from 21° to 55°; the water was found by selective absorption, the mixed vapors from the saturated solution being passed over calcium chloride and the absorbed water found by weighing. The results obtained are about $^1/_3$ lower than those of Groschuff and myself; the presumption is that the absorption of water was not complete.

For the composition of the other phase (benzene in water) a reliable method has not yet been devised. The existing figures are few. Hantzsch[27] has a value of 0.113% for the solubility of benzene in water, determined by fractional distillation of the saturated solution. Herz[8] gives the figure 0.08% at 22°, obtained by direct measurement of benzene dissolved. I have calculated[23b] from the freezing-point depression of water saturated with benzene that the solubility at 0° is about 0.15%. Moore and Roaf[29] have found the same value, 0.15%, for 15°. No great reliance can be placed upon any one of these figures, and a truly reliable method is greatly to be desired.

Summary

1. It is proposed that all methods for determining solubility be classified on the basis of the phase rule, as *thermostatic, plethostatic or barostatic.*
2. A volumetric method, thermostatic in character, is proposed for the determination of the mutual solubility of liquids.
3. The mutual solubility of ethyl ether and water has been determined by the volumetric method between the temperature of the quadruple point (—3.83°) and 30°, slightly below the boiling point.
4. A method is proposed for determining the solubility of water in a limited list of organic liquids by means of silver perchlorate.
5. The solubility of water in benzene has been determined by this method from the temperature of the quadruple point (5.4°) to the boiling point (69.5°).

NEW YORK, N. Y.

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

THE ATOMIC WEIGHT OF GALLIUM

BY THEODORE W. RICHARDS AND WILLIAM M. CRAIG

Received February 10, 1923

The atomic weight of gallium has received less attention than almost any other atomic weight, largely because of the scarcity of this element. Until very recently our knowledge of the subject was confined chiefly to the work of the discoverer, Lecoq de Boisbaudran, who determined the atomic weight in two ways.[1] By igniting gallium ammonium alum he obtained the value 70.1; and by converting the metal into the oxide

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[29] Moore and Roaf, *Proc. Roy Soc.*, **77B**, 96 (1905).

[1] Lecoq de Boisbaudran, *Compt. rend.*, **86**, 941 (1878).

(through the nitrate[2]) he obtained the value 69.7. The mean value 69.9 has been generally adopted.

The present investigation upon this subject was made possible by the fact that the Bartlesville Zinc Company of Bartlesville, Oklahoma, in redistilling a very large quantity of zinc in order to attain great purity, had accumulated a large mass of comparatively non-volatile residues, (consisting chiefly of lead) which contained a considerable quantity of gallium. The first portion of this material was provided through the great kindness of Mr. F. G. McCutcheon of the Company, and we desire here to express again our thanks to him for his generosity. The major portion of the crude residue containing gallium was purchased later from the Company. Our earlier work upon gallium,[3] carried out with this material, paved the way for the present research, which has required nearly 4 years for its completion.[4]

Preparation of Materials

Gallium.—The residues from the retorts, consisting chiefly of lead, contained on the average only 0.1% of gallium. Accordingly, it was necessary to work on a large scale. In all, 60 kg. of lead, yielding about 60 g. of gallium, was used. After preliminary efforts, using the methods outlined by others, the following succession of operations was adopted. The lead was milled to fine shavings, dissolved (in half-kg. portions) in dil. nitric acid added gradually, and largely precipitated with a slight excess of dil. sulfuric acid. After evaporation of the filtrate to the point of the copious evolution of sulfur trioxide, in order to remove the nitric acid, the residual semi-solid mass was dissolved in water and diluted until about 5 *N* in sulfuric acid. After the removal of the further precipitate of lead sulfate, the filtrate was treated with hydrogen sulfide in the cold, whereby the remainder of the lead, the copper and traces of other heavy metals were separated. Upon further dilution (until about 0.5 *N* in acid) the boiling solution was again treated with hydrogen sulfide, which precipitated most of the arsenic and possibly other sulfides needing a low hydrogen-ion concentration for their removal.

The filtrate was boiled to expel hydrogen sulfide, and solid sodium carbonate was added until a precipitate was barely perceptible. From this neutralized solution, gallium hydroxide was precipitated by means of ammonium hydroxide, an excess of this reagent being avoided. The gelatinous precipitate, after settling, was washed several times by decantation

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[2] This process always yields a result somewhat too low. See Richards and Rogers, *Proc. Am. Acad.*, **28,** 200 (1893).

[3] (a) Richards, Craig and Sameshima, THIS JOURNAL, **41,** 131 (1919). (b) Richards and Boyer, **41,** 133 (1919); (c) **43,** 274 (1921).

