

electrolysis, accords, at least qualitatively, with a conception reached from an earlier study of palladium. This conception is that hydrogen when evolved electrolytically enters the metal of the electrode in a transitional form, which produces a diminution of the resistance of the metal; and this transitional form, in the cases in which the gas in question is largely occluded, passes gradually into another, which has the opposite effect upon the resistance. Indications have also been obtained that the conduct of oxygen is similar to that of hydrogen.

The quantity of the transitional form present when continued electrolysis has led to a steady state of resistance, is dependent upon the current density. In the case of hydrogen, at least, it may reach very high values. The consequent diminution of electrical resistance is also large in the case of hydrogen, but much smaller in that of oxygen, when the current densities are the same.

The transitional form of hydrogen appears to be responsible for the major part of the changes of dimensions produced in palladium by electrolytic occlusion.

In the more persistent, or "alloy" form, the hydrogen is firmly held by palladium up to a critical temperature which has not been determined, but which lies probably not far from 300°. At this temperature hydrogen begins to be evolved rapidly.

The foregoing observations are of interest because of the important role in the mechanism of the electrode processes, which they seem to make it necessary to assign to reactions occurring within the electrode.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY.]

### GALLIUM.<sup>1</sup>

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This article deals with the spectroscopic detection of gallium, indium, and zinc; the purification of gallium; the determination of gallium, and of gallium, indium, zinc, and aluminum in the presence of one another; and the preparation and properties of two new salts of gallium, and the properties of some salts that had previously been prepared.

#### Material.

The crude material employed in this investigation consisted of about 35 g. of an alloy consisting chiefly of gallium and indium, which was generously presented to us by Mr. Kurt Stock, Superintendent of the Bartlesville

<sup>1</sup> This article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by J. Allington Bridgman in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Zinc Company, Bartlesville, Oklahoma.<sup>1</sup> It would have been of interest to determine the percentages of gallium and indium in the alloy before undertaking the preparation of pure gallium from the material, but this was not possible because at the beginning of the investigation no method of accurately determining gallium and indium in the presence of each other was known. Results that were obtained during the process of purification of the gallium indicated, however, that the alloy contained not over 8% of indium, somewhat less than 1% of zinc, and traces of cadmium and copper.

### Spectroscopic Detection of Gallium, Indium and Zinc.

Before taking up the study of the purification of gallium, it was necessary to develop some method by means of which the purity of the various preparations of gallium might be ascertained as the work proceeded. The two elements whose presence in the gallium was chiefly to be expected were indium and zinc, because they are associated in largest amount with the gallium in the alloy. The spectroscopic examination of the material naturally suggested itself as the best method to employ, and inasmuch as no statements have hitherto appeared in the literature as to the delicacy of the spectroscopic detection of these 3 elements in the presence of one another, this subject was first investigated. Two types of spectra were studied: spark spectra, which were observed with the eye, and arc spectra, which were photographed.

### The Detection of Gallium and Indium by Means of Their Spark Spectra.

There were needed for these tests a solution of a salt of gallium that was substantially free from indium, and a solution of a salt of indium free from gallium.

The first of these was prepared by dissolving a portion of the original alloy in aqua regia, and freeing the solution from indium by adding an excess of potassium hydroxide and boiling the solution.<sup>2</sup> The precipitated indium hydroxide which, as we later ascertained, carries with it some gallium hydroxide, was removed by filtration, and metallic gallium was separated from the alkaline filtrate by electrolysis. The metal was dissolved in aqua regia, and ammonium hydroxide was added. The precipitated hydroxide was washed, dried and ignited, and yielded 1.0819 g. of gallium oxide. This product was dissolved in 10 cc. of conc. hydrochloric acid, and the resulting solution was diluted to 25 cc. This solution of gallium chloride, which contained 0.0322 g. of gallium per cc., was used in the spectroscopic tests.

<sup>1</sup> For descriptions of the separation of this alloy from spelter, see Hillebrand and Scherrer, *J. Ind. Eng. Chem.*, 8, 225 (1916); Browning and Uhler, *Am. J. Sci.*, 41, 351 (1916).

<sup>2</sup> Lecoq de Boisbaudran, *Compt. rend.*, 95, 410 (1882).

A solution of indium chloride free from gallium was prepared by dissolving in water a portion (0.7988 g.) of the pure indium chloride prepared by F. C. Mathers<sup>1</sup> in this laboratory in connection with his work on the atomic weight of indium. The solution was diluted to 25 cc. and hence contained 0.0166 g. of indium per cc.

The apparatus that was employed for the observation of the spark spectra consisted of a Krüss spectroscope, induction coil capable of giving a spark about one inch in length, and small glass cups for holding the solutions. The cup was made by fusing a piece of platinum wire into the end of a piece of glass tubing 7 mm. in diameter, and then cutting off the tube about 6 mm. from the closed end. Such a cup holds about three drops of liquid.

**Detection of Gallium.**—Twenty cc. of hydrochloric acid was added to 80 cc. of water. Into this diluted acid one drop of the solution of gallium chloride (1 cc. = 0.0322 g. Ga) was introduced. Three drops of this very dilute solution of gallium chloride were then brought into one of the glass spark cups, and the spark spectrum of the solution was examined. The best results were obtained with a short spark and a heavy current through the primary of the coil. A second drop of the solution of gallium chloride was then added to the diluted hydrochloric acid, and a sample of the resulting solution was spectroscopically examined as before. This was repeated until the limits of the test were established. The following table gives the lower limits of concentration at which the two principal lines of gallium could be thus detected:

TABLE I.  
Spectroscopic Detection of Gallium.

No.	Grams of gallium in 100 cc.	Mg. of gallium in spark cup.	Gallium line. $\lambda = 4172$ .	Gallium line. $\lambda = 4033$ .
1.....	0.0030	0.0046	Faint	Not visible
2.....	0.0046	0.007	Distinct	Not visible
3.....	0.0072	0.014	Distinct	Very faint
4.....	0.0154	0.023	Distinct	Distinct

These results show that, under the conditions described, 0.0046 mg. of gallium can be detected by ocular observation of the spark spectrum of a solution of gallium chloride, and that both of the principal lines of the spark spectrum are visible when 0.014 mg. of gallium as chloride is present.

**Detection of Indium.**—The procedure was the same as that for the detection of gallium. The lower limits of concentration at which the two principal lines of indium could be detected were found to be as follows:

TABLE II.  
Spectroscopic Detection of Indium.

No.	Grams of indium in 100 cc.	Mg. of indium in spark cup.	Indium line. $\lambda = 4511$ .	Indium line. $\lambda = 4102$ .
1.....	0.0009	0.0013	Faintly visible	Not visible
2.....	0.0017	0.0026	Distinct	Not visible
3.....	0.0043	0.0065	Strong	Faintly visible

<sup>1</sup> THIS JOURNAL, 29, 485 (1907).

These results show that it is possible, in this manner, to detect 0.0013 mg. of indium, and that both of the principal lines of the spark spectrum of indium are visible when 0.0065 mg. of indium as chloride is present.

**Detection of Indium in the Presence of Gallium.**—It sometimes is the case that the lines of one element are masked or are rendered difficultly visible to the eye when a large amount of another element is present. For this reason the spark spectra of a series of solutions that contained both gallium chloride and indium chloride were examined in order to determine the limit of visibility of the indium spectrum when a preponderating amount of gallium is present. The results are given in Table III.

TABLE III.  
Spectroscopic Detection of Indium in the Presence of Gallium.

No.	Grams in 100 cc.		Mg. in spark cup		Indium line.		% indium relative to gallium.
	of indium.	of gallium.	of gallium.	of indium.	$\lambda = 4511.$	$\lambda = 4102.$	
1	3.12	0.00191	3.1	0.0019	Faintly visible	Not visible	0.06
2	2.91	0.0043	2.9	0.0043	Distinct	Faintly visible	0.15
3	2.89	0.0074	2.8	0.0073	Distinct	Distinct	0.26

From these results it is seen that the delicacy of the method of detecting indium by means of its spark spectrum is almost as great in the presence of a relatively large amount of gallium as it is when indium alone is present. When the gallium in the spark cup amounts to only 3 mg., the presence in it of 0.0019 mg. of indium, 0.06% of the weight of the gallium, may be detected by this method.

**Detection of Gallium in the Presence of Indium.**—The spark spectra of solutions containing minute amounts of gallium chloride and relatively large quantities of indium chloride were next examined to ascertain the delicacy of the test for gallium.

TABLE IV.  
Spectroscopic Detection of Gallium in the Presence of Indium.

No.	Grams in 100 cc.		Mg. in spark cup		Gallium line.		Per cent. gallium relative to indium.
	of indium.	of gallium.	of indium.	of gallium.	$\lambda = 4172.$	$\lambda = 4033.$	
1	1.63	0.0030	1.63	0.0030	Very faint	Not visible	0.18
2	1.61	0.0046	1.61	0.0046	Distinct	Not visible	0.28
3	1.52	0.0134	1.52	0.0134	Distinct	Very faint	0.83
4	1.47	0.0175	1.47	0.0175	Distinct	Distinct	1.12

The delicacy of this method of detecting gallium is thus seen to be almost as great when a preponderating amount of indium is present as it is when gallium alone is examined. When the indium in the spark cup amounts to only 1.63 mg., the presence in it of 0.003 mg. of gallium, 0.18% of the weight of the indium, may be detected by this method.

