

in the potassium chloride in this mixture is the same (0.504) as it is in dilute potassium chloride solutions, the proportion of the current carried by its ions was found to be 0.573, and the proportion carried by the ions of the potassium sulfate to be 0.427. By multiplying these values by the measured specific conductance of the mixture, the partial specific conductances of the two salts in the mixture were obtained.

The partial specific conductance of the potassium chloride so obtained was found to be 2.0 per cent. larger, and that of the potassium sulfate 5.2 per cent. smaller, than the values calculated by the principle, previously tested only by conductance measurements, that each salt in the mixture has an ionization equal to that which it has when present alone in a solution in which its ions have a concentration equivalent to that of the common ion in the mixture, the ionization being taken equal to the ratio  $\Delta\eta/\Delta_0\eta_0$ , in which  $\Delta$  and  $\Delta_0$  represent the equivalent conductances, and  $\eta$  and  $\eta_0$  the viscosities, of solutions of the separate salts at the ion concentration in question and at zero concentration.

BOSTON, MASS.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

## A REVISION OF THE ATOMIC WEIGHT OF IRON.

[THIRD PAPER.]

### THE ANALYSIS OF FERROUS BROMIDE.

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CONTENTS: 1. Introduction. 2. Purification of Materials. 3. Preparation of Ferrous Bromide for Analysis. 4. Method of Analysis. 5. Balance and Weighing.

#### I. Introduction.

The atomic weight of iron has already been subjected to two investigations in this laboratory. In one<sup>1</sup> ferric oxide was analyzed by reduction, in the other<sup>2</sup> the per cent. of bromine in ferrous bromide was determined. The first investigation yielded as a result 55.883 (O = 16.000), a value somewhat lower than the one in general use at the time, 56.0. The result of the second investigation, 55.871 (Ag = 107.93) confirmed so closely the value resulting from the oxide analysis, that, since the methods of the two investigations differ so radically, the matter was allowed to rest at this point until very recently. During the last few years much evidence has been brought forward to show that the older value for the atomic weight of silver, 107.93, is several hundredths of a unit too high and that the probable value lies at least as low as 107.88. With this lower value for silver and a correspondingly lower value for bromine the atomic weight of iron calculated from the bromide

<sup>1</sup> Richards and Baxter, *Proc. Am. Acad.*, 35, 253 (1900).

<sup>2</sup> Baxter, *Ibid.*, 39, 245 (1903).

analyses is 55.845. The agreement of this corrected value with the result of the analysis of the oxide is far from satisfactory. It becomes imperative therefore to discover, if possible, the cause of the difficulty and to determine which of the early results is more reliable.

Neither of the methods mentioned above is entirely free from difficulties. In the oxide method, either the presence of magnetic oxide in the ferric oxide or incomplete reduction would have caused too high a result to be obtained. Since in the experiments by Richards and Baxter, the oxide was made from the nitrate by ignition in air, it is not easy to believe that an error from the first cause actually exists. On the other hand, very prolonged ignition at a high temperature in a current of hydrogen is necessary to insure even apparently complete reduction of ferric oxide to metal. Two indications of complete reduction were obtained by Richards and Baxter, one of which was constancy in the weight of the metal when repeatedly ignited in hydrogen, the other of which was complete solubility of the metal in dilute acid. Either of these tests might be misleading, however, since oxide might be so coated over with metal as to prevent or delay further reaction with the hydrogen, while it is well known that the solubility of ferric oxide in acid is increased by the presence of ferrous salts. It is true that gases occluded by the ferric oxide and released during reduction might have caused too great a loss in weight and hence have lowered the observed atomic weight of iron. But careful tests were made for occluded gases and no appreciable quantity was detected.

While the analysis of halogen salts for halogen has been found to be one of the most satisfactory methods of atomic weight determination, the analysis of ferrous bromide, as carried out by Baxter, was subject to a slight uncertainty. The bromide was made by sublimation in porcelain tubes and contained between one- and two-tenths of one per cent. of sodium bromide extracted from the tubes. The proportion of sodium bromide was unfortunately not as constant as could be desired, hence the correction which was applied for this impurity may be slightly in error.

On the whole, however, the ferrous bromide analysis seemed more satisfactory, and, since fused-quartz apparatus, which was not available for the earlier investigation, presented the possibility of many improvements in the preparation and analysis of the salt, it was decided, in taking up the subject anew, first to repeat the analysis of ferrous bromide.

## 2. Purification of Materials.

*Water.*—The ordinary distilled water of the laboratory was used in the preliminary stages of the purification of some of the materials used in this research, but for most purposes the laboratory supply was twice

redistilled, first from alkaline permanganate, and then from very dilute sulfuric acid. Condensers of block tin were employed and rubber or cork connections were entirely avoided. In general, the water was collected in Jena glass flasks, but for special purposes either platinum or quartz receivers were used.

*Nitric Acid.*—Commercial c. p. nitric acid was purified by two distillations through a quartz condenser with the rejection of the first third of the distillate in each distillation. Nitric acid distilled in this way does not contain more than the merest trace of chlorine, if the original acid is fairly pure. Here also quartz or platinum receivers were used whenever traces of alkalis were to be avoided.

*Sulfuric Acid.*—The best commercial article was distilled from a non-tubulated glass retort into an air-cooled flask. The first portion of the distillate was rejected. This acid was never used where a trace of alkali would have been harmful.

*Ammonia.*—Pure commercial ammonia of sp. gr. 0.90 was heated in a glass-stoppered boiling flask and the gas was absorbed in the purest water.

*Solid Reagents.*—Potassium permanganate, potassium dichromate, potassium and ammonium oxalates and oxalic acid were purified by several crystallizations from aqueous solution, with centrifugal drainage.

