

and hydroxyl ion has been studied with the following results.

1. When carbon dioxide is carefully excluded, the reaction appears to be strictly bimolecular in character with no complications due to side reactions or reverse reactions up to more than 90% completion.

2. The second order rate constants are independent of the initial concentrations of each reactant over the range investigated.

3. The absence of any appreciable kinetic salt effect in water and in alcohol-water mixtures has been demonstrated by the constancy of rate con-

stants over a considerable range of ionic strength in the presence and absence of added salts.

4. A decrease in the dielectric constant of the solvent increases the rate of the reaction in good agreement with the theory of Harned and Samaras.

5. The energy of activation has been determined in a solvent of fixed composition (water) and in two mixed solvents of constant gross dielectric constant. The relation between the two energies of activation is in agreement with the predictions of Svrbely and Warner.

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The Sesquioxide and Hydroxides of Gallium

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Gallium is among those metals whose hydroxides are amphoteric and tend to precipitate in a highly hydrous and gelatinous condition, with properties varying widely depending upon the details of the methods used in their preparation. Because equilibrium is exceedingly difficult to establish in such hydrous systems, the isolation of definite compounds and the study of the stability relationships between these compounds is not easily accomplished. Weiser¹ and Milligan and Weiser² have reviewed the work which has been done on the system gallium oxide-water. Alpha and beta modifications of the oxide and a compound $\text{Ga}_2\text{O}_3 \cdot \text{H}_2\text{O}$ or $\text{GaO}(\text{OH})$ have been reported but our knowledge of the system has been very incomplete.

purpose of obtaining more exact information concerning the phases which occur, their stability ranges and relationships, and their properties. Improved methods for establishing equilibrium with the help of fused mineralizing agents and of superheated steam in a bomb have been used to supplement the common dehydration studies.

Experimental

Identification of Phases Appearing.—The substances obtained by the various experimental methods were identified by chemical analysis and by X-ray and microscopic examination.

The compositions of the samples were determined by ascertaining the amount of water lost upon ignition in platinum at 1200–1300° after the sample had first been dried to constant weight in the air at 105°.

All of the samples secured were very finely divided and only the powder X-ray diffraction method could be applied. The samples were examined with Mo $K\alpha$ radiation in a General Electric X-ray diffraction apparatus. The characteristic spectra which were found for the various substances isolated are mapped in Fig. 1.

The patterns obtained for $\beta\text{-Ga}_2\text{O}_3$ and $\text{GaO}(\text{OH})$ check with those reported by Milligan and Weiser² for $\beta\text{-Ga}_2\text{O}_3$ and $\text{Ga}_2\text{O}_3 \cdot \text{H}_2\text{O}$. That for $\alpha\text{-Ga}_2\text{O}_3$ is similar to the one reported by the same investigators for $\alpha\text{-Ga}_2\text{O}_3$ using Cu $K\alpha$ radiation, except that the lines are displaced. The pattern for $\text{Ga}(\text{OH})_3$ is new, since this compound has not been isolated before.

All of the samples were examined by means of the microscope. In most cases the particles were so small that, even when oil immersion methods were used, little information concerning the products could be obtained. Under the most favorable conditions a few of the products contained crystals large enough for optical study.

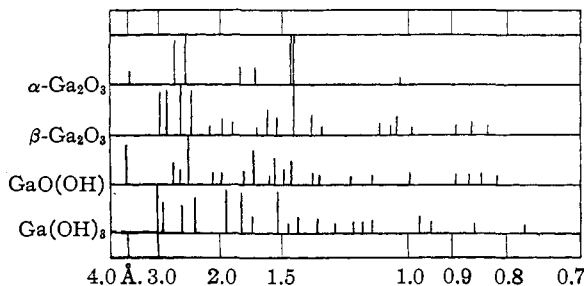


Fig. 1.—Diagrams of the X-ray diffraction patterns obtained with Mo $K\alpha$ radiation.

In the present investigation a comprehensive study of the system has been undertaken with the

(1) Weiser, "Inorganic Colloid Chemistry," Vol. II, John Wiley and Sons, Inc., New York City, 1935.

