nearly identical values of 1.1221 and 1.1218 for the ratio $\lambda_{Cl}(C = 0)/\lambda_{Cl}(0.05\ N\ KCl)$ in light and heavy water, respectively. La Mer and Chittum[21] have shown recently from theory and experiment that the salt conductance ratio Λ_0/Λ_c is very nearly constant for these two solvents and their mixtures. We thus have

$$\lambda_0(N_{D_2O}) = (\lambda_0/\lambda_c)_{H_2O}\ \lambda_c(N_{D_2O}) \qquad (4)$$

in which λ_c and λ_0 are the conductances of a given ion constituent at concentration C and at infinite dilution, respectively. Substitution in equation (4) of the value for $\lambda_c(N_{D_2O})$ given for the chloride ion by equation (2) and 1.1221 for the ratio $(\lambda_0/\lambda_c)_{H_2O}$ gives

$$\lambda_0(Cl^-) = 76.34 - 16.23\ N_{D_2O} + 2.58\ N^2_{D_2O}$$

a relation that may be used in determining the limiting transference number of any chloride in any H_2O–D_2O mixture for which the limiting salt conductance is known.

The authors wish to thank Professor La Mer and Dr. Chittum of Columbia University for many helpful suggestions concerning experimental technique.

Summary

Transference and conductance measurements on solutions of several electrolytes in deuterium oxide and its mixtures with water have been made. The investigation included 0.05 N solutions of potassium and hydrogen–deuterium chlorides in a wide range of H_2O–D_2O mixtures. The conductance of the chloride ion constituent from these two chlorides varies nearly linearly with the mole fraction of deuterium oxide in the mixed solvent. The hydrogen–deuterium component, on the other hand, shows wide variations from linearity, thus indicating a complex conductance mechanism.

Measurements have also been made on solutions of sodium, potassium and hydrogen–deuterium chlorides at several concentrations in nearly pure ($N_{D_2O} = 0.9935$) deuterium oxide. From these data limiting values of the ion conductances have been computed for heavy water.

NEW YORK, N. Y. RECEIVED JUNE 29, 1937

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[21] La Mer and Chittum, THIS JOURNAL, **58**, 1642 (1936).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE RICE INSTITUTE]

X-Ray Studies on the Hydrous Oxides. VIII. Gallium, Indium and Thallic Oxides[1]

BY W. O. MILLIGAN AND HARRY B. WEISER

The composition of precipitated alumina prepared and aged under varying conditions has been established with considerable certainty as a result of numerous dehydration and X-ray diffraction studies.[2] The present paper is concerned with the composition of the precipitated oxides of other members of the aluminum family about which but little authentic information was available.

A. Hydrous Gallium Oxide

A review[2] (pp. 120–121) of the earlier work on precipitated gallium oxide leads to the conclusion that the freshly formed gel is a hydrous oxide amorphous to X-rays, and not a hydrate. If the fresh gel is dissolved in ammonia and reprecipitated by dilution, a granular product is obtained which gives a definite X-ray diffraction pattern different from that of the anhydrous oxide. This material must be either a definite hydrate or a new modification of the oxide. Havestadt and Fricke[3] found that the composition may be represented by the formula $3Ga_2O_3 \cdot 5H_2O$ both when dried at 100° and when dried over phosphorus pentoxide at room temperature, but this evidence is insufficient to establish the existence of a definite hydrate.

Goldsmidt, Barth and Lunde[4] found that the precipitated oxide gave a distinctive X-ray diffraction pattern up to a temperature of 350° but when heated to 420–440° it gave a new pattern[5] similar to that from α-Al_2O_3; hence this product was designated as α-Ga_2O_3. Heating to 650° gave a second modification of gallium

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[1] Preliminary results were reported at the New York Meeting of the American Chemical Society, April, 1935.

[2] *Cf.* Weiser, "Inorganic Colloid Chemistry," Vol. II, John Wiley and Sons, Inc., New York City, 1935, pp. 90–100.

