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X-RAY STUDIES ON THE HYDROUS OXIDES

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**A Thesis
Submitted to the
Faculty of the Rice
Institute in Partial
Fulfillment of the
Requirements for
the Degree of
Doctor of
Philosophy**

Deposited Jan. 1950

Houston, Texas

May 15, 1934

UMI Number: 3079804

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X-RAY STUDIES ON THE HYDROUS OXIDES

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CHAPTER I

HYDROUS AND HYDRATED OXIDES

The addition of a solution of an alkali hydroxide to a solution of a heavy metal salt usually gives a voluminous, gelatinous precipitate containing an amount of water depending upon the conditions of formation and subsequent treatment of the sample. Drying under arbitrary conditions often results in a water content consistent with the formation of definite metal hydroxides, hydrates, or hydrated hydroxides. Early investigators invariably assumed the existence of numerous hydrates to account for the variable water content of their preparations. While many definite hydrates and hydroxides are known to exist, it must be clearly recognized that the mere analysis of an arbitrarily dried gelatinous precipitate cannot establish the existence of such a compound. This fact was first clearly recognized by van Bommel(1) who investigated by vapor pressure methods several hydrous precipitates including SiO_2 , Al_2O_3 , SnO_2 , etc. This classic work paved the way for the rapid development of the study of the hydrous oxides which has taken place since 1920. The investigations of Weiser(2), Hüttig(3), Willstätter(4), Simon(5), Fricke(6), and their coworkers have thrown considerable light on this class of compounds. While many of the cherished hydrates of the early investigators have been shown to be non-existent, in many cases modern methods of investigation have shown the situation in many cases to be much more complicated than it was formerly supposed. Examples of this will be given in following sections of this paper.

For the purposes of this paper a hydrous oxide shall be defined as an adsorptive oxide containing an amount of adsorbed water depending upon the

conditions of formation and treatment of the sample. A hydrate shall be considered to be a definite, crystalline, chemical compound. In most definite "hydroxides" it has been shown by x-ray analysis that the crystal lattice consists of metal ions and hydroxyl ions, and that in certain "hydrates", H_2O groups are arranged around some central group after the manner of Werner complexes. "Hydroxides" may also contain additional chemically bound water over and above the true hydroxide. However, since in so many cases the complete structure has not been determined by x-ray analysis no attempt shall be made, in general, to distinguish between "hydroxides" and "hydrates". It is not considered that anything would be gained by using the terms "water of crystallization" and "water of constitution".

If it is possible to obtain large crystals of a preparation under examination, there need be no difficulty in determining the amount of combined water, however in the case of the typical hydrous oxides and hydrous hydrated oxides, the extreme insolubility of the compounds gives precipitates in such a finely-divided form that no individual crystals can be detected using even the microscope. Indeed before x-ray analysis established the fact of their crystallinity, it was questioned if they were really crystalline.

Methods of investigation which give the most useful and trustworthy results are phase rule and x-ray studies. A brief description of these methods as used in this paper will be given in the next two paragraphs before proceeding to specific systems investigated.

Dehydration Isobars and Isotherms. The systems hydrate-oxide(or lower hydrate)-water vapor and oxide-water vapor are both two component systems. Application of the phase rule shows that the systems should be univariant and bivarient respectively. The types of curves expected are shown as dotted

lines in Figs. 1 and 2. Actual curves represented by the unbroken lines usually do not follow sharp right angles, but are rounded off because of variations in particle size, lattice distortion, and lattice strain. Complications may arise in the interpretation of dehydration curves in cases where the product of dehydration is a powerful desiccating agent. Examples of this will be discussed in Chapter II.

X-RAY ANALYSIS. One of the most important results of x-ray analysis was the proof that many, if not all, colloids are crystalline. Since most hydrous and hydrous hydrated oxides are only submicroscopically crystalline, it is evident that their study is greatly facilitated by the use of x-ray methods. If it can be shown that the powder x-radiogram of a gel or hydrous oxide is identical with that of the anhydrous oxide, then the absence of hydrates is proven. When hydrates are formed each has its own distinctive pattern. If the existence of a hydrate is once established, its presence in a gel or gelatinous precipitate can be shown at once by x-ray methods.

In the following chapters of this paper phase rule and x-ray methods will be applied to a number of the more important hydrous oxides and hydrous hydrated oxides.

Figure 1

I hydrous oxide; II hydrate; III hydrous hydrate; isobars

Figure 2

I hydrous oxide; II hydrate; III hydrous hydrate; isotherms

References for Chapter I

- (1) van Bemmelen: Z. anorg. allgem. Chem., (1890-); "Die Absorption", (1910).
- (2) Weiser and coworkers: J. Phys. Chem., (1920-); "The Hydrous Oxides", (1926).
- (3) Hüttig and coworkers: Z. anorg. allgem. Chem., (1922-); Kolloid-Z., (1924-).
- (4) Willstätter and coworkers: Ber., (1924-).
- (5) Simon and coworkers: Z. anorg. allgem. Chem., (1925-); Kolloid-Z., (1925-).
- (6) Fricke and coworkers: Z. anorg. allgem. Chem.; Kolloid-Z., (1924).

CHAPTER II

ALUMINA

The addition of a base to a solution of an Al salt gives a highly gelatinous precipitate usually designated as $\text{Al}(\text{OH})_3$. While considerable evidence indicates that the first formed gelatinous mass is hydrous Al_2O_3 , and not an aluminium oxide hydrate such as $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, a number of older as well as more recent investigations point to the existence of a hydrate or series of hydrates in the freshly precipitated gel.

A critical survey of the evidence for and against the existence of definite hydrates in precipitated alumina was made 8 years ago(1). Since that time the situation has been complicated by the interpretation put on vapor pressure and x-ray data obtained more especially by Hüttig and Willstätter. In the present paper are given: (A) An historical summary in tabular form of vapor pressure and x-ray data on (1) precipitated alumina and (2) the trihydrate of alumina. (B) An x-ray study of (1) Hüttig aluminas, (2) Willstätter aluminas, (3) precipitated alumina aged at 100 degrees C., (4) aged alumina decomposed by heat, (5) alumina formed by the thermal decomposition of hydrated aluminium chloride, (6) alumina formed by the decomposition of gibbsite, and (7) artificial gibbsite.

A. HISTORICAL

(1) Precipitated Alumina.

Composition. The precipitate formed by the interaction of NH_4OH and a soluble Al salt will henceforth be designated as precipitated alumina. Different investigators have assigned various formulas to the precipitate dried in

different ways. Some typical results are summarized in Table I. It is apparent that while certain investigators, especially van Bommel and Shidei, question the existence of hydrates, others, notably Hüttig and Willstätter, believe that a part of the water is chemically bound in the orthodox sense of the word to give definite hydrates. The work of Willstätter and Hüttig will receive critical consideration in the experimental portion of this chapter.

The vapor pressure data of Shidei on precipitated alumina commands special attention. He treated AlCl_3 solution with NH_4OH , washed the resulting precipitate by decantation several times and then dialysed it for 11 days at 50-60 degrees C. The resulting precipitate was free of Cl^- and SO_4^{--} but still contained a trace of ammonia. The vapor pressure curve at constant temperature for this precipitate was determined in a specially designed apparatus. Extreme care was taken to obtain equilibrium conditions. Final values were obtained in some experiments only after over 70 days. The curve reproduced in Fig. 1 shows clearly that no definite hydrates are formed under the conditions of Shidei's experiment. It was assumed that the water present has formed a solid solution in the alumina; but it is more probable that the water is retained by adsorption forces on the surface of the finely-divided crystals of anhydrous alumina or monohydrate.

X-Ray Data. A number of investigators have examined precipitated alumina by x-ray diffraction methods. Haber(9) obtained no diffraction effect in the precipitate from an ultrafiltered alumina prepared by Grun's method. He concluded from this that the gel is amorphous when thrown down in the cold but gradually assumes an ordered structure. Frick and Weaver(10), on the other hand, observed one broad diffraction band from a precipitate formed at room temperature and a weak pattern from one thrown down at 100 degrees C. Bohn (11)

Table I
Composition of Precipitated Alumina

Investigator	Method of drying	Composition mols H ₂ O/Al ₂ O ₃	Investigator's conclusions
van Bommel(2)	Air-dried	4.3 to 4.5	Indefinite hydrates except possibly a trihydrate
Carnelly and Walker(3)	Air-dried	5	Either no hydrates or a large number of hydrates
	at 65 degrees, C.	3	
	at 160-200	2	
	at 250-290	1	
	at 350	0	
Allan(4)		Precipitated	Composition determined by the method of drying
		Cold Hot	
	air-dried	3.03 2.89	
	Over H ₂ SO ₄ at 100 degrees	2.020 2.04 2.015 1.88	
Guichard(5)	Air-dried	6.59	The di- and tri-hydrates exist in the cold ppt.
Hettig and co-workers(6)	Aged under varying conditions	3 to 1	A series of hydrates are formed
Willstätter and coworkers(7)	Pptd. under varying conditions	3 to 1	Definite hydrates are formed.
Shidei(8)	Varying pressure	See Fig. 1	No hydrates

FIG. 1
Vapor Pressure-Composition Diagram for Precipitated Alumina (after Shidei)

Table II
Precipitated Aluminas used in X-Ray Diffraction Studies

Investigator	Treatment	Composition mols H ₂ O/Al ₂ O ₃	No. in Fig. 2
Biltz and Lehrer(12)	Dried:		
	At 100 degrees C.	1.03	-
	with liquid NH ₃	1.15	-
	with liquid NH ₃	2.995	1
	with acetone	2.88	2
	with liquid NH ₃	2.04	-
	with liquid NH ₃	1.00	3
	with acetone	1.00	-
	with acetone	1.71	-
	with liquid NH ₃	1.49	-
	with liquid NH ₃	1.98	4
	with acetone	3.16	-
	with acetone	2.39	-
	with acetone	2.55	-
	with liquid NH ₃	2.98	5
de Jong(13)	pptd. and dried 40-45°C.	--	6
	pptd. and dried 100°C.	--	-
Rocksby(14)	Dehydration of gibbsite 250°C. 1		7
	pptd. at 20°C.	--	similar to 7
	pptd. at 100°C.	--	similar to 7

obtained a well-defined pattern which he described as similar to some "banxites" is a precipitate thrown down at 100°. These qualitative observations have been extended by more recent quantitative work which has been summarized in Table II and Fig. 2^f. Because of the similarity in the x-radiograms from a number of the samples, it is necessary to reproduce only a few of them. The numbers in

^fFor Fig. 2 see: Weiser and Milligan: J. Phys. Chem., 36, 3013 (1932).

in the last column of the table correspond to the numbers of the x-ray patterns shown in the figure. It will be noted that all of Biltz and Lehrer's samples yield similar but not identical diffraction effects. Rocksby examined a number of preparations formed with varying concentrations of ammonium hydroxide at both room temperature and at 100° . The x-ray patterns from the several samples were identical except for a slight variation in the width of the lines, showing that the conditions of preparation influence the particle size. The lines were quite diffuse but the positions were the same with the product formed by the thermal decomposition of gibbsite. Further discussion of Rocksby's results will be given in a later section, but it is evident that precipitated alumina must be considered to be made up essentially of finely-divided particles having this crystal lattice.

(2) The Crystalline Trihydrates.

The mineral gibbsite occurs in nature in the form of well-defined crystals. The artificial preparation of this compound has been accomplished in a variety of ways. Thus Bonsdorff(15) and Bayer(16) dissolved alumina gel in KOH and allowed the solution to stand in a closed vessel until crystals appeared. Similarly, Goudriaan(17) dissolved Al in NaOH and allowed the solution to stand in the air, and Fricke(18) passed CO_2 slowly into cold alkali aluminate solution or slowly hydrolyzed the aluminate by dilution. While the composition of the several preparations corresponds to the formula $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, there is a difference of opinion as to whether the artificial preparations are identical in crystal structure with gibbsite. This point has been investigated by x-ray diffraction methods. The results are summarized in Table III and a number of x-ray diagrams are reproduced in Fig. 3. Except for the results of Biltz and Lehrer, the evidence is fairly conclusive that ~~the~~ the artificial preparations

Figure 3

X-Ray Diagrams of Natural and Artificial Alumina Trihydrates

1. $\text{Al}_2\text{O}_3 \cdot 3.06\text{H}_2\text{O}$ after Biltz and Lehrer
2. Artificial gibbsite after Biltz and Lehrer
3. α - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ after Damerell et al
4. α - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ Damerell's sample by Weiser and Willigan
5. gibbsite after Rocksby
6. α - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ after Rocksby
7. ? ? ? after Hansen and Brownmiller
8. Gibbsite after Hansen and Brownmiller
9. Gibbsite after Jo Jong
10. Gibbsite, γ - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ by W. and M.
11. "Bauxite" by W., and M.
12. Artificial gibbsite, γ - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ by W. and M.
13. Diaspore, α - $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ by W. and M.

