version of a part of the radioactivity into luminous energy. We have found the direct determination of k_1 and k_2 for potassium uranyl nitrate to be impracticable, on account of the impossibility of making uniform thin films. The activity of a thick film was found to be 0.369, which is in almost exact agreement with the calculated value, 0.368 (Table II). It is therefore probable that the proportion of radioactive energy converted into luminous energy is, at most, very small.

Our conclusions may be summarized as follows:

(1) Absorption of radioactivity is, like activity itself, an atomic property, independent of the form of chemical combination.

(2) The absorption by unit weight per unit area is, for any element, inversely proportional to the square-root of its atomic weight.

(3) The radioactivity of a thick film of any pure uranium compound may be calculated from a knowledge of its chemical composition.

A REVISION OF THE ATOMIC WEIGHT OF MANGANESE.

BY GREGORY PAUL BAXTER AND MURRAY ARNOLD HINES.

Received August 2, 1906.

THE following table, taken from Clarke's "A Recalculation of the Atomic Weights"[1] gives a brief resumé of previous work upon the atomic weight of manganese which has other than historical interest.

$O = 16.000$

Berzelius: Ann. Physik. Chem. 18, 74 (1830).
$MnCl_2 : 2AgCl$ 55.12
Turner: Trans. Roy. Soc. Edinb. 11, 143 (1831).
$MnCl_2 : 2AgCl$ 54.92
Dumas: Ann. Chem. Pharm. 113, 25 (1860).
$MnCl_2 : 2Ag$ 54.98
von Hauer: J. pr. Chem. 72, 360 (1857).
$MnSO_4 : MnS$ 54.91
Schneider: Ann. Physik. Chem. 107, 605 (1859).
$Mn : 2CO_2$ 54.03
Rawack: Ibid.
$Mn_3O_4 : H_2O$ 54.08
Dewar and Scott: Proc. Roy. Soc. 35, 44 (1883).
$AgMnO_4 : AgMnO$ 54.86

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[1] Smith. Misc. Coll., Constants of Nature, Part V, p. 283 (1897).

$AgMnO_4 : 2KBr$ 55.02

Marignac: Arch. sci. phys. nat. [3] 10, 21 (1883).

$MnO : MnSO_4$ 55.01

Weeren: Dissertation, Halle (1890).

$MnO : MnSO_4$ 55.00

$MnS : MnSO_4$ 55.00

From these results Clarke computes the most probable value to be 54.987.

The close agreement of the greater part of these determinations is striking, the experiments of Schneider and Rawack being the only ones which indicate a value for manganese very different from 55.0. The variations of their results from the others is not surprising, however, since manganoso-manganic oxide and manganous oxalate, with which they worked, are undoubtedly difficult to obtain in a pure condition. The remaining determinations all fall within limits 0.26 of a unit apart, and all but two agree within 0.16 of a unit. Our present knowledge concerning the variety of atomic weights upon which the above determinations are based is not sufficiently certain[1] to lead to the expectation of closer agreement from such widely different methods.

For this investigation the substances chosen for examination were manganous chloride and bromide, since the analysis of halogen compounds may be effected with great accuracy. Furthermore, these compounds have not been investigated by any of the more recent experimenters except Dewar and Scott,[2] who performed one analysis each of the chloride and bromide and obtained the values 54.91 and 54.97 respectively.

PURIFICATION OF MATERIALS.

Water.—All of the water used in either the purification or the analyses was twice distilled, once from a dilute alkaline solution of potassium permanganate and then from a very dilute sulphuric acid solution. Block-tin condensers were used in both distillations and the apparatus contained no rubber or cork connections. The water was collected as a rule in Jena glass flasks, although for special purposes either platinum or quartz receivers were substituted.

Reagents.—Acids and ammonia also were distilled shortly

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[1] Richards and Wells: Publications of the Carnegie Institution, No. 28, 67 (1905); Report of the International Committee on Atomic Weights, this Journal, 28, 6 (1906).

[2] Loc. cit.

before use, either platinum or quartz condensers and receivers being employed when necessary. Solid reagents were recrystallized, usually with centrifugal drainage.

Vessels.—Special pains were taken in all the work to prevent the introduction of alkalies or silica into the purest materials, by avoiding as far as possible the use of glass vessels.

Manganous Bromide.—Four different specimens of manganous bromide were employed, which were obtained from different sources and were purified in different ways. In the case of Samples A and B, purification of the manganese from other heavy metals was accomplished by recrystallization of Merck's "chemically pure" potassium permanganate. Sample A was crystallized three times only, while Sample B was thus treated ten times, the last two crops of crystals being thoroughly drained from the mother-liquors by means of a centrifugal.

