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ATOMIC WEIGHT OF GALLIUM

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ABSTRACT

In this determination of the atomic weight of gallium, weighed portions of the pure metal were converted to the hydroxide, the sulphate, and the nitrate, respectively. These were then heated until they were changed to the oxide, Ga_2O_3, which was finally ignited at 1,200 to 1,300° C. By this procedure, the atomic weight is related directly to that of oxygen.

Preliminary tests showed that the metal was free from an appreciable film of oxide and did not contain occluded gases. The highly ignited oxide, obtained through the hydroxide or the sulphate, contained no gases and was not appreciably hygroscopic. The oxide obtained by igniting the nitrate was less satisfactory. To make possible the correction of the weights to the vacuum standard, the density of the oxide was also determined, and found to be 5.9_5 g/cm^3.

The value for the atomic weight based on this work is 69.74.

CONTENTS

I. INTRODUCTION

The atomic weight of gallium was determined by Lecoq de Boisbaudran soon after he discovered the element,[1] and later by T. W. Richards and W. M. Craig.[2] Boisbaudran's determinations were made by converting gallium ammonium alum to gallic oxide and by converting the metal to the oxide through the nitrate. He obtained 70.12 and 69.70, respectively, as values for the atomic weight by these two methods. Richards and Craig prepared pure gallium trichloride ($GaCl_3$)

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[1] Compt. rend. **86**, 941 (1878) and J. Chem. Soc. (Abstracts) **34**, 646 (1878).

[2] J. Am. Chem. Soc. **45**, 1155 (1923).

and determined the quantity of chlorine in combination with the gallium by precipitating and weighing the chlorine as silver chloride, thus relating the atomic weight of gallium to that of silver (107.88) through chlorine (35.458). Their result, 69.716, becomes 69.720, if the present value for the atomic weight[3] of chlorine, 35.457, is used in the calculation. The scarcity of gallium and the difficulty of obtaining it in the pure state probably account for the fact that so few determinations of its atomic weight have been made.

Recently metallic gallium, at least 99.999 percent pure, was prepared by one of the authors,[4] and it was deemed advisable to determine the atomic weight, with this very pure metal as the starting point. The most obvious and attractive method seemed to be that of converting the metal to the oxide through the hydroxide, the sulphate, and the nitrate, respectively, thus directly relating the atomic weight to that of oxygen and avoiding errors that might exist in determinations by less direct methods.

II. PRELIMINARY TESTS

At the outset, it was necessary to make sure that both the metal and the oxide, Ga_2O_3, are suitable for this type of work. T. W. Richards and E. F. Rogers[5] found that many oxides, especially those obtained by igniting the nitrate, contained gases which they did not succeed in driving out by heating in a vacuum or by heating with a blast lamp. These authors determined the gases by dissolving the oxides in acids and then measuring the volume of the gases liberated. Obviously their work was confined to oxides, such as those of magnesium, zinc, and nickel, which are soluble in acids.

In the present work it was found that gallic oxide, ignited at 1,100 to 1,300° C, is insoluble in acids, but that it can be dissolved in hot diluted hydrochloric acid (2+3)[6] if the oxide has not been heated above 850° C. In the method employed by us for the determination of the atomic weight, the oxide was heated at 1,200 to 1,300° C until constant weight was attained, but it seemed reasonable to assume that if it could be shown that the oxide ignited at 850° C contained no gases, then an oxide prepared in a similar way and finally ignited at 1,200 to 1,300° C would be very unlikely to contain any.

Three 0.5-g portions of gallic oxide were therefore prepared by igniting the hydroxide, the sulphate, and the nitrate, respectively, for 5 hours at 800 to 850° C. These were then dissolved in 20 ml of diluted hydrochloric acid (2+3) in a glass tube of such shape that any liberated gases would be trapped in a small graduated portion of the tube.[7] Before use, the diluted hydrochloric acid was heated on the steam bath in a manner similar to that employed in dissolving the gallic oxide, to make certain that dissolved gases that could be liberated by such heating would be expelled. A bubble of gas, the volume of which was estimated to be about 0.1 ml, was obtained from the oxide derived from the nitrate. The others did not yield a trace of gas.