[4] A very brief statement of the outcome was presented to the *Société Chimique de France* on July 12th, 1922, and published in its *Bulletin,* **31,** 929 (1922).

with a siphon. It contained chiefly hydroxides of gallium, indium and zinc. Excess of potassium hydroxide, with portions of which the precipitate was successively treated, dissolved the first and last named hydroxides very readily, but had little effect upon the indium compound. Nevertheless, enough of the latter was dissolved[5] to necessitate a far more effective method of separation. The alkaline solution (containing gallium, some indium and a trace of zinc) was neutralized with sulfuric acid; subsequently ammonia was added until a precipitate barely began to form. After the addition of more ammonium sulfate this solution was electrolyzed with a current of 10 amperes, the cathode being a rod of stout platinum wire extending 10 cm. into the solution, and the anode consisting of platinum foil.

Metallic zinc and indium were deposited at first; but since even the first deposit contained some gallium, it was redissolved and re-electrolyzed separately. As the electrolysis proceeded, yielding more gallium, the boiling solution gradually deposited upon the bottom of the vessel an insoluble basic gallium ammonium sulfate as a fine granular powder. During the electrolysis traces of arsine were evolved and much of the arsenic remaining in the preparation was eliminated in this disagreeable and unwholesome fashion. The basic salt, which contained nearly all the gallium (since but little was deposited electrolytically under the conditions described above) formed a new and effective mode of purification. It was dissolved in a slight excess of potassium hydroxide and electrolyzed successfully in the alkaline solution. A large excess of potassium hydroxide must be avoided in this electrolysis; otherwise there is formed a potassium gallium alloy which acts upon water and acid but slightly, considering the large percentage of potassium present.

The gallium thus obtained was treated first with warm conc. nitric acid in order to remove the more soluble metals present, and then (after washing) with dil. sulfuric acid. As already pointed out,[6] gallium has a tendency to become passive. Under some conditions, moreover, small liquid drops of the metal fail to coalesce, probably because of the formation of a film of oxide. Sulfuric acid at once produces coalescence, doubtless dissolving the thin superficial coat. Probably the film of oxide is the cause of the fact that metallic gallium, like the similar metal aluminum, remains apparently bright for years in dry air. The gallium dissolved in the acids used for washing was of course recovered by subjection to the processes just described.

Earlier work had shown that the removal of the last traces of zinc and perhaps of some other metals was not an easy matter.[6] Two methods

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[5] The statement of others that the separation is almost quantitative does not, of course, apply to work of the precision aimed at in the present study. Uhler and Browning, *Am. J. Sci.*, [IV] **42**, 389 (1916).

[6] Ref. 3c, p. 276.

have been found effective; first, fractional crystallization of the metal, which removes all impurities not isomorphous; and, second, heating to a high temperature in a vacuum,[7] which removes more volatile substances, especially zinc and arsenic. Accordingly, to make assurance doubly sure, the material used in this case was subjected successively to both treatments, as follows.

The purified metal obtained by electrolysis solidified at a temperature only slightly below 29.75°, the normal freezing point of gallium. This is strong evidence of purity. In order to eliminate any residual trace of other non-isomorphous metals, the following process was employed. The liquid metal obtained by electrolysis was placed in a watch glass cooled merely by the air of the room (25°). The point of a small platinum wire provided with a minute fragment of solid gallium was introduced into the liquid metal and a crystal of solid gallium was allowed to grow slowly upon it. The large crystal thus obtained was removed to a second watch glass, and the liquid metal adhering to its surface was removed by rubbing the crystal upon the glass. In this manner most of the adhering liquid was removed, since liquid gallium, like water, adheres to clean, dry glass. Following this procedure, the metal was fractionally crystallized by 8 crystallizations. The purest sample was crystallized at least 5 times, the additional 3 recrystallizations having been undertaken in order to augment the yield. The diagram (Fig. 1) illustrates the details of the process.

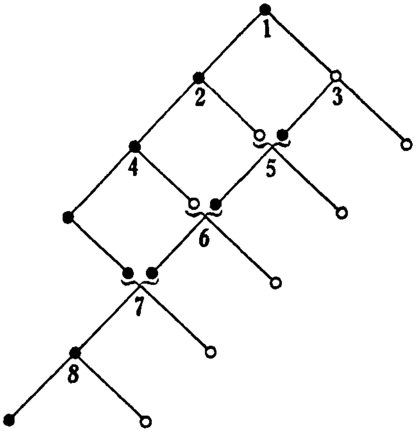

Fig. 1.—Fractional crystallization of metallic gallium. Black circles denote crystals; white circles, fused metal. Only the crystals indicated on the extreme left were used in this work.

