TABLE I

SUMMARY OF DERIVED DATA AT 25°[a]

Substance	Mol. wt.	Density	$-\Delta U_B$[b], kcal./mole	$-\Delta H_R$, kcal./mole	$-\Delta H_f°$, kcal./mole	$\Delta F_f°$, kcal./mole
Ti	47.90	4.51	224.86 ± 0.22	225.52 ± 0.23	225.52 ± 0.23[c]	212.33 ± 0.23[c]
TiO	63.90	4.92	101.25 ± 0.12	101.61 ± 0.12	123.91 ± 0.28	116.92 ± 0.28
Ti_2O_3	143.80	4.56	87.78 ± 0.10	88.11 ± 0.10	362.93 ± 0.48	342.31 ± 0.48
Ti_3O_5	223.70	4.15	89.36 ± 0.05	89.65 ± 0.05	586.69 ± 0.69	553.12 ± 0.69

[a] Errors are uncertainty interval. [b] At 30°. [c] Datum for TiO_2.

that the slight increase in weight on ignition of the combustion product (used to correct for incomplete combustion) was due to some higher oxide between the one burned and TiO_2 is not excluded by this work; consequently, the uncertainties in the final results have been increased when necessary to account for this.

The value 225.3 ± 0.3 kcal./mole obtained by Neumann, *et al.*,[2d] for the heat of formation, $-\Delta H_f°$, of TiO_2 from combustion measurements on titanium metal is in good agreement with the value obtained here. No combustion measurements for the other oxides of titanium appear in the literature. However, Nasu[18] determined the equilibrium H_2O/H_2 ratio for the reduction of TiO_2 in an iron tube and from his measurements calculated $-\Delta H_{298} = 388.1$ kcal./mole for the heat of formation of Ti_2O_3. Brewer[19] subsequently has used Nasu's data and other considerations in estimating the heats of formation at 298°K. of TiO, Ti_2O_3 and Ti_3O_5 as −127, −381 and −605 kcal./mole, respectively. The National Bureau of Standards[13] has also listed values for the standard heats of formation in kcal./mole as: Ti_2O_3, −367; Ti_3O_5, −584; TiO_2, −218. Although all of these values are of the correct order of magnitude, their accuracy is by no means comparable to that of the direct determinations reported here.

Using entropy data listed by Kelley,[16] free energies of formation from the elements at 1 atm. pressure and 298°K. were calculated (see Table I). Further calculations of free energy changes at ordinary temperatures show that both TiO and Ti_2O_3 are thermodynamically stable to disproportionation; the reaction, $Ti_3O_5 = Ti_2O_3 + TiO_2$, has a small negative ΔF; and decomposition of Ti_3O_5 into TiO_2 and TiO, or Ti, is precluded.

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[18] N. Nasu, *J. Chem. Soc. Japan*, **56**, 659 (1935).

[19] L. Brewer, "Thermodynamic Properties of the Oxides," University of California Radiation Laboratory Report-104, July 1948.

[CONTRIBUTION FROM THE ALUMINUM RESEARCH LABORATORIES]

Analogies in the Gallia and Alumina Systems. The Preparation and Properties of Some Low-Alkali Gallates[1]

BY L. M. FOSTER AND H. C. STUMPF

Gallium, appearing in Group III of the periodic table, shows great resemblance to aluminum in its chemical properties, and occurs to a very small extent in all natural aluminous materials. The similarity of the ionic radii of the two elements (0.57 Å. for aluminum, 0.62 Å. for gallium) permits mixed crystal formation, and a number of compounds, particularly oxides of gallium, have been observed which are isomorphous with the corresponding aluminum compounds.

In the aluminum system there are a considerable number of oxide and hydrated oxide phases. The older established forms are: alpha trihydrate (gibbsite), beta trihydrate (bayerite), alpha monohydrate (boehmite), beta monohydrate (diaspore), gamma alumina, and alpha alumina (corundum).[1] "Beta" alumina was originally thought to be another allotropic modification of anhydrous alumina, but it has since been found to be an alkali aluminate containing about 5% soda.[2]

Jellinek and Fankuchen[3] reported that the various X-ray powder diffraction patterns which can be obtained for gamma alumina can be interpreted as arising from specimens of different crystallite size, and that "gamma" represents a continuous transformation sequence in the nearly anhydrous alumina, ending in corundum at high temperature. Stumpf, *et al.*,[4] however, interpreted the patterns as arising from a number of discrete crystalline phases, the nature and proportion of which depend on the thermal treatment given the sample. These phases were arbitrarily designated gamma, delta, eta, theta, kappa and chi.

Striking analogies have been observed between the aluminas and gallias which contribute appreciably to our understanding of the two systems.

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[1] Presented in part at the Seventh Annual Pittsburgh Conference on X-Ray and Electron Diffraction, November, 1948. The system of Greek letter designation used here is that introduced by J. D. Edwards, F. R. Frary and Z. Jeffries, "The Aluminum Industry, Vol. I—Aluminum and Its Production," McGraw-Hill Book Company, Inc., New York, N. Y., 1930.