In order to free the manganese from potassium and convert it into the bromide, the following processes were employed with Sample A: First the permanganate was dissolved in water and was reduced by passing sulphur dioxide into the solution. This sulphur dioxide was made by heating copper turnings with concentrated sulphuric acid and was purified from copper compounds mechanically carried along by passing through three gas washing-bottles, each containing a solution of sulphurous acid, and one column of beads moistened with a similar solution. From the solution of potassium and manganous sulphates the manganese was precipitated by the addition of an alkaline solution of ammonium carbonate. The manganous carbonate was washed with water until the washings were free from sulphates, then it was dissolved in nitric acid, which had been redistilled until free from chlorine, and the manganous nitrate was recrystallized six times from a solution strongly acid with nitric acid, four times in a glass vessel, twice in platinum. Usually it was necessary to start crystallization by inoculation, and cooling with ice was found advisable for the sake of economy in material. From a dilute solution of the purified nitrate in a platinum vessel, the manganese was again precipitated as carbonate, by means of ammonium carbonate which had been freshly made by passing pure carbon dioxide into distilled ammonia in a platinum flask. The resulting manganous carbonate, after thorough washing with water containing a small amount of ammonia to prevent colloidal solution of the carbonate, was readily converted into bromide by solution in hydrobromic acid. Since it was probable that the carbonate contained occluded nitrate, and since a portion of the material had been oxidized to the manganic state during the washing, it was obvious that bromine would be set free during the solution in hydrobromic acid. The use of a platinum vessel for this purpose was therefore precluded. In order to avoid the introduction of silica, instead of glass vessels, quartz dishes were employed. These have been shown to be practically insoluble in acid solutions.[1] The free bromine was expelled from the solution of manganous bromide by prolonged heating on a steam-bath in a quartz dish. Finally it was crystallized six times, thrice in quartz, and, after filtration with a platinum funnel, thrice in platinum with centrifugal drainage after each crystallization. The crystals were dried as far as possible over stick potash in a vacuum desiccator. From the mother-liquors, by means of six similar crystallizations, Sample A_2 was obtained.

In the conversion of Sample B from permanganate to bromide minor changes were introduced. The ammonium carbonate was prepared in a pure state by distilling a solution of commercial ammonium carbonate in a platinum still. Instead of expelling free bromine from the solution of manganous bromide by prolonged heating upon the steam-bath, the solution was evaporated as far as possible upon the steam-bath and the residue was heated to 200° in an electric oven. The bromide was dissolved in water, and after filtration of the solution, was crystallized three times in a platinum dish. The third crop of crystals is designated as Sample C_1.

Sample C_1 was prepared from a commercial specimen of pyrolusite. This was first dissolved in hydrochloric acid and the solution was boiled to expel chlorine. Hydrogen sulphide was passed into the diluted solution of manganous chloride to saturation, and the precipitate of sulphur and sulphides was removed by filtration. After the excess of hydrogen sulphide had been expelled by boiling, the solution was fractionally precipitated with sodium hydroxide until the precipitate was free from iron. Finally, the manganese was precipitated with ammonium carbonate and the precipitate was washed and dissolved in nitric

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[1] Mylius and Meusser: Z. anorg. Chem. 44, 221 (1905). See also page 1565 of this paper.

acid. The nitrate was recrystallized and converted into bromide exactly as in the case of Sample A.

The source of Sample D was Merck's "chemically pure" manganous sulphate. A solution of 500 grams of this salt was first saturated with hydrogen sulphide, and the precipitate, which consisted chiefly of manganous sulphide, was removed by filtration. After the addition of a small amount of ammonia, hydrogen sulphide was again passed into the solution to saturation, and the precipitate discarded. In a similar way third and fourth fractions of sulphide were removed. Next the solution was thrice fractionated with small portions of potassium hydroxide, the precipitate being rejected in each case. Then the manganese was twice precipitated as carbonate by means of ammonium carbonate and the manganous carbonate was converted into bromide exactly as in the case of Sample B. The first crop of thrice recrystallized bromide is designated Sample D_1, a second similar crop obtained from the mother-liquors is Sample D_2.

Manganous Chloride.—Two samples of manganous chloride were prepared. Sample B corresponded in its purity to Sample B of manganous bromide, since both were made by dissolving the same specimen of manganous carbonate. The solution of the carbonate in hydrochloric acid, which had been distilled with a quartz condenser, was evaporated to dryness in a quartz dish and was heated to 200° in an electric oven. Then the filtered aqueous solution was evaporated to crystallization in a platinum dish and the first crop of crystals was twice recrystallized (Sample B_1). The mother-liquors also yielded a crop of thrice recrystallized salt (Sample B_2).

The mother-liquors of the manganous nitrate of Samples B and D were combined and recrystallized six times, three times in glass and three times in platinum, and from this pure nitrate Sample E_1 of manganous chloride was prepared as above.

Hydrobromic Acid.—Commercial bromine was freed from chlorine by twice converting the bromine into hydrobromic acid by means of thoroughly washed hydrogen sulphide and water, and heating the hydrobromic acid, after distillation, with recrystallized potassium permanganate. The bromine was thus twice distilled from a bromide, the bromide in the second distillation being almost free from chloride. Iodine was eliminated by boiling the hydrobromic acid in each case with a small quantity of permanganate and rejecting the bromine set free. A portion of the final product, when converted into ammonium bromide by means of ammonia, and added to a solution of 3.46875 grams (in vacuum) of pure silver, yielded 6.03855 grams (in vacuum) of fused silver bromide, whence the ratio of silver to silver bromide is 57.443, while 57.445 is the value to be expected.[1]

By treating this bromine, covered with water, with washed hydrogen sulphide, hydrobromic acid was again produced. The solution was boiled, after mechanical separation of the greater part of the free sulphur and bromide of sulphur, and was then filtered. In order to remove the sulphuric acid produced during the action of the bromine upon the hydrogen sulphide, the hydrobromic acid was first distilled. Then it was diluted, and a small quantity of recrystallized barium hydroxide was added to precipitate last traces of sulphuric acid. The slight precipitate of barium sulphate was collected upon a filter, and the acid was three times distilled with rejection of the first and last portions, with a glass retort and condenser. Finally the acid was once distilled with the use of a quartz condenser. The product of the final distillation was collected in quartz vessels and was used immediately for dissolving the manganous carbonate. That this acid was free from solid impurities, such as alkalies and silica, was shown by evaporating 30 cc. in a weighed platinum crucible. No weighable residue remained after the crucible had been heated to very dull redness.