#### The Detection of Traces of Indium and Zinc by Means of Their Arc Spectra.

Although the spark spectrum was found to yield very satisfactory results in the detection of minute amounts of gallium and indium, it did not prove

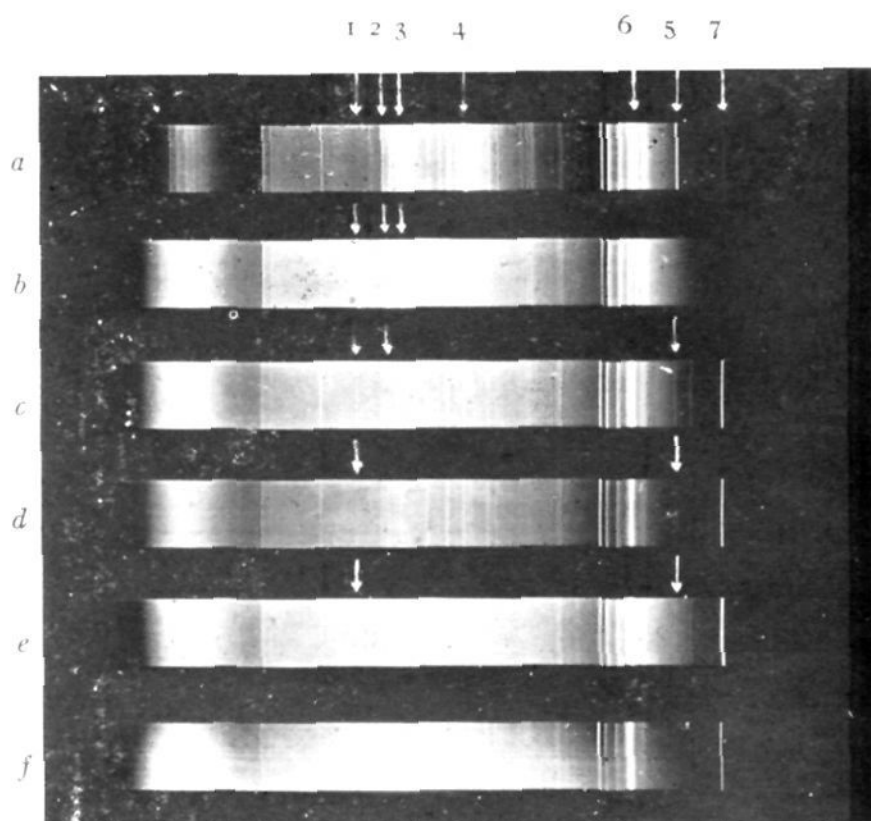


Fig. 1.

1 Zn  $\lambda = 4811$ . 2 Zn  $\lambda = 4722$ . 3 Zn  $\lambda = 4680$ . 4 In  $\lambda = 4511$ .  
 5 In  $\lambda = 4102$ . 6 Ga  $\lambda = 4172$ . 7 Ga  $\lambda = 4033$ .



to be sufficiently sensitive for the detection of traces of zinc. For this reason the arc spectra of different mixtures of gallium, indium, and zinc were next studied, the spectra in this series of observations being photographed on non-halation orthochromatic plates manufactured by the Eastman Kodak Company. A pyrogallol developer prepared according to the formula of the same company gave excellent results.

Both a Steinheil grating spectrometer and a Hilger wave-length spectrometer were used in the beginning, but the Hilger instrument, being found to give much the stronger lines, was exclusively employed in the later measurements.

The arc was formed between graphite rods 12 mm. in diameter. The upper rod was roughly pointed at the end. A depression was hollowed out in the upper end of the lower terminal. Before these electrodes were used, they were treated first with boiling hydrochloric acid and then with boiling water. A solution of the material to be examined was placed in the depression in the end of the lower rod and was then evaporated to dryness.

It was found that the faint lines due to minute amounts of zinc and indium showed most distinctly on the plates when the slit was fairly wide and the exposures were quite short, from 5 to 10 seconds. Longer exposure strengthened the lines of the spectrum somewhat, but this was more than offset by the greater effect upon the plate of the continuous spectrum from the arc, which seriously reduced the contrasts in the photographs.

The indium line,  $\lambda = 4102$ , and the zinc line,  $\lambda = 4811$ , serve best to show the presence of these two elements because none of the strong lines due to the electrodes lies near them.

Fig. 1 shows photographs of the arc spectra of our preparations of the chlorides of indium, zinc, and gallium, and of mixtures of gallium chloride with the other two salts: *a* is the spectrum from indium chloride that contained a slight amount of gallium; *b* is the spectrum from zinc chloride; *c* is the spectrum from 0.021 g. of gallium chloride (see *f*) to which 0.03% of zinc and 0.03% of indium had been added; *d* is the spectrum from 0.021 g. of gallium chloride (see *f*) to which 0.01% of zinc and 0.01% of indium had been added; *e* is the spectrum from 0.021 g. of gallium chloride (see *f*) to which 0.005% of zinc and 0.005% of indium had been added; *f* is the spectrum from 0.021 g. of gallium chloride that had been purified by double distillation of the chloride (see page 1543).

In *c* the lines of zinc,  $\lambda = 4811$  and  $\lambda = 4722$ , and the indium line,  $\lambda = 4102$  (0.03% of each element being present), are distinctly visible. In *d*, where the amounts of zinc and indium are 0.01%, the chief lines of these elements are still discernible. In *e* the amounts of zinc and indium

are each only 0.005% of the gallium present. The lines  $\lambda = 4811$  (zinc) and  $\lambda = 4102$  (indium) are here just visible.

These results furnish conclusive evidence that the gallium chloride which we prepared by double distillation of the compound in the manner later to be described, could not have contained as much as 0.005% of either indium or zinc.

#### THE PURIFICATION OF GALLIUM.

##### Preliminary Examination of the Alloy of Gallium and Indium.

The alloy received from Mr. Stock was found to be rather slowly attacked by either nitric acid or hydrochloric acid alone. Hot aqua regia acted vigorously upon it, but complete solution resulted only after quite prolonged treatment.

One and three-tenths g. of the alloy was placed in a solution of 7 g. of potassium hydroxide in 50 cc. of water, and the liquid was heated to boiling. A rapid evolution of gas resulted, and this was accelerated when a piece of platinum was placed in contact with the alloy; yet even after the solution had been boiled for 15 hours, a considerable portion of the metal remained undissolved. This residue was next dropped into molten potassium hydroxide. The two substances reacted so violently that this method of treatment was abandoned because of the comparatively small amount of material at our disposal. It is possible, however, that this reaction might rapidly convert the gallium into a soluble compound of that element, and thus separate it from indium in a single, simple operation.

To ascertain approximately the amount of indium in the alloy, 6.6207 g. of the material was dissolved in aqua regia and the solution was boiled for several minutes with an excess of a solution of potassium hydroxide. The precipitate which resulted was collected on a filter, and yielded on ignition 0.6486 g. of oxide which, had it been pure indium oxide, would have been equivalent to 0.5365 g. of indium. This corresponds to 8.13% of indium in the alloy. Spectroscopic examination showed, as was expected, that the precipitate was not pure indium, and, moreover, that it contained gallium. No further attempts were made at this stage of the investigation to determine the composition of the alloy because of the lack of analytical methods. The procedure for the quantitative separation of the constituents of the alloy that will be described later was developed only after all of the alloy had been dissolved and the gallium had been separated.

##### The Electrolysis of Solutions Containing Gallium.

Boisbaudran<sup>1</sup> obtained metallic gallium by electrolyzing a solution of basic gallium sulfate in potassium hydroxide. Schucht makes the brief statement<sup>2</sup> that "gallium, like zinc, is thrown down completely at the

<sup>1</sup> *Ann. chim. phys.*, 10, 100 (1877).

<sup>2</sup> *Berg. und Hüttenmännische Zeit.*, 39, 121 (1880); *Chem. News*, 41, 280 (1880).



negative pole in a pure state." Ehrlich<sup>1</sup> electrolyzed a "galliferous alkaline solution" from which metallic gallium was deposited in the form of fine needles. Kunert<sup>2</sup> electrolyzed a solution of gallium hydroxide in potassium hydroxide; the current from 10 large Bunsen cells deposited 0.1 g. of pure gallium per hour.

Browning and Uhler<sup>3</sup> electrolyzed a solution of gallium hydroxide in sodium hydroxide, the metal separating as liquid globules at ordinary temperature, and in the form of a "tree" when the electrolyte was cooled to about 0°.

Experimental examination of the deposition of gallium by electrolysis of a solution of gallium hydroxide in a solution of fixed alkali hydroxide showed that the metal is separated very slowly. Moreover, it seemed probable that gallium electrolytically deposited from a strongly alkaline solution would be contaminated with the alkali metal, a supposition that seems to be supported by the observation of Boisbaudran and Jungfleisch<sup>4</sup> that gallium, thus prepared, decrepitates in hot water, and by the statement of Browning and Uhler that the gallium "trees" liberate a gas when brought into contact with water. For these reasons, it was sought to develop a method for the electrolytic deposition of metallic gallium from an acid solution, and to then study the separation of gallium from indium and zinc by this means.

The electrolytic deposition of indium from acid solution was satisfactorily developed<sup>5</sup> a comparatively short time ago. This element is the immediate group analog of gallium. For this reason it seemed probable that the method that gave excellent results with indium, the electrolysis of an aqueous solution of the sulfate, might prove applicable to the deposition of gallium. If the electrolyte contained both gallium and indium, it appeared to be reasonably certain that sharp separation of the two elements would not be effected by a single electrolysis, but it was hoped that fractional electrolysis would gradually first remove indium, and would finally yield deposits of gallium substantially free from indium.

A mixture of the hydroxides of gallium and indium was dissolved in sulfuric acid, 10 cc. of sulfuric acid (sp. gr., 1.4) was added in excess, and the solution was diluted to 350 cc. It was then electrolyzed with a current of 4 amperes, the cathode of sheet platinum being 8 x 3 cm. At the end of 3 hours and 40 minutes 0.0418 g. of metal had been deposited on the cathode. This plate was then placed in another beaker containing

<sup>1</sup> *Chem. Ztg.*, **9**, 78 (1885); *Chem. News*, **51**, 115 (1885).

<sup>2</sup> *Chem. Ztg.*, **9**, 1826 (1885); *Ber.*, **19**, 7R (1886).

<sup>3</sup> *Am. J. Sci.*, **42**, 389 (1916).

<sup>4</sup> *Compt. rend.*, **86**, 475 (1878).

<sup>5</sup> Dennis and Geer, *THIS JOURNAL*, **26**, 437 (1904); Thiel, *Ber.*, **37**, 175 (1904); Mathers, *THIS JOURNAL*, **29**, 485 (1907).

dil. sulfuric acid, and was made the anode. The deposit readily dissolved as sulfate.

The spark spectrum of this solution showed gallium and indium lines of about equal intensity. A second deposit obtained from the first solution by electrolysis lasting 3 hours weighed 0.0108 g. This was dissolved from the platinum cathode in the manner above described. The spark spectrum of its solution showed the gallium lines much more strongly than those of indium. The residual solution gave a strong spark spectrum of gallium but no indium lines.

The method was next used with a larger portion of material, 6.4113 g. of the original alloy being employed. This was dissolved in dil. (1 : 10) sulfuric acid by immersing the alloy in 75 cc. of the acid, making contact with it by means of a platinum wire that projected slightly through the end of a glass tube, inserting in the acid the same platinum cathode as was used before, and electrolyzing with the alloy as anode. The liquid alloy and the solution were stirred with a jet of air throughout the electrolysis. A potential difference of about 12 volts was maintained between the electrodes. This gave at the beginning a current of about one ampere, but when nearly all of the alloy had been converted to sulfate, the current had dropped to about 0.1 ampere. A slight deposit which formed on the cathode during the solution of the alloy was found to consist of indium, gallium and zinc.