[2] R. R. Ridgway, A. A. Klein and W. J. O'Leary, *Trans. Electrochem. Soc.*, **70**, 71–88 (1936).

[3] M. H. Jellinek and I. Fankuchen, *Ind. Eng. Chem.*, **37**, 158 (1945); **41**, 2259 (1949).

[4] H. C. Stumpf, A. S. Russell, J. W. Newsome and C. M. Tucker, *ibid.*, **42**, 1398 (1950).

Experimental

Gallia Monohydrate.—A number of workers have prepared and studied a definite crystalline monohydrate of gallia.[5,6,7,8]

In the present investigation it was observed that a dense, granular precipitate could be obtained easily, in a short time, by digesting gelatinous gallium hydroxide in the supernatant liquor from which it was precipitated, or simply by washing the precipitate comparatively free of ions with water. Very seldom, however, did these procedures yield products that gave sharp Debye–Scherrer powder patterns. Generally patterns were obtained that indicated a structural relationship to the monohydrate, but the lines were considerably broadened and indistinct, indicating extremely small crystallite size. It was possible to circumvent the gelatinous stage completely by precipitating the gallium from either hot or cold sodium gallate solutions with carbon dioxide. Here again, however, the products seldom gave sharp X-ray patterns. Only by washing a precipitate repeatedly by decantation with hot water, over a period of several days, was it possible to get a product whose Debye–Scherrer pattern was sharp and well defined. After this method of aging was adopted it made little difference how the original precipitate was obtained. Good preparations were made by gassing hot or cold sodium gallate solutions with carbon dioxide, by neutralizing sodium gallate solutions with dilute hydrochloric acid and by neutralizing dilute gallium chloride solutions with ammonia, sodium bicarbonate or sodium hydroxide.

The only crystalline product obtained by drying precipitates prepared as above, at about 100°, was a monohydrate with the aluminum diaspore structure. Generally such material, regardless of the length of drying at that temperature, contained about 11.5% total water, whereas the theoretical water content of the monohydrate is 8.78%.

Reproduction of the Debye–Scherrer X-ray powder diffraction patterns of gallia monohydrate and diaspore are shown as A and B of Fig. 1. (All were made with filtered CuK radiation in a 14.45 cm. powder camera.)

Laubengayer and Engle[8] reported the preparation of a gallia trihydrate. A product obtained by digesting a gelatinous gallium hydroxide precipitate in saturated steam at 167° had a water content approximately that of a trihydrate, and gave an X-ray pattern different from those of the monohydrate, or the anhydrous oxides. The pattern they reported does not correspond to either alpha or beta alumina trihydrate—the only ones known in the alumina system. In two attempts to duplicate their experiment, we obtained only the monohydrate.

The fact that, according to our experiments, there is only one hydrate of gallia—that isomorphous with diaspore—suggests that gallium might be found enriched in diasporic minerals. Indeed, information available from the literature, particularly from Boehm[7] and Einecke,[9] indicated that the gallium content of a few samples of European diaspores was 10–100 times greater than that of non-diasporic bauxites. In the present investigation 30 high-alumina ore samples were analyzed spectroscopically for trace elements. The group consisted of 20 samples that were predominantly gibbsite, 5 that were predominantly boehmite, 4 that were predominantly diaspore clay and 1 that was essentially pure disapore.[10] The gallium oxide amounted to 0.007 to 0.014% of the aluminum oxide content of all of the bauxite and diaspore clay samples. The concentration in the diaspore sample was 0.02%, showing only slight enrichment.

Alpha Gallia.—The preparation of a gallium sesquioxide with the corundum structure was first reported by Goldsmidt, *et al.*[5] They designated this form as alpha gallia to indicate the analogy to the alumina system. It can be formed by heating the monohydrate in air at about 400°.