[3] Havestadt and Fricke, *Z. anorg. allgem. Chem.*, **188**, 357 (1930); *cf.* Fricke and Blencke, *ibid.*, **143**, 183 (1925); Fricke, *Z. Elektrochem.*, **30**, 393 (1924).

[4] Goldsmidt, Barth and Lunde, *Skrifter Norske Videnskaps-Akad. i. Oslo, I. Mat.-Natur. Klasse*, No. 7, 24 (1925).

[5] *Cf.* Zachariasen, *ibid.*, No. 4, 18 (1928).

oxide which was believed to be either rhombic or monoclinic, and was designated as β-Ga_2O_3. More recently these observations have been confirmed by Centola.[6] Although it is customary to designate the modification that is stable at the highest temperature as α, the next lower as β, etc.,[7] we have chosen to retain the original nomenclature to avoid any possible confusion.

Neogi and Nandi[8] reported recently that gallium oxide gel dried in air consists of $Ga_2O_3 \cdot 3H_2O$, and the gel dried in a vacuum consists of $Ga_2O_3 \cdot 2H_2O$. The only evidence offered in support of the existence of these alleged hydrates is the analysis of the samples.

The X-ray data of Havestadt and Fricke, of Goldsmidt, Barth and Lunde, and of Centola show that precipitated gallium oxide may give a definite X-ray diffraction pattern which is distinct from the patterns of either anhydrous modification of the oxide. There is no direct evidence to prove or disprove that the gel is a definite hydrate.

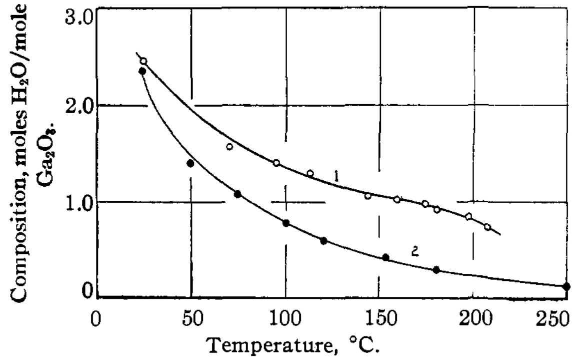

Fig. 1.—Dehydration isobars of: (1) hydrous gallium oxide monohydrate; (2) hydrous gallium oxide.

Experimental

Formation. Sample A.—Just enough ammonia was added to a solution of gallium chloride to redissolve the precipitated gel. The resulting solution was placed in a desiccator over sulfuric acid for about two weeks, at the end of which time most of the gallium oxide had reprecipitated. The sample was washed by decantation to remove chloride and was air-dried at room temperature.

Sample B.—To 100 cc. of a 0.1 *M* solution of gallium chloride at 25° was added a slight excess of ammonia, and the resulting white gelatinous precipitate was allowed to remain in contact with the supernatant liquid. In twenty-four hours the gel was transformed into a granular powder which was washed by the aid of the centrifuge with 50-cc. portions of water, until the wash water was free of chloride, and then air-dried at room temperature.

Sample C.—This was prepared like Sample B, except that the gallium chloride solution was at 100°. Although the precipitate was allowed to stand for twenty-four hours at room temperature in contact with the mother liquid, the transformation to the more granular powder did not take place. The higher temperature of precipitation would be expected to render the precipitate less soluble, and there was little or no excess ammonia left in the solution. This sample was washed and dried in the same manner as Sample B.

Dehydration.—Samples A and C were dehydrated isobarically in an apparatus already described[9] at an aqueous vapor pressure of 23.6 mm., allowing ample time for equilibrium to be established at each temperature. The dehydration isobars are given in Fig. 1. The experimental points represent the average of two distinct runs which agree within ±0.02 mole of water per mole of gallium oxide. It will be noted that the isobar for sample C (Fig. 1, No. 2) is a typical desorption curve for a hydrous oxide, giving no indication of hydrate formation. The isobar for sample A (Fig. 1, No. 1), on the other hand, is that of a hydrous monohydrate. The composition $Ga_2O_3 \cdot 1.67H_2O$ obtained by Havestadt and Fricke, for a sample prepared in a similar manner and dried at 100°, falls fairly close to the curve when one considers that the aqueous pressure could not have been 23.6 mm.