The purest crystals (melting at 29.75°) were then placed into a boat of fused silica, and the liquefied metal was heated for about 24 hours in a large, evacuated silica tube at 800° to 850°. It is only very slightly volatile under these conditions. The product failed to show the slightest spectroscopic evidence of zinc, lead, indium or arsenic after a searching test with a Féry spectrometer. Finally the gallium was etched with nitric and with sulfuric acid, washed with distilled water, separated into small droplets, solidified, and dried in a desiccator.

The very pure gallium thus obtained was then converted into chloride according to the method which has already been described,[3] a method very

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[7] P. E. Browning attained the same result by heating in hydrogen. Ref. 5, p. 398.

similar to that independently and almost simultaneously employed by Dennis and Bridgman.[8] The subsequent distillation of the chloride afforded a further excellent means of eliminating impurities, if any were still present. The apparatus used for this purpose was made wholly of glass, sealed together. Each piece of glass, before being sealed into the apparatus, was thoroughly washed. After the assemblage had been completed, every trace of water was removed by repeated evacuation and filling with thoroughly dried air. The diagram (Fig. 2) illustrates the assemblage. Because at several stages of the procedure it was necessary to change connections, and stopcocks in the chief train were inadmissible (for fear of contaminations introduced by their lubrication) the magnetic valve (which has already been briefly described,[9] and which is illustrated herewith, (Fig. 3)) was used. It differed from the valve used

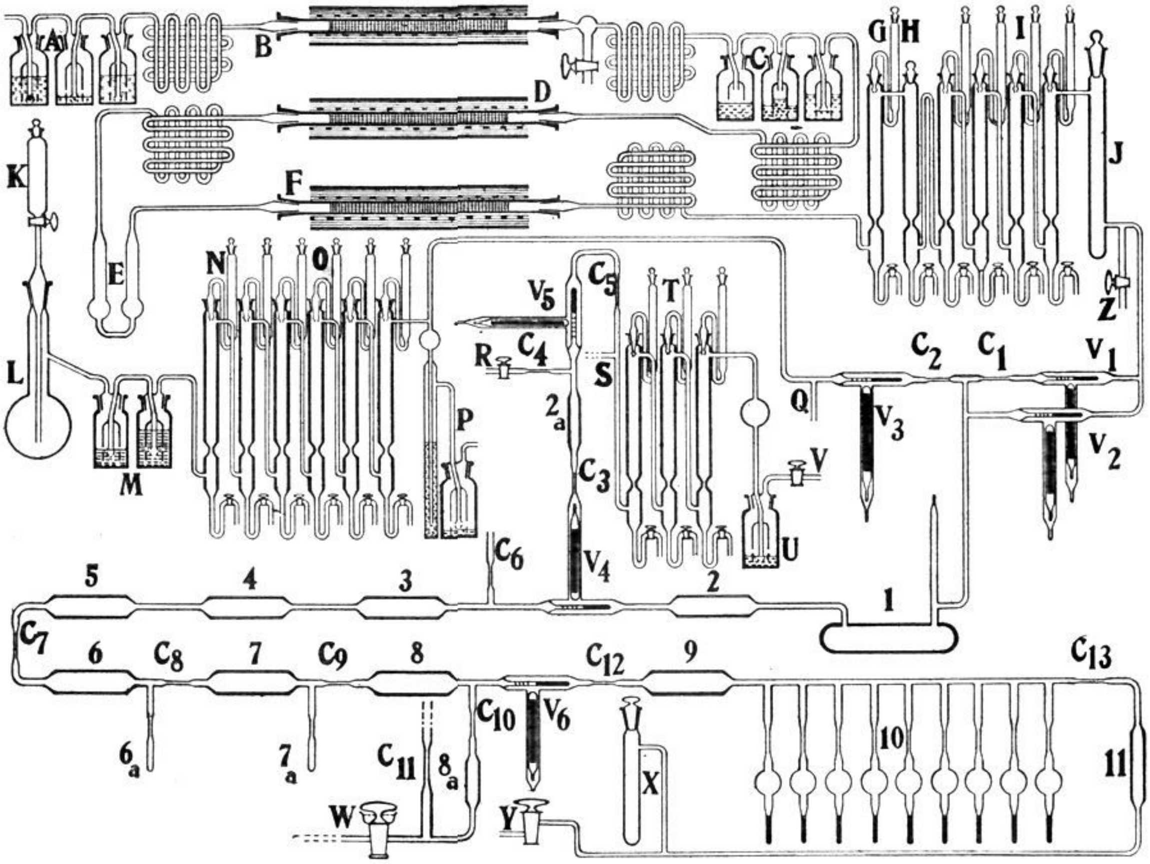

Fig. 2.—Apparatus for distillation and sublimation of gallium chloride. The apparatus for preparing pure nitrogen extends from *A* to *J;* that for preparing pure chlorine from *K* to *Q*. Gallium was converted to chloride in Receptacle 1 and fractionally sublimed in the receptacles from 2 to 10, as described in the text. The diagram is not drawn to scale.