*Silver.*—The sample of silver used in this investigation was purified by methods which have been thoroughly tested in this laboratory.<sup>1</sup> Silver chloride was precipitated from strongly acid solution and after thorough washing by decantation, was reduced by means of sugar and sodium hydroxide. The metal was washed and fused upon charcoal before a blowpipe and the surface impurities were removed from the buttons by scrubbing with sea sand and etching with dilute nitric acid. The cleansed buttons were dissolved in nitric acid, and the solution, after neutralization, was precipitated with ammonium formate which had been prepared with distilled materials. Again the metal was thoroughly washed with water and fused with even more care than before in a porcelain crucible lined with the purest lime. The resulting buttons were in turn cleansed by etching with dilute nitric acid and were next converted into electrolytic crystals in a cell in which a concentrated, nearly neutral solution of silver nitrate served as electrolyte, and a pile of the buttons served as anode, the cathode being a stick of very pure silver from another preparation. After the crystals had been thoroughly washed with water, they were fused in a current of hydrogen in a porcelain boat lined with the purest lime. The boat was provided with cavities so that the buttons of silver varied considerably in size,

<sup>1</sup> See especially Richards and Wells, *Pub. Car. Inst.*, 28, 16 (1905); THIS JOURNAL, 27, 472.

from 2 to 5 grams. The final product was freed from adhering lime by etching with dilute nitric acid and, after being washed with the purest water, it was dried, first in air at 100°, finally in a vacuum at about 500°.

A second sample was prepared in an exactly similar fashion by Dr. H. C. Chapin<sup>1</sup> for work upon the atomic weight of neodymium, except that it was necessary to cut the product into smaller fragments by means of a fine jeweler's saw. Surface contamination with iron from the saw was removed by etching with successive portions of dilute nitric acid until the acid remained free from iron. This specimen was used only in Analysis 13 and 27. Both specimens have already been used in a determination of the atomic weights of iodine and silver and have been found to give results identical with those of other very pure specimens of silver.<sup>2</sup>

*Hydrobromic Acid.*—This substance was prepared from bromine which had been carefully freed from chlorine and iodine by processes which have repeatedly been shown to be effective for the purpose in this laboratory. Commercial bromine was first distilled from solution in saturated aqueous potassium bromide. A portion of the product was next converted into potassium bromide by addition to a solution of twice recrystallized potassium oxalate, and the remainder of the bromine was distilled from solution in this potassium bromide, which must have been at any rate nearly free from chloride. Although in these two distillations from a bromide, the bromine must have been very effectually freed from chlorine, still another similar distillation was carried out later. The next step consisted in converting the bromine to hydrobromic acid. Hydrogen, made by the action of water on "hydrone," was purified and dried by scrubbing with water and passing over fused potassium hydroxide. This hydrogen was charged with a very nearly equivalent amount of bromine by bubbling through the latter substance at about 45° and the mixture was passed over hot platinized asbestos in a hard glass tube. The resulting hydrobromic acid was absorbed in the purest water. Needless to say, no cork or rubber connections were used in the apparatus for synthesizing hydrobromic acid except to connect the hydrogen generator to the purifying apparatus. In order to free the hydrobromic acid from iodine the solution was twice boiled for some time, after the addition of a small amount of the specimen of bromine which was used in the preparation of the acid, and finally with a small quantity of chlorine-free potassium permanganate. The hydrobromic acid solution was next distilled and then was converted into bromine by heating with a nearly equivalent amount of chlorine-free permanganate. In this way, since only five-eighths of the bromine is set free,

<sup>1</sup> *Proc. Am. Acad.*, 46, 213 (1910); *THIS JOURNAL*, 33, 16 (1911).

<sup>2</sup> Baxter, *THIS JOURNAL*, 32, 1591 (1910).

the product received a third distillation from a bromide. The bromine was again converted into hydrobromic acid in the way already described, and the acid solution was freed from excess of free halogen by boiling and finally by distillation. Three different specimens of hydrobromic acid prepared in the same way, all gave identical results as far as could be determined.

Fuming hydrobromic acid was made by saturating the constant-boiling solution at  $0^{\circ}$  with hydrobromic acid gas synthesized as above. Especial care was taken to avoid an excess of bromine in the synthesizing apparatus.

*Iron.*—The preparation of pure iron has been discussed in the earlier papers upon the atomic weight of iron. Essentially the same methods were used in the purification of the three specimens employed in this investigation.

Sample A was made from very pure iron ribbon. After solution in redistilled nitric acid the ferric nitrate was three times crystallized from concentrated nitric acid with centrifugal drainage after each crystallization. All the operations, even the centrifugation, were performed in platinum vessels.

The nitrate was next dried and partially decomposed by heating on an electric stove in a platinum dish. The resulting mixture of oxide and basic nitrate was reduced to metal by means of ammonia, generated from a concentrated solution by means of solid sodium hydroxide and dried by the same substance. During the reduction, the oxide was contained in porcelain boats which were placed in a hard glass tube. Fused or ground connections were employed in the apparatus throughout. This sample of metal was used only for preliminary preparations.

Very pure metallic iron prepared by the American Rolling Mills Co. served as the starting point in the preparation of Sample B. It contained sulfur 0.019 per cent., phosphorus 0.003 per cent., carbon 0.018 per cent., silicon, trace, manganese, trace, copper 0.05 per cent.

In the purification of this material exactly the same course was followed as in the case of Sample A, except that the nitrate was crystallized five times from concentrated nitric acid, and the oxide was reduced in hydrogen, generated electrolytically from a solution of potassium hydroxide and dried by solid potassium hydroxide.

