# THE CONSTITUTION OF COLLOIDAL SYSTEMS OF THE HYDROUS OXIDES[1]

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## I. INTRODUCTION

"Hydrous oxide" is the general term applied to the gelatinous precipitates thrown down from salt solutions above a critical pH value which varies for different salts. The term as we have used it for more than a quarter of a century implies that the gel water is held by the oxide by means of adsorption and capillary forces; hence the water content of a given hydrous oxide is the accidental result of the conditions of formation and drying and the age of the sample. The gels of ferric oxide, chromic oxide, titania, zirconia, and silica are typical hydrous oxides.

The elements of water are combined with certain oxides in definite stoichiometric ratios to give hydrated oxides or hydroxides, such as $MgO \cdot H_2O$ or $Mg(OH)_2$, $Al_2O_3 \cdot 3H_2O$ or $Al(OH)_3$, $Fe_2O_3 \cdot H_2O$ or $FeOOH$, $SnO \cdot 0.5H_2O$, etc. Wherever the application of x-ray analytical methods discloses the presence of hydroxyl groups, it is customary to designate the preparation as a hydroxide rather than as a hydrated oxide, but the terms are used interchangeably. Gelatinous precipitates of such compounds are called hydrous hydrates or hydrous hydroxides.

On standing, the primary colloidal particles of hydrous oxides and hydroxides grow or coalesce and lose gel water spontaneously, causing the mass to assume a less gelatinous and more granular character. This aging or spontaneous transformation from a loose voluminous precipitate to a granular mass is accompanied by a decrease in the solubility, the adsorbability, and the peptizability of the compound.

The view that the hydrous oxide gels and sols consist of colloidal particles of oxide or of a simple hydrate with adsorbed and entrained water was defended by van Bemmelen (2) a half-century ago, but this rather elementary concept of the constitution of colloidal systems of the hydrous oxides is not accepted by certain investigators in this field. For example,

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[1] Presented by Harry B. Weiser before the general meeting at the Ninety-fifth Meeting of the American Chemical Society, held in Dallas, Texas, April, 1938.

Willstätter, Krause, Kohlschütter, and Morley and Wood believe that the freshly precipitated oxide gels are best regarded as hydrates or orthohydroxides and that the aging process consists either of a polymerization or of a condensation involving the splitting off of water from one or more molecules of orthohydroxide to give polyhydroxides of gradually increasing complexity.

In the preface to a series of books on colloid chemistry the editor, Jerome Alexander, warns against any deceptive appearance of simplicity in nature and cautions, facetiously, that "It is we who are simple, not nature." Although no scientist would deny the complexity of most natural phenomena, it does not follow that the units of every system in nature must necessarily be of a complex character. At the risk of appearing old-fashioned and elementary minded, we shall present two types of experimental evidence that give strong support to the claim that most oxide gels and sols consist of agglomerates of minute crystals of oxide or simple hydrate (or hydroxide) rather than of polymerized bodies or condensation products of varying degrees of complexity. The evidence is derived from the simultaneous application of the time-honored phase rule technique and of the more recent x-ray diffraction analysis.

### *Experimental procedures*

The application of the phase rule to the problem of the constitution of hydrous oxides has frequently led to erroneous conclusions in the past because of the nature of the systems and because of faulty technique. The temperature–composition curves at constant pressure (isobars) and the pressure–composition curves at constant temperature (isotherms) for hydrous oxide hydrates or hydroxides are, as a rule, not sharply defined step-curves. Moreover, the dehydration product may be highly hygroscopic, thereby modifying the form of the curve. Finally, in most instances the dehydration of the heavy metal oxides at constant pressure is reversible only over a very narrow range, and days or even weeks may be required to establish an equilibrium state at each temperature. If these characteristics of the systems under consideration are recognized, phase rule data may be obtained that are usually capable of definite interpretation.

In the laboratory of The Rice Institute, isobars are obtained by the simple expedient of heating the samples to constant weight at each temperature in a thermostatically controlled, hot-air oven through which is passed continuously air saturated with water vapor at 25°C. The isothermal dehydration is accomplished in an apparatus shown diagrammatically in figure 1. The general method of procedure consists in pumping off a definite amount of water and measuring the vapor pressure of the resulting product at constant temperature by means of a manometer filled with "vacuum pump oil" of known density. The changes in composition are followed (*1*) by direct weighing of the sample tube with contents, (*2*) by collecting in a drying tube and weighing the water vapor pumped off at each pressure, or (*3*) by direct weighing of the sample with the

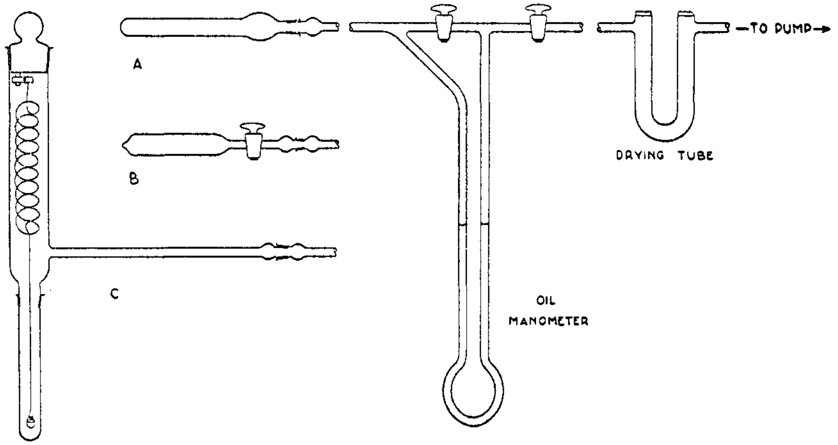


FIG. 1. Apparatus for isothermal dehydration

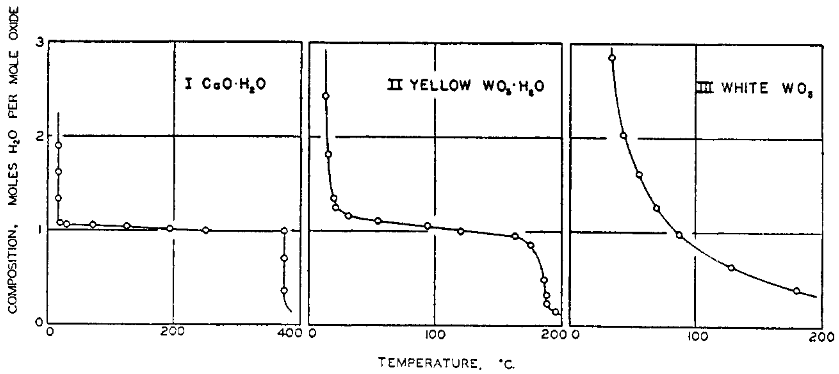


FIG. 2. Dehydration isobar for (*1*) hydrate or hydroxide, (*2*) hydrous hydrate, (*3*) hydrous oxide (after Hüttig).

McBain–Bakr balance (27). In figure 2 are given isobars which are typical of (*a*) macroscopic hydrates or hydroxides, (*b*) hydrous hydrates or hydroxides, and (*c*) hydrous oxides.

If the phase rule curve for a hydrous gel shows a definite point of inflection like that given in I of figure 2, there is no question but that the elements of water are combined with the oxide in a definite stoichiometric ratio. In II the upper portion of the curve represents the loss of adsorbed or hydrous water by the hydrate; the middle portion corresponds chiefly to the loss of combined water; and the lower portion corresponds chiefly to the loss of water adsorbed by the anhydrous oxide. The rounded corners of the step are the result of the colloidal nature of the hydrous hydrate. In such colloidal precipitates there exists a wide variation in crystal size, and there is more or less crystal lattice distortion and crystal lattice strain. These facts, together with the marked tendency of both the hydrate and the dehydration product to adsorb water, account for the absence of sharp breaks in the dehydration curves of colloidal oxide hydrates. Hüttig (17) accounts for the form of the curve by assuming that only a part of the hydrate water is held definitely in place in the crystal lattice, whereas a part is "osmotically bound" or in solid solution and so may move about with more or less freedom. The evidence in support of Hüttig's point of view is not convincing. As a matter of fact, this type of curve is frequently obtained when the elements of water are present as —OH groups rather than as $H_2O$ molecules. Damerell (8, 9, 10) attributes the loss of water by a hydrate below a definite decomposition temperature to surface dehydration of extremely minute crystals without lattice rearrangement. This view is likewise unsatisfactory, since one gets a similar form of curve even with macroscopic crystals. In any event, for certain hydrous hydrates the corners are rounded to such an extent that the point of inflection corresponding to a hydrate is slight or may be absent altogether. Under these conditions examination of the dehydration product at intervals by the technique of x-ray diffraction may assist greatly in establishing the constitution of the colloidal material.

X-ray diffraction patterns are obtained by us with either a Seemann or a Philips-Metalix x-ray diffraction apparatus, using filtered Cu $K_\alpha$ x-radiation. The samples for examination are sealed in capillary tubes of Lindemann glass, which is quite transparent to x-rays.