Hydrochloric Acid.—The "chemically pure" acid was boiled for some time, after the addition of a small quantity of potassium permanganate. Then it was twice distilled in glass, the middle portion only being collected, and finally once in quartz shortly before use.

Nitric Acid.—This acid was twice distilled, all but the last third of the distillate being rejected in each distillation. This acid gave no test for chloride in a nephelometer.

Silver.—Five different specimens of silver were employed, a portion of each one of which had already been used in an atomic weight research, and had been shown to be of the highest grade of purity. Two of these specimens, Samples H and J, were used

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[1] Baxter: "A Revision of the Atomic Weight of Bromine," Pr. Am. Acad. 42, 201 (1906).

in an investigation upon the atomic weight of iodine by one of us.[1] Sample H was prepared from silver nitrate which had been seven times recrystallized from nitric acid, five times recrystallized from water, and finally precipitated with ammonium formate. Sample J was precipitated once as silver chloride, electrolyzed once, and finally precipitated with ammonium formate. Sample K was employed in our investigation upon the atomic weight of cadmium.[2] This sample was thrice precipitated as silver chloride and once electrolyzed. Sample L was precipitated once as chloride, once as metal by ammonium formate and was once electrolyzed. This sample has been used in the analysis of cadmium bromide.[3] Sample M was prepared for an investigation upon the atomic weight of bromine, and had been twice electrolyzed after a preliminary purification.[4] Samples H, J and L also were used in the latter research, and were found to give values identical with those obtained with sample M. All five samples were finally fused in a current of pure hydrogen in a lime boat. The fused lumps were cleaned with dilute nitric acid, cut into fragments either with a clean steel chisel and anvil, or with a jeweler's saw, treated with dilute nitric acid until free from iron, washed, dried, and finally heated to about 300° in a vacuum.

THE ANALYSIS OF MANGANOUS BROMIDE.

The method of analysis was essentially that already frequently employed in this laboratory for the analysis of metallic halides. Weighed portions of the halides, after fusion in hydrobromic or hydrochloric acid, were first titrated against weighed portions of pure silver. Then the precipitated silver salts were collected and weighed.

The apparatus used for the fusion of the manganous bromide in a current of nitrogen and hydrobromic acid gases, was used in the preparation of ferrous bromide by one of us,[5] and is a modification of apparatus used for a similar purpose in determinations of the atomic weights of cobalt,[6] nickel,[7] and uranium[8] in this labora-

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[1] Baxter: Pr. Am. Acad. 41, 78 (1905).

[2] Baxter and Hines: This Journal, 27, 225 (1905).

[3] Baxter, Hines and Frevert: Ibid. 28, 770 (1906).

[4] Baxter: Pr. Am. Acad. 42, 207 (1906).

[5] Baxter: Ibid. 39, 246 (1903).

[6] Richards and Baxter: Ibid. 33, 117 (1897).

[7] Richards and Cushman: Ibid. 33, 99 (1897).

[8] Richards and Merigold: Ibid. 37, 378 (1902).

tory. A mixture of air and ammonia was passed over heated rolls of copper gauze and the excess of ammonia was removed by means of sulphuric acid. The gas was then purified and dried in an apparatus constructed wholly of glass, with ground joints, which consisted of a tower filled with beads moistened with silver nitrate solution to remove sulphur compounds, two similar towers containing dilute sulphuric acid to eliminate last traces of ammonia, and two towers filled with granular fused potassium hydroxide to absorb moisture and carbon dioxide. The partially dried gas, after bubbling through pure bromine in a small flask, passed into a second flask containing hydrobromic acid in which washed red phosphorus was suspended, to convert the bromine into hydrobromic acid. A U-tube, also containing red phosphorus and hydrobromic acid, removed traces of bromine which escaped reduction in the flask. Two additional U-tubes containing beads moistened with concentrated hydrobromic acid only, served to eliminate phosphorus compounds which, in the investigation upon ferrous bromide,[1] were found to accompany the hydrobromic acid if the phosphorous acid in the reduction flask was allowed to become very concentrated. Finally the mixture of nitrogen and hydrobromic acid gases was thoroughly dried, first by pure fused calcium bromide, and then by resublimed phosphorus pentoxide.

The manganous bromide, contained in a weighed platinum boat, was heated gently in a current of nitrogen, purified as above and dried by phosphorus pentoxide, until the greater part of the crystal water was expelled, then strongly in a current of nitrogen and hydrobromic acid until fused. After the salt had cooled, the hydrobromic acid was displaced by nitrogen and this in turn by air which had been passed over solid potassium hydroxide, concentrated sulphuric acid and phosphorus pentoxide. As stated before, the purifying apparatus was constructed wholly of glass, in such a way that by means of stop-cocks any one gas or mixture of gases could be employed, to the exclusion of the others. The boat was then transferred to the weighing-bottle in which it was originally weighed, and the stopper was inserted without an instant's exposure of the salt to moisture, by means of the bottling apparatus which has been frequently described in

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[1] Loc. cit.

papers from this laboratory.[1] The weighing-bottle was then allowed to stand in a desiccator near the balance case for some time before it was weighed.