The purification of Sample C was even more thorough. The specimen of metal from the American Rolling Mills Co. was used here also. The block of iron, which was sawed from a larger piece, was washed first with ether, next with alcohol and finally with water. A superficial layer was then removed by etching with dilute nitric acid and the block was again washed with water. Upon dissolving the metal in

redistilled hydrochloric acid, a small amount of insoluble matter remained, chiefly carbon in all probability. Without filtering, the solution was diluted with water and treated with hydrogen sulfide for some time, and a slight precipitate, consisting chiefly of sulfur and copper sulfide, was removed by filtration. On treating the solution twice more with hydrogen sulfide, only sulfur was precipitated. In this way all but traces of metals whose sulfides are insoluble in acids must have been eliminated.

In order to free the iron in particular from cobalt and nickel, it was next precipitated as ferric hydroxide by means of ammonia. First the ferrous chloride solution was oxidized by boiling for some time with a considerable amount of nitric acid, and after dilution it was poured, with continual agitation, into a hot solution of recrystallized ammonium nitrate containing a very large excess of redistilled ammonia. The precipitate was then washed many times by decantation. The process was next repeated, after dissolving the hydroxide in nitric acid. Preliminary experiments with iron containing known amounts of nickel showed that this method could be relied upon to remove traces of the latter element, although the complete elimination of large amounts is relatively slow. It is to be noted that, since the atomic weights of cobalt and nickel are so close to that of iron, the effect of a very considerable percentage of cobaltous or nickelous bromide in the ferrous bromide would be small.

The next step was to dissolve the ferric hydroxide in redistilled sulfuric acid and to reduce the iron electrolytically from the ferric to the ferrous state. This was done with a large platinum dish as cathode, and a platinum spiral of small surface as anode. The solution of ferric sulfate was concentrated in the first place, so that on cooling the reduced solution ferrous sulfate crystallized out. After removal of the crystals the electrolysis was continued and another crop of crystals obtained. By repeating these operations several times, almost all the iron was eventually recovered as ferrous sulfate. Metallic iron was then deposited electrolytically upon a platinum dish from a concentrated solution of recrystallized ammonium oxalate. During this electrolysis no manganese dioxide was deposited upon the anode, showing that the material was essentially free from this element. The metallic deposit was thoroughly washed with water and dissolved in the purest nitric acid. A small insoluble residue of carbon remained, which was removed by filtration through asbestos in a filtering apparatus consisting of only quartz and platinum. The asbestos had been digested for some time with aqua regia to remove soluble matter, and thoroughly washed with water. During the crystallization of the ferrous sulfate and the electrolytic deposition of the metal, aluminium and chromium as well as alkali metals

and silica must have been eliminated. Further treatment of this specimen was exactly similar to that of Sample B.

*Ferrous Bromide.*—Ferrous bromide was made by dissolving the different preparations of pure iron in the constant-boiling solution of hydrobromic acid in a quartz dish. The acid was freshly distilled through a quartz condenser, and was collected in a quartz vessel. Although the reduction of the ferric oxide to metal was probably more or less incomplete, all three specimens of iron gave clear solutions. At first, the solution of the iron was carried on inside a large desiccator filled with very pure hydrogen, and by means of an electrical heater constructed with platinum wire inside the desiccator the solution was evaporated to crystallization. The crystals were rapidly removed from the solution and centrifugally drained in platinum Gooch crucibles. Although a portion of the material oxidized to ferric bromide in this operation, the large preponderance of ferrous salts effectually prevented solution of platinum. The crystals of ferrous bromide were then recrystallized in a similar manner from constant-boiling hydrobromic acid in a quartz dish, and after centrifugal drainage were preserved in a quartz dish in a desiccator containing sticks of potassium hydroxide. Sample A of ferrous bromide was prepared in this way from Sample A of iron.

Sample B of ferrous bromide was made from Sample B of iron in essentially the same way except that during the preparation of this sample it was found more convenient to dissolve the iron in hydrobromic acid in the air on an electric stove as rapidly as possible and to crystallize in the air. Although some oxidation unavoidably takes place, the greater portion of the ferric salt passes into the mother liquors. Since during the subsequent preparation of the ferrous bromide for weighing, all ferric salt is decomposed, slight oxidation is of no consequence. Sample B of ferrous bromide was three times crystallized from hydrobromic acid solution.

Sample C<sub>1</sub> of ferrous bromide was made from Sample C of iron in the same way and was crystallized five times from hydrobromic acid. Sample C<sub>2</sub> was obtained from the mother liquors of Sample C<sub>1</sub>, after evaporation and reduction with metallic iron, and was crystallized five times. Sample C<sub>3</sub> resembled Sample C<sub>1</sub>, except that the hydrobromic acid solution of ferrous bromide was filtered through asbestos in the platinum-quartz filtering tube, and then the salt was crystallized four times. The asbestos was digested with constant-boiling hydrobromic acid solution before use.

### 3. Preparation of Ferrous Bromide for Analysis.

As in the analysis of many other metallic bromides in this laboratory, the ferrous bromide was prepared for weighing by fusion in a current of nitrogen and hydrobromic acid gases. In the earlier work upon ferrous bromide

fusion was unnecessary, since the salt was prepared by sublimation in a current of dry gases, and therefore contained only superficial moisture and ferric salt which could be eliminated by heating at a temperature below the fusing point. In the present instance, however, the salt contained at least four molecules of crystal water and possibly included ferric bromide. While in several recent investigations<sup>1</sup> it has been found possible to expel crystal water from hydrated crystals almost completely by heating them to a temperature at which they effloresce without melting, traces of moisture seem to be invariably retained. The desirability of fusing the ferrous bromide was therefore evident. Several difficulties were met in carrying out this operation. In the first place, in several preliminary experiments where the bromide was fused in a current of nitrogen and hydrobromic acid gases in a platinum boat, a superficial alloy of iron and platinum was formed. Whether this was due to dissociation of the salt or to the presence of a small proportion of hydrogen in the nitrogen was not determined. A similar difficulty met by Baxter and Coffin<sup>2</sup> in the fusion of cobaltous chloride in a current of pure hydrochloric acid gas leads one to believe that the former explanation is the real one. The only other material available for containing the salt during fusion was fused quartz. Fortunately experiments showed that ferrous bromide could be fused in a boat of this material in an atmosphere containing hydrobromic acid gas without attacking the quartz boat appreciably and without decomposition of the salt.