In the following section the results of some observations on the constitutions of typical hydrous oxide gels, obtained by using phase rule and x-ray diffraction technique, will be described; in the last section the results of the direct examination of hydrous oxide sols by x-ray diffraction analysis will be considered.

## II. HYDROUS OXIDE GELS

### *A. Alumina*

Two well-defined hydrates of alumina exist in nature: $\gamma\text{-}Al_2O_3\cdot 3H_2O$ (gibbsite) and $\alpha\text{-}Al_2O_3\cdot H_2O$ (diaspore). Diaspore has not been prepared in the laboratory, but gibbsite is readily obtained by allowing alumina gel thrown down from the salt solution with ammonia or alkali to age in the cold, especially in the presence of alkali, and by the slow hydrolysis of alkali aluminate. A sample of synthetic γ-$Al_2O_3 \cdot 3H_2O$ was subjected to isobaric dehydration (58), waiting until equilibrium was established at each temperature. Samples heated for 2 hr. (insufficient for equilibrium to be set up) at various temperatures were examined by x-ray diffraction. The results are shown graphically in figure 3. It will be seen that γ-$Al_2O_3 \cdot 3H_2O$ loses $2H_2O$ to give γ-$Al_2O_3 \cdot H_2O$ as an intermediate product which, in turn, goes over to γ-$Al_2O_3$, and finally to α-$Al_2O_3$ at elevated temperatures. This dehydration isobar is quite similar to that obtained by L. H. Milligan (32) for an artificial gibbsite and by Fricke and Severin (14) for a natural gibbsite. All the curves are alike in showing a rounded step corresponding to $Al_2O_3 \cdot 3H_2O$ and in giving no indication whatsoever of the formation of a monohydrate as an intermediate product between γ-$Al_2O_3 \cdot 3H_2O$ and γ-$Al_2O_3$. But the x-ray evidence is indisputable that a colloidally dispersed intermediate phase is obtained, which gives a distinctive diffraction pattern corresponding to γ-$Al_2O_3 \cdot H_2O$ (böhmite). The chemical individuality of this compound is evidenced by the fact that Fricke and Severin obtained macroscopic crystals of it by heating commercial $Al_2O_3 \cdot 3H_2O$ to 350–750°C. at a pressure of 200 atm. Hüttig and Peter (20) prepared a similar product by heating the trihydrate in a bomb tube at 200 atm. Particularly good crystals result on heating 4 to 20 per cent aluminum nitrate containing up to 20 per cent nitric acid at 320–360°C. and 200–300 atm.

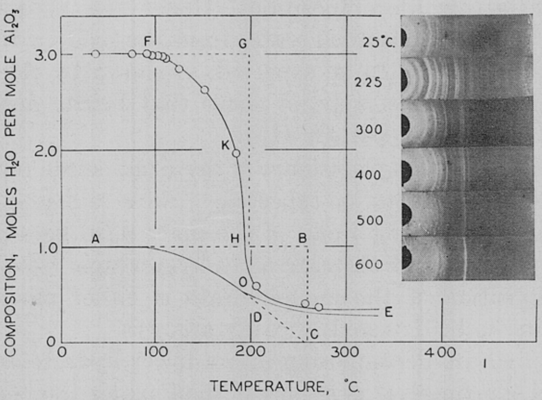


FIG. 3. Dehydration isobar and x-ray diffraction photographs of aluminas

Although the existence of γ-$Al_2O_3 \cdot H_2O$ is established, this compound does not give a "step" dehydration isobar. Moreover, it was found

(58) that the x-ray diffraction pattern for γ-$Al_2O_3 \cdot H_2O$ persists below a composition corresponding to $Al_2O_3 \cdot 0.35H_2O$. This anomalous behavior caused us at one time to doubt whether the intermediate product was a true hydrate; therefore it calls for special consideration.

Application of the phase rule to the two-component system monohydrate–oxide–water vapor shows that the system should be univariant, giving an isobar (58) represented by the dotted lines *AB* and *BC* in figure 3. Theoretically the curve should drop to zero composition at a definite temperature but, as we have pointed out, this never occurs with a colloidally dispersed hydrate; instead, a part of the water is lost below the true decomposition temperature of the mass of the hydrate, and the curve takes the rounded form *ADC*. Now if the oxide formed by the dehydration of the hydrate is highly hygroscopic, it will adsorb most of the water vapor formed by the decomposition. Hence the actual dehydration measured is the loss of adsorbed water from the oxide. In such cases a bivariant type of curve is to be expected, as shown by the solid line *AE* in figure 3. It is this last type of curve that Fricke and Severin (14) obtained for both α- and γ-$Al_2O_3 \cdot H_2O$.

We may now explain the persistence of the x-radiogram for γ-$Al_2O_3 \cdot H_2O$, where it would ordinarily not be expected. The x-radiogram of the monohydrate should persist along a part of the curve *ADC* because some of the compound is present, and the extremely hygroscopic γ-$Al_2O_3$ formed by partial decomposition of the monohydrate is either amorphous or too finely crystalline to be detected by x-ray analysis.

In a higher hydrate decomposing into a lower hydrate and finally into the anhydrous substance, it is apparent that, under the conditions noted above, the isobar alone will fail completely to detect the lower hydrate. The theoretical curves for a trihydrate decomposing into a monohydrate, and this in turn into the oxide, are given by the broken lines *FGHBC* in figure 3. Experimentally the composition of the trihydrate remains constant only to point *F*, where some water is lost, giving a small amount of water vapor and monohydrate. As this process continues along the line *FKH*, all the trihydrate decomposes rapidly to monohydrate. Then the lower hydrate loses water to the point *O*; hence the line *FKH* continues past the theoretical composition of the monohydrate to *O*. This decomposition of monohydrate gives the highly adsorptive γ-$Al_2O_3$, the presence of which causes the dehydration curve to follow the course *HOE* for the reasons given above.

Because of the extreme hygroscopicity of γ-$Al_2O_3$, the dehydration curve of γ-$Al_2O_3 \cdot H_2O$ shows such a marked variation from the theoretical curve that its existence as intermediate product in the dehydration of γ-$Al_2O_3 \cdot 3H_2O$ has not been detected by phase rule technique. This is an extreme case, but it is not unique. Adsorption of water by the dehydration product is responsible for the shape of the lower portion of the dehydration isobars of all colloidal oxide hydrates or hydroxides.

$\alpha$-$Al_2O_3 \cdot 3H_2O$ or bayerite is a metastable compound isomeric with gibbsite, the stable modification. The dehydration isobar of bayerite is similar in essential respects to that of gibbsite.

The highly gelatinous precipitate thrown down at room temperature on adding ammonia to an aluminum salt solution gives the characteristic x-ray diffraction pattern of $\gamma$-$Al_2O_3 \cdot H_2O$. The patterns from the gel precipitated from nitrate and from chloride solutions are reproduced in figure 4, a and b. The series of alleged hydrates of alumina described by Prutton, Maron, and Unger (39) were prepared from aluminum chloride solution, and are probably $\gamma$-$Al_2O_3 \cdot H_2O$ with varying amounts of adsorbed water.

Alumina gel free from other salts is best obtained by the action of amalgamated aluminum on water (68). Pure aluminum (99.6 per cent aluminum) is amalgamated in a mercuric chloride solution, washed thoroughly, and then placed in water. The gels prepared by its action for 24 hr. on boiling water and on cold water were examined by x-rays; the patterns are reproduced in figure 4, c and d. The gel thrown down in the hot gives the pattern of highly dispersed $\gamma$-$Al_2O_3 \cdot H_2O$; on the other hand, the gel obtained in the cold gives the typical patterns of $\alpha$-$Al_2O_3 \cdot 3H_2O$ or bayerite. Under the conditions described, the $\gamma$-$Al_2O_3 \cdot H_2O$ first precipitated in the cold is transformed into $\alpha$-$Al_2O_3 \cdot 3H_2O$. If sufficient time were allowed, this metastable compound would have gone to $\gamma$-$Al_2O_3 \cdot 3H_2O$, gibbsite.

Failure in the past to recognize that $\gamma$-$Al_2O_3 \cdot H_2O$ precipitated in the cold ages spontaneously in the cold, first to metastable $\alpha$-$Al_2O_3 \cdot 3H_2O$ and finally to stable $\gamma$-$Al_2O_3 \cdot 3H_2O$, has caused considerable confusion in interpreting the x-ray data of different investigators. It is now known, however, that samples of the metastable isomer are likely to contain more or less of the stable isomer, and that this apparently accounts for the differences in the bayerite patterns obtained by different people and for the presence in them of lines corresponding to $\gamma$-$Al_2O_3 \cdot 3H_2O$. In a study of the transformation from alumina monohydrate to trihydrate by isobaric dehydration and x-ray diffraction methods, Hüttig was led to conclude that a continuous series of crystalline hydrates between the two extreme compositions was formed. It is very much more probable that the intermediate products are not definite chemical individuals as Hüttig (19, 21) suggests, but are mixtures of $\gamma$-$Al_2O_3 \cdot H_2O$, $\alpha$-$Al_2O_3 \cdot 3H_2O$, and $\gamma$-$Al_2O_3 \cdot 3H_2O$ in varying amounts, depending on the conditions of precipitation and the age and treatment of the samples.