(2) Milligan and Weiser, *THIS JOURNAL*, **59**, 1670 (1937).

Preparation of α -Ga₂O₃ and β -Ga₂O₃.—These were prepared in quantity so they could be used in equilibrium studies.

Although it has been reported that α -Ga₂O₃ is obtained by various methods, in this investigation great difficulty was encountered in the preparation of samples which gave the characteristic X-ray diffraction pattern. The best method was found to be similar to that of Goldschmidt, Barth, and Lunde.³ A hot concentrated solution of sodium bicarbonate was added to a dilute solution of gallium chloride, held at boiling, to give complete precipitation of the gallium. The gelatinous precipitate was washed free of chloride ion with hot water. During the washing the precipitate appeared to age, becoming less gelatinous. After being dried in the air at room temperature for an hour the solid was placed in a platinum crucible and heated in a muffle furnace in the air at 425°. The water content of some samples decreased to between 1.5 and 4% inside of twenty-four hours of heating and the products gave good X-ray diffraction patterns for α -Ga₂O₃. Frequently, however, under the same controlled conditions, samples would retain up to 20% of water even after being held for periods up to two weeks at 425°, and these samples gave very poor or no X-ray diffraction patterns. This experience shows how difficult it is to approach equilibrium in this system. Anhydrous α -Ga₂O₃ could not be obtained because, at the high temperatures necessary for dehydration, the α -Ga₂O₃ inverted to β -Ga₂O₃.

β -Ga₂O₃ was obtained by precipitating the gelatinous hydroxide by any of the common methods, washing it free of ions, and igniting it above 600°. These preparations gave the characteristic X-ray diffraction patterns for β -Ga₂O₃ but always consisted of extremely minute crystals. One would expect crystal growth upon long ignition at high temperatures but none was observed.

Samples of anhydrous gallium oxide obtained by the thermal decomposition of oxy salts of gallium, such as the oxalate, nitrate, or camphorate, were so finely divided that no X-ray diffraction patterns were obtained for them.

Fusion-Quenching Studies.—In order to get information about the range of stability of β -Ga₂O₃ the fusion-quenching method was used. This method has given good results in the study of other oxide systems where the changes are sluggish.⁴ In each of a series of experiments 0.1 g. of a given gallium oxide preparation was mixed with a few drops of water and the desired amount of a flux suitable for speeding up the rate of inversion. The mixture was held in a platinum crucible at a given constant temperature long enough to allow the attainment of equilibrium and to give opportunity for crystal growth, and then was quenched by dropping the crucible into cold water. The oxide was washed free of the soluble flux and dried in the air at 95°. The phases obtained were identified by microscopic and X-ray examination.

The eutectic mixture of 44.6% lithium chloride and 55.4% potassium chloride, found to be so satisfactory as a flux for the study of germanium dioxide,⁴ was used with gallium oxide. The large number of experiments made with this flux are summarized in Table I.

TABLE I

FUSION-QUENCHING EXPERIMENTS USING KCl-LiCl FLUX

Expt.	Temp., °C. (±5°)	LiCl- KCl, mg.	Time, hours	Form of Ga ₂ O ₃	
				Used	In product
1	420	2	47	No pattern	Trace GaO(OH)
2	420	50	47	No pattern	Trace β -Ga ₂ O ₃
3	420	2	60	No pattern	No pattern
4	420	2	60	No pattern	No pattern
5	380	2	30	β -Ga ₂ O ₃	β -Ga ₂ O ₃
6	600	2	18	β -Ga ₂ O ₃	β -Ga ₂ O ₃
7	800	2	1	β -Ga ₂ O ₃	β -Ga ₂ O ₃
8	1000	2	0.5	β -Ga ₂ O ₃	β -Ga ₂ O ₃
9	1000	2	5	β -Ga ₂ O ₃	β -Ga ₂ O ₃
10	1000	3	20	β -Ga ₂ O ₃	β -Ga ₂ O ₃
11	1000	3	50	β -Ga ₂ O ₃	β -Ga ₂ O ₃
12	1000	50	20	β -Ga ₂ O ₃	β -Ga ₂ O ₃