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[3] J. Am. Chem. Soc. **57**, 787 (1935)

[4] James I. Hoffman, J. Research NBS **13**, 665 (1934) RP734.

[5] Proc. Am. Acad. Arts, Sci. **28**, 200 (1893).

[6] This denotes two volumes of concentrated hydrochloric acid (specific gravity 1.18) diluted with three volumes of water. This system of specifying diluted acids is used throughout this paper. If no dilution is specified, the concentrated reagent is meant.

[7] The method of determination was essentially that used by Richards and Rogers. Proc. Am. Acad. Arts Sci., **28**, 200 (1893).

The foregoing determinations strongly indicated that gallic oxide, derived from the hydroxide or the sulphate by igniting to constant weight at temperatures above 850° C, would not contain any gases, but a direct determination on a portion of oxide, ignited at 1,300° C, was deemed highly desirable. A 0.5-g portion was accordingly placed in a platinum tubulated crucible containing 6 g of borax that had previously been fused to free it from gases. The crucible was then sealed to a manometer and evacuated. The volume of the evacuated system was about 40 cc. The borax and gallic oxide were fused at the lowest temperature possible. During the heating required for the fusion the mercury in the manometer remained practically stationary, and when the tube had cooled to the original temperature, the mercury stood at its original level. This indicated the absence of any gases in the gallic oxide, but a similar determination on a 0.5-g portion of zinc oxide, prepared by igniting the nitrate and known to contain 0.30 ml of gas,[8] yielded only about 0.1 ml of gas. Subsequent tests showed that the viscous molten borax in the quantity used can hold 0.3 ml of gas in an evacuated system, at the temperature that was permissible, even though no large bubbles are visible.

The foregoing procedure was then modified so that it included fusion in borax and measurement of the gas after solution of the cooled melt in acid. The fusion was made in the tubulated platinum crucible as described, the platinum top of the crucible was removed after cooling, and a glass top, fitted with a graduated tube, was sealed in its place. Diluted hydrochloric acid (2+5) was then added, and the liberated gases were measured. Aside from the fact that solution of the melt was very slow, this latter part of the procedure was essentially the same as that used in determining the gases in the oxide directly by solution in acid. The borax in all the determinations and blanks was heated in a vacuum for 3 hours before use. Three blank determinations on 6-g portions of borax ($Na_2B_4O_7.10H_2O$) yielded 0.10, 0.15, and 0.10 ml of gas, respectively. Two determinations on 0.5 g of Ga_2O_3, derived from the hydroxide and sulphate, yielded 0.15 and 0.15 ml of gas, respectively. A single determination on a sample of zinc oxide, known to contain 0.30 ml of gas, yielded 0.25 ml after subtracting 0.10 ml as a blank for the borax. This method is not to be recommended for accurate work on the determination of gases in insoluble oxides because the blanks are too high and inconsistent, but for the present purpose the results show that either no gas or a negligible quantity is contained in gallic oxide obtained by igniting the hydroxide or the sulphate, and finally heating to 1,300° C.

Of all the oxides investigated by Richards and Rogers, that of magnesium, prepared by igniting the nitrate, contained the most gas. For example, one 0.5-g portion which had been heated over the blast lamp for 1¼ hours contained 5.86 ml of gas (mostly nitrogen and oxygen). If it could be shown that prolonged ignition at 1,300° C would expel all gases from this oxide, it was deemed probable but not necessarily certain that similar ignitions would free gallic oxide from gases, provided any were present. A 5-g portion of magnesium oxide was prepared by igniting the nitrate and finally heating for 2 hours at 1,100° C. By dissolving in acid and measuring the volume

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[8] The amount was determined by dissolving in acid and measuring the volume as previously indicated.

of the evolved gases, a 1.0-g portion of this oxide yielded 3.1 ml of gas. The remainder of the oxide was then heated for 1½ hours at 1,300° C and the quantity of gas determined in a 1.0-g portion. A volume of 1.7 ml was found. The remaining oxide was then heated at 1,300° C for an additional period of 7 hours. A 1.0-g portion of this yielded only 0.25 ml of gas. As the oxide in all determinations of the atomic weight to be reported in this paper was heated at 1,300° C for at least 15 hours, it is probable that any gases would have been expelled, if they had been present in the oxide at the beginning of the ignition.