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[8] Dennis and Bridgman, THIS JOURNAL, **40,** 1540 (1918).

[9] This magnetic valve was first used by us in this work during the winter of 1917–18 [(a) Ref. 3a, p. 132], and later by one of us in collaboration with Dr. H. Krepelka [(b) THIS JOURNAL, **42,** 2226 (1920)], as well as by Hildebrand and Buehrer, [(c) *ibid.,* **42,** 2215 (1920)].

by Bruner and by Briscoe[10] (which could not conveniently have been used in our elaborate apparatus) in that magnetism rather than gravitation was the agency employed for breaking the fine inner tube and thus establishing communication between the previously separated portions of the apparatus.

The pure gallium, contained in the receptacle 1 of this assemblage, was converted by means of pure chlorine into the two chlorides of gallium, $GaCl_2$ and $GaCl_3$. After complete conversion into the trichloride, the substance was distilled or sublimed 9 times in succession, in chlorine, in pure nitrogen, and in a vacuum, and was finally distilled into the bulbs in which it was weighed for analysis. The successive steps demanded by this elaborate succession of processes may be briefly detailed as follows. When about 17 g. of gallium had been cautiously introduced into receptacle 1, through the vertical tube, the latter was sealed and the whole apparatus was thoroughly dried again in the manner already described. Thereupon, pure dry nitrogen was passed through the chlorine apparatus, by means of a special connection between *Z* (near *J*) and *K*, the gas finding egress through *Q*, and thus sweeping out all the air. By closing the stopcock *Z*, sealing *Q*, and opening magnetically the valves V_1, V_3 and V_5, the nitrogen stream was then diverted through the train from V_1 to V_5, including the protecting towers containing sulfuric acid (*T*). In due time the stopcock at *V* was closed, thus driving the nitrogen through the valve V_3 and backwards through the last sulfuric acid tower of the chlorine apparatus. Thus all oxygen was removed from the vessels in which the synthesis was to be effected. When this had been accomplished, the nitrogen apparatus was temporarily disconnected by sealing the capillary tube C_1. The other closed magnetic valve V_2 remained available, so that nitrogen could be used in a later stage of the process. An electric oven having been placed around receptacle 1, containing the gallium, the chlorine stream was started. Diluted at first with nitrogen and thoroughly dried by sulfuric acid in the towers *O*, the halogen gradually attacked the gallium, at first forming dichloride, which covered the metal with a thin liquid film. This film prevented violent combustion, which might have broken the tube.

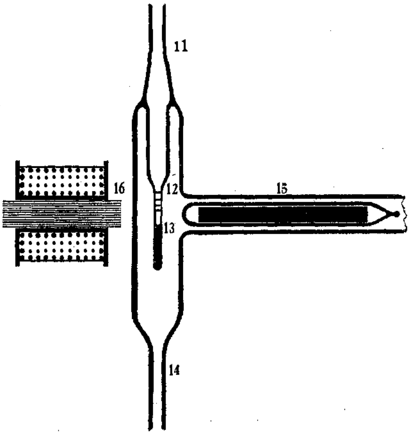

Fig. 3.—The magnetic valve. A bar of soft iron (15), enclosed in a strong glass tube, breaks the capillary at the file scratches (12) when the electro magnet (16) is actuated, thus opening communication between 11 and 14.

After about a third of the gallium had been converted into the chlorides, the temperature of the electric oven was raised from its previous temperature (95°) to about 120°, while Vessels 2 and 2a were cooled with filter paper wet with ice water, in order to condense evaporated gallium trichloride. All the metal having combined with halogen, the temperature of the electric oven was gradually raised to about 200°, at which temperature gallium trichloride evaporates rapidly. Because the chlorine stream was continued, most, if not all, of the dichloride still present was converted into trichloride during the distillation. Nearly all of the gallium trichloride was thus distilled into

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[10] Bruner and Bekier, *Z. Elektrochem.*, **18,** 369 (1912). Briscoe and Little *J. Chem. Soc.*, **105,** 1324 (1914).