Next the boat was transferred to a flask and the salt was dissolved in about 300 cc. of the purest water. The weighing-bottle was rinsed and the rinsings were added to the solution. Then the solution was filtered into the glass stoppered precipitating flask through a tiny filter to collect a trace of insoluble matter, and the filter-paper and residue were ignited in a weighed porcelain crucible.

From the weight of manganous bromide very nearly the requisite quantity of pure silver could be calculated. This silver was weighed out and dissolved, in a flask provided with a column of bulbs to prevent loss of silver by spattering, in distilled nitric acid diluted with an equal volume of water. After the silver was dissolved, the solution was diluted to twice its volume and was heated until free from nitrous fumes. Then it was still further diluted until not stronger than 1 per cent., and was slowly added with constant stirring to the 1 per cent. solution of manganous bromide in the precipitating flask. After having been shaken for some time, the solution was allowed to stand several days, one week in the case of Analyses 14 and 15, with occasional shaking, until the supernatant liquid was clear. Thirty cc. portions of the solution were then tested with hundredth-normal solutions of silver nitrate and sodium bromide in the nephelometer for excess of bromide or silver, and, if necessary, either standard silver nitrate or sodium bromide solution was added, and the process of shaking and testing repeated, until the amounts of bromide and silver in the solution were equivalent. If the solution was perfectly clear when tested, and contained no considerable excess of bromide or silver, the test solutions were discarded, since they contained only negligible amounts of silver bromide, otherwise they were returned to the flask and a correction was applied for the silver bromide thus introduced.

As soon as the exact end-point of the titration had been found, about four centigrams of silver nitrate in excess were added to precipitate dissolved silver bromide, and the flask was again shaken and allowed to stand until clear. The precipitate of silver bromide was collected upon a weighed Gooch crucible after it

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[1] Richards and Parker: Pr. Am. Acad. 32, 59 (1896).

had been washed with water by decantation about ten times. Next it was heated for several hours at 140°, then for two hours at about 230° in an electric air-bath, and, after it had cooled in a desiccator, it was weighed. In order to determine how much moisture was retained by the precipitate, in each case it was transferred as completely as possible to a clean porcelain crucible and weighed; then the salt was fused by heating the small crucible, contained in a large covered crucible, and again weighed. The fused salt was light yellow as a rule, showing that no appreciable reduction had taken place. The asbestos mechanically detached from the Gooch crucible together with a minute quantity of silver bromide which occasionally escaped the crucible, was collected from the filtrate and wash-waters upon a small filter, the ash of which was treated with nitric and hydrobromic acids before weighing. Although the filtrates and first wash-waters were essentially free from dissolved silver bromide, the subsequent wash-waters usually contained a trace of silver bromide. The amount of dissolved salt was determined with the nephelometer by comparison with standard bromide solutions.

Several difficulties were met in carrying out the analyses. In the first place it proved difficult to wash the platinum boat absolutely clean. When rinsed with cold water only, and dried at 100°, the weight was in many cases a few hundredths of a milligram greater than before fusion of the bromide. Ignition to redness of the boat thus treated then produced a slight loss in weight. Rinsing with hot water reduced the gain in weight of the boat after drying but did not wholly prevent a slight loss on ignition. The cause of the variation was not discovered, hence it seems safer in the calculations to use the weight of the boat after drying. The total variation is so slight, however, that it scarcely affects the final result.

Two other difficulties arose from the fact that when a solution of a manganous salt, even as dilute as the filtrates from analyses, is filtered through filter-paper, in spite of long-continued washing a small amount of manganese is tenaciously retained by the paper. This was discovered from the fact that the asbestos residues always contained manganese. In Analyses 31 to 33 it was found possible to eliminate the manganese completely by washing the filter finally with 5 per cent. hydrobromic acid. In two cases (Analyses 29 and 30) the residues were analyzed for manganese and were found to contain 0.00023 and 0.00057 gram of Mn_3O_4 respectively.

The average of these two quantities is, however, larger than the total residue in some cases, hence this value can not be used to correct the previous analyses. In order to determine accurately the proper correction for this error, a solution containing manganous nitrate in the proportion in which it was usually contained in the filtrate of an analysis, was passed through filter-paper and the filters were then washed as thoroughly as possible with water. The ash of these papers invariably contained manganese, the weights of manganic oxide in several experiments being found to be 0.00018, 0.00011, 0.00006, 0.00018 and 0.00005 gram with an average of 0.00012 gram. This quantity was subtracted from the weight of asbestos shreds in all cases except Analyses 31 to 33, where the paper was washed with hydrobromic acid.

The residue obtained by the filtration of the manganous bromide proved to contain manganese and to be free from detectable amounts of platinum and silica. Probably this insoluble residue consisted chiefly of oxides of manganese, although prolonged fusion in hydrobromic acid failed to reduce materially the proportion of insoluble matter. The discovery of adsorption in the case of manganous nitrate led to the suspicion that at least a portion of this residue was due to adsorption of manganese compounds by the filter-paper. In order to test this point a solution of manganous bromide, containing about 5 grams in 200 cc., after one filtration was again filtered through a second filter about 3 cm. in diameter. Filters of this size were used in filtering the manganous bromide solution in the analyses. This filter was then washed with water as thoroughly as in an analysis, and was ignited. The weight of manganic oxide obtained was 0.00008 gram. Two repetitions of the experiment yielded 0.00008 and 0.00010 gram respectively. If, as is probable, the manganese is adsorbed, not as bromide, but as some basic compound, possibly as manganic hydroxide, the bromine would have remained partially, if not wholly, in the solution. In that case a suitable correction could be applied by subtracting from the weight of the residue the average of the quantities of manganese adsorbed in the above experiments. An attempt to prevent the difficulty by adding dilute sulphuric acid to the solution of manganous bromide did not diminish the extent of the adsorption. Hence a negative correction of 0.00009 gram is applied to the residues in all cases.