In Expts. 1 and 2 the gallium oxide samples used had been precipitated at 70° by ammonium hydroxide, washed, and dried at 400° for two hundred and fifty hours, a procedure which gives α -Ga₂O₃. They had given no X-ray diffraction patterns. Faint X-ray diffraction patterns were obtained for the products, with indications that in 1, with a small amount of flux, crystals of GaO(OH) were formed, whereas in 2, with a large proportion of flux and presumably better conditions for obtaining equilibrium, β -Ga₂O₃ was formed. In 3 the sample used was anhydrous oxide obtained by the ignition of gallium oxalate at 590° while that used in 4 was from ignition of gallium camphorate at 590°. The products gave no patterns. In expts. 5 through 12 β -Ga₂O₃, which had been ignited at 1000° and which gave the characteristic X-ray pattern, was used. In this series the temperature was varied between 380 and 1000°, the amount of flux between 2 and 50 mg., and the time of heating between one-half and fifty hours. The products all gave the pattern for β -Ga₂O₃ and microscopic examination showed no crystal growth. It is apparent that the LiCl-KCl flux does promote inversion somewhat but is not a very effective mineralizing agent for this system, since no appreciable crystal growth of gallium oxide was obtained.

Sodium carbonate, potassium bisulfate, and potassium sulfide were also used as fluxes in such fusion-quenching experiments. A sample of α -Ga₂O₃, giving the proper X-ray diffraction pattern, was converted to β -Ga₂O₃ when heated with potassium bisulfate at 420° for fifty-eight hours. In all the other experiments, in some of which the temperature was raised to 1400°, β -Ga₂O₃ either persisted or was formed. The fusion-quenching experiments indicate that β -Ga₂O₃ is the stable form of the oxide in the range studied, 380 to 1400°.

Hydrothermal-Quenching Studies.—The hydrothermal-quenching method, employing as the inversion catalyzer water or an aqueous solution confined in a vapor tight bomb, has been shown to be effective for establishing equilibrium in oxide systems, such as germanium dioxide.⁴ This technique was used for studying various gallium oxide preparations and was found to give much better crystal growth than the fusion-quenching method.

In these experiments the gallium preparation plus six or seven cc. of water was placed in a platinum thimble in the stainless steel bomb and held at constant temperature in

(3) Goldschmidt, Barth, and Lunde, *Skrifter Norske Videnskaps-Akad. i Oslo I. Mat.-Natur. Klasse*, No. 7, 24 (1925).

(4) Laubengayer and Morton, *THIS JOURNAL*, 54, 2305 (1932).

the bomb furnace for a period thought to be long enough to give equilibrium.

The capacity of the bomb was 15 cc. and the addition of 6 cc. of water ensured the presence of liquid water at all temperatures below its critical point and, presumably, the partial aqueous vapor pressures in the bomb in these experiments were the saturation aqueous vapor pressures for these temperatures. At 374°, the critical temperature for water, the aqueous vapor pressure in the bomb must have been about 220 atmospheres.

After removal from the furnace the bomb was rapidly air-quenched and the product was examined by X-ray and microscopical methods to identify the phases present. In some cases the percentage of water associated with the product after it was dried at 105° was determined. Table II summarizes these experiments.

In expts. 1, 2, and 3, the material used was the gelatinous preparation obtained by precipitating gallium with ammonium hydroxide between 30 and 40° and washing free of ions. Hydrothermal treatment gave GaO(OH) as shown by the X-ray diffraction pattern and by the percentages of water present in 1 and 3: calcd. 8.77%.