Vessel 2, leaving only a small portion of this substance and a slight gray residue (probably sodium chloride taken from the glass) in Vessel 1. The first and most volatile portion of the distillate showed a slightly pink tint, due to a trace of some unknown substance, which we proceeded immediately to eliminate. Before the second distillation the halide in Vessel 2 was digested for several hours at about 90° in chlorine, in order to insure the complete conversion of the gallous into the gallic form. The temperature having been raised to 145°, and with a slow stream of chlorine still passing, a small amount of the gallium chloride was distilled into Vessel 2a, in order to eliminate any possible low-boiling contaminations. Vessel 2a was then sealed off at the capillary C_3, and C_5 also was sealed in order to preserve this specimen which was not used for analysis. During the synthesis and subsequent distillations just mentioned, Valve V_4 was heated to 250° to prevent condensation there. The tube C_{11} was connected with the drying towers through the tube S, and the whole latter part of the apparatus was then very thoroughly dried. Pure dry nitrogen was passed through this section of the assemblage by connecting the stopcock Z with C_6, and this latter capillary was then sealed, making the apparatus ready for further distillation.

After Valve V_4 had been opened magnetically, about $^9/_{10}$ of the gallium chloride was distilled into No. 3 at a temperature of 220° while the chlorine stream continued to pass through the train, and the distillation in chlorine was repeated from Vessel 3 to Vessel 4, again leaving a small residue. These three distillations and prolonged digestion in an atmosphere of chlorine were deemed sufficient to convert the gallium from dichloride completely to trichloride, especially when consideration was taken of the wide difference in the boiling points of these 2 substances (about 530° and 220°, respectively) and the fact that the distillate was distinctly greenish in color because of dissolved chlorine.

The dissolved chlorine had, of course, to be removed. Accordingly, the distillate in Vessel 4 was melted and allowed to solidify several times in succession in a slow stream of pure nitrogen, which was admitted by sealing C_2 and opening V_2 magnetically. The product was then pure white, and any trace of chlorine which may have remained was eliminated by distilling into Vessel 5 in a stream of nitrogen at a temperature kept low (about 140°) to prevent dissociation. A second distillation in nitrogen into Vessel 6 continued the fractional purification, since a fraction of residue remained in each case. At this stage in the proceedings, the very pure substance and the remaining portion of the apparatus were cut off from the gas connections by sealing the capillaries C_7 and C_{11}; and the residual nitrogen was completely exhausted through Stopcock W, which was lubricated with sulfuric acid and sealed above with paraffin (according to a suggestion by Krepelka). By heating Vessel 6 to about 75° the gallium chloride was then sublimed in a vacuum into Vessel 7, the first portion of the sublimate having been collected and sealed in 6a. Vessel 6 was then removed by the sealing of C_8; the halide was sublimed at a temperature of only about 60° from Vessel 7 to 8, and again some of the first portion of sublimate collected in 7a. Sublimation, of course, combines the advantages of distillation and crystallization. Yet another sublimation in a vacuum conveyed the material, after the opening of the magnetic valve V_6, into Vessel 9. From this vessel, by suitable regulation of its temperature and that of each connecting tube and bulb (of the group numbered 10), the substance was fractionated at a temperature of 120° to 145° into the successive bulbs, the respective temperatures of the several bulbs determining the point of accumulation. Tube 11 was provided as a reservoir in case of accident, and Tube X contained phosphorus pentoxide to assist in drying the tubes in a vacuum before the distillations. Before the final distillation the capillary C_{13} was plugged with gallium chloride by suitable arrangement of temperatures, so as to prevent the premature escape of any of the substance into the safety receptacle 11. The volatile salt, when solidified in a capillary, formed a very convenient stopper for preventing its own egress.

The collecting bulbs 10 were of the type already used repeatedly in such work.[11] In Fig. 2, they are shown in horizontal projection; when viewed in vertical projection their arrangement appeared as in the upper part of Fig. 4. This arrangement was found to be important to prevent fracture at the moment of sealing. During the distillation each capillary, after its bulb had been filled, was temporarily sealed with a small solid plug of gallium chloride by suitable cooling; and after the whole apparatus had cooled, each of these plugs in turn was carefully melted and the capillaries were sealed at the bend by means of a small blowpipe. Subsequently, the walls of the capillary were melted together and bent into a hook in the fashion shown in Fig. 4.