In a study of the lake formation process ten years ago (51) it was observed that alumina gel (from amalgamated aluminum in the cold) lost its adsorption capacity for alizarin much more readily when prepared in the absence of chloride than when prepared in the presence of chloride. This was attributed, at the time, to the action of chloride in preventing the transformation of highly unsaturated atoms of aluminum on the surface of the gel into the normal lattice of crystalline alumina. We now know that the presence of chloride slowed down the following transformation: $\gamma\text{-}Al_2O_3 \cdot H_2O \rightarrow \alpha\text{-}Al_2O_3 \cdot 3H_2O \rightarrow \gamma\text{-}Al_2O_3 \cdot 3H_2O$. In the absence of chloride this transformation of very highly dispersed $\gamma\text{-}Al_2O_3 \cdot H_2O$ takes place fairly rapidly with the formation of larger crystals, chiefly of $\alpha\text{-}Al_2O_3 \cdot 3H_2O$, having a relatively low adsorption capacity, whereas in the presence of chloride the highly colloidal $\gamma\text{-}Al_2O_3 \cdot H_2O$ is more stable, and the gel retains its strong adsorption capacity for a longer period of time.

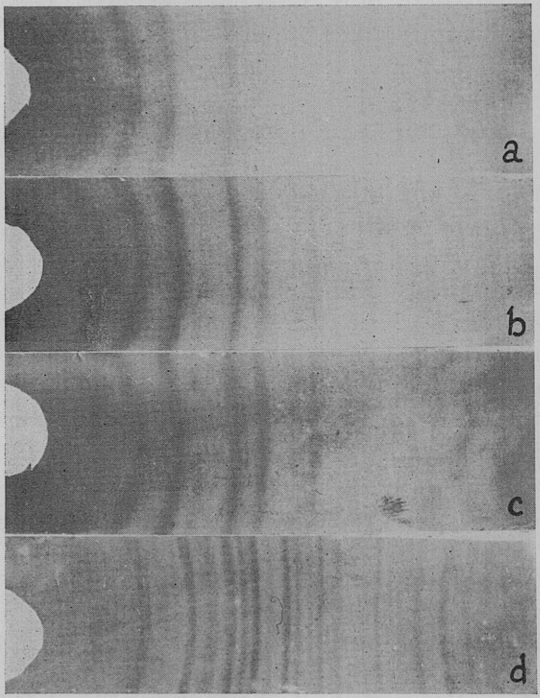


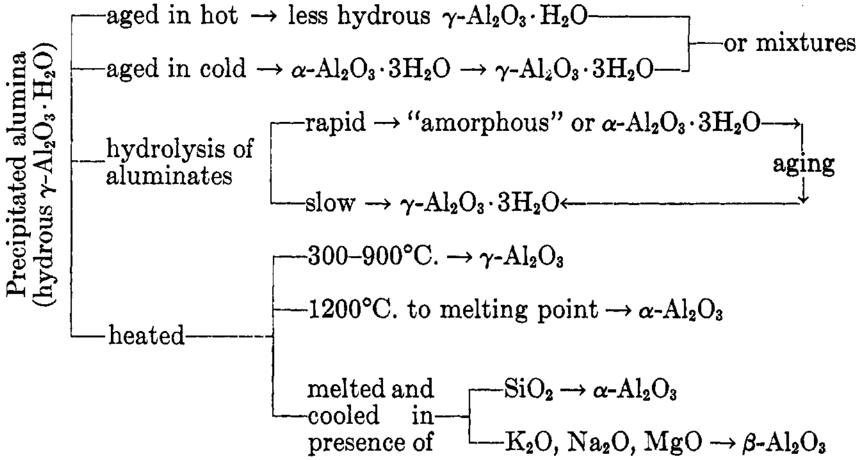
FIG. 4. X-ray diffraction photographs: $\gamma\text{-}Al_2O_3 \cdot H_2O$ from (*a*) nitrate solution, (*b*) chloride solution, (*c*) amalgamated aluminum in the hot; and (*d*) $\alpha\text{-}Al_2O_3 \cdot 3H_2O$ from amalgamated aluminum in the cold.

Willstätter and Kraut (64) describe several hydrous aluminas, differing in reactivity and adsorptive power, prepared by precipitating aluminum sulfate with ammonia under varying conditions. A suspended precipitate into which steam was conducted for 5 hr. was a pale yellow plastic mass, *A*; without the steam treatment, it was a very pale yellow plastic mass, *B*; precipitated with more dilute ammonia it was a pure white, very voluminous, and very finely divided substance, *C*. An intermediate variety, *b*, prepared by the dialysis of aluminum chloride with frequent additions of small quantities of ammonia, was claimed to be related chemically to *B* but resembled *A* in adsorptive power; a modified form of *C*, precipitated at 60°C., had an adsorptive capacity similar to that of *B*; and a new (67) form of *A*, claimed to be $Al_2O_3 \cdot 2H_2O$, was obtained by carrying out the precipitation at approximately 50°C., washing by decantation four times, followed by the addition of 15 per cent ammonia, and further washing by decantation until peptization started. As a result of dehydration experiments with the gels, Willstätter claimed that he obtained various hydrates which gave certain temperature intervals of almost constant water content. Thus precipitates obtained at low hydroxide-ion concentration and washed with acetone, which was tacitly assumed to remove adsorbed water, analyzed approximately for trihydrate; and precipitates obtained with excess ammonia in the hot gave what were assumed to be polyaluminum hydroxides, such as $2Al(OH)_3 \cdot H_2O$, $4Al(OH)_3 \cdot 3H_2O$, and so on up to $8Al(OH)_3 \cdot 7H_2O$. X-ray analysis of the several preparations (3, 54) showed that most of Willstätter's alleged hydrates have no existence in fact. Thus the preparations *A*, *B*, and "new" *A* all gave the x-ray pattern of the monohydrate $\gamma$-$Al_2O_3 \cdot H_2O$, less sharp than the patterns of the gels from the chloride and nitrate (figure 4). If the preparations originally $\gamma$-$Al_2O_3 \cdot H_2O$ are aged under suitable conditions in the cold, lines corresponding to $\alpha$-$Al_2O_3 \cdot 3H_2O$ or $\gamma$-$Al_2O_3 \cdot 3H_2O$ may appear also in the x-radiogram. But Willstätter's gels are at the outset essentially $\gamma$-$Al_2O_3 \cdot H_2O$, which differ in particle size and in degree of hydration, and hence they show marked differences in their behavior toward reagents and in their adsorption capacity for dyes and enzymes.

Thiessen and Thater (44) prepared an electrolyte-free gel by the hydrolysis of aluminum ethylate. The fresh, highly hydrous gel gave a smooth pressure–composition curve, but an aged, more granular gel showed a point of inflection in the pressure–composition curve corresponding to $Al_2O_3 \cdot 3H_2O$. The fresh gel was probably hydrous $\gamma$-$Al_2O_3 \cdot H_2O$, and the aged gel gave the x-ray pattern of $\alpha$-$Al_2O_3 \cdot 3H_2O$.

Finally, one appears justified in concluding that the freshly formed and aged gels of precipitated alumina are not polyhydroxides or condensation products but are agglomerates of minute crystals of $\gamma$-$Al_2O_3 \cdot H_2O$, $\alpha$-$Al_2O_3 \cdot 3H_2O$, $\gamma$-$Al_2O_3 \cdot 3H_2O$, or mixtures of these three in varying amounts depending on the conditions of preparation. The crystal structure of none of these compounds is known with certainty, but $\alpha$-$Al_2O_3 \cdot H_2O$ (diaspore) and $\gamma$-$Al_2O \cdot 3H_2O$ (gibbsite) have been investigated recently by Ewing (12) and Megaw (31).

The various transformations of precipitated alumina are shown in the following diagram:



### *B. Gallia*

Gallia, like alumina, forms a definitely crystalline trihydrate (24a)[2] and a hydrous monohydrate under suitable conditions. The gel, freshly precipitated at room temperature by the addition of alkali to a gallium salt, is hydrous $Ga_2O_3$. On standing in contact with ammonium hydroxide or on reprecipitation from a solution in ammonium hydroxide, hydrous $Ga_2O_3$ is transformed into hydrous $Ga_2O_3 \cdot H_2O$, which gives a dehydration isobar with a point of inflection corresponding to a monohydrate and a distinct x-ray diffraction pattern.

The gel thrown down at 100°C. consists of larger particles of hydrous $Ga_2O_3$ than are formed in the cold. Because of the lower solubility of the larger particles the gel does not age to monohydrate as readily as the oxide precipitated at room temperature. The dehydration isobar of the 100°C.-gel is continuous, and the x-ray diffraction pattern consists of two or three broad bands. Samples heated to higher temperatures show a progressive decrease in the width of the most prominent diffraction bands and the appearance of additional bands, indicating that the hydrous oxide is recrystallizing to form larger primary particles as the temperature is increased.