THE ANALYSIS OF MANGANOUS CHLORIDE.

The apparatus employed for the fusion of manganous chloride was very similar to that used in the fusion of the bromide. Hydrochloric acid gas was generated by dropping concentrated sulphuric acid into concentrated hydrochloric acid. The gas was freed from spray in a gas washing-bottle, and was dried in five towers filled with beads moistened with concentrated freshly boiled sulphuric acid. From the towers the gas passed into the bottling apparatus in which the salt was fused in a current of hydrochloric acid and bottled in pure dry air as described above. This apparatus also was made wholly of glass with the exception of the air-drying towers which were closed with rubber stoppers. Since the salt was not heated in air no error could arise from this source.

In a few preliminary experiments the hydrochloric acid gas was passed finally over freshly sublimed phosphorus pentoxide, but this drying agent was subsequently eliminated since it was found to introduce volatile phosphorus compounds into the hydrochloric acid and thus into the manganous chloride, if the latter was moist. The effect of this difficulty upon previous work in this laboratory in the case of the analysis of chlorides which were fused in a current of hydrochloric acid gas, has been discussed elsewhere,[1] and has been shown to have been negligible. In the same place it has also been shown that hydrochloric acid gas attacks sulphuric acid to so slight an extent that the latter may safely be used to dry the former.

Although at first sight it is to be expected that hydrobromic acid, if dried by means of phosphorus pentoxide, would act upon this substance in a way similar to the action of hydrochloric acid gas, it has been shown[2] that no such difficulty exists if the hydrobromic acid is as dilute as in our work, the maximum concentration attainable by passing nitrogen through bromine at ordinary temperatures and then over phosphorus being not greater than 30 per cent. by volume.

The principal point of difference between the analyses of manganous bromide and manganous chloride was occasioned by the

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[1] Baxter, Hines and Frevert: This Journal, **28**, 779 (1906).

[2] Ibid. **28**, 781 (1906).

greater solubility of silver chloride. This introduced no difficulty in the case of the titrations, although the opalescence in both nephelometer tubes was of course more marked at the end-point. In order to make the precipitation of the silver chloride more complete, however, a much larger excess of silver nitrate was necessary than in the case of silver bromide, about fifteen hundredths of a gram being added in each analysis. Furthermore, the precipitate was washed at first with a solution of silver nitrate containing four hundredths of a gram in a liter, although the final six washings were performed with water. The silver chloride dissolved in both filtrate and washings was determined by comparison as previously described. Here even the filtrate showed a trace of dissolved silver chloride.

In the case of manganous chloride also the extent of the adsorption of manganese compounds by the filter-paper was investigated by filtering a solution of the salt through a filter-paper, and, after thoroughly washing the paper, determining the residue after ignition. The correction for adsorption thus found, 0.00006 gram, is in some cases larger than the weight of the residue minus the loss in weight of the boat, owing possibly to the fact that not all the platinum lost by the boat is collected upon the filter-paper. At any rate the uncertainty introduced by applying the correction wherever possible is very small.

The filter upon which the asbestos shreds were collected was washed with warm dilute hydrochloric acid to eliminate adsorbed manganese compounds, so that no correction for adsorption is here necessary. This acid was then tested for silver chloride with the nephelometer, and if any was found it was added to the main weight of this substance.

In Analyses 32, 33, 34, 35 and 38 the silver nitrate was added to the manganous chloride, while in Analyses 36 and 37 precipitation was performed in the reverse fashion.

The possibility of the existence of manganic compounds in the salts was considered. In order to determine whether or not this was the case, one specimen of manganous chloride, after fusion in hydrochloric acid, was tested for manganic compounds by adding a solution of starch paste and potassium iodide. No coloration resulted even after the addition of hydrochloric acid, although a trace of permanganate produced immediate coloration in the same solution.

The fused salts were pink in the case of both the chloride and the bromide, hence Forchhammer's statement that the pink color of manganous salts is due to the presence of manganic compounds is incorrect.[1]

It has already been shown that chlorides and bromides which have been fused and allowed to solidify in an acid atmosphere occlude none of the gas, for they give neutral solutions.[2]

The Nephelometer.—The nephelometer employed for the estimation of slight opalescences has already been described in detail by Richards and Wells.[3] All the precautions necessary for the accurate use of this instrument were carefully observed. The two tubes to be compared were always of the same size. The source of light in the nephelometer was so adjusted that tubes containing exactly equal amounts of precipitate gave identical readings. It was found advantageous to insert a plate of ground glass between the source of light and the test-tubes. In making up the test solutions, great pains were taken that the concentration of electrolytes in the two solutions and the conditions of precipitation should be as nearly as possible the same. Final readings were taken only after the ratio between the two tubes had become constant.

Vacuum Corrections.—In order to find accurately the vacuum corrections for manganous bromide and chloride, it was necessary to determine the densities of these two salts. The experiments were carried out exactly as described in our determinations of the specific gravities of cadmium halides,[4] with the following results:

Density of $MnBr_2$.