X-ray Examination.—The following preparations were examined with Mo Kα radiation in a General Electric X-ray diffraction apparatus: (1) Sample A, air-dried; (2) Sample A, dehydrated at 113°; (3) Sample A, dehydrated to 207°; (4) Sample A, heated to 850°. The results are given in chart form in Fig. 2. The following samples held in Mark tubes were examined with Cu Kα radiation, using a Philips X-ray tube and camera 57 mm. in diameter: (1) Sample A, air-dried; (2) Sample B, air-dried; (3) Sample C, dehydrated to 100°; (4) Sample C, dehydrated to 150°; (5) Sample C, dehydrated to 250°; (6) Sample C, dehydrated to 450°; (7) Sample C, heated to 600°; (8) Sample A, heated to 625°; (9) Sample C, heated to 900°. Sample C was examined also at other temperatures between 100 and 450° but the patterns showed no differences and are not included as separate diagrams. The exposure time was 30–60 minutes for the

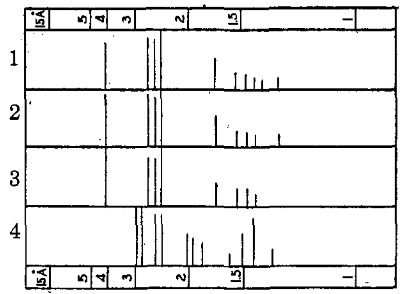

Fig. 2.—Diagram of the X-ray diffraction patterns of: (1, 2, 3) gallium oxide monohydrate; (4) β-Ga_2O_3.

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[6] Centola, *Congr. intern. quim. pura aplicada, 9th Congr., Madrid*, **3**, 230 (1934).

[7] Sosman, "The Properties of Silica," Chemical Catalog Co., Inc., New York City, 1927, p. 43.

[8] Neogi and Nandi, *J. Indian Chem. Soc.*, **13**, 399 (1936).

[9] Weiser and Milligan, *J. Phys. Chem.*, **38**, 513 (1934); This Journal, **58**, 1262 (1936).

diffraction patterns obtained with Cu Kα radiation. The results are given in chart form in Fig. 3, and some of the negatives are reproduced in Fig. 4.