To test the gallic oxide for hygroscopicity, a 4-g portion, which had been ignited for 15 hours at 1,300° C, was exposed in an uncovered crucible for 24 hours at relative humidities between 35 and 50 percent. The total gain in weight was only 0.2 mg.

Further tests showed that no change in weight (within the limits of accuracy of weighing) occurred when this strongly ignited oxide was heated for 1 hour at 1,300° C, in an atmosphere of oxygen or nitrogen. This, in addition to the fact that in the ignition of one 4-g portion of oxide no detectable change in weight took place during a period of 46 hours of heating in air at 1,300° C, indicates that the oxide is not appreciably volatile, that it shows no tendency to dissociate at this temperature, and that it contains no lower oxide.

By taking into consideration (1) that gallic oxide, derived from the hydroxide or the sulphate by igniting at 850° C, contains no gas, (2) that either no gas or a negligible quantity was found in the oxide, ignited at 1,300° C, by fusion with borax and solution of the melt in acid, (3) that an oxide like that of magnesium, known to contain gases, tends to lose them on prolonged ignition at 1,300° C, (4) that the highly ignited oxide is not appreciably hygroscopic, and (5) that the oxide shows great stability under varying conditions, it was concluded that this oxide, Ga_2O_3, ignited at 1,300° C, is a suitable compound to use in determining the atomic weight of gallium.

III. PREPARATION AND TESTING OF MATERIALS USED

1. METALLIC GALLIUM

(a) PREPARATION

Two portions of metallic gallium were prepared by the method previously described.[9] Both were at least 99.999 percent pure on the basis of tests given in the reference just cited. One portion of pure metal was that used in determining the melting point [10] and was prepared from crude metal obtained about 15 years ago from Bartlesville, Okla. The other portion was prepared from impure metal recently obtained from the same district.

(b) TESTS FOR OCCLUDED GASES

At no time was there any evidence of the liberation of gases when crystals of the metal were melted under water. Such a test, however, was not regarded as conclusive. A single crystal, weighing 3.5167 g, was placed in a small porcelain boat and weighed, using a similar boat as a counterpoise. The counterpoise and the boat containing the

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[9] James I. Hoffman, J. Research NBS **13**, 665 (1934) RP734.

[10] Wm. F. Roeser and James I. Hoffman, J. Research NBS **13**, 673 (1934) RP735.

metal were heated for 30 minutes at 300° C in a stream of hydrogen and then gradually cooled to room temperature in hydrogen. No change in weight was detected. After this the boat containing the gallium was placed in a small Pyrex-glass tube, which was then sealed to a manometer.

After evacuating the system, the gallium in the tube was heated for 30 minutes at 300 to 400° C, after which the system was cooled to room temperature. The mercury stood at the original level, and the gallium in the boat did not show any detectable change in weight. It was therefore concluded that no significant amount of gases was occluded in the crystals. The vapor pressure of gallium is so low (approximately 0.002 mm of Hg at 1,000° C)[11] that loss by volatilization at temperatures below 1,000° C is probably insignificant for any reasonably short period of heating.

(c) TESTS FOR A FILM OF OXIDE ON THE SURFACE OF THE CRYSTALS

The surface of the crystals of metal used in this work was so bright that there seemed small chance that any appreciable film of oxide existed, but the possibility remained that a very thin film might escape simple visual observation. Accordingly, a 4.7-g portion of gallium in the form of small crystals (to give maximum surface for minimum weight of metal) was placed in a hard-glass tube connected to a source of hydrogen and at the outlet to a small tube containing anhydrous magnesium perchlorate, $Mg(ClO_4)_2$. The hydrogen was preheated at about 650° C in a tube containing copper gauze, and the resulting gases were passed through a tube containing ascarite (sodium hydroxide on asbestos) and then through another containing anhydrous magnesium perchlorate, before being admitted into the tube containing the gallium. The metal was heated for 1 hour at 680 to 700° C in a stream of this purified hydrogen, and the increase in weight of the tube containing the anhydrous magnesium perchlorate at the exit end of the hard-glass tube was noted. This increase (0.7 mg) was the same as the average obtained in three blank determinations, which indicated that no appreciable film of oxide was present.