Table III
Artificial Gibbsite and Similar Preparations

Investigator	Method or Sample	X-Ray Pattern Obtained	No. in Fig. 3
Biltz and Lehrer(19)	Pptd. by NH_4OH at 70°C . and dried with acetone	Unlike gibbsite	1
	Bondorff's Method	Somewhat like gibbsite	2
Damerell(20)	Pptd. alumina aged in the cold	Different than gibbsite	3
Weiser and Milligan	Damerell's sample	" " " "	4
Fricke and coworkers(21)	Slow hydrolysis in cold of aluminates	Identical with gibbsite	-
	Rapid hydrolysis of aluminates	Different from "	-
L.H. Milligan(22)	Bayer's Method	Identical with "	-
Rocksby(23)	Mineral Gibbsite	Gibbsite pattern	5
	Goudriaan's Method	Different from "	6
Hansen and Brownmiller(24)	Goudriaan's Method	Unlike gibbsite	7
	Mineral gibbsite	Gibbsite pattern	8
de Jong(25)	Mineral gibbsite	Gibbsite pattern	9
Weiser and Milligan	Mineral Gibbsite	" "	10
	Mineral "bauxite"	" "	11
	Bondorff's Method	" "	12
	Goudriaan's Method	" "	13
	Mineral Diaspore	Diaspore pattern	14

are either identical with α - or γ - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ or mixtures. Our x-radiograms of (1) a mineral gibbsite, (2) a mineral "bauxite", and (3) artificial gibbsites obtained by Bonsdorff's and Goudriann's methods were identical as nearly as could be determined (Fig. 3: 10, 11, and 12). It is not obvious why the differences in the x-radiograms of the various investigators for the apparently same product should exist. However as will be pointed out in the section "Synthesis of Gibbsite" in the experimental part of this paper, it is probable that the differences are the result of obtaining varying amounts of the alpha and gamma trihydrates.

B. EXPERIMENTAL

(1) Preparations according to Hettig's Procedures.

Hettig and coworkers(26) prepared a number of alumina precipitates and studied them by isobaric dehydration and x-ray diffraction methods. The gel freshly precipitated in the cold, appeared to be amorphous and to lose water continuously with increasing temperature. On standing at ordinary temperatures the fresh gel went over gradually into $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. According to Hettig the transformation was not direct; but a series of crystalline intermediate hydrates between $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ was believed to form. Every member of this series of hydrates manifested its individuality by a definite step-curve.

Hettig and Kostelitz recognized two more or less separate and distinct aging processes; (a) gelatinous alumina, which consists of alumina and adsorbed water, reacts with the adsorbed water to form a series of compounds ending with $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$; (b) a lower alumina hydrate, assumed to be $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ with adsorbed water, reacts with the adsorbed water giving a series of compounds with $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ as the final product. These two processes are represented in Figs. 4 and 5, respectively. In Fig. 4 the transformation is from I to II to III to IV in which I represents the non-crystalline $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, II, and III, intermediate hydrates and IV, gibbsite. The second process is represented in

FIG. 4

Temperature-Composition Curves of Precipitated Alumina (after Hüttig, I)

FIG. 5

Temperature-Composition Curves of Precipitated Alumina (after Hüttig, II)

in Fig. 5 in which the changes are from 1 which is the curve for the monohydrate through 2, 3, 4, and 5, the curves for intermediate hydrates, and 6, the curve for the trihydrate.

X-radiograms of the several products were found to exhibit differences each from the other. This was likewise interpreted to mean that each was a definite chemical individual intermediate between non-crystalline alumina, a monohydrate, and the trihydrate.

It is well known that differences in the mode of preparation of a definite material may influence the particle size and thus the width (sharpness) of the lines on the x-ray diffraction pattern; but differences in the position and relative intensities of the lines require further explanation. The differences in the position may be accounted for as a result of (1) formation of a solid solution with water in varying amounts, (2) experimental errors inherent in the apparatus employed, (3) error in calibration of individual films, (4) and samples being mixtures rather than pure definite compounds as Hettig and Kestelitz assumed their intermediate products to be. Of course, no significance can be attached to slight differences in visually estimated intensities. Unfortunately Hettig's x-ray data are recorded only in chart form on a small scale, and it is altogether impossible to make any accurate comparisons with the results of other people.

Preparation and Treatment of Samples. In the present investigation samples of precipitated aluminas were prepared and aged as nearly as possible in accord with the procedures of Hettig and Kestelitz. Both the K and L series of samples were investigated. To prepare the former, one liter of 2 N NH_4OH was added with stirring to 90 g of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ dissolved in 200 cc of water at room temperature. The resulting hydrous precipitate was placed in 250 cc wide-mouthed bottles and washed ten times by the aid of the centrifuge using 200 cc portions of water. At the conclusion of the washing, the gel was almost

chloride free and sol formation has begun. The sample was divided into five parts as shown in Table IV.

The L samples were made by adding 48 cc of 25 % NH_4OH at 48°C . to 548 cc of a solution containing 118 g $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and 37.6 g of NH_4Cl . The resulting precipitate was washed as above described and four samples were aged as shown in Table IV.

Table IV
Aging of Precipitated Al uminas

Samples	Method of Aging
K_1 and L_1	In a closed desiccator over 10% H_2SO_4 ; K_1 15 weeks and L_1 18 weeks
K_1^*	Same as K_1 for 29 weeks
K_2 and L_2	In the open air but protected from dust for 27 weeks
K_3 and L_3	In a closed desiccator for 31 weeks
K_4 and L_4	Over water in a closed desiccator for 22 weeks

X-Ray Examination. The samples above described were air-dried, powdered, and placed in thin nonex capillary tubes, one end of which contained a sample of very pure NaCl which was used to calibrate each film. X-ray diffraction patterns were obtained with the General Electric x-ray diffraction apparatus. The results are given in Table V, and the diagrams of the patterns are shown in Fig. 6. The interplanar spacings d_{hkl} , $\text{\AA}$ are expressed in Angstrom units; I represents the relative intensity, estimated on such a scale that 10 means the most intense line.

Table V
X-Ray Diffraction Data for Aluminas Prepared by Hüttig's Methods

K ₁ '		K ₁ ''		K ₂		K ₃		K ₄		L ₁		L ₃		L ₄	
D	I	D	I	D	I	D	I	D	I	D	I	D	I	D	I
4.65	10	4.76	9	4.75	8	4.79	10	4.75	10	3.18	7	4.79	10	3.18	7
4.32	10	4.31	9	4.36	8	4.34	10	4.39	9	2.36	8	4.39	9	2.36	8
3.22	3	3.18	4	3.19	2	3.19	4	3.22	5	1.85	10	3.22	5	1.85	10
2.36	4	3.46	2	2.39	2	2.47	2	2.47	2	1.43	6	2.47	3	1.43	4
2.22	10	2.37	3	2.22	10	2.37	3	2.37	3	1.31	4	2.37	3	1.31	4
2.00	2	2.26	1	1.99	1	2.26	1	2.22	10	1.13	2	2.22	10		
1.87	2	2.22	10	1.90	1	2.22	10	2.01	2			2.01	2		
1.71	6	1.99	1	1.789	1	2.00	2	1.89	2			1.89	2		
1.55	1	1.885	1	1.721	5	1.89	1	1.72	8	L ₂		1.72	8		
1.44	5														
1.38	3	1.770	1	1.436	3	1.77	1	1.64	1			1.64	1		
1.33	4	1.709	7	1.390	2	1.72	7	1.60	1			1.60	1		
1.21	1	1.639	1			1.65	1	1.56	1	3.18	7	1.56	1		
1.16	1	1.589	1			1.60	1	1.44	3	2.36	8	1.44	3		
1.13	1	1.550	1			1.55	2	1.39	2	1.85	10	1.39	2		
		1.431	4			1.44	3	1.33	2	1.43	6	1.33	2		
		1.389	3			1.39	3	1.21	1	1.31	4	1.21	1		
		1.327	4			1.21	4			1.13	2				
		1.204	2			1.21	2								

It is significant that Hüttig's K samples formed in the cold are all quite similar and that they are probably mostly $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. The L samples formed at higher temperatures give patterns almost identical with that of $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ except L_3 which is similar to the K samples. It is altogether probable that this difference is the result of the varying conditions of aging.

(2) Preparations According to Willstätter's Procedures.

Samples of several aluminas were made according to the procedures of Willstätter and coworkers and were examined by the x-ray diffraction method.

Preparation of Sample A. One liter of a solution containing 100 g of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ at 100°C was added to a solution of one liter of 6 N NH_4OH at 50°C . with vigorous stirring, after which steam was passed into the mixture for 5 hours, adding more ammonia from time to time. The resulting precipitate was washed free from sulfate and chloride by ordinary decantation and finally by the aid of the centrifuge. A portion of the sample was dried over P_2O_5 for 30 days and then contained 21.72 % water. Willstätter and Kraut's similar product dried over H_2SO_4 contained a percent of water corresponding approximately to the formula $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$.

B. This preparation was precipitated like A, but instead of passing steam into it, the sample was heated on a steam bath for 30 minutes at 65°C ., then washed nearly free from sulfate and chloride.

D. About 65 g of alumina (calculated as $\text{Al}(\text{OH})_3$) were dissolved in a solution of 70 g of KOH in 450 cc of water. The resulting solution was filtered diluted to 5 liters, and CO_2 passed in rapidly. After thorough washing the sample was dried over P_2O_5 for 30 days.

Now A. Willstätter, and Kraut, and Hummel (27) have recently modified the procedure for preparing the A sample which is claimed to give the definite hydrate $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$. A sample was made according to this procedure: A solution of

250 g $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ in 750 cc of water was warmed to 48°C . and poured rapidly with vigorous mechanical stirring into 2.5 liters of 15 % by weight NH_4OH also at 49°C .; the temperature rose to about 50°C . The resulting mixture was stirred for 30 minutes, and diluted to 12 liters with distilled water. The precipitate was washed by decantation 4 times after which 1 liter of 15 % NH_4OH was added, and stirred for 5 minutes, followed by dilution to 12 liters with distilled water. The washing by decantation was continued until peptization began. About 2 days were required for these operations in accordance with the requirements of Willstätter. The resulting precipitate was then washed with acetone and ether. Samples were dried, A_1 in vacuum, A_2 over P_2O_5 in vacuum, and A_3 at 110°C . in air.

X-Ray Examination. X-radiograms were made of the 6 samples above described. The position and relative intensities of the lines in the several samples are shown in Table VI and the diagrams for two of the samples only are reproduced in Fig. 7 (5 and 6). It is evident that all of Willstätter's samples formed by precipitation in the hot have the same structure, which is that of $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. The D Sample obtained by rapid hydrolysis of aluminate in the cold gave an x-radiogram in which no lines could be detected.

Table VI

X-Ray Data for Willstätter's Preparations

A		B		D		New A_1		New A_2		New A_3	
D	I	D	I	D	I	D	I	D	I	D	I
3.16	7	3.15	5	No lines or bands visible							
2.34	8	2.36	7								
1.85	10	1.85	10			1.85	10	2.35 6		1.85 10	
		1.61	0.1					1.85 10		1.85 10	
1.43	8	1.43	8			1.43	7	1.43 7		1.43 8	
1.31	6	1.32	6					1.31 5			
1.13	2	1.13	1

FIG. 6
X-Ray Diffraction Diagrams of Precipitated Aluminas prepared according to Hüttig's Procedures

FIG. 7
X-Ray Diffraction Diagrams of Precipitated Aluminas prepared in Various Ways

(3) Aging of Precipitated Alumina at 100°C.

Since a survey of reported work indicated that different products are obtained on aging hydrous alumina in the hot and in the cold, the following systematic procedure^{*} was carried out: 200 g of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ was dissolved in 500 cc of water and 125 cc of 15 N NH_4OH was added with vigorous^o stirring. A sample containing the suspended oxide was removed at once and the remainder was heated to boiling under a reflux condenser. The boiling was continued several weeks, samples being removed from time to time and washed and dried according to the following procedure: Each sample was washed 7 times by the aid of the centrifuge with 50 cc portions of distilled water followed by 5 washings with 50 cc portions of acetone and then dried at 50°C. No significance is attached to this particular procedure but it was followed with all samples so that the various compositions are comparable. Willstätter believes that washing with acetone removes all the adsorbed water, leaving only chemically combined water. This appears to be definitely in error. However, in the present experiments washing with acetone was used as a convenient^{ent} method of removing much of the water without the necessity of heating to a high temperature which might decompose definite hydrates, assuming they were present. After drying according to the above procedure the composition was determined and x-radiograms made. The relationship between the age of the sample and the water content of the precipitate is given in Table VII and shown graphically in Fig. 8. The x-ray diffraction data are given in Table VIII and Fig. 7. The results are quite conclusive. The precipitate is almost amorphous when first formed but aging in the hot gradually causes a transformation to the crystalline form which shows the same lines on the x-radiogram as Willstätter's A and B samples.