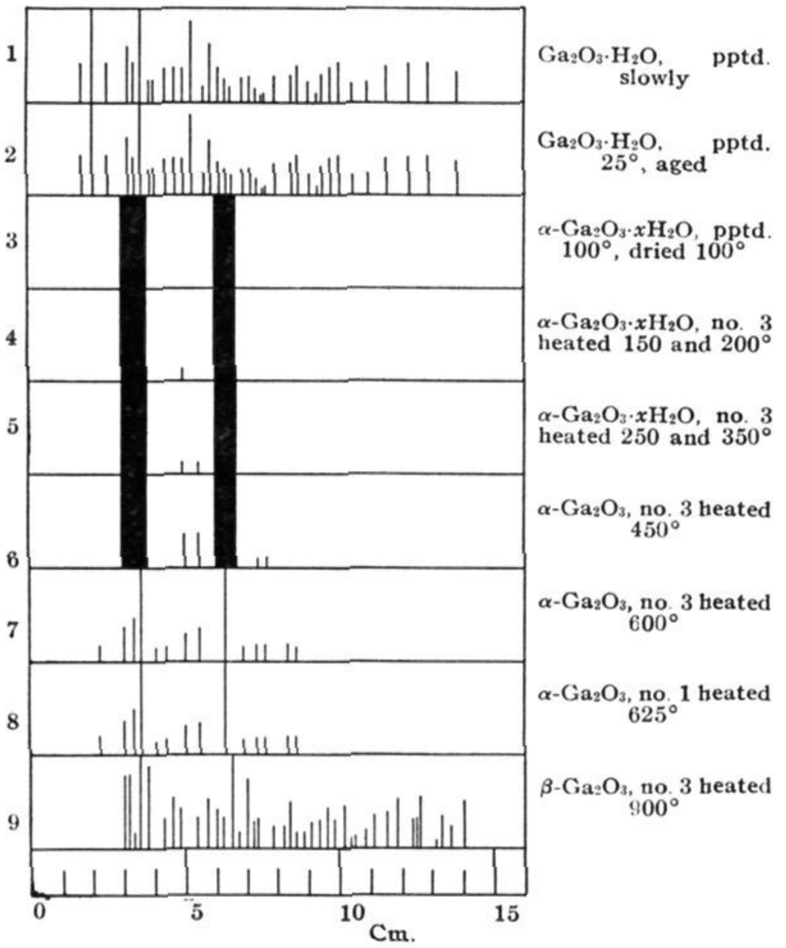

Fig. 3.—Diagrams of the X-ray diffraction patterns of gallium oxide preparations.

Samples A and B (Fig. 3, nos. 1 and 2) give identical X-ray patterns distinct from either α- or β-Ga_2O_3. This evidence, combined with the results of isobaric dehydration, leaves little doubt but that these samples consist of a hydrous monohydrate, $Ga_2O_3 \cdot H_2O$. The pattern for the air-dried sample C consists of two broad bands. Heating to higher temperatures gradually resolves these two broad bands and brings out additional lines to give the α-Ga_2O_3 pattern. Sample C may be assumed to consist of particles of hydrous α-Ga_2O_3 so finely divided that the X-ray diffraction pattern shows only two or more broad bands. A gel prepared at room temperature by adding less ammonia than required to precipitate all the gallium, was examined as rapidly as possible while still moist, using Cu Kα radiation. The resulting pattern was identical with the one from sample C with the addition of the diffraction bands of water. This pattern is not included in the chart.

B. Hydrous Indium Oxide

From a survey[2] (pp. 121–123) of earlier dehydration work on precipitated indium oxide, it would appear that the gel is a hydrous oxide rather than a hydrous hydrate.

Goldsmidt, Barth and Lunde[4] noted that precipitated indium oxide gave a good X-ray diffraction pattern. Weiser and Milligan[10,11] obtained a sharp pattern from a moist gel made by ultrafiltration of an indium oxide sol prepared by precipitation of an indium nitrate solution with ammonia, followed by washing and peptization with dilute hydrochloric acid. More recently[12] an indium oxide sol containing 22.1 g. of indium oxide per liter prepared by peptization of the well-washed ammonia precipitate with a few drops of hydrochloric acid, was examined *directly* by an X-ray diffraction method. The sol was flowed through the camera in an uninclosed column. The resulting pattern was identical with the pattern obtained[10,11] for the moist gel or air-dried powder. These observations suggest that the precipitated oxide is a hydrate, and the following experiments support this view.

Experimental

Formation.—A slight excess of ammonia was added to indium chloride solutions (made by dissolving metallic indium in dilute hydrochloric acid and evaporating in a vacuum desiccator over potassium hydroxide) at 25 and 100°. The cold precipitated sample was highly gelatinous, whereas the hot precipitated oxide was powdery. The latter was left in contact with the supernatant liquid at 100° for several hours. The precipitates were washed almost free of chloride and air-dried at room temperature.