The solution of the sulfates of these three metals, obtained in this manner by electrolysis, was evaporated to dryness, the residue was dissolved in water, and the solution was diluted to 100 cc. This was electrolyzed, the anode being a sheet of platinum, and the cathode a platinum rod that projected about 12 mm. into the solution. The solution was stirred by a jet of air. A current of four amperes yielded in two hours a deposit that weighed 0.0410 g.

The spark spectrum of a solution of this deposit in hydrochloric acid showed strong lines of gallium and indium, but the lines of zinc were only faintly visible. The first solution was further electrolyzed for 2 hours and 10 minutes longer at 0.6 to 0.8 ampere, 0.0861 g. being deposited on the cathode. The spark spectrum of the solution of this deposit in hydrochloric acid again showed strongly the lines of gallium and indium, and very faintly the lines of zinc. A further electrolysis of one hour and forty minutes at 0.6 ampere yielded 0.0545 g. of deposit, which, when dissolved, showed strong lines of indium and gallium, whereas the zinc lines were scarcely visible.

A portion of the original solution from which these 3 deposits had been separated was concentrated, and its spark spectrum showed strong lines of gallium, faintly visible lines of indium, but no lines of zinc.

Ten further fractional electrolyses of this solution were then made,

the time required for each deposit varying from 1.5 hours to 5 hours with a current of from 0.6 to 1.0 ampere. Each deposit was dissolved in hydrochloric acid and the spark spectrum of the resulting solution was examined. In every case strong gallium lines were seen, but the spectrum of indium became gradually weaker, being scarcely visible in the last fractions.

Seven more fractions were deposited on a rotating rod of platinum which was bent into a wavy form for the purpose of stirring the solution. In the later fractions in this last series the gallium lines were strong and the  $\alpha$ -line of indium was faintly visible.

These results show that by means of fractional electrolysis of a slightly acid solution of the sulfates of gallium, indium, and zinc, zinc may be removed entirely, and gallium may be obtained almost free from indium.

Moreover the electrolytic deposition of a small amount of metal from a slightly acid solution of the sulfates and the subsequent examination of the spark spectrum of the solution of this deposit in hydrochloric acid affords a much more delicate qualitative test for traces of indium and zinc than can be obtained by direct examination of the spark spectrum of the original solution.

For use in the further investigation of methods for the separation of gallium from accompanying elements, about 25 g. of gallium in the form of various salts was treated in such a way as to remove most of indium and zinc associated with it. This was done by boiling the solution with an excess of the solution of sodium hydroxide to remove indium as completely as possible. After the indium hydroxide had been removed by filtration, the solution was made acid and zinc was precipitated by the addition of a solution of potassium mercuric thiocyanate (see page 1548). The precipitate of zinc mercuric thiocyanate was filtered off and the mercury in the filtrate was precipitated as sulfide and was removed by filtration. The gallium in the filtrate was thrown down as the hydroxide by ammonium hydroxide. This gallium hydroxide was dissolved in sulfuric acid and the solution was diluted to 800 cc. The solution then contained about 25 g. of gallium as sulfate. The deposition of gallium by electrolysis from this solution under varying conditions showed certain interesting phenomena. When a portion of the solution was electrolyzed with a cathode consisting of a rotating rod of platinum, the liberated gallium formed a black suspension. Another portion of the solution was treated with sufficient sodium hydroxide to redissolve the gallium hydroxide, and this resulting solution was electrolyzed with a cathode consisting of a sheet of platinum 8 x 3 cm., the current being from 2 to 4 amperes. During this electrolysis a portion of the metal formed a black suspension that settled very slowly. The larger part of the metallic gallium was deposited on the cathode and as the solution was kept above the melting

point of the metal, globules of the gallium dropped from the cathode into a glass cup immediately beneath it. It was noticed that while the concentration of the gallium in this solution was still high, a layer of reddish liquid collected at the bottom of the beaker at the end of nearly every period of the electrolysis. The electrolysis was carried on only during the day and this reddish liquid collected to the depth of about 12 mm. during the night. The colorless liquid above this red layer was decanted through a filter and the red solution was then poured upon the filter. The red liquid could be seen flowing through the stem of the funnel, but when this struck the colorless liquid below, the red color disappeared and a black suspension of metallic gallium formed in the liquid. When the concentration of gallium in the electrolyte became less, the red liquid ceased to form. It seems probable that the red color is due to a colloidal suspension of gallium which perhaps exists in this form only in a solution that contains a definite concentration of sodium hydroxide.

When the metal that was deposited by electrolysis was allowed to stand overnight under water, it became coated with a black film. If this metal is then placed in boiling, dilute nitric acid for a time, it regains its lustre and retains it either under water or in the air. After the gallium had been treated for some minutes with boiling dil. nitric acid, it was washed with water, was then caused to solidify by touching it with a particle of solid gallium, and this metal was kept over calcium chloride until used for the chlorination described below.

#### The Distillation of Gallium Chloride.

Zinc chloride boils at  $730^{\circ}$ . Indium trichloride volatilizes very slightly at  $440^{\circ}$ , and only slowly at  $600^{\circ}$ . Gallium trichloride melts at  $75.5^{\circ}$  and boils at 215 to  $220^{\circ}$ . These facts warranted the study of the fractional distillation of the anhydrous chlorides of zinc, indium, and gallium, with a view to ascertaining whether gallium chloride free from zinc and indium might be thus prepared.

A preliminary chlorination and distillation was made with a portion of the original alloy. A glass tube of about 2 cm. diameter was slightly bent in the middle, and a portion of the alloy (3.3962 g.) was placed in the lowest part of the bent tube. A small oven constructed of asbestos board<sup>1</sup> was placed around this portion of the tube. Dry chlorine was passed through the tube and the oven was heated to  $240^{\circ}$ . Some of the resulting chlorides distilled and condensed in the cold portion of the tube beyond the oven. The spark spectrum of this material showed faint lines of indium and zinc, and strong lines of gallium.

An apparatus of the form shown in Fig. 2 was then constructed, the tube A being of Jena glass. About 4 g. of the alloy was placed in A, dry chlorine was passed into the tube and the lower end of A was heated to

<sup>1</sup> Dennis, "Gas Analysis," p. 202.

start the reaction between the alloy and the chlorine. The heat of reaction then suffices to complete the chlorination and it causes some of the

chloride to distil to the upper portion of the tube, nearly to the side-arm. After chlorination was complete, a Snowdon electric furnace<sup>1</sup> was brought up around the tube A and this was then heated to about 230°. This caused a portion of the chlorides to distil

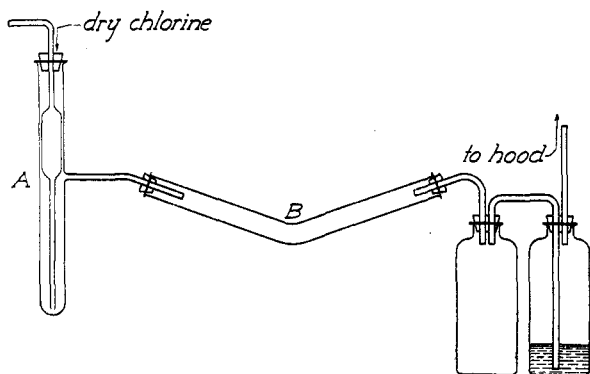


Fig. 2.

over into B. The temperature was raised to 250° and the distillation was continued for about one hour. The spark spectrum of the material that condensed in B showed the presence of a preponderating amount of gallium, and the lines of indium were only faintly visible. The material remaining in the tube A showed strong lines of gallium, indium and zinc.

Purified gallium chloride from the tube B (Fig. 2) was again distilled in chlorine, the side-arm for the apparatus in this case being fused to a tube

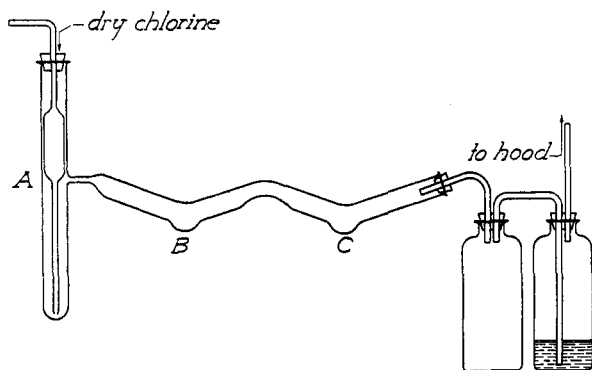


Fig. 3.

of Jena glass that had two depressions, B C (Fig. 3). Gallium chloride was melted and poured into the tube A. Dry chlorine was passed through the apparatus and A was heated to from 220 to 240° in a Snowdon furnace. Gallium chloride that condensed in B was then distilled

over into the depression C by heating the tube B with the flame of a Bunsen burner. The spark spectrum of the chloride that condensed in C showed very faintly the  $\alpha$ -line of the indium spectrum when a large amount of the material was placed in the spark cup.

The above preliminary experiments gave reason to suppose that several successive distillations of gallium chloride in a current of chlorine would free it from indium and zinc. These distillations were carried out in a tube

<sup>1</sup> *Cornell Chemist*, 4, 13 (1914).

of Pyrex glass of about 20 mm. external diameter, bent into a series of 9 depressions (Fig. 4). The tube was constricted between the depressions. 5.3978 g. of the original alloy was placed in the first bend A, and dried chlorine was conducted through a glass tube, the end of which dipped

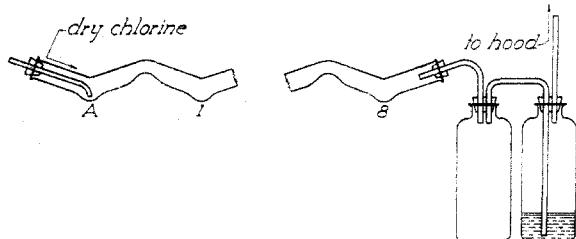


Fig. 4.

below the surface of the alloy. The reaction between the chlorine and alloy was started by heating the latter with a Bunsen flame. The action was at first violent, the union of the chlorine with the metals being accompanied by the emission of a bluish light and a play of incandescent particles throughout the tube in the neighborhood of the sample. When a layer of the molten chloride had formed above the metal, the chlorination proceeded quietly.