In order to test the efficacy of this procedure, a determination was made in which 2 mg of Ga_2O_3 was substituted for the metallic gallium, immediately after the latter was removed. The absorbing tube in this case showed a net increase in weight of 0.4 mg. A preliminary determination on 9.5 mg of Ga_2O_3 had yielded a net increase in weight in the absorbing tube of 1.8 mg. Strictly quantitative conversion of all the oxygen in the Ga_2O_3 could not be expected because it is not certain whether a lower oxide or the metal is formed by reduction in hydrogen at 680 to 700° C. A. Dupré[12] stated that at a cherry-red heat a lower oxide of gallium is formed, and that at a bright red heat the metal is formed. A. Brukl[13] stated that the lower oxide, Ga_2O, is volatile. In the attempts to reduce the Ga_2O_3 just mentioned, some of the lower oxide must have been formed because a grayish sublimate appeared on the cooler part of the hard glass tube between the heated portion and the exit end. Regardless of the stage of reduction, the

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[11] P. Hartech, Z. physik. Chem. **134**, 1 (1928).

[12] Compt. rend. **86**, 720 (1878).

[13] Z. anal. Chem. **86**, 92 (1931).

results indicate that if an appreciable amount of oxide had existed in the metal it would have been detected.

The crystals of metallic gallium were also subjected to two types of optical examination [14] to discover whether there was an oxide coating. A microscopical examination showed that there could be no such coating except as an optically uniform film less than 3 μ (1 μ=.001 mm) thick. To cover the case of films thinner than this, the crystals were examined for the structural colors of thin films.

When an optically reflecting metal surface coated by a transparent film of uniform thickness is illuminated with white light, part of the light is reflected, and part enters the film. This latter is partly reflected and partly absorbed by the metal surface. After multiple reflections, the light which emerges has suffered constructive or destructive interference, depending on the thickness and index of refraction of the film, and on the phase change and angle of the reflection. With normal incidence and negligible phase change at reflection from either surface (as would be expected for a transparent oxide film in optical contact with a metal), a deficiency of blue is observed as a straw color for a film 0.06 μ thick with a refractive index of 1.5. If the film is thicker, the color is brighter and varies according to the sequence of white-center thin-film colors. As the observations are made at increasingly oblique angles, the order of any such color decreases, the change being readily apparent. In the case where a relative phase change of one-half wave length occurs between the two reflections (as would be expected for an oxide film not in optical contact with the metal), a film 0.06 μ thick with a refractive index of 1.5 is gray at normal incidence, but rapidly darkens when viewed at greater obliquities.

The colors of thin films can be produced artificially upon a metal resembling the sample of gallium in polish and reflectivity, by evaporating upon its surface a very pure, very dilute aqueous solution of gelatin or a pure dilute solution of collodion made with anhydrous alcohol and ether. The colors, including the pale straw, corresponding to an optical difference of 0.18 μ (twice the optical thickness of the film), are readily seen and decrease in order as the obliquity of observation increases.

When the face of a gallium crystal was observed under diffused white light, there was no change of its gray color as the crystal was rotated about an axis normal to the direction of observation and lying in the face under observation. This, taken in conjunction with the limits established by the microscopical examination and the fact that gallium is a gray and not a white metal, showed that if a film of oxide with a refractive index as high as 1.5 is present at all, it can not be thicker than 0.06 μ.

Assuming that a cubical crystal, 0.5 cm on an edge, is covered with a film of oxide, 0.06 μ thick, and assuming the density of both the metal and the oxide to be 6, the maximum weight of the oxygen in the film could be only about 0.000014 g and would affect the total weight by only about 1 part in 50,000.

(d) TEST FOR CHLORIDES IN THE CRYSTALS OF METALLIC GALLIUM

Since the metal had been crystallized under dilute hydrochloric acid, a test for chlorides was made by dissolving a crystal, weighing

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[14] The optical examinations were made by Charles Proffer Saylor, chemical microscopist at the National Bureau of Standards.

approximately 0.5 g, in diluted sulphuric acid (1+4), neutralizing nearly all the excess acid with ammonium hydroxide, and adding silver nitrate to the faintly acid solution. No turbidity appeared. Under similar conditions, a turbidity appeared in a solution to which 0.02 mg of chloride ion in the form of HCl had been added. It should be noted that pure gallium dissolves very slowly in dilute sulphuric acid.