Dehydration.—The dehydration isobars given in Fig. 5 show clearly that the samples of the hot and cold precipitates are definite trihydrates containing a small additional amount of adsorbed water. As would be expected, the more hydrous oxide prepared at 25° decomposes at a lower temperature than the more granular material made at 100°. This is a striking example of the influence of pri-

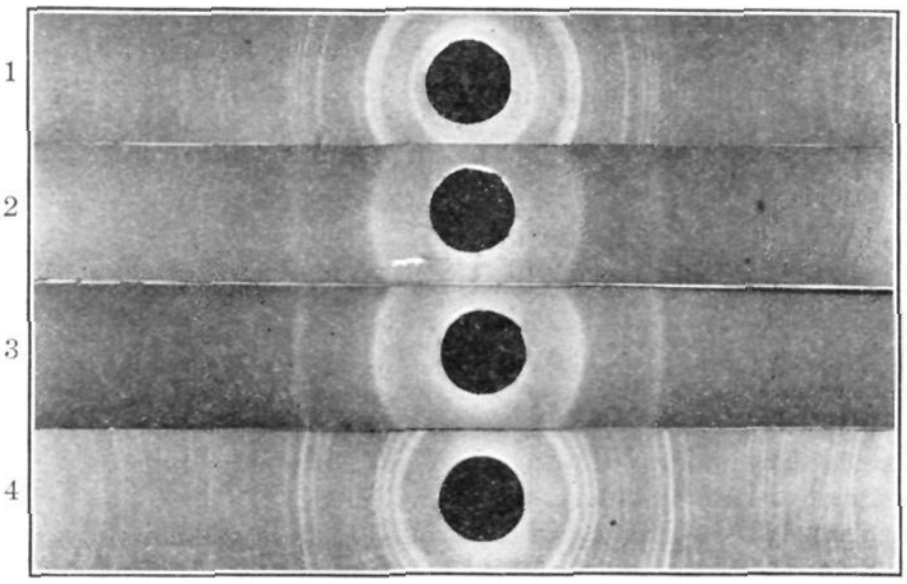

Fig. 4.—X-ray diffraction patterns of: (1) gallium oxide monohydrate; (2) hydrous α-Ga_2O_3; (3) α-Ga_2O_3; (4) β-Ga_2O_3.

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[10] Weiser and Milligan, *J. Phys. Chem.*, **40**, 1 (1936).

[11] Weiser and Milligan, *Trans. Faraday Soc.*, **32**, 358 (1936).

[12] Milligan and Weiser, *J. Phys. Chem.*, **40**, 1095 (1936).

mary particle size on the temperature of decomposition. Carnelley and Walker[13] obtained a smooth temperature-composition curve for the precipitated oxide. This apparent discrepancy is explained by the fact that these early investigators waited only an hour for equilibrium to be established at each point on the curve, and, furthermore, no attempt was made to control the aqueous vapor pressure within their apparatus. To confirm this explanation of Carnelley and Walker's smooth curve, an isobar was run, waiting only thirty minutes at each point. This isobar was continuous, showing no indication whatsoever of hydrate formation. This curve is not given here since it is without value, except as an illustration of erroneous results of faulty technique.

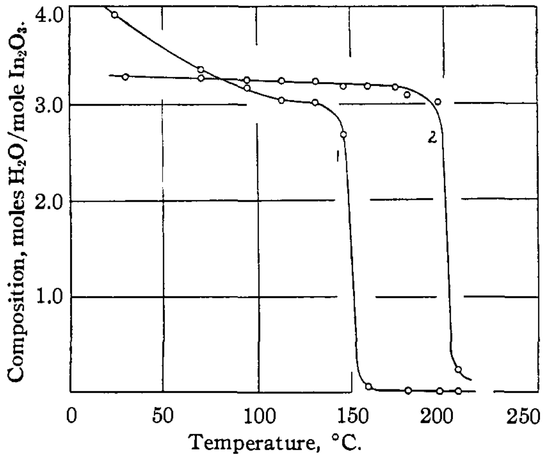

Fig. 5.—Dehydration isobars of indium oxide trihydrate or indium hydroxide precipitated at: (1) 25°; (2) 100°.

X-ray Examination.—Samples of the indium oxide trihydrate prepared in the hot and in the cold, and heated to various temperatures, as well as of anhydrous indium oxide were examined with Mo $K\alpha$ radiation, using the General Electric X-ray diffraction apparatus. The results obtained are given in chart form in Fig. 6. Reproductions of the X-radiograms of the trihydrate prepared at 25 and 100°, and of the anhydrous oxide are shown in Fig. 7.