The second difficulty lay in the preparation of pure hydrobromic acid gas. In most previous investigations in this laboratory the method which has been used is to saturate nitrogen gas with bromine and then to pass the mixture through concentrated hydrobromic acid solution containing red phosphorus. Both before the hydrobromic acid solution becomes saturated with the gas and after a considerable amount of phosphorous acid has accumulated in the solution, volatil phosphorus compounds are likely to accompany the mixture of nitrogen and hydrobromic acid gases,<sup>3</sup> even if they are thoroughly scrubbed in a series of U-tubes containing saturated hydrobromic acid solution. This method was therefore used only in three of the preliminary experiments.

The method employed by Richards and Hönigschmid<sup>4</sup> in the fusion of calcium bromide, that of saturating hydrogen with bromine and passing it over hot platinum, is unsuited to the case of ferrous bromide on account of the occasional large excess of hydrogen in the hydrobromic acid gas.

<sup>1</sup> Baxter and Tilley, *THIS JOURNAL*, 31, 210 (1909). Baxter and Chapin, *Proc. Am. Acad.*, 46, 237 (1910); *THIS JOURNAL*, 33, 21.

<sup>2</sup> *THIS JOURNAL*, 28, 1584 (1906).

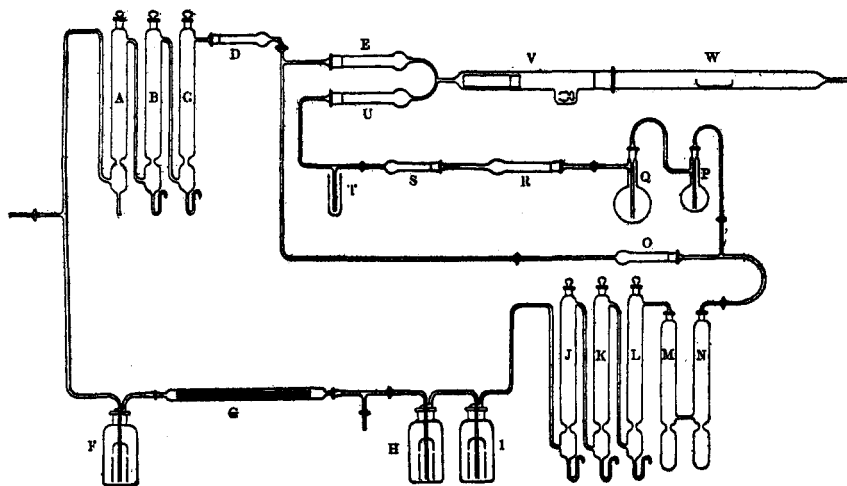
<sup>3</sup> Baxter, *Proc. Am. Acad.*, 39, 247 (1903).

<sup>4</sup> *THIS JOURNAL*, 32, 1583 (1910).



A more satisfactory method was found in charging the nitrogen with hydrobromic acid gas by passing it through fuming hydrobromic acid solution. In this way all possibility of contamination with phosphorus was avoided.

The apparatus for preparing the various gases was as follows: Nitrogen was obtained by passing air through concentrated ammonia solution in the bottle F (see figure) and then over hot copper gauze in the hard-



glass tube G. The excess of ammonia was removed by dilute sulfuric acid in the bottles H and I. The gas was then conducted through a tower, J, filled with beads moistened with silver nitrate solution, two similar towers, K and L, containing dilute sulfuric acid to eliminate last traces of ammonia, and two towers, M and N, filled with sticks of fused potassium hydroxide to absorb carbon dioxide and moisture. In the first three experiments the partially dried gas, after bubbling through bromine in a small flask, passed into a second flask containing concentrated hydrobromic acid solution in which carefully washed red phosphorus was suspended, to convert the bromine into hydrobromic acid. A U-tube, also containing red phosphorus and hydrobromic acid solution, removed traces of bromine which escaped reduction in the flask. Two additional U-tubes, containing beads moistened with concentrated hydrobromic acid solution only, served to eliminate volatil phosphorus compounds. Finally the mixture of nitrogen and hydrobromic acid gases was thoroughly dried by means of fused calcium bromide.

In all except the first three experiments the nitrogen was charged with hydrobromic acid gas by bubbling through fuming hydrobromic acid solution in the bulbs P and Q. The mixture was dried by means of fused calcium bromide in the tube R, and, after being freed from a possible

trace of bromine by anhydrous ferrous bromide in the tube S, was passed a second time over fused calcium bromide in the tube U. The fuming hydrobromic acid solution contained ferrous bromide to prevent the evolution of bromine.

When desired, the nitrogen could be passed directly through the phosphorus pentoxide tubes, O and E, into the bottling apparatus VW in which the fusion took place. Air was purified and dried by passing over silver nitrate in the tower A, fused potassium hydroxide in the tower B, concentrated sulfuric acid in the tower C, and phosphorus pentoxide in the tubes D and E.

All connections in the apparatus were made of fused or ground glass. No lubricant whatever was used on the ground joints and stopcocks which came in contact with hydrobromic acid but these joints were so long and so well ground that there could have been no diffusion inward. Either concentrated sulfuric acid or Ramsay desiccator grease was used for lubrication in the nitrogen and air apparatus.