The results of observations (34) on precipitated gallia are summarized in figure 5. It is apparent that the upper curve exhibits a point of inflec-

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[2] Added to proof.

tion corresponding to a monohydrate, although this might very well be overlooked if it were not for the simultaneous x-ray diffraction data. The diffraction pattern for $Ga_2O_3 \cdot H_2O$ (5) is entirely different from that of $\gamma$-$Al_2O_3 \cdot H_2O$.

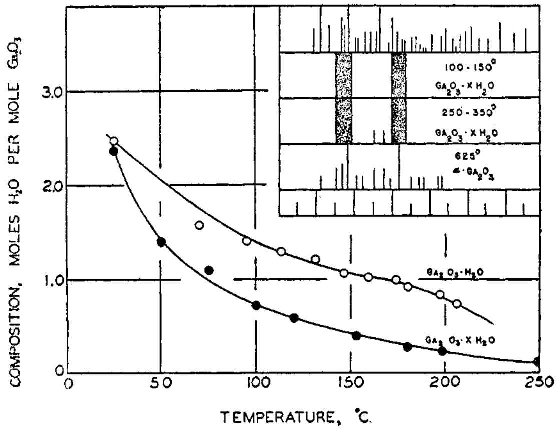


FIG. 5. Dehydration isobars and x-ray diffraction patterns of gallias

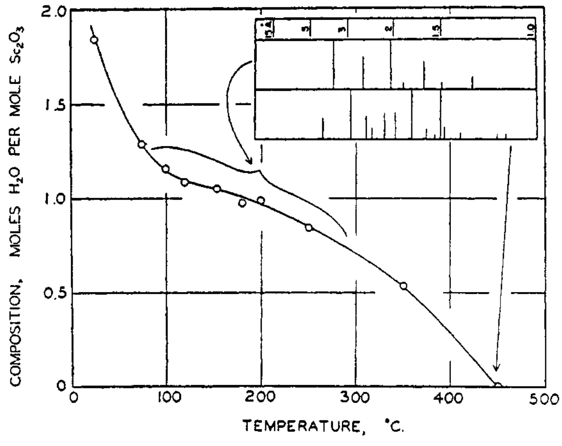


FIG. 6. Dehydration isobar and x-ray diffraction patterns for hydrous scandium oxide monohydrate

### C. *Scandia*

Scandia gel precipitated either at room temperature or at 100°C. is a highly gelatinous mass which gives a definite dehydration isobar corresponding to hydrous $Sc_2O_3 \cdot H_2O$. Figure 6 (63) gives the dehydration and x-ray data for a gel thrown down at 25°C. The alleged compound of

Štěrba-Böhm and Melichar (41), $[2Sc(OH)_3]\cdot H_2O$, gives the same diffraction pattern as the precipitated gel, $Sc_2O_3\cdot H_2O$.

For purposes of comparison, the diffraction patterns of $\gamma$-$Al_2O_3\cdot H_2O$, $Sc_2O_3\cdot H_2O$, and $Ga_2O_3\cdot H_2O$ are shown together in figure 7. The close resemblance between the pattern of $Sc_2O_3\cdot H_2O$, which gives a monohydrate dehydration isobar, and that of $\gamma$-$Al_2O_3\cdot H_2O$, which does not give a monohydrate isobar, indicates a similarity in both constitution and crystal structure.

### *D. The hydrous oxides of tin*

*Hydrous stannic oxide.* As early as 1812 Berzelius called attention to differences between the hydrous oxide formed by precipitation of stannic chloride with alkali and the product resulting from the action of nitric acid on tin. Since both preparations give a very slight acid reaction when shaken with water, they are commonly designated as orthostannic and metastannic acid, respectively. Earlier chemists regarded them as distinct chemical individuals with sharply defined differences.

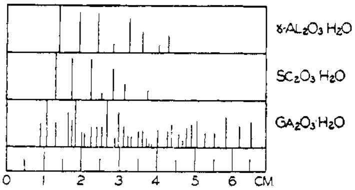


FIG. 7. Diagrams of the x-ray diffraction patterns for the hydrous monohydrates of the oxides of aluminum, scandium, and gallium.

Early investigators reported the preparation of a variety of supposedly definite oxide hydrates and hydrated acids of tin, obtained by drying the different preparations under suitable conditions, but extended investigations of van Bemmelen (2), Lorenz (26), Mecklenburg (30), and Weiser (50) failed to establish the existence of any preparation in which the elements of water are combined in a definite stoichiometric ratio. In recent years, however, Willstätter (65, 66) and his collaborators have adopted the older view that the behavior of different oxides could best be explained by assuming the existence of more or less stable hydrates. Willstätter claimed that all adsorbed water was removed from a gel by drying rapidly in a vacuum or by leaching with acetone. The composition of a gel formed in a special way and dried by the acetone method at −35° to +10°C. was represented by the formula $Sn(OH)_4\cdot 4H_2O$; when the gel was dried at room temperature it analyzed for $Sn(OH)_4$, which was regarded as the first member of a series of ortho- or $\alpha$-stannic acids. In an aqueous medium

$Sn(OH)_4$ was supposed to go over into other less basic members of the series. Thus by suitable conditions of precipitation and drying with acetone at 0° to 10°C., orthodistannic acid was supposedly formed; at 35° to 46°C. orthotristannic acid; and so on. Different so-called metastannic acids were likewise prepared and formulas assigned to many of them.

As evidence of hydrate formation Willstätter cites the regions of almost constant water content in the temperature–composition curves of acetone-dried preparations. Such evidence is altogether inconclusive, particularly in view of the fact that the nature and location of the "flats" in the curves are determined almost exclusively by the history of the sample. Such behavior was noted by van Bemmelen almost forty years before Willstätter. The adsorptive capacity of a true hydrous oxide for water at different stages of dehydration is determined by the physical character of the preparation; hence a "flat" corresponding to a hydrate is purely accidental and can be duplicated only by following a set method of procedure in precipitating, aging, and drying. Willstätter's comparison of the behavior of hypothetical, high molecular, hydrated stannic acids with their groups Sn:O and Sn·OH to that of carbohydrates with their groups C:O and C·OH appears to us highly fantastic and illusionary. As Posnjak (37) pointed out in 1926: "Willstätter and his collaborators did not bring forth a single new fact, but rather take the problem back some fifty years and only add to the confusion."

In support of his criticism of Willstätter's point of view Posnjak showed that samples of the so-called ortho- and meta-stannic acids give identical x-ray diffraction patterns, which in turn are identical with that of the mineral cassiterite, anhydrous $SnO_2$. This result has been confirmed by Yamada (70), Förster (13, 16), Hüttig and Döbling (18), and others, so that there is no question about the facts. The ortho- and meta-acids ($\alpha$- and $\beta$-oxides) are not isomers but are structurally identical stannic oxide with more or less adsorbed water. The differences in properties cannot be traced to differences in composition or crystal structure, but are due to differences in size and extent of coalescence of primary crystalline particles into secondary aggregates.

Although precipitated stannic oxide, as ordinarily prepared, is always hydrous $SnO_2$ and forms no hydrates or hydroxides, simple, condensed, or polymerized, Thiessen and Körner (43) claim that a stannic oxide gel prepared by the slow hydrolysis of an alcoholic solution of stannic ethylate gives isobars and isotherms that indicate the formation of no less than six definite hydrates. This could not be confirmed by us (55), as is shown by the dehydration isobar given in figure 8, together with similar isobars for typical $\alpha$- and $\beta$-oxides. In every instance smooth curves were obtained, indicating the absence of hydrates. The change in direction of the curve for a Thiessen–Körner preparation at 60–70°C. is due not to hydrate formation but to the presence of some adsorbed alcohol on the sample. The breaks in the curves of Thiessen and Körner may result from faulty technique, possibly from the failure to allow sufficient time for equilibrium to be established under a given set of conditions. Finally, x-ray diffraction examination of gels obtained by dehydrating a Thiessen–Körner preparation to temperatures corresponding to alleged hydrates, all give a band pattern corresponding to cassiterite, indicating that the several alleged hydrates consist of stannic oxide of varying degrees of agglomeration and with varying amounts of adsorbed water.

Thiessen claims that his hydrates are metastable bodies which have to be caught "on the run," and that we missed them by attempting to get

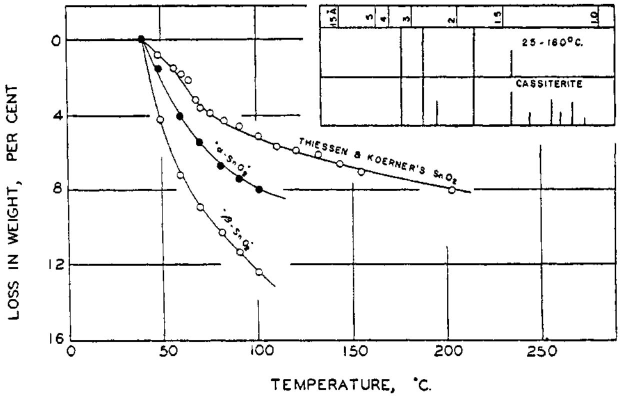


FIG. 8. Dehydration isobars and x-ray diffraction patterns for hydrous stannic oxide

points on the curve corresponding to equilibrium conditions. It is a brave man who trusts phase rule data obtained under non-equilibrium conditions. Moreover, it is not obvious why metastable hydrates should give the x-ray diffraction pattern for the anhydrous oxide, unless one wants to assume that the samples examined were mixtures of a hydrate amorphous to x-rays and the anhydrous oxide, and that only the pattern of the latter showed up. If this assumption were true, the "steps" would not come at exact stoichiometric ratios as found by Thiessen and coworkers, but at a lower ratio of $H_2O$ to oxide, which would be determined by the relative amounts of the "amorphous hydrate" and crystalline anhydrous oxide present.