After the metals in the alloy had been completely converted to chlorides, the portion of the tube marked A was surrounded by the asbestos oven mentioned above, and was heated from 220 to 250°. A portion of the chlorides distilled over into depression 1. The chloride was successively distilled in this manner from one section to the next until it finally was collected in the last section, No. 8, of the tube. The distillation of the chloride from one depression to the next was effected by slipping over the glass tube the barrel of a porous cup from which the bottom had been cut off, and which had been wrapped with nichrome ribbon so that it could be electrically heated. This heating tube was about 7 cm. in diameter and 15 cm. long. In distilling the chloride from section 1 to section 2, the heating tube was placed around depression 1, and the current was adjusted to raise the temperature to 254°. In the succeeding distillations the heating tube was moved along until it covered the section containing the chloride and the current was adjusted to give a temperature ranging from 235 to 245°. A slow current of chlorine was passed through the tube during the distillations. The spark spectrum of the material which condensed in section 8 of the tube, and which consisted chiefly of gallium chloride, still showed faintly the lines of indium and zinc. The indium spectrum was stronger than from the material obtained in the preceding experiment.

The failure to obtain pure gallium chloride by these 8 distillations may have been due either to (1) insufficient vertical rise between the different depressions in the distilling tube, which might allow the chlorides of zinc and indium to be carried along mechanically; or to (2) overheating during the chlorination of the alloy, which might cause either the distillation of

some zinc chloride, or the distillation of indium monochloride or indium dichloride before the conversion of the indium to the trichloride was complete; these lower chlorides of indium would first be formed, and they are more volatile than the trichloride.

To remove the first of these possible difficulties an apparatus of different form was constructed (Fig. 5). This was blown entirely of Jena glass and the tubes A and D were fitted at the top with widened inlet tubes that were ground into the necks of the two distilling tubes. The gallium chloride from the two preceding experiments, which was nearly free from zinc and indium, was

melted and poured into the tube A. Glass wool that had previously been washed with hydrochloric acid and carefully dried was inserted in A and D around the inlet tubes. The chlorides were distilled from A into D in

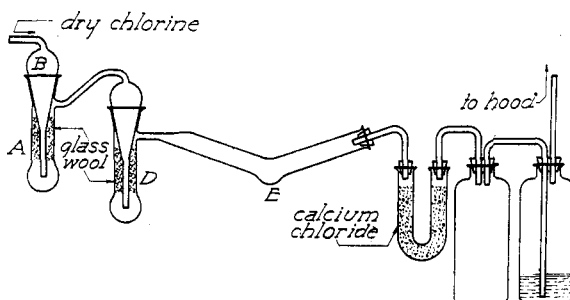


Fig. 5.

a current of dry chlorine by heating A with a Snowdon furnace from 230 to 255°. The material that condensed in D showed the lines of neither zinc nor indium. This chloride was removed from D, dissolved in water, and its solution was electrolyzed with a rotating rod of platinum as cathode until a small amount of metal was deposited. The spark spectrum of the solution of this deposit in hydrochloric acid showed the lines of neither zinc nor indium.

Because of the success of this method of distillation in freeing gallium chloride from indium and zinc, it was decided to convert the large amount

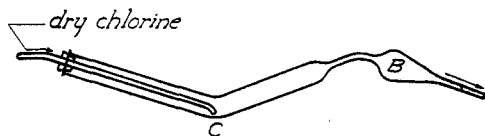


Fig. 6.

of metallic gallium that had been prepared by electrolysis (see page 1538) to the chloride, and to subject this chloride to all distillations. This gallium was nearly free from indium

and zinc. The chlorination of the metallic gallium was carried out in the bent tube C (Fig. 6) of Jena glass that was fused to the inlet tube B of the flask A (Fig. 5). Metallic gallium was placed at the depression C and the chlorination was made as described above, B not being connected with A during the procedure. This avoided the possibility of the distillation of zinc chloride and lower chlorides of indium into A and D during the chlorination of the metal. After chlorination was complete, the tube B was inserted into the neck of the

flask A, and C was warmed to such a temperature as caused the chlorides to melt and flow down into A. The current of chlorine was continued through the apparatus and A was heated in a Snowdon furnace while the chloride distilled through the glass wool from A into D. When all of the chlorides had condensed in D, the heating of A was discontinued and the furnace was brought up around the tube D and the chloride was again distilled through the glass wool into the tube E, where it condensed.

In the first chlorination and double distillation, 5.009 g. of the purified metallic gallium was employed. A slight leakage of the vapor of gallium chloride into the outer air took place through the ground joints at the top of A and D. This was stopped in the next distillation by sealing these joints with water glass.

A second portion of gallium weighing 9.2982 g. was chlorinated and distilled and then a third sample weighing 8.4075 g. was later chlorinated and distilled.

The residue left in A after the first two samples had been distilled over was tested for the presence of zinc with the microscope, using solid potassium mercuric thiocyanate,<sup>1</sup> and zinc was found to be present.

The residue remaining in C where the chlorination was carried on and the chloride that condensed in D gave no test for zinc by this method. This method, however, has been found to be not wholly reliable for the detection of minute amounts of zinc in the presence of large amounts of gallium.<sup>2</sup>

In an attempt to increase the delicacy of this microscopical test for zinc, the gallium chloride was first volatilized at 250° and the test was then applied to the residue, but the results were not successful. The most satisfactory method for determining the purity of the gallium chloride prepared by the above method was found to be the photographing of the arc spectrum of the material (see page 1535). This redistilled gallium chloride was found to be spectroscopically free from zinc and indium, and by the method above described it was shown that it could not contain more than 0.005% of either of these two elements. Two successive distillations of gallium chloride in the apparatus shown in Fig. 4 therefore yield a product of high purity.

#### THE DETERMINATION OF GALLIUM ALONE, AND OF GALLIUM, INDIUM, ZINC AND ALUMINUM IN THE PRESENCE OF ONE ANOTHER.

##### The Determination of Gallium.

Lecoq de Boisbaudran<sup>3</sup> determined gallium by adding to a solution of a salt of gallium an excess of ammonium hydroxide and then boiling

<sup>1</sup> Behrens, *Z. anal. Chem.*, 30, 141 (1891).

<sup>2</sup> Ruth E. Chipman, "The Mercuric Sulfocyanates as Reagents in Microscopic Qualitative Analysis." A thesis presented to the Faculty of the Graduate School of Cornell University, June, 1917.

<sup>3</sup> *Ann. chim. phys.*, [6] 2, 181 (1884).



the solution until it turned litmus paper red. This precipitated the gallium as the hydroxide, and Boisbaudran stated that the presence of salts of the alkali metals or of the alkaline earths did not affect the results. From 1 to 1.5 mg. of gallium per liter of solution was, however, unprecipitated.

Trial was made of this method of Boisbaudran by adding ammonium hydroxide to a solution of gallium chloride that contained about 0.05 g. of gallium oxide. The solution was then boiled and it was found necessary to continue the boiling for from 30 to 45 minutes to effect the removal of the excess of ammonium hydroxide. Although the precipitate of gallium hydroxide was somewhat granular, much of it adhered to the sides of the beaker and could not be detached. Another portion of the solution of gallium chloride was precipitated by ammonium hydroxide after ammonium chloride had first been added. The precipitate in this case was somewhat more gelatinous, but a portion of it adhered firmly to the sides of the beaker.

Because of this difficulty, two other precipitants were next tried, and to render it possible to ascertain the accuracy of these new methods, a solution of gallium of known concentration was prepared from some of the gallium chloride that had been purified by distillation. A sample of this gallium chloride was dissolved in water, an excess of ammonium hydroxide was added, and the resulting gallium hydroxide was washed, dried, and ignited to gallium oxide over a Bunsen flame. This oxide was then pulverized in an agate mortar, was reheated, and was then cooled in a stoppered weighing bottle. 0.6471 g. of this oxide was heated with 1.5 cc. of conc. sulfuric acid, the resulting gallium sulfate was dissolved in water, and the solution was diluted to 250 cc. in a measuring flask. This flask was calibrated to hold 10 times the volume of a 25 cc. buret that was subsequently used to measure portions of the solution.

The first reagent that was used for the precipitation of the gallium was sodium trinitride,  $\text{NaN}_3$ .

**Precipitation of Gallium Hydroxide by Sodium Trinitride.**—Portions of 25 cc. each of the slightly acid solution of gallium sulfate just described were diluted to about 250 cc. Solid sodium trinitride was added to each solution and the solutions were then vigorously boiled for various lengths of time. The resulting precipitates of gallium hydroxide, which settled well, were collected on ashless filters and were washed, dried, and ignited to gallium oxide over the Bunsen flame. The oxide was in each case ignited in a porcelain crucible, was cooled in a desiccator and was then quickly weighed.

In determination No. 3, in which the boiling was continued for 10 minutes, the precipitate adhered somewhat to the sides of the beaker, and this explains the low weight of gallium oxide. When the solution

was boiled for a shorter time, Nos. 1, 2 and 4, the results were fairly satisfactory in each case and the presence of as much as 15 g. of ammonium chloride did not affect the accuracy of the method. The use of sodium trinitride, however, is open to two objections: the powerful physiological action of the hydronitric acid that is liberated when the solution is boiled, and the difficulty of obtaining on the market a supply of sodium trinitride of satisfactory purity. For these reasons sodium sulfite was substituted for sodium trinitride.

TABLE V.  
Precipitation of Gallium Hydroxide by Sodium Trinitride.

No.	Weight of $Ga_2O_3$ taken. Gram.	Weight of $NaN_3$ added. Gram.	Time of boiling. Minutes.	Other salts added.	Weight of $Ga_2O_3$ found. Gram.
1.....	0.0647	0.5	1-2	None	0.0650
2.....	0.0647	0.5	5	None	0.0660
3.....	0.0647	0.5	10	None	0.0623
4.....	0.0647	0.5	4	15 g. $NH_4Cl$	0.0657

**Precipitation of Gallium Hydroxide by Sodium Sulfite.**—A portion of the same solution as was used above was precipitated by adding about one g. of solid hydrated sodium sulfite to the solution and boiling for 4 minutes. The precipitate was easily collected by filtration, but ignition to the oxide showed that precipitation had not been complete. 0.0784 g. of gallium oxide was present in the solution and the precipitate weighed 0.0728 g. A further small amount of sodium sulfite was added to the filtrate which was again boiled, and the precipitate yielded on ignition 0.0054 g. of gallium oxide. In the precipitation of further portions of the solutions 1.5 g. of sodium sulfite was added in each case. The results are given in Table VI.

TABLE VI.  
Precipitation of Gallium Hydroxide by Sodium Sulfite.