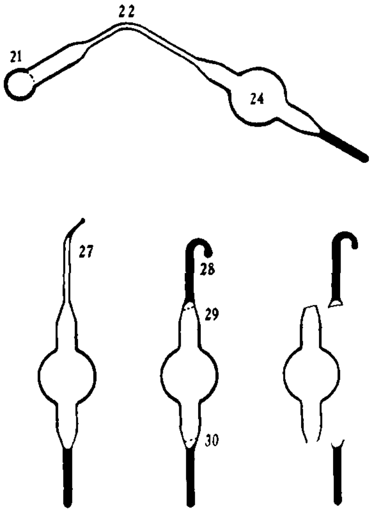

Fig. 4.—Bulbs for weighing anhydrous gallium chloride. The upper diagram shows the position of bulb when receiving gallium chloride by sublimation or distillation. The lower diagrams represent a bulb during the subsequent stages of procedure.

The elaborate apparatus, and the succession of operations just described were not perfected all at once. They were evolved with the help of experience gained in three preliminary trials, more or less successful, but each indicating needed improvements. The final assemblage functioned perfectly.

Thus 8 successive samples of gallium chloride were obtained. Each had been distilled or sublimed 9 times with rejection each time of a small portion of the least volatile part, and usually also of a small portion of the most volatile part. The substance thus obtained was a very beautiful preparation of perfect transparency and without a trace of color. The remaining substance in the sealed vessel 7, which is still unbroken, has in the course of time distilled from one portion of the vessel to another, at room temperature, leaving no visible residue and developing into perfect crystals of remarkable beauty. The specimens actually analyzed must have been, if possible, even purer than this. The temperature of sublimation was so low that (in the absence of any excess of chlorine or acid) the substance could hardly have attacked the glass walls of its receptacle appreciably during the latter part of its progress, and certainly no appreciable amount of sodium chloride could have distilled or sublimed at a temperature of 75°. Therefore, these samples were analyzed with confidence in their purity.

The other substances employed were purified by the usual means.

Sulfuric Acid was obtained by the double distillation of a very pure commercial specimen, only the middle third in each case being used.

Hydrochloric Acid was freed from any possible trace of bromine and iodine by

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[11] For example see Richards and Rogers, *Proc. Am. Acad.*, **31,** **166** (1895). Baxter, Moore and Boylston, This Journal, **34**, 259 (1912). Ref. 3a. Especially Ref. 9b.

boiling with small successive amounts of pure permanganate and was then twice distilled, and the first and last thirds of the distillate were rejected.

Nitric Acid was purified in usual fashion and carefully tested in the nephelometer to prove the absence of halogen.

Chlorine was prepared by the action of pure potassium permanganate on pure 10% hydrochloric acid; the speed of the evolution was regulated by change of temperature.

Silver had been prepared by recrystallization of the nitrate, precipitation as metallic silver by pure ammonium formate, reconversion into the nitrate and reprecipitation, fusion into metallic buttons, electrolysis (using the pure metal as anode in a solution of pure silver nitrate), and then fusion of the electrolytic product in hydrogen in boats of pure lime. The very pure metal thus obtained was, when necessary, cut on a clean anvil with a clean chisel, etched with nitric acid, rinsed thoroughly with water, and dried by heating in a vacuum. For this pure metal we are greatly indebted to Dr. N. F. Hall, who kindly left for us the remainder of a considerable amount prepared for his work on isotopic lead and the silver coulometer.[12]

Phosphorus pentoxide was twice successively resublimed from a porcelain boat in an electrically heated tube of refractory glass during the passage of dry oxygen.

Water was thrice distilled; first, from dil. alkaline permanganate, then from a trace of sulfuric acid to hold ammonia, and finally, again after the addition of a trace of potassium hydroxide, to retain any possible trace of acid. Especial care was taken to prevent, by means of baffles, the projection of any drops of the liquid to be distilled into the distillate (See Fig. 5).

Nitrogen was prepared by the convenient method described in other papers,[13] and shown diagrammatically in Fig. 2 (A to J).

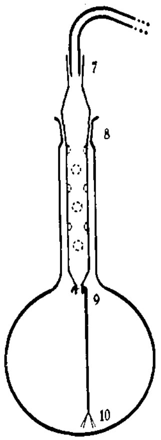

Fig. 5.—Still for pure water. The perforated tube ground into the neck of the flask greatly assisted in preventing projected drops from entering the distillate. Markovnikov tubes were suspended from its lower end. The still was constructed wholly of Pyrex glass, the condenser tube of pure block tin.

Method of Analysis

One of the bulbs containing anhydrous gallic chloride was used for each analysis. In order to correct the results to the vacuum standard, the exterior volume of each of these bulbs had to be determined by noting its loss of weight in water when suspended by a fine thread from the balance arm. Subsequently, the bulb was carefully cleaned with nitric acid and distilled water, and wiped dry with a chemically clean, lintless cloth. Two fine scratches were made with a safety razor blade, ground to a fine file edge upon a carborundum stone, and the powdered glass was removed by the cloth. The bulb thus prepared, after long standing in a desiccator, was ready for the analytical process and was carefully weighed on a very sensitive balance.