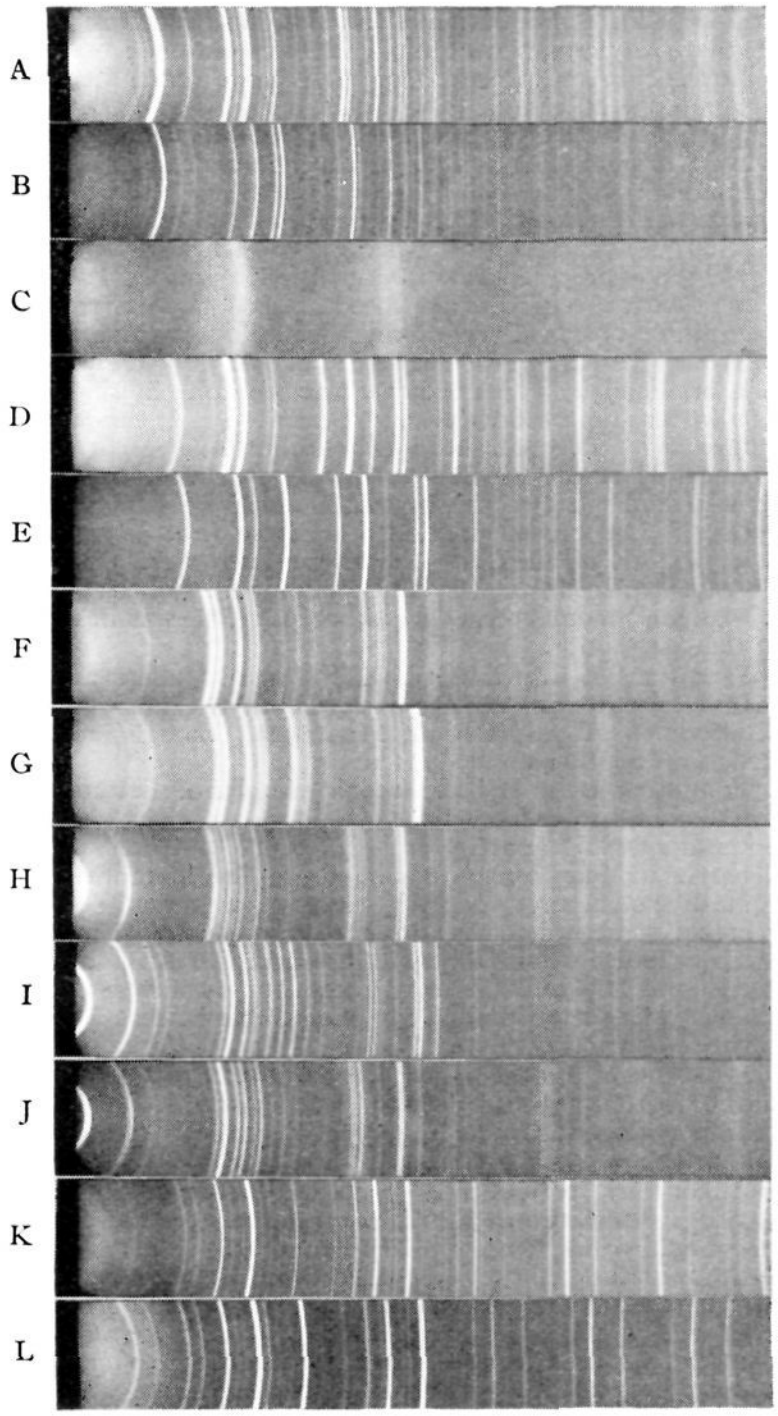

Fig. 1.—X-Ray powder patterns of gallium and aluminum oxide phases:

A: Gallia monohydrate, $a = 4.49$, $b = 9.78$, $c = 2.97$.
B: Beta alumina monohydrate (diaspore), $a = 4.43$, $b = 9.36$, $c = 2.80$.
C: Decomposition product of gallium nitrate.
D: Alpha gallia, $a = 5.30$, $\alpha = 56°4'$, density (computed) 6.48.
E: Alpha alumina (corundum), $a = 5.13$, $\alpha = 55°6'$.
F: High temperature form of gallia (theta-like).
G: Theta alumina.
H: Low sodium gallate, $a = 5.70$, $c = 22.8$.
I: Low sodium aluminate, beta alumina (Monofrax), $a = 5.56$, $c = 22.6$.
J: Low potassium gallate, $a = 5.80$, $c = 23.5$.
K: Low lithium gallate, $a = 8.21$.
L: Low lithium aluminate, $a = 7.94$.

Difficulties encountered in making a good preparation of alpha gallia were mentioned by Laubengayer and Engle[8] and inferred by Milligan and Weiser.[6] The latter workers obtained patterns which consisted of two broad diffuse bands, by heating gelatinous precipitates at various temperatures up to 450°. At higher temperatures, a slight amount of additional structure was discernible. On heating such a preparation to 600°, they got a pattern which they designated as alpha. If the very diffuse pattern they reported

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[5] V. M. Goldsmidt, T. Barth and G. Lunde, *Skrifter Norske Videnskaps-Akad., Oslo, I. Mat. Naturv. Klasse*, No. 7, 24 (1925).

[6] W. O. Milligan and H. B. Weiser, THIS JOURNAL, **59**, 1670 (1937).

[7] J. Boehm and G. Kahan, *Z. anorg. u. allgem. Chem.*, **238**, 350 (1938).

[8] A. W. Laubengayer and H. R. Engle, THIS JOURNAL, **61**, 1210 (1939).

[9] E. Einecke, "Das Gallium," Leopold Voss, Leipzig, 1937.

[10] The sample of diaspore was from a deposit near Chester, Mass., generously supplied by the Museum of Natural History, Springfield, Mass.

was a faithful reproduction of the film, however, it is doubtful that truly crystalline alpha gallia was obtained.

In the present investigation these same difficulties were encountered initially. The following preparations were employed as starting materials: 1, the gelatinous precipitate from neutralizing dilute gallium chloride solution with ammonium hydroxide, washed by centrifugation with cold water, dried at 105°; 2, the precipitate obtained as in 1, digested in hot water until it became granular, dried at 105°; 3, the granular precipitate obtained by gassing cold sodium gallate with carbon dioxide, dried at 105°; 4, the granular precipitate obtained by gassing hot (90°) sodium gallate solution with carbon dioxide, dried at 105°; 5, the precipitate obtained by neutralizing dilute gallium chloride solution with sodium bicarbonate, dried at 105°; 6, the product obtained by decomposing gallium nitrate at 325°. The patterns of all preparations were very diffuse and in general consisted of the two diffuse bands noted by Milligan and Weiser. The carbon dioxide precipitate (no. 3) gave the best pattern of the group, but the lines were wide and slightly displaced from the corresponding lines of the pattern of the good monohydrate whose preparation was described in the last section.