No.	Weight of $Ga_2O_3$ taken. Gram.	Time of boiling. Minutes.	Other salts present.	Weight of $Ga_2O_3$ found. Gram.
1.....	0.0647	10-12	10 g. $NH_4Cl$	0.0649
2.....	0.0647	6-7	10 g. $NH_4NO_3$	0.0661
3.....	0.0647	7	10 g. $(NH_4)_2SO_4$	0.0641

The results are quite satisfactory even when fairly large amounts of ammonium salts are present. It was found that the solutions could be boiled for a much longer time than when sodium trinitride was used, without causing the precipitate to adhere to the walls of the beaker.

A slight modification of this method of precipitation which avoids the introduction of sodium salts into the solution was later employed in the determination of gallium in a sample of caesium gallium selenate alum (see page 1558). A solution of ammonium sulfite, which was prepared by saturating ammonium hydroxide with sulfur dioxide, was substituted

for solid sodium sulfite. A value of 13.33% of  $\text{Ga}_2\text{O}_3$  as against a calculated value of 13.31% in the alum was obtained.

In making weighings of gallium oxide it was observed that this substance, like the oxides of aluminum and indium, is quite hygroscopic, and in all of the analyses that are later described the crucible that contained the gallium oxide was placed in a stoppered weighing bottle as soon as it was removed from the desiccator, and was weighed in that bottle.

In the determinations of gallium described below, gallium was precipitated by sodium sulfite, the procedure being as follows: If ammonium chloride or hydrochloric acid is not already present in the solution, a few cc. of hydrochloric acid is added, the solution is then made slightly alkaline with ammonium hydroxide, and about 1.5 g. of hydrated sodium sulfite is dissolved in the solution. This weight of sodium sulfite suffices for the precipitation of 0.1 g. of gallium oxide, and the amount of gallium should usually not be permitted to exceed this amount because otherwise the precipitate of gallium hydroxide is so bulky as to render difficult its filtration and washing. After the sodium sulfite has been dissolved in the solution, hydrochloric acid is carefully added until the solution is distinctly acid to litmus paper. The solution is then vigorously boiled for about 6 minutes. The resulting precipitate of gallium hydroxide is allowed to settle and is then filtered on an ashless filter paper and washed until the wash water is free from chlorides. The precipitate is dried and is ignited with the paper over the Bunsen flame in a porcelain crucible. The crucible is placed in a desiccator while still warm and is afterwards transferred to a stoppered weighing bottle for weighing.

The precipitation of gallium by this method is usually complete, but it nevertheless is advisable to add a small amount of sodium sulfite to the filtrate and to boil that for some minutes to ascertain whether gallium is present. If insufficient hydrochloric acid was added before the solution was first boiled, some gallium may be retained in solution by the alkali resulting from the hydrolysis of the sodium sulfite. To guard against this error, the filtrate, after boiling with a small amount of sodium sulfite and the removal of any precipitate that may form, should be acidified with acetic acid and boiled for 20 minutes. Any gallium hydroxide that appears on this treatment is collected, ignited and weighed, and its weight added to that of the oxide already obtained.

#### **Precipitation of Zinc as Zinc Mercuric Thiocyanate from Solutions that Contain Gallium.**

Zinc forms a difficultly soluble double salt with mercuric thiocyanate. Gallium does not. To ascertain whether this fact could be utilized to separate zinc from gallium, a solution that contained the sulfates of gallium and zinc was made slightly acid with sulfuric acid and an excess of a solution of potassium mercuric thiocyanate was added. After several

hours, the precipitate of zinc mercuric thiocyanate was removed by filtration. The filtrate was treated with hydrogen sulfide to precipitate the mercury, the mercuric sulfide was filtered off, the filtrate was boiled to remove hydrogen sulfide, and ammonium hydroxide was then added until the solution was slightly alkaline. Acetic acid was next added in slight excess, and the gallium that was present was precipitated as the hydroxide by boiling this solution. This hydroxide was dissolved in a slight excess of sulfuric acid, the solution was diluted to 100 cc., and the metals in the resulting solution were fractionally deposited by electrolysis on a rotating platinum rod, using a current of 2 to 3 amperes. Spectroscopic examination of the deposits on the cathode showed that zinc and gallium were present in all of them, zinc predominating in the early fractions, and gallium in the later ones. These results showed that zinc was not completely precipitated by potassium mercuric thiocyanate under the conditions above described.

While this work was in progress, however, an investigation of this method for the determination of zinc was completed in this laboratory by Mr. C. S. Hoyt<sup>1</sup> working under the direction of Professor G. E. F. Lundell. These investigators established the conditions under which the precipitation of the zinc should be made, and careful observance of their directions gave us very satisfactory results.

The reagent is prepared by dissolving 27 g. of mercuric chloride and 39 g. of potassium thiocyanate in one liter of water. The solution of the zinc salt to be precipitated should not contain more than 0.1 g. of zinc in 200 cc., and this volume of solution should contain about 2 cc. of conc. nitric acid or sulfuric acid. The solution of potassium mercuric thiocyanate is added by drops to the solution of zinc, which is constantly stirred during the addition of the precipitant. In making a determination of zinc, the reagent is added until a precipitate begins to form, and from this point 20 cc. of the precipitant is added for every 0.1 g. of zinc estimated to be present. After precipitation is complete, the contents of the beaker are allowed to stand for several hours. The precipitate is then collected in a Gooch crucible, is washed with water that contains 20 cc. of the reagent per liter, and is then dried at 105–110°. The zinc factor for this precipitate is 0.1314.

The accuracy of the separation of zinc from gallium by this improved method was tested by precipitating the zinc from a slightly acid solution containing known amounts of zinc and gallium. After the precipitate of zinc mercuric thiocyanate had been removed by filtration, 10 cc. of hydrochloric acid was added to the filtrate and the mercury in the solu-

<sup>1</sup>C. S. Hoyt, "The Zinc Mercuric Sulfoeyanate Method for the Determination of Zinc," a thesis presented to the Faculty of the Graduate School of Cornell University, June, 1917; also, Lundell and Bee, *Trans. Am. Inst. Metals*, Sept., 1914.

tion was precipitated by hydrogen sulfide. The mercuric sulfide was filtered off, the filtrate was boiled to expel hydrogen sulfide, and the gallium was then thrown down by sodium sulfite (see page 1547), and was weighed as the oxide. The results of two analyses, which are given in Table VII, show that the method is quite satisfactory for the determination of zinc and gallium in the presence of each other.

TABLE VII.  
The Separation of Zinc from Gallium.

No.	Weight of zinc taken. Gram.	Weight of zinc found. Gram.	Weight of gallium oxide taken. Gram.	Weight of gallium oxide found. Gram.
1.....	0.0939	0.0929	0.0828	0.0823
2.....	0.0939	0.0937	0.0828	0.0830

### Preliminary Experiments upon the Determination of Gallium, Indium, Zinc and Aluminum in the Presence of One Another.

Solutions of salts of gallium, zinc, indium, and aluminum of known concentrations were prepared as follows:

A solution of gallium sulfate was made in the manner above described and its concentration was ascertained by precipitation of gallium by sodium sulfite.

Indium chloride that had been prepared by Mathers<sup>1</sup> was dissolved in water and measured portions of this solution were boiled with a slight excess of ammonium hydroxide. The precipitated indium hydroxide was ignited to the oxide, which was then allowed to cool, was moistened with nitric acid, was reignited and was weighed as  $\text{In}_2\text{O}_3$ .

Pure zinc sulfate was dissolved in water and the strength of the solution was determined by precipitation with potassium mercuric thiocyanate.

The concentration of a solution of aluminum sulfate was determined by the usual method of precipitation with ammonium hydroxide.

Portions of these 4 solutions, carefully measured from burets, were used to prepare the mixtures that were employed in the study of the analytical separation and determination of the 4 elements.

**Separation and Determination of Gallium and Indium.**—Solutions that contained known amounts of gallium and indium were each diluted to 200 cc. A small amount of hydrochloric acid was added to each solution and a solution of sodium hydroxide was run in until the liquid was neutral. 1.5 g. of sodium hydroxide in excess was then added and the solution was boiled for several minutes. The resulting precipitate of indium hydroxide was collected on a filter and washed, and was then redissolved in hydrochloric acid and the indium reprecipitated by again boiling with an excess of 1.5 g. of sodium hydroxide. This precipitate was removed by filtration and was washed; it was then dissolved in hydrochloric acid,

<sup>1</sup> *Loc. cit.*

and the indium was determined by precipitation with ammonium hydroxide in the manner previously described. The alkaline filtrates from the two precipitations of indium were combined and were acidified with hydrochloric acid. The gallium was precipitated by sodium sulfite, the precipitate was collected on a filter and washed, was dissolved in hydrochloric acid and the gallium was reprecipitated with sodium sulfite, and was finally weighed as the oxide.

TABLE VIII.

## The Separation of Gallium from Indium.

No.	Weight of Ga <sub>2</sub> O <sub>3</sub> taken. Gram.	Weight of Ga <sub>2</sub> O <sub>3</sub> found. Gram.	Weight of In <sub>2</sub> O <sub>3</sub> taken. Gram.	Weight of In <sub>2</sub> O <sub>3</sub> found. Gram.
1.....	0.0828	Not det.	0.0647	0.0660
2.....	0.0828	0.0834	0.0647	0.0662
3.....	0.0828	0.0828	0.0647	0.0676

The results for gallium are satisfactory, but those for indium are somewhat high. Later determinations of indium in the presence of gallium by this method yielded, however, very satisfactory results. (See Table XV.)

**Separation and Determination of Gallium and Zinc.**—Solutions containing known amounts of gallium and zinc were diluted to about 200 cc., and two cc. of sulfuric acid was added to each solution. The zinc was precipitated from these solutions by potassium mercuric thiocyanate. Ten cc. of hydrochloric acid was added to each filtrate and the mercury in the filtrate was precipitated by hydrogen sulfide. After removal of the mercuric sulfide by filtration, the solutions were boiled to remove hydrogen sulfide, and the gallium was precipitated by sodium sulfite. It will be seen that the results for both gallium and zinc by this method are quite satisfactory.

TABLE IX.

## The Separation of Gallium from Zinc.

No.	Weight of zinc taken. Gram.	Weight of zinc found. Gram.	Weight of Ga <sub>2</sub> O <sub>3</sub> taken. Gram.	Weight of Ga <sub>2</sub> O <sub>3</sub> found. Gram.
1.....	0.0939	0.0929	0.0828	0.0823
2.....	0.0939	0.0937	0.0828	0.0830

**Separation and Determination of Gallium and Aluminum.**—Solutions of salts of gallium and aluminum of known concentration were prepared and the aluminum was precipitated as a hydrated chloride<sup>1</sup> by a modification of the method of Gooch.<sup>2</sup>

In Determination No. 1. (see Table X), 60 cc. of hydrochloric acid was added to the solution containing gallium and aluminum and 60 cc. of ether was then added. The flask was immersed in cold water and the liquid was saturated with hydrogen chloride. The resulting precipitate

<sup>1</sup> Dennis, *Z. anorg. Chem.*, **9**, 339 (1895).