2. CHEMICAL REAGENTS

Nitric acid, hydrochloric acid, sulphuric acid, and ammonium hydroxide were the only reagents used. The acids, bought on the specifications for analytical reagent chemicals recommended by the Committee on Analytical Reagents of the American Chemical Society, were of such good quality that it was not necessary to purify them. None of them yielded a nonvolatile residue exceeding 0.2 mg when 100-ml portions were evaporated and the residue ignited. As less than 25 ml of the combined acids was involved in any determination, and especially since exactly the same quantities were used in blank determinations, these small amounts of impurities were entirely negligible. The ammonium hydroxide was prepared by passing gaseous ammonia into distilled water contained in a Pyrex flask whose inside surface was covered with paraffin. A 100-ml portion of this ammonium hydroxide yielded a residue weighing less than 0.1 mg, even after the solution had stood in the flask for over 3 months.

3. PLATINUM CRUCIBLES

In work involving prolonged ignitions at high temperatures, it is essential that the crucibles do not change in weight or that two or more crucibles are available that change weight at a uniform rate. The former requirement cannot be met in the case of platinum crucibles.[15] In the determinations of all the results reported in this paper, one platinum crucible, from a series of four having the same composition,[16] was used as a tare. The whole set was heated in a platinum-wound muffle furnace for 5 hours at 1,200 to 1,300° C, cooled and weighed. Then the crucibles were again heated for 15 to 25 hours at 1,200 to 1,300° C, cooled, and weighed. If any crucible, compared with the tare, showed an apparent change in weight of as much as 0.1 mg during this latter period of heating, it was not used. It might be added that in the beginning of the work it was not unusual for at least one crucible out of four to fail to meet these requirements. However, after repeated ignitions, polishings with fine sand, and treatments with hydrochloric acid, all the crucibles remained remarkably constant in weight, as compared with the tare, during successive heatings.

IV. PROCEDURES

1. CONVERSION OF METALLIC GALLIUM TO GALLIC OXIDE THROUGH THE HYDROXIDE

For the conversion of the metal to the oxide, Ga_2O_3, through the hydroxide, one or more crystals were carefully weighed to the nearest

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[15] E. Wichers and R. Gilchrist, Serviceability of platinum laboratory ware of various compositions, Publication pending; Abstract in Tech. News Bull. 217, National Bureau of Standards, p. 47 (1935).

[16] Two sets of four crucibles each were used throughout this work. The one was platinum containing about 0.4 percent of iridium, the other was platinum containing about 3.5 percent of rhodium. No difference in performance was noted.

0.05 mg, transferred to a 250-ml Pyrex beaker, and dissolved in a mixture of 40 ml of distilled water, 5 ml of sulphuric acid, 5 ml of nitric acid, and 5 ml of hydrochloric acid. For the determination of a "blank", a dilute solution of aluminum chloride, containing aluminum equivalent to 0.00378 g of Al_2O_3, was transferred to a similar beaker to which the same quantities of reagents had been added. The solution of aluminum chloride was prepared by diluting a more concentrated solution which had been carefully standardized by precipitating the aluminum with ammonium hydroxide and igniting the precipitate to the oxide. From this point the solutions in the two beakers were subjected to the same treatments, and the proper correction for the aluminum added to the "blank" was applied at the end of the determination. The small amount of aluminum chloride was added to the blank to serve as a gatherer of traces of impurities that might otherwise have escaped precipitation.