Samples 1–6 were held at 500° for two hours and reexamined. In no case was a pattern obtained that was characteristic in all respects of alpha gallia, though indeed a structural relation was indicated.

In another series of experiments, samples of material prepared as in 4 were heated for one hour at various temperatures, about 25° apart, from 167 to 625°. There was no sharp transition from a monohydrate-like stucture to an alpha-like structure. Rather, there was a gradual development of structure at the lower temperatures, then little further change at the higher temperatures. An additional sample was held at 500° for 29 hours, but its pattern did not differ significantly from that of the sample held at 500° for only one hour.

A pattern of the decomposition product of gallium nitrate (no. 6, heated two hours at 500°) is shown in C of Fig. 1. This is representative of the type of patterns obtained in this series.

In contrast to these results, it was observed that if the starting material for a heating experiment was the crystalline monohydrate with a sharp characteristic powder pattern, an alpha gallia was obtained in the 400 to 600° range that had a similarly sharp pattern, corresponding line for line, with alpha alumina. Alpha gallias with essentially identical patterns were obtained by heating monohydrate samples prepared by gassing cold sodium gallate with carbon dioxide, by neutralizing gallium chloride solution with sodium bicarbonate or ammonia, and by neutralizing sodium gallate solution with hydrochloric acid. The only requirement was that the original precipitates be aged in such a way as to give good monohydrate patterns. The inference here is that alpha gallia is formed by removal of water from the crystalline monohydrate, and is not formed if this phase is circumvented by removing the water before the monohydrate structure is fully developed. The powder patterns of alpha gallia and alpha alumina are given as D and E of Fig. 1.

Surface Area of Alpha Gallia.—The gallia powder patterns, such as C of Fig. 1, are very similar in character to those of the gamma aluminas, with different position and intensity of bands, of course. This suggested that these gallias would have similar sorptive properties. A Brunauer–Emmett–Teller sorption system of conventional design was employed for the measurements, using *n*-butane gas at 0°. The area of the *n*-butane molecule was taken as 39.0 Å.[2] The description of the samples and the measured areas are as follows:

1. Material prepared by heating an unaged carbon dioxide precipitate at 500° for one hour in vacuum. This material gave a diffuse powder pattern before the final heat treatment, and a similarly diffuse pattern like C, Fig. 1, after the heat treatment; area 1.76 × 10^4 sq. meter/mole (94 sq. meter/g.).
2. Material from the decomposition of gallium nitrate at 500°. This material also had a very diffuse pattern (C, Fig. 1); area 1.86 × 10^4 sq. meter/mole (99 sq. meter/g.).
3. True alpha gallia, which had a characteristic corundum-like pattern such as D, Fig. 1; area 0.45 × 10^4 sq. meter/mole (24 sq. meter/g.).

The area for the most sorptive commercial gamma alumina is about 3 × 10^4 sq. meter/mole (294 sq. meter/g.). Thus the sorptive gallias have areas about two-thirds as large as the most sorptive alumina, on a molar basis, and about four times as large as well-crystallized alpha gallia. It should be borne in mind that no intensive investigation was carried out to determine the optimum conditions of activation of the gallia samples. Had this been done, samples of even larger area undoubtedly could have been prepared.

Samples of the most sorptive gallia (gallium nitrate decomposition product) and the least sorptive, well crystallized, alpha gallia were examined with the electron microscope. The alpha gallia crystals were ellipsoids, about 1 micron long, and had built-up, step-like ends, indicating that they were probably composed of smaller, well-developed crystallites of the rhombohedral class. The highly-sorptive gallium nitrate product showed no characteristic crystal habit. Particle size ranged from something smaller than could be resolved with the instrument, to large clumps, several microns in diameter. The latter undoubtedly were aggregates of smaller particles. This semi-crystalline nature is characteristic of highly sorptive materials.

Theta-like Gallia.—Goldsmidt, *et al.*,[5] reported the preparation of a second allotropic form of anhydrous gallium oxide. This form results from heating alpha gallia at about 600°, and above, in air. It is also formed by igniting gallium nitrate, acetate, oxalate, etc., at high temperatures, and is the only stable form up to the melting point (*ca.* 1700°). The workers cited noted some similarity between the pattern of this form of gallia and that of the low-alkali aluminate, "beta," alumina, $Na_2O{\cdot}11Al_2O_3$. At that writing "beta" alumina was thought to be a truly allotropic modification of pure alumina and on that basis they designated the high-temperature-stable form as beta gallia. This terminology has carried through in the literature to the present time. This designation was unfortunate, for it was found in the present investigation that, whereas the diffraction pattern of this form of gallia shows some resemblance to that of the alkali aluminate, it is almost identical to that of theta alumina. With a small regular shift due to the slightly different parameters the two patterns can be superimposed.