Density of Toluene 25°/4° = 0.86156.

Weight of $MnBr_2$ in vacuum. Grams.	Weight of toluene displaced in vacuum. Gram.	Density of $MnBr_2$. 25°/4°.
3.0098	0.5914	4.385
3.0342	0.5963	4.384
	Average,	4.385

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[1] Ann. Phil, N. S. 1, 50 (1821).

[2] Richards: Pr. Am. Acad. 29, 59 (1893); This Journal, 24, 376 (1902); Richards and Baxter: Pr. Am. Acad. 34, 367 (1899); Baxter and Hines: This Journal, 27, 227 (1905).

[3] Am. Ch. J. 31, 235 (1904); 35, 510 (1906).

[4] Ibid. 31, 220 (1904).

Density of $MnCl_2$.
Density of toluene 25°/4° = 0.86166.

Weight of $MnCl_2$ in vacuum. Grams.	Weight of toluene displaced in vacuum. Gram.	Density of $MnCl_2$. 25°/4°.
1.9436	0.5617	2.982
2.8532	0.8266	2.974
3.1202	0.9035	2.976
	Average,	2.977[1]

All weights were reduced to the vacuum standard by applying the following corrections for each apparent gram of substance.

	Specific gravity.	Vacuum correction.
Weights	8.3	
$MnBr_2$	4.385	+0.000129
$MnCl_2$	2.977	+0.000259
AgBr	6.473	+0.000041
AgCl	5.56	+0.000071
Ag	10.50	−0.000031
Toluene	0.862	+0.00126

The balance was a new Troemner, No. 10, and was easily sensitive to one-fiftieth of a milligram with a load of less than 50 grams. The weights, which were of brass, gold-plated, were occasionally carefully standardized to hundredths of a milligram. The corrections did not vary with time, however. All weighings were made by substitution, with tare vessels as nearly like those being weighed as possible.

The atomic weights involved in the calculations are assumed to be as follows: Ag = 107.930; Br = 79.953;[2] Cl = 35.473.[3]

Series I.	$MnBr_2 : 2Ag$	54.959
" II.	$MnBr_2 : 2AgBr$	54.955
" III.	$MnCl_2 : 2Ag$	54.958
" IV.	$MnCl_2 : 2AgCl$	54.958
	Average,	54.958

The close agreement of the averages of the four series is conclusive evidence that no serious error, such as occlusion by the silver halides, affected the method of analysis. This is strikingly shown by the ratio between the silver used and the silver halide obtained in the same analysis.

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[1] Shröder obtained the value 2.478. Dichtigkeitsmessungen, Heidelberg, 1873.

[2] Baxter: Pr. Am. Acad., 42, 201 (1906).

[3] Richards and Wells: Publications of the Carnegie Institution, No. 28 (1905).

THE ATOMIC WEIGHT OF MANGANESE.

Series I. $MnBr_2 : 2Ag$.

$Ag = 107.930$. $Br = 79.953$.

Number of analysis.	Sample of $MnBr_2$.	Sample of Ag.	Weight of $MnBr_2$ in vacuum. Grams.	Corrected weight of residue. Gram.	Change in weight of boat. Gram.	Weight of Ag in vacuum. Grams.	Weight of Ag added or subtracted. Gram.	Corrected weight of $MnBr_2$. Grams.	Corrected weight of Ag. Grams.	Atomic weight of manganese.
1	A_2	K	6.53738	0.00000	—0.00004	6.56772	—0.00017	6.53738	6.56755	54.962
2	A_1	K	4.81026	0.00019	+0.00002	4.83243	—0.00005	4.81005	4.83238	54.957
3	C_1	K	4.88124	0.00027	0.00000	4.90354	0.00000	4.88097	4.90354	54.960
4	C_1	H	5.63234	0.00022	—0.00007	5.65833	—0.00020	5.63219	5.65813	54.964
5	A_1	H	5.79927	0.00008	—0.00005	5.82610	—0.00010	5.79924	5.82600	54.963
6	C_1	J	6.59033	0.00046	+0.00004	6.62051	—0.00010	6.58983	6.62041	54.957
7	B_1	H	4.19917	0.00016	—0.00010	4.21809	+0.00030	4.19911	4.21839	54.967
8	A_1	J	3.59834	0.00015	+0.00010	3.61478	0.00000	3.59809	3.61478	54.957
9	B_1	J	5.16345	0.00019	—0.00008	5.18711	0.00000	5.16334	5.18711	54.965
10	B_1	K	3.92230	0.00014	—0.00010	3.94021	+0.00021	3.92226	3.94042	54.959
11	B_1	K	4.49181	0.00032	—0.00009	4.51220	+0.00030	4.49158	4.51250	54.953
12	C_1	H	3.60099	0.00016	+0.00012	3.61746	—0.00010	3.60071	3.61736	54.960
13	D_1	H	4.77414	0.00022	0.00000	4.79602	+0.00018	4.77392	4.79620	54.951
14	D_1	J	3.57674	0.00015	—0.00001	3.59323	—0.00004	3.57660	3.59319	54.957
15	D_2	H + J	5.69991	0.00026	—0.00007	5.72586	+0.00055	5.69972	5.72641	54.948
									Average,	54.959

THE ATOMIC WEIGHT OF MANGANESE.

Series II. $MnBr_2 : 2AgBr$.

$Ag = 107.930$. $Br = 79.953$.