<sup>2</sup> "Methods in Chemical Analysis," 1912, p. 214.

of hydrated aluminum chloride was filtered on a Gooch crucible and was washed with a mixture of 30 cc. of hydrochloric acid and 30 cc. of ether, which had been saturated with hydrogen chloride. The precipitate was then dissolved in water and the aluminum was determined by precipitation with ammonium hydroxide. A small amount of sulfuric acid was added to the filtrate from the precipitation of aluminum chloride and the liquid was then heated until the ether and most of the hydrochloric acid had been driven off; the gallium in the solution was then thrown down by sodium sulfite.

In Determination No. 2, only 25 cc. of hydrochloric acid and 25 cc. of ether were added before the solution was saturated with hydrogen chloride. A mixture of 25 cc. of hydrochloric acid and 25 cc. of ether, saturated with hydrogen chloride, was used to wash the precipitate.

TABLE X.  
The Separation of Gallium from Aluminum.

No.	Weight of $Al_2O_3$ taken. Gram.	Weight of $Al_2O_3$ found. Gram.	Weight of $Ga_2O_3$ taken. Gram.	Weight of $Ga_2O_3$ found. Gram.
1.....	0.0841	0.0831	0.0828	0.0844
2.....	0.0841	0.0825	0.0083	0.0098

These results were not satisfactory, but further experience with the method enabled us to obtain quite accurate analyses by this method. (See Table XVII.)

**Separation and Determination of Gallium, Indium and Zinc. First Method.**—Solutions that contained known amounts of gallium, indium, and zinc, gallium preponderating, were diluted to about 100 cc. Zinc was precipitated by the addition of 25 cc. of potassium mercuric thiocyanate. After several hours' standing, the precipitate was removed by filtration and the mercury in the filtrate was thrown down by hydrogen sulfide. The filtrate from this last filtration was boiled to remove hydrogen sulfide, and the indium and gallium were then separated and determined by the method described on page 1549.

TABLE XI.  
The Separation of Gallium, Zinc and Indium. First Method.

No.	Weight of $Ga_2O_3$ taken. Gram.	Weight of $Ga_2O_3$ found. Gram.	Weight of zinc taken. Gram.	Weight of zinc found. Gram.	Weight of $In_2O_3$ taken. Gram.	Weight of $In_2O_3$ found. Gram.
1.....	0.0828	0.0833	0.0038	0.0041	0.0065	0.0030
2.....	0.0828	0.0833	0.0188	0.0196	0.0129	0.0075

The results for gallium were quite satisfactory but those for zinc were high and those for indium were quite low. This may have been due to the presence of indium either in the precipitate of zinc mercuric thiocyanate, or in the precipitate of mercuric sulfide when the mercury is removed from the filtrate from the zinc precipitation. To throw light

upon this point a solution that contained only indium and zinc was prepared and the zinc was precipitated as zinc mercuric thiocyanate. The excess of mercury was removed from the filtrate by hydrogen sulfide and the indium was precipitated by ammonium hydroxide.

TABLE XII.  
The Separation of Zinc and Indium.

No.	Weight of zinc taken. Gram.	Weight of zinc found. Gram.	Weight of $\text{In}_2\text{O}_3$ taken. Gram.	Weight of $\text{In}_2\text{O}_3$ found. Gram.
1	0.0939	0.0969	0.0649	0.0494

The result for zinc was quite high, and the precipitate of zinc mercuric thiocyanate was found to contain indium when examined before the spectroscope. This method, therefore, does not furnish a satisfactory means of determining zinc and indium in the presence of each other.

**Second Method.**—Solutions containing known amounts of gallium, indium and zinc were prepared, and the indium was separated and determined by double precipitation with sodium hydroxide in the manner described on page 1549. The alkaline filtrates from this double precipitation were combined, and the solution was neutralized with sulfuric acid. The zinc in this solution was determined by precipitation with potassium mercuric thiocyanate. The mercury in the filtrate from this precipitate was removed by hydrogen sulfide and the gallium in the filtrate was determined by double precipitation with sodium sulfite (page 1547).

TABLE XIII.  
The Separation of Gallium, Zinc and Indium. Second Method.

No.	Wt. of $\text{Ga}_2\text{O}_3$ taken. Gram.	Wt. of $\text{Ga}_2\text{O}_3$ found. Gram.	Wt. of zinc taken. Gram.	Wt. of zinc found. Gram.	Wt. of $\text{In}_2\text{O}_3$ taken. Gram.	Wt. of $\text{In}_2\text{O}_3$ found. Gram.
1	0.0828	0.0813	0.0186	0.0171	0.0130	0.0129
2	0.0828	0.0827	0.0367	0.0337	0.0323	0.0318
3	0.0828	0.0821	0.0939	0.0926	0.0647	0.0650
4	0.0828	0.0817	0.0075	0.0049	0.0065	0.0063
5	0.0083	0.0079	0.0939	0.0944	0.0323	0.0335
6	0.0828	Not det.	0.0188	0.0161	0.0130	0.0120
7	0.0083	0.0061	0.0939	0.0942	0.0194	0.0195
8	0.0083	0.0085	0.0075	0.0050	0.0647	0.0680

In Determinations Nos. 3, 5 and 7, an excess of 3 g. of sodium hydroxide instead of the usual amount of 1.5 g. was employed for the first precipitation of indium hydroxide. In Determinations Nos. 1 and 2, the precipitated indium hydroxide was dissolved in hydrochloric acid. In the other determinations it was dissolved in sulfuric acid. It was found that in some cases zinc was present in the filtrate from the final precipitation of indium by ammonium hydroxide. Consequently, in all of the determinations except Nos. 1 and 2, this filtrate was treated with potassium mercuric thiocyanate and any precipitate that formed was



added to the main precipitate of zinc mercuric thiocyanate. An examination of the table will show that the results for gallium and indium were quite satisfactory in nearly every case, but that those for zinc were inaccurate especially when the amount of zinc was small.

**Third Method.**—Solutions containing known amounts of gallium, indium and zinc were diluted to about 200 cc. and 2 cc. of sulfuric acid (sp. gr., 1.84) was added to each solution. Zinc was precipitated as zinc mercuric thiocyanate in the usual manner. After standing for several hours, this precipitate was collected on an asbestos filter in an unweighed Gooch crucible and was washed with a solution containing 20 cc. of potassium mercuric thiocyanate reagent in one liter. The precipitate was then treated on the asbestos mat in the crucible alternately with a few drops of a strong solution of sodium hydroxide and a few drops of conc. hydrochloric acid until it was dissolved. Four cc. of acid was sufficient to effect solution of the precipitate. The resulting solution was then diluted to about 200 cc. and the excess of acid was neutralized with sodium hydroxide. Two cc. of conc. sulfuric acid and 20 cc. of the potassium mercuric thiocyanate reagent were then added. The contents of the beaker were allowed to stand for several hours, and the precipitate was collected in a weighed Gooch crucible which was then dried and weighed.

The combined filtrates from the two precipitations of zinc mercuric thiocyanate had a volume of about 500 cc. Ten cc. of hydrochloric acid was added to the solution, the mercury was precipitated by hydrogen sulfide, the mercuric sulfide was filtered off, and the filtrate was freed from hydrogen sulfide by boiling. The indium and gallium in the solution were determined by the method described on page 1549.

TABLE XIV.

The Separation of Gallium, Zinc and Indium. Third Method.

No.	Wt. of Ga <sub>2</sub> O <sub>3</sub> taken. Gram.	Wt. of Ga <sub>2</sub> O <sub>3</sub> found. Gram.	Wt. of zinc taken. Gram.	Wt. of zinc found. Gram.	Wt. of In <sub>2</sub> O <sub>3</sub> taken. Gram.	Wt. of In <sub>2</sub> O <sub>3</sub> found. Gram.
1 . . . . .	0.0828	0.0840	0.0076	0.0077	0.0064	0.0014
2 . . . . .	0.0166	0.0163	0.0188	0.0188	0.0647	0.0502
3 . . . . .	0.0083	0.0094	0.0939	0.0939	0.0130	0.0039

It will be seen that the results for zinc were very satisfactory and that those for gallium were fairly accurate. The amount of indium, however, was low in each case and it was found that the precipitate of mercuric sulfide gave a strong spectrum of indium.

**The Separation and Determination of Gallium, Indium, Zinc and Aluminum.**—Solutions that contained known amounts of gallium, indium, zinc and aluminum were treated essentially as outlined on page 1552, up to the first precipitation of gallium by sodium sulfite. In this precipitation the hydroxides of both gallium and aluminum were precipitated by sodium sulfite and this mixture of hydroxides was then dissolved in hy-

drochloric acid, and the gallium and aluminum were then separated by the method already described on page 1550.

TABLE XV.

## The Separation of Gallium, Zinc, Indium and Aluminum.

No.	Wt. of Ga <sub>2</sub> O <sub>3</sub> taken. Gram.	Wt. of Ga <sub>2</sub> O <sub>3</sub> found. Gram.	Wt. of In <sub>2</sub> O <sub>3</sub> taken. Gram.	Wt. of In <sub>2</sub> O <sub>3</sub> found. Gram.	Wt. of zinc taken. Gram.	Wt. of zinc found. Gram.	Wt. of Al <sub>2</sub> O <sub>3</sub> taken. Gram.	Wt. of Al <sub>2</sub> O <sub>3</sub> found. Gram.
1.....	0.0828	0.0797	0.0323	0.0320	0.0376	0.0363	0.0841	0.0852
2.....	0.1056	0.1052	0.0323	0.0328	0.0376	0.0381	0.0841	0.0840
3.....	0.0414	0.0429	0.0647	0.0655	0.0939	0.0939	0.0280	0.0273

The results given in the table show that the determination of each of the 4 elements was fairly satisfactory in all of the 3 analyses.

These preliminary experiments upon the analytical separation of gallium, indium, zinc and aluminum indicated that the most accurate results would be obtained by the determination of zinc and gallium in one sample and of indium and gallium in a second sample, the aluminum being determined in either of the two samples.

Further investigation in this direction led to the adoption of the procedure described below.

#### Method of Analysis of Mixtures Containing Gallium, Indium, Zinc and Aluminum.

Neutral or slightly acid solutions of two samples of the material to be analyzed are prepared. Sample 1 in which zinc and gallium (and aluminum) are to be determined should not contain more than 0.1 g. of zinc. Sample 2 in which indium and gallium (and aluminum) are to be determined should not contain more than 0.1 g. of indium. The accurate determination of zinc is made in Sample 1; that of indium in Sample 2. Gallium and aluminum may be determined in whichever of the two samples these elements are present in amounts most suitable for analysis.