The solutions in both beakers were evaporated until fumes of sulphuric acid just appeared. They were then cooled, any acid on the inside surface of the beakers was washed down with a jet of water, and the evaporation was repeated to make sure that all chlorides were removed, because chlorides, carried down by the gelatinous precipitate of gallium hydroxide, might result in volatilization of gallium (as $GaCl_3$) during the subsequent ignition.[17] The solutions were again cooled, diluted to 150 ml, a few drops of methyl red indicator added, and then ammonium hydroxide was added until the color of the indicator just turned yellow. The beakers were allowed to stand on the steam bath for 5 minutes. Then the precipitates were transferred to large ashless filters and washed a few times with hot water. The filtrates were slightly acidified with sulphuric acid, evaporated to a volume of 40 to 50 ml, and ammonium hydroxide was again added until the color of methyl red just turned to yellow. After a digestion of 15 minutes on the steam bath, these solutions were allowed to stand over night at room temperature, and any precipitate which separated was removed by filtration and combined with the first precipitate. A dilute solution of ammonium nitrate, whose pH was adjusted to about 6.2, was used for washing this last precipitate.

These filtrates were transferred to clean platinum dishes and heated until nearly all ammonium salts and sulphuric acid were expelled. A few drops of hydrochloric acid and 5 ml of water were added to the residue. The dishes and contents were heated on the steambath for a few minutes, and the solutions were poured through small filters. The filtrates, having volumes of about 10 ml, were neutralized with ammonium hydroxide as before and allowed to stand for 24 hours. As no precipitate appeared in either case, it was concluded that the last of the gallium had been obtained in the preceding precipitation and that all of the aluminum had been precipitated in the case of the blank.

The filters containing the precipitates were transferred to platinum

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[17] The fact that almost identical results were obtained for the atomic weight by the three different procedures described in this paper indicates that no loss of gallium occurs when the sulphate is ignited to the oxide or when a solution containing gallium chloride and an excess of sulphuric acid is heated until copious fumes of sulphuric acid are evolved. Further evidence on this point is furnished by the following tests: A solution of gallium sulphate was carefully standardized by precipitating the gallium with cupferron and igniting it to the oxide. One ml of the solution was found to contain 0.003120 g of Ga_2O_3. Two 20-ml portions of this solution (each equivalent to 0.0624 g of Ga_2O_3) were transferred to platinum crucibles and 1 ml of sulphuric acid was added to each. To one was also added 3 ml of hydrochloric acid. The excess of acid was evaporated by heating, first on the steam bath and then indirectly in a radiator. The dry residue was finally ignited to constant weight in the same manner as was done in the standardization. The results obtained, 0.0625 g, and 0.0625 g, respectively, show that no volatilization took place.

crucibles which had been tested for constancy of weight, as previously described. The precipitate containing the aluminum was placed in the crucible used as a tare. After the precipitates were dried in an oven, the crucibles were partially covered and placed in a cold muffle furnace which was gradually heated to about 1,200° C during the course of 6 to 8 hours. The residues were then heated in the tightly covered crucibles at 1,200 to 1,300° C until constant weight was obtained. All final weights remained constant within 0.1 mg during heating for at least 25 hours between 1,200 and 1,300° C, and one of the ignited precipitates was heated for 46 hours between these two temperatures without showing any change in weight. In all weighings the platinum crucible containing the small quantity of aluminum oxide, which was negligibly hygroscopic, was used as a counterpoise. The weight of the residue in the crucible containing the gallic oxide represented the weight of the oxide plus any blank, while the weight of the residue in the crucible used as a tare represented the weight of the aluminum oxide plus the blank. The weights of the blanks, therefore, cancelled each other, and in calculating results, 0.00378 g was subtracted from the weight of the blank because aluminum chloride, equivalent to this weight of aluminum oxide, was added to it in the beginning. Concentrated sulphuric acid was used as the drying agent in the desiccator.

The true weight of gallic oxide was therefore found by subtracting the weight of the crucible used as a tare plus its contents from that of the crucible containing the gallic oxide plus its contents (after making the correction for the aluminum added to the blank). All weighings were made to the nearest 0.05 mg, and all weights were corrected to the vacuum standard. In making these corrections the value, 5.9_1 was used for the density of the solid metal, and 5.9_5 as the density of the oxide, Ga_2O_3. The former is given in the International Critical Tables, vol. 1, p. 104 (1926), but, as no value for the density of the oxide is reported, a determination was made by E. L. Peffer of the volumetric section of the National Bureau of Standards. For this purpose, the pure oxide, obtained in the foregoing procedure, was used. With carbon tetrachloride as the test liquid, a value of 5.97 g/cm³ was obtained at 27° C. From observations made in kerosene as the test liquid, a value of 5.93 g/cm³ was found. The value used, 5.9_5, is the average of the results obtained by the two procedures.