*Hydrous stannous oxide.* The precipitate obtained by the interaction of stannous salts and an alkali is usually erroneously formulated as $Sn(OH)_2$. Bury and Partington (7) claim that the precipitate dried in vacuum over phosphorus pentoxide has the composition $3SnO \cdot 2H_2O$.

Actually, the gel is hydrous $SnO \cdot 0.5H_2O$, as evidenced by the phase rule and x-ray data shown graphically in figure 9 (56). The white or faintly yellow gel thrown down from stannous chloride solution with ammonia was washed practically free from chloride, first by the centrifuge until peptization started and then with a supercentrifuge. Air-dried samples were subjected to isobaric dehydration in a current of nitrogen and examined by x-rays at intervals. The results show conclusively that the preparation is a hydrous hemihydrate which starts to decompose at a temperature of 120°C. to give $\alpha$-SnO. Comparable to the behavior of copper hydroxide, the gel of $SnO \cdot 0.5H_2O$ dehydrates spontaneously to $\alpha$-SnO at room temperature in the presence of excess alkali. It is also dehydrated by the action of light, especially in the absence of free ammonia.

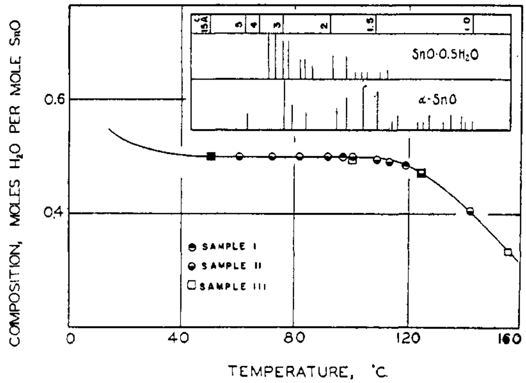


FIG. 9. Dehydration isobar and x-ray diffraction patterns of stannous oxides

## *E. Titania*

The hydrous oxides of $TiO_2$, $ZrO_2$, and $ThO_2$ are always described as existing in both an alpha-(or ortho-) and a beta-(or meta-)modification. Actually, in every case the relationship between the two alleged isomers is the same as exists between the so-called alpha- and beta-stannic oxides.

The product commonly referred to as orthotitanic acid is a white gelatinous precipitate thrown down by the addition of ammonia or alkali hydroxide to a solution of tetravalent titanium salt. Metatitanic acid is a granular, difficultly soluble preparation obtained (*1*) by aging the orthotitanic acid, (*2*) by the action of nitric acid on titanium, or (*3*) by hydrolysis of boiling solutions of titanium chloride. These alleged acids or oxide hydrates do not exist; both are hydrous oxides, as evidenced by the form of the dehydration isobars (57) shown in figure 10. Here again, the difference between the two preparations in solubility, adsorbability, and peptizability is a question of specific surface and not of isomerism. Aging involves not the condensation or polymerization of orthohydroxides, but the growth, coalescence, and agglomeration of primary particles into coarser aggregates.

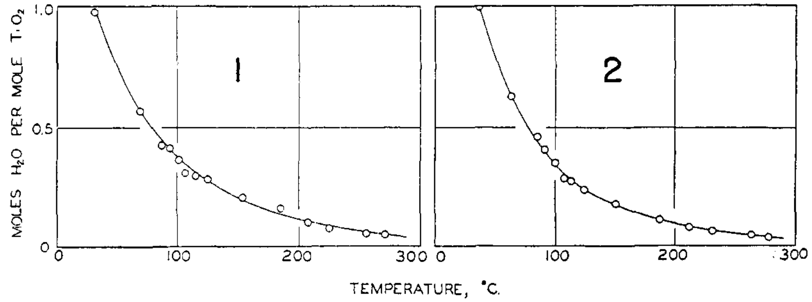


Fig. 10. Dehydration isobars for hydrous titanium dioxide: 1, precipitated at room temperature; 2, oxidation of $Ti_2O_3 \cdot xH_2O$ in air.

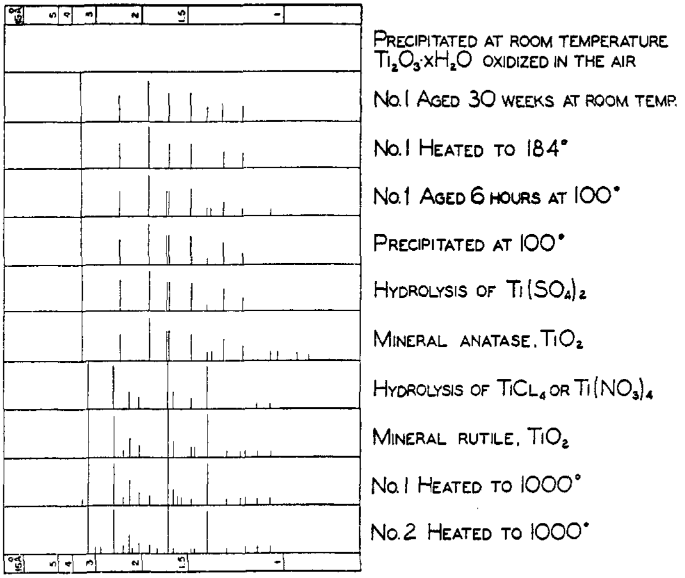


Fig. 11. Diagrams of the x-ray diffraction patterns of titanias

A summary of the x-ray diffraction data (57) obtained with titanias prepared and treated in different ways is given in figure 11. It is an interesting fact that the gel formed by hydrolysis of titanium chloride or nitrate gives an x-radiogram corresponding to the rutile modification of titania, whereas hydrolysis of titanium sulfate under similar conditions gives the anatase modification of the oxide. The gel precipitated from titanium chloride or nitrate solutions at 100°C. with ammonia gives a pattern corresponding to anatase. This behavior may well be of primary importance in connection with the manufacture of titania pigments.

The aging of the freshly precipitated oxide is a continuous process, which can be followed by observing (*1*) the sharpening of the anatase lines in the x-ray diffraction pattern, (*2*) the decrease in the adsorption capacity for dyes, and (*3*) the falling off in the solubility and peptizability in hydrochloric acid. In the light of the phase rule and x-ray studies, there seems no experimental justification for assuming, as Morley and Wood (35) do, that the change in physical character of the gelatinous oxide on aging is due to the formation of complex salt-like condensation products by the molecules of alleged hydroxides functioning both as acid and as base.

### *F. Hydrous ferric oxide*

*The brown gel.* The brown gel of hydrous ferric oxide, frequently misnamed ferric hydroxide, is commonly prepared by the addition of a base to a solution of ferric salt. Since a small integral ratio between oxide and water may be realized by drying the gel under suitable conditions, hydrates of the oxide have been reported from time to time, but most of the experimental evidence indicates that the brown precipitate gives no hydrates on isobaric or isothermal dehydration. The isobars (40) of two gels thrown down at room temperature are typical desorption curves showing no indication of the presence of $Fe(OH)_3$ or any other hydrate (figure 12). Curve 1 is for a relatively coarse sample formed by precipitation of a ferric nitrate solution with ammonia, and curve 2 is for a finer grained sample thrown down from a ferric chloride solution with ammonia. The gel freshly formed in the cold is amorphous to x-rays, but after standing at room temperature in contact with water for several weeks it gives a band diffraction pattern corresponding to $\alpha$-$Fe_2O_3$ or hematite (59), and after several months the aging has progressed to the point where the sample gives a sharp hematite pattern. The aging of the brown gel consists in the growth of $\alpha$-$Fe_2O_3$ crystals too small to give a characteristic x-radiogram into crystals large enough to give sharp diffraction lines. This transformation takes place slowly at room temperature but more rapidly at high temperature. The gel thrown down at 100°C. gives at once a band pattern of $\alpha$-$Fe_2O_3$; if maintained for a few hours at this temperature, it gives a sharp line pattern. A gel precipitated at 50°C. and held at this temperature for a few hours gives broad diffraction bands corresponding to $\alpha$-$Fe_2O_3$. It would appear, therefore, that the brown gel precipitated at room temperature is hydrous $\alpha$-$Fe_2O_3$.