C. Hydrous Thallic Oxide

The reddish brown, highly hydrous precipitate of thallic oxide is usually assumed to be a monohydrate, but Hüttig and Mytyzek[14] showed that the X-radiograms of the hydrous precipitate and the anhydrous oxide are identical.

A crystalline hydrate of thallic oxide, $Tl_2O_3 \cdot 3H_2O$, stable to a temperature of 340°, is said[15] to be formed by prolonged fusion of precipitated thallic oxide with potassium hydroxide and subsequent treatment of the yellow mass of glittering spangles with water. The evidence for hydrate formation is not conclusive.

Experimental

Formation.—Following Carnegie's directions, a slight excess of ammonia was added to a solution of thallic chloride at 25°. The resulting reddish-brown precipitate was washed by decantation until the wash water was free of chloride, and added carefully, while still moist, to molten potassium hydroxide in a nickel crucible. The mixture of thallic oxide and potassium hydroxide was heated for sixty hours. Before the molten mass was allowed to cool, numerous bright, lustrous, golden spangles could be seen floating in the liquid. After cooling, the alkali was washed out with water by decantation. A small amount of unchanged dark thallic oxide was removed by sedimentation from the yellow crystal-like particles; the latter were dried at 80° and ground to a reddish powder.

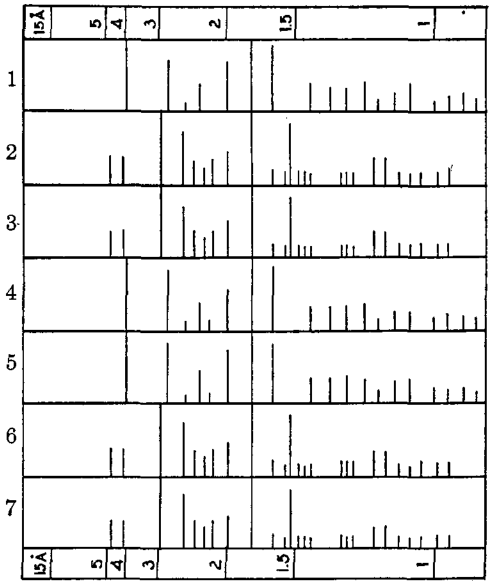

Fig. 6.—Diagrams of the X-ray diffraction patterns of: (1) indium oxide trihydrate or indium hydroxide precipitated at 25°; (2) No. 1 heated to 159°; (3) No. 1 heated to 207°; (4) indium oxide trihydrate or indium hydroxide precipitated at 100°; (5) No. 4 heated to 113°; (6) No. 4 heated to 207°; (7) No. 1 heated to 850°, anhydrous In_2O_3.

X-ray Examination.—X-radiograms were obtained for this material, and for ignited thallic oxide, in a Seemann-Bohlin type camera, using Cu $K\alpha$ radiation. The exposure time was 600 milliampere minutes. A chart of the resulting patterns is given in Fig. 8. It is apparent that the pattern of the alleged thallic oxide trihydrate is identical with the pattern of the anhydrous thallic oxide. The golden color and spangle-like appearance are due to the state of physical aggregation, and not to the formation of a definite hydrate or of a new crystalline modification of the anhydrous oxide.

Summary

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

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[13] Carnelley and Walker, *J. Chem. Soc.*, **53**, 88 (1888).

[14] Hüttig and Mytyzek, *Z. anorg. allgem. Chem.*, **192**, 187 (1930).

[15] Carnegie, *Chem. News*, **60**, 113 (1889).