Table VII

Age and Composition of Precipitated Alumina

Age hours	Composition % water	Numbers in Table 8 Fig.7		Age hours	Composition % water	Numbers in Table 8 Fig.7	
0	74.73	1	-	96.5	24.15	7	2
1	-----	2	-	168	-----	8	3
3	40.89	3	1	237	22.51	9	-
14.5	-----	4	2	335	-----	10	-
24	34.65	5	2	504	-----	11	-
72	26.88	6	2	1009	19.35	12	4

Table VIII

X-Ray Diffraction Data for Alumina Aged at 100°C.

1		2		3		4		5		6	
D	I	D	I	D	I	D	I	D	I	D	I
No lines or bands visible in No.'s 1 and 2				1.85	10	1.84	10	1.84	10	1.84	10
				1.43	10	1.43	9	1.43	9	1.43	9
						1.32	5	1.33	5	1.33	5
7		8		9		10		11		12 and 12a	
D	I	D	I	D	I	D	I	D	I	D	I
1.84	10	2.38	8	3.15	6	3.15	5	3.16	5	3.18	5
1.43	9	1.84	10	2.34	7	2.33	7	2.33	7	2.36	8
1.33	5	1.43	9	1.85	10	1.85	10	1.85	10	1.85	10
		1.33	5	1.43	9	1.44	8	1.43	8	1.43	8
				1.32	5	1.33	5	1.33	5	1.13	2
				1.14	2	1.14	2	1.14	1

FIG. 8
Time-Composition Curve of Precipitated Alumina aged at 100°C.

FIG. 9

(4) Dehydration of Alumina Aged at 100°C.

Since all the samples described in the preceding paragraph were treated with acetone and dried at 50°C., it was thought desirable to dry some of these at higher temperatures and thereby reduce the water content. Thus sample 12 having a composition 19.35 % water when dried at 50°C. was heated for about 3 hours at 160°C. (sample 12a) at which temperature the composition became 10.38 %, which corresponds to $\text{Al}_2\text{O}_3 \cdot 0.65\text{H}_2\text{O}$. X-ray examination showed that the crystal structure had not changed, the results for 12 and 12a being identical. If the phase rule be applied without modification, it is proven that the material is not a monohydrate. However as will be shown below this material is actually a monohydrate. This point will be further discussed under the heading: Interpretation of Dehydration Curves.

Polymorphism of Alumina. It has been demonstrated that at least four polymorphic forms of anhydrous alumina exist: (1) α - Al_2O_3 , which occurs in nature as corundum and has been prepared artificially by heating ordinary alumina to 1800°C. (28); (2) β - Al_2O_3 , prepared by allowing molten α - Al_2O_3 containing 0.5 % MgO (29) or 5 % Na_2O (30) to cool slowly; and (3) γ - Al_2O_3 , formed by heating precipitated alumina in the neighborhood of 300-900°C.; and finally (4) δ - Al_2O_3 , recently prepared by allowing molten α - Al_2O_3 containing 5 % Li_2O to cool slowly (32, 33).

In 1928 Parravano and Montoro (34) reported the formation of another modification of alumina by heating $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ for 15 days. Biltz and Lehrer (35) called this modification ζ - Al_2O_3 . However in 1929 Parravano and Omorato (36) reported a serious error in the 1928 paper. "The spectrum reported in the work cited and attributed to be from alumina at 250°C. was due to an exchange of samples".

For the purposes of comparison the x-ray diffraction patterns of the α , β , γ , and δ modifications of alumina together with that of γ - $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ are given in chart form in Fig. 9. There can be no doubt that each of the five samples possesses a crystal structure entirely different from the others.

(5) Thermal Decomposition of Aluminium Chloride.

In view of the error in Parravano and Montero's report experiments were carried out to determine, if possible, what form of alumina results from the decomposition of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. In the first experiment 5 g of the salt was placed in an electric oven at 150°C . In 10 hours the temperature rose to 250° and the sample was maintained at this temperature for 2 hours. X-ray examination showed the resulting product to be amorphous. A second sample prepared by heating 17 hours at 225° and a third by heating at 250° for 30 days likewise proved to be amorphous. It was then decided to carry out the dehydration at a lower temperature. Accordingly, a sample was heated for 72 hours at 165 – 170° . This treatment was insufficient to decompose the hydrate completely; hence the sample was washed with hot water until nearly chloride free and then dried at 60° . X-ray examination showed that a crystalline product resulted which was identical with γ - $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ as shown diagrammatically in Fig. 7 (g).

(6) Thermal Decomposition of Gibbsite.

Gibbsite, γ - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, starts to decompose on heating to a temperature somewhat below 200° . Rocksby obtained an x-radiogram of the product formed by thermal decomposition at a temperature of 250° . Under these conditions the composition of the product was represented by the formula $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. Since the x-radiogram is different from that of diaspor, it was considered that this material was an isomer of diaspor. This will be further discussed in a following section of this chapter.

(7) Synthesis of Gibbsite.

In the historical portion of this chapter was included the diagram for the x-ray pattern of an artificial gibbsite which we prepared (Fig. 3, 12). The sample was made in the following way: To a solution of 56.1 g of KOH in 300 cc of water were added 10 g of Al strips, a little at a time to avoid frothing and excessive heating. The resulting solution was filtered, placed in a stoppered flask, and allowed to stand. Upon examination 30 days later, the flask was covered with a micro-crystalline powder. This material was carefully washed, and dried at 60°, and submitted to x-ray examination. The results obtained are given in Table IX and Fig. 3 (10, 11, and 12).

The above method of synthesizing gibbsite is similar to that of Goudriaan. A sample prepared by Bonsdorff's method which is essentially the same as Goudriaan's gave an identical x-radiogram. It will be recalled that Rocksby obtained different x-radiograms from samples made by these two methods, not the same as gibbsite. This is explained by the fact that a second isomer of gibbsite exists (Fricke's bayerite, $\alpha\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$). This material occurs as an intermediate product in these methods of preparing gibbsite. This second trihydrate has recently been proven to be actually a definite chemical compound(37). This question is further discussed in a following section of this present paper under the title: Interpretation of Dehydration Curves.

Discussion of Results

From the experiments above described and from earlier observations of Haber, Fricke, and Weaver, and others, it is evident that alumina, freshly precipitated by the interaction of cold solutions of ammonia or alkali and a soluble Al salt, is either amorphous or contains such extremely minute crystals that it gives little or no diffraction effect. When the gelatinous precipitate

Table IX
X-Ray Data for Gibbsite and Diaspore

10 Gibbsite Mineral D I		11 "Bauxite" Mineral D I		12 Gibbsite Artificial D I		13 Diaspore Mineral D I	
4.85	10	4.85	10	4.85	10	4.00	10
4.34	9	4.34	9	4.36	8	2.57	8
3.31	1	3.31	1			2.34	8
3.12	1	3.12	1			2.13	10
2.45	7	2.45	7	2.45	6	2.08	2
2.38	7	2.38	7	2.38	6	1.82	1
2.26	1	2.26	1	2.26	3	1.71	2
2.17	3	2.17	3	2.17	3	1.63	10
2.04	3	2.04	3	2.04	3	1.54	1
1.990	2	1.990	2	1.985	3	1.50	2
1.907	2	1.907	2	1.911	3	1.47	2
1.798	3	1.798	3	1.795	3	1.40	8
1.741	4	1.741	4	1.741	3	1.38	1
1.681	5	1.681	5	1.680	4	1.34	1
1.642	0.1	1.642	0.1			1.32	1
1.580	1	1.580	1			1.29	1
1.448	4	1.448	4	1.448	4		
1.404	6	1.404	6	1.404	5		
1.352	2	1.352	2				
1.312	1	1.312	1				

is allowed to age in the hot a crystalline phase appears which gives gradually an x-ray pattern identical with that from aluminas obtained by the thermal decomposition of gibbsite, γ - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, at 250° and from the thermal decomposition of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. Long continued aging causes the crystals to grow as evidenced by the increase in the sharpness of the lines on the x-ray pattern. Thus, by referring to Table VIII and Fig. 7 it will be seen that the gel aged for an hour gives a pattern showing only general scattering; but after two or three hours two rather broad bands appear. Continued aging for several days finally results in a pattern quite similar to the one resulting from the dehydration of gibbsite at 250° . As the material dehydrates no change in the position of the lines is noted showing that the gel is not a solid solution of alumina and water. The gel is therefore hydrous alumina or a hydrous alumina hydrate. The question as to which of these two possibilities represents the facts will be discussed further in the following section.

INTERPRETATION OF DEHYDRATION ISOBARS AND ISOTHERMS

Alumina Hydrates.

Two years ago(56) it was concluded as a result of x-ray and dehydration studies that only two hydrates of alumina exist: γ - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (gibbsite) and α - $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (diaspore). No indication was found at that time for the existence of a second trihydrate α - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (Fricke's Bayerite) or for a second monohydrate γ - $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (bohmite). From the available evidence, it was believed that precipitated alumina was hydrous " δ - Al_2O_3 " rather than hydrous γ - $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. In the light of more recent developments it now appears that certain of these conclusions must be modified and extended.

Alpha Alumina Trihydrate.

While our first paper was in the process of publication an article by Fricke and Severin(44) appeared in which definite evidence was presented to prove that α - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (bayerite), isomeric with gibbsite, exists as a defin-

its trihydrate. The α - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ gives a distinctive x-ray diffraction pattern and a dehydration isobar characteristic of a trihydrate. Synthetic γ - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ is formed by the slow hydrolysis of aluminates (Bonsdorff and Goudriaan). On the other hand, if the separation takes place relatively quickly, the metastable isomer, α - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, is the first formed and goes over spontaneously into γ - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ in the course of a few weeks contact with dilute alkali. We failed to observe the formation of α - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ either by the method of Goudriaan or that of Bonsdorff, since the precipitate remained in contact with the alkali 30 days before it was subjected to x-ray analysis and therefore was entirely γ - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$.

A pure sample of α - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ prepared by Mr. R.P. Rocksby has been examined by the x-ray diffraction method. Comparison of the x-ray pattern of α - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ shows that some of the samples previously considered (56) to be mixtures of γ - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and " δ - Al_2O_3 ", contained considerable amounts of α - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. For example, diagrams 3, 4, and 6 of Fig. 3 and 1-5 and 8 of Fig. 6 are for samples made up largely of α - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$.

γ - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ vs. δ - Al_2O_3 .

More than twelve years ago L.H. Milligan (53) dehydrated a sample of artificial gibbsite in a current of air containing a known amount of water vapor. The dehydration isobar showed conclusively that the sample was a trihydrate but gave no indication whatsoever of the formation of a monohydrate. Since both Rocksby (54) and ourselves have obtained a material that gives the same x-ray diffraction pattern as γ - $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (bohmite) by the thermal dehydration of γ - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (gibbsite) it is important to explain, if possible, why the isobars fail to reveal the presence of a monohydrate.

Dehydration Isobar of Artificial Gibbsite. A sample of γ - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ was dehydrated in an apparatus similar to that of L.H. Milligan previously described (57). Special care was taken to ensure equilibrium values. It was found that many days were required at the lower temperatures and many hours at the higher temperatures. The results are shown graphically in Fig. 10. It is apparent that the isobar gives no evidence whatsoever of the formation of monohydrate. X-ray analysis of samples taken at intervals from a second container give the results shown in Table X.

A dehydration isobar almost identical with Fig. 10 was obtained by Fricke and Severin for gibbsite (44). They also made isobars for the α gibbsite or bayerite and for both γ - $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (diaspore) and γ - $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (bohmite). These curves, reproduced in Fig. 11, are noteworthy since extreme care was taken to ensure equilibrium. In some cases several weeks were required to get a single point and the value recorded was taken only after the system remained in equilibrium for 8-25 days.