In the final drying of the hydrobromic acid phosphorus pentoxide was not used on account of the danger of the formation of volatil phosphorus compounds.<sup>1</sup> Calcium bromide was chosen for this purpose, because its first hydrate has a very low aqueous pressure, 0.2 mm. at 25°, *i. e.*, one liter of moist gas passed over fused calcium bromide retains only 0.0002 gram of moisture.<sup>2</sup> The aqueous tension changes very slightly with the temperature. Furthermore, this salt is easily prepared. Fused zinc bromide is a less efficient drying agent. The aqueous pressure of its lowest hydrate is 1.2 mm. at 25°, and increases rather rapidly with the temperature.<sup>3</sup>

The ferrous bromide contained in the weighed quartz boat was placed in the heating tube W of the bottling apparatus,<sup>4</sup> and after air had been expelled by nitrogen and then by a mixture of nitrogen and hydrobromic acid gases, the tube was gradually heated until the water of crystallization began to evaporate rapidly.<sup>5</sup> There was never any appearance of melting at this point. As soon as dehydration appeared to be complete, the temperature was still further raised until the ferrous bromide fused. The salt was allowed to solidify, and while cooling, the mixture of nitrogen and hydrobromic acid gases was replaced by nitrogen, and this in turn by dry air when the tube was cold. While the tube was being swept out with nitrogen and air, a portion of the current of gas was sent backward through the tube U and the trap T, in order to avoid

<sup>1</sup> Baxter, Hines and Frevert, *THIS JOURNAL*, 28, 779 (1906).

<sup>2</sup> From results by Baxter and Warren, published in this number of *THIS JOURNAL*, p. 342.

<sup>3</sup> *Ibid.*

<sup>4</sup> Richards and Parker, *Proc. Am. Acad.*, 32, 59 (1896).

<sup>5</sup> At about 200°, Dammer, *Handb. anorg. Chem.*, 4, 761.

all possibility of contamination with hydrobromic acid. Finally the boat was pushed into the weighing bottle contained in the socket of V the bottling apparatus, and the stopper was inserted, all in the current of pure dry air. Several hours' standing in a desiccator near the balance always preceded the weighing of the bottle with its contents. In the preliminary series of experiments the fusion tube was of hard glass but in the final series of experiments this was replaced by a tube of transparent fused quartz. This quartz tube remained essentially unattacked during the final series of experiments. The tube was electrically heated by means of a removable mica sleeve wound with "Nichrome" resistance ribbon.

#### 4. Method of Analysis.

The procedure for the determination of the bromine in ferrous bromide was essentially that already frequently employed in the analysis of bromides in this laboratory. A solution of the salt was titrated against a weighed very nearly equivalent amount of silver and then the precipitated silver bromide was collected and determined gravimetrically. However, owing to the reducing effect of ferrous solutions upon solutions of silver salts, preliminary oxidation of the ferrous iron to the ferric state was found necessary in the earlier research upon ferrous bromide.

The salt was dissolved in about 200 cc. of pure water containing two drops of redistilled sulfuric acid. The acid was necessary, since ferrous bromide dissolved in pure water alone oxidizes rapidly and gives a copious precipitate of basic salt. After dilution to at least 600 cc. in a three-liter glass-stoppered precipitating flask, a solution was added containing ninety-nine per cent. of the amount of thrice crystallized potassium dichromate necessary to complete the oxidation and five per cent. more than the theoretical amount of distilled sulfuric acid. In order to avoid loss of bromine by evaporation from the surface of the solution, the dichromate was introduced through a funnel with a fine tip reaching to the bottom of the liquid. The solutions were allowed to mix largely by diffusion, aided by occasional very gentle agitation, and the flask was kept closed for some time after the introduction of the dichromate. When the oxidation is effected in this way, absolutely no evidence of free bromine can be obtained in the atmosphere above the solution, although we found experimentally that less than 0.01 mg. of bromine could easily be detected by the odor in an empty three-liter flask.

Very nearly the exact amount of the purest silver to combine with the ferrous bromide was weighed out and dissolved in redistilled nitric acid which had been diluted with an equal volume of water, in a flask provided with a column of bulbs to catch possible splatterings. The solution was further diluted and heated until free from nitrous acid, and then was again diluted until not more concentrated than tenth-nor-

mal. This solution was next added to the ferrous bromide solution which also had been diluted until more dilute than tenth-normal. After thorough mixing by shaking, the flask with its contents was allowed to stand for several days with occasional shaking until the supernatant liquid seemed perfectly clear. The solution was then tested for an excess of bromide or silver in a nephelometer<sup>1</sup> with careful observance of all the precautions necessary in the use of this instrument. If a deficiency in either bromide or silver was observed, a suitable amount of a thousandth-normal solution of sodium bromide or silver nitrate was added and the shaking and testing were repeated. This process was continued until the amounts of bromide and silver were equivalent. The test portions, since they contained only negligible amounts of silver and bromine, were discarded.

In order to determine whether appreciable occlusion had taken place, in Analyses 9 and 25, and 13 and 27, the precipitates were allowed to stand in contact with their mother liquors for 3 and 2 weeks respectively after the end point had apparently been reached. No change in end point with the time could be detected. In Analyses 13 and 27, moreover, the precipitation was carried out in the reverse fashion by adding the bromide solution to the silver solution. The results of these analyses were no different from those of the others. Further evidence that no occlusion took place is furnished by the ratio of silver to silver bromide (see page 333).