As in the case of aluminum bromide, the solution of the salt in water was conducted with great care to avoid loss of halogen, by a method essen-

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[12] Richards and Hall, This Journal, **39**, 531 (1917); **38**, 2045 (1916).

[13] See for example, Ref. 9b, p. 2225.

tially similar to that which had worked so satisfactorily in the former case. Upon the bottom and sides of a large, stout, glass-stoppered Erlenmeyer flask, about 0.2 liter of the purest water was frozen during continued rotation.[14] The weighed, scratched bulb was carefully slid down upon the ice at the bottom of the inclined flask, with scrupulous precautions as to cleanliness. The stopper was then replaced, covered with several thicknesses of chemically clean cloth, and firmly tied. In a temperature of about —20° (maintained by solid carbon dioxide and alcohol), the flask was carefully shaken so as to break both ends of the bulb at the places previously scratched. Danger of breaking the flask was averted by the protective coating of ice. Only a few small fragments of glass, besides the bulb and its solid ends, resulted from the fracture. Very slowly the ice was then allowed to melt, the flask being so tilted that the water, only drop by drop, was able to act upon the solid gallium chloride. In this way loss of hydrochloric acid, which might be caused by the high heat of solution of gallium chloride and the tendency of the salt to hydrolyze, was prevented as much as possible. The water held by capillarity in the two ends of the bulb formed effective water seals and allowed no fumes to escape into the flask; but even if a trace had escaped it would have been held by the large surface of ice.

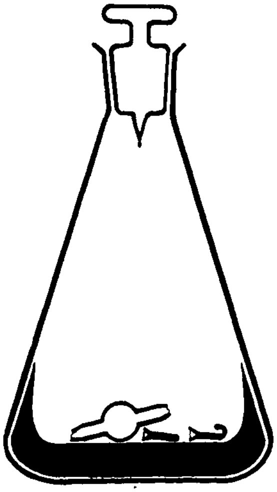

Fig. 6.—Arrangement for dissolving gallium chloride. This diagram represents the stout Erlenmeyer flask coated with ice below, in which, while still cold, the gallium chloride bulbs were fractured.

When the dissolving of the gallium chloride had been satisfactorily accomplished, the solution was diluted with purest water and filtered through a weighed Gooch-Munroe crucible with the usual analytical precautions. The thistle tube used for receiving the filter crucible extended almost to the bottom of the receiving flask. It was provided with holes at intervals in the sides of the stem, to prevent spattering and also the possibility that liquid might be forced backward through change of pressure. After great care had been taken to transfer every trace of broken glass to the crucible, the latter with its contents was carefully dried and weighed. The weight of the glass was, of course, corrected to the vacuum standard.

To the solution of gallium chloride thus transferred to a smoothly ground glass-stoppered 3-liter Erlenmeyer flask, was then added a solution of a carefully weighed amount of pure silver known from preliminary experiments to be very nearly that required to precipitate all of the chlorine.

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[14] This device was employed by Richards and Krepelka, Ref. 9b.

Each step of this process, as well as of the subsequent adjustment to exact equivalence by means of the nephelometer, was conducted with the greatest care, in a manner already often described, in a photographic dark room. No especially new feature entered into this part of the work, although perhaps unusually meticulous precautions were observed. In two of the experiments the silver chloride thus resulting was weighed, but these experiments could hardly be considered as more than preliminary. The series finally accepted left little to be desired.

Preliminary Results

The preliminary work briefly published in 1919 did not pretend to be a determination of the atomic weight. The original material had not been very carefully purified, and the method of dissolving the gallium chloride at that time might have led to loss of hydrochloric acid. Moreover, the salt may have contained a trace of water; therefore, it is not surprising that the result was too high. Accidents vitiated to a greater or less extent 3 subsequent series of distillations, but several careful analyses of the product obtained from them showed that the atomic weight could not be far from 69.7. The two practice analyses involving the weighing of the silver chloride gave the value 69.74. Hence, the better part of the preliminary work, considered as a whole, pointed to a value of about 69.72. These determinations are not worth giving in detail, but they afforded highly valuable preparation for the final series of determinations.

Final Determinations

The data of one of the final analyses may be given in full in order to make clear the necessary corrections.