The results obtained by converting the metal to the oxide through the hydroxide are shown in table 1.

TABLE 1.—*Results obtained for the atomic weight of gallium by converting the metal to the oxide through the hydroxide*

[In making the weighings, only 0's and 5's were recorded in the fifth decimal place. Figures other than these are a result of the correction of the recorded values to the vacuum standard, and hence are still subject to the same uncertainty as the recorded values.]

No.	Wt of metal	Wt of Ga_2O_3	Calculated atomic weight
	g	g	
1 [a]	0.86526	1.16307	69.73_0
2 [a]	1.25888	1.69205	69.75_0
3 [b]	1.23368	1.65815	69.75_3
4 [b]	3.45532	4.64464	69.72_7
5 [b]	2.97452	3.99838	69.72_5
			69.73_7=Average.

[a] =first lot of metal. [b] =second lot of metal.

2. CONVERSION OF METALLIC GALLIUM TO GALLIC OXIDE THROUGH THE SULPHATE

The metal was weighed, dissolved, and the nitric and hydrochloric acids removed by evaporation as in the previous procedure. Pyrex beakers of 100-ml capacity were used, and exactly the same quantities of acid were carried along as a blank in a similar beaker. The gallium sulphate and excess sulphuric acid were transferred to a platinum crucible that had been tested for constancy of weight as compared with a similar crucible as a tare in the manner previously described. The contents of the beaker containing the blank were transferred to the crucible used as a tare. The small beakers were repeatedly rinsed with water and the rinsings added to the contents of the crucibles. These additions were made possible by evaporating part of the water from the crucibles between rinsings.

When it was certain that all the gallium sulphate had been transferred, as much as possible of the water was evaporated on the steam-bath. Then the crucibles were partially covered and transferred to radiators, and heat was very gradually applied until the excess sulphuric acid was volatilized. The crucibles and contents were next placed in a muffle furnace which was gradually heated until sulphur trioxide began to be evolved. This occurred at about 700° C, and during this evolution, the temperature was regulated to remain practically constant in order to avoid too rapid a decomposition of the sulphate, which might result in mechanical losses. After sulphur trioxide ceased to be evolved, the crucibles were tightly covered, and the temperature was raised to 1,200 to 1,300° C. The ignition was then continued until constant weight was obtained. A somewhat longer period of ignition was required than in the case of the hydroxide, but no particular difficulty in arriving at constant weight was experienced. The results obtained by this procedure are shown in table 2. All weights are reduced to the vacuum standard.

TABLE 2.—*Results obtained for the atomic weight of gallium by converting the metal to the oxide through the sulphate*

No.	Wt of metal	Wt of Ga_2O_3	Calculated atomic weight
	g	g	
1[a]	1.15767	1, 55604	69.74_5
2[a]	1.53230	2.05967	69.73_3
3[b]	2.48716	3.34320	69.73_0
4[a]	3.09080	4.15443	69.74_1
			69.73_7=Average.

[a] =first lot of metal.
[b] =second lot of metal.

3. CONVERSION OF METALLIC GALLIUM TO GALLIC OXIDE THROUGH THE NITRATE

The metal was weighed to the nearest 0.05 mg, transferred to a 100-ml Pyrex beaker, and dissolved in a mixture of 40 ml of distilled water, 5 ml of hydrochloric acid, and 5 ml of nitric acid. Exactly the same quantities of acid were carried along as a blank in a similar beaker. When solution was complete, the water and excess of acids were evaporated on the steam bath. Ten ml of diluted nitric acid

(1 + 1) was added to both the blank and the beaker containing the gallium, and the solutions were evaporated as far as possible on the steam bath. This addition of nitric acid and the evaporation were repeated 5 times to make as certain as possible that all chlorides were expelled. After the last evaporation, the residue in the beaker containing the gallium was dissolved in 10 ml of diluted nitric acid (1 + 1) and transferred to a platinum crucible which had been carefully weighed and tested for constancy of weight. The contents of the beaker containing the blank were treated with a like amount of acid and transferred to the crucible used as a tare.