After the exact end point had been reached in each analysis, an excess of about 6 centigrams of silver nitrate was added and the flask was again thoroughly shaken. When the supernatant liquid was clear, the precipitate was thoroughly washed with pure water and collected upon a Gooch-Munroe-Neubauer crucible which had been heated to constant weight at 170° in an electric oven. The crucible and contents were heated for about 15 hours at the same temperature in the electric oven before being weighed. The greater part of the silver bromide was transferred to a porcelain crucible and the residual moisture was estimated by determining the loss in weight upon fusion. With two exceptions the fused silver bromide was light yellow and transparent. In these two analyses red particles of some iron compound were visible in the bromide and the results of these analyses were lower than those of the others. These two analyses are omitted from the table of results.

The precipitating flask was carefully rinsed with ammonia, and the silver bromide content of the solution was compared nephelometrically with known bromide solutions. The quantity found in this way was always less than one-tenth of a milligram.

While silver bromide is essentially insoluble in a solution containing

<sup>1</sup> Richards and Wells, *Am. Chem. J.*, **31**, 235 (1904); **35**, 510 (1906).

a bromide or a silver salt, it dissolves slightly in pure water. The first few washings, owing to the excess of silver nitrate in the filtrate, undoubtedly did not dissolve an appreciable amount of the bromide. Even the later washings, amounting to about one liter, could hardly have become saturated with bromide. The correction actually applied in each analysis for solubility of the silver bromide, 0.0001 gram per liter, certainly can not be far from the correct one.<sup>1</sup>

### 5. Balance and Weighing.

All the weighings were performed in a Troemner balance No. 10, easily sensitive to 0.02 milligram. The gold-plated brass weights were standardized from time to time by the method described by Richards.<sup>2</sup> No changes of more than a few hundredths of a milligram were found, however. Variations in the weights of containing vessels owing to changing atmospheric conditions were avoided by using counterpoises of the same material and as nearly as possible of the same shape and volume. The following vacuum corrections were applied:

	Specific gravity.	Vacuum correction.
Weights.....	8.3 <sup>3</sup>	....
Silver.....	10.49 <sup>4</sup>	— 0.000031
Silver bromide.....	6.473 <sup>5</sup>	+ 0.000041
Ferrous bromide.....	4.636 <sup>6</sup>	+ 0.000114

In the following tables are given the results of all the analyses completed, except three which met with known mishaps. The analytical work was performed wholly by Mr. Thorvaldson.

#### ATOMIC WEIGHT OF IRON.

Ag = 107.88.

Br = 79.916.

#### Preliminary Series I. FeBr<sub>2</sub> : 2Ag.

Number of analysis.	Sample of FeBr <sub>2</sub> .	Weight of FeBr <sub>2</sub> in vacuum. Grams.	Weight of Ag. in vacuum. Grams.	Weight of Ag added. Gram.	Corrected weight of Ag in vacuum. Grams.	Ratio FeBr <sub>2</sub> : 2 Ag.	Atomic weight of iron.
1	A	3.45339	3.45441	0.00040	3.45481	0.999589	55.840
2	A	3.04933	3.05030	0.00025	3.05055	0.999600	55.841
3	A	2.9007	2.9018	0.0001	2.9019	0.999586	55.839
4	B	3.0873	3.0884	0.0001	3.0885	0.999611	55.844
5	B	3.50278	3.50416	0.00010	3.50426	0.999577	55.837
6	B	4.05239	4.05379	0.00025	4.05404	0.999593	55.840
7	B	4.08516	4.08653	0.00030	4.08683	0.999593	55.840
Average,						0.999593	55.840

<sup>1</sup> Böttger finds the solubility to be 0.00008 g. per liter at 20°, *Z. physik. Chem.*, 46, 602 (1903). Kohlrausch gives the value 0.00011 at 21°, *Ibid.*, 50, 356 (1905).

<sup>2</sup> THIS JOURNAL, 22, 144 (1900).

<sup>3</sup> Baxter, *Proc. Am. Acad.*, 42, 209 (1906); THIS JOURNAL, 28, 1321.

<sup>4</sup> Richards and Wells, *Pub. Car. Inst.*, 28, 11 (1905); THIS JOURNAL, 27, 466.

<sup>5</sup> Baxter and Hines, *Am. Chem. J.*, 31, 224 (1904).

<sup>6</sup> Baxter, *Proc. Am. Acad.*, 39, 251 (1903).

FINAL SERIES I.  $\text{FeBr}_2 : 2\text{Ag}$ .

Number of analysis.	Sample of $\text{FeBr}_2$ .	Weight of $\text{FeBr}_2$ in vacuum. Grams.	Weight of Ag in vacuum. Grams.	Weight of Ag added or subtracted. Gram.	Corrected weight of Ag in vacuum. Grams.	Ratio $\text{FeBr}_2 : 2\text{Ag}$ .	Atomic weight of iron.
8	B	5.03555	5.03769	0.00005	5.03774	0.999565	55.834
9	$\text{C}_2$	6.06309	6.06557	0.00000	6.06557	0.999592	55.840
10	$\text{C}_2$	5.59258	5.59492	-0.00010	5.59482	0.999599	55.842
11	$\text{C}_1$	5.89767	5.90014	0.00000	5.90014	0.999581	55.838
12	C	4.48546	4.48732	0.00010	4.48742	0.999563	55.834
13	B	5.41562	5.41794	0.00005	5.41799	0.999563	55.834
14	A	6.50002	6.50272	0.00005	6.50277	0.999577	55.837
15	$\text{C}_1$	3.56564	3.56719	0.00000	3.56719	0.999565	55.834
16	B	5.32434	5.32662	-0.00020	5.32642	0.999609	55.844
17	$\text{C}_2$	6.38845	6.39124	-0.00030	6.39094	0.999610	55.844
18	$\text{C}_2$	6.37952	6.38223	-0.00010	6.38213	0.999591	55.840
Total,		60.64794			60.67313	0.999585	55.838

Average, 0.999583 55.838

## ATOMIC WEIGHT OF IRON.

Ag = 107.880.