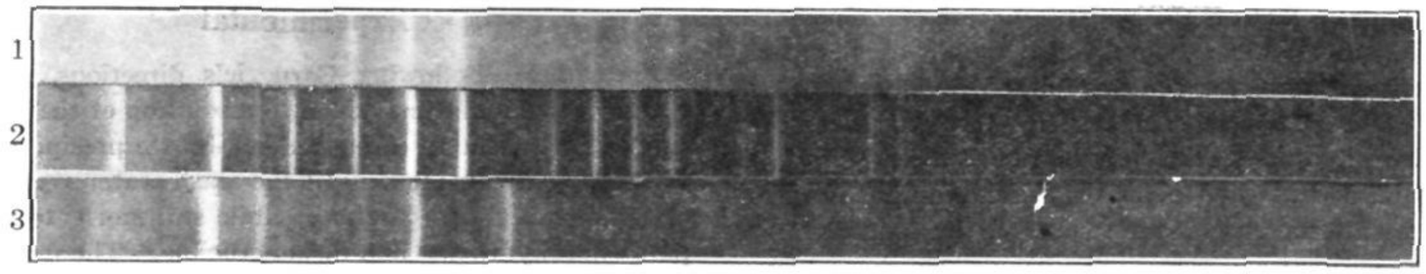

Fig. 7.—X-ray diffraction patterns of: (1) $In_2O_3 \cdot 3H_2O$ precipitated at 25°; (2) $In_2O_3 \cdot 3H_2O$ precipitated at 100°; (3) anhydrous In_2O_3.

1. The alleged tri- and dihydrates of gallium oxide reported by Neogi and Nandi are either hydrous gallium oxide, hydrous gallium oxide monohydrate, or a mixture, depending upon the exact conditions of precipitation.

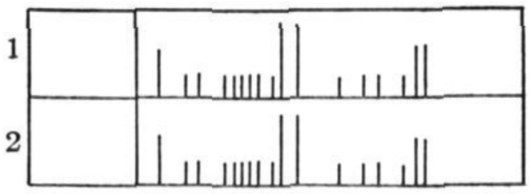

Fig. 8.—Diagram of the X-ray diffraction patterns of Tl_2O_3: (1) prepared by Carnegie's method; (2) prepared by precipitation and ignited at 850°.

2. The precipitate freshly formed at room temperature by the addition of alkali to a gallium salt is hydrous gallium oxide.

3. On standing in contact with ammonium hydroxide solution or by reprecipitation from a solution in ammonium hydroxide, hydrous gallium oxide is transformed into a definite monohydrate which gives a characteristic dehydration isobar and X-ray diffraction pattern.

4. The precipitate formed at 100° consists of hydrous gallium oxide. Because of the lower solubility of the larger particles, it does not age to the monohydrate as readily as the oxide precipitated at room temperature.

5. Hydrous gallium oxide precipitated at 100° gives a continuous dehydration isobar. The X-ray diffraction pattern consists of two or three broad bands. Samples heated to temperatures between 100 and 250° show a progressive decrease in the width of the most prominent diffraction bands, as well as the presence of a few additional bands. This indicates that the hydrous gallium oxide is recrystallizing to form larger primary particles as the temperature is increased.

6. The precipitate formed by the addition of alkalies or ammonium hydroxide to indium salt solutions at room temperature or at 100°, is indium oxide trihydrate or indium hydroxide.

7. The dehydration isobar for indium oxide trihydrate or hydroxide shows a break, corresponding to a definite compound. The sample formed at 100° decomposes at a somewhat higher temperature than the one precipitated at room temperature. This furnishes a good example of the influence of primary particle size on the decomposition temperature.

8. Indium oxide trihydrate or indium hydroxide precipitated at room temperture or at 100° gives a characteristic X-ray diffraction pattern, distinct from the pattern of the anhydrous oxide. The sample prepared at the higher temperature shows the sharper diffraction lines, indicating that the primary particle size is larger.

9. Carnegie's alleged thallic oxide trihydrate has been found to give an X-ray diffraction pattern identical with anhydrous thallic oxide. The golden color and spangle-like appearance of Carnegie's preparation results from the state of physical aggregation.

HOUSTON, TEXAS

RECEIVED MAY 17, 1937