Number of analysis.	Sample of $MnBr_2$.	Weight of $MnBr_2$ in vacuum. Grams.	Corrected weight of residue. Gram.	Change in weight of boat. Gram.	Weight of AgBr in vacuum. Grams.	Loss on fusion. Gram.	Corrected weight of asbestos. Gram.	Weight of AgBr from wash-waters. Gram.	Corrected weight of $MnBr_2$. Grams.	Corrected weight of AgBr. Grams.	Atomic weight of manganese.
16	A_2	5.58461	0.00037	+0.00008	9.76524	0.00032	0.00069		5.58416	9.76561	54.964
17	A_2	5.63458	0.00022	+0.00004	9.85295	0.00030	0.00073	0.00007	5.63432	9.85345	54.961
18	A_2	6.53738	0.00000	−0.00004	11.43246	0.00029	0.00078	0.00005	6.53738	11.43300	54.957
19	A_1	4.81026	0.00019	+0.00002	8.41199	0.00024	0.00031		4.81005	8.41206	54.959
20	C_1	4.88124	0.00027	0.00000	8.53619	0.00022	0.00039	0.00006	4.88097	8.53642	54.950
21	C_1	5.63234	0.00022	−0.00007	9.84971	0.00009	0.00046		5.63219	9.85008	54.954
22	C_1	6.52653	0.00017	+0.00010	11.41232	0.00018	0.00061	0.00018	6.52626	11.41293	54.968
23	A_1	5.79927	0.00008	−0.00005	10.14153	0.00013	0.00061	0.00005	5.79924	10.14206	54.957
24	A_1	3.59834	0.00015	+0.00010	6.29262	0.00014	0.00023		3.59809	6.29271	54.952
25	B_1	5.16345	0.00019	−0.00008	9.02941	0.00005	0.00023	0.00004	5.16334	9.02959	54.966
26	B_1	3.92230	0.00014	−0.00010	6.85939	0.00012	0.00012	0.00041	3.92226	6.85968	54.951
27	B_1	4.49181	0.00032	−0.00009	7.85527	0.00015	0.00059		4.49158	7.85571	54.942
28	C_1	3.60099	0.00016	+0.00012	6.29731	0.00014	0.00023		3.60071	6.29740	54.949
29	D_1	4.77414	0.00022	0.00000	8.34878	0.00020	0.00057		4.77392	8.34915	54.951
30	D_1	3.57674	0.00015	−0.00001	6.25541	0.00018	0.00046		3.57660	6.25569	54.933
31	D_2	5.69991	0.00026	−0.00007	9.96830	0.00020	0.00030		5.69972	9.96840	54.947

Average, rejecting analysis 30, 54.955

Average of Series I and II, 54.957

THE ATOMIC WEIGHT OF MANGANESE.

Series III. $MnCl_2 : 2Ag$.

Ag = 107.930. Cl = 35.473.

Number of analysis.	Sample of $MnCl_2$.	Sample of Ag.	Weight of $MnCl_2$ in vacuum. Grams.	Corrected weight of residue. Gram.	Change in weight of boat. Gram.	Weight of Ag in vacuum. Grams.	Weight of Ag added or subtracted. Gram.	Corrected weight of $MnCl_2$. Grams.	Corrected weight of Ag. Grams.	Atomic weight of manganese.
32	B_2	L	4.62985	0.00017	—0.00002	7.93730	+0.00010	4.62970	7.93740	54.960
33	B_1	L	3.52899	....	—0.00001	6.05071	—0.00030	3.52899	6.05041	54.958
34	B_1	L	3.30881	0.00000	—0.00010	5.67299	—0.00020	3.30881	5.67279	54.960
35	E_1	L	3.56859	0.00014	+0.00002	6.11818	0.00000	3.56843	6.11818	54.955
36	E_1	K	3.45114	0.00023	+0.00008	5.91647	—0.00010	3.45083	5.91637	54.958
37	B_1	L	4.47948	0.00008	—0.00015	7.68015	—0.00020	4.47948	7.67995	54.959
38	E_1	M	3.92089	0.00002	—0.00005	6.72232	—0.00005	3.92089	6.72227	54.958

Average, 54.958

Series IV. $MnCl_2 : 2AgCl$.

Number of analysis.	Sample of $MnCl_2$.	Weight of $MnCl_2$ in vacuum. Grams.	Corrected weight of residue. Gram.	Change in weight of boat. Gram.	Weight of AgCl in vacuum. Grams.	Loss on fusion. Gram.	Weight of asbestos. Gram.	Weight of AgCl from wash-waters. Gram.	Corrected weight of $MnCl_2$. Grams.	Corrected weight of AgCl. Grams.	Atomic weight of manganese.
39	B_2	4.62985	0.00017	—0.00002	10.54532	0.00006	0.00017	0.00098	4.62970	10.54641	54.957
40	B_1	3.52899	....	—0.00001	8.03616	0.00013	0.00046	0.00219	3.52899	8.03868	54.962
41	B_1	3.30881	0.00000	—0.00010	7.53598	0.00014	0.00040	0.00107	3.30881	7.53731	54.959
42	E_1	3.56859	0.00014	+0.00002	8.12767	0.00005	0.00042	0.00128	3.56843	8.12932	54.950
43	E_1	3.45114	0.00023	+0.00008	7.85947	0.00012	0.00053	0.00141	3.45083	7.86129	54.952
44	B_1	4.47948	0.00008	—0.00015	10.20110	0.00007	0.00078	0.00191	4.47948	10.20372	54.963
45	E_1	3.92089	0.00002	—0.00005	8.92964	0.00004	0.00038	0.00142	3.92089	8.93140	54.962