Gallium nitrate was prepared by dissolving gallium metal in concentrated nitric acid in a platinum dish. The sirupy solution was taken up in water and evaporated down three times. The salt was then decomposed at about 500° and the product finally ignited at the highest temperature of the bunsen flame. The powder patterns of the theta-like gallia and theta alumina are shown as F and G of Fig. 1.

Hereafter, in this paper. the high temperature form of gallia will be referred to as the "theta-like" form. However, it is emphasized that this form is not merely similar to theta alumina, but identical to it in crystal structure, with allowances for the slightly different ion size.

An interesting observation in this connection is the manner in which gallium metal goes into solution. As is well known, very pure gallium dissolves extremely slowly in hot nitric acid in a glass vessel. Solution is faster in a platinum dish, where electrolytic attack can take place. Even in platinum, however, solution is very slow because, in the boiling acid, a vapor film between the two metals disrupts the electric current. If the solution is cooled so as to be quiescent, attack appears to be rapid at first, but after a few minutes the gallium becomes covered with a voluminous layer of a black product (which we suggest is gallium suboxide, Ga_2O) and there is no apparent further attack. This material does not dissolve in the cold acid but does so readily when the solution is boiled again. By alternately boiling and cooling, considerable gallium can be dissolved in a short time.

Low Alkali Gallates ($Na_2O{\cdot}11Ga_2O_3$ and $K_2O{\cdot}11Ga_2O_3$).—In view of the analogies in the gallia and alumina systems noted thus far, it was reasonable to expect the existence of the gallium counterpart of the low-alkali aluminates, sodium and potassium "beta" alumina, $Na_2O{\cdot}11Al_2O_3$ and $K_2O{\cdot}11Al_2O_3$.

"Beta" alumina is observed to separate from various fused baths containing a large proportion of alumina and a small proportion of the alkali oxide. It is also formed to a considerable extent when high-alkali Bayer process alumina is fused. These methods were not suitable for preparing the analogous gallium compounds because of the rather large amount of material required. The sodium compound was made, however, in the following manner: About 10% of ignited gallium oxide—the theta-like form—was added to sodium fluoride. One gram portions of this were fused in platinum crucibles and held molten for various times at various temperatures. The material was then cooled, and the masses extracted with boiling water. The insoluble material from a charge which had been held at 1010° for ten minutes consisted almost entirely of a compound that was isomorphous, by X-ray, with sodium "beta" alumina. The small amount of other material present was either unreacted chunks of the original oxide or long needles of an unidentified compound. This compound was possibly one of the gallium fluoride–sodium fluoride complexes. There are several such complexes of aluminum fluoride—cryolite chiolite, etc.—and probably comparable complexes of gallium fluoride exists. No attempt was made to identify this compound further.

The most perfect gallate crystals were very thin, transparent, hexagonal plates, about 50 microns across.

Sodium analysis was made on about 25 mg. of the plates that had been separated with the aid of a microscope. *Anal.* Calcd. for 11 $Ga_2O_3 \cdot Na_2O$: Na_2O, 2.9. Found: Na_2O, 3.4. The analytical figure was probably high because of the difficulty in effecting a clean separation of the beta plates from the unidentified needles, which undoubtedly have a high sodium content.

A preparation of a low-potassium gallate was also made in a similar manner, using potassium fluoride instead of sodium fluoride. The product consisted of extremely fine crystals whose shape could not be determined under the microscope. *Anal.* Calcd. for 11 $Ga_2O_3 \cdot K_2O$: K_2O, 4.4. Found: K_2O, 4.7.

The powder patterns of the low-sodium gallate, a commercial sodium "beta" alumina called "Monofrax"[11] and the low-potassium gallate are shown as H, I, and J, Fig. 1.

Lithium Gallate.—The low-lithium aluminate, "zeta" alumina, is formed by the combination of lithium and aluminum oxides. Its preparation parallels that of the sodium and potassium compounds, but it has the cubic spinel lattice.[12] The "ideal" composition appears to be $LiAl_5O_8$,[13] but it exhibits the ability of spinels to dissolve a large excess of the major oxide component without a significant change in structure. Thus the first lithium aluminate, prepared by Barlett[12] and named "zeta" by her, contained but 0.35% Li_2O.

Laubengayer and Engle[8] used the eutectic mixture of lithium and potassium chlorides as a mineralizing agent in an attempt to convert the theta-like gallia (their beta) back to alpha. They reported that there was no conversion and the theta-like form remained as the only product. However, the conditions of their experiments, particularly those at high temperature, seemed ideal for the formation of either the low-potassium or low-lithium gallate so part of their work was repeated by the present authors.

To 0.5 g. of ignited gallia was added 0.25 g. of the chloride eutectic (44.6% LiCl, 55.4% KCl). A few drops of water were added and the mixture was stirred well to insure intimate contact of the components. After slow drying, the mixture was heated to 1000° in a platinum crucible and maintained at that temperature for four hours. (In the last experiment of Laubengayer and Engle a similar mixture was held at 1000° for 20 hours.) The cooled and crushed material was leached free of chloride ion with boiling water. The insoluble residue was found by X-ray to be isomorphous with the low-lithium "zeta" alumina and to have a lithium content, as determined by photometric analysis, of 1.33% (2.87% Li_2O). The powder patterns of this lithium gallate and the lithium aluminate are shown as K and L of Fig. 1. The interplanar spacings of the three strongest lines for each of the six gallia phases are given in Table I.