As much as possible of the water and acid in both crucibles was evaporated on the steambath. After this the crucibles were partially covered, placed in radiators, and very slowly heated to about 400° C. They were then transferred to a muffle furnace and gradually heated until the nitrate was decomposed, after which they were tightly covered and heated to 1,300° C. The residue obtained in one of two determinations attained constant weight only after it had been heated for 20 hours at 1,300° C. The other did not attain constant weight in 25 hours. This sluggishness in coming to constant weight was attributed to the retention of gases referred to earlier in this paper. In order to determine whether constant weight could be obtained at all, 5 ml of water, 2 ml of sulphuric acid, and 3 ml of hydrofluoric acid were added to the residue and to the blank. The water and acids were evaporated, and the residue was ignited as in the case of the sulphate. Constant weight was obtained by gradually heating to 1,300° C and then igniting at this temperature for 10 hours.

The two results obtained by this procedure are given in table 3, the first of which is included here, even though it was not gotten by simple direct ignition of the nitrate but by the additional treatment with sulphuric and hydrofluoric acids just described. The procedure involving the ignition of the nitrate is not to be recommended.

TABLE 3.—*Results obtained for the atomic weight of gallium by converting the metal to the oxide through the nitrate*

No.	Wt of metal	Wt of Ga_2O_3	Calculated atomic weight
	g	g	
1[a]	0.78420	1.05411	69.73$_0$
2[a]	.80495	1.08196	69.74$_0$
			69.73$_5$=Average.

[a]=first lot of metal.

V. DISCUSSION OF RESULTS

The weights were carefully calibrated by the mass section of the National Bureau of Standards before this work was started and after it was finished, and the proper corrections were made. By the use of a platinum crucible as a counterpoise, the use of brass weights in excess of 4 g was avoided. Errors caused by the effect of changes in humidity on the brass weights were therefore so small that they were entirely negligible.

The balance used was sensitive to 0.05 mg, and yielded weighings reproducible within 0.05 mg. Tests showed that the inequality of the balance arms could cause a maximum error of only 0.01 mg in any of the determinations. This permitted direct weighing, although a few weighings were made by substitution.

These considerations show that the limit of uncertainty in a single weighing of either the metal or the oxide was 0.05 mg. If the errors were in the same direction in weighing the metal as in weighing the oxide, they were practically without effect, but if they were in opposite directions, errors of considerable magnitude were introduced. In the compound, Ga_2O_3, oxygen constitutes only about one-fourth of the weight, so that in the conversion of metallic gallium to gallic oxide, the relative increase in weight is small. A small error made in weighing the metal or the oxide will, therefore, cause a relatively large error in the calculated atomic weight. For example, in the case of the result, 69.74_5, obtained by converting 1.15767 g of gallium to oxide (no. 1, table 2), if the weight of the metal had been recorded 0.05 mg too high and the weight of the oxide 0.05 mg too low, the calculated atomic weight would have been 69.76_5. If the errors in weighing had been reversed, the calculated atomic weight would have been 69.72_4. This shows that an error of ± 0.02 can exist in this result, although this is improbable. The smaller weights of gallium were used in the beginning of the work because it was not thought possible to convert the larger quantities of hydroxide or sulphate to oxide without mechanical loss. Later it was found that the conversion of 3.0 g of metal, through either the hydroxide or the sulphate, offered no particular difficulties.

It is evident that the conversion of large amounts of metal to oxide will minimize errors of this kind, and that a weighted average is more reliable than the general average because the former gives added importance to the results obtained by the conversion of large quantities of metal to oxide. The weighted average, 69.73_5, obtained by basing the calculation on the total weight of gallium and the total weight of gallic oxide in the 11 determinations, differs only slightly from the simple general average, 69.73_7. The substantial agreement between this value, 69.73_5, and that of Richards and Craig, 69.720, obtained by an entirely different ratio, not only adds to the reliability of the two values, but it also indicates that no appreciable separation of isotopes occurred in either determination unless the remote assumption is made that such separation could have been practically the same in both cases.

The rounded value for the atomic weight of gallium, based on conversion of the metal to gallic oxide, is 69.74.

WASHINGTON, August 29, 1935.