Average, 54.958

Average of Series III and IV, 54.958

				Ag : AgBr.
Analyses	1	and	18	57.4438
"	2	"	19	57.4459
"	3	"	20	57.4426
"	4	"	21	57.4425
"	5	"	23	57.4439
"	8	"	24	57.4439
"	9	"	25	57.4457
"	10	"	26	57.4432
"	11	"	27	57.4423
"	12	"	28	57.4421
"	13	"	29	57.4454
"	14	"	30	57.4387
"	15	"	31	57.4456
			Average,	57.4435

Average, rejecting analyses 14 and 30, 57.4439

The most probable value for this ratio has recently been shown to be 57.4453.[1]

Richards and Wells have proved beyond question that the ratio of silver to silver chloride is as low as 75.2634,[2] a value which is identical with that obtained from the analysis of manganous chloride.

				Ag : AgCl.
Analyses	32	and	39	75.2615
"	33	"	40	75.2662
"	34	"	41	75.2628
"	35	"	42	75.2607
"	36	"	43	75.2595
"	37	"	44	75.2662
"	38	"	45	75.2656
			Average,	75.2632

It is interesting to tabulate the analyses according to the specimens of material employed.

Average of analyses with samples	A_1	and	A_2	of	$MnBr_2$	54.959
" " " " "	B_1			"	"	54.958
" " " " "	C_1			"	"	54.958
" " " " "	D_1	"	D_2	"	"	54.951[3]
" " " " "	B_1	"	B_2	"	$MnCl_2$	54.960
" " " " "	E_1			"	"	54.956
					Average,	54.957

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[1] Baxter: Loc. cit.

[2] Loc. cit.

[3] Analysis 30 is rejected.

Average of analyses with sample H of Ag	54.958
" " " " " J " "	54.961
" " " " " K " "	54.959
" " " " " L " "	54.959
" " " " " M " "	54.958
Average,	54.959

The purification of Sample B was exceptionally thorough. In the first place potassium permanganate is isomorphous with a comparatively limited number of substances, so that the initial purification by a large number of crystallizations of this substance may be expected to have eliminated every trace of impurity of heavy metals. In the second place the final product had been many times recrystallized in the form of two other compounds of manganese. It is almost inconceivable that any impurity could have eluded this large number of crystallizations in three different forms. That such a prolonged purification was unnecessary is shown by the agreement of the results from the other samples with that from Sample B. Even in the case of Samples A, C, D and E the final product had been recrystallized in at least two forms. The slightly lower results in the case of Sample D differ from the others by an amount no greater than the possible experimental error, and can not be considered to indicate that the composition of this sample is different from that of the others.

The various samples of silver also yielded essentially the same result, which confirms the statement as to the identity of the different samples made on page 1566.

There can be little doubt that the final average of all four series, 54.96, represents with accuracy the relation of the atomic weight of manganese to that of silver 107.930. This value is in such close agreement with the value derived from previous investigations, that until the relation of oxygen to silver is more accurately known, no change in the atomic weight of manganese need be made from the value 55.0, now accepted by the International Committee on Atomic Weights.

The main results of this research may be briefly summarized as follows:

(1) The atomic weight of manganese, referred to silver 107.930, is found to be 54.96, by analysis of both manganous bromide and manganous chloride.

(2) The specific gravity of manganous bromide at 25°, referred

to water at 4°, is found to be 4.385, and that of manganous chloride under the same conditions is found to be 2.977.

We are deeply indebted to the Carnegie Institution of Washington for funds which have made this investigation possible, and also to Dr. Wolcott Gibbs and the Cyrus M. Warren Fund for Research in Harvard University for many indispensable platinum vessels.

CHEMICAL LABORATORY OF HARVARD COLLEGE,
CAMBRIDGE, MASS., July, 1906.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF COBALT.

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FOURTH PAPER.—THE ANALYSIS OF COBALTOUS CHLORIDE.

SOME years ago the atomic weight of cobalt was investigated in this laboratory by the determination of the ratios of cobaltous bromide to silver and to silver bromide,[1] and of cobaltous bromide,[2] cobaltous chloride,[3] and cobaltous oxide[3] to cobalt. From these investigations the probable value for the atomic weight of cobalt was found to be 58.995 (Ag = 107.930), the most satisfactory results being obtained through the analysis of cobaltous bromide.

The determination of the cobalt in cobaltous chloride was effected by reduction of the salt in a current of hydrogen. The salt was not obtained in a state of absolute purity, and it was necessary to apply corrections for the impurities, so that at the time very little value was attached to the result, 59.072.[4] In the present investigation it has been found possible with the help of the newly available quartz apparatus to prepare the salt in a state of greater purity, and the analysis of this new material confirms

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[1] Richards and Baxter: Pr. Am. Acad. 33, 115 (1897).

[2] Ibid. 34, 351 (1899).

[3] Ibid. 35, 61 (1899).

[4] The value found from two analyses was 59.044, upon the assumption that the atomic weight of chlorine is 35.456 (Ag = 107.930). Recent determinations in this laboratory by Richards and Wells (Publications of the Carnegie Institution, No. 28, 1905) have shown that the value of the latter constant is as high as 35.473. This change in the atomic weight of chlorine produces an increase in the atomic weight of cobalt of 0.028.