The only physical evidence of the formation of hydrate or hydroxide by dehydration of the brown gel was furnished by the phase rule studies of Thiessen and Köppen (42) on a gel thrown down by the slow hydrolysis of ferric ethylate. During the isothermal dehydration of this gel, Thiessen and Köppen reported breaks corresponding to no less than eight and possibly ten different hydrates: $Fe_2O_3 \cdot nH_2O$, where $n$ = 5.0, 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0, and 0.5. We have repeated these experiments and failed to find any indication of a break corresponding to any one of the remarkable series of "Thiessen hydrates." A typical set of isotherms is reproduced in figure 13 (59). Thiessen questioned the purity of our preparations, and so the experiments were repeated with a gel formed by

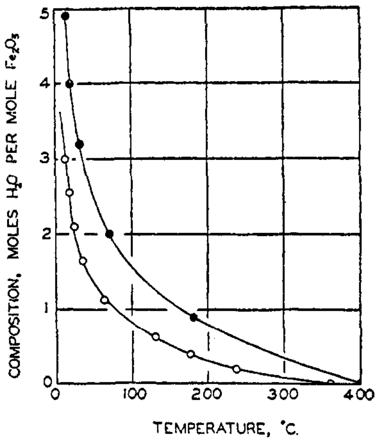


FIG. 12. Dehydration isobars for hydrous ferric oxides

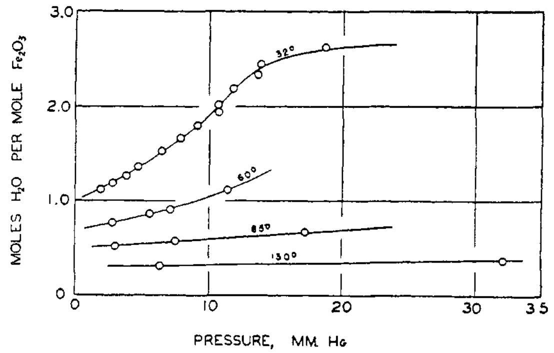


FIG. 13. Dehydration isotherms for $Fe_2O_3 \cdot xH_2O$ prepared by Thiessen's method

slow hydrolysis at 15°C. of a specially prepared sample of ferric ethylate. Again, smooth dehydration isotherms were obtained. The only real difference between our experimental procedure and that of Thiessen is that we allowed time for equilibrium to be substantially established at each pressure, whereas Thiessen waited for a length of time which he knew was insufficient for equilibrium to be set up. Thiessen justified his unusual procedure in phase rule work because of the supposed transient nature of the alleged hydrates. In our observations of the rate at which equilibrium is established we failed to detect any indication of such metastable hydrates.

Krause (24) and his collaborators claim the existence of ortho- and meta-hydroxides of iron, as well as a variety of products of aging, on the basis of the results of procedures involving the synthesis of silver ferrites. Krause assigns definite molecular structures to the freshly formed gels and interprets the changes on aging to polymerization, ring closure, aggregation, oxygen bridging, etc. This view ignores the results of x-ray diffraction and phase rule work. At best it is of limited application, since even the highly hydrous 100°C.-gel is $\alpha$-$Fe_2O_3$ with adsorbed and capillary-bound water. Willstätter and coworkers (64, 66) likewise claim that the water in the brown gel is held in part as chemically combined water and in part as capillary-bound water. They claim to be able to remove the capillary water by washing with acetone, leaving definite hydrates the composition of which depends on the conditions of drying. As we have seen, these claims are not justified by Willstätter's experiments and are not taken seriously by most people.

*Hydrous ferric oxide monohydrates.* Two monohydrates of ferric oxide exist in nature: $\alpha$-$Fe_2O_3 \cdot H_2O$, or göthite, and $\gamma$-$Fe_2O_3 \cdot H_2O$, or lepidocrocite. These give characteristic x-ray diffraction patterns and step dehydration isobars, $\alpha$-$Fe_2O_3 \cdot H_2O$ yielding $\alpha$-$Fe_2O_3$ and $\gamma$-$Fe_2O_3 \cdot H_2O$ yielding $\gamma$-$Fe_2O_3$.

The $\alpha$-monohydrate may be synthesized (*1*) by oxidation of ferrous salts under suitable conditions, (*2*) by aging the brown gel in 2 *M* potassium hydroxide at 150°C., and (*3*) by slow hydrolysis of most ferric salts. The last procedure is probably the simplest. In 1920 it was observed (49) that a solution of ferric acetate which had stood for a week or two at room temperature gave a yellow precipitate on prolonged boiling to remove the excess acetic acid followed by coagulating the resulting sol. From a freshly formed acetate solution treated in the same way, a red coagulum was obtained. It was believed at the time that both the yellow and red preparations were hydrous ferric oxides which differed from each other in physical structure, but it is now known from x-ray analysis that the yellow coagulum was hydrous $\alpha$-$Fe_2O_3 \cdot H_2O$ and the red was hydrous $\alpha$-$Fe_2O_3$. Posnjak and Merwin (38) obtained the same compound from dilute solutions of ferric sulfate; more concentrated solutions yielded a basic salt. The results of observations with a number of ferric salts are summarized in table 1 (59).

The $\gamma$-modification of $Fe_2O_3 \cdot H_2O$ is synthesized preferably by the oxidation of ferrous iron compounds under conditions that favor the formation of an intermediate iron complex (1).

TABLE 1

*Slow hydrolysis of ferric salts*

| SALT HYDROLYZED | PRODUCT IDENTIFIED BY X-RAY ANALYSIS |
|---|---|
| Sulfate | $\alpha$-$Fe_2O_3 \cdot H_2O$ or $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$ |
| Nitrate | $\alpha$-$Fe_2O_3 \cdot H_2O$ |
| Nitrate (with trace of $\beta$-$Fe_2O_3 \cdot H_2O$) | $\alpha$-$Fe_2O_3 \cdot H_2O$ |
| Bromide | $\alpha$-$Fe_2O_3 \cdot H_2O$ |
| Oxalate | $\alpha$-$Fe_2O_3 \cdot H_2O$ |
| Acetate | $\alpha$-$Fe_2O_3 \cdot H_2O$ |
| Chloride | $\beta$-$Fe_2O_3 \cdot H_2O$ |

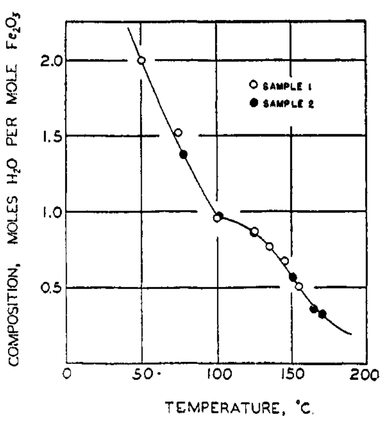


FIG. 14. Dehydration isobar for $\beta$-FeOOH

In table 1 it will be noted that when aqueous solutions of ferric chloride are allowed to stand at room temperature or are heated slowly to 60–100°C., a yellow hydrous precipitate is deposited which is not $\alpha$-$Fe_2O_3 \cdot H_2O$. Since the precipitate contains chloride and gives a distinctive x-radiogram, it is frequently regarded as a basic salt. We have found, however, that practically all the chloride may be removed without modifying the x-radiogram. Moreover, the dehydration isobar corresponds to that of a hydrous monohydrate. The results (60) of isobaric dehydration examination are summarized in figure 14.

The yellow precipitate from ferric chloride has been named β-ferric oxide monohydrate to distinguish it from the α- and γ-monohydrates. Kolthoff (23) believes that the compound should be formulated β-FeO(OH) and that the chloride it carries down with it is isomorphous FeOCl in solid solution. Kolthoff may be right, but his experimental evidence is insufficient to justify his conclusions.

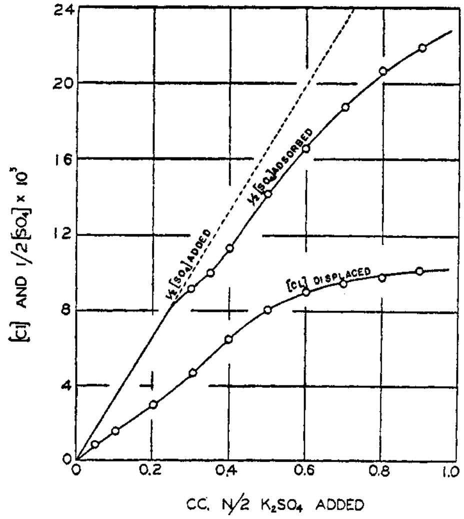


FIG. 15. Simultaneous displacement of chloride and adsorption of sulfate on titrating alumina sol with potassium sulfate

## III. HYDROUS OXIDE SOLS

Sols of the hydrophobic type, which includes most of the hydrous oxides, can be prepared fairly free from electrolytes, but it was demonstrated first by Thomas Graham and confirmed repeatedly thereafter that, in the absence of protecting colloids, some electrolyte must be present in the sols to ensure their stability. Thus ferric oxide sol formed by hydrolysis of ferric chloride or by peptization of the hydrous oxide gel with ferric chloride always contain more or less chloride. Sorum sols containing no detectable chloride either contain a trace of some other electrolyte or are protected by some material derived from the dialyzing membrane during the prolonged dialysis.