TABLE I

INTERPLANAR SPACINGS OF PRINCIPAL X-RAY LINES OF GALLIUM OXIDE PHASES (IN ÅNGSTRÖMS) (RELATIVE INTENSITIES IN PARENTHESES)

Gallia monohydrate	4.08 (1)	2.40 (0.9)	1.69 (0.9)
Alpha gallia	2.63 (1)	1.66 (0.9)	2.48 (0.7)
Theta-like gallia	1.44 (1)	2.80 (0.9)	2.53 (0.9)
Low-sodium gallate	11.25 (1)	5.68 (0.8)	1.45 (0.7)
Low-potassium gallate	11.5 (1)	2.79 (0.8)	5.9 (0.7)
Low-lithium gallate	2.46 (1)	1.45 (0.9)	1.58 (0.8)

Thermal Studies of the Alpha-Theta Transition.—We have in the gallia and alumina systems the unusual phenomenon of a complete reversal in the order of a phase transition. In the alumina system, theta alumina transforms to alpha in the neighborhood of 1000°. In the gallia system, alpha gallia transforms to the theta-like form in the neighborhood of 600°. It has been assumed that the gamma aluminas (where gamma is taken to include theta) are monotropically metastable with respect to alpha alumina, since a large evolution of heat has been observed in going from gamma to alpha in the neighborhood of 1000°. This transition temperature is meaningless then and, in the presence of suitable catalysts, it should be possible to lower it considerably. Indeed, Edwards and Tosterud[14] observed that the transition to corundum frequently did not occur up to about 1150° in the absence of mineralizing agents, but in the presence of ammonium fluoride, aluminum fluoride, cryolite or hydrogen fluoride, among others, corundum was obtained at as low as 850°. If it can be assumed that the heat evolution accompanies the transition from theta to alpha alumina, then it would be reasonable to look for a heat absorption in going from alpha to the theta-like gallia, taking into consideration the great similarity in aluminum and gallium chemistry and in the physical and thermodynamic properties of their compounds.

Apparatus was constructed which consisted of a solid stainless steel cylinder, $1\,^3/_4''$ long by $1\,^1/_8''$ diameter, in both ends of which were drilled $^3/_8''$ holes $^7/_8''$ deep which served as receptacles to hold quartz vials containing the oxide sample and blank. A thermocouple well was drilled into the block from the side to a position midway between the two receptacles. One junction of a chromel–alumel differential thermocouple was supported in the center of the sample and the other in the blank. The temperature of the block was taken as the blank temperature. A supplementary experiment, wherein the two were compared directly, showed this to be approximately true. The unit was placed in a 1-foot long, open-end tube furnace of $1\,^1/_2''$ bore. A high heating rate was employed (about 25° per minute near 1000°), since it was found that this decreased the time required for a transition to take place and sharpened the exothermal peaks considerably.

The potential across the differential thermocouple was measured with a Leeds and Northrup, Type K, potentiometer.

Measurements were made on three different substances: alpha gallia, amorphous alumina and theta alumina. In Fig. 2 the temperature differential between the sample and the blank is plotted against the blank temperature for three representative experiments. The experiments were repeated several times and, except for minor differences, the effects were reproducible. The curves are accurate tracings of the experimental points, which were too numerous and close together to include in the figure.

All samples showed an initial cooling of about 10° which is attributed to the evaporation of water from the highly sorptive specimens. The blanks, having been ignited at high temperatures, would not pick up much moisture during the loading operation. The small persistent temperature differences occasionally observed between a sample and blank could have resulted from non-uniform heating zones in the furnace. No significance is attached to the other small variations in the curves.

Alpha gallia was prepared by heating the monohydrate at 500° for 18 hours in a slow air stream. Ignited gallia was used as the blank. This was prepared by heating the monohydrate at the highest temperature of the bunsen flame. One sharp exothermal peak was observed with a take-off temperature of about 700°. The expected endothermal effect was not in evidence. In supplementary experiments the heating was interrupted at the points marked 1 and 2 on the curve, and the samples were removed and cooled rapidly. Sample 1 was entirely alpha gallia. Sample 2 was entirely the theta-like gallia.

Amorphous alumina was made by decomposing aluminum nitrate nonahydrate at 600°. To insure reproducibility of the results, 2% ammonium fluoride was added as a

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(11) Obtained from the Carborundum Company.

(12) H. W. Barlett, *J. Am. Ceram. Soc.*, **15**, 361 (1932).

(13) E. Kordes, *Z. Krist.*, **91**, 193–228 (1935).

(14) J. D. Edwards and M. Tosterud, unpublished work carried out in these Laboratories in 1929.