TABLE II
HYDROTHERMAL-QUENCHING EXPERIMENTS

Expt.	Sample used	Temp., °C. (=3°)	Time, hours	% H ₂ O	Product X-ray pattern
1	Gelatinous ppt.	110	106	13.8	GaO(OH)
2	Gelatinous ppt.	150	100		GaO(OH)
3	Gelatinous ppt.	248	135	9.1	GaO(OH)
4	Gelatinous ppt.	150	96		GaO(OH)
5	Gelatinous ppt.	167	89	24.5	Ga(OH) ₃
6	Gelatinous ppt.	170	96		Ga(OH) ₃
7	Gelatinous ppt.	170	166		GaO(OH)
8	Gelatinous ppt.	177	99		Ga(OH) ₃ , GaO(OH)
9	Gelatinous ppt.	250	86	10.5	GaO(OH)
10	Gelatinous ppt.	250	86	8.4	GaO(OH)
11	Gelatinous ppt.	250	86	8.9	GaO(OH)
12	Gelatinous ppt.	285	96	10.3	GaO(OH)
13	Gelatinous ppt.	300	89	3.3	GaO(OH), β-Ga ₂ O ₃
14	Gelatinous ppt.	315	96	3.1	β-Ga ₂ O ₃
15	Gelatinous ppt.	330	120	0.3	β-Ga ₂ O ₃
16	Gelatinous ppt.	350	96	.7	β-Ga ₂ O ₃
17	Gelatinous ppt.	375	96	.2	β-Ga ₂ O ₃
18	Gelatinous ppt.	400	101	.4	β-Ga ₂ O ₃
19	Gelatinous ppt.	420	74	.0	β-Ga ₂ O ₃
20	Gelatinous ppt.	430	118		β-Ga ₂ O ₃
21	Cryst. Ga(OH) ₃	305	161		β-Ga ₂ O ₃
22	Cryst. Ga(OH) ₃	420	107	1.0	β-Ga ₂ O ₃
23	GaO(OH)	305	161		β-Ga ₂ O ₃
24	GaO(OH)	420	102	0.0	β-Ga ₂ O ₃
25	α-Ga ₂ O ₃	250	64		GaO(OH)
26	α-Ga ₂ O ₃	305	161		GaO(OH)
27	β-Ga ₂ O ₃	250	84		β-Ga ₂ O ₃
28	β-Ga ₂ O ₃	400	168	.0	β-Ga ₂ O ₃
29	β-Ga ₂ O ₃	450	150		β-Ga ₂ O ₃
30	Ga ₂ O ₃ from oxalate	425	70		β-Ga ₂ O ₃
31	Ga ₂ O ₃ from camphorate	425	70		β-Ga ₂ O ₃

In expts. 4 through 20 the gelatinous gallium preparation, precipitated at 90° by ammonium hydroxide, was washed well and then introduced, while still moist, into the bomb with 6 cc. of water. Here it was found that GaO(OH) was formed in the range 150 to 300° but that at 167° crystalline Ga(OH)₃, with a distinctive X-ray diffraction pattern and a water content close to the theoretical value, 22.4%, was obtained. This crystalline

normal hydroxide also was formed in expt. 6 during a period of ninety-six hours at 170°. But in expt. 7, when a temperature of 170° was again maintained and the period of heating was lengthened to one hundred and sixty-six hours and better opportunity was given for equilibrium to be established, GaO(OH) was formed. Experiment 8, run at 177° for ninety-nine hours, gave both Ga(OH)₃ and GaO(OH). At and above 300° β-Ga₂O₃ was obtained and was shown to be the stable phase, since in expts. 21 and 22 Ga(OH)₃, held at 305° and 420° respectively, was converted to β-Ga₂O₃ and in expts. 23 and 24 GaO(OH) at 305 and 420°, respectively, gave β-Ga₂O₃. In expt. 25 at 250° a sample which had given the α-Ga₂O₃ pattern was converted to GaO(OH). In expt. 26 α-Ga₂O₃ at 305° gave GaO(OH). Experiments 12, 13, 14, 23, and 26 fix the upper limit of stability of GaO(OH) in the bomb at 300 ± 5°.

Samples of β-Ga₂O₃ in expts. 27, 28, and 29 were not changed by hydrothermal treatment between 250 and 450° although, according to preceding experiments at 250°, conversion to GaO(OH) might be expected. Either β-Ga₂O₃ is stable at 250° or the inversion rate of its well-formed crystals is inappreciable. In expts. 30 and 31 the oxides prepared by ignition of the oxalate and camphorate, too finely divided to give an X-ray diffraction pattern, were converted at 425° to the definitely crystalline β-Ga₂O₃.

