by redetermining the $CuSO_4$–H_2O isotherm at 25°.

2. The concentrations of alcohol solutions in equilibrium with the various hydrate pairs in the above system are given.

3. A new tentative value for the vapor pressure of the pair $CuSO_4$–$CuSO_4.H_2O$ is given.

4. The above method for the first time has been applied to the system Al_2O_3–H_2O at 25°.

5. The experimental results point to the existence of the hydrates $Al_2O_3 \cdot 3H_2O$, $Al_2O_3 \cdot 2.5H_2O$, $Al_2O_3 \cdot 2H_2O$, and possibly also $Al_2O_3 \cdot 1.5H_2O$. The study was not carried any lower.

6. At 25° no hydrates above $Al_2O_3 \cdot 3H_2O$ have been found. Above this point water seemed to be adsorbed and entrained.

7. The vapor pressures of the various hydrates are given.

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[21] Thiessen and Thater, *Z. anorg. allgem. Chem.*, **181**, 417 (1929).