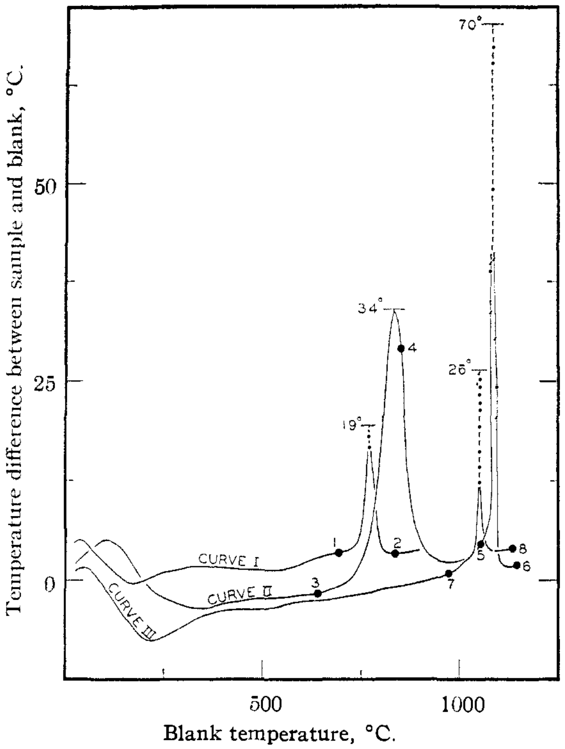

Fig. 2.—Heating curves of gallium and aluminum oxides: curve I, alpha gallia; curve II, amorphous alumina; curve III, theta alumina.

mineralizing agent. This was mixed in thoroughly, then the material was held at 600° again for 18 hours to decompose the ammonium fluoride.[15] The blank was prepared by heating some of this material at 1250° for three hours.

Two exothermal effects were observed, the first setting in in the neighborhood of 700° and the second at about 1000°. Samples were taken in supplementary experiments at the points shown. These were found to be: 3-amorphous alumina, 4-gamma alumina[16]; 5-gamma plus 5–10% alpha, 6-entirely alpha.

It was surprising that sample 5 contained no theta, since it has been assumed that theta is always an intermediary between gamma and alpha. It was necessary then to investigate the behavior of theta alumina.

Theta alumina was made by heating beta trihydrate (bayerite) at 1000° in steam for one hour. Two per cent. ammonium fluoride was then added and decomposed as before. This material gave pattern G of Fig. 1. The first exothermal peak was absent, as expected. The second peak was greatly reduced in magnitude over that resulting from the transition of gamma to alpha in the previous experiment. This suggests that in the first experiment (Curve II) the large exothermal effect was a super-position of a large heat of crystallization of gamma on the heat of transition of theta to alpha. It is reasonable to assume that this additional energy is that which is released in going from gamma to theta, but that theta is short-lived under the conditions of the experiment and goes immediately over to corundum without appearing in sample 5.

Discussion

The transitions in the gallia system which were observed in this investigation are compared with the alumina transitions in Fig. 3. Temperature increases from bottom to top of the diagram, but absolute placement along a vertical line is arbitrary. The arrow leading from alpha alumina monohydrate, through theta, to alpha alumina, is broken to indicate the omission of the phases which with theta, have been collectively designated as the "gamma aluminas." It is the contention of Jellinek and Fankuchen[3] that in the alumina system all of the gammas, including theta, are only manifestations of a continual increase of crystallite size leading finally to corundum. Since the reversed order of the theta-alpha transition is observed in the gallia system, this view is untenable, at least as regards theta, and this form must be regarded as a discrete crystal phase as proposed by Stumpf, *et al.*[4]

The transition from theta to alpha alumina is in the direction that would be expected from the densities of the two forms (theta, *ca.* 3.87; alpha, 3.99). In the gallia system, however, there exists the unusual situation where the dense alpha structure (6.48, computed) transforms to the less dense theta structure (5.95 experimental)[17] with increasing temperature.

The alpha to theta transition is unambiguous. The starting material and transformed product gave similarly sharp X-ray patterns indicating that both phases consisted of well-developed crystals; hence, there should be little or no heat of crystallization within a phase. It is impossible to prepare completely anhydrous alpha gallia, and presumably some of the remaining water is lost during the transformation to the theta-like form. This could not account for the exothermal peak, however, since the loss of water would be an endothermal process and tend to diminish the over-all effect. Alpha gallia must be regarded then as a metastable phase. This same conclusion was reached by Laubengayer and Engle on the basis of their fluxing experiments with lithium and potassium chlorides. The possibility of getting the low-lithium gallate in such experiments, however, complicates the interpretation of their results.

The fact that the high temperature form of gallia appears to be monotropic tempts one to question the usual assumption that alpha alumina is also monotropic. However, to decide definitely whether or not a reversal in the direction of the heat of transition would be expected in the alumina system, requires more detailed knowledge of the crystals than is available at present. It is possible that the exothermal effects near 1000° shown in Curves II and III of Fig. 2 result from crystallization within a phase immediately prior to the theta-alpha transition. The extremely small crystallite size of theta alumina may permit this. A small endothermal effect occurring near the same temperature might then be obscured by the larger exothermal effect. The very rapid falling off of the second peak of Curve II suggests that such an effect might be present. The experiments are by no means conclusive in this respect, however, the more work is indicated.