The hydrothermal experiments show that, under the conditions prevailing in the bomb with water present under considerable pressures, GaO(OH) is the stable phase between 110 and 300° while above 300° β-Ga₂O₃ is stable. Well-formed crystals of Ga(OH)₃ were obtained in some cases at from 167 to 177° but these apparently are metastable. Ga(OH)₃ should be less stable when the aqueous vapor pressures are lower than those which prevailed in the bomb in expts. 5 and 6. In order to test this a sample of crystalline Ga(OH)₃ was placed in the bomb with only 3 cc. of water and was heated at 167° for sixty-four hours. This was calculated to give an aqueous vapor pressure of about 7 atmospheres. After quenching the crystals were found to be unchanged. The experiment was repeated at 167° with only the dry crystals of Ga(OH)₃ present. No change took place in sixty-four hours. The temperature was raised to 250° and the Ga(OH)₃ plus 3 cc. of water was heated for sixty-four hours. No change occurred. Once the crystals of Ga(OH)₃ are obtained they apparently decompose very slowly and this rate does not seem to be affected much by lowering the aqueous vapor pressure in the bomb.

The hydrothermal treatment gave definite crystalline growth but this growth was extremely slow and even in the most successful experiments the crystals were still minute. This method gave the best approach to equilibrium thus far obtained. α-Ga₂O₃ was never obtained in the bomb where relatively high aqueous vapor pressures prevailed.

Dehydration Studies.—Dehydration curves were run for: (1) the gelatinous precipitate used in expts. 1, 2, and 3, Table II, (2) the crystalline Ga(OH)₃ obtained in expt. 5, and (3) the crystalline GaO(OH) obtained in expt. 12. In each case the sample was heated in a loosely covered platinum crucible in the air in a furnace which could be maintained at constant temperature ± 5° until equilibrium

was approached as closely as possible and the loss of water over a period of twenty-four hours became negligible. The total loss in weight at this temperature was determined and then the sample was exposed to the next higher temperature and the dehydration continued in the same manner, the total period of heating being about three hundred hours. The curves secured by plotting the moles of water in the sample per mole of Ga_2O_3 against the temperature are given in Fig. 2.

Curve 1 for the gelatinous precipitate shows a break corresponding to the composition of $\text{Ga}(\text{OH})_3$. However, this break is at about 600° and real equilibrium was obviously not attained in spite of the protracted periods of heating. No break corresponding to $\text{GaO}(\text{OH})$ is noted in this curve but this is not surprising since the hydrothermal experiments have shown that $\text{GaO}(\text{OH})$ is not stable above 300° . This curve differs from the smooth desorption curve given by Milligan and Weiser² for the dehydration of hydrous gallium oxide but it is to be noted that their samples were allowed to age. This gave conditions favorable for the growth of well formed $\alpha\text{-Ga}_2\text{O}_3$ crystals which would gradually lose the adsorbed water when heated.

Curve 2 for crystalline $\text{Ga}(\text{OH})_3$ has a decided break at about 220° , indicating decomposition of this compound, and then gives a flat which corresponds to the composition $\text{Ga}_2\text{O}(\text{OH})_4$. This is the only evidence obtained in this investigation of the possible existence of a so-called dihydrate as reported by Neogi and Nandi⁵ and is not strong enough to establish the formation of such a compound. Samples prepared according to their directions gave no new X-ray diffraction pattern which could be assigned to this compound. Curve 2 is in rough agreement with the evidence secured by hydrothermal methods for the decomposition of $\text{Ga}(\text{OH})_3$. The extremely slow rate of decomposition of crystals of $\text{Ga}(\text{OH})_3$ is indicated in the curve by the high temperatures necessary to give anhydrous gallium oxide.