Br = 79.916.

Preliminary Series II.  $\text{FeBr}_2 : 2\text{AgBr}$ .

Number of analysis.	Sample of $\text{FeBr}_2$ .	Weight of $\text{FeBr}_2$ in vacuum. Grams.	Weight of AgBr in vacuum. Grams.	Loss on fusion. Gram.	Corrected weight of AgBr in vacuum. Grams.	Ratio $\text{FeBr}_2 : 2\text{AgBr}$ .	Atomic weight of iron.
19	A	3.45339	6.01412	0.00054	6.01358	0.574265	55.853
20	A	3.04933	5.31057	0.00028	5.31029	0.574228	55.841
21	B	3.50278	6.10048	0.00015	6.10033	0.574195	55.831
22	B	4.05239	7.05799	0.00047	7.05752	0.574195	55.831
						0.574221	55.840

FINAL SERIES II.  $\text{FeBr}_2 : 2\text{AgBr}$ .

Number of analysis.	Sample of $\text{FeBr}_2$ .	Weight of $\text{FeBr}_2$ in vacuum. Grams.	Weight of AgBr in vacuum. Grams.	Loss on fusion. Gram.	Corrected weight of AgBr in vacuum. Grams.	Ratio $\text{FeBr}_2 : 2\text{AgBr}$ .	Atomic weight of iron.
23	B	5.03555	8.76960	0.00010	8.76950	0.574212	55.837
24	$\text{C}_2$	6.06309	10.55911	0.00022	10.55889	0.574216	55.839
25	$\text{C}_2$	5.59258	9.73988	0.00014	9.73974	0.574202	55.834
26	$\text{C}_1$	5.89767	10.27065	0.00008	10.27057	0.574230	55.844
27	B	5.41562	9.43199	0.00028	9.43171	0.574193	55.830
28	A	6.50002	11.31990	0.00032	11.31958	0.574227	55.843
29	$\text{C}_1$	3.56564	6.21000	0.00013	6.20987	0.574189	55.829
30	B	5.32433	9.27263	0.00026	9.27237	0.574216	55.839
31	$\text{C}_2$	8.51818	14.83494	0.00026	14.83468	0.574207	55.836
32	$\text{C}_2$	6.38845	11.12550	0.00014	11.12536	0.574224	55.842
33	$\text{C}_2$	6.37952	11.11011	0.00040	11.10971	0.574229	55.844
Total,		64.68065			112.64198	0.574214	55.838

Average, 0.574213 55.838

Average of Final Series I and II, 55.838

In seeking to discover the most probable value for the atomic weight of iron indicated by the foregoing data, it is only fair to bear in mind that the first experiments of a series are almost invariably influenced by incidental experimental errors which are largely eliminated in later experiments. Furthermore, the first three samples of ferrous bromide to be analyzed were fused in hydrobromic acid prepared from bromine and red phosphorus and hence, may have contained traces of phosphorus, while a hard glass tube was used in the fusion of the next four samples. We have therefore collected in the two preliminary series the first seven analyses, made in the summer and fall of 1909. The two final series were completed during the winter of 1909-10 after a very considerable intermission and are, in our opinion, much more satisfactory and less subject to avoidable errors.

The averages of the two final series agree perfectly, showing that so far as the estimation of the bromine is concerned no serious constant error exists. This is further indicated in the following table where the ratio of silver used and silver bromide obtained in the different pairs of analyses is recorded.

	Preliminary.	Ag : AgBr.
Analyses	1 and 19	0.574502
	2 and 20	0.574460
	5 and 21	0.574438
	6 and 22	0.574428
	Average,	0.574457
	Final.	
	8 and 23	0.574461
	9 and 24	0.574451
	10 and 25	0.574432
	11 and 26	0.574471
	13 and 27	0.574444
	14 and 28	0.574471
	15 and 29	0.574439
	16 and 30	0.574440
	17 and 32	0.574448
	18 and 33	0.574464
	Average,	0.574452

The average ratio agrees with the value to be expected, 0.574453.<sup>1</sup>

The different samples of ferrous bromide appear to be exactly similar as far as can be told by the results of the analyses. The following table contains a comparison of the averages from the different samples in the final series.

<sup>1</sup> Baxter, *Proc. Am. Acad.*, 42, 210 (1906); THIS JOURNAL, 28, 1332.

Sample.	FeBr <sub>2</sub> : 2Ag.	FeBr <sub>2</sub> : 2AgBr.	Average.
A	55.837	55.843	55.840
B	55.837	55.835	55.836
C	55.839	55.838	55.839
Average,	55.838	55.839	55.838

In the final series 60.64794 grams of ferrous bromide combined with 60.67313 grams of silver, whence the atomic weight of iron is 55.838, while 64.68065 grams of ferrous bromide produced 112.64198 grams of silver bromide, the amount to be expected if the atomic weight of iron is 55.838.

No matter how the results are treated, the outcome is the same. This method indicates a value for the atomic weight of iron of 55.838 if silver is taken as 107.88.