**Determination of Zinc and Gallium (and Aluminum) in Sample 1.**—The neutral or slightly acid solution of the sample is diluted to 200 cc. and two cc. of conc. sulfuric acid is added. The reagent solution of potassium mercuric thiocyanate (see page 1548) is then added drop by drop to the solution which is vigorously stirred throughout the addition. After the precipitate has begun to form, 20 cc. more of the precipitant is added and the solution is allowed to stand for several hours with occasional stirring. The precipitate is then collected in an unweighed Gooch crucible and is washed with a solution that is prepared by diluting 20 cc. of potassium mercuric thiocyanate reagent to 1 liter. A few drops of a concentrated solution of sodium hydroxide and then a few drops of conc. hydrochloric acid are alternately poured upon the precipitate and between successive additions of these reagents small quantities of water are run through the crucible. The precipitate should be entirely dissolved by the

use of not more than 4 cc. of hydrochloric acid. If this solution of the zinc precipitate is acid, it is neutralized with sodium hydroxide; if it is alkaline, it is neutralized with sulfuric acid. It is then diluted to 200 cc., two cc. of conc. sulfuric acid is added, and the zinc is precipitated with 20 cc. of the potassium mercuric thiocyanate reagent in the manner above described. After several hours' standing, the precipitate is filtered through a weighed Gooch crucible and is washed with the dilute solution of potassium mercuric thiocyanate above mentioned. The precipitate is then dried in the crucible at 105–110° and is weighed. The zinc factor is 0.1314.

If it is desired to determine gallium, or gallium and aluminum, in this sample, the filtrates from the two precipitations of zinc are combined, 5 cc. of conc. hydrochloric acid is added to the solution and the mercury is precipitated by hydrogen sulfide. The precipitate of mercuric sulfide is filtered off and washed. The filtrate is boiled to expel hydrogen sulfide and is then neutralized with sodium hydroxide. 1.5 g. of sodium hydroxide dissolved in a little water is then added to the solution which is next boiled for several minutes. The resulting indium hydroxide is collected on a filter paper and is washed with hot water and the filtrate is set aside. The precipitate of indium hydroxide is then redissolved in hydrochloric acid, the solution is diluted to 100 cc., 1.5 g. of sodium hydroxide is added and the solution is again boiled to reprecipitate indium as the hydroxide. This precipitate is collected on a filter and is washed with hot water; the filtrate from this precipitation is then combined with the filtrate from the first precipitation. 1.5 g. of hydrated sodium sulfite ( $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ ) is dissolved in a little water and is added to the solution. Hydrochloric acid is next run in, a drop at a time, until the solution is distinctly acid to litmus paper. The liquid is then boiled for about 6 minutes. The resulting precipitate consists of gallium hydroxide together with aluminum hydroxide, if aluminum is also present. It is collected on a filter paper and is washed with a little hot water. To make sure that the precipitation of gallium has been complete, a small amount of sodium sulfite is added to the filtrate and the solution is boiled for several minutes. If no precipitate results, the solution is made slightly acid with acetic acid and is boiled for a further 20 minutes. Any additional precipitate from either of these treatments is added to the precipitated hydroxide first obtained.

*If no aluminum is present*, the gallium hydroxide is dissolved in hydrochloric acid and the solution is diluted to 200 cc. The solution is then made slightly alkaline with ammonium hydroxide and 1.5 g. of hydrated sodium sulfite is then added. The solution is then made slightly acid with hydrochloric acid and is boiled for about 6 minutes. The resulting precipitate of gallium hydroxide is collected on an ashless filter paper and

is washed with water until free from chlorides. The filtrate should be tested as above described to ascertain whether the precipitation of gallium has been complete. The gallium hydroxide is dried on the paper and is incinerated over the Bunsen flame and weighed as  $\text{Ga}_2\text{O}_3$ .

*If aluminum is present*, the precipitate of the hydroxides of gallium and aluminum is dissolved in not more than 25 cc. of conc. hydrochloric acid. An equal volume of ether is added to this solution. The flask is immersed in cold water, and the solution is saturated with hydrogen chloride. The precipitated hydrated aluminum chloride is collected on an unweighed Gooch filter. The precipitate is washed with a small amount of a cold mixture of equal volumes of conc. hydrochloric acid and ether, this mixture having first been saturated with hydrogen chloride. The precipitate is then dissolved in water and the aluminum is determined by precipitation with ammonium hydroxide in the usual manner. The filtrate from the aluminum chloride precipitate contains the gallium. One cc. of sulfuric acid is added to this solution which is then boiled until most of the ether and hydrochloric acid have been expelled. The solution is then diluted to 200 cc., and the gallium is determined by precipitation with sodium sulfite in the manner above described.

#### **Determination of Indium and Gallium (and Aluminum) in Sample 2.**

—Sample 2, in which indium is to be determined, is diluted to 100 cc., and 1.5 g. of sodium hydroxide in excess of the amount of this substance required to neutralize the solution is added. The liquid is then boiled for several minutes and the resulting precipitate of indium hydroxide is collected on a filter paper, is washed with hot water, and is then dissolved in hydrochloric acid. This solution is neutralized with sodium hydroxide as before, 1.5 g. of sodium hydroxide is then added and the solution is boiled for several minutes. This second precipitate of indium hydroxide is dissolved in hydrochloric acid, ammonium hydroxide is added until the solution is slightly alkaline, and the liquid is boiled for several minutes. The precipitated indium hydroxide is collected on an ashless filter paper, is washed with hot water and is then dried. It is next ignited in a weighed crucible over a Bunsen flame, the crucible is allowed to cool, the oxide is moistened with a few drops of nitric acid, is heated carefully to remove the excess of nitric acid, and is then again highly heated over a Bunsen flame, and is weighed as  $\text{In}_2\text{O}_3$ .

The alkaline filtrates from the two precipitations of indium by sodium hydroxide contain the gallium and aluminum that may have been present in the sample. To determine these two elements, the solution is neutralized with sulfuric acid and then one cc. of conc. sulfuric acid is added for every 100 cc. of the solution. Zinc is precipitated from this acid solution by the addition of from 30 to 40 cc. of the potassium mercuric thiocyanate reagent. The contents of the beaker are allowed to stand for several

hours and the precipitate is then collected on a filter and is washed with a solution containing 20 cc. of the potassium mercuric thiocyanate reagent to the liter. Five cc. of hydrochloric acid is added to the filtrate and mercury is then precipitated by hydrogen sulfide, the mercuric sulfide is removed by filtration and is washed, and the filtrate is then freed from hydrogen sulfide by boiling. Gallium and aluminum may then be determined in this solution by the method described under "Sample 1."

The oxides of gallium, indium and aluminum are somewhat hygroscopic. For this reason the crucible that contains the ignited oxide should in each case be weighed in a stoppered weighing bottle.

Results that were obtained in analyses of mixtures containing gallium, indium, zinc and aluminum by the use of the methods just described are given in the following tables:

TABLE XVI.  
Determination of Zinc and Gallium in Sample 1.

No.	Zinc taken. Gram.	Zinc found. Gram.	Ga <sub>2</sub> O <sub>3</sub> taken. Gram.	Ga <sub>2</sub> O <sub>3</sub> found. Gram.	In <sub>2</sub> O <sub>3</sub> present. Gram.
1.....	0.0076	0.0077	0.0828	0.0840	0.0064
2.....	0.0188	0.0188	0.0166	0.0163	0.0647
3.....	0.0939	0.0939	0.0083	0.0094	0.0130

TABLE XVII.  
Determination of Indium, Gallium (and Aluminum) in Sample 2.

No.	In <sub>2</sub> O <sub>3</sub> taken. Gram.	In <sub>2</sub> O <sub>3</sub> found. Gram.	Ga <sub>2</sub> O <sub>3</sub> taken. Gram.	Ga <sub>2</sub> O <sub>3</sub> found. Gram.	Al <sub>2</sub> O <sub>3</sub> taken. Gram.	Al <sub>2</sub> O <sub>3</sub> found. Gram.	Zinc present. Gram.
1.....	0.0323	0.0328	0.1056	0.1052	0.0841	0.0840	0.0376
2.....	0.0647	0.0655	0.0414	0.0429	0.0280	0.0273	0.0939
3.....	0.0323	0.0320	0.0828	0.0797	0.0841	0.0852	0.0376
4.....	0.0130	0.0129	0.0828	0.0813	None	..	0.0188
5.....	0.0323	0.0318	0.0828	0.0827	None	..	0.0367
6.....	0.0647	0.0650	0.0828	0.0821	None	..	0.0939
7.....	0.0065	0.0063	0.0828	0.0817	None	..	0.0075
8.....	0.0323	0.0335	0.0083	0.0079	None	..	0.0939
9.....	0.0194	0.0195	0.0083	0.0061	None	..	0.0939
10.....	0.0647	0.0680	0.0083	0.0085	None	..	0.0075

#### A STUDY OF CERTAIN SALTS OF GALLIUM.

##### Gallium Selenate.

A solution of gallium selenate was prepared by placing gallium hydroxide in an amount of selenic acid insufficient to dissolve all of the hydroxide, and heating the acid nearly to boiling. After several hours of digestion, the solution was freed from the excess of gallium hydroxide by filtration and the filtrate was evaporated at room temperature. The crystals that separated were drained on a Witt plate by suction. The salt is very soluble and it is difficult to obtain crystals that are satisfactory for microscopic examination. The crystals show oblique extinction and they therefore belong either to the monoclinic or to the triclinic system.

The salt was dried to constant weight in the air and was then analyzed. Selenium was determined by placing a weighed sample of the salt in conc. hydrochloric acid and heating this to boiling to reduce selenic acid to selenious acid. The selenious acid was then reduced to free selenium by passing sulfur dioxide through the hot solution. The precipitated selenium was collected on a weighed Gooch crucible and was dried at  $110^{\circ}$  and weighed. Gallium was determined in the filtrate by the sodium sulfite method.

Calc. for  $\text{Ga}_2(\text{SeO}_4)_3 \cdot 16\text{H}_2\text{O}$ :  $\text{Ga}_2\text{O}_3$ , 21.90;  $\text{SeO}_3$ , 44.49;  $\text{H}_2\text{O}$ , 33.61. Found:  $\text{Ga}_2\text{O}_3$ , 21.77, 21.66, Av., 21.71;  $\text{SeO}_3$ , 44.49, 44.24, Av., 44.36;  $\text{H}_2\text{O}$ , by difference, 33.98.