Curve 3 for the crystalline $\text{GaO}(\text{OH})$ shows that this loses little water in the air until heated to nearly 300° . The sharp break there gives further evidence that this substance exists as a definite compound, decomposing to yield the nearly anhydrous oxide at 400° , and is in line with the hydrothermal experiments which show that $\text{GaO}(\text{OH})$ is not stable above 300° . This curve is similar to that reported for gallium oxide monohydrate by Milligan and Weiser.²

The dehydration studies confirm the evidence secured by the hydrothermal method for the existence and stability of $\text{Ga}(\text{OH})_3$ and $\text{GaO}(\text{OH})$.

The Properties of $\alpha\text{-Ga}_2\text{O}_3$.—This modification of gallium sesquioxide has been obtained only in the hydrous condition as a microcrystalline powder, the largest crystals being only about one micron in length. The solubility of $\alpha\text{-Ga}_2\text{O}_3$ appears to be very low in water but it reacts slowly with dilute mineral acids. When heated to 600° in the air it inverts slowly to $\beta\text{-Ga}_2\text{O}_3$. In the presence of fused mineralizing agents this inversion to the beta form was observed at 420° . In the hydrothermal bomb the inversion takes place at 305° and above. The inversion has not been shown to be reversible. Below 305° hydrous $\alpha\text{-Ga}_2\text{O}_3$ is converted in the bomb to $\text{GaO}(\text{OH})$.

(5) Neogi and Nandi, *J. Indian Chem. Soc.*, **13**, 399 (1936).

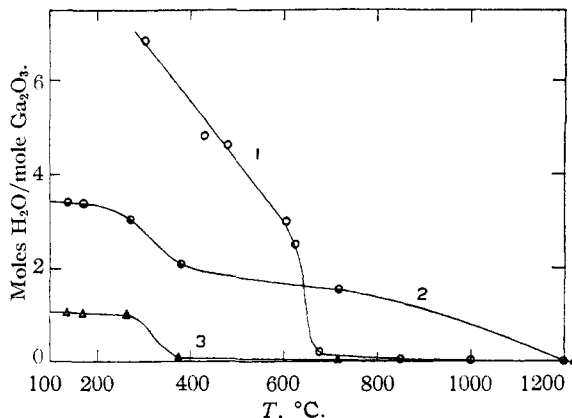


Fig. 2.—Dehydration isobars.

The Properties of $\beta\text{-Ga}_2\text{O}_3$.—This form has been shown to be stable in the range 300 to 1400° and probably is stable up to the melting point.³ Since $\beta\text{-Ga}_2\text{O}_3$ has not been converted to any other substance below 300° it is possible that it is stable at all temperatures and that the system is monotropic. In the present investigation the best crystals were obtained by the hydrothermal method at 420° in expt. 19. These crystals are biaxial, probably monoclinic poly-twins, exhibiting octahedral symmetry. They vary in length from seven to 25 microns. The refractive index for the fast component is 1.92 and for the slower 1.95.

$\beta\text{-Ga}_2\text{O}_3$ is insoluble in dilute and concentrated mineral acids. The very fine crystalline powder is taken partially into colloidal suspension by boiling it with concentrated hydrochloric acid for a long time. It should be noted that $\beta\text{-Ga}_2\text{O}_3$ formed in the bomb at 420° and then dried in the air at 105° was anhydrous whereas, when this oxide is made by ignition of the gelatinous precipitate in the air, it is necessary to heat it as high as 1200 to 1300° to drive off all the water. The better developed crystals resulting from long treatment in the bomb might be expected to be relatively free of water.

Properties of $\text{GaO}(\text{OH})$.—Well formed but small crystals of gallium hydroxy-oxide were obtained in the hydrothermal bomb between 110 and 300° .⁶ These crystals are obliquely truncated prisms about 6 microns in length. They show parallel extinction in all views. The refractive index parallel to the long axis is slightly greater than 1.84 and perpendicular to the long axis slightly less than 1.84 for some views and slightly greater for other views. This indicates a biaxial character. The crystals are stable at room temperature in the air and may be dried at 105° without decomposition. $\text{GaO}(\text{OH})$ is soluble in dilute mineral acids.