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(15) Presumably the ammonium fluoride decomposes to ammonia, which is evolved, and hydrogen fluoride, which reacts with some of the alumina to form very well-dispersed aluminum fluoride, which then serves as the mineralizing agent.

(16) This is true gamma according to the designation of Stumpf, *et al.*,[4] not to be confused with the older designation which included all of the anhydrous phases between the hydrates and corundum (see Introduction). The pattern was diffuse, indicating very small crystallite size.

(17) G. E. F. Lundell and J. I. Hoffman, *J. Research Natl. Bur. Standards*, **15**, 409 (1935).

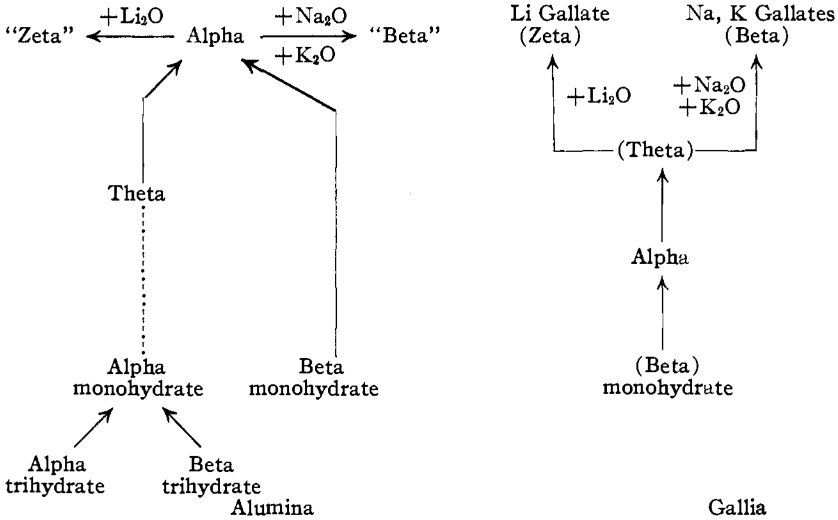

Fig. 3.—Transformations in the alumina and gallia systems. The gallia phases in parentheses are so designated to show the relationship to the alumina phases.

It is seen from Fig. 3 that no well-crystallized gallium oxide was found that did not have an exact counterpart in the alumina system. The compound that Laubengayer and Engle assumed was a trihydrate does not fit into the scheme; since the pattern they reported does not resemble either the alpha or beta alumina trihydrates—the only ones recognized in the alumina system. This by itself does not rule out the existence of a hydrate unique to the gallium system, and quite possibly those workers have prepared one. However, in view of the fact that we were unable to reproduce their results, it would be well to withold acceptance of this hydrate until conditions for its formation are more definitely established.

The low-alkali gallates, whose preparation is given here, have not been reported before. The character of their Debye–Scherrer patterns, and the alkali contents determined analytically, leave no doubt that they are completely analogous to the so-called "beta" and "zeta" aluminas. The manner in which these compounds were formed warrants some consideration. Obviously some alkali oxide was required. This must have been formed in small amounts by the reaction of part of the gallium oxide with the alkali halides. (In no case was all of the original oxide recovered.) It was fortuitous that this reaction took place to just the right extent. If it had proceeded much farther with the formation of considerable alkali oxide, the final product would undoubtedly have been the 1:1 alkali gallate, $MGaO_2$, whereas extensive reaction would, of course, have converted most of the original oxide to halide. This latter situation obtained when alumina was added to sodium fluoride. The only product isolated was cryolite, Na_3AlF_6.

Goldsmidt, *et al.*, designated the theta-like gallia as beta because some similarity in position and in intensity of the lines of the gallia pattern to those of the so-called "beta" aluminas suggested a structural relationship between them, though the gallia was stated to be of lower symmetry. The similarity is seen in Fig. 1. It should be noted, however, that the one very intense line near the origin of the so-called "beta" patterns is completely missing from the patterns of the theta-like oxide. If there is, indeed, a structural relationship between theta and the alkali gallates, this would help in explaining how the gallates are formed by the addition of an alkali oxide to the theta-like form. In the alumina system, however, we find a discrepancy, for the "beta" aluminate is ordinarily formed at temperatures where corundum is stable rather than theta. It is not unreasonable to assume that corundum reverts to a transient theta structure before becoming the aluminate.

Summary

1. No crystal phase of gallia was found which does not have an exact counterpart in the alumina system.

2. Suitable conditions were found for preparing well-crystallized gallia monohydrate and alpha gallia.

3. The high-temperature form of gallia, which bears the designation beta in the literature, has been shown to be isomorphous with theta alumina.

4. Sodium, potassium, and lithium gallates have been prepared whose structures are completely analogous to the corresponding compounds in the alumina system that bear the names "beta" and "zeta" in the literature.

5. Thermal studies have shown that a considerable evolution of heat accompanies the transition from alpha gallia to the theta-like form, indicating that alpha gallia is metastable in the temperature range considered. A large heat of crystallization was evolved when amorphous alumina crystallized to gamma. A very large exothermal effect was observed when gamma alumina transformed to corundum. The last effect is not readily explained.

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