When the sample of the crystalline gallium selenate was dried in the air, 2.5145 g. of the salt lost 0.2810 g., which corresponds to 5.94 molecules of water. Consequently the salt that was dried by suction contains about 22 molecules of water.<sup>1</sup>

These results indicate that a hydrate of gallium selenate containing 16 molecules of water exists, and that it is also probable that when gallium selenate crystallizes from aqueous solution at room temperature, the salt contains 22 molecules of water of crystallization.

The solubility of this air-dried, crystalline gallium selenate was determined by placing an excess of the salt in water in a stoppered bottle, heating the contents of the bottle to  $25^{\circ}$  in a thermostat for 6 hours, and then pipetting off samples of the supernatant, saturated solution and weighing them. The gallium in these samples was determined by the sodium sulfite method.

Weight of saturated solution taken. Gram.	Weight of $\text{Ga}_2\text{O}_3$ found. Gram.
0.7558	0.0908
0.6192	0.0749

The average of these values is 0.1205 g. of  $\text{Ga}_2\text{O}_3$  per g. of solution. One part of the salt therefore dissolves in 1.74 parts of water at  $25^{\circ}$ , and 100 cc. of the solution contains 57.58 g. of gallium selenate.

### Caesium Gallium Selenate Alum.

A solution containing gallium selenate, caesium selenate, and some free selenic acid was evaporated at room temperature. The crystals were separated from the mother liquor and were dried in the air. They showed the octahedral form characteristic of the alums.

Caesium was determined by precipitation with chloroplatinic acid, selenium by precipitation as free selenium, and gallium by precipitation with ammonium sulfite in the filtrate from the selenium determination. The water of crystallization was determined by drying a sample of the salt to constant weight at about  $180^{\circ}$ .

<sup>1</sup> The same degree of hydration, namely 22 molecules of water, was found to exist in a sample of gallium sulfate that was dried by simply pressing the crystals between sheets of filter paper.

Calc. for  $\text{CsGa}(\text{SeO}_4)_2 \cdot 12\text{H}_2\text{O}$ :  $\text{Cs}_2\text{O}$ , 19.96;  $\text{Ga}_2\text{O}_3$ , 13.31;  $\text{SeO}_3$ , 36.07;  $\text{H}_2\text{O}$ , 30.65.  
 Found:  $\text{Cs}_2\text{O}$ , 19.78;  $\text{Ga}_2\text{O}_3$ , 13.33;  $\text{SeO}_3$ , 35.73;  $\text{H}_2\text{O}$ , 30.33.

These results show that the salt has the formula  $\text{CsGa}(\text{SeO}_4)_2 \cdot 12\text{H}_2\text{O}$  and that it is therefore a typical alum.

The solubility of this alum in water at  $25^\circ$  was determined in the manner described under the selenate.

Weight of saturated solution taken. Grams.	Weight of $\text{Ga}_2\text{O}_3$ found. Gram.
2.0702	0.0109
2.0422	0.0109

The average of these results is 0.0053 g. of  $\text{Ga}_2\text{O}_3$  per g. of solution. One part of the salt therefore dissolves in 24.1 parts of water at  $25^\circ$ , and 100 cc. of the solution contains 4.15 g. of the alum.

#### Ammonium Gallium Sulfate Alum and Caesium Gallium Sulfate Alum.

During the process of extraction of germanium from certain material in this laboratory there were obtained residual solutions that were rich in zinc sulfate, and that contained about 30% of sulfuric acid. Spectroscopic examination of these solutions showed the presence of gallium.

Lecoq de Boisbaudran<sup>1</sup> separated traces of indium from gallium by utilizing the fact that ammonium gallium alum is quite insoluble in 70% alcohol. It therefore seemed probable that separation of this alum from alcoholic solution might furnish a convenient means for the recovery of gallium from such residues as those above mentioned. The development of such a method made necessary the determination of the approximate solubility of ammonium gallium alum, and since the corresponding caesium alum would doubtless be even less soluble, a sample of that compound was prepared and its solubility was determined.

A sample of each of these two alums was placed in a small bottle, an amount of water insufficient to completely dissolve the sample was added to each, and the mixture were held at  $25^\circ$  in the thermostat for 6 hours. The gallium present in weighed amounts of the saturated, supernatant solution was then determined.

The solubilities were then determined for each of the alums, using first 50% alcohol and next 70% alcohol. After the mixtures had been held in the thermostat at  $25^\circ$  for 6 hours, 40 cc. of the supernatant liquid was pipetted off in each case and was evaporated to dryness. Each residue was then heated for two hours at  $150^\circ$  and was weighed as the mixture of the anhydrous sulfate of gallium with ammonium sulfate or with caesium sulfate. The solubilities of each of the alums in a mixture of 35 cc. of water, 50 cc. of absolute ethyl alcohol, and 15 cc. conc. hydrochloric acid was then determined. The gallium in samples of 40 cc. of the saturated, supernatant solution was precipitated by the sodium sulfite method.

The results of these various determinations follow:

<sup>1</sup> *Compt. rend.*, **95**, 410 (1882).

**Solubility of Ammonium Gallium Sulfate Alum.**—(1) In water.

Weight of saturated solutions taken. Grams.	Weight of $Ga_2O_3$ found. Gram.
1.0248	0.0463
0.7010	0.0309

The average of these values is 0.0446 g. of  $Ga_2O_3$  per g. of solution. One part of the salt therefore dissolves in 3.24 parts of water at 25°, and 100 cc. of the solution contains 30.84 g. of the alum.

## (2) In 50% alcohol.

40 cc. of the saturated solution of the alum gave a residue that weighed 0.0049 g., which corresponds to 0.0411 g. of  $Ga_2O_3$  or 0.2170 g. of ammonium gallium alum per liter of solution. One part of the salt therefore dissolves in 4600 parts of 50% alcohol at 25°, and 100 cc. of the solution contains 0.0217 g. of the alum.

## (3) In 70% alcohol.

40 cc. of the saturated solution of the alum gave a residue that weighed 0.0020 g., which corresponds to 0.0166 g. of  $Ga_2O_3$  or 0.0875 g. of ammonium gallium alum per liter of solution. One part of the salt therefore dissolves in 11,400 parts of 70% alcohol at 25°, and 100 cc. of the solution contains 0.00875 g. of the alum.

(4) In a solution containing 35 cc. of water, 50 cc. of absolute alcohol, 15 cc. of conc. sulfuric acid.

40 cc. of the saturated solution of the alum yielded 0.0122 g. of  $Ga_2O_3$ , which corresponds to 0.305 g. of  $Ga_2O_3$  or 1.613 g. of ammonium gallium alum per liter of solution. One part of the salt therefore dissolves in 620 cc. of this solution at 25°, and 100 cc. of the solution contains 0.1613 g. of the alum.

**The Solubility of Caesium Gallium Sulfate Alum.**—(1) In water.

Weight of saturated solution taken. Grams.	Weight of $Ga_2O_3$ found. Gram.
2.0812	0.0048
1.7305	0.0040

The average of these values is 0.0023 g. of  $Ga_2O_3$  per g. of solution. One part of the salt therefore dissolves in 66.2 cc. of water at 25°, and 100 cc. of the solution contains 1.51 g. of the alum.

## (2) In 50% alcohol.

40 cc. of the saturated solution gave a residue that weighed 0.0010 g., which corresponds to 0.0059 g. of  $Ga_2O_3$  or 0.0387 g. of caesium gallium alum per liter of solution. One part of the salt therefore dissolves in 25,800 parts of 50% alcohol at 25°, and 100 cc. of the solution contains 0.00387 g. of the alum.

## (3) In 70% alcohol.

40 cc. of the saturated solution of the alum gave a residue that weighed 0.0009 g., which corresponds to 0.0054 g. of  $Ga_2O_3$  or 0.0356 g. of caesium gallium alum per liter of solution. One part of the salt therefore dissolves in 28,000 parts of 70% alcohol at 25°, and 100 cc. of the solution contains 0.00356 g. of the alum.

(4) In a solution containing 35 cc. of water, 50 cc. of absolute alcohol, and 15 cc. of conc. sulfuric acid.

40 cc. of the saturated solution of the alum yielded 0.0014 g. of  $Ga_2O_3$ , which corresponds to 0.0350 g. of  $Ga_2O_3$  or 0.228 g. of caesium gallium alum per liter of solution. One part of the salt therefore dissolves in 4,380 parts of this solution at 25°, and 100 cc. of the solution contains 0.0228 g. of the alum.



### Summary.

1. The spark spectra and the arc spectra of gallium, indium and zinc have been studied, and the delicacy of the spectroscopic detection of gallium and indium alone and in the presence of each other ascertained. Gallium chloride prepared by double distillation is found to contain less than 0.005% of either indium or zinc.

2. The purification of gallium by fractional electrolysis, and the preparation of pure gallium chloride by distillation are described.

3. Methods for the determination of gallium alone and of gallium, indium, zinc and aluminum in the presence of one another have been developed.

4. Two new salts of gallium, gallium selenate, and caesium gallium selenate alum, have been prepared. The solubilities of ammonium gallium sulfate alum and of caesium gallium sulfate alum in water, in 50% alcohol and in 70% alcohol, have been measured.

ITHACA, N. Y.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MCGILL UNIVERSITY.]

## UNSATURATION AND MOLECULAR COMPOUND FORMATION.

By O. MAASS AND J. RUSSELL.

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It has been shown that organic substances containing oxygen, such as the alcohols and ethers, form additive compounds with the halogens and halogen hydrides. The hypothesis put forward to account for the existence of these compounds is based on the supposed tetravalency of oxygen and the consequent formation at low temperatures of compounds, commonly called oxonium compounds.

In the course of an investigation<sup>1</sup> of these oxonium compounds several systems of non-oxygen-containing substances and the halogen hydrides were examined with the object of showing that, in the absence of oxygen, compounds are not formed. The system chloroform-hydrobromic acid illustrated this. But contrary to expectations toluene was found to form an addition compound with hydrobromic acid similar to an oxonium compound, and further experiments showed that toluene and chlorine combine to form such compounds. The present investigation has been carried out with the object of ascertaining the nature of these toluene compounds by determining whether aromatic and unsaturated hydrocarbons in general combine in a similar manner.

Modern theories of molecular compound formation are reverting more and more to a modified form of Berzelius' views. Molecules are supposed to combine in virtue of residual forces which, too small to hold the molecules together at high temperatures, come into play at low temperatures

<sup>1</sup> THIS JOURNAL, 34, 1273 (1912).