Properties of $\text{Ga}(\text{OH})_3$.—Gallium hydroxide, not previously described, was obtained from the gelatinous precipi-

(6) Böhm and Kahan, *Z. anorg. allgem. Chem.*, **238**, 350 (1938), recently have reported that they obtained $\text{GaO}(\text{OH})$ by precipitating gallium from a chloride solution with ammonium hydroxide and aging the gelatinous precipitate for six days under water. They also obtained $\text{GaO}(\text{OH})$ by heating the gelatinous precipitate at 290° with water in a quartz tube at 70 to 80 atmospheres pressure. This preparation gave an X-ray diffraction pattern similar to diaspor and had a water content corresponding to the formula $\text{GaO}(\text{OH})$.

tate by the hydrothermal method at around 167° as a very fine powder which gave a characteristic powder X-ray diffraction pattern. The crystals were too small to study with the microscope even with the use of an oil-immersion objective. $\text{Ga}(\text{OH})_3$ is soluble in dilute mineral acids but is not appreciably soluble in water.

Discussion

The probable mechanism of the precipitation of gallium as the gelatinous precipitate and of the subsequent aging of this precipitate may be outlined on the basis of the experimental data now available. The size of the gallium ion is such that one may expect a coordination number of six with respect to oxygen.⁷ In solution the ion will therefore be hexahydrated. With increase in hydroxyl ion concentration protons will be removed from the coordinated water molecules, with progressive formation of hydroxyl groups about the gallium to produce a gelatinous system approximating the normal hydroxide in composition. This is associated with a considerable amount of adsorbed water. The aging of this material apparently involves the loss of the adsorbed water and condensation of the hydroxyl groups with the splitting out of water. Under favorable conditions, such as exist in a bomb with high aqueous vapor pressures, the crystalline normal hydroxide may be obtained but this compound has not been isolated at lower aqueous vapor pressures. Slow aging of the gel at room temperature, or at higher temperatures with high aqueous vapor pressures, involves condensation to $\text{GaO}(\text{OH})$. More rapid aging at elevated temperatures and low aqueous vapor pressures gives the hydrous alpha form of the sesquioxide.⁸ These various forms persist at low temperatures but at higher temperatures they slowly are converted to $\beta\text{-Ga}_2\text{O}_3$. The changes in properties noticed during the aging process are to

(7) L. C. Pauling, *THIS JOURNAL*, **55**, 1895 (1933).

(8) Milligan and Weiser have reported obtaining an X-ray diffraction pattern consisting of bands when they examined the fresh gelatinous precipitate by means of $\text{Cu K}\alpha$ radiation and believe that these bands indicate the presence of hydrous $\alpha\text{-Ga}_2\text{O}_3$. We have repeated this work with $\text{Cu K}\alpha$ radiation and do get weak bands but it seems very doubtful whether this pattern can be interpreted as proving that the precipitate is predominantly $\alpha\text{-Ga}_2\text{O}_3$.

be attributed to the changes in composition and aggregation which occur.

The system gallium sesquioxide-water resembles that of aluminum oxide-water closely, as is to be expected from the similar nature of the gallium and aluminum ions. The very sluggish changes and the extremely small tendency for crystalline growth in these systems is particularly to be noted. In this respect they follow the lead of boric oxide which is so difficult to obtain in the crystalline form. This reluctance to crystallize readily seems to be much greater for the oxides of the third group than for the oxides of silicon, germanium, and tin and there is available no explanation to account for this.

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Summary

1. The system gallium sesquioxide-water has been studied by fusion quenching, hydrothermal quenching and dehydration methods, with the use of X-ray, microscopical, and chemical analytical methods for the identification of the phases which occur.

2. The hydrothermal quenching method has been found to afford the best conditions for approaching equilibrium and for the growth of crystals in this system which is characterized by very sluggish changes.

3. The compounds isolated in the system include hydrous $\alpha\text{-Ga}_2\text{O}_3$, $\beta\text{-Ga}_2\text{O}_3$, $\text{GaO}(\text{OH})$, and $\text{Ga}(\text{OH})_3$, the last not having been reported before. The properties of these substances and their ranges of stability have been studied.

4. The mechanism of the precipitation of gallium and the aging of the gelatinous precipitate are discussed.

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