Certain possible constant errors need to be discussed. In two analyses of ferrous bromide prepared from meteoric iron, described in the following paper in the atomic weight of meteoric iron, the oxidation of the ferrous bromide to the ferric state before the precipitation of the silver bromide was carried out with ninety-eight instead of ninety-nine per cent. of the theoretical dichromate necessary. These two analyses yielded results very slightly lower than analyses with similar material in which ninety-nine per cent. of the theoretical dichromate was used, owing possibly to reduction of silver salts by the residual ferrous salt. The question naturally arises whether ninety-nine per cent. of dichromate is enough to prevent reduction of silver salts. In this connection it must be remembered that the ferrous salt was from the moment of solution undergoing continual oxidation, and that in reality less than one per cent. remained unoxidized after the addition of the dichromate. As the solution was always allowed to stand several hours after the addition of the dichromate, before precipitation, this oxidation must have been very considerable. Secondly, the average ratio of silver used to silver bromide obtained has exactly the proper value, which indicates that the silver bromide contained no excess of silver. This point is substantiated by the appearance of the fused silver bromide, which, as has already been stated, was light yellow and transparent. Furthermore, the reducing effect of ferrous salts on silver salts diminishes with the concentration of both substances. For instance, while a 0.5 per cent. acid solution of ferrous sulfate gave a precipitate of silver with an equal amount of a 0.06 per cent. solution of silver nitrate on standing over night, the same ferrous solution gave no precipitate with a 0.03 per cent. solution of silver nitrate. Similarly a 0.1 per cent. solution of ferrous sulfate gave no precipitate with even a 20 per cent. solution of silver nitrate. Since in an analysis the concentration of silver nitrate used



in precipitation was never over one per cent., while, if one per cent. of the ferrous bromide was unoxidized, the concentration of the latter substance could never have been higher than 0.003 per cent., the possibility of reduction was certainly small.

Although one of us<sup>1</sup> has already shown that it is possible to free ferrous bromide from ferric salt by heating in a current of nitrogen and hydrobromic acid gases to about 400°, the experiment for the detection of ferric salt was repeated with the fused ferrous bromide. The salt fused as described above was transferred to the weighing bottle in an atmosphere of nitrogen. The stopper of the weighing bottle was then removed and a freshly boiled and cooled, slightly acid solution of ammonium thiocyanate was quickly poured into the bottle, completely filling the bottle. The bottle was again stoppered and allowed to stand until the ferrous bromide was dissolved. Although the solution did not remain perfectly colorless, the color of the ferric thiocyanate was not strong. By comparison with solutions of known amounts of ferric iron the quantity of ferric bromide was found to be less than 0.05 milligram. So slight an amount of oxidation as this might well have occurred during the solution of the salt. At any rate it is obviously unnecessary to apply a correction of this magnitude.

The question of the neutrality of the ferrous bromide is difficult to settle, in particular because a basic precipitate is formed by oxidation as soon as the salt is dissolved in water. In many similar instances, however, where metallic bromides have been fused and allowed to solidify in hydrobromic acid gas, the salts have been found to be essentially neutral, hence it is fair to assume that this is the case with ferrous bromide also, especially since the concentration of the hydrobromic acid gas was never very high during the fusion. Furthermore, if the salt was not neutral, such variations in the method of heating and fusing as actually occurred would be expected to produce variations in the basicity or acidity of the salt. That such variations were inappreciable is indicated by the agreement of the different results.

None of the specimens of fused ferrous bromide gave a perfectly clear solution, even when dissolved in water containing considerable acid. The insoluble substance consisted of a trace of black material, undoubtedly carbon, since it disappeared when collected on a filter and ignited, and a very small amount of a light colored precipitate visible only under the most favorable conditions. The quantity of both kinds of material varied somewhat in different fusions and in the most successful experiments the insoluble material was almost entirely absent. Variations in the manner and speed of heating the ferrous bromide seemed to have no perceptible effect on the quality of the fused material.

<sup>1</sup> Baxter, *Proc. Am. Acad.*, 39, 246 (1903).

Finally the attempt was made to determine the weight and composition of the residue. Acidified solutions of fused ferrous bromide were filtered through tiny filters, and the papers were thoroughly washed. The filtrates seemed perfectly clear. The filters were ignited and the residues weighed in platinum crucibles. Since many salts of heavy metals are adsorbed from solution by filter paper,<sup>1</sup> blank experiments were carried out by filtering again the once filtered solutions. In four experiments the residues obtained from the original material weighed 0.30, 0.14, 0.15, and 0.12 milligram, while three blank experiments yielded 0.13, 0.13 and 0.12 milligram of ignited residue. The four residues were boiled with aqua regia, and the solution was evaporated. The solution was found to contain a trace of iron, while a slight insoluble gray residue which appeared to be silica remained. Whatever the composition of the residue, its weight is insignificant. If the residue was silica, it may have been extracted from the quartz boat which lost in weight at the rate of a few hundredths of a milligram in each analysis.

The uncertainty introduced by the last three considerations is not large enough to affect the second decimal place in the atomic weight of iron. The rounded-off value 55.84 confirms the earlier work on ferrous bromide as closely as could be expected while the greater purity of the ferrous bromide which we prepared gives greater probability to the result of this research than to that of the earlier one on the bromide. Since the bromide method of atomic weight investigation has been thoroughly tested with numerous metallic bromides, the results of this investigation are entitled to greater weight than the earlier results from the analysis of ferric oxide. Until the opportunity is offered for investigating farther the analysis of ferric oxide, it seems decidedly safer to employ the lower value for the atomic weight of iron yielded by the analysis of ferrous bromide.

In the following paper is described a continuation of this research by the determination of the atomic weight of meteoric iron.

We are particularly indebted to the Carnegie Institution of Washington for pecuniary assistance in carrying out this investigation and also to the Cyrus M. Warren Fund for Research in Harvard University for indispensable platinum vessels.

Following is a summary of the chief results of this investigation:

1. A new method of preparing very pure ferrous bromide is described.
2. The analysis of this salt indicates that the atomic weight of iron is 55.838 referred to silver 107.880. If silver is assumed to have the atomic weight 107.870, iron becomes 55.833.

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<sup>1</sup> Baxter and Hines, *THIS JOURNAL*, 28, 1569 (1906). Baxter and Wilson, *Proc. Am. Acad.*, 43, 369 (1907); *THIS JOURNAL*, 30, 191.