Table X

X-Ray Diffraction Data Obtained during the Dehydration of γ - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$

Temperature, °C.	Type of Pattern
35-150	γ - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (gibbsite)
185	γ - $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (bohmite) and γ - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$
205-410	γ - $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$

In the light of the above work there can be no question about the facts. The monohydrates formed by the decomposition of γ - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ does not undergo decomposition at a definite temperature as a real hydrate usually does. Indeed in the experiment shown in Fig. 10, a sample at 410° having a composition of approximately $\text{Al}_2\text{O}_3 \cdot 0.34\text{H}_2\text{O}$ gave the x-radiogram of γ - $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ only. This

Figure 10
Thermal Dehydration Isobar of γ - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (synthetic gibbsite)

Figure 11

Thermal Dehydration Isobars of α and γ - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and α -
and γ - $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (after Friske and Severin)

Fig. 23

Fig. 24

Fig. 25

Temperature °C

would be impossible if the hydrate were behaving in a normal way. Furthermore, Fricke and Severin's curve for the monohydrate is a typical description curve showing no indication whatsoever of a break. It is this sort of evidence which formerly lead us to believe that the alleged monohydrate was not a true hydrate but an alumina with adsorbed water.

The only evidence advanced by Rocksby(54) is support of the view that the product of the thermal dehydration of $\gamma\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ is a monohydrate, was an analysis of the product. But the dehydration curves of L.H. Milligan, Fricke and Severin, and ourselves show that this composition was accidental and could not possibly have been an equilibrium value. More recently Edwards and Testerud(43) claimed that the compound formed by heating precipitated alumina under pressure analysed for a monohydrate, gave the $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ x-ray pattern, and exhibited a thermal arrest in the heating curve. The first two lines of evidence will not definitely distinguish between a monohydrate and a hydrous alumina with the right amount of adsorbed water and an arrest in the heating curve of an oxide-water system does not necessarily indicate the presence of a true hydrate(47). In this case the arrest might be offered as evidence of a polymorphic change from $\delta\text{-Al}_2\text{O}_3$ to $\gamma\text{-Al}_2\text{O}_3$. However preparations which give the $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ pattern can be obtained in well-defined microscopic crystals which analyze for monohydrate. Thus Fricke and Severin(44) obtained it by heating commercial alumina to $350\text{--}370^\circ$ at a pressure of 200 atmospheres. Hüttig and Peters(48) prepared a similar product by heating the trihydrate in a bomb tube at 200 atmospheres. Particularly good crystals were made by heating 4-20% $\text{Al}(\text{NO}_3)_3$ containing up to 20% HNO_3 at $320\text{--}360^\circ$ and 200-300 atmospheres(49,50). In the light of this positive evidence there can no longer be any doubt that böhmite is $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. But having reached

this conclusion one is obliged to explain the absence of a sign of a break corresponding to the monohydrate in the dehydration isobars of γ - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and γ - $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

Interpretation of the Dehydration Isobars. Application of the phase rule to the two component system hydrate-oxide-water vapor, shows that the system should be univariant. The type of isobar is given by the dotted lines in Fig. 12. Theoretically, the curve should drop to zero composition at a definite temperature but actually the isobars are rounded off as shown in the figure by the broken line ADC. This is due to a loss of part of the water below the true decomposition temperature of the mass of the hydrate on account of lattice distortion, strain in the crystals, and variation in crystal size. However if the oxide formed by the dehydration of the hydrate is highly hygroscopic, it will adsorb most of the water vapor, Hence the actual dehydration measured, is the loss of adsorbed water from the oxide. In such a case a bivariant type of curve is to be expected, as shown by the solid line AE in Fig. 12. It is precisely this last type of curve which Fricke and Severin obtained for both α - and γ - $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

We can now explain the persistence of the x-radiogram of the monohydrate where it would ordinarily not be expected to exist. The x-radiogram for the monohydrate should persist along the broken curve ADC because some monohydrate exists as such and the highly hygroscopic γ - Al_2O_3 (38,39,41,42,52,55,58) formed by partial decomposition of the former is either amorphous or too finely crystalline to be detected by x-ray analysis.

In the case of a higher hydrate decomposing first into a lower hydrate and finally into the anhydrous substance, it is apparent that under the conditions noted above, the isobar will completely fail to detect the lower hydrate.

Figure 12

Isobaric equilibrium in the system hydrate-oxide-water vapor

100-1000

1000 1000

12. 1. 1964

Figure 13

**Isocharic equilibrium in the system hydrate-lower hydrate-oxide-
water vapor**

Figure 14

Thermal Dehydration Isober of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (after Linck and Jung)

In Fig. 13 the theoretical curves for the case of a trihydrate decomposing into a monohydrate and this in turn to the oxide are given by the dotted lines. The actual experimental curve is given by the solid line. The composition of the trihydrate remains constant until at point F some water is lost giving a small amount of water vapor and monohydrate. As this process continues along FK and along KH all the trihydrate decomposes rapidly giving monohydrate. Now at this temperature the lower hydrate loses water to point O and hence the line FKH continues past the theoretical composition of the monohydrate to the point O. This decomposition of the monohydrate gives the highly adsorptive oxide, the presence of which causes the dehydration to proceed along the line HOE for the reason given above.

Although the case under consideration is unusual it is not unique. Thus a curve, reproduced herein as Fig. 14, somewhat similar to the one shown in Fig. 13 is obtained for the dehydration of gypsum which yields plaster of Paris as an intermediate product. (40, 41, 45, 46, 51) Everybody agrees that the latter compound is $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ but this would not follow from the dehydration curve which is like HKH in Fig. 13 rather than like HOE. Here

again, the highly hygroscopic character of the anhydrite resulting from the decomposition of the hemihydrate adsorbs a part of the water and the dehydration of this hydrous material determines the form of the curve.

SUMMARY

The results of this investigation are as follows:

1. X-ray diffraction studies have been carried out on aluminas precipitated under widely varying conditions in order to determine what definite hydrates of alumina exist.

2. The evidence indicates that there are but four alumina hydrates:

α - and γ - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and α - and γ - $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, (using Haber's notation).

3. Samples prepared according to the procedures of Hüttig and coworkers were found by x-ray diffraction methods to be either α - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ or γ - $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

4. Samples prepared by the methods of Willstätter and coworkers were found by x-ray studies to be either γ - $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ or to give no diffraction pattern.

5. No indication was found for a series of definite hydrates corresponding to those reported by Hüttig and Willstätter and their coworkers.

6. The artificial trihydrate prepared by the methods of both Bonsdorff and Goudriaan give identical x-ray diffraction patterns under the experimental conditions described in this paper.

7. Slow hydrolysis of an aluminate solution gives a definite metastable alumina hydrate α - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (bayerite) different from γ - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (gibbsite).

Ageing of this metastable hydrate especially in contact with alkali gives γ - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. The present authors overlooked the labile modification at one time since they allowed the products made by the method of Goudriaan and Bonsdorff to stand in contact with alkali for 30 days. That α - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ is a definite trihydrate has been conclusively proven by dehydration isobars recently obtained by Fricke and Severin.

8. Dehydration isobars of γ - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ made by L.H. Milligan, over twelve years ago, and by Fricke and Severin and the present authors more recently, show no indication whatsoever of the formation of a monohydrate. However x-ray examination of the intermediate dehydration product gives the pattern attributed to γ - $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (böhmite). This is the same material that the present authors formerly considered to be hydrous " δ - Al_2O_3 " because of the form of the dehydration curve.

9. Well-defined macroscopic crystals of $\gamma\text{-Al}_2\text{O}_3\cdot\text{H}_2\text{O}$ have been made (Fricke and Severin, Hüttig and Peters, Ipatiev); but the dehydration isobar of the compound is a typical desorption curve.

10. In this chapter an explanation is suggested for the apparently anomalous behavior of the dehydration curves of both $\gamma\text{-Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$ and $\gamma\text{-Al}_2\text{O}_3\cdot\text{H}_2\text{O}$, based on the fact that the thermal decomposition of the latter gives a very highly adsorptive oxide ($\gamma\text{-Al}_2\text{O}_3$) which adsorbs most of the water vapor. Dehydration of this hydrous oxide gives a bivalent curve.

11. The various transformations of precipitated alumina may be tabulated in the following diagram, which is a revision of the diagram already reported (56):

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CHAPTER III

STANNIC OXIDE

The question of the so-called stannic oxides and the existence of definite hydrates of stannic oxide have been the subject of repeated investigations from the time of Berzelius to the present. The colloidal nature of the so-called stannic oxides was investigated by van Bemmelen(1), and by Mecklenburg(2) who concluded that the alpha and beta acids were both hydrous oxides differing from each other in the size of the particles. This same conclusion was reached by Weiser(3) twelve years ago. Investigations made at that time showed that there was no definite dividing line between the two preparations, and that the beta oxide consisted of the larger particles. Gutbier, Hüttig, and Böbling(4) concluded from pressure-temperature curves that no definite hydrates(5) were formed. The x-ray diffraction patterns of the various samples as well as those of Mecklenburg which had aged for several years, showed that the original hydrous oxide was apparently amorphous and that the aged products exhibited a gradual formation of a crystal lattice identical with the mineral cassiterite, SnO_2 . X-radiograms made by Yamada(6) of several different preparations (7), all revealed a structure identical with the anhydrous oxide. Further x-ray patterns of the so-called alpha and beta stannic acids were made by Posnjak(8) who demonstrated clearly that the structure of both is identical with the anhydrous stannic oxide; and that the difference in the two oxides is due to a difference in particle size, the beta being the larger. This is in accordance with the observations of Mecklenburg and of Weiser. Hydrous SnO_2 was dried in a vacuum over P_2O_5 by Ferster(9) who concluded from x-ray data that the products obtained had the structure of cassiterite. X-radiograms of the

fresh gel and the products resulting from the aging and heating of colloidal SnO_2 were obtained by Böhm(10). His published photographs show clearly the gradual increase in particle size from the original hydrous oxide to the anhydrous SnO_2 , the lattice in all cases remaining identical with that of cassiterite.

In view of all the apparently conclusive evidence that is available, it would appear that the question of the nature of the so-called stannic oxides should be considered a settled one; but such is not the case. In a recent investigation Thiessen and Koerner(11) claim that a stannic oxide gel prepared by the slow hydrolysis of stannic ethylate gives pressure-composition and temperature-composition curves that indicate the formation of a series of hydrates. From temperature-composition data the following hydrates are claimed: $\text{SnO}_2 \cdot n\text{H}_2\text{O}$, where n equals 2.5, 2.0, 1.75, 1.5 and from temperature-composition curves: n equals 1.0, and 0.5. X-radiograms of the several preparations were made, but no definite results were obtainable by this method. It was claimed that the lattice undergoes a slight expansion as the water content decreases(12), but the "strong diffuse blackening" of the film renders impossible the making of exact measurements.

Experimental

In view of the theoretical importance of the existence or non-existence of a series of SnO_2 hydrates, it is the purpose of the present paper to consider (1) the dehydration of stannic oxides at temperatures which are said to give definite hydrates; and (2) the examination of these reputed hydrates by x-ray diffraction methods.

I. The Thermal Dehydration of Hydrous Stannic Oxide.

A. Stannic Oxide Prepared by Thiessen and Koerner's Method.

Preparation of Oxide. The stannic oxide was prepared according to the procedure outlined in detail by Thiessen and Koerner. Sodium ethylate made

by adding metallic sodium to absolute alcohol was allowed to react with an anhydrous SnCl_4 solution in absolute alcohol in accord with the following equation: $\text{SnCl}_4 + 4\text{NaOC}_2\text{H}_5 \rightarrow \text{Sn}(\text{OC}_2\text{H}_5)_4 + 4\text{NaCl}$. All reactions were carried out with extra precautions to prevent the entrance of water vapor into the apparatus or solutions. The resulting mixture of stannic ethylate and sodium chloride was digested on a water bath, and finally the latter was filtered off. An amount of the alcoholic solution of ethylate equivalent to 25 g of anhydrous SnO_2 was added to 5 liters of absolute alcohol. The resulting solution was allowed to stand with occasional stirring in a flask with a neck 5 cm in diameter. Moisture from the air hydrolyzed the stannic ethylate, the process being complete in about 26 days. The gelatinous precipitate of SnO_2 was filtered off, washed with one liter of absolute alcohol in 100 cc portions, dried with suction on a filter paper, and kept in a glass-stoppered bottle until used.

Rate of Dehydration. The SnO_2 gel made by the above method consists of SnO_2 , alcohol, and water. Thiessen and Koerner obtained a composition-temperature curve by heating the sample at definite temperatures for 15 minutes over CaCl_2 . The resulting curve is shown in Fig. 1. The breaks in the curve are indicative of the formation of the definite hydrates $\text{SnO}_2 \cdot \text{H}_2\text{O}$, and $\text{SnO}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$.

It would not be expected that an equilibrium state would result from heating samples for only 15 minutes, and Thiessen and Koerner give no data to show whether or not this is the case. It was thought desirable to determine the time required for equilibrium at a given temperature, before proceeding to obtain the temperature-composition curve. To do this a sample was placed in an electric oven with the temperature adjusted to 50°C . The sample was re-

FIG. 1
Temperature-Composition Curve of Stannic Oxide (after Thiessen and Koerner)

FIG. 2
Rate of Dehydration of Stannic Oxide at 50°C

moved at intervals, allowed to cool, weighed, and the heating continued. The resulting curve showing the relation between composition and time of heating is given in Fig. 2. It will be observed that about 8 hours is required to attain equilibrium at the temperature stated. As would be expected, equilibrium is established more rapidly at higher temperatures; thus at 160 degrees, 2 or 3 hours is sufficient.

The form of the time-composition curve is what would be expected from a material containing water, and a little alcohol; the rate of drying is quite rapid at first and then falls off, decreasing to a relatively low value before the composition becomes constant. This means that, at first, alcohol and some of the water comes off followed by the greater portion of the water leaving the last trace of water^② which, as is well known, is very difficult to remove.

The Composition-Temperature Curve. In the light of the above experiments a composition-temperature curve was obtained, taking care to heat the sample at each temperature for at least 12 hours to ensure the establishment of equilibrium. Two samples were taken: the first was allowed to cake into a lump as the heating proceeded, and the second was pre-dried enough to allow it to be powdered. The samples were placed in weighing bottles, and heated to constant weight over calcium chloride at a definite temperature, after which the temperature was raised and the heating continued. The dehydration was carried out in a thermo-regulated electric oven, the temperature of which was constant within 0.5° . For temperatures below 100° a thermometer was used that had been calibrated against a standard thermometer checked by the Bureau of Standards. Above 100° an accurate thermometer was employed which had been checked against the standard thermometer below 100° . The results obtained are given

in Table I and in Fig. 3.

B. Alpha and Beta Stannic Oxides.

For the purposes of comparison dehydration curves were obtained for samples of the so-called alpha and beta stannic oxides. A sample of the alpha oxide was prepared by the addition of a slight excess of ammonium hydroxide to a solution of SnCl_4 . The resulting gelatinous precipitate was washed by centrifuging, and finally air-dried until it could be powdered. The beta oxide was prepared by treating pure metallic tin with concentrated HNO_3 , washing and drying the resulting product in the air. The results of both samples are given in Table II and in Fig. 4 (13). The dehydration was carried out as described in the preceding paragraph. The percentage loss of weight of Thiessen and Koerner's stannic oxide was calculated at each temperature and the results shown in the third curve of Fig. 4 (13).

The significance of the curves obtained from the various preparations will be discussed after a consideration of the results found by x-ray examination of the alleged hydrates of Thiessen and Koerner.

II. X-Ray Examination of Thiessen and Koerner's Stannic Oxide.

Separate samples of SnO_2 prepared by the method of Thiessen and Koerner were heated to temperatures that should [#]give hydrates according to the composition-pressure and composition-temperature curves of these investigators. The following temperatures were chosen: 25° , 36° , 50° , 90° , and 160° . Specimens of the heated samples were sealed in tubes of "nonex" glass ([#]special glass made of materials of low atomic weight) and x-radiograms made by the powder method in the usual manner, using a General Electric x-ray diffraction apparatus. In each case the pattern of NaCl was obtained on the same film for purposes of calibration. The interplanar spacings and the visually estimated relative intensities are given in Table III and in chart form in Fig. 5. The spacings are in ⁰Angstrom units and the intensities on such a scale that the

FIG. 3
Temperature-Composition Curve of Stannic Oxide prepared by Hydrolysis of Stannic Ethylate

FIG. 5
X-Ray Diffraction Patterns for Stannic Oxides: Thiessen and Koerner's Preparations dehydrated at (1) 25°C, (2) 36°C, (3) 50°C, (4) 90°C, and (5) 160°C, (6) The Mineral SnO₂.

Table I

The Thermal Dehydration of Thiessen and Keerner's SnO_2

temperature °C	not powdered		powdered	
	weight of SnO_2		weight of SnO_2	
	sample g	%	sample g	%
39.6	0.9073	83.25		
40.6	.9069	83.29		
48.4	.8997	83.95		
56.3	.8933	84.56		
60.2	.8899	84.88		
63.6	.8857	85.28		
67.8	.8753	86.29	0.3996	86.13
69.8	.8735	86.47	.3989	86.28
74.5	.8707	86.75	.3971	86.67
78.6	.8690	86.92	.3964	86.82
81.6	.8674	87.08	.3953	87.06
85.7	.8671	87.11	.3950	87.13
90.0	.8654	87.28	.3943	87.29
95.4	.8637	87.45	.3935	87.46
100.4	.8598	87.85	.3916	87.89
104.7	.8575	88.09	.3908	88.07
110.0	.8549	88.35	.3894	88.38
116.0	.8540	88.45	.3889	88.50
120.0	.8536	88.49	.3888	88.52
123.5	.8531	88.54	.3887	88.54
132.3	.8510	88.76	.3870	88.93
143.2	.8465	89.23	.3847	89.46
154.0	.8428	89.68	.3833	89.79
202.0	.8283	91.19	.3780	91.05

most intense line is designated as 10.

Discussion of Results

Composition-temperature curves of hydrous stannic oxide have been previously obtained by Carnelly and Walker(14) and by van Bommel(15). The smooth curves obtained by these investigators were quite similar to those for the alpha and beta stannic oxides, shown in Fig. 4. The curve obtained from the preparation of Thiessen and Koerner is similar except for a change in its direction at about 60-70°. The reason for this is obvious when it is recalled that the material consists of SnO_2 , water, and a little alcohol. The odor of alcohol is still apparent in a sample that had been heated to 40° and there is no question but that traces of alcohol persist up to the boiling point. As has been seen, samples of SnO_2 containing water only give a smooth, continuous curve. Samples containing alcohol but no water would be expected to give a curve of the same type, but would reach the maximum sooner. In the case under consideration, in which both loss of alcohol and loss of water are superimposed on the same curve, the two effects added together algebraically would be expected to give a curve of the shape found experimentally to hold. Since Thiessen and Koerner did not allow sufficient time for equilibrium to be established, the breaks in their curves are without significance as far as hydrate formation is concerned. This point has already been adequately discussed by Posnjak in connection with the similar results of Willstätter and ⁴Kraut.

Since the crystal lattice of all the products formed at various temperatures is identical with the mineral cassiterite, SnO_2 , with respect to the position and intensity of the lines on the x-radiogram, no definite hydrates

of SnO_2 are actually formed. The only difference in the diffraction effects is that the size of the particle, as indicated by the width of the lines in the products obtained by dehydration, are smaller than those which compose the mineral cassiterite. It should be noted from Table III and Fig. 5 that the interplanar spacings do not change (within the expected experimental error for such wide lines) with varying amounts of water, as would be the case if the SnO_2 and water formed a solid solution. This shows that the water must be adsorbed on the surface of the finely-divided crystals.

Hydrous SnO_2 , whether in the so-called alpha or beta form or formed by the method of Thiessen and Koerner, consist of very small crystals of SnO_2 which adsorb water or water and alcohol in the Thiessen preparation. When the latter material is dehydrated, at temperatures up to about $60-70^\circ$ most of the alcohol and some of the water is driven off, the dehydration proceeds in a uniform manner at temperatures above this point where little alcohol is left as in the case of the familiar alpha and beta preparations.

Thiessen and Koerner found that the general blackening of the film upon which the x-ray diffraction patterns were recorded precluded accurate measurements, and concluded that the method was not suitable for distinguishing the presence or absence of hydrate formation. No such difficulties are encountered, however, when the proper exposure is made, and a special glass of low atomic weight is used. Indeed in photographs published by Thiessen and Koerner the identity of these products with the mineral SnO_2 is clearly shown. It is true, of course, that the broad, diffuse lines cannot be read as accurately as the sharper lines; nevertheless all lines recorded in Table III are clearly visible on the original negatives.

Summary

The results of this investigation are as follows:

1. Hydrous stannic oxide has been prepared by the hydrolysis of stannic ethylate according to the method of Thiessen and Koerner, who claim that a series of definite hydrates of SnO_2 results from the thermal dehydration of this material.
2. Composition-temperature curves have been obtained under conditions that ensure the establishment of equilibrium. The curves are smooth indicating the absence of hydrates. Breaks in the curves of Thiessen and Koerner were due to failure to allow sufficient time for equilibrium to be established under a given set of conditions.
3. X-radiograms of preparations obtained by dehydration at definite temperatures, show that the products are made up of particles of SnO_2 of varying size with varying amounts of adsorbed water; no definite hydrates are formed. This confirms the observations of Gutbier, Hüttig, and Döbling; Posnjak; Yamada; Weiser; and others.
4. The claim of Thiessen and Koerner, that the x-ray diffraction method is not suitable for determining the presence or absence of hydrates, has been shown not to be valid; on the contrary, when the proper precautions are taken the results are definite and conclusive.

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CHAPTER IV

STANNOUS OXIDE

Anhydrous Stannous Oxide. Stannous oxide was prepared by Berzelius(1) by the addition of potassium carbonate in excess to a solution of stannous salt. Gay Lussac(2) obtained a hydrous precipitate with ammonium hydroxide, and dehydrated this material by boiling under water until a black SnO appeared. Ditte(3) stated that the presence of ammonium hydroxide prevented the alleged transformation to the anhydrous oxide; however if the ammonia is boiled off, the dehydration proceeds. An excess of alkali, insufficient to dissolve the oxide, favors the transformation(4). Sandall(5) prepared a black form of SnO by grinding fused SnCl_2 with $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. The blue-black oxide of Berzelius became brownish-green when pounded or ground. Upon heating, an olive-green color developed(6). Frémy evaporated a dilute solution of ammonium chloride in which precipitated SnO was suspended; when crystals of ammonium chloride appeared, the hydrous material was said to change to a cinnabar-colored powder which was transformed to greenish-brown upon rubbing with a hard body. Moth(7) obtained a red oxide by digesting the hydrous material with acetic acid, but Bury and Partington(8) were unable to prepare this form. Frankel and Snipischsky(9) added sodium hydroxide to a solution of SnCl_2 ; the white precipitate was transformed into a blue powder when boiled for several hours on a water bath of saturated sodium chloride solution. Frémy believed that three modifications of SnO exist, namely: 1. the blue-black, crystalline oxide made by digesting hydrated SnO with excess alkali, 2. the olive-green powder made by heating the black modification, and 3. the cinnabar-colored powder resulting from the slow evaporation of a suspension

of precipitated SnO in dilute ammonium chloride solution.

Precipitated Stannous Oxide. The precipitate obtained by the interaction of solutions of stannous salts and an alkali has been formulated $\text{Sn}(\text{OH})_2$, although there is no evidence that such is the case. Froust(10) found that an excess of potassium carbonate gave a white precipitate containing 5 % water. Schaffner(11) believed that ammonium hydroxide gave a basic salt. Potassium carbonate was said to give a precipitate that had the composition $23\text{SnO} \cdot \text{H}_2\text{O}$ when dried below 80°C .

Table I

Precipitated from SnCl_2 by	Color	Dried	Composition % water
NaOH	Yellow tinge	Vacuum, P_2O_5 , 14 da.	7.11
Na_2CO_3	Yellow tinge	CaCl_2 , P_2O_5 , KOH , 14 da.	8.54
NH_4OH	Yellow when dried	P_2O_5	8.32
NH_4OH (CO_2 atmosphere)	Yellow when dried	P_2O_5	8.82
Na_2CO_3 (CO_2 atmosphere)	Yellow, when dried	Vacuum, P_2O_5 , 14 da.	7.4
NaOH and Na_2CO_3	-----	110°C ., air bath	2.5

Ten years ago Bury and Partington(12) investigated the hydrous precipitate prepared in several ways; the various methods used are listed herein as Table I. These investigators concluded that all samples were the same except the last, and that the composition was $33\text{SnO} \cdot \text{H}_2\text{O}$. It was observed(13), that when precipitated SnO stood in a glass vessel, the portion in contact with the glass darkened. Bury and Partington attributed this to the action of alkali traces on the surface of the glass, since it is well known that excess

alkali favors the transformation to the blue-black oxide. This view was apparently substantiated by the observation that samples kept in silica tubes did not blacken.

Brown and Henke(14) treated SnCl_2 solution in a glass cylinder with sodium carbonate. The first preparation was white when precipitated and slightly yellow when dried. Subsequent precipitates darkened before washing was complete. The blackening was said to begin along the sides of the glass cylinder coincident with the scratches on the glass caused by a stirring rod. Washing with concentrated hydrochloric acid had no effect, but treatment with NaOH prevented further blackening of the precipitate. Brown and Henke believed that the first black particles act as catalysts to produce further blackening, but offer no explanation as to the formation of the initial particles. The theory of Bury and Partington would have predicted that treatment with alkali would produce more rather than less blackening. It is probable that some other factor is entering in. This is suggested by Roth's observation that one of his preparations rapidly turned black upon exposure to sunlight.

The present investigation includes 1. an examination of the various modifications of SnO by x-ray diffraction methods in order to determine whether the differences in color and other properties are due to the existence of polymorphic forms, to varying particle size, or to some combination of these effects; 2. a study of precipitated SnO to find out whether it is a hydrous oxide or a hydrous hydrate; and to determine the conditions that effect the blackening.

Experimental

Anhydrous Stannous Oxide.

A. Blue-Black C-SnO_2 A solution of 25 g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 200 cc of water was cleared up with HCl and 20 g of NaOH in 200 cc of water was added. A white or faintly yellow precipitate formed which turned to a blue-black powder upon

heating to boiling. This powder was washed thoroughly by decantation and was dried for 18 hours at 110°C .

B. Brownish-Green α - SnO . A portion of A was ground in an agate mortar; this treatment gave a brownish-green powder.

C. Greyish-Green β - SnO . Another portion of A was heated in a vacuum in a pyrex tube. At about 550°C the blue-black crystals were transformed to a greyish-green powder.

Attempts to prepare the red forms of Roth and of Fremy were unsuccessful, in confirmation of the results of Bury and Partington.

Samples of each of the above described preparations were sealed in nemex glass tubes, and x-ray diffraction photographs were obtained using the General Electric X-Ray Diffraction Apparatus. Pure NaCl was used to calibrate the film. The results are given in Table II and Fig. 1. The interplanar spacings d_{hkl} are expressed in Angstrom units; and the relative, estimated intensities, I , are expressed on such a scale that 10 means the most intense line on a given film. The pattern obtained from α - SnO corresponds to a tetragonal structure of the PbO type(15) with $a_0 = 3.78 \text{ \AA}$ and $c_0 = 4.79 \text{ \AA}$. The calculated density is 6.51. The results are almost identical with the values found by Levi(16) who obtained $a_0 = 3.77 \text{ \AA}$ and $c_0 = 4.77 \text{ \AA}$. The pattern of β - SnO was not studied further. The results indicate that SnO exists in two polymorphic forms: α - SnO , the blue-black tetragonal form which is brownish-green when in a finely-divided state; and β - SnO , the greyish-green modification prepared by heating the α - SnO to above 550°C . Shortly after these results were first published (17) the existence of a second modification of SnO was independently confirmed by Kaysselitz and Kohlmeier (18) who observed a thermal effect at 490°C in the heating curve of α - SnO . It was shown quantitatively that decomposition to SnO_2 and Sn was negligible at this temperature. (19) Since in the experiments described above the sample was heated up rapidly and the temperature of 550°C was the point where the change seemed complete, it would be expected that the true transformation temperature would be somewhat lower.

Table I

X-Ray Diffraction Data for Anhydrous and Hydrated SnO

A & B		C		Samples D		E		F	
α -SnO		β -SnO		2SnO·H ₂ O Air-dried		2SnO·H ₂ O Dried 115°C		α -SnO from 2SnO·H ₂ O	
D	I	D	I	D	I	D	I	D	I
4.79	4	3.38	10	3.53	10	3.52	10	4.79	4
2.96	10	2.99	5	3.32	10	3.32	10	3.37	2
2.68	5	2.92	5	2.99	10	2.98	9	2.97	10
2.40	3	2.88	9	2.82	9	2.79	9	2.68	5
1.890	4	2.66	9	2.64	1	2.51	4	2.40	3
1.787	7	2.08	1	2.51	4	2.40	4	1.90	4
1.595	9	2.02	4	2.40	4	2.27	3	1.895	7
1.482	8	1.769	8	2.27	3	1.925	5	1.595	9
1.369	1	1.675	2	1.925	5	1.771	5	1.489	8
1.336	2	1.595	2	1.776	5	1.691	1	1.339	2
1.220	1	1.496	2	1.690	1	1.624	1	1.221	1
1.195	1	1.414	2	1.625	1	1.575	1	1.168	3
1.165	3	1.294	2	1.572	1	1.466	1	1.100	1
1.099	1	1.204	2	1.406	1	1.405	1	1.074	2
1.072	2	1.096	2					1.026	2
1.027	2							0.993	1
1.012	1							0.899	1
0.992	1							0.882	1
0.932	1							0.847	1
0.900	1							0.838	1
0.879	1							0.802	1
0.872	1							0.770	1
0.850	1								
0.839	1								
0.798	1								
0.749	1								
0.712	1

FIG. 1

X-Ray Diffraction Diagrams of Stannous Oxides and Stannous Oxide Hemihydrate

FIG. 2

Composition-Temperature Curve of Stannous Oxide Hemihydrate

The result of 490°C obtained by Keysseritz and Kehlmeier confirms this.

Hydrous Hydrated Stannous Oxide

Stannous oxide hydrate was precipitated from a freshly prepared and filtered HCl solution of SnCl_2 by addition of NH_4OH . Upon the addition of the NH_4OH the temperature fell from that of the room to about 60°C. The white or faintly yellow colored, hydrous precipitate was washed first with ammonia and then with water by centrifuging at 3000 r.p.m. until peptization began. A very stable sol resulted before the precipitate was chloride free; centrifuging for over an hour at 3000 r.p.m. failed to produce coagulation. Accordingly, further purification was carried out by washing with a supercentrifuge at 36000 r.p.m. After repeated washing only a trace of chloride remained. The precipitate was then air-dried until it could be powdered, and a sample was placed in a weighing bottle and was dehydrated by heating in an electric oven in a stream of dry nitrogen, which was purified by passing through a heated pyrex combustion tube containing copper freshly reduced by hydrogen from cupric oxide wire. The nitrogen was not rendered completely oxygen free, since continued heating at high temperatures resulted in some oxidation of the oxide. However oxidation is negligible in the temperature range for which results are reported. The isobaric temperature-composition curve that was obtained with three separate samples is plotted in Fig. 2. The composition when dried in the manner described at 50°C was found to be, % SnO : observed 93.70, 93.71, 93.74; calculated for $2\text{SnO} \cdot \text{H}_2\text{O}$, 93.74. It is apparent from the form of the curve that the hydrated SnO has the composition corresponding to the hemihydrate, $2\text{SnO} \cdot \text{H}_2\text{O}$. As the dehydration proceeds, the sample becomes decidedly yellow by the time the temperature reaches 100°C; at higher temperatures a grey or green color appears. The change in color from the white or faintly yellow to the permanent deeper yellow, is a continuous one. The nature of this change will be discussed in the second paragraph following.

X-radiograms were obtained for the following samples: D, $2\text{SnO} \cdot \text{H}_2\text{O}$, air-dried; E, $2\text{SnO} \cdot \text{H}_2\text{O}$, dried at 110° ; and F, $\alpha\text{-SnO}$ prepared by heating $2\text{SnO} \cdot 2\text{H}_2\text{O}$ to about 400° in a vacuum. The results are given in Table II and Fig. 1. For purposes of comparison, G, the pattern of SnO_2 is also included in Fig. 1. It will be observed that the crystal structure of the hemi-hydrate is different from either the $\alpha\text{-SnO}$ or the $\beta\text{-SnO}$, and that the product of thermal decomposition is $\alpha\text{-SnO}$, provided the temperature is kept below 550°C , the transition temperature for the α to β transformation.

Since the x-radiograms for hemi-hydrate dried in the air and at 110° are the same, the change in color from white or faintly yellow to decidedly yellow, cannot be due to isomerism; but must be due to a change in particle size or physical character. From the width of the lines on the x-radiograms, it appears that the deep yellow material has the larger particles. Thus crystal growth takes place as the hemi-hydrate is heated.

Darkening of Hydrated SnO on Exposure to Light. Stannous chloride in slight excess was treated with NH_4OH in a pyrex flask in the dark. Test tubes were filled with portions of the suspension and stoppered and aged as given in Table III. The samples exposed to light were left in a test-tube rack in ordinary daylight. The others were kept in a closed cupboard in a dark room, and were examined at intervals. Inspection of Table III makes it clear that the nature of the containing vessel has little or nothing to do with the darkening; but that it is caused by the action of light. In order to test further the effect of light and the effect of the nature of the surface of the containing vessel, another experiment was carried out. Hydrated SnO was precipitated from a slight excess of SnCl_2 by NH_4OH in a pyrex flask in diffused daylight. Within 5 minutes after precipitation, samples were placed in soft glass cylinders treated as in Table IV.

Table III
Color after

Container	Kept in dark				Exposed to light			
	5 min.	2 hrs.	1 wk.	2 wks.	5 min.	2 hrs.	1 wk.	2 wks.
Soft glass	White	White	White	White	White	Grey	Green-grey	Green
Pyrex	White	White	White	White	White	Grey	Green-grey	Green
Fused Silica	White	White	White	White	White	Grey	Green-grey	Green

Table IV

Color after

Time	Exposed to light				Kept in dark			
	New cylinder		Scratched cylinder		New cylinder		Scratched cylinder	
	washed with		washed with		washed with		washed with	
	HCl	NaOH	HCl	NaOH	HCl	NaOH	HCl	NaOH
5 min.	White	White	White	White	White	White	White	White
15 min.	Grey	Grey	Grey	Grey	White	White	White	White
1 da.	Green	Green	Green	Green	White	White	White	White
3 da.	Green	Green	Green	Green	White	White	White	White
1 wk.	Green	Green	Green	Green	White	White	White	White
18 mo.	Green	Green	Green	Green	White	White	White	White

The coloration begins on the side of the glass nearest the most intense illumination. In each of the above described series of experiments, a portion of each precipitate was made alkaline with NH_4OH and allowed to stand in the light in a pyrex flask. Only slight darkening takes place, and the original white or faint yellow may become slightly keener. As is well known, a solution of SnCl_2 in dilute HCl hydrolyzes, precipitating out a white, creamy substance upon standing. Since in the experiments described, an excess of SnCl_2 is present, one would expect the same thing to happen; and such is the case. However, there is no danger of confusion as to color, as the deposit forms in a separate thin, upper layer.

Two samples (not included in the tables) one with a slight excess of stannous chloride and the other with a slight excess of ammonium hydroxide, after standing for several weeks, contained some blue-black crystals which were proven by microscopic and x-ray examination to be α -SnO. It is apparent that the blackening process consists of a transformation of the white or faintly yellow $2\text{SnO} \cdot \text{H}_2\text{O}$ first to anhydrous α -SnO in the finely-divided form, and second to blue-black α -SnO as the particles increase in size. This dehydration is accelerated by the action of light, especially in the absence of free ammonia. The nature of the containing vessel and its surface is of minor if not negligible importance. The failure of Bury and Partington to observe darkening in silica was probably due to their use of an opaque vessel.

Summary

The following is a brief summary of the results of this investigation:

1. Stannous oxide has been found to exist in two polymorphic forms: α -SnO which is blue-black in large crystals and brownish-green when powdered; and β -SnO which is greyish-green. The transformation temperature from the alpha to the beta form is approximately 550°C .
2. The crystal structure of α -SnO is tetragonal, of the PbO type with $a_0 = 3.78 \text{ \AA}$ and $c_0 = 4.79 \text{ \AA}$.
3. The precipitate formed by the interaction of solutions of stannous salt and ammonium hydroxide has been found by a temperature-composition isobar and x-ray diffraction studies to be a hemihydrate, $2\text{SnO} \cdot \text{H}_2\text{O}$.
4. Stannous oxide hemihydrate is dehydrated into α -SnO by (a) the action of excess alkali, (b) the action of light especially in the absence of free ammonia, and (c) heating to temperatures below the transformation temperature to the beta form.

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CHAPTER V

TITANIUM DIOXIDE

Tetravalent titanium, like tin, is said to form two distinct acids: ortho or alpha titanic acid and meta or beta titanic acid. Since the work of several investigators has shown that the stannic acids(13) are in reality hydrous stannic oxides differing essentially in the size of the primary particles, it seems not unlikely that the so-called titanic acids are also hydrous oxides whose properties are determined by the size and physical character of the particles.

The product commonly called orthotitanic acid or alpha titanic acid, is a white gelatinous precipitate formed by the addition of ammonia or alkali hydroxide to a solution of a tetravalent titanium salt. The highly hydrous gel is readily soluble in dilute acids and is easily peptized by dilute alkalis and suitable salts to give stable sols. On the otherhand, the product referred to as metatitanic acid or beta titanic acid, is a granular, difficultly soluble, and but slightly peptizable substance obtained (a) by the interaction of nitric acid and titanium, (b) by the aging under water of the precipitated gel of the so-called orthotitanic acid slowly in the cold and more rapidly in the hot, (c) by precipitation in the hot, (d) and by hydrolysis of solutions of tetravalent titanium salts.

The composition of the preparations referred to above varies with the method of formation and the subsequent treatment. The only evidence for the existence of the definite hydrates corresponding to the formulas of the acids that earlier investigators (2, 5, 9, 10, 11, 12) have assumed, is the analysis

of the products formed and dried at arbitrary conditions. Carmelly and Walker(1) obtained a smooth temperature-composition isobar for a precipitated gel and hence concluded that no definite hydrates were formed, unless it is assumed that a large number exist, each stable over a very narrow temperature range. Morley and Wood(8) prefer to assume that the change from the so-called alpha to beta form consists of a condensation to salt-like complexes, but there is no experimental justification for this point of view. More recently Gutbier and coworkers (3) obtained smooth composition-temperature isobars for several preparations, indicating the absence of definite hydrates of titania.

No systematic x-ray study of the constitution of the alleged titanic acids has been made. Hedvall(4) states that "titanium hydroxide" precipitated at some unspecified temperature is crystalline, since it gives a good interference pattern both when moist or when dried at room temperature. On the other hand Gutbier and coworkers(3) report that the freshly precipitated products give no diffraction pattern, but the gels thrown with ammonia at 20°C. to 100°C. and subsequently ignited give the pattern of the mineral rutile or a mixture of rutile and anatase, and the product obtained by oxidizing $Ti_2O_3 \cdot xH_2O$, followed by heating to 490°C., the x-ray pattern of anatase.

In the following section will be given the dehydration isobars of two typical gels of titanium dioxide and the results of the x-ray examination of the precipitated oxides obtained under widely varying conditions.

Experimental

1. Preparation of Samples

Precipitation with Ammonia. A solution of 17 g. of titanium tetrachloride in 75 cc of 6 N hydrochloric acid was treated with ammonia at room temperature and the resulting precipitate washed thoroughly by decantation by the aid of the centrifuge until only a trace of chloride remained. This sample, which

will be designated as No. 1, was treated in different ways, as given in Table II. A second sample, designated as No. 6, was prepared by treating a boiling solution of the tetrachloride with a small excess of ammonia, boiling the mixture for 15 minutes, and finally washing and drying as sample No. 1.

Oxidation of $Ti_2O_3 \cdot xH_2O$. A solution of 8 g. of titanium trichloride in 100 cc of water was treated with 15 cc of 15 N ammonia, the mixture diluted to 400 cc and allowed to oxidize in the air. The original black precipitate changed rapidly to a gray color which changed slowly to white on conducting a current of air into the suspension. This precipitate (No. 2) was thoroughly washed and air-dried at room temperature.

Hydrolysis. A dilute solution of titanium tetrachloride in hydrochloric acid was hydrolysed by boiling for four hours, using a reflux condenser. The resulting granular precipitate was washed with hot water and air-dried at room temperature. Similar preparations were made by the hydrolysis of the nitrate and sulfate.

2. Isobaric Dehydration

Temperature-composition isobars for sample No. 1 precipitated at room temperature and sample No. 2 made by the oxidation of $Ti_2O_3 \cdot xH_2O$ were obtained in the following way. The samples in glass-stoppered weighing bottles were placed in a thermostated electric oven through which dry air was circulated at the rate of 72 liters per hour. The air was dried by passing it through a large calcium chloride tower, a sulfuric acid bottle, and finally through a tower filled with glass wool and phosphorus pentoxide. The rate was measured with a calibrated oil-filled flow meter left permanently in the line. The air was filtered through cotton just before passing into the oven. The air was preheated by passing through a 15-foot coil of glass tubing inside the

oven and was then conducted into a small enameled pan with a loose fitting cover, which held the samples. This arrangement is similar to that of L.H. Milligan(6). The temperatures were measured with standardized thermometers and a standardized thermocouple. The temperature was kept constant to within 1 to 2 °C. To attain equilibrium conditions at a given temperature, each sample was heated at least four days and in some cases for as long as thirty days. In general, less time was required to attain equilibrium at higher temperatures than at lower temperatures. The results are given in Table I and Figure 1. In agreement with the results of Gutbier and coworkers(3), the smooth isobars for both samples indicate the absence of hydrates corresponding to the alleged acids.

3. X-Ray Analysis

The specimens listed in Table II were examined as described in preceding papers in this series. The diffraction data are given in Table III and are shown in chart form in Fig. 2 for purposes of comparison.

Densitometer curves for the films from samples 1,4,6 and 8 are given in Fig. 3. These curves were obtained with a simplified and inexpensive recording photodensitometer that has already been described(7). From these data it is apparent that the samples precipitated in the cold gave little or no x-ray diffraction pattern, whereas both the aged oxide and the one thrown down at 180°C. give the anatase pattern. The precipitate freshly formed in the cold consists either of amorphous TiO_2 with adsorbed water, or what is more likely, of anatase crystals so minute that little or no x-ray diffraction is observed.

As already noted, Hedvall(4) obtained an x-ray diffraction with a precipitated titania. Since both Gutbier and coworkers and ourselves failed to get a pattern with the cold precipitated oxide, it is probable that Hedvall's precipitate was obtained in the hot and that the pattern showed the lines of

FIG. 1. DEHYDRATION ISOBARS OF HYDROUS TiO_2

1. Precipitated at room temperature. 2. Made by oxidation of $\text{Ti}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ in air.

FIG. 2. CHART OF X-RAY DIFFRACTION PATTERNS

FIG. 3. DENSITOMETER CURVES OF X-RAY DIFFRACTION PATTERNS

Table I

Thermal Dehydration Isobars of Hydrrous Titanium Dioxides

Temperature	Composition		Temperature	Composition	
	Mols H ₂ O/ per mol TiO ₂			Mols H ₂ O per mol TiO ₂	
°C	No.1 Pptd. room temperature	No.2 Oxidation of Ti ₂ O ₃ ·xH ₂ O	°C	No.1 Pptd. room temperature	No.2 Oxidation of Ti ₂ O ₃ ·xH ₂ O
35.1	0.970	1.030	122.5	0.288	0.291
71.3	0.562	0.590	150	0.218	0.217
87.2	0.425	0.454	184	0.184	0.154
92.6	0.415	0.402	205	0.114	0.101
100.0	0.362	0.361	224	0.081	0.084
105.4	0.308	0.306	255	0.054	0.061
110.0	0.295	0.296	270	0.046	0.053

Table II
X-Ray Examination of Hydrrous Titanium Dioxides

Sam- ple No.	Method of Preparation	Results
1	Precipitated at room temperature	No visible lines or bands
3a	No.1 aged at room temperature 14 weeks	No visible lines or bands
3	No.1 aged at room temperature 30 weeks	Anatase pattern, very broad bands
5	No.1 aged 6 hours at 100°C.	Anatase pattern, broad bands
4	No.1 heated to 184°C.	Anatase pattern, broad bands
11	No.1 heated to 1000°C.	Rutile pattern (and trace anatase?)
6	Precipitated at 100°C.	Anatase pattern, broad bands
2	Oxidation of $Ti_2O_3 \cdot xH_2O$	No lines or bands visible
14	No.2 heated to 184°C.	No lines or bands visible
12	No.2 heated to 1000°C.	Rutile pattern (and trace anatase?)
9	Hydrolysis of $TiCl_4$	Rutile pattern, broad bands
9a	Hydrolysis of $Ti(NO_3)_4$	Rutile pattern, broad bands
7	Hydrolysis of $Ti(SO_4)_2$	Anatase pattern, broad bands
10	Mineral rutile, TiO_2	Rutile pattern, sharp lines
8	Mineral anatase, TiO_2	Anatase pattern, sharp lines
13	Mineral brookite, TiO_2	Brookite pattern, sharp lines

Table III
X-Ray Diffraction Data for TiO₂

anhydrous TiO_2 (anatase modification) as we observed.

The samples ignited at about 1000°C . consist for the most part of rutile. Inspection of Table III shows that sample No. 11 gives in addition to the rutile pattern very weak lines at $3.51 \text{ \AA}$ and $1.895 \text{ \AA}$. It will be observed that the two most intense anatase lines are $3.49 \text{ \AA}$ and $1.883 \text{ \AA}$. It seems likely that a small amount of unchanged anatase is present in this ignited sample. Sample No. 12 also consists of rutile with the addition of lines of weak intensity at $3.00 \text{ \AA}$, $2.11 \text{ \AA}$, $1.89 \text{ \AA}$. Since the sample was precipitated originally from TiCl_3 solution and oxidized in the air, it may contain some impurity not present in the other samples.

Summary

The following is a brief summary of the results of this investigation:

1. X-ray diffraction examination of hydrous titanium dioxide freshly precipitated at room temperature or freshly prepared by the oxidation of $\text{Ti}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ gives no lines or bands. Thermal dehydration isobars for these two samples show that the water is given off in a continuous manner. The dehydration experiments of Guthrie and coworkers are confirmed. There is no indication of any definite hydrates.
2. Aging under water at room temperature for 14 weeks of hydrous titanium dioxide precipitated at room temperature produces no change detectable by x-ray methods. Further aging of the sample for 30 weeks at room temperature or 6 hours at 100°C . under water, gives minute crystals of anatase, TiO_2 ; heating of the freshly precipitated material to 184°C . gives anatase.
3. Hydrous titanium dioxide precipitated at 100°C . shows the x-ray-gram of anatase.

4. Hydrous titanium dioxide prepared by the hydrolysis at the boiling point of solutions of titanium tetrachloride and nitrate, show the x-radiogram of rutile, while hydrolysis of titanium sulfate under similar conditions gives anatase.

5. The product obtained by ignition at approximately 1000°C. of the hydrous oxide precipitated in the cold, shows the x-radiogram of rutile with indications of the presence of a little unchanged anatase.

6. X-ray analysis and thermal dehydration isobars indicate that no hydrates of titanium dioxide have been prepared.

7. Precipitated titanium dioxide is a hydrous oxide consisting, especially when precipitated or aged in the hot, essentially of anhydrous TiO_2 (anatase modification) and adsorbed water.

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CHAPTER VI

YELLOW HYDROUS BETA-FERRIC OXIDE MONOHYDRATE

Aqueous solutions of ferric chloride allowed to stand for a long time at room temperature or heated slowly to 60-100°C deposit a yellow, hydrous precipitate containing an amount of chloride depending upon the conditions of formation. This material is usually considered to be a definite basic chloride of some kind. The compositions obtained by various investigators for this material are summarized in Table I.

X-ray diffraction examination by Böhn(3) of the yellow precipitate from a sol aged for twenty years showed the material to be distinct from α - or γ -Fe₂O₃·H₂O or α - or γ -Fe₂O₃. Schikker(14) pointed out that the x-ray pattern of the precipitate obtained by slowly heating a solution of 35 g of FeCl₃·6H₂O in ⁴1 liter of water to 90°C was identical with Böhn's preparation and different from Stirrman's definite FeOCl (15). Schikker considers it probable that his preparation is not a true basic chloride, but is a monohydrate of ferric oxide. The fact that the material in question has never been proven to be a definite basic chloride is recognized by Hellner and Zocher(7) who designate it as a "hypothetical basic chloride".

Fischer(6) and Schikker(14) have both observed that a sudden loss of about 1 mol of water per mol of ferric oxide occurs upon dehydration, although no data has been given. Fischer, in the absence of x-ray diffraction data, was not aware that his yellow precipitate was any different from the already known yellow monohydrate of ferric oxide. Consideration of all the known facts, point to the conclusion that the yellow, hydrous material

Table I

The Preparation and Composition of Alleged Basic Ferric Chlorides

Investigator	Preparation and Treatment	Ratio Fe:Cl	Conclusion
Wittstein(18)	Yellow-brown powder from aged FeCl_3 solution; dried at 50°C .	2.33	A basic salt
Ordway(11)	Dilute FeCl_3 solution deposits a yellow substance on boiling	4.5	A basic salt
Béchamp(2)	Boiled FeCl_3 with H_2O , washed ppt. rapidly and dried 100°C .	4.5	
Picton and Linder (13)	Evaporated in vacua a FeCl_3 sol.	6.33	Definite basic salts
Cameron and Robinson(5)	Phase rule study system Fe_2O_3 - HCl - H_2O at 25°C .		No basic salts
Fischer(6)	Ppt. from FeCl_3 solution loses 1 mol H_2O / mol Fe_2 suddenly		No basic salts.
Pickering(12)	Yellow ppt. made by heating FeCl_3 solution	8	A basic salt
Neidle(10)	Hot dialysis of Fe_2O_3 sol containing FeCl_3 gives a yellow sol		Sol contains basic salts
Weiser(16)	Yellow ppt. by slow hydrolysis of FeCl_3 solutions; red-brown ppt. from rapid hydrolysis		No basic salts
Stirman(15)	Heated a FeCl_3 solution 270 - 410°C .	1	Definite crystals of FeOCl
Böhm(3)	Aged Fe_2O_3 sol gave a yellow ppt. whose x-ray pattern is distinct from α - and γ - Fe_2O_3 or- $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$		Assumed a basic chloride
Britten(4)	Titration of FeCl_3 with NaOH gave a yellowish ppt. at $P_H \approx 6.6$	6.67	Assumed basic salt
Bary(1)	Yellow filaments by slow evaporation of a Fe_2O_3 sol	7	Assumed basic salt
Schikorr(14)	Dialysis or heating of FeCl_3 gave a yellow ppt.	8	a basic saltm but more likely a hydrate

is actually a definite monohydrate of ferric oxide, distinct from the α - or γ - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$. That this hypothesis is correct is shown in the experimental portion of this chapter which follows in the next paragraph.

Experimental

1. Preparation of Samples

Malfitano(8) observed that ferric chloride solutions slowly heated to 100°C give a yellow colloid, while rapid heating gives a reddish-brown one. Studies of the hydrolysis of ferric chloride solutions by Weiser(16) made 15 years ago showed that the color depends upon the rate of heating. At that time in the absence of x-ray data, it was concluded that the yellow product was a hydrous ferric oxide of particle size larger than the ordinary brownish-red and smaller than the brick red ferric oxide. The yellow color was attributed to the size of the particles. The necessity for the slow heating of the ferric chloride solution has since been recognized by most investigators, in particular by Schikker(14) and Hellner and Zoehrer(7).

Hydrolysis of Ferric Chloride Solutions. One hundred cc portions of freshly prepared ferric chloride solutions were placed in 125 cc flasks with reflux condenser attached, and heated to boiling during a period of about 45 minutes. Table II summarizes the results from one series of experiments. In all cases except the most dilute solutions, a yellow sol or yellow precipitate is obtained, which upon further heating goes over to a brick-red colored precipitate. Quantities of five samples were prepared for further examination as follows:

Sample A. A solution containing 100 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 4 liters of water was heated slowly to 95°C and digested for 24 hours at this temperature.

Table II
Hydrolysis of Ferric Chloride Solutions

FeCl ₃ solution used Molarity	Color and Physical Character of Precipitate or Sol after a time of			
	5 minutes	1 hour	2 hours	3 days
0.01	yellow solution	clear red sol	clear red sol	Brick red
0.02	yellow solution	-----	red sol	Brick red
0.03	yellow solution	-----	reddish-yellow [#] sol	Brick red
0.04	yellow solution	-----	yellow sol	Brick red
0.05	yellow-brown sol.	Yellow ppt.	yellow sol	Brick red
0.25	reddish-brown ^{""}	Yellow ppt.	yellow ppt.	Brick red
0.50	reddish-brown "	Yellow ppt.	yellow ppt.	Brick red
0.75	reddish-brown "	yellow pppt.	yellow ppt.	Brick red
1.00	reddish-brown "	cloudy	yellow ppt.	Brick red

The resulting yellow precipitate was separated from the supernatant liquid by centrifuging and was washed once with distilled water. Attempts to wash with distilled water again gave a very stable sol. The sample was dried to constant weight at 60°C.

Sample B. A second sample was prepared by heating a solution containing 25 g per liter of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ for 24 hours, followed by washing once with water, and 8 times with acetone, using the centrifuge. This sample was dried for 24 hours at 140°C. Heating to this temperature gave a slightly less bright yellow color.

Sample C. A solution containing 100 g per liter of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was heated slowly to 85-90°C during a period of 3 hours, and digested for 12 hours at this temperature. The supernatant liquid was decanted off, and the remaining precipitate was subjected to continuous, hot dialysis using a Cellophane membrane.

Sample D. Approximately 500 cc of 0.5 and 1.0 N solutions of ferric chloride were heated slowly to 90°C, washed with water once, and 6 times with 150 cc portions of 1.0 N NH_4OH , using the centrifuge. The samples were dried at 120°C. A second sample from the 1.0 N ferric chloride was prepared in the same manner, but was dried at 92°C.

Sample E. One hundred g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 4 liters of water, heated slowly to about 65°C, and digested for 24 hours at this temperature. The precipitate was washed twice with water in 3 liter portions, and 20 times with 12 liter portions of dilute NH_4OH , by decantation. This sample contained less chloride than any other. It is apparent that washing by decantation alone, rather than using the centrifuge, was a more effective method of removing the chloride. The precipitate was not matted down in the

in the bottom of the flask as when the centrifuge was used. This allowed the precipitate to peptize at once upon the addition of the dilute ammonia, forming an unstable sol. Spontaneous precipitation of this sol in a few hours gave a flocculant precipitate that settled fairly easily. These conditions appear favorable for the replacement of nearly all of the chloride with ammonia or ammonium hydroxide. After washing with ammonia, the precipitate was washed several times with water, until only a trace of ammonia was left.

The chloride content of samples A-E is summarized in Table III. It is apparent that the composition depends upon the method of formation and the subsequent treatment of the sample. Since in sample E the ratio Fe:Cl reached nearly 38, the product can hardly be considered as a basic chloride.

2. Thermal Dehydration Isobars

Sample A was thermally dehydrated in an apparatus described(17) in detail elsewhere (see Chapter V). The results obtained are given in Table IV and in Fig. 1. The color changes from yellow to brick-red coincident with the sudden loss of water between 150 and 184°C. X-ray analysis of the brick-red product shows it to be α -Fe₂O₃.

The dehydration isobar for sample E is given in ~~Table V~~ and Fig. 2. The apparatus used in this experiment was an improvement on the one used previously(17). A constant water vapor-pressure was obtained by bubbling air through a bottle of water in a thermostat at 25°C. The air saturated at 25°C was passed through traps to remove any water vapor carried over mechanically, through a flow meter, and finally through a larger preheating coil of glass tubing inside the constant temperature oven. The air was passed through the apparatus at a rate of about 360 liters per hour, in expectation that the time required for equilibrium might be reduced. The results for the purer sample E show more clearly that it is a definite hydrate, and that ~~the~~ decomposition

Figure 1
Thermal Dehydration Isobar of Sample A

Figure 2
Thermal Dehydration Isotherm for Sample E

Table III
Composition of Beta-Monohydrate

Sample	Treatment of the Sample	% H ₂ O	Ratio Fe:Cl
A	Washed once, dried at 60°C.	7.76	4.79
B	Acetone-washed, dried at 140°C.	5.8	6.4
C	Dialysed for 2 weeks, dried at 71°C.	3.52	10.96
	Dialysed for 3 weeks, dried at 110°C.	2.99	---
	Dialysed for 8 weeks, dried at 110°C.	3.04	---
D	Ammonia washed with centrifuge, dried at 120°C.	1.87	---
	Ammonia washed with centrifuge, dried at 120°C.	1.44	---
	Ammonia washed with centrifuge, dried at 92°C.	1.39	28
E	Ammonia washed by decantation only, dried in air at room temperature for 6 hours	0.87	37.8

Table IV
Thermal Dehydration of Beta-Fe₂O₃·H₂O, Sample A

Temperature °C.	Loss of Weight %	Temperature °C.	Loss of Weight %
35.1	0.0	122.5	4.06
71.3	1.71	150	5.21
87.2	2.49	184	18.83
92.6	2.72	205	19.19
100.0	2.96	224	19.37
105.4	3.46	255	19.57
110.0	3.58	270	19.64

temperature is located more accurately than in the determination on sample A.

3. X-Ray Analysis

Examination of all the samples described above, using the same methods described in previous chapters of this paper, gave identical results. The pattern is distinctly different from the other ferric oxides and hydrates. For purposes of comparison, the x-radiograms of α - and γ - Fe_2O_3 and α - and γ - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ together with that from samples A-E, are given in chart form in Fig. 3. Careful examination of the films reveals no trace of any of the α - Fe_2O_3 lines. It is apparent that little or no "amorphous" ferric oxide can be present, especially in the samples dialysed in the hot since under those conditions any present would be expected to age rapidly to α - Fe_2O_3 .

The brick-red precipitates listed in Table II were all found to be α - Fe_2O_3 , as would be expected.

Crystal Structure of Beta-Ferric Oxide Monohydrate. Both α - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (goethite) and γ - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (lepidocrocite) have an orthorhombic structure. The lattice constants(19) are:

	a_0	b_0	c_0	$a:b:c$
α - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$	4.60 Å	10.01	3.04	0.459:1:0.303
γ - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$	3.85	12.5	3.07	0.308:1:0.246

An attempt has been made to suggest a structure for the supposed beta-mono-hydrate.

Trial and error gave the results listed in Table VI. It will be observed that the experimental data agrees with an orthorhombic structure having the following lattice constants: $a_0 = 5.28$; $b_0 = 10.24$; $c_0 = 3.34$; $a:b:c = 0.516:1:0.326$. The agreement between the observed and calculated values shows that

Table VI
X-Ray Diffraction Data

Calculated			Observed			
hkl	D	I	D	D	D	D
100	5.280	4	5.3	5.4	5.4	5.3
001	3.340	8	3.34	3.33	3.30	3.30
200	2.640	4	2.63	2.63	2.63	2.62
040	2.560	10	2.56	2.54	2.54	2.53
031	2.298	2	2.31	2.28	2.28	2.28
221	1.950	7	1.953	1.945	1.943	1.941
300	1.760	2	1.760	1.751	1.750	1.745
012	1.612	8	1.644	1.640	1.630	1.635
132	1.418	1	1.448	1.444	1.436	1.440

Figure 3

X-Ray Diffraction Patterns for Ferric Oxides and Hydrates

the lattice is either orthorhombic with the constants stated or a structure so close to it that they cannot be distinguished by the methods used. The density of the sample was found to be 3.14 when measured by the density bottle method. Flotation in a solution of potassium iodide and mercuric iodide gave a result of 3.2 ± 0.1 . The density calculated from the x-ray data is 3.245 for a unit cell containing two molecules of $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$. This is independent evidence that the material under examination is actually a monohydrate of ferric oxide and not a definite basic chloride.

Discussion of Results

The fact that ferric chloride solutions of widely varying concentrations give upon slow hydrolysis, hydrous yellow substances with identical x-radiograms, but varying chloride content, proves that a definite chemical compound has been formed, and that no appreciable amounts of other crystalline phases are present, but does not tell us the composition of the material. The dehydration isobars show that about 1 mol of water per mol of ferric oxide is chemically combined, indicating that the material is a monohydrate. It remains to consider whether the material is a monohydrate of ferric oxide or a monohydrate of a definite basic salt. In view of the fact that the chloride content can be reduced so that the ratio $\text{Fe}:\text{Cl}$ is almost 38, without any indications of decomposition such as hydrolysis of a higher basic chloride; it is difficult to believe we are dealing with a definite basic chloride. Furthermore, assuming the material to be a monohydrate of ferric oxide, the density calculated from x-ray data agrees with the experimental value. There can be little doubt but that this yellow, hydrous material is a definite,

hydrous monohydrate of ferric oxide containing traces of adsorbed chloride. Since the two well known monohydrates are termed α - and γ - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, we have decided to designate the third modification as β - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

SUMMARY

The results of this investigation may be summarized as follows:

1. Slow hydrolysis of solutions of ferric chloride of varying concentrations give a yellow, hydrous precipitate containing varying amounts of chloride.
2. X-ray analysis of all these precipitates yields identical results.

The pattern obtained is distinctly different from α - and γ - Fe_2O_3 and α - and γ - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

3. Purification by hot dialysis gives a ratio $\text{Fe}:\text{Cl} \approx 12$; washing with dilute ammonium hydroxide and finally with water gives a ratio $\text{Fe}:\text{Cl} \approx 38$, without any indications of decomposition.

4. Thermal dehydration isobars show that the material is a monohydrate.

5. Contrary to the opinions of many previous investigators, but in agreement with the observations of Fischer and Schiktor, the yellow material obtained by the slow hydrolysis of ferric chloride solutions is a hydrous ferric oxide monohydrate containing an amount of adsorbed chloride depending on the conditions of preparation and treatment of the sample.

6. It is suggested that this monohydrate be designated as β - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

7. The x-ray data obtained by the powder method agrees with an orthorhombic lattice having the unit cell dimensions: $a_0 = 5.28$; $b_0 = 10.24$; $c_0 = 3.34$; $a:b:c = 0.516:1:0.326$. The observed and calculated densities agree if the unit cell contains two molecules of $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

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