The presence of chloride in the dialyzed sols led Wyrouboff and Verneuil (69) to suggest that the various preparations contain basic salts or chlorides of condensed hydroxides. This idea was further extended and developed by Duclaux (11), Malfitano (28, 29), Hantzsch and Desch (15), and Linder and Picton (25). Thus the constitution of ferric oxide sols was represented by such formulas as:

$$[20Fe(OH)_3 \cdot FeCl_3]_n \quad \text{and} \quad [45Fe(OH)_3 \cdot FeCl_3]_n$$

The view that the oxide sols are oxysalts or basic salts meets with serious objection at the outset, since definite oxychlorides or basic chlorides are obtained, if at all, only under special conditions. No oxychloride of aluminum has been established with certainty, and but one ferric oxychloride has been identified, Stirnemann's FeOCl, prepared by heating a solution of ferric chloride in a bomb tube between 270° and 410°C. The idea that Graham's ferric oxide sol, formed by peptization with ferric chloride, contains a basic salt gained support from Böhm's claim that the particles in an aged sol gave an x-radiogram for a basic salt identical with that said to result from the slow hydrolysis of ferric chloride. But, as we have seen, the alleged basic salt is in reality $\beta$-$Fe_2O_3 \cdot H_2O$ containing varying amounts of adsorbed chloride, depending on the conditions of formation and the treatment.

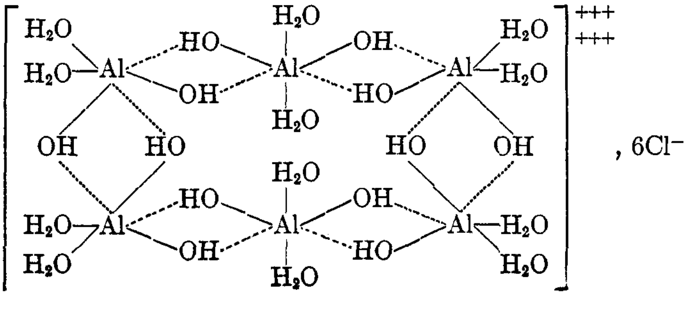
Pauli (36) considers the colloidal particles in hydrous oxide sols to be complex ions resulting from ionization of complex electrolytes allied to the Werner compounds. Since the composition of a given sol varies with the condition of preparation, he represents it by a general formula. For hydrous ferric oxide sol this is

$$[xFe(OH)_3 \cdot yFeOCl \cdot FeO]^+, \ (Cl^-)$$

in which $x = 32$ to $350$ and $y = 4$ to $5.7$.

Although we agree in a general way with Pauli's formulation, it is difficult to justify the details of the above formula, since no one has established the existence of $Fe(OH)_3$, and FeOCl is obtained only under special conditions in a bomb tube at elevated temperatures.

Thomas and coworkers (45, 46, 47, 48) suggest that the dispersed phase in hydrous oxide sols, such as alumina sol formed by peptizing the gel from amalgamated aluminum in dilute hydrochloric acid, consists of olated and possibly oxolated aluminum oxychloride complexes of the Werner type resembling the polyol basic chromic salts formulated by Bjerrum. Thomas formulates one such olated nucleus as follows:



Larger complexes are assumed to result from dissociation of any of the water molecules in nuclei like the above and olation among such nuclei through the hydroxo groups thus formed. The existence of such complexes was assumed to account, among other things, for the observation that the pH value of the sol is raised by the stepwise addition of neutral salts, the anion order being oxalate > acetate > sulfate > halides > nitrate. The increase in pH value was attributed to replacement of OH groups by the anion of the added salt, followed by the union of the displaced OH radicals with hydrogen ion to form water.

Now we have seen that the gel formed by the action of amalgamated aluminum on water at 100°C. is $\gamma\text{-}Al_2O_3 \cdot H_2O$, and we shall see that the dispersed phase in a sol prepared by Thomas' procedure is $\gamma\text{-}Al_2O_3 \cdot H_2O$. As already pointed out, we do not know the exact crystal structure of $\gamma\text{-}Al_2O_3 \cdot H_2O$, but it is probably similar to that of diaspore, $\alpha\text{-}Al_2O_3 \cdot H_2O$, which has been represented as AlO(OH) (12). In any event, when the crystal structure of $\gamma\text{-}Al_2O_3 \cdot H_2O$ is known, the structure of the dispersed phase in Thomas' alumina sol will be the same.

Since hydrous oxide sols formed in the presence of chloride, say, always contain more or less chloride, Thomas believes that such sols should be designated as metallic oxychloride sols rather than as hydrous oxide sols. He recognizes that the term "ferric oxychloride hydrosol" is objectionable, since it connotes a definite chemical compound when no such meaning is intended. Nevertheless, he prefers to refer to hydrous oxide sols as oxysalt sols, since the colloidal particles are not pure hydrous oxides or hydroxides. To be consistent, the metal sols and salt sols should be renamed, since the dispersed phase is not pure metal and salt, respectively. It is difficult to see what would be gained by introducing such a change in our terminology. The ratio of iron to chlorine in a ferric oxide sol has been variously reported as 6, 42, 84, 396, 2700, and higher. To designate a sol with a low chloride content as an oxychloride sol is like calling precipitated barium sulfate a chlorosulfate because it contains some adsorbed barium chloride.

It is now quite generally recognized that the stability of a positive silver halide sol results from preferential adsorption of silver ions by unsaturated secondary valence forces on the surface of the crystals. The crystals may also contain some adsorbed silver nitrate. Similarly, a hydrous oxide sol formed in the presence of metallic chloride, hydrochloric acid, and their corresponding ions will contain varying amounts of the several components, depending on the precise method of formation and purification of the sol. The positive charge on a given sol is due to the preferential adsorption of metallic ion and hydrogen ion, just as the positive charge on a positive silver halide sol is due to preferential adsorption of silver ion. It is unnecessary to attribute the charge to the presence of an "ionogenic complex attached to the surface" (Pauli), unless the presence of such a complex is known or rendered highly probable. Thus, to assume the presence of a simple salt like FeOCl on the surface of the particles of a ferric oxide sol goes well beyond the established facts.

In recent years investigations have been made of the various phenomena that accompany the stepwise addition of coagulating electrolytes to sols (52, 53, 62). For example, the addition of sulfate to a sol of hydrous alumina results in adsorption of sulfate and displacement of chloride from a diffuse ionic layer surrounding the particles. Figure 15 is typical of such adsorption and displacement curves. To account for the observed facts, the constitutions of two typical hydrous oxide sols are represented as follows:

$$\begin{array}{c|c|c} [(x\mathrm{Fe_2O_3}\cdot y\mathrm{HCl}\cdot z\mathrm{H_2O}) & \mathrm{Fe}_m{}^{+++}\mathrm{H}_n{}^{+}] & (3m + n - q)\mathrm{Cl}^-,\ q\mathrm{Cl}^- \\ \text{Solid phase} & \text{Inner ionic} & \text{Diffuse outer} \\ & \text{layer} & \text{ionic layer} \end{array}$$

and

$$\begin{array}{c|c|c} [(x\gamma\text{-}\mathrm{Al_2O_3}\cdot \mathrm{H_2O}\cdot y\mathrm{HCl}\cdot z\mathrm{H_2O} & \mathrm{Al}_m{}^{+++}\mathrm{H}_n{}^{+}] & (3m + n - q)\mathrm{Cl}^-,\ q\mathrm{Cl}^- \\ \text{Solid phase} & \text{Inner ionic} & \text{Diffuse outer} \\ & \text{layer} & \text{ionic layer} \end{array}$$

This formulation of the constitution of certain oxide sols is accepted by Iyer (22), but he suggests that the diffuse portion of the double layer contains displaceable hydroxide ions as well as chloride ions. The displacement of hydroxide ions by the anions of neutral salts would account for the increase in pH value emphasized by Thomas, but it seems questionable whether hydroxide ions will be present in the outer portion of the ionic double layer in sols having a pH value of 4 to 5. We have attributed the increase in pH value of alumina sol on adding neutral salts, especially those with multivalent anions, to increase in adsorption of hydrogen ion in the presence of a strongly adsorbed anion. This increase in the adsorption of cations in the presence of strongly adsorbed anions is a general phenomenon that has been observed repeatedly with various types of adsorbents, such as carbon and fibers, as well as the hydrous oxides. It may be that a part of the increase in pH value on adding neutral salts to alumina sol is due to the replacement of OH groups from $\gamma\text{-}Al_2O_3\cdot H_2O$ by the added ion, but the existence of such an interchange is still questionable. If this happens, it means that anions such as $C_2H_3O_2^-$, $Cl^-$, and $SO_4^{--}$ displace OH groups from the crystals of $\gamma\text{-}Al_2O_3\cdot H_2O$ or $\gamma\text{-}AlO\cdot OH$. The experiment should be tried with crystals of $\gamma\text{-}Al_2O_3\cdot H_2O$ above the colloidal range in size where adsorption phenomena, which will produce a similar effect on the pH value, take place to a relatively small extent. It must be kept in mind that with salts such as citrate, oxalate, and acetate buffer action will tend to increase the pH value of the sol–electrolyte mixtures above that of the sol alone.