Table I

Analytical Data for Analysis D; Bulb 7

	G.	G.
Wt. of bulb + sample (in air)..........	5.76651	
Exterior volume of bulb = 2.845 cc.		
Exterior volume of brass weights = 0.695 cc.		
Vacuum correction for bulb[15]...........	+0.00260	
Wt. of bulb + sample (in a vacuum)....	5.76911	5.76911
Wt. of empty bulb (in air)...............	2.48904	
Vacuum correction for glass[15]...........	+0.00085	
Wt. of empty bulb (in a vacuum).......	2.48989	2.48989
Wt. of gallium chloride (in a vacuum)...		3.27922

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[15] The specific gravities of silver, glass and brass were taken as 10.5, 2.5 and 8.4, respectively, in calculating the reduction of the weights to the vacuum standard. The value for glass was determined with a piece of the tubing used for making the bulbs. The atmospheric conditions at the times of weighing varied little from the normal of 760 mm. pressure and 20°, but for certainty they were duly observed.

TABLE I (*Continued*)

	G.	G.
Silver (wt. in air)	6.02808	
Vacuum correction[15]	−0.00017	
Silver (wt. in a vacuum)	6.02791	
Chloride added in titration	−0.00103	
(expressed as its equivalent of silver)		
Vacuum weight of silver required for exact nephelometric balance	6.02688	6.02688
Calculated atomic weight		69.718

There follow the data and results of the four final and most trustworthy determinations, which were consecutive since fortunately no accident necessitated the rejection of any result after the final series had been begun. The values are referred to the atomic weights, Ag = 107.88, and Cl = 35.458.

TABLE II

DATA AND RESULTS OF FINAL SERIES OF DISTILLATIONS

Bulb No.	Vac. wt. of gallium chloride	Vacuum wt. of silver	Calc. atomic weight
1	3.40649	6.26079	69.718
2	4.56208	8.38446	69.722
3	2.55769	4.70108	69.707
7	3.27922	6.02688	69.718
		Av.	69.716

Evidently the fractionation yielded essentially the same product at its end as at its beginning. The analysis of the contents of other bulbs was inhibited by lack of time; but it could hardly have changed the result of the series.

Since these results are so much more consistent with each other than those of any other determinations of the atomic weight of gallium, and since, moreover, the method by which they were determined is one which has been tested for many years and found in similar cases to be trustworthy, one can hardly doubt that the outcome, 69.716, represents very nearly the true atomic weight of gallium. As would be expected, it falls between the two results of Lecoq de Boisbaudran.

One of the interesting outcomes of the work is the conclusion that, granting the validity of the "whole number rule" of Harkins and Aston, the value 69.72 indicates the existence of at least two isotopes in gallium.

We are indebted once more to the Carnegie Institution of Washington, as well as to an anonymous benefactor of this Laboratory, for generous financial support in this investigation. To the University of Texas we are grateful for hospitable accommodation during part of the preliminary work of refining the crude material which was carried on by one of us in summer.

Summary

This paper recounts a determination of the atomic weight of gallium by means of the analysis of gallium chloride. The gallium which formed the starting point was very carefully purified, converted into chloride by the action of pure chlorine, and fractionated in this form. The fractionation was effected by distillation and sublimation in chlorine, in nitrogen, and in a vacuum. The salt was analyzed by essentially the same method as that employed in the case of aluminum bromide, and yielded the result Ga = 69.716, if silver is 107.88 and chlorine is 35.458.

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[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON]

THE SYSTEM, CALCIUM OXIDE–CARBON DIOXIDE

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Received February 10, 1923

Previous Investigations and Purpose of the Present Work

The reaction between calcium oxide and carbon dioxide has long been the subject of investigation. Comparatively few workers, however, have sought the behavior of calcium carbonate when it is subjected to conditions of relatively high temperature and pressure. The reason for this is doubtless found in the fact that difficulties of experimentation at pressures in the neighborhood of a thousand megabars and at temperatures above 1000° are great. Nevertheless, a knowledge of the pressure-temperature relations of this simple system is necessary before further exact knowledge can readily be obtained of systems which contain mixtures of calcium carbonate with other carbonates or with silica. From systems, either with or without the presence of water, would crystallize minerals such as the dolomites and silicate carbonate compounds of which spurrite and cancrinite are examples. We hope that the present work may serve as a basis for the further investigation of the natural conditions which have given rise to the formation of many complex minerals containing calcium carbonate as one constituent.

In the following pages are described an apparatus which has proved reasonably satisfactory for such experimentation, and the results which have been obtained in the 2-component system, calcium oxide–carbon dioxide, the reaction being represented by the equation, $CaCO_3 = CaO + CO_2$.

Of the equilibria data already obtained at lower pressures and temperatures, which may be controlled in apparatus of thin-walled tubes, only