From the evidence obtained by titration of oxide sols with neutral salts there is no necessary reason for assuming that the sols are colloidal electrolytes consisting of basic salts or Werner complexes. On the contrary, the indirect evidence suggests that the dispersed phase consists essentially of hydrous oxide (or simple hydrate or hydroxide).

Since x-ray diffraction analysis has proven helpful in determining the constitution of gels, one would expect this technique to be useful with sols. Until recently, however, the application of x-ray diffraction methods to sols has been indirect; the sols have been coagulated or ultrafiltered and the resulting gel, either dry or moist, has been examined. For example, we found (61) that the moist gels obtained by ultrafiltration of alumina, stannic oxide, and indium hydroxide sols gave the patterns of $\gamma$-$Al_2O_3 \cdot H_2O$, $SnO_2$, and $In_2O_3 \cdot 3H_2O$ or $In(OH)_3$, respectively. Although it is often assumed that the sol particles have the same constitution in the sol state as in the gel from the sol, only the direct examination of the sols by x-ray diffraction methods can decide whether this is the case.

Björnståhl (4) first examined gold and silver sols directly by allowing them to flow through a tube of gold-beater's skin centered in the x-ray camera and obtained patterns like those for metallic gold and silver respectively. The important investigations of Böhm and Niclassen (6) on the gels of various hydrous and hydrated oxides and hydroxides have been supposed by some people to include studies on sols in the sol state, but in a private communication Böhm writes: „Die Aufnahmen für die Arbeit in der Z. f. anorganische Chemie, **132,** 1 (1924) wurden, wie Sie richtig vermuten, an den meist fruchten *Ruckstanden* von Solen nach dem Koagulation oder Eindampfen (so beim Crum'schen Sol) gemacht.“ In the same communication Böhm states that he and Ganter examined *liquid sols* of aged ferric oxide and vanadium pentoxide by allowing them to flow through a Mark tube and observed some indication of orientation of the needle-like particles.

In 1934 we examined directly a Péan de St. Gilles ferric oxide sol which we sealed in a Nonex glass tube and exposed to x-rays for 96 hr. in a General Electric apparatus. The resulting diffraction pattern was the same as that for $\alpha$-$Fe_2O_3$. The experiment was not altogether convincing, since such long exposure to x-rays may have caused partial coagulation of the sol.

The chief difficulties in the direct examination of sols by x-rays are as follows: (*a*) the relatively low concentration of the solid phase, (*b*) the scattering of the x-rays by the water in the sample, and (*c*) the possibility of coagulation of the sol by x-rays. The first and second diffculties were obviated by using fairly concentrated sols and the third by flowing the sols continuously through the camera (33). Some objections may be made to flowing the sol through a tube of any kind; hence the sols were allowed to flow in an unenclosed column in the same way that Debye originally examined liquids. A Debye–Scherrer type of camera was employed, a diagram of which is shown in figure 16. Cu $K_\alpha$ x-radiation from a Philips cross-focus tube was used. The exposure time was 30–60 min. To identify the patterns from the several sols, x-radiograms (33) were made from the corresponding powders. The results obtained from pure water, the various sols, and the corresponding solid materials are given in the usual chart form in figure 17, and reproductions of the patterns for cerium dioxide sol and cerium dioxide powder are given in figure 18.

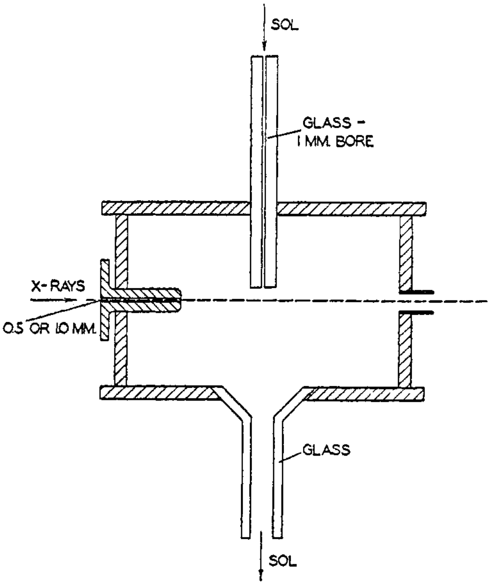


FIG. 16. Camera for the direct x-ray diffraction examination of sols

The results are conclusive. In every instance the sol pattern is a composite of the patterns of pure water and of simple oxide or oxide hydrate (or hydroxide). If the sol is weak or the primary crystals very minute, the water bands predominate in the pattern, whereas with stronger sols or larger primary crystals, the water bands appear less pronounced. As in the gels, the dispersed phases in typical hydrosols of the oxides are not polymerized bodies or condensation products but consist essentially of aggregates of minute crystals of simple oxide or of simple hydrate or hy-

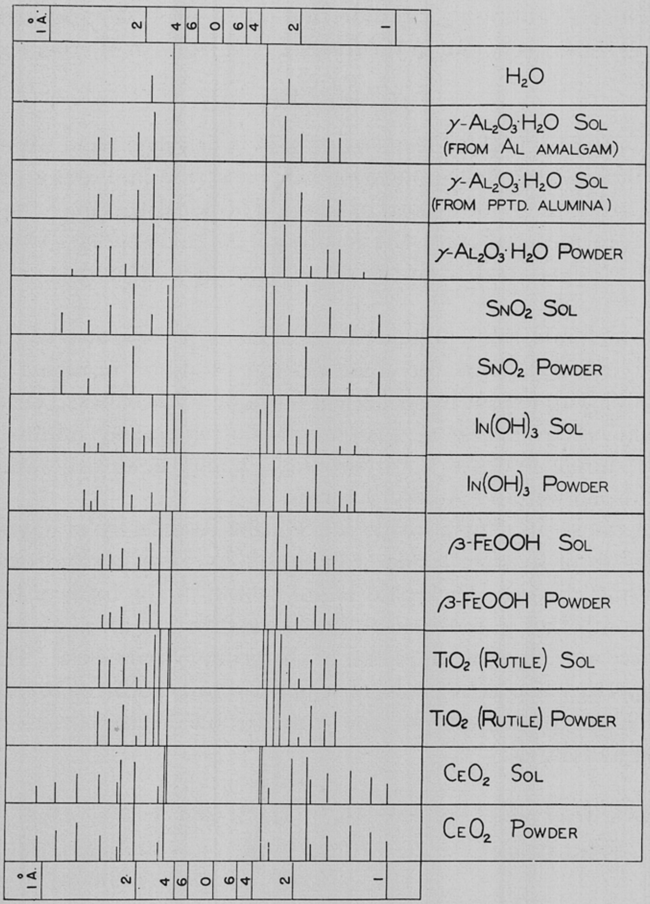


FIG. 17. Diagrams of the x-ray diffraction patterns of sols and the corresponding precipitates

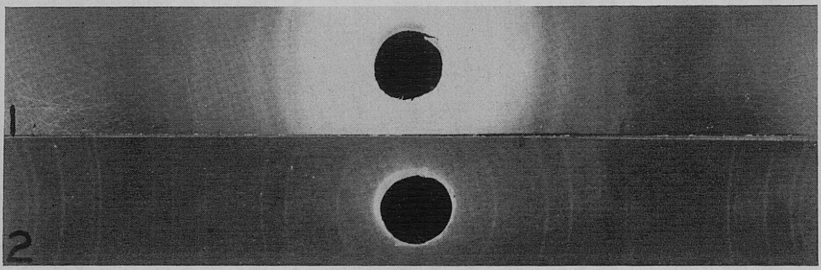


FIG. 18. X-ray diffraction patterns of (*1*) cerium dioxide sol, examined directly in the sol state, and (*2*) cerium dioxide powder.

droxide. In sols containing chloride there is no experimental justification for assuming that it is bound in the form of basic salts or Werner complexes.

## IV. SUMMARY

1. The constitution of hydrous oxide gels is deduced from experimental evidence obtained by the application of phase rule and x-ray diffraction techniques to a number of typical oxides. The constitution of the hydrous oxide sols is formulated from the results of potentiometric "titration" of sols with electrolytes and from the direct examination of the sols by x-ray diffraction methods.

2. It is concluded that, in general, gelatinous precipitates of the oxides are not polymerized bodies or condensation products resulting from the splitting off of water from hypothetical metallic hydroxides. Instead, the gels are believed to consist of agglomerates of extremely minute crystals of oxide or simple hydrate (or hydroxide), which hold large amounts of water by adsorption and capillary forces.

3. The particles in typical oxide sols consist essentially of aggregates of minute crystals of hydrous oxide or of simple hydrate (or hydroxide). In sols containing chloride, the latter is not bound in the form of basic salts or Werner complexes in most cases, but is adsorbed in an amount depending on the size and physical character of the primary particles. To account for the properties of positive sols, of which alumina sol from amalgamated aluminum is a typical example, the constitution of the particles may be represented as follows:

$$\begin{array}{ccc} [(x\gamma\text{-}Al_2O_3\cdot H_2O\cdot yHCl\cdot zH_2O) & Al_m^{+++}H_n^{+}] & (3m+n-q)Cl^-,\ qCl^- \\ \text{Solid phase} & \text{Inner ionic layer} & \text{Diffuse outer ionic layer